General Chemistry for Gee-Gees

GENERAL CHEMISTRY FOR GEE-GEES

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MEET THE AUTHORS

Kevin Roy

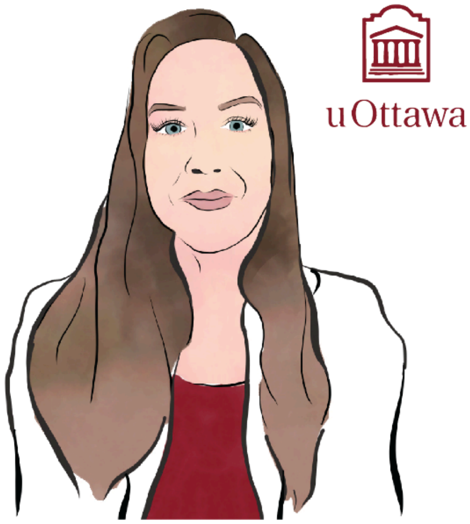
Kevin Roy completed his Honours Bachelor of Science at uOttawa in 2019 and is currently completing his M.D. at the uOttawa School of Medicine. In 2018, Kevin was working on a research project that evaluated the effects of an open education resource in an undergraduate chemistry classroom. During that time, he was introduced to the open textbook movement. Kevin learnt about how a team led by a professor from the University of Toronto enlisted students to adapt an open textbook for an undergraduate classroom. After attending this presentation, Kevin was inspired to create a student-led adaptation of an open textbook for a large undergraduate class in the Faculty of Science: a project for students, by students. It is his hope that this project will serve as an example of how undergraduate students can advocate for and even create open education resources at their academic institution.

Mahdi Zeghal

Mahdi is a current medical student at the University of Ottawa. Being native to Ottawa, he completed his high school studies in the nation's capital and his post-secondary undergraduate studies in Biomedical Sciences at uOttawa. Mahdi's been involved in many opportunities to educate others for many years, and what was once just a common part of his extracurriculars now became his passion. He continues to actively seek involvement in education initiatives and opportunities, including promoting medicine to interested students, advocating for improved medical education, and teaching others how to engage with medical learners in large- and small-group settings. He sincerely hopes that this open textbook, being an incredible project and initiative spanning many months of hard work, will serve to help students excel in CHM 1301/1311 and perhaps even gain an appreciation for the study of chemistry.

Jessica Thomas

Jessica is currently an undergraduate chemical engineering student at the University of Ottawa. Throughout her academic career, Jessica has found herself tutoring, peer-teaching, and now, creating unique content to further the education of new chemistry students. Jessica hopes that this open textbook allows students better access to course material beyond the confines of a heavy and expensive general chemistry textbook. She hopes the reader enjoys this work; despite any challenging questions it may contain.

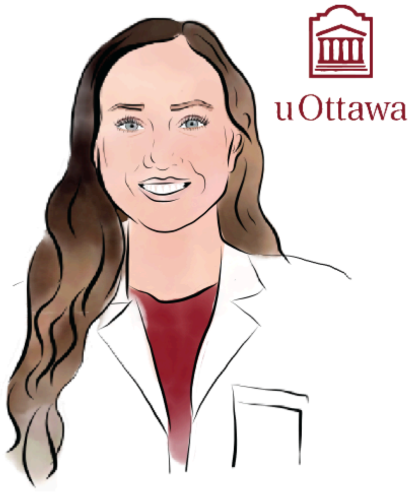


Dr. Kathy-Sarah Focsaneanu

Kathy-Sarah Focsaneanu (known as “Dr. Fox” to her students) received both her bachelor’s and Ph.D. in chemistry from uOttawa, working in the Scaianoresearch group, which specializes in photochemistry – the study of the interaction of matter and light. During her Ph.D., she also worked as a TA in several courses and fell in love with teaching. After finishing her doctorate, Dr. Fox was very fortunate to join the Faculty of Science as a teaching-intensive Science Lecturer. Now, her focus is on incorporating new teaching technologies and techniques into the Chemistry classroom and carrying out small research projects in Chemistry Education.

Geneviève O’Keefe

Geneviève O’Keefe is an undergraduate student at the University of Ottawa with the Faculty of Science, pursuing an H.B.Sc. in Biopharmaceutical Sciences with a specialization in Medicinal Chemistry. Geneviève has a passion for research and education in undergraduate chemistry and is keen to help widen the accessibility of this science amongst the student population. Her involvement in this project was motivated by her own personal experiences as an undergraduate science student relating to purchasing expensive course materials. She hopes that this resource will prove to be useful and valuable to the

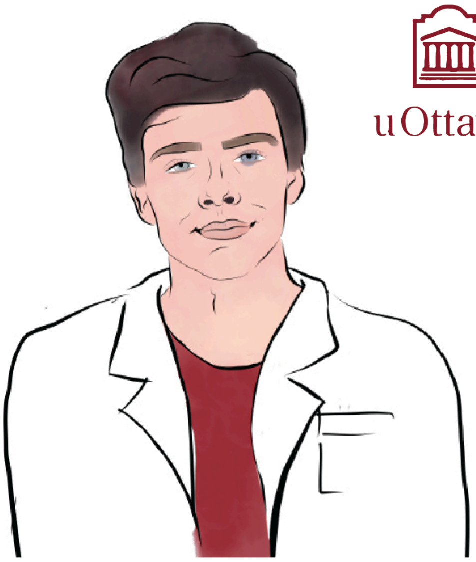


University of Ottawa student population specifically. Upon graduating in 2021, she intends on pursuing a Ph.D. in Organic Chemistry at the University of Alberta.

Dr. Brandi West

Brandi West received her B.Sc. (Honours) in chemistry from Trent University in 2006. During her honours project, she developed an interest in physical chemistry that lead her to earn an M. Sc. from Queen's University in 2009. She then joined the mass spectrometry facility at the University of Ottawa, where she earned her Ph. D. in 2014. Her research focused on the thermodynamics and kinetics of gas-phase reactions. Her passion for physical chemistry and mass spectrometry led her to complete a PDF position at the University of Auckland, New Zealand (2015) where she investigated the thermodynamic properties of aerogels using MALDI imaging. Upon her return to Canada, Dr. West rejoined the mass spectrometry facility before accepting her current position as a part-time professor at the University of Ottawa in 2018. Dr. West has had the opportunity to teach a range of physical and analytical chemistry courses, along with general chemistry. In her free time, Dr. West enjoys a diverse range of pastimes; from sewing and quilting to bingeing the latest sci-fi show or getting together with family and friends to play a new board game.

Derek Fraser-Halberg



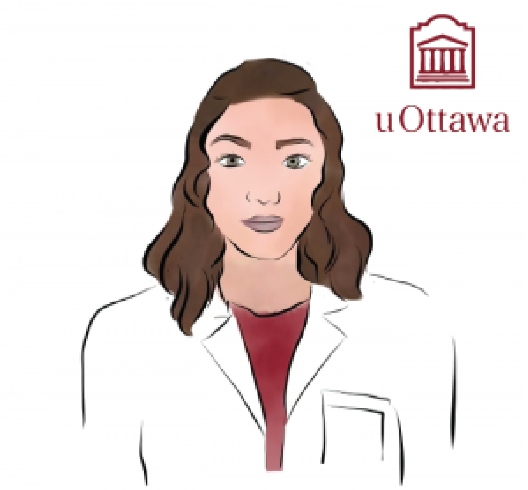
Derek is currently a second-year Biochemistry Science student at the University of Ottawa. Derek finds that extending the knowledge he has gained through the years of being a biochemistry student is not only enjoyable for himself, but helpful to others. His unique ability to readily explain hard to understand subjects in a simple manner has given him the opportunity to assist students in ways such as: helping his classmates with the courses they are taking, advocating for better educational standards to those less fortunate, and creating resources to better cater to the needs of students. This open textbook is an extension of Derek's passion to help and create a better learning environment for students and teachers. Derek actively seeks ways in which he can engage and help people with the knowledge he has gained throughout his years of education. He truly believes that his efforts in helping others, whether it's to CHM 1301/1311 students, or anyone interested in learning, will serve to benefit the greater good and advance society as a whole.

Nathan Biniam

Nathan Biniam is currently a second-year student at the University of Ottawa enrolled in the Biomedical Sciences program. Nathan enjoys assisting members in his community and is deeply interested in both neuroscience and technology. As an active member of his community, Nathan has been involved in several opportunities to assist others. Over the last few years he has taken part in many educational initiatives and opportunities, whether it be leading school clubs or tutoring individuals struggling in the sciences. Among the many educational initiatives he is involved in, the open textbook has been an excellent addition to his passion for helping educate others. As a student who has completed the course, Nathan believes the textbook will be an excellent resource to help students both transcend in CHM 1301/1311 and develop a general appreciation for chemistry.

Leanne Trepanier

Leanne Trepanier is currently enrolled as an undergraduate student in the B.Sc. Nursing program at the University of Ottawa. Since she is of the opinion that chemistry can be involved in everyday life, even outside of a science major, she was thrilled to collaborate on this project. Leanne is excited to share this open education resource with those taking General Chemistry at the University of Ottawa to help them acknowledge the clear links between chemistry and the world surrounding them. Being a university undergraduate student, she is also aware of the cost of learning materials which are normally necessary for courses. Having this free, accessible resource online, she hopes that it will enable all students to gain a deep understanding of general chemistry, without any economic discrimination.



Debby Pinos

Debby is a current undergraduate biochemistry student with a minor in computer sciences at the University of Ottawa. Having developed a passion for learning and research, Debby loves to help her friends and peers by organizing study groups and tutoring sessions. Working on the open textbook has given her the opportunity to be part of this movement to support other students' educations. Debbie believes that education is priceless, and she feels fortunate to be a part of this project. She hopes that the students in CHM 1301/1311 will benefit from this free resource and advance in their studies.

ACKNOWLEDGEMENTS

Dear students,

University is expensive. As a graduate of the Faculty of Science and a former student enrolled in Principles of General Chemistry, I speak from experience when I say that with the cost of tuition, textbooks, online learning tools and more, the cost of a university education adds up very quickly!

It is my greatest hope that the General Chemistry for Gee-Gees textbook can help relieve some of the financial stresses that you face as a post-secondary student at the University of Ottawa, by being free to use as an open education resource. I hope this textbook not only peaks your interest in chemistry and helps you succeed in the course, but also shows you the positive impact that open education resources can have on a community. Open education resources are not bound by traditional copyright licenses and are instead licensed under a Creative Commons license. The Creative Commons license is based on the belief that when we share, everyone wins. This textbook is for students, by students and came to fruition because students came together to support one another. I hope this textbook can be an example to you that as students, our voice is powerful when we join together to advocate for change.

There are many people that I need to thank for their roles in bringing this project to life. Firstly, thank you Dr. Kathy-Sarah Focsaneanu for all your contributions to this project. Thank you for listening to students, believing in students and for continually being devoted to improving yourself as an educator for your students. Thank you Dr. Alison Flynn and Dr. Mélanie Brunet for helping mold the early vision of the project. Thank you Mahdi Zeghal and Jessica Thomas for taking that vision and creating the framework to bring it to life. Thank you Dr. Alain St-Amant for supporting this project in every possible way, even with all the roles that you play pulling you in every direction. Thank you Geneviève O'Keefe, Nathan Biniam, Derek Fraser-Halberg, Dr. Brandi West, Leanne Trepanier and Debbie Pinos for all your outstanding contributions that have made this project possible. Lastly, and certainly not least, thank you to the Thinking Ahead Giving Back Chartwell fund, the Science Students' Association, the Faculty of Science and the Office of the Associate Vice-President Student Affairs for investing in students and funding the adaptation of this open textbook.

I sincerely hope you enjoy the textbook... as much as a textbook can be enjoyed!

Happy learning,

Kevin Roy

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CHAPTER 1

1.1 - THE MOLE

The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains but by the quantity of each type of atom or ion. For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for the amount of substances, the *mole*, which remains indispensable in modern chemical science.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A **mole** is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. To further illustrate this idea, 1 pair = 2 things, 1 dozen = 12 things, and 1 mole = 6.022×10^{23} things. One Latin connotation for the word "mole" is "large mass" or "bulk," which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named **Avogadro's number (N_A)** or the Avogadro constant in honour of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of "per mole," a conveniently rounded version being 6.022×10^{23}/mol.

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The **molar mass** of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see Figure 1.1.1).

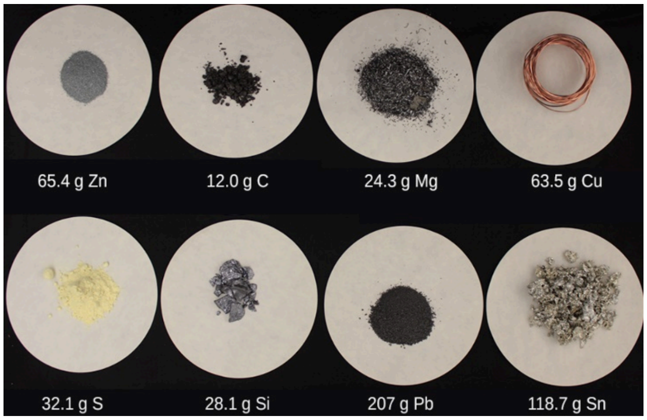


Figure 1.1.1. Each sample contains 6.022 × 10^{23} atoms —1.00 mol of atoms. Top row (from left to right): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. Bottom row (from left to right): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in atomic mass units, or amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure 1.1.2).

Figure 1.1.2. Each sample contains 6.02 × 10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

Table 1.1.1. Quantitative properties of selected elements.

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022 × 1023
H	1.008	1.008	6.022 × 1023
O	16.00	16.00	6.022 × 1023
Na	22.99	22.99	6.022 × 1023
Cl	35.45	33.45	6.022 × 1023

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see Figure 1.1.3). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.

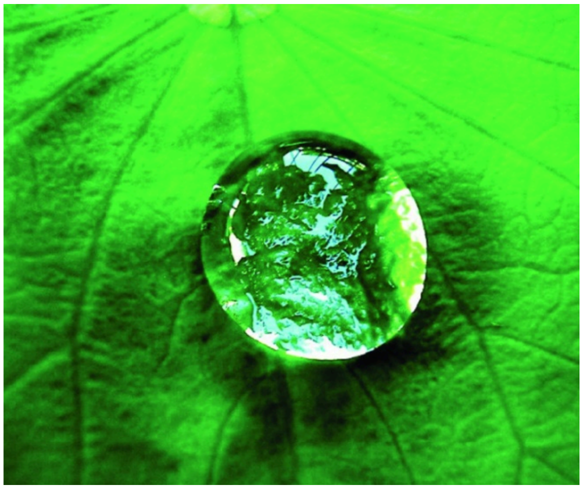


Figure 1.1.3. The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: "tanakawho"/Wikimedia commons)

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate the number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

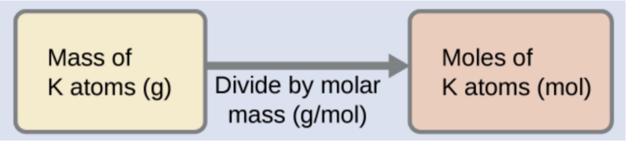
Example 1.1.1 – Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated daily average requirement for dietary potassium is 4.7 g. What is the estimated daily average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth of the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit (not the dimension, as the same variable is being expressed using a different method but essentially expressing the same data) "g" cancels and the answer has units of "mol:"

$$4.7\ g\ K\left(\frac{mol\ K}{39.10\ g}\right) = 0.12\ mol\ K$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation since it is a bit greater than 0.1 mol.

Check Your Learning 1.1.1 – Deriving Moles from Grams for an Element

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Answer

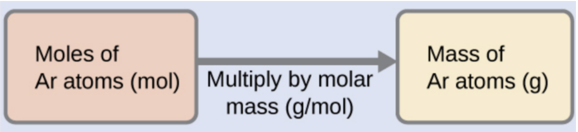
n = 0.360 mol

Example 1.1.2 – Deriving Grams from Moles for an Element

A litre of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a litre of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth ($\sim 10^{-3}$) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4}\ mol\ Ar \left(\frac{39.95\ g}{mol\ Ar}\right) = 0.037\ g\ Ar$$

The result is in agreement with our expectations, around 0.04 g Ar.

Check Your Learning 1.1.2 – Deriving Grams from Moles for an Element

What is the mass of 2.561 mol of gold?

Answer

m = 504.4 g

Example 1.1.3 – Deriving Number of Atoms from Mass for an Element

Copper is commonly used to fabricate electrical wire (Figure 1.1.4.). How many copper atoms are in 5.00 g of copper wire?

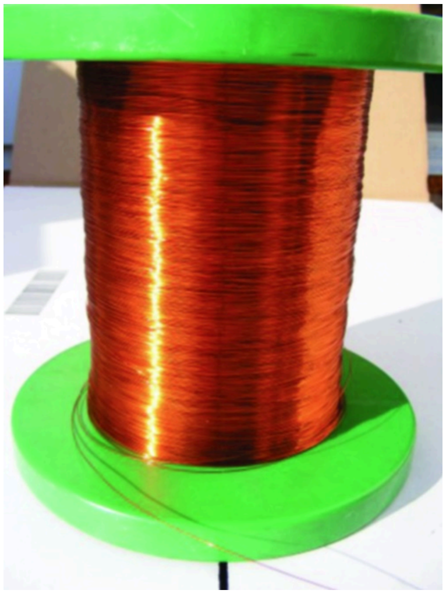
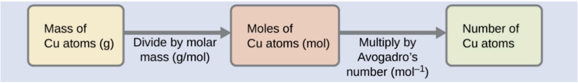


Figure 1.1.4. Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to the number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth of the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

$$5.00\ g\ Cu \cdot \left(\frac{mol\ Cu}{63.55\ g}\right) \cdot \left(\frac{6.022\times 10^{23}\ atoms}{mol}\right) = 4.74 \times 10^{22}\ atoms\ of\ copper$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

Check Your Learning 1.1.3 – Deriving Number of Atoms from Mass for an Element

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Answer

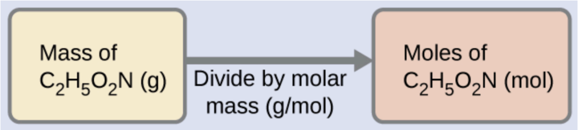
4.586×10^{22} Au atoms

Example 1.1.4 – Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element:



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	**Quantity (mol element / mol compound)**	**Molar Mass (g / mol element)**	**Subtotal (**
C	2	x 12.01	= 24.02
H	5	x 1.008	= 5.040
O	2	x 16.00	= 32.00
N	1	x 14.01	= 14.01
		Molecular mass (g / mol compound)	**75.07**

The provided mass of glycine (~28 g) is a bit more than one-third of the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

$$28.35\ g\ glycine \cdot \left(\frac{mol\ glycine}{75.07\ g}\right) = 0.378\ mol\ glycine$$

This result is consistent with our rough estimate.

Check Your Learning 1.1.4 – Deriving Moles from Grams for a Compound

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer

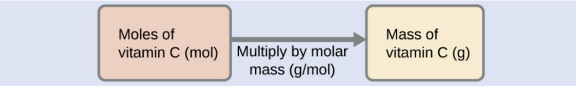
$n = 0.073$ mol

Example 1.1.5 – Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation, we get:

$$1.42 \times 10^{-4}\ mol\ vitamin\ C \left(\frac{176.124\ g}{mol\ vitamin\ C}\right) = 0.0250\ g\ vitamin\ C$$

This is consistent with the anticipated result.

Check Your Learning 1.1.5 – Deriving Grams from Moles for a Compound

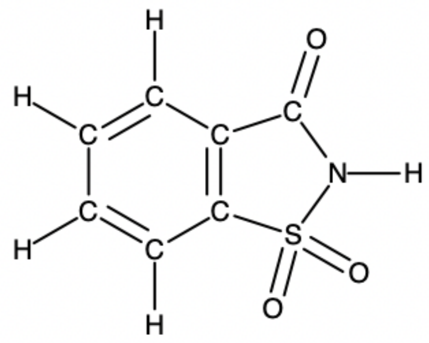
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer

$m = 14.2$ g

Example 1.1.6 – Deriving the Number of Atoms and Molecules from the Mass of a Compound

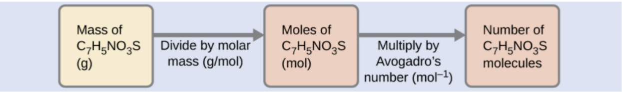
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0 mg (0.0400 g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of a compound is computed by first deriving the number of moles, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ g\ C_7H_5NO_3S \left(\frac{mol\ C_7H_5NO_3S}{183.18\ g\ C_7H_5NO_3S}\right)\left(\frac{6.022 \times 10^{23}\ C_7H_5NO_3S\ molecules}{1\ mol\ C_7H_5NO_3S}\right) = 1.31 \times 10^{20}\ C_7H_5NO_3S\ molecules$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31 \times 10^{23}\ C_7H_5NO_3S\ molecules \left(\frac{7\ C\ atoms}{1\ C_7H_5NO_3\ molecule}\right) = 9.20 \times 10^{21}\ atoms$$

Check Your Learning 1.1.6 – Deriving the Number of Atoms and Molecules from the Mass of a Compound

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Answer

9.545×10^{22} molecules C_4H_{10}; 9.545×10^{23} atoms H

Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's **percent composition**, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%\,H = \frac{mass\ H}{mass\ compound} \times 100\%$$

$$\%\,C = \frac{mass\ C}{mass\ compound} \times 100\%$$

If the analysis of a 10.0 g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%\,H = \frac{2.5\ g\ H}{10.0\ g\ compound} \times 100\% = 25\%$$

$$\%\,C = \frac{7.5\ g\ C}{10.0\ g\ compound} \times 100\% = 75\%$$

A chemical compound is the combination of two or more elements. If you are studying a chemical compound, you may want to find the percent composition of a certain element within that chemical compound. The equation for percent composition is:

$$\%\ composition = \frac{Mass\ of\ element}{Molecular\ mass} \times 100\%$$

Equation 1.1.1. Percent composition.

If you want to know the percent composition of the elements in a compound, follow these steps:

Steps to Solve:

1. Find the molar mass of all the elements in the compound in grams per mole.

2. Find the molecular mass of the entire compound.

3. Divide the component's molar mass by the entire molecular mass.

4. You will now have a number between 0 and 1. Multiply it by 100 to get percent composition!

Tips for solving:

The compounds will always add up to 100%, so in a binary compound, you can find the percent of the first element, then subtract from 100% to determine the percent of the second element.

If using a calculator, you can store the overall molar mass to a variable such as "A". This will speed up calculations, and reduce typographical errors.

These steps are outlined in Example 1.1.7.

Example 1.1.7 – Percent Composition

Find the percent composition of phosphorus pentachloride (PCl_5).

Solution

Find the molar mass of all elements in the compound:

$$P = 30.974\ g$$

$$Cl = 5(35.453\ g) = 177.265\ g$$

Find the molecular mass:

$$PCl_5 = 30.974\ g + 177.265\ g = 208.239\ g$$

Divide each molar mass by the molecular mass and multiply by 100:

$$P = \frac{30.974\ g}{208.239\ g} \times 100\% = 14.87\%$$

$$Cl = \frac{177.265\ g}{208.239\ g} \times 100\% = 85.13\%$$

Therefore, phosphorus pentachloride is 14.87% P and 85.13% Cl by mass.

Check Your Learning 1.1.7 – Percent Composition

Find the percent composition of hydrochloric acid (HCl).

Answer

HCl is 2.76 % hydrogen and 97.24 % chlorine by mass.

★ Questions

1. Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2. Which has the largest number of molecules? Explain why.

2. Which contains the greatest mass of oxygen: 0.75 mol of ethanol (C_2H_5OH), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why.

3. How are the molecular mass and the molar mass of a compound similar and how are they different?

4. Calculate the molar mass (in g/mol) of each of the following:

(a) The anesthetic halothane, $C_2HBrClF_3$

(b) The herbicide paraquat, $C_{12}H_{14}N_2Cl_2$

(c) Caffeine, $C_8H_{10}N_4O_2$

(d) Urea, $CO(NH_2)_2$

(e) A typical soap, $C_{17}H_{35}CO_2Na$

5. Determine the number of moles of the compound and the number of moles (in mol) of each type of atom in each of the following:

(a) 25.0 g of propylene, C_3H_6

(b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$

(c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)

(d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$

(e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

6. Determine the mass (in grams) of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) 1.6×10^{-3} mol Na_2SO_4

(d) 6.854×10^{3} mol glucose, $C_6H_{12}O_6$

(e) 2.86 mol $Co(NH_3)_6Cl_3$

★★ Questions

7. One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

8. A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

9. Which of the following represents the least number of molecules?

(a) 20.0 g of H_2O (18.02 g/mol)

(b) 77.0 g of CH_4 (16.06 g/mol)

(c) 68.0 g of CaH_2 (42.09 g/mol)

(d) 100.0 g of N_2O (44.02 g/mol)

(e) 84.0 g of HF (20.01 g/mol)

Answers

1. Since there is 1 mole of each, they all have the same number of molecules.

2. Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

3. The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

4. (a) 197.382 g/mol; (b) 257.163 g/mol; (c) 194.193 g/mol; (d) 60.056 g/mol; (e) 306.464 g/mol

5. (a) 0.594 mol C_3H_6, 1.78 mol C, 3.56 mol H; (b) 4.08×10^{-5} mol $C_2H_5NO_2$, 8.15×10^{-5} mol C, 2.04×10^{-4} mol H, 4.08×10^{-5} mol N, 8.15×10^{-5} mol O; (c) 40.06 mol $C_{13}H_{16}N_2O_4F$, 520.79 mol C, 640.98 mol H, 80.12 mol N, 160.24 mol O, 40.06 mol F; (d) 0.81 mol $Cu_4(AsO_3)_2(CH_3CO_2)_2$, 0.81 mol Cu, 0.40 mol As, 2.02 mol O, 0.81 mol C, 1.21 mol H; (e) 1.80×10^{-3} mol $C_6H_4(CO_2H)(CO_2CH_3)$, 0.016 mol C, 0.014 H, 7.22×10^{-3} mol O

6. (a) 0.819 g; (b) 307 g; (c) 0.23 g; (d) 1.235×10^{6} g (1235 kg); (e) 765 g

7. 0.107 mol Na, 6.43×10^{22} atoms Na

8. 0.865 servings, or about 1 serving.

9. (a) 20.0 g H_2O represents the least number of molecules since it has the least number of moles.

1.2 – DETERMINING CHEMICAL FORMULAE

Now that you've obtained a good understanding of 1) the basis of chemical bonding in ionic and covalent compounds and 2) the mole concept and its relation to masses and molar masses, we can now integrate this knowledge in this section. Here, we begin our discussion on expressing and understanding the chemical formulas for compounds and using these formulas to write out balanced chemical equations.

Chemical Formulas

A **molecular formula** is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The **structural formula** for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure 1.2.1). The use of lines in structural formulas represent covalent bonds that hold the atoms together (by the sharing of electrons between atoms) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

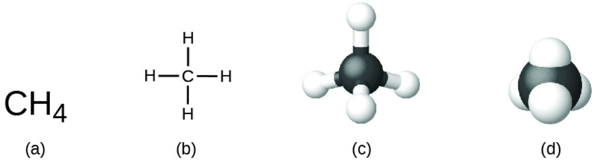


Figure 1.2.1. A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms (e.g. carbon and the noble gases including helium, neon, and argon), some exist naturally as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. In other words, in their natural standard states, oxygen and nitrogen exist as diatomic molecules and very rarely as single oxygen or nitrogen atoms in their natural standard state. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 1.2.2).

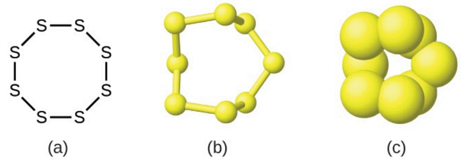


Figure 1.2.2. A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is extremely important to note as you move forward in chemistry that a subscript following a symbol and a number in front of a symbol do not represent the same thing. For example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are covalently bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 1.2.3).

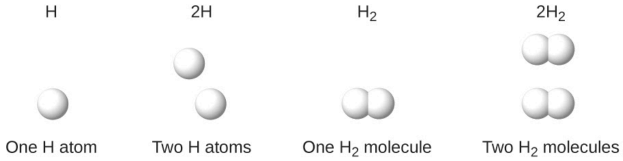


Figure 1.2.3. The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

It's important to note that the **empirical formula** is not the same as the molecular formula (that was discussed at the beginning of this section); in a molecular formula, the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound whereas the empirical formula only gives the *simplest whole-number ratio of atoms/ions* in the compound.

Empirical formulas are often a first step in determining a molecular formula. The following example highlights the difference between empirical formulas and molecular formulas. A molecule, on the other hand, is made up of atoms covalently bonded together to form a single discrete unit. If we take a molecule of ethyne, C_2H_2, and multiply it's formula by 2 to get C_4H_4, we no longer get ethyne but cyclobutadiene, C_4H_4, which has a different structure and different properties (Figure 1.2.4).

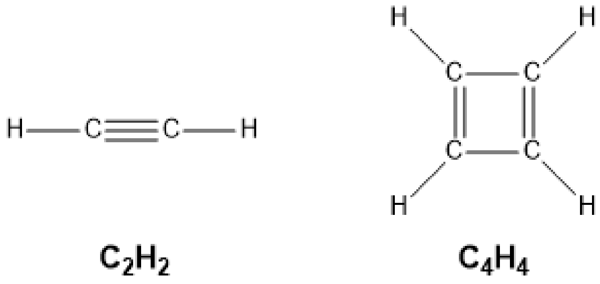


Figure 1.2.4. Structural formula for ethyne, C_2H_2, and cyclobutadiene, C_4H_4.

As we'll discuss in greater detail in the final chapter on molecular bonding, ionic compounds form lattice structures that always have a whole-number multiple of repeating formula units. As long as we add whole number multiples of formula units of the same ionic compound, we could hypothetically have an infinitely large lattice structure. Hence, for the sake of simplicity, we use the empirical formula to describe the simplest ratio of ions. Table salt is denoted as NaCl since in any lattice structure of any size, whether you have 10 Na^+ and 10 Cl^- or 1000 Na^+ and 1000 Cl^-, there must always be one sodium cation (Na^+) for each chloride anion (Cl^-). Even if we write $Na_{10}Cl_{10}$, it will always be simplified to NaCl, and the identity of the compound remains the same.

In sum, the empirical formulas give you the ratio of different elements in a molecule and molecular formulas give you the actual number of atoms in the molecule.

Let's look at another example: the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure 1.2.5) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O (but remember: this formula doesn't denote the actual structure of the molecule – CH_2O corresponds to formaldehyde, which is used for preserving biological specimens and even bodies of deceased persons!). Note that a molecular formula is always a whole-number multiple of an empirical formula.

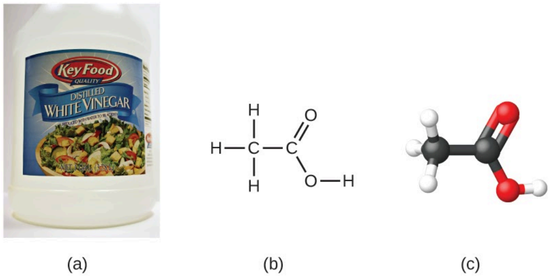


Figure 1.2.5. (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Determination of Empirical Formulas

The most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, we must keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. To accomplish this, we can use molar masses to convert the mass of each element to a number of moles. We then consider the moles of each element relative to each other, converting these numbers into a whole-number ratio that can be used to derive the empirical formula of the substance.

Consider a sample of a compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.17\ g\ C \times \frac{1\ mol\ C}{12.01\ g\ C} = 0.142\ mol\ C$$

$$0.287\ g\ H \times \frac{1\ mol\ H}{1.008\ g\ H} = 0.284\ mol\ H$$

Thus, we can accurately represent this compound with the formula $C_{0.142}H_{0.248}$. Of course, per accepted convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$C_{\frac{0.142}{0.142}}H_{\frac{0.248}{0.142}}\ or\ CH_2$$

(Recall that subscripts of "1" are not written but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2. This may or not be the compound's *molecular formula* as well; however, we would need additional information to make that determination (as discussed later in this section).

Consider as another example a sample of a compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$Cl_{0.150}O_{0.525} = Cl_{\frac{0.150}{0.150}}O_{\frac{0.525}{0.150}} = ClO_{3.5}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, we must multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure 1.2.6 outlines this procedure in flow-chart fashion for a substance containing elements A and X.

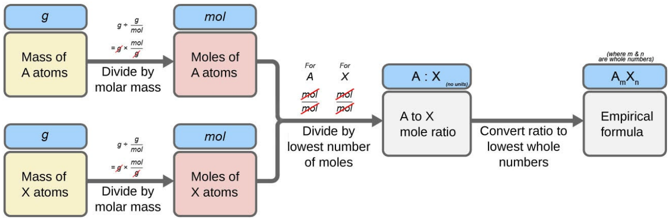


Figure 1.2.6. The empirical formula of a compound can be derived from the masses of all elements in the sample.

Example 1.2.1 – Determining a Compound's Empirical Formula from the Masses of Its Elements

A sample of the black mineral hematite (Figure 1.2.7), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?

Figure 1.2.7. Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

Solution

For this problem, we are given the mass in grams of each element. Begin by finding the moles of each:

$$34.97\ g\ Fe\left(\frac{mol\ Fe}{55.85\ g}\right) = 0.6261\ mol\ Fe$$

$$15.03\ g\ O\left(\frac{mol\ O}{16.00\ g}\right) = 0.9394\ mol\ O$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.000\ mol\ Fe$$

$$\frac{0.9394}{0.6261} = 1.500\ mol\ O$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

$$2(Fe_1O_{1.5}) = Fe_2O_3$$

The empirical formula is Fe_2O_3.

Check Your Learning 1.2.1 – Determining a Compound's Empirical Formula from the Masses of Its Elements

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Answer

N_2O_5

Deriving Empirical Formulas from Percent Composition

With regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

Example 1.2.2 – Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29 % C and 72.71% O (Figure 1.2.8). What is the empirical formula for this gas?

Figure 1.2.8. An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the "percentage" unit, whose name is derived from the Latin phrase *per centum* meaning "by the hundred." Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\%\ C = \frac{27.29\ g\ C}{100\ g\ compound}$$

$$72.71\%\ O = \frac{72.71\ g\ O}{100\ g\ compound}$$

The molar amounts of carbon and hydrogen in a 100 g sample are calculated by dividing each element's mass by its molar mass:

$$27.29\ g\ C\left(\frac{mol\ C}{12.01\ g}\right) = 2.272\ mol\ C$$

$$72.71\ g\ O\left(\frac{mol\ O}{16.00\ g}\right) = 4.544\ mol\ O$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272\ mol\ C}{2.272} = 1$$

$$\frac{4.544\ mol\ O}{2.272} = 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

Check Your Learning 1.2.2 – Determining an Empirical Formula from Percent Composition

What is the empirical formula of a compound containing 40.0 % C, 6.71 % H, and 53.28 % O?

Answer

CH_2O

Deriving Empirical Formulas from Combustion Analysis

The elemental composition of hydrocarbons (organic compounds consisting entirely of carbon and hydrogen atoms) and related compounds containing C, H and other elements may be determined via **combustion analysis**. In combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas (O_2), resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product (Figure 1.2.9). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.

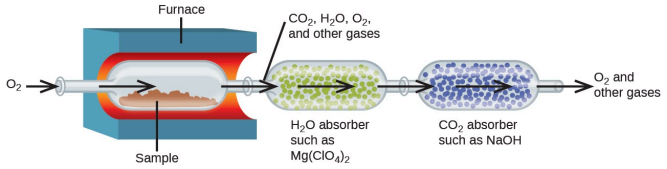


Figure 1.2.9. This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

Combustion Analysis Problems – Underlying Assumption

You'll frequently come across combustion analysis problems as you practice determining empirical (and later on molecular) formulas from data obtained on the collection of combustion products. For all combustion analysis problems you come across, always keep in the back of your mind the following underlying assumption – *the combustion reaction is complete*. In other words, assume that there are no other side-products produced in the combustion reaction; only the product compounds mentioned in the problem are formed. Therefore, for hydrocarbons and compounds containing C, H, and O, this means that only gaseous carbon dioxide and water are produced. For other compounds containing other elements such as S and N, you can expect to see other compounds form as well, including SO_2 and NO_2; these will be mentioned in the question to help you determine the identity of the unknown compound.

If it were an incomplete combustion, side-products such as carbon monoxide, carbon (soot), and nitric oxide (NO) would form, making it extremely difficult, if not impossible, to determine the composition of elements and identity of your sample.

Example 1.2.3 – Combustion Analysis

Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. Combustion analysis of a 0.00126 g sample of polyethylene yields 0.00394 g of CO_2 and 0.00161 g of H_2O. What is the empirical formula of polyethylene?

Solution

The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide (CO_2), and all the hydrogen in the sample is converted to water, H_2O (note that the sample, being a hydrocarbon, is represented by C_xH_y):

$$C_xH_y\,(s) + \text{excess}\ O_2\,(g)\ \ ?\ \ x\,CO_2\,(g) + y\ 2H_2O\,(g)$$

Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts *x* and *y* are needed.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively. With these molar amounts, the empirical formula for the compound may be written as described in the previous chapter of this text. An outline of this approach is given in the following flow chart:

$$mol\ C = 0.00394\ g\ CO_2 \times \frac{1\ mol\ CO_2}{44.01\ g} \times \frac{1\ mol\ C}{1\ mol\ CO_2} = 8.95 \times 10^{-5}\ mol\ C$$

$$mol\ H = 0.00161\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.02\ g} \times \frac{2\ mol\ H}{1\ mol\ H_2O} = 1.79 \times 10^{-4}\ mol\ H$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is:

$$\frac{mol\ H}{mol\ C} = \frac{1.79 \times 10^{-4}\ mol\ H}{8.95 \times 10^{-5}\ mol\ C} = \frac{2\ mol\ H}{1\ mol\ C}$$

The empirical formula for polyethylene is CH_2.

Check Your Learning 1.2.3 – Combustion Analysis

A 0.00215 g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of CO_2 and 0.00148 g of H_2O by combustion analysis. What is the empirical formula for polystyrene?

Answer

CH

Example 1.2.4 – Combustion Analysis

Salicylic acid is used to make aspirin. It contains only carbon, oxygen, and hydrogen. Combustion of a 43.5 mg sample of this compound produced 97.1 mg of CO_2 and 17.0 mg of H_2O. What is the empirical formula of salicylic acid?

Answer

The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide (CO_2), all the hydrogen in the sample is converted to water (H_2O), and all of the oxygen is converted to either carbon dioxide or water.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively:

$$mol\ C = 0.0971\ g\ CO_2 \times \frac{1\ mol\ CO_2}{44.01\ g/mol} \times \frac{1\ mol\ C}{1\ mol\ CO_2} = 2.21 \times 10^{-3}\ mol\ C$$

$$mol\ H = 0.0170\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.02\ g/mol} \times \frac{2\ mol\ H}{1\ mol\ H_2O} = 1.89 \times 10^{-3}\ mol\ H$$

Knowing the molar masses of carbon and hydrogen, we can convert these molar values into masses; consequently, these will represent the mass of carbon and hydrogen in the sample:

$$mass\ C = 2.21 \times 10^{-3}\ mol \times \frac{12.01\ g}{1\ mol\ C} = 0.0265\ g$$

$$mass\ H = 1.89 \times 10^{-3}\ mol \times \frac{1.008\ g}{1\ mol\ H} = 0.00190\ g$$

If we know the mass of the sample and the mass of carbon and hydrogen individually in the sample, the remaining mass must be oxygen, for which we find its molar amount:

$$m_O = m_{sample} - m_C - m_H$$

$$m_O = 0.0435\ g - 0.0265\ g - 0.00190\ g$$

$$m_{\text{O}} = 0.0151\ \text{g}$$

$$mol\ O = 0.0151\ g \times \frac{1\ mol\ O}{16.00\ g} = 9.44 \times 10^{-4} mol\ O$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The C-to-O and H-to-O molar ratio is

$$\frac{mol\ C}{mol\ O} = \frac{2.21 \times 10^{-3}\ mol\ C}{9.44 \times 10^{-4}\ mol\ O} \approx \frac{2.33\ mol\ C}{1\ mol\ O} \rightarrow \times 3 \rightarrow \frac{7\ mol\ C}{3\ mol\ O}$$

$$\frac{mol\ H}{mol\ O} = \frac{1.89 \times 10^{-3}\ mol\ H}{9.44 \times 10^{-4}\ mol\ O} \approx \frac{2.00\ mol\ H}{1\ mol\ O} \rightarrow \times 3 \rightarrow \frac{6\ mol\ H}{3\ mol\ O}$$

Hence, the empirical formula for salicylic acid is $C_7H_6O_3$.

Check Your Learning 1.2.5 – Combustion Analysis

A 2.0714 g sample containing carbon, hydrogen, and oxygen was burned in a combustion analysis apparatus; 1.928 g of H_2O and 4.709 g of CO_2 were produced. Separately, the molar mass of the sample was found to be 116.16 g/mol. Determine the empirical formula of the sample.

Answer

Empirical formula: C_3H_6O

Determination of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the box below). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

In Case You're Interested...Mass Spectrometry

Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 1.2.10):

the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons

the cations pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball-bearing rolling past a magnet is deflected to a lesser extent than that of a small steel BB)

the ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a mass spectrum) is made – the height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio.

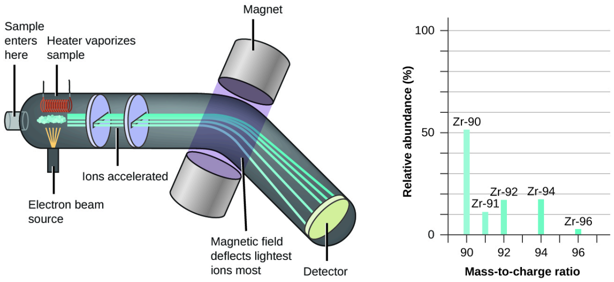


Figure 1.2.10. Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.

For more information you can check out the following videos (podcast video #1; educational video #2 from the Royal Society of Chemistry) that explain and animate the process of mass spectrometry.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its **empirical formula mass**. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule, which we designate as *n*:

$$\frac{molecular\ or\ molar\ mass\ (amu\ or\ g/mol)}{empirical\ formula\ mass\ (amu\ or\ g/mol)} = n\ formula\ units/molecule$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by *n*, as shown by the generic empirical formula A_xB_y:

$$(A_xB_y)_n = A_{nx}B_{ny}$$

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180\ amu/molecule}{30\ \frac{amu}{formula\ unit}} = 6\ formula\ units/molecule$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(CH_2O)_6 = C_6H_{12}O_6$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

Example 1.2.4 – Determination of Molecular Formulas

Nicotine (Figure 1.2.11), an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02 % C, 8.710 % H, and 17.27 % N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

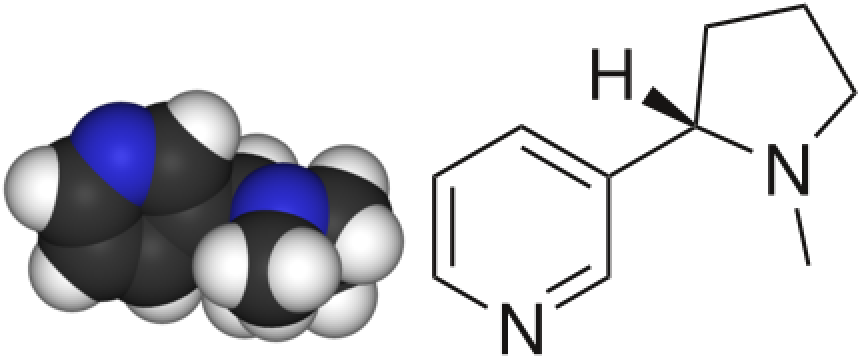


Figure 1.2.11. 2D and 3D structure of nicotine

Solution

Determining the molecular formula from the provided data will require a comparison of the compound’s empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound’s empirical formula. Assuming a convenient, a 100 g sample of nicotine yields the following molar amounts of its elements:

$$(74.02\ g\ C)\left(\frac{1\ mol\ C}{12.01\ g\ C}\right) = 6.163\ mol\ C$$

$$(8.710\ g\ H)\left(\frac{1\ mol\ H}{1.01\ g\ H}\right) = 8.624\ mol\ H$$

$$(17.27\ g\ N)\left(\frac{1\ mol\ N}{14.01\ g\ N}\right) = 1.233\ mol\ N$$

Next, we calculate the molar ratios of these elements relative to the least abundant element, N.

$$6.163\ mol\ C/\ 1.233\ mol\ N = 5$$

$$8.264\ mol\ H/\ 1.233\ mol\ N = 7$$

$$1.233\ mol\ N/\ 1.233\ mol\ N = 1$$

$$\frac{1.233}{1.233} = 1.000\ mol\ N$$

$$\frac{6.163}{1.233} = 4.998\ mol\ C$$

$$\frac{8.624}{1.233} = 6.994\ mol\ H$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

We calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57\ g\ nicotine}{0.2500\ mol\ nicotine} = \frac{162.3\ g}{mol}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3\ g/mol}{81.13\ \frac{g}{formula\ unit}} = 2\ formula\ units/molecule$$

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2$$

Check Your Learning 1.2.6 – Determination of Molecular Formulas

A sample of a chromium compound has a molar mass of 76.09 g/mol. Elemental analysis of the compound shows that it contains 47.37 % carbon, 10.59 % hydrogen, and 42.04 % oxygen. What is the molecular formula of the compound?

Answer

Cr_2O_3

It is important to be aware that it may be possible for the same atoms to be arranged in different ways. Compounds with the same molecular formula may have different atom-to-atom bonding and, therefore different structures and properties, these are known as **isomers**. You'll learn much more about different types of isomers in CHM 1321 (Organic Chemistry I).

Writing and Balancing Chemical Equations

When atoms gain or lose electrons to yield ions or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas (as we've seen so far in this section) that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change/reaction involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure 1.2.12, with space-filling molecular models shown in the lower half of the figure.

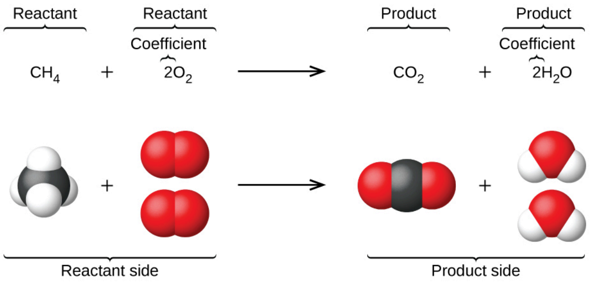


Figure 1.2.12. The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called **reactants**, and their formulas are placed on the left side of the equation.

2. The substances generated by the reaction are called **products**, and their formulas are placed on the right side of the equation.

3. Plus signs (+) separate individual reactant and product formulas, and an arrow (?) separates the reactant and product (left and right) sides of the equation.

4. The relative numbers of reactant and product species are represented by **coefficients** (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure 1.2.13). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

One methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.

One dozen methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.

One mole of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

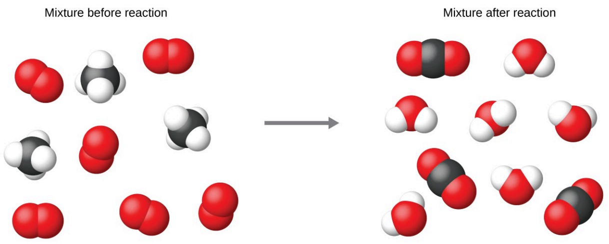


Figure 1.2.13. Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

Balancing Equations

The chemical equation is called balanced when an equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction of Figure 1.2.12, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is:

$$\left(1\ CO_2\ molecule \times \frac{2\ O\ atoms}{CO_2\ molecule}\right) + \left(2\ H_2O\ molecules \times \frac{1\ O\ atom}{H_2O\ molecule}\right)$$
$$= 4\ O\ atoms$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$CH_4 + 2O_2 \text{ ? } CO_2 + 2H_2O$$

Element	Reactants	Products	Balanced?
C	1 x 1 = 1	1 x 1 = 1	1 = 1, yes
H	4 x 1 = 4	2 x 2 = 4	4 = 4, yes
O	2 x 2 = 4	(1 x 2) + (2 x 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example, the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$H_2O \rightarrow H_2 + O_2 \text{ (unbalanced)}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	1 x 2 = 2	1 x 2 = 2	2 = 2, yes
O	1 x 1 = 1	1 x 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2H_2O \rightarrow H_2 + O_2 \text{ (unbalanced)}$$

Element	Reactants	Products	Balanced?
H	2 x 2 = 4	1 x 2 = 2	4 ≠ 2, no
O	2 x 1 = 2	1 x 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2H_2O \rightarrow 2H_2 + O_2 \text{ (balanced)}$$

Element	Reactants	Products	Balanced?
H	2 x 2 = 4	2 x 2 = 4	4 = 4, yes
O	2 x 1 = 2	1 x 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the **balanced equation** is, therefore:

$$2H_2O \rightarrow 2H_2 + O_2$$

Example 1.2.5 – Balancing Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \rightarrow N_2O_5 \text{ (unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	1 x 2 = 2	1 x 2 = 2	2 = 2, yes
O	1 x 2 = 2	1 x 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$N_2 + 5O_2 \rightarrow 2N_2O_5 \text{ (unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 x 2 = 2	2 x 2 = 4	2 ≠ 4, no
O	5 x 2 = 10	2 x 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2N_2 + 5O_2 \rightarrow 2N_2O_5 \text{ (balanced)}$$

Element	Reactants	Products	Balanced?
N	2 x 2 = 4	2 x 2 = 4	4 = 4, yes
O	5 x 2 = 10	2 x 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Check Your Learning 1.2.7 – Balancing Equations

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer

$2NH_4NO_3$? $2N_2 + O_2 + 4H_2O$

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \rightarrow H_2O + CO_2 \text{ (unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \rightarrow 3H_2O + 2CO_2 \text{ (unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $^7/_2$, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \frac{7}{2}O_2 \rightarrow 3H_2O + 2CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2C_2H_6 + 7O_2 \rightarrow 6H_2O + 4CO_2$$

Finally with regard to balanced equations, recall that convention dictates the use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is indeed balanced:

$$3N_2 + 9H_2 \rightarrow 6NH_3$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Balancing Chemical Equations – Additional Practice

Balancing chemical equations is an extremely important and fundamental skill you'll need to master to succeed in general chemistry and many other chemistry-related courses.
This interactive tutorial lets you review and practice balancing some equations, as well as this link that generates chemical reactions for you to balance.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*). These notations are illustrated in the example equation here:

$$Na\,(s) + 2H_2O\,(l) \rightarrow 2NaOH\,(aq) + H_2\,(g)$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

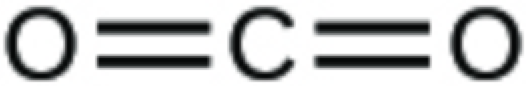
$$CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}$$

Other examples of these special conditions will be encountered in more depth in later chapters.

★ Questions

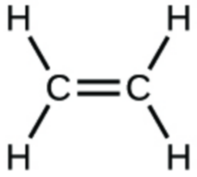
1. Write the molecular and empirical formulas of the following compounds

(a)

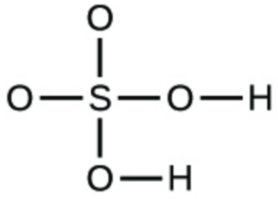


(b)

(c)



(d)



2. Open the Build a Molecule simulation and select the "Larger Molecules" tab. Select an appropriate atoms "Kit" to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the "Kit" to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on "3D" to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms in any way to make a different compound? If so, draw its structural formula and state its name.

(c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).

3. Calculate the following to four significant figures:

(a) the percent composition of ammonia, NH_3.

(b) the percent composition of photographic "hypo," $Na_2S_2O_3$.

(c) the percent of calcium ion in $Ca_3(PO_4)_2$.

★★ Questions

4. Determine the empirical formulas for compounds with the following percent compositions:

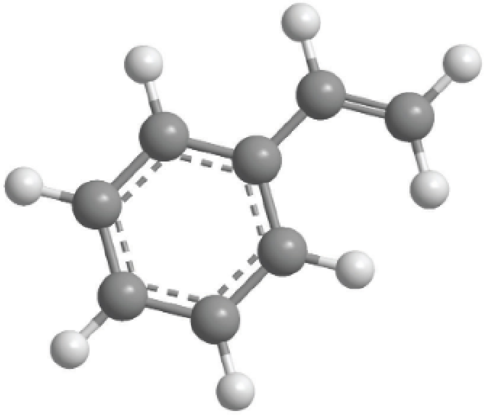
(a) 43.6 % phosphorus and 56.4 % oxygen

(b) 28.7 % K, 1.5 % H, 22.8 % P, and 47.0 % O

5. Dichloroethane, a compound that is often used for dry cleaning, contains carbon, hydrogen, and chlorine. It has a molar mass of 99 g/mol. Analysis of a sample shows that it contains 24.3 % carbon and 4.1 % hydrogen. What is its molecular formula?

6. A major textile dye manufacturer developed a new yellow dye. The dye has a percent composition of 75.95 % C, 17.72 % N, and 6.33 % H by mass with a molar mass of about 240 g/mol. Determine the molecular formula of the dye.

7. How many moles of CO_2 and H_2O will be produced by combustion analysis of 0.010 mol of styrene?



Styrene

8. Combustion of a 34.8 mg sample of benzaldehyde, which contains only carbon, hydrogen, and oxygen, produced 101 mg of CO_2 and 17.7 mg of H_2O.

(a) What was the mass of carbon and hydrogen in the sample?

(b) Assuming that the original sample contained only carbon, hydrogen, and oxygen, what was the mass of oxygen in the sample?

(c) What was the mass percentage of oxygen in the sample?

(d) What is the empirical formula of benzaldehyde?

(e) The molar mass of benzaldehyde is 106.12 g/mol. What is its molecular formula?

★ Questions (Part 2)

9. Balance the following equations:

(a) PCl_5 *(s)* + H_2O *(l)* → $POCl_3$ *(l)* + HCl *(aq)*

(b) Cu *(s)* + HNO_3 *(aq)* → $Cu(NO_3)_2$ *(aq)* + H_2O *(l)* + NO *(g)*

(c) H_2 *(g)* + I_2 *(s)* → HI *(s)*

(d) Fe *(s)* + O_2 *(g)* → Fe_2O_3 *(s)*

(e) Na *(s)* + H_2O *(l)* → NaOH *(aq)* + H_2 *(g)*

(f) $(NH_4)_2Cr_2O_7$ *(s)* → Cr_2O_3 *(s)* + N_2 *(g)* +H_2O *(g)*

(g) P_4 *(s)* + Cl_2 *(g)* → PCl_3 *(l)*

(h) $PtCl_4$ *(s)* → Pt *(s)* + Cl_2 *(g)*

10. Write a balanced molecular equation describing each of the following chemical reactions.

(a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.

(b) Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapour.

(c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.

(d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.

★★ Questions (Part 2)

11. A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

(a) The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.

(b) The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.

(c) Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.

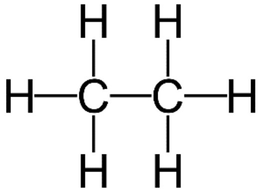
(d) The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.

(e) Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

Answers

1. (a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

2. (a) Ethane



(b) There are no other ways to arrange the atoms.

(c) n/a

3. (a) 17.8% H, 82.2% N; (b) 29.1% Na, 30.4% O, 40.6% S; (c) 38.8% Ca, 41.3% O, 20.0% P

4. (a) P_2O_5 (b) KH_2PO_4

5. $C_2H_4Cl_2$

6. $C_{15}H_{15}N_3$

7. Moles of CO_2: 0.08 mol CO_2, moles of H_2O: 0.04 mol H_2O

8. (a) 27.6 mg C and 1.98 mg H; (b) 5.2 mg O; (c) 15%; (d) C_7H_6O; (e) C_7H_6O

9. (a) $PCl_5\,(s) + H_2O\,(l) \rightarrow POCl_3\,(l) + 2\,HCl\,(aq)$

(b) $3\,Cu\,(s) + 8\,HNO_3\,(aq) \rightarrow 3\,Cu(NO_3)_2\,(aq) + 4\,H_2O\,(l) + 2\,NO\,(g)$

(c) $H_2\,(g) + I_2\,(s) \rightarrow 2\,HI\,(s)$

(d) $4\,Fe\,(s) + 3\,O_2\,(g) \rightarrow 2\,Fe_2O_3\,(s)$

(e) $2\,Na\,(s) + 2\,H_2O\,(l) \rightarrow 2\,NaOH\,(aq) + H_2\,(g)$

(f) $(NH_4)_2Cr_2O_7\,(s) \rightarrow Cr_2O_3\,(s) + N_2\,(g) + 4\,H_2O\,(g)$

(g) $P_4\,(s) + 6\,Cl_2\,(g) \rightarrow 4\,PCl_3\,(l)$

(h) $PtCl_4\,(s) \rightarrow Pt\,(s) + 2\,Cl_2\,(g)$

10. (a) $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$

(b) $2\,C_4H_{10}\,(g) + 13\,O_2\,(g) \rightarrow 8\,CO_2\,(g) + 10\,H_2O\,(g)$

(c) $MgCl_2\,(aq) + 2\,NaOH\,(aq) \rightarrow Mg(OH)_2\,(s) + 2\,NaCl\,(aq)$

(d) $2\,H_2O\,(g) + 2\,Na\,(s) \rightarrow 2\,NaOH\,(s) + H_2\,(g)$

11. (a) $CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$

(b) $CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(s)$

(c) $Ca(OH)_2\,(s) + MgCl_2\,(aq) \rightarrow Mg(OH)_2\,(s) + CaCl_2\,(aq)$

(d) $Mg(OH)_2 + 2HCl\,(aq) \rightarrow MgCl_2\,(aq) + H_2O\,(l)$

(e) $MgCl_2 \rightarrow Mg_2 + 2HCl\,(aq)$, Cathode: $Mg2+ + 2e^- \rightarrow Mg\,(s)$, Anode: $2Cl^-\,(aq) \rightarrow Cl_2\,(g) + 2e^-$

1.3 – REACTION STOICHIOMETRY

The Stoichiometry of Balanced Chemical Equations

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing the classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's **stoichiometry**, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Food preparation, for example, offers an appropriate comparison. A recipe for making eight pancakes calls for 1 cup pancake mix, ¾ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is:

1 cup mix + ¾ cup milk + 1 egg → 8 pancakes

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is:

$$24\ pancakes \times \frac{1\ egg}{8\ pancakes} = 3\ eggs$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. The coefficients in the balanced equation are used to derive **stoichiometric factors** that permit the computation of the desired quantity. To illustrate this idea, consider the production of ammonia by the reaction of hydrogen and nitrogen:

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

This equation shows ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\ NH_3\ molecules}{3\ H_2\ molecules}\ or\ \frac{2\ doz\ NH_3\ molecules}{3doz\ H_2\ molecules}\ ot\ \frac{2\ mol\ NH_3\ molecules}{3\ mol\ H_2\ molecules}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 1.3.1 – Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure 1.3.1)?

$$2\ Al + 3\ I_2 \rightarrow 2\ AlI_3$$

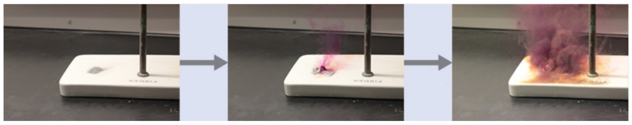
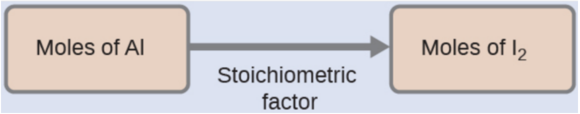


Figure 1.3.1. Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapour. (credit: modification of work by Mark Ott)

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is 3 mol I_2, 2 mol Al. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\begin{aligned} mol\ I_2 &= 0.429\ mol\ Al \times \frac{3\ mol\ I_2}{2\ mol\ Al} \\ &= 0.644\ mol\ I_2 \end{aligned}$$

Check Your Learning 1.3.1 – Moles of Reactant Required in a Reaction

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3\ Ca(OH)_2 + 2\ H_3PO_4$? $Ca_3(PO_4)_2 + 6\ H_2O$?

Answer

$n = 2.04$ mol

Example 1.3.2 – Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$$

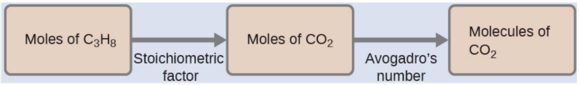
Solution

The approach here is the same as for the previous example, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require the use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3\ mol\ CO_2}{1\ mol\ C_3H_8}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75\ mol\ C_3H_8 \times \frac{3\ mol\ CO_2}{1\ mol\ C_3H_8} \times \frac{6.022 \times 10^{23}\ CO_2\ molecules}{mol\ CO_2}$$
$$= 1.4 \times 10^{24}\ CO_2\ molecules$$

Check Your Learning 1.3.2 – Number of Product Molecules Generated by a Reaction

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2\ NH_3 + CaSO_4 + 2\ H_2O$$

Answer

4.8×10^{24} NH_3 molecules

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

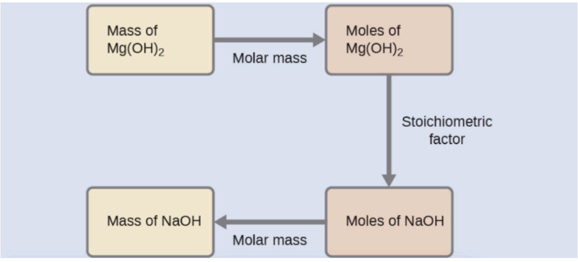
Example 1.3.3 – Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$MgCl_2\,(aq) + 2\ NaOH(aq) \rightarrow Mg(OH)_2\,(s) + 2\ NaCl\,(aq)$$

Solution

We must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in the following flow chart:



$$16\ g\ Mg(OH)_2 \times \frac{1\ mol\ Mg(OH)_2}{58.3\ g\ Mg(OH)_2} \times \frac{2\ mol\ NaOH}{1\ mol\ Mg(OH)_2} \times \frac{40.0\ g\ NaOH}{mol\ NaOH} = 22\ g\ NaOH$$

Check Your Learning 1.3.3 – Relating Masses of Reactants and Products

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\ Ga + 3\ O_2$? $2\ Ga_2O_3$.

Answer

$m = 39.0$ g

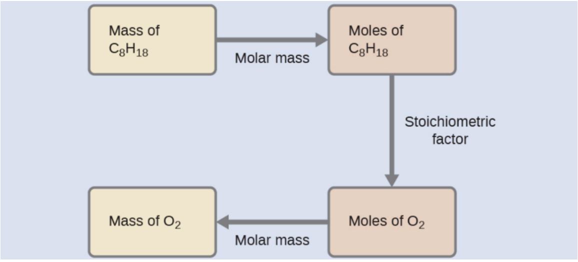
Example 1.3.4 – Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$$

Solution

The approach required here is the same as for the previous example, differing only in that the provided and requested masses are both for reactant species.



$$702\ g\ C_8H_{18} \times \frac{1\ mol\ C_8H_{18}}{114.23\ g\ C_8H_{18}} \times \frac{25\ mol\ O_2}{2\ mol\ C_8H_{18}} \times \frac{32.00\ g\ O_2}{mol\ O_2} = 2.46 \times 10^3\ g\ O_2$$

Check Your Learning 1.3.4 – Relating Masses of Reactants

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the following equation?

$$Fe_2O_3 + 3\ CO\ ?\ 2\ Fe + 3\ CO_2$$

Answer

$m = 13.22$ g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure 1.3.2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

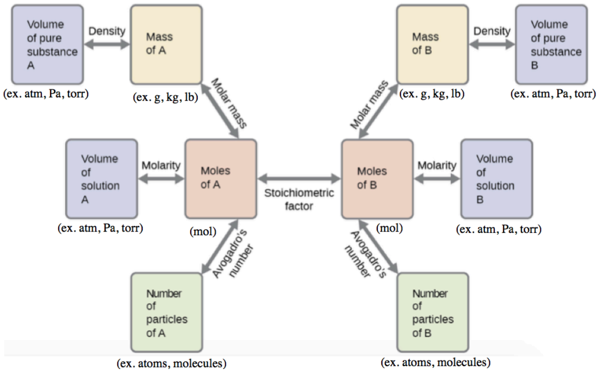


Figure 1.3.2. The flow chart depicts the various computational steps involved in most reaction stoichiometry calculations.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 1.3.3):

1 slice of cheese + 2 slices of bread → 1 sandwich

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread leftover. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

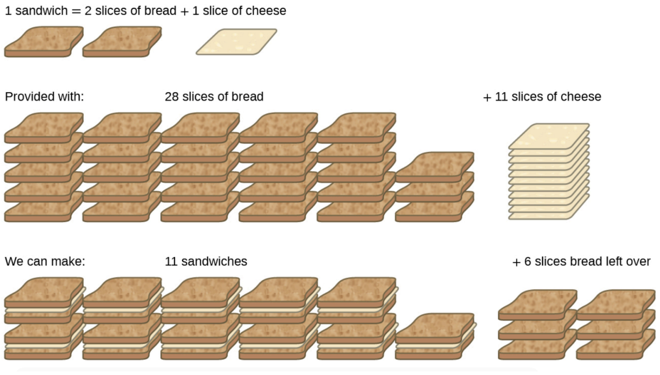


Figure 1.3.3. Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the **limiting reactant**, and the other substance is the **excess reactant**. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. The reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example in the previous paragraph, the complete reaction of the hydrogen would yield:

$$mol\ HCl\ produced = 3\ mol\ H_2 \times \frac{2\ mol\ HCl}{1\ mol\ H_2} = 6\ mol\ HCl$$

The complete reaction of the provided chlorine would produce:

$$mol\ HCl\ produced = 2\ mol\ Cl_2 \times \frac{2\ mol\ HCl}{1\ mol\ Cl_2} = 4\ mol\ HCl$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure 1.3.4).

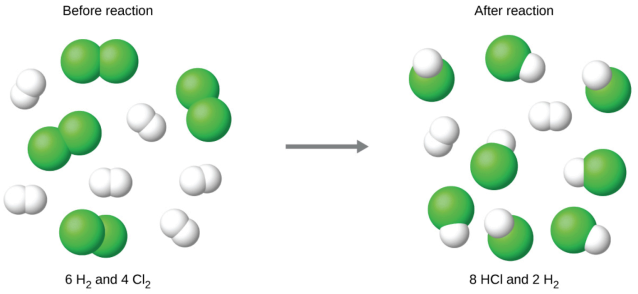


Figure 1.3.4. When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

Example 1.3.5 – Identifying the Limiting Reactant

Silicon nitride is a very hard and high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\ Si\ (s) + 2\ N_2\ (g) \rightarrow Si_3N_4\ (s)$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$mol\ Si = 2.00\ g\ Si \times \frac{1\ mol\ Si}{28.09\ g\ Si} = 0.0712\ mol\ Si$$

$$mol\ N_2 = 1.50\ g\ N_2 \times \frac{1\ mol\ N_2}{28.02\ g\ N_2} = 0.0535\ mol\ N_2$$

The provided Si: N_2 molar ratio is:

$$\frac{0.0712\ mol\ Si}{0.0535\ mol\ N_2} = \frac{1.33\ mol\ Si}{1\ mol\ N_2}$$

The stoichiometric Si: N_2 ratio is:

$$\frac{3\ mol\ Si}{2\ mol\ N_2} = \frac{1.5\ mol\ Si}{1\ mol\ N_2}$$

Comparing these ratios shows that Si is provided in a less-than stoichiometric amount, and so is the limiting reactant. Alternatively, compute the amount of product expected for the complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield:

$$mol\ Si_3N_4\ produced = 0.0712\ mol\ Si \times \frac{1\ mol\ Si_3N_4}{3\ mol\ Si} = 0.0237\ mol\ Si_3N_4$$

while the 0.0535 moles of nitrogen would produce:

$$mol\ Si_3N_4\ produced = 0.0535\ mol\ N_2 \times \frac{1\ mol\ Si_3N_4}{2\ mol\ N_2} = 0.0268\ mol\ Si_3N_4$$

Since silicon yields a lesser amount of product, it is the limiting reactant.

Check Your Learning 1.3.5 – Identifying the Limiting Reactant

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water? How much excess reagent remains once the reaction has gone to completion?

Answer

O_2 is the limiting reagent and 3.75 g of O_2 remains in excess.

Percent Yield

The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriately balanced chemical equation, is called the **theoretical yield** of the reaction. In practice, the amount of product obtained is called the **actual yield**, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete. Some products are difficult to collect without some loss, so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its **percent yield**:

$$percent\ yield = \frac{actual\ yield}{theoretical\ yield} \times 100\%$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when the percent yield is calculated.

Example 1.3.6 – Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

$$CuSO_4\,(aq) + Zn\,(s) \rightarrow Cu\,(s) + ZnSO_4\,(aq)$$

What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

$$1.274\ g\ CuSO_{4(aq)} \times \frac{1\ mol\ CuSO_{4(aq)}}{159.62\ g\ CuSO_{4(aq)}} \times \frac{1\ mol\ Cu}{1\ mol\ CuSO_{4(aq)}} \times \frac{63.55\ g\ Cu}{1\ mol\ Cu} = 0.5072\ g\ Cu$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be:

$$percent\ yield = \frac{actual\ yield}{theoretical\ yield} \times 100\%$$

$$percent\ yield = \frac{0.392\ g\ Cu}{0.5072\ g\ Cu} \times 100\%$$

$$percent\ yield = 77.3\%$$

Check Your Learning 1.3.6 – Calculation of Percent Yield

You use the following reaction to produce Freon (CF_2Cl_2) from CCl_4 and HF:

$$CCl_4 + 2\ HF \rightarrow CF_2Cl_2 + 2\ HCl$$

This reaction has a yield of 75 %. Knowing this, how much HF (in kg) is needed to produce 10 kg of Freon?

Answer

m = 4.40 kg

★ Questions

1. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:

(a) The number of moles (in mol) and the mass of chlorine (in grams), Cl_2, required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.

(b) The number of moles (in mol) and the mass (in grams) of oxygen formed by the decomposition of 1.252 g of mercury (II) oxide.

(c) The number of moles (in mol) and the mass (in grams) of sodium nitrate, $NaNO_3$, required to produce 128 g of oxygen. ($NaNO_2$ is the other product.)

(d) The number of moles (in mol) and the mass (in grams) of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.

(e) The number of moles (in mol) and the mass (in grams) of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)

(f) The number of moles and the mass of $C_2H_4Br_2$ formed by the reaction of 12.85 g of ethene with an excess of Br_2.

2. I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation:

$$2\ CuCl_2 + 4\ KI \rightarrow 2\ CuI + 4\ KCl + I_2$$

(a) How many molecules of I_2 are produced?

(b) What mass of I_2 is produced (in grams)?

3. Silver is often extracted from ores such as $K[Ag(CN)_2]$ and then recovered by the reaction:

$$2\ K[Ag(CN)_2]\ (aq) + Zn\ (s) \rightarrow 2\ Ag\ (s) + Zn(CN)_2\ (aq) + 2\ KCN\ (aq)$$

(a) How many molecules of $Zn(CN)_2$ are produced by the reaction of 35.27 g of $K[Ag(CN)_2]$?

(b) What mass of $Zn(CN)_2$ is produced (in grams)?

4. Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO_2, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much (mass, in grams) SiO_2 is required to produce 3.00 kg of SiC.

★★ Questions

5. In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

6. A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(s)$$

7. Freon-12, CCl_2F_2, is prepared from CCl_4 by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of CCl_2F_2 from 32.9 g of CCl_4. Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield.

8. Citric acid, $C_6H_8O_7$, a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. What mass of citric acid (in grams) is produced from exactly 1 metric ton (1.000×10^3 kg) of sucrose if the yield is 92.30 %? The equation representing this reaction is:

$$C_{12}H_{22}O_{11} + H_2O + 3\,O_2 \rightarrow 2\,C_6H_8O_7 + 4\,H_2O$$

9. Outline the steps needed to determine the limiting reactant when 30.0 g of propane, C_3H_8, is burned with 75.0 g of oxygen. Determine the limiting reactant.

10. What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation:

$$Li + N_2 \rightarrow Li_3N \text{ (unbalanced)}$$

11. Uranium can be isolated from its ores by dissolving it as $UO_2(NO_3)_2$, then separating it as solid $UO_2(C_2O_4)\cdot 3H_2O$. Addition of 0.4031 g of sodium oxalate, $Na_2C_2O_4$, to a solution containing 1.481 g of uranyl nitrate, $UO_2(NO_3)_2$, yields 1.073 g of solid $UO_2(C_2O_4)\cdot 3H_2O$.

$$Na_2C_2O_4 + UO_2(NO_3)_2 + 3\,H_2O \rightarrow UO_2(C_2O_4)\cdot 3H_2O + 2\,NaNO_3$$

Determine the limiting reactant and the percent yield of this reaction.

12. The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.

(a) What is the limiting reactant when 0.200 mol of P_4 and 0.200 mol of O_2 react according to:

$$P_4 + 5\,O_2 \text{ ? } P_4O_{10}$$

(b) Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

Answers

1. (a) $Cl_2\,(g) + 2\,Na\,(s) \rightarrow 2\,NaCl\,(aq)$, 0.435 mol Na, 0.217 mol Cl_2, 15.4 g Cl_2

(b) $2\,HgO\,(s) \rightarrow 2\,Hg\,(s) + O_2\,(g)$, 0.005780 mol HgO, 2.890×10^{-3} mol O_2, 9.248×10^{-2} g O_2

(c) $2\,NaNO_3\,(s) \rightarrow O_2\,(g) + 2\,NaNO_2\,(s)$, 8.00 mol $NaNO_3$, 6.8×10^2 g $NaNO_3$

(d) $C\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$, 1665 mol CO_2, 73.3 kg CO_2

(e) $CuCO_3\,(s) \rightarrow CuO\,(s) + CO_2\,(g)$, 18.86 mol CuO, 2.330 kg $CuCO_3$

(f) $C_2H_4Br_2 \rightarrow C_2H_4 + Br_2$, 0.4580 mol $C_2H_4Br_2$, 86.05 g $C_2H_4Br_2$

2. (a) 1.28×10^{23} molecules; (b) 26.9 g

3. (a) 5.337×10^{22} molecules; (b) 10.41 g $Zn(CN)_2$

4. 4.50 kg, SiO_2, $SiO_2 + 3\,C \rightarrow SiC + 2\,CO$

5. Yes – recognize that there is a 2:1 mole ratio of HNO_3 : Na_2CO_3 in the balanced chemical equation for this neutralization reaction. Hence, we need at least 2 moles of Na_2CO_3 for every 1 mole of HNO_3 to neutralize all of the acid. The given quantities (in kg) correspond to molar quantities of 39.67 mol HNO_3 : 18.87 mol Na_2CO_3; this is a 2:1 mole ratio (2X more sodium carbonate than acid). Therefore, sufficient Na_2CO_3 was used to neutralize all of the acid.

6. 92.0 %

7. Percent yield = 48.3 %, g CCl_4 ? mol CCl_4 ? mol CCl_2F_2 ? g CCl_2F_2

8. 1.03 tonnes

9. (1) Determine the balanced chemical equation: $C_3H_6 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$; (2) Using the given masses and the reactants' molar mass, find the moles for both propane and oxygen; (3) With the moles found in the previous step, find the mole of carbon dioxide with the mole ratios based on the balanced chemical equation; (4) With these two values, determine the mass of carbon dioxide. The reactant which results in the smallest mass of carbon dioxide is the limiting reactant. In this case it is **oxygen**.

10. Li is the limiting reactant

11. $Na_2C_2O_4$ is the limiting reactant. percent yield = 86.6 %

12. (a) O_2 is the limiting reactant; (b) 88 %

1.4 – SOLUTION STOICHIOMETRY

Molarity

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a solid mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (see Figure 1.4.1.). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.

Figure 1.4.1. Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

Solutions

We have previously defined solutions as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce some of the basic properties of solutions.

The relative amount of a given solution component is known as its **concentration**. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the **solvent** and may be viewed as the medium in which the other components are dispersed, or **dissolved**. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an **aqueous solution**.

A **solute** is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as **dilute** (of relatively low concentration) and **concentrated** (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications. **Molarity (*M*)** is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 litre (1 L) of the solution:

$$M = \frac{mol\ solute}{L\ solution}$$

Example 1.4.1 – Calculating Molar Concentrations

A 355 mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of the solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$M = \frac{mol\ solute}{L\ solution} = \frac{0.133\ mol}{355\ mL \times \frac{1\ L}{1000\ mL}} = 0.375\ M$$

Check Your Learning 1.4.1 – Calculating Molar Concentrations

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Answer

M = 0.05 mol/L

Example 1.4.2 – Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from the previous example?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in the previous example, 0.375 mol/L:

$$M = \frac{mol\ solute}{L\ solution}$$

$$mol\ solute = M \times L\ solution$$

$$mol\ solute = 0.375\ \frac{mol\ sugar}{L} \times (10\ mL \cdot \frac{1\ L}{1000\ mL}) = 0.004\ mol\ sugar$$

Check Your Learning 1.4.2 – Deriving Moles and Volumes from Molar Concentrations

What volume (mL) of the sweetened tea described in the previous example contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

V = 80 mL

Example 1.4.3 – Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 1.4.2) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500 L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?

Figure 1.4.2. Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute's molar mass to obtain the amount of solute in moles:

First, find the number of moles of the solute:

$$25.2\ g \times \frac{1\ mol\ CH_3CO_2H}{60.052\ g\ CH_3CO_2H} = 0.420\ g\ CH_3CO_2H$$

Next, we find the molarity:

$$M = \frac{mol\ solute}{L\ solution}$$

$$M = \frac{0.420\ mol\ solute}{0.500\ L\ solution}$$

$$M = 0.839\ M$$

In other words:

$$M = \frac{mol\ solute}{L\ solution} = 0.839\ M$$

$$M = \frac{0.839\ mol\ solute}{1.00\ L\ solution}$$

Check Your Learning 1.4.3 – Calculating Molar Concentrations from the Mass of Solute

Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer

0.674 mol/L

Example 1.4.4 – Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30 mol/L solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in the second example:

$$M = \frac{mol\ solute}{L\ solution}$$

$$mol\ solute = 5.30\ \frac{mol\ NaCl}{L} \times 0.250\ L = 1.325\ mol\ NaCl$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325\ mol\ NaCl \times \frac{58.44\ g\ NaCl}{mol\ NaCl} = 77.4\ g\ NaCl$$

Check Your Learning 1.4.4 – Determining the Mass of Solute in a Given Volume of Solution

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200 mol/L solution of calcium chloride?

Answer

5.55 g $CaCl_2$

When performing calculations stepwise, as in the previous example, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In the previous example, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (see the next example). This eliminates intermediate steps so that only the final result is rounded.

Example 1.4.5 – Determining the Volume of Solution Containing a Given Mass of Solute

In the Example 1.4.3, we found the typical concentration of vinegar to be 0.839 mol/L. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$g\ solute \times \frac{mol\ solute}{g\ solute} = mol\ solute$$

Then, use the molarity of the solution to calculate the volume of the solution containing this molar amount of solute:

$$mol\ solute \times \frac{L\ solute}{mol\ solute} = L\ solute$$

Combining these two steps into one yields:

$$g\ solute \times \frac{mol\ solute}{g\ solute} \times \frac{L\ solution}{mol\ solute} = L\ solution$$

$$75.6\ g\ CH_3CO_2H \left(\frac{mol\ CH_3CO_2H}{60.05\ g}\right)\left(\frac{L\ solution}{0.839\ mol\ CH_3CO_2H}\right) = 1.50\ L\ solution$$

Check Your Learning 1.4.5 – Determining the Volume of Solution Containing a Given Mass of Solute

What volume of a 1.50 mol/L KBr solution contains 66.0 g KBr?

Answer

V = 0.370 L

Other Units for Solution Concentrations

Mass Percentage

Earlier in this chapter, we introduced percent composition as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The **mass percentage** of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$mass\ percentage = \frac{mass\ of\ component}{mass\ of\ solution} \times 100\%$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent. When expressing mass percent, you can use any measurement system you choose, but the same units must be used on both the top and the bottom of the equation and the denominator is always 100 (for example: g/100 g, oz/100 oz).

Mass percentage is also referred to by similar names such as *percent mass, percent weight, weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including % mass, % weight, and *(w/w)%*. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle (Figure 1.4.3) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4 %. Therefore, a 100.0 g sample of bleach would contain 7.4 g of NaOCl.

Figure 1.4.3. Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4 % NaOCl by mass.

Example 1.4.6 – Calculation of Percent by Mass

A 5.0 g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1 %. Substituting the given masses into the equation defining mass percentage yields:

$$\%\ glucose = \frac{3.75\ mg\ glucose \times \frac{1\ g}{1000\ mg}}{5.0\ g\ spinal\ fluid} \times 100\% = 0.075\%$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 mol/L).

Check Your Learning 1.4.6 – Calculation of Percent by Mass

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04 mol/L solution of CH_3OH to 500.0 mL?

Answer

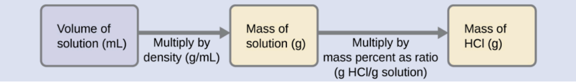
14.8 %

Example 1.4.7 – Calculations using Mass Percentage

"Concentrated" hydrochloric acid is an aqueous solution of 37.2 % HCl by mass that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

Solution

The HCl concentration is near 40%, so a 100 g portion of this solution would contain about 40 g of HCl. Since the solution density isn't greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or 5 × 40 = 200 g. In order to derive the mass of solute in a solution from its mass percentage, we need to know the corresponding mass of the solution. Using the solution density given, we can convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flow chart:



For proper unit cancellation, the 0.500 L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/100 g solution:

$$500\ mL\ solution\left(\frac{1.19\ g\ solution}{mL\ solution}\right)\left(\frac{37.2\ g\ HCl}{100\ g\ solution}\right) = 221\ g\ HCl$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

Check Your Learning 1.4.7 – Calculations using Mass Percentage

What volume of concentrated HCl solution contains 125 g of HCl?

Answer

V = 282 mL

Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a **volume percentage**, % vol or *(v/v)%*:

$$volume\ percentage = \frac{volume\ solute}{volume\ solution} \times 100\%$$

Example 1.4.8 – Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70 % by volume aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

Per the definition of volume percentage, the isopropanol volume is 70 % of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$(355\ mL\ solution)\left(\frac{70\ mL\ isopropyl\ alcohol}{100\ mL\ solution}\right)\left(\frac{0.785\ g\ isopropyl\ alcohol}{1\ mL\ isopropyl\ alcohol}\right)$$
$$= 195\ g\ isopropyl\ alcohol$$

Check Your Learning 1.4.8 – Calculations using Volume Percentage

Wine is approximately 12 % ethanol (CH_3CH_2OH) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

Answer

n = 1.5 mol ethanol

Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A **mass-volume percent** is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, a physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (*m/v*), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood (Figure 1.4.4).

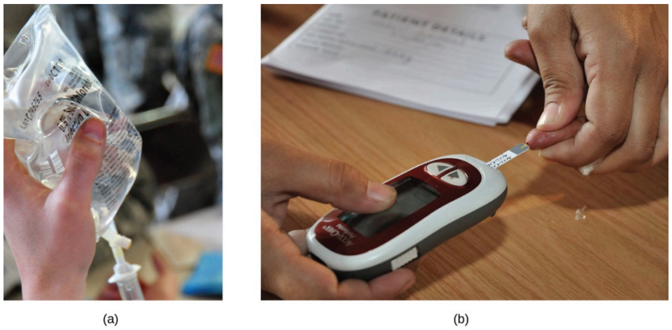


Figure 1.4.4. “Mixed” mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (*m/v*). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by “The National Guard”/Flickr; credit b: modification of work by Biswarup Ganguly)

Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as **parts per million (ppm)** or **parts per billion (ppb)**. The units, pm and ppb, can also be defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$ppm = \frac{mass\ solute}{mass\ solution} \times 10^6\ ppm$$

$$ppb = \frac{mass\ solute}{mass\ solution} \times 10^9\ ppb$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the Environmental Protection Agency (EPA) has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure 1.4.5).

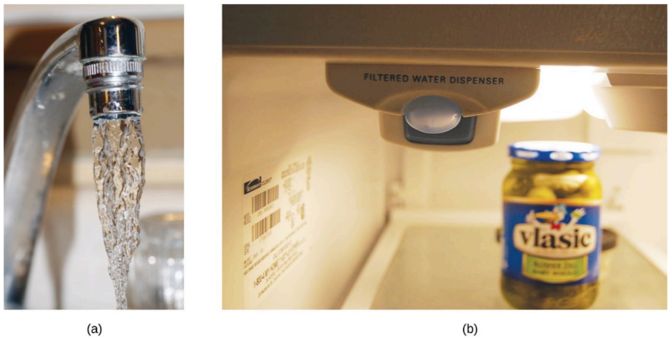


Figure 1.4.5. (a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons)

Example 1.4.9 – Calculation of Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

$$15\ ppb \times \frac{1\ ppm}{10^3\ ppb} = 0.015\ ppm$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$ppb = \frac{mass\ solute}{mass\ solution} \times 10^9\ ppb$$

$$mass\ solute = \frac{ppb\ \times\ mass\ solution}{10^9\ ppb}$$

$$mass\ solute = \frac{15\ ppb\ \times\ 300\ mL \times \frac{1.00\ g}{mL}}{10^9\ ppb} = 4.5 \times 10^{-6} g$$

Finally, convert this mass to the requested unit of micrograms:

$$4.5 \times 10^{-6} g = \frac{1\ \mu g}{10^{-6}\ g} = 4.5\ \mu g$$

Check Your Learning 1.4.9 – Calculation of Parts per Million and Parts per Billion Concentrations

(a) Your tap water contains 4.0 ppm fluoride. A conspiracy website says fluoride is dangerous and you can be poisoned if you consume more than 5.0 grams of it. If you drink 6 glasses (each glass is 0.40 L) of tap water per day, how long until you consume 5.0 grams of fluoride (assuming it NEVER leaves your body?).

(b) A 50.0 g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Answer

a. 520 days

b. 9.6 ppm, 9600 ppb

Molality

A final way to express the concentration of a solution is by its molality. The **molality (*b*)** of a solution is the moles of solute divided by the kilograms of solvent. A solution that contains 1.0 mol of NaCl dissolved into 1.0 kg of water is a “one-molal” solution of sodium chloride. The symbol for molality is a lower-case *b* written in italics.

$$Molality\ (b) = \frac{moles\ of\ solute}{kilograms\ of\ solvent} = \frac{mol}{kg}$$

Molality differs from molarity only in the denominator. While molarity is based on the litres of solution, molality is based on the kilograms of solvent. Concentrations expressed in molality are used when studying the properties of solutions related to vapour pressure and temperature changes. Molality is used because its value does not change with changes in temperature. The volume of a solution, on the other hand, is slightly dependent upon temperature.

Example 1.4.10 – Molality

Determine the molality of a solution prepared by dissolving 28.60 g of glucose ($C_6H_{12}O_6$) into 250 g of water.

Solution

Convert grams of glucose to moles and divide by the mass of the water in kilograms:

$$28.60\ g\ C_6H_{12}O_6 \times \frac{1\ mol\ C_6H_{12}O_6}{180.18\ g\ C_6H_{12}O_6} = 0.1587\ mol\ C_6H_{12}O_6$$

$$\frac{0.1587\ mol\ C_6H_{12}O_6}{0.250\ kg\ H_2O} = 0.635\ mol/kg\ C_6H_{12}O_6$$

The answer represents the moles of glucose per kilogram of water and has three significant figures.

Molality and molarity are closely related in value for dilute aqueous solutions because the density of those solutions is relatively close to 1.0 g/mL. This means that 1.0 L of solution has nearly a mass of 1.0 kg. As the solution becomes more concentrated, its density will not be as close to 1.0 g/mL and the molality value will be different than the molarity. For solutions with solvents other than water, the molality will be very different than the molarity. Make sure that you are paying attention to which quantity is being used in a given problem.

Water as a Universal Solvent

Water is dubbed a *universal solvent* because it dissolves many substances due to strong interactions between water molecules and those of other substances. Entropy is another driving force for a liquid to dissolve or mix with other substances (just know for now that entropy describes matter and/or energy dispersal within a system or the measure of the *disorder* of a system). Mixing increases disorder or entropy. You will learn more about entropy in CHM2131/CHM2132.

Hydrophobic effect and hydrophilic effect

Because of its high dipole moment and ability to donate and accept protons for hydrogen bonding, water is an excellent solvent for polar substances and electrolytes, which consist of ions. Molecules that strongly interact with or love water molecules are **hydrophilic**, due to hydrogen bonding, polar-ionic or polar-polar attractions. Nonpolar molecules that do not mix with water are **hydrophobic** or **lipophilic** because they tend to dissolve in oil. Large molecules such as proteins and fatty acids that have hydrophilic and hydrophobic portions are **amphipathic** or **amphiphilic**. Water molecules strongly intermingle with hydrophilic portions by means of dipole-dipole interaction or hydrogen bonding. This will be examined in detail in CHM1321.

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 1.4.6).

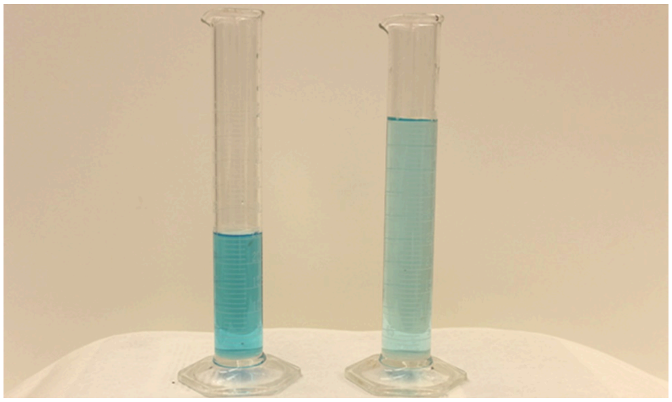


Figure 1.4.6. Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott)

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, we can achieve a particular concentration. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, these pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents (Figure 1.4.7).

Figure 1.4.7. A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of $KMnO_4$ in a flask. (credit: modification of work by Mark Ott)

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the molar amount of solute in a solution (n) is equal to the product of the solution's molarity (M) and its volume in litres (L):

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1 L_1$$

$$n_2 = M_2 L_2$$

where the subscripts "1" and "2" refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution,* $n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1 L_1 = M_2 L_2$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and litres as the unit of volume, other units of concentration and volume are more commonly used. The dilution equation is often written in the more general form:

$$C_1 V_1 = C_2 V_2$$

where C and V are concentration is expressed in moles/litre and volume is litres, respectively.

Example 1.4.11 – Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00 mol/L solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution's concentration to be less than one-half of 5 mol/L. We will compare this ballpark estimate to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850\ L \times 5.00\ \frac{mol}{L}}{1.80\ L} = 2.36\ M$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 mol/L).

Check Your Learning 1.4.11 – Determining the Concentration of a Diluted Solution

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04 mol/L solution of CH_3OH to 500.0 mL?

Answer

0.102 mol/L CH_3OH

Example 1.4.12 – Volume of a Diluted Solution

What volume of 0.12 mol/L HBr can be prepared from 11 mL (0.011 L) of 0.45 mol/L HBr?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 mol/L) is slightly more than one-fourth of the original concentration (0.45 mol/L), we would expect the volume of the diluted solution to be roughly four times the original volume, around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\ M)(0.011\ L)}{(0.12\ M)}$$

$$V_2 = 0.041\ L$$

The volume of the 0.12 mol/L solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

Check Your Learning 1.4.10 – Volume of a Diluted Solution

A laboratory experiment calls for 0.125 mol/L HNO_3. What volume of 0.125 mol/L HNO_3 can be prepared from 0.250 L of 1.88 mol/L HNO_3?

Answer

V = 3.76 L

Example 1.4.13 – Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 mol/L KOH is required to prepare 5.00 L of 0.100 mol/L KOH?

Solution

We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 mol/L is roughly one-sixteenth that of the stock solution (1.59 mol/L), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 litres. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\ M)(5.00\ L)}{(1.59\ M)}$$

$$V_1 = 0.314\ L$$

Thus, we would need 0.314 L of the 1.59 mol/L solution to prepare the desired solution. This result is consistent with our rough estimate.

Check Your Learning 1.4.11 – Volume of a Concentrated Solution Needed for Dilution

What volume of a 0.575 mol/L solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00 mol/L glucose solution?

Answer

$V = 0.261$ L

Molecular, Complete Ionic, and Net Ionic Equations

So far, we have looked only at molecular equations. These are the balanced reaction equations where we have accounted for all the atoms involved in the reaction. For some reactions, this isn't the whole story. In the cases where we have ionic compounds dissolved in water, we need to go one step further.

Let us consider the **precipitation reaction** for the formation of barium sulfate. **Precipitation** is a process in which a homogeneous solution reacts to form a solid product (known as the precipitate) The complete chemical equation for this reaction can be written to describe what happens, and such an equation is useful in making chemical calculations:

$$\underbrace{\mathrm{BaCl_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\,NaCl(aq)}}_{\text{Complete Chemical Equation}}$$

However, the complete chemical equation does not really represent the microscopic particles (that is, the ions) present in the solution. Thus we might write below the **complete ionic equation,** where the aqueous salts are written as their individual ions:

$$\underbrace{\mathrm{Ba^{2+}(aq)} + \overbrace{\mathrm{2\,Cl^-(aq)}}^{\text{spectator}} + \overbrace{\mathrm{2\,Na^+(aq)}}^{\text{spectator}} + \mathrm{SO_4^{2-}(aq) \longrightarrow BaSO_4(s)} + \overbrace{\mathrm{2\,Na^+(aq)}}^{\text{spectator}} + \overbrace{\mathrm{Cl^-(aq)}}^{\text{spectator}}}_{\text{Complete Ionic Equation}}$$

The complete ionic equation is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behaviour of ions, not the specific compound from which they came. A precipitate of $BaSO_4$*(s)* will form when *any* solution containing Ba^{2+}*(aq)* is mixed with *any* solution containing SO_4^{2-} *(aq)* (provided concentrations are not extremely small). This happens independently of the Cl^- *(aq)* and Na^+ *(aq)* ions in the complete ionic equation. These ions are called **spectator ions** because they do not participate in the reaction. When we want to emphasize the independent behaviour of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of $BaSO_4$, the net ionic equation is”

$$\underbrace{Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)}_{\text{Net Ionic Equation}}$$

Example 1.4.14 – AgCl Precipitation

When a solution of $AgNO_3$ is added to a solution of $CaCl_2$, insoluble AgCl precipitates. Write three equations (complete chemical equation, complete ionic equation, and net ionic equation) that describe this process.

Solution

Complete Chemical Equation:

$$2\,AgNO_3\,(aq) + CaCl_2\,(aq) \rightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)$$

The proper states and formulas of all products are written and the chemical equation is balanced.

Complete Ionic Equation:

$$2\,Ag^+\,(aq) + 2\,NO_3^-\,(aq) + Ca^{2+}\,(aq) + 2\,Cl^-\,(aq) \rightarrow 2\,AgCl\,(s) + Ca^{2+}\,(aq) + 2\,NO_3^-\,(aq)$$

AgCl is a solid so it does not break up into ions in solution.

Net Ionic Equation:

$$Ag^+\,(aq) + Cl^-\,(aq) \rightarrow AgCl\,(s)$$

All spectator ions are removed.

Check Your Learning 1.4.12 – AgCl Precipitation

Write balanced net ionic equations to describe a reaction that may occur when K_2CO_3 and $SrCl_2$ are mixed.

Answer

$$Sr^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow SrCO_3\,(s)$$

Example 1.4.15 – Combining Na_2SO_4 and NH_4I

Write a balanced net ionic equation to describe any reaction which occurs when the solutions of Na_2SO_4 and NH_4I are mixed.

Solution

Complete Chemical Equation:

$$Na_2SO_4\,(aq) + NH_4I_2\,(aq) \rightarrow 2\,NaI\,(aq) + (NH_4)_2SO_4\,(aq)$$

Both products are aqueous so there is no net ionic equation that can be written.

Check Your Learning 1.4.13 – Combining Na_2SO_4 and NH_4I

Write balanced net ionic equations to describe a reaction which may occur when $FeSO_4$ $Ba(NO_3)_2$ are mixed.

Answer

$$Ba^{2+}\,(aq) + SO_4^{\ 2-}\,(aq) \rightarrow BaSO_4\,(s)$$

The occurrence or nonoccurrence of precipitates can be used to detect the presence or absence of various species in solution. A $BaCl_2$ solution, for instance, is often used as a test for the presence of $SO_4^{\ 2-}$ ions. There are several insoluble salts of Ba, but they all dissolve in dilute acid except for $BaSO_4$. Thus, if $BaCl_2$ solution is added to an unknown solution that has previously been acidified, the occurrence of a white precipitate is proof of the presence of the $SO_4^{\ 2-}$ ion.

$AgNO_3$ solutions are often used in a similar way to test for halide ions. If an $AgNO_3$ solution is added to an acidified unknown solution, a white precipitate indicates the presence of Cl^- ions, a cream-coloured precipitate indicates the presence of Br^- ions, and a yellow precipitate indicates the presence of I^- ions (Figure 1.4.8). Further tests can then be made to see whether perhaps a mixture of these ions is present. When $AgNO_3$ is added to tap water, a white precipitate is almost always formed. The Cl^- ions in tap water usually come from the Cl_2 which is added to municipal water supplies to kill microorganisms.

Figure 1.4.8. The three common silver halide precipitates: AgI, AgBr and AgCl (left to right). The silver halides precipitate out of solution, but often form suspensions before settling. Image used with permission (CC BY-SA 3.0; Cychr).

Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose, it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

★ Questions

1. Determine the molarity for each of the following solutions:

(a) 0.444 mol of $CoCl_2$ in 0.654 L of solution

(b) 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution

(c) 0.2074 g of calcium hydroxide, $Ca(OH)_2$, in 40.00 mL of solution

(d) 10.5 kg of $Na_2SO_4{\cdot}10H_2O$ in 18.60 L of solution

(e) 7.0×10^{-3} mol of I_2 in 100.0 mL of solution

(f) 1.8×10^{4} mg of HCl in 0.075 L of solution

2. What is the mass of the solute in 0.500 L of 0.30 *M* glucose, $C_6H_{12}O_6$, used for intravenous injection? Outline the steps necessary to answer the question.

3. Calculate the number of moles and the mass of the solute in each of the following solutions:

(a) 2.00 L of 18.5 mol/L H_2SO_4, concentrated sulfuric acid

(b) 100.0 mL of 3.8×10^{-5} mol/L NaCN, the minimum lethal concentration of sodium cyanide in blood serum

(c) 5.50 L of 13.3 mol/L H_2CO, the formaldehyde used to "fix" tissue samples

(d) 325 mL of 1.8×10^{-6} mol/L $FeSO_4$, the minimum concentration of iron sulfate detectable by taste in drinking water

4. What is the molarity of $KMnO_4$ in a solution of 0.0908 g of $KMnO_4$ in 0.500 L of solution? Outline the steps necessary to answer the question.

5. Calculate the molarity of each of the following solutions:

(a) 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum

(b) 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia

(c) 1.49 kg of isopropyl alcohol, C_3H_7OH, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol

(d) 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20 °C

6. There is about 1.0 g of calcium, as Ca^{2+}, in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?

7. A 9.00 g sample contains 45.0 mg of dissolved sugar. What is the percent by mass of sugar in this solution?

★★ Questions

8. A cleaning solution is 4% by mass sodium hypochlorite (bleach). If you use 70 g of cleaning solution to clean your bathroom, how much bleach was used?

9. Your beer is 7% alcohol by volume. How much pure alcohol did you actually drink if your bottle contains 7 fl oz and you have had two and a half bottles?

10. You mix 73 µL of loading dye with 1000 µL of DNA. How much loading dye is there in the solution by volume percent.

11. Your blood sugar reading is 0.2% (*m/v*). How many grams of sugar are in your body (assuming you contain 5.1 L of blood)?

12. Suppose the vinegar you use is 0.76 mol/L acetic acid (CH_3COOH). What is the concentration of your vinegar in ppm?

13. Suppose you mix 50 mL $CoCl_2$ in 0.654 L of solution. What is the concentration of the resulting mixture in ppb?

14. You add 3.6 g of H_2SO_4 to 10.0 g of water. What is the molality of this solution?

15. You have 1 L of saline solution (NaCl) at 0.15 mol/L. What is the molality of the solution if NaCl has a density of 2.16 g/cm^3 (hint: 1 cm^3 = 1 mL)?

16. If 4.12 L of a 0.850 mol/L H_3PO_4 solution is diluted to a volume of 10.00 L, what is the concentration of the resulting solution?

★ Questions (Part 2)

17. What is the final concentration of the solution produced when 225.5 mL of a 0.09988 mol/L solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

18. An experiment in a general chemistry laboratory calls for a 2.00 mol/L solution of HCl. How many mL of 11.9 mol/L HCl would be required to make 250 mL of 2.00 mol/L HCl?

19. Write out the complete chemical equation, complete ionic equation, and net ionic equation for the mixture of $Ca(NO_3)_2$ *(aq)* and H_3PO_4 *(aq)*.

20. Write out the complete chemical equation, complete ionic equation, and net ionic equation for the mixture of KCl *(aq)* and $Pb(NO_3)_2$ *(aq)*.

21. Indicate what type, or types, of reaction each of the following represents:

(a) Ca *(s)* + Br_2 *(l)* ? $CaBr_2$ *(s)*

(b) $Ca(OH)_2$ *(aq)* + 2 HBr *(aq)* ? $CaBr_2$ *(aq)* + 2 H_2O *(l)*

(c) C_6H_{12} *(l)* + 9 O_2 *(g)* ? 6 CO_2 *(g)* + 6 H_2O *(g)*

Answers

1. (a) 0.679 mol/L; (b) 1.00 mol/L; (c) 0.06998 mol/L; (d) 1.75 mol/L; (e) 0.070 mol/L; (f) 6.6 mol/L

2. 27 g; Determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass.

3. (a) 37.0 mol H_2SO_4; 3.63×10^3 g H_2SO_4; (b) 3.8×10^{-6} mol NaCN; 1.9×10^{-4} g NaCN; (c) 73.2 mol H_2CO; 2.20 kg H_2CO; (d) 5.9×10^{-7} mol $FeSO_4$; 8.9×10^{-5} g $FeSO_4$

4. 1.15×10^{-3} mol/L; Determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity.

5. (a) 5.04×10^{-3} mol/L; (b) 0.499 mol/L; (c) 9.92 mol/L; (d) 1.1×10^{-3} mol/L

6. 0.025 mol/L

7. 0.5%

8. 2.8 g

9. 36.23 mL

10. 6.8%

11. 1.02 kg

12. 45719.97 ppm

13. 71 022 727 ppb

14. 3.67 mol/kg

15. 0.069 mol/kg

16. 0.35 mol/L

17. 0.50 mol/L

18. 42 mL

19. Complete: $3\ Ca(NO_3)_2 + 2\ H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\ HNO_3$

Complete Ionic: $3\ Ca^{2+} + 6\ NO_3^{-} + 6\ H + 2\ PO_4^{3-} \rightarrow Ca_3(PO_4)_2 + 6\ H + 6\ NO_3^{-}$

Net Ionic: $3\ Ca^{2+} + 2\ PO_4^{3-} \rightarrow Ca_3(PO_4)_2$

20. Complete: $Pb(NO_3)_2\,(aq) + 2\ KI\,(aq) \rightarrow PbI_2\,(s) + 2\ KNO_3\,(aq)$

Complete Ionic: $Pb^{2+}\,(aq) + 2\ NO_3^{-}(aq) + 2\ K^{+}\,(aq) + 2\ I^{-}\,(aq) \rightarrow PbI_2\,(aq) + 2\ K^{+}\,(aq) + 2\ NO_3^{-}(aq)$

Net Ionic: $Pb^{2+}\,(aq) + 2\ I^{-}\,(aq) \rightarrow PbI_2\,(aq)$

21. (a) oxidation-reduction (addition); (b) acid-base (neutralization); (c) oxidation-reduction (combustion)

1.5 – REDOX REACTIONS

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term ***oxidation*** *was originally used to describe chemical reactions involving O_2, a term which you may be familiar with within the context of real-life scenarios and applications like the browning of some fruits and the implication of antioxidants. However, in the sciences, its meaning has evolved to refer to a broad and important reaction class known as oxidation-reduction (redox) reactions. A few examples of such reactions will be used to develop a clear picture of this classification, and we'll use the stoichiometry skills you've learned throughout this chapter to balance redox reactions and solve amounts/concentrations of reactants/products.*

Oxidation-Reduction (Redox) Reactions

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2\,\mathrm{Na}\,(s) + \mathrm{Cl_2}\,(g) \rightarrow 2\,\mathrm{NaCl}\,(s)$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$2\,\mathrm{Na}\,(s) \rightarrow 2\,\mathrm{Na^+}\,(s) + 2\,e^-$$

$$\mathrm{Cl_2}\,(g) + 2\,e^- \rightarrow 2\,\mathrm{Cl^-}\,(s)$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, recall the "*s*" indicates that the resulting ions are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

Oxidation = loss of electrons

Reduction = gain of electrons

Table 1.5.1. Tips & tricks – Oxidation & reduction acronyms.

Here's are two acronyms you can easily use to remember the difference between oxidation and reduction: **1) OIL RIG** **OIL** = ***O****xidation* ***I****s* ***L****oss (of electrons)* **RIG** = ***R****eduction* ***I****s* ***G****ain (of electrons)* **2) LEO** *says* **GER** **LEO** *(zodiac sign for the lion)* = ***L****ose* ***E****lectrons –* ***O****xidation* **GER** *(like a lion growl – *grrr*)* = ***G****ain* ***E****lectrons –* ***R****eduction*

In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium.

Reducing agent = species that is oxidized
Oxidizing agent = species that is reduced

Hence, given that the electrons are transferred from one reactant to another, it's important to remember that if something has been oxidized (it lost electrons), then something else has been reduced (gained those electrons).

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding HCl:

$$H_2\,(g) + Cl_2\,(g) \rightarrow 2\,HCl\,(g)$$

The product of this reaction is a covalent compound, so the transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion:

The oxidation number of an atom in its elemental form is zero (e.g. O_2, Cl_2, Na).

The oxidation number of a monatomic ion is equal to the ion's charge (e.g. +1 for Na^+, -2 for O^{2-}).

The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Oxidation numbers for common nonmetals are usually assigned as follows:

Hydrogen: +1 when combined with nonmetals (e.g. H_2O), −1 when combined with metals and boron

Oxygen: −2 in most compounds (e.g. H_2O), sometimes −1 (so-called peroxides, O_2^{2-}), very rarely −1/2 (so-called superoxides, O_2^-), might be +2 or -1 when coupled to a more electronegative centre (such as F) or a group 1 or group 2 metal

Halogens: −1 for F always (e.g. HF), −1 for other halogens when combined with metals, nonmetals (except O), and other halogens lower in the group

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

A few tips to keep in mind as you solve problems involving determining oxidation numbers in compounds: 1) if two rules appear to contradict each other, follow the rule that appears higher on the list; 2) for a multi-atom species, figure out the easy oxidation states first, then solve for the other unknown atoms.

Example 1.5.1 – Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

(a) H_2S

(b) SO_3^{2-}

(c) Na_2SO_4

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{Charge on } H_2S = 0 = (2 + 1) + (1 \times x)$$
$$x = 0 - (2 \times (+1)) = -2$$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{Charge on } SO_3^{2-} = -2 = (3 \times (-2)) + (1 \times x)$$
$$x = -2 - (3 \times (-2)) = +4$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

$$\text{charge on } SO_4^{2-} = -2 = (4 \times (-2)) + (1 \times x)$$
$$x = -2 - (4 \times (-2)) = +6$$

Check Your Learning 1.5.1 – Assigning Oxidation Numbers

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

(a) $K\underline{N}O_3$

(b) $\underline{Al}H_3$

(c) $\underline{N}H_4^+$

(d) $H_2\underline{P}O_4^-$

Answer

(a) N, +5; (b) Al, +3; (c) N, −3; (d) P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist – see Example 1.5.2 "Describing Redox Reactions".) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\text{Oxidation} = \text{increase in oxidation number}$$
$$\text{Reduction} = \text{decrease in oxidation number}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

Types of Redox Reactions – Combustion

Several subclasses of redox reactions are recognized, including **combustion reactions** in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions (Figure 1.5.1) are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10\,\text{Al}\,(s) + 6\,\text{NH}_4\text{ClO}_4\,(s) \rightarrow 4\,\text{Al}_2\text{O}_3\,(s) + 2\,\text{AlCl}_3\,(s) + 12\,\text{H}_2\text{O}\,(g) + 3\,\text{N}_2\,(g)$$

Figure 1.5.1. Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. (credit: modification of work by NASA)

Check out this brief video showing the test-firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

Types of Redox Reactions – Single-displacement (Replacement)

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$\text{Zn}\,(s) + 2\,\text{HCl}\,(aq) \rightarrow \text{ZnCl}_2\,(aq) + \text{H}_2\,(g)$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$\text{Cu}\,(s) + 2\,\text{AgNO}_3\,(aq) \rightarrow \text{Cu(NO}_3)_2\,(aq) + 2\,\text{Ag}\,(s)$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue colour (Figure 1.5.2).

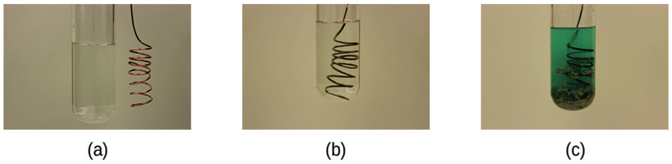


Figure 1.5.2. (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-coloured silver metal on the wire and development of a blue colour in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example 1.5.2 – Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

(a) $ZnCO_3\,(s) \rightarrow ZnO\,(s) + CO_2\,(g)$

(b) $2\,Ga\,(l) + 3\,Br_2\,(l) \rightarrow 2\,GaBr_3\,(s)$

(c) $2\,H_2O_2\,(aq) \rightarrow 2\,H_2O\,(l) + O_2\,(g)$

(d) $BaCl_2\,(aq) + K_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2\,KCl\,(aq)$

(e) $C_2H_4\,(g) + 3\,O_2\,(g) \rightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

(a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(b) This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga (*l*) to +3 in $GaBr_3$ (*s*). The reducing agent is Ga (*l*). Bromine is reduced, its oxidation number decreasing from 0 in Br_2 (*l*) to −1 in $GaBr_3$ (*s*). The oxidizing agent is Br_2 (*l*).

(c) This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in H_2O_2 (*aq*) to 0 in O_2 (*g*). Oxygen is also reduced, its oxidation number decreasing from −1 in H_2O_2 (*aq*) to −2 in H_2O (*l*). For disproportionation reactions, the same substance functions as an oxidant and a reductant.

(d) This is not a redox reaction since oxidation numbers remain unchanged for all elements.

(e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in C_2H_4 (*g*) to +4 in CO_2 (*g*). The reducing agent (fuel) is C_2H_4 (*g*). Oxygen is reduced, its oxidation number decreasing from 0 in O_2 (*g*) to −2 in H_2O (*l*). The oxidizing agent is O_2 (*g*).

Check Your Learning 1.5.2 – Describing Redox Reactions

This equation describes the production of tin (II) chloride:

$$\mathrm{Sn}\,(s) + 2\,\mathrm{HCl}\,(g) \rightarrow \mathrm{SnCl_2}\,(s) + \mathrm{H_2}\,(g)$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer

Yes, a single-replacement reaction. Sn (*s*) is the reductant, HCl (*g*) is the oxidant.

Balancing Redox Reactions – The Half-Reaction Method

The redox reactions discussed so far tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation was relatively simple. Balancing other reactions becomes more complicated when they take place in aqueous media that often involves water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the **half-reaction method**, which splits oxidation-reduction reactions into their oxidation "half" and reduction "half" to make finding the overall equation easier. This method involves the following general steps:

Write out the net ionic form of the reaction (see the preceding section "Solution Stoichiometry" to refresh your memory on expressing net ionic equations).

Separate this equation into its two half-reactions representing the redox process.

Balance all elements except oxygen and hydrogen.

Balance oxygen atoms by adding H_2O molecules.

Balance hydrogen atoms by adding H^+ ions.

Balance the net charge on each side by adding electrons.

If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.

Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.

Verify your final reaction (check that the number of atoms and the total charges are balanced).

Redox reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important:

Acidic solution: follow all steps 1-9 as normal.

Basic solution: follow all steps 1-9 as normal, add two additional "steps" to step 5 :

- Add OH^- ions to *both* sides of the equation in numbers equal to the number of H^+ ions. A common mistake students make is that they add OH^- to only one side of the equation, but just like in math equations, if you add one element to one side, you *must* add it to the other side as well (hence, add the same number of OH^- ions to *both* sides!).
- On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.

Example 1.5.3 – Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron (II) to yield iron(III) and chromium(III) in an acidic solution.

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

Solution

1. *Write the two half-reactions*. Each half-reaction will contain one reactant and one product with one element in common.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

2. *Balance all elements except oxygen and hydrogen*. The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+}$$

3. *Balance oxygen atoms by adding* H_2O *molecules*. The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

4. *Balance hydrogen atoms by adding* H^+ *ions.* The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$$Fe^{2+} \rightarrow Fe^{3+}$$
$$Cr_2O_7^{2-} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

5. *Balance charge by adding electrons*. The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} ion). Adding one electron to the right side brings that side's total charge to (3+) + (1−) = 2+, and charge balance is achieved. The chromium half-reaction shows a total charge of (1 × 2−) + (14 × 1+) = 12+ on the left side (1 $Cr_2O_7^{2-}$ ion and 14 H^+ ions). The total charge on the right side is (2 × 3+) = 6 + (2 Cr^{3+} ions).

Adding six electrons to the left side will bring that side's total charge to ((12+) + (6−)) = 6+, and charge balance is achieved.

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

$$Cr_2O_7^{2-} + 14\ H^{+} + 6\ e^{-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

Note: At this point, make sure you always check that one of your equations has the electron(s) on the reactants side, while the other equation has the electron(s) on the products side. If this isn't the case, it's a clear sign that you've done something wrong – go back and check your work to find the error(s).

6. *Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction*. To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$$6\ Fe^{2+} \rightarrow 6\ Fe^{3+} + 6\ e^{-}$$

$$Cr_2O_7^{2-} + 14\ H^{+} + 6\ e^{-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

A good way to qualitatively check your work when balancing both half-reactions is by recalling your understanding of oxidation and reduction. For the first reaction, $6\ Fe^{2+} \rightarrow 6\ Fe^{3+} + 6\ e^{-}$, the oxidation state of iron goes up from +2 and +3, and there are electrons being lost in the products side, so it's the oxidation half-reaction. For the second reaction, the oxidation state of chromium goes down from +6 to +3, and electrons are gained in the reactants side, so it's the reduction half-reaction.

7. Add the balanced half-reactions and cancel species that appear on both sides of the equation.

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^{+} + 6\ e^{-} \rightarrow 6\ Fe^{3+} + 6\ e^{-} + 2\ Cr^{3+} + 7\ H_2O$$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^{+} \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

A final check of atom and charge balance confirms the equation is balanced.

Element	**Reactants**	**Products**
Fe	6	6
Cr	2	2
O	7	7
H	14	14
Charge	+24	+24

Check Your Learning 1.5.3 – Balancing Redox Reactions in Acidic Solution

In acidic solution, hydrogen peroxide reacts with Fe^{2+} to produce Fe^{3+} and H_2O. Write a balanced equation for this reaction.

Answer

$$H_2O_2\,(aq) + 2\,H^+\,(aq) + 2\,Fe^{2+} \rightarrow 2\,H_2O\,(l) + 2\,Fe^{3+}$$

Example 1.5.4 – Balancing Redox Reactions in Basic Solution

Balance the following reaction equation in basic solution:

$$MnO_4^-\,(aq) + Cr(OH)_3\,(s) \rightarrow MnO_2\,(s) + CrO_4^{2-}\,(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction:

$$\text{Oxidation (unbalanced): } Cr(OH)_3\,(s) \rightarrow CrO_4^{2-}\,(aq)$$

$$\text{Reduction (unbalanced): } MnO_4^-\,(aq) \rightarrow MnO_2\,(s)$$

Starting with the oxidation half-reaction, we can balance the chromium:

$$\text{Oxidation (unbalanced): } Cr(OH)_3\,(s) \rightarrow CrO_4^{2-}\,(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the "leftover" hydrogen appears as five H^+ on the right side:

$$\text{Oxidation (unbalanced): } Cr(OH)_3\,(s) + H_2O\,(l) \rightarrow CrO_4^{2-}\,(aq) + 5\,H^+\,(aq)$$

The left side of the equation has a total charge of [0], and the right side a total charge of [−2 + 5 × (+1) = +3]. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{Oxidation (balanced): } Cr(OH)_3\,(s) + H_2O\,(l) \rightarrow CrO_4^{2-}\,(aq) + 5\,H^+\,(aq) + 3\,e^-$$

Checking the half-reaction:

Cr: Does (1 x 1) = (1 x 1)? Yes.

H: Does (1 x 3 + 1 x 2) = (5 x 1)? Yes.

O: Does (1 x 3 + 1 x 1) = (4 x 1)? Yes.

Charge: Does [0] = [1 x (-2) +5 x (+1) + 3 x (-1)]? Yes.

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:

$$\text{Reduction (unbalanced): } MnO_4^-\,(aq) + 4\,H^+\,(aq) \rightarrow MnO_2\,(s) + 2\,H_2O\,(l)$$

Then add three electrons to the left side to balance the charge:

$$\text{Reduction (balanced): } MnO_4^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \rightarrow MnO_2\,(s) + 2\,H_2O\,(l)$$

Make sure to check the half-reaction:

Mn: Does (1 x 1) = (1 x 1)? Yes.

H: Does (4 x 1) = (2 x 2)? Yes.

O: Does (1 x 4) = (1 x 2 + 2 x 1)? Yes.

Charge: Does [1 x (-1) + 4 x (+1) + 3 x (-1)] = [0]? Yes.

Collecting what we have so far:

Oxidation (balanced): $Cr(OH)_3\,(s) + H_2O\,(l) \rightarrow CrO_4^{2-}\,(aq) + 5\,H^+\,(aq) + 3\,e^-$

Reduction (balanced): $MnO_4^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \rightarrow MnO_2\,(s) + 2\,H_2O\,(l)$

In this case, both half-reactions involve the same number of electrons; therefore, simply add the two half-reactions together.

$$Cr(OH)_3\,(s) + H_2O\,(l) + MnO_4^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \rightarrow MnO_2\,(s) + 2\,H_2O\,(l) + CrO_4^{2-}\,(aq) + 5\,H^+\,(aq) + 3\,e^-$$

$$Cr(OH)_3\,(s) + MnO_4^-\,(aq) \rightarrow MnO_2\,(s) + H_2O\,(l) + CrO_4^{2-}\,(aq) + H^+\,(aq)$$

Checking each side of the equation:

Mn: Does (1 x 1) = (1 x 1)? Yes.

Cr: Does (1 x 1) = (1 x 1)? Yes.

H: Does (1 x 3) = (2 x 1 + 1 x 1)? Yes.

O: Does (1 x 4 + 1 x 3) = (1 x 4 + 1 x 2 + 1 x 1)? Yes.

Charge: Does [1 x (-1)] = [1 x (-2) + 1 x (+1)]? Yes.

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:

$$OH^-\,(aq) + Cr(OH)_3\,(s) + H_2O\,(l) + MnO_4^-\,(aq) \rightarrow MnO_2\,(s) + H_2O\,(l) + CrO_4^{2-}\,(aq) + (H^+ + OH^-)\,(aq)$$

$$OH^-\,(aq) + Cr(OH)_3(s) + H_2O\,(l) + MnO_4^-\,(aq) \rightarrow MnO_2\,(s) + 2H_2O\,(l) + CrO_4^{2-}\,(aq)$$

Checking each side of the equation:

Mn: Does (1 x 1) = (1 x 1)? Yes.

Cr: Does (1 x 1) = (1 x 1)? Yes.

H: Does (1 x 1 + 1 x 3) = (2 x 2)? Yes.

O: Does (1 x 1 +1 x 4 + 1 x 3) = (1 x 4 + 1 x 2 + 2 x 1)? Yes.

Charge: Does [1 x (-1) + 1 x (-1)] = [1 x (-2)]? Yes.

This is the balanced equation in basic solution.

Check Your Learning 1.5.4 – Balancing Redox Reactions in Basic Solution

Balance the following in the type of solution indicated.

(a) $H_2 + Cu^+$? Cu (acidic solution)

(b) $H_2 + Cu(OH)_2$? Cu (basic solution)

(c) $Fe + Ag^+$? $Fe^{2+} + Ag$

(d) Identify the oxidizing agents in reactions (a), (b), and (c).

(e) Identify the reducing agents in reactions (a), (b), and (c).

Answer

(a) $H_2\,(g) + Cu^{2+}\,(aq)$? $2\,H^+\,(aq) + Cu\,(s)$;

(b) $H_2\,(g) + Cu(OH)_2\,(s)$? $2\,H_2O\,(l) + Cu\,(s)$;

(c) $Fe\ (s) + 2\ Ag^{+}\ (aq)$? $Fe^{2+}\ (aq) + 2\ Ag\ (s)$;

(d) Recall oxidizing agent = species reduced: (a) Cu^{2+}; (b) $Cu(OH)_2$; (c) Ag^{+}

(e) Recall reducing agent = species oxidized: (a) H_2; (b) H_2; (c) Fe

★ Questions

1. Determine the oxidation states of the elements in the following compounds:

(a) NaI

(b) $GdCl_3$

(c) $LiNO_3$

(d) H_2Se

(e) Mg_2Si

(f) RbO_2, rubidium superoxide

(g) HF

2. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a)H_3PO_4

(b) $Al(OH)_3$

(c) SeO_2

(d) KNO_2

(e) In_2S_3

(f.) P_4O_6

3. Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

(a) $Mg\ (s) + NiCl_2\ (aq) \rightarrow MgCl_2\ (aq) + Ni\ (s)$

(b) $PCl_3\ (l) + Cl_2\ (g) \rightarrow PCl_5\ (s)$

(c) $C_2H_4\ (g) + 3\ O_2\ (g) \rightarrow 2\ CO_2\ (g) + 2\ H_2O\ (g)$

(d) $Zn\ (s) + H_2SO_4\ (aq) \rightarrow ZnSO_4\ (aq) + H_2\ (g)$

(e) $2\ K_2S_2O_3\ (s) + I_2\ (s) \rightarrow K_2S_4O_6\ (s) + 2\ KI\ (s)$

(f) $3\ Cu\ (s) + 8\ HNO_3\ (aq) \rightarrow 3\ Cu(NO_3)_2\ (aq) + 2\ NO\ (g) + 4\ H_2O\ (l)$

4. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

(a) $Al\ (s) + F_2\ (g) \rightarrow$

(b) $Al\ (s) + CuBr_2\ (aq) \rightarrow$ (single displacement)

(c) $P_4\ (s) + O_2\ (g) \rightarrow$

(d) $Ca\ (s) + H_2O\ (l) \rightarrow$ (products are a strong base and a diatomic gas)

5. When heated to 700–800 °C, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.

6. The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?

★★ Questions

7. Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

(a) Sn^{4+} *(aq)* → Sn^{2+} *(aq)*

(b) $[Ag(NH_3)_2]$ *(aq)* → Ag^{+} *(s)* + NH_3 *(aq)*

(c) Hg_2Cl_2 *(s)* → Hg *(l)* + Cl^{-} *(aq)*

(d) H_2O *(l)* → O_2 *(g)* (in acidic solution)

(e) IO_3^{-} *(aq)* → I_2 *(s)*

(f) SO_3^{2-} *(aq)* → SO_4^{2-} *(aq)* (in acidic solution)

(g) MnO_4^{-} *(aq)* → Mn^{2+} *(aq)* (in acidic solution)

(h) Cl^{-} *(aq)* → ClO_3^{-} *(aq)* (in basic solution)

8. Balance each of the following equations according to the half-reaction method:

(a) Sn^{2+} *(aq)* + Cu^{2+} *(aq)* → Sn^{4+} *(aq)* + Cu^{+} *(aq)*

(b) H_2S *(g)* + Hg_2^{2+} *(aq)* → Hg *(l)* + S *(s)* (in acid)

(c) CN^{-} *(aq)* + ClO_2 *(aq)* → CNO^{-} *(aq)* + Cl^{-} *(aq)* (in acid)

(d) Fe^{2+} *(aq)* + Ce^{4+} *(aq)* → Fe^{3+} *(aq)* + Ce^{3+} *(aq)*

(e) HBrO *(aq)* → Br^{-} *(aq)* + O_2 (*g*) (in acid)

9. Balance each of the following equations according to the half-reaction method:

(a) MnO_4^{-} *(aq)* + NO_2^{-} *(aq)* → MnO_2 *(s)* + NO_3^{-} *(aq)* (in base)

(b) MnO_4^{2-} *(aq)* → MnO_4^{-} *(aq)* + MnO_2 *(s)* (in base)

(c) Br_2 (l) + SO_2 *(g)* → Br^{-} *(aq)* + SO_4^{2-} *(aq)* (in acid)

10. Balance the following in acidic solution:

(a) $H_2O_2 + Sn^{2+} \rightarrow H_2O + Sn^{4+}$

(b) $PbO_2 + Hg \rightarrow Hg_2^{2+} + Pb^{2+}$

(c) $Al + Cr_2O_7^{2-} \rightarrow Al^{3+} + Cr^{3+}$

11. Balance the following in basic solution:

(a) SO_3^{2-} *(aq)* + $Cu(OH)_2$ *(s)* → SO_4^{2-} *(aq)* + Cu(OH)

(b) O_2 *(g)* + $Mn(OH)_2$ *(s)* → MnO_2 *(s)*

(c) NO_3^{-} *(aq)* + H_2 *(g)* → NO *(g)*

(d) Al *(s)* + CrO_4^{2-} *(aq)* → $Al(OH)_3$ *(s)* + $Cr(OH)_4^{-}$ *(aq)*

Answers

1. (a) Na +1, I -1; (b) Gd +3, Cl -1; (c) Li +1, N +5, O -3; (d) H +1, Se -2; (e) Mg +2, Si -4; (f) Rb -1, O +0.5; (g) H +1, F -1

2. (a) H +1, P +5, O −2; (b) Al +3, H +1, O −2; (c) Se +4, O −2; (d) K +1, N +3, O −2; (e) In +3, S −2; (f) P +3, O −2

3. (a) Mg: oxidized, 0 → +2, reducing agent, Ni: reduced, +2 → 0, oxidizing agent;

(b) P: oxidized, +3 → 5, reducing agent, Cl: reduced, 0 → -1, oxidizing agent;

(c) C: oxidized, -2 → +4, reducing agent, O: reduced, 0 → -2, oxidizing agent;

(d) Zn: oxidized, 0 → +2, reducing agent, H: reduced, +1 → 0, oxidizing agent;

(e) S: oxidized, +2 → +5/2, reducing agent, I: reduced, 0 → -1, oxidizing agent;

(f) Cu: oxidized, 0 → +2, reducing agent, N: reduced, +5 → +2, oxidizing agent

4. (a) $2\,Al\,(s) + 3\,F_2\,(g) \rightarrow 2\,AlF_3\,(s)$

(b) $Al\,(s) + CuBr_2\,(aq) \rightarrow 3\,Cu\,(s) + 2\,AlBr_3\,(aq)$

(c) $P_4\,(s) + O_2\,(g) \rightarrow P_4O_{10}\,(s)$

(d) $Ca\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(aq) + H_2\,(g)$

5. $C_{diamond}\,(s) + O_2\,(g) \rightarrow CO_2\,(g)$

6. $H_2\,(g) + F_2\,(g) \rightarrow CO_2\,(g)$

7. (a) $Sn^{4+}\,(aq) + 2e^- \rightarrow Sn^{2+}\,(aq)$

(b) $[Ag(NH_3)_2]\,(aq) + e^- \rightarrow Ag^+\,(s) + NH_3\,(aq)$

(c) $Hg_2Cl_2\,(s) + 2\,e^- \rightarrow Hg\,(l) + Cl^-\,(aq)$

(d) $2\,H_2O\,(l) \rightarrow O_2\,(g) + 4\,H^+\,(aq) + 4\,e^-$

(e) $6\,H_2O\,(l) + IO_3^-\,(aq) + 10\,e^- \rightarrow I_2\,(s) + 12\,OH^-\,(aq)$

(f) $H_2O\,(l) + SO_3^{2-}\,(aq) \rightarrow SO_4^{2-}\,(aq) + 2\,H^+\,(aq) + 2\,e^-$

(g) $8\,H^+\,(aq) + MnO_4^-\,(aq) + 5\,e^- \rightarrow Mn^{2+}\,(aq) + 4\,H_2O\,(l)$

(h) $Cl^-\,(aq) + 6\,OH^-\,(aq) \rightarrow ClO_3^-\,(aq) + 3\,H_2O\,(l) + 6\,e^-$

8. (a) $Sn^{2+}\,(aq) + 2\,Cu^{2+}\,(aq) \rightarrow Sn^{4+}\,(aq) + 2\,Cu^+\,(aq)$

(b) $H_2S\,(g) + Hg_2^{2+}\,(aq) + 2\,H_2O\,(l) \rightarrow 2\,Hg\,(l) + S\,(s) + 2\,H_3O^+\,(aq)$

(c) $5\,CN^-\,(aq) + 2\,ClO_2\,(aq) + 3\,H_2O\,(l) \rightarrow 5\,CNO^-\,(aq) + 2\,Cl^-\,(aq) + 2\,H_3O^+\,(aq)$

(d) $Fe^{2+}\,(aq) + Ce^{4+}\,(aq) \rightarrow Fe^{3+}\,(aq) + Ce^{3+}\,(aq)$

(e) $2\,HBrO\,(aq) + 2\,H_2O\,(l) \rightarrow 2\,H_3O^+\,(aq) + 2\,Br^-\,(aq) + O_2\,(g)$

9. (a) $2\,MnO_4^-\,(aq) + 3\,NO_2^-\,(aq) + H_2O\,(l) \rightarrow 2\,MnO_2\,(s) + 3\,NO_3^-\,(aq) + 2\,OH^-\,(aq)$

(b) $3\,MnO_4^{2-}\,(aq) + 2\,H_2O\,(l) \rightarrow 2\,MnO_4^-\,(aq) + MnO_2\,(s) + 4\,OH^-\,(aq)$

(c) $Br_2\,(l) + SO_2\,(g) + 2\,H_2O\,(l) \rightarrow 2\,Br^-\,(aq) + SO_4^{2-}\,(aq) + 4\,H^+\,(aq)$

10. (a) $2\,H^+ + H_2O_2 + Sn^{2+} \rightarrow H_2O + Sn^{4+}$

(b) $4\,H^+ + PbO_2 + 2\,Hg \rightarrow Hg_2^{2+} + Pb^{2+} + 2\,H_2O$

(c) $2\,Al + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 2\,Al^{3+} + 2\,Cr^{3+} + 7\,H_2O$

11. (a) $SO_3^{2-}\,(aq) + 2\,Cu(OH)_2\,(s) \rightarrow SO_4^{2-}\,(aq) + 2\,Cu(OH) + H_2O$

(b) $O_2\,(g) + 2\,Mn(OH)_2\,(s) \rightarrow 2\,MnO_2\,(s) + 2\,H_2O$

(c) $2\,NO_3^-\,(aq) + 3\,H_2\,(g) + 2\,H_2O \rightarrow NO\,(g) + 2\,OH^-\,(aq)$

(d) $Al\,(s) + CrO_4^{2-}\,(aq) + 4\,H_2O \rightarrow Al(OH)_3\,(s) + Cr(OH)_4^-\,(aq) + OH^-\,(aq)$

CHAPTER 2

2.1 – INTERMOLECULAR FORCES

The States of Matter

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (E_k) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' E_k provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 2.1.1 illustrates how changes in physical state may be induced by changing the temperature, hence, the average E_k, of a given substance.

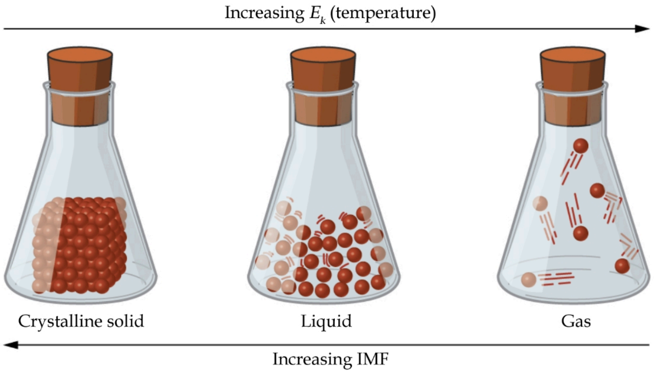


Figure 2.1.1. Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in Figure 2.1.1, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold glass as the water vapour in the air is cooled by the cold glass, as seen in Figure 2.1.2.

Figure 2.1.2. Condensation forms when water vapour in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their E_k. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure.

We define **Standard Temperature and Pressure (STP)** for gases as 0 °C and 1.00 bar (1 bar = 100 000 Pa = 0.987 atm) to establish convenient conditions for comparing the molar volumes of gases. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 2.1.3.

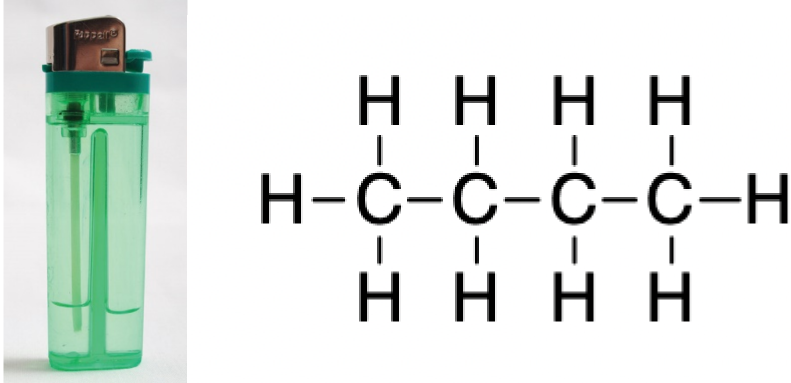


Figure 2.1.3. Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough E_k to overcome the attractive IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later section of this chapter.

Forces Between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 2.1.4 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules of energy. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy: 430 kilojoules.

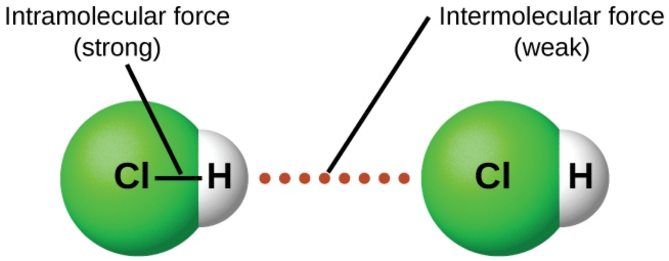


Figure 2.1.4. *Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as **van der Waals forces**, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the **London dispersion force** in honour of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. Dipoles are present in molecules where there is an unequal dispersion of charge. If there is increased electron density on one end of the molecule, we would label this area with a delta minus (δ^-). This then means that the other end of the molecule has a decreased electron density therefore, it is labelled with a delta plus (δ^+). These labels are shown in Figure 2.1.5. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 2.1.5.

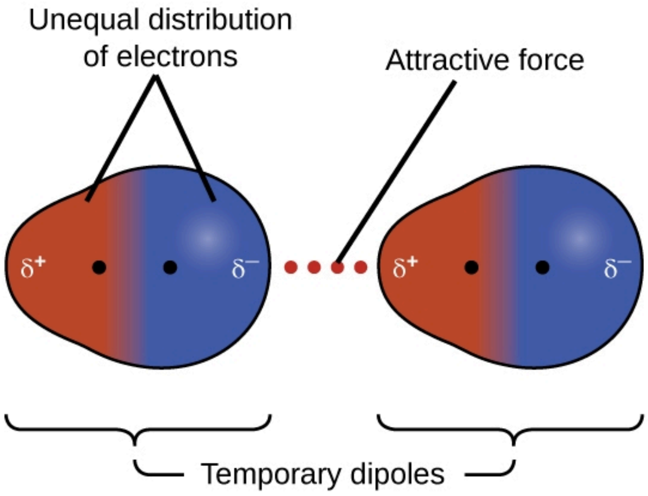


Figure 2.1.5. Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in the following table.

Table 2.1.1. Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

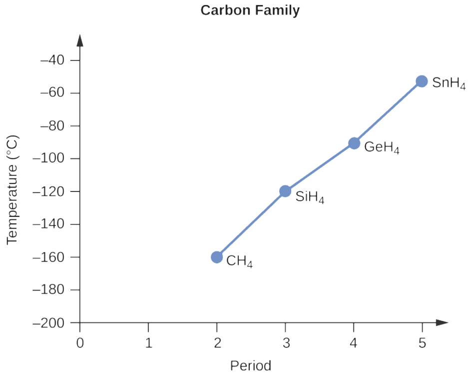
Example 2.1.1 – London Forces and Their Effects

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

You may recall chemical bonding and molecular geometry from high school chemistry. All of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 < SiH_4 < GeH_4 < SnH_4$.

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:



Check Your Learning 2.1.1 – London Forces and Their Effects

Order the following hydrocarbons from lowest to highest boiling point:
C_2H_6, C_3H_8, and C_4H_{10}.

Answer

$C_2H_6 < C_3H_8 < C_4H_{10}$. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore $C_2H_6 < C_3H_8 < C_4H_{10}$.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 2.1.6) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

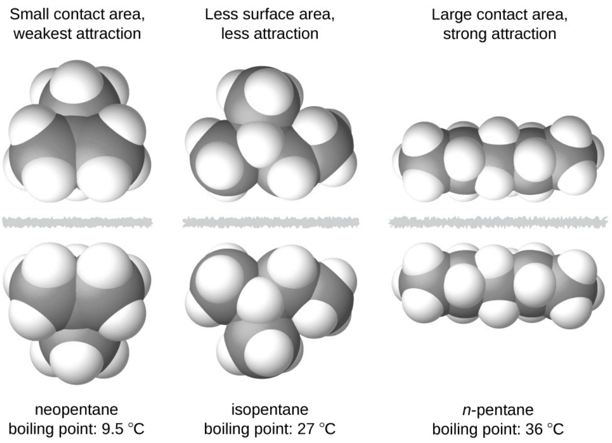


Figure 2.1.6. The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko (shown in Figure 2.1.7) with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally non sticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

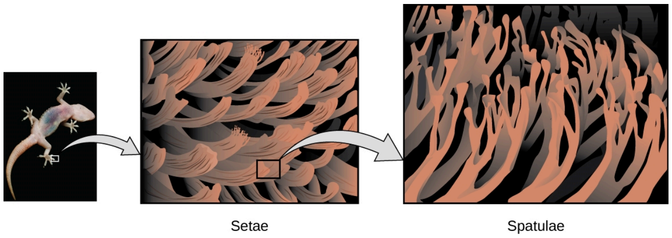


Figure 2.1.7. Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

Dipole-Dipole Attractions

You may recall from your high school chemistry class on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule — a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a **dipole-dipole attraction**—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 2.1.8.

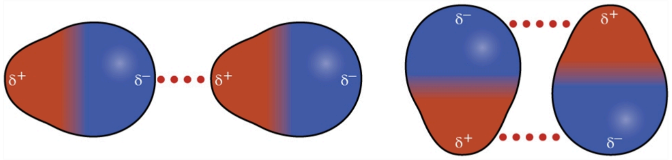


Figure 2.1.8. This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average E_k. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to condense to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

Example 2.1.2 – Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

Check Your Learning 2.1.2 – Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom. These three elements have very high values of *electronegativity*, the ability of an atom to attract electron density in a chemical bond towards its own nucleus (defined and discussed in Section 9.3). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for a F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. Examples of hydrogen bonds include $HF \cdots HF$, $H_2O \cdots HOH$, and $H_3N \cdots HNH_2$, in which the hydrogen bonds are denoted by dots. Figure 2.1.9 illustrates hydrogen bonding between water molecules.

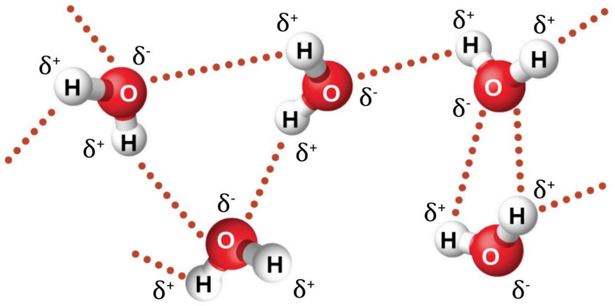


Figure 2.1.9. Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3, PH_3, AsH_3, and SbH_3), group 16 hydrides (H_2O, H_2S, H_2Se, and H_2Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 2.1.10. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.

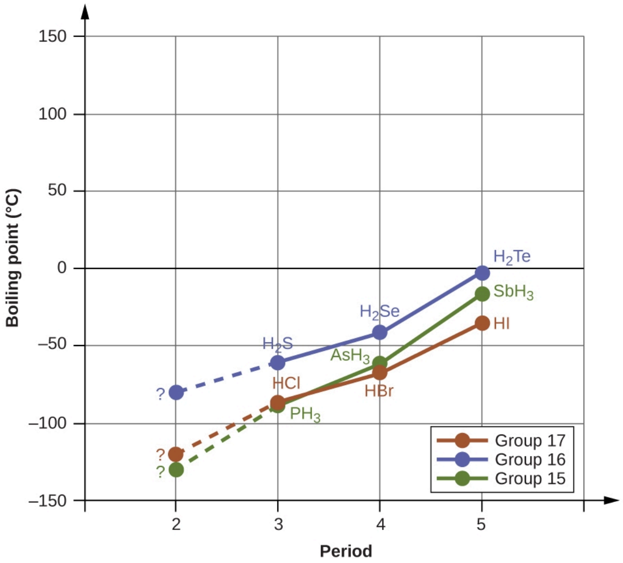


Figure 2.1.10. For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 2.1.11. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

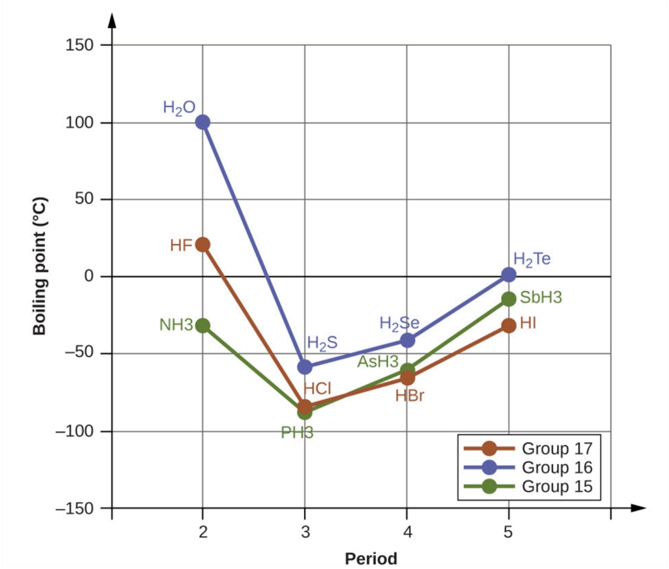


Figure 2.1.11. In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

Example 2.1.3 – Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

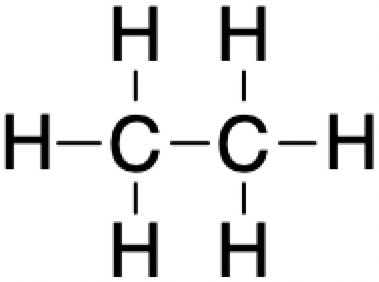
Solution

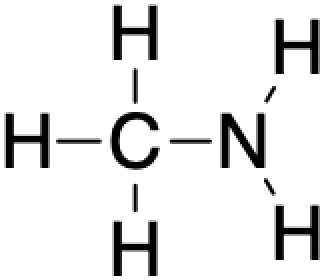
The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

Check Your Learning 2.1.3 – Effect of Hydrogen Bonding on Boiling Points

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C.

Predict the relative melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.





Answer

CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses two N–H bonds and therefore will exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. Therefore, the melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. Our prediction is confirmed by literature values: CH_3NH_2 has a melting point of −93 °C and a boiling point of −6 °C.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-) parallel chains of repeating nucleotides, which form its well-known double-helical structure, as shown in Figure 2.1.12.

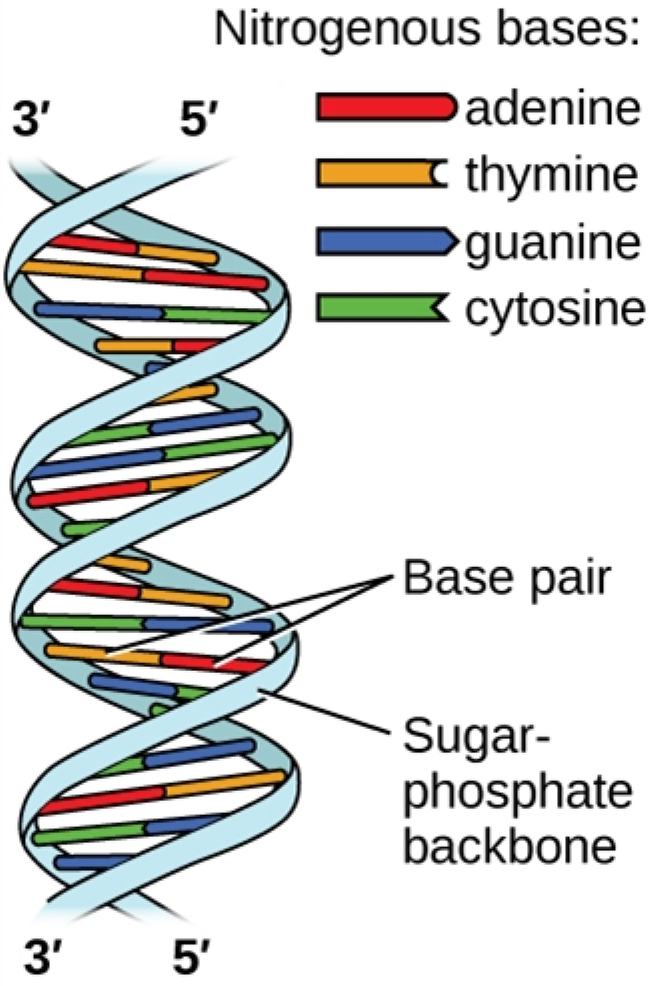


Figure 2.1.12. Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 2.1.13.

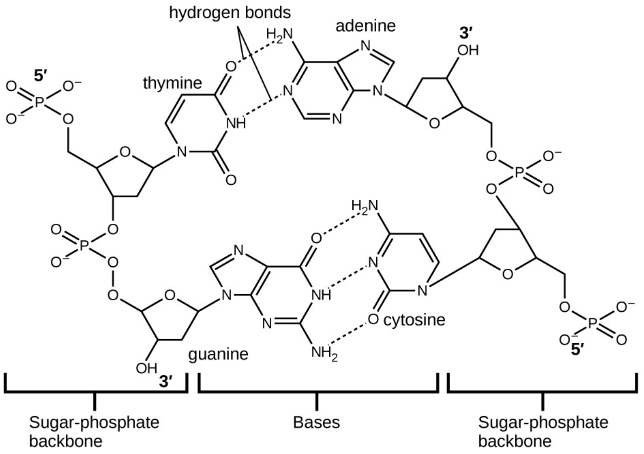


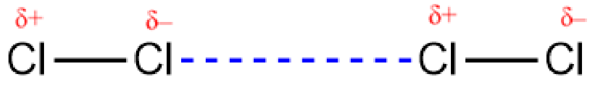
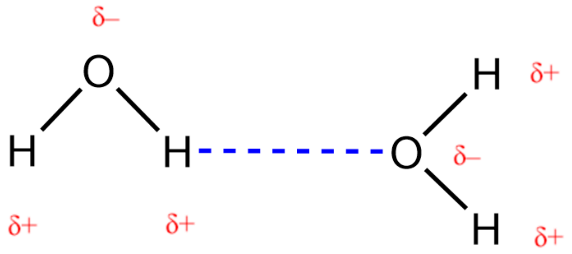
Figure 2.1.13. The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Summary

Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as van der Waals forces), and hydrogen bonds. Dipole–dipole interactions arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. London dispersion forces are due to the formation of instantaneous dipole moments in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an induced dipole in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more polarizable than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. Hydrogen bonds are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cage-like structure that is less dense than liquid water. Table 2.1.2 summarizes relative bond energies of intermolecular forces.

Table 2.1.2 Relative Bond Energies of Intermolecular Forces

Intermolecular Force	**Diagram**	**Energy (kJ/mol)**[†]
London dispersion		Under 4 – 63
Dipole-dipole		2 – 8
Hydrogen bonds		4 – 50

[†] Ege, Seyhan (2003) Organic Chemistry: Structure and Reactivity. Houghton Mifflin College. ISBN 0618318097. pp. 30–33, 67.

Questions

★ Questions

1. Open the PhET States of Matter Simulation to answer the following questions:

    (a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?

    (b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.

    (c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

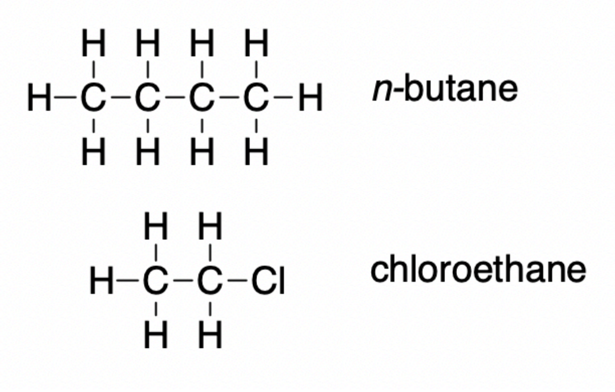
2. Define the following and give an example of each:

    (a) Dispersion force

    (b) Dipole-dipole attraction

    (c) Hydrogen bond

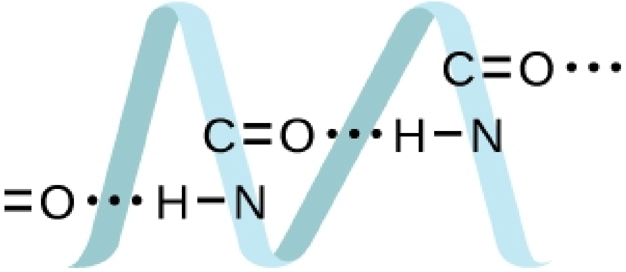
3. On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses.



4. The melting point of H_2O *(s)* is 0 °C. Would you expect the melting point of H_2S *(s)* to be −85 °C, 0 °C, or 185 °C? Explain your answer.

5. Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

6. Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



7. Identify the intermolecular forces present in the following solids:

(a) CH_3CH_2OH

(b) $CH_3CH_2CH_3$

(c) CH_3CH_2Cl

Answers

1. (a) Similarities: Solid and liquid are more dense compared to gas. The higher temperature the system has, the faster the molecular move. Differences: For water, the liquid state is denser than solid state; while other solids are denser than their liquid state. Different substances have different temperatures.

Temperature	Neon	Argon	Oxygen	Water
Solid	-260 °C	-230 °C	-242 °C	-116 °C
Liquid	-247 °C	-187 °C	-204 °C	55 °C
Gas	-218 °C	-84 °C	-79 °C	536 °C

The higher temperature they have, the stronger IMF the substances have.

(b) The potential energy first decreases in the negative region, and then keeps increasing. When the distance between two atoms is greater than ε, the total force on each atom is attractive and large enough to matter. When the distance between two atoms is ε, the attractive (van der Waals) and repulsive (electron overlap) forces balance. At this point, the whole system has the lowest potential energy.

2. (a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (example: Ar).

(b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (example: ICI molecules attract one another by dipole-dipole interaction).

(c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, or nitrogen atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (example: HF···HF).

3. Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction is therefore stronger, leading to a higher boiling point.

4. −85 °C. Water has stronger hydrogen bonds so it melts at a higher temperature.

5. The higher the melting point reflects stronger intermolecular forces. In this case, silane has the strongest intermolecular forces whereas sulfide has the weakest. Although, the polarity cannot be directly determined based on the melting points.

6. H-bonding is the principle IMF holding the DNA strands together. The H-bonding is between the N−H and C=O.

7.

(a) Hydrogen bonding and dispersion forces

(b) Dispersion forces

(c) Dipole-dipole attraction and dispersion forces

2.2 – GASES AND THE PERIODIC TABLE

The geometric structure and the physical and chemical properties of atoms, ions, and molecules usually do *not* depend on their physical state; the individual water molecules in ice, liquid water, and steam, for example, are all identical. In contrast, the macroscopic properties of a substance depend strongly on its physical state, which is determined by intermolecular forces and conditions such as temperature and pressure.

Figure 2.2.1 shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (H_2, N_2, O_2, F_2, and Cl_2). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (O_3), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25 °C and 1.0 atm, commonly referred to as "room temperature and pressure"). Gallium (Ga), which melts at only 29.76 °C, can be converted to a liquid simply by holding a container of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

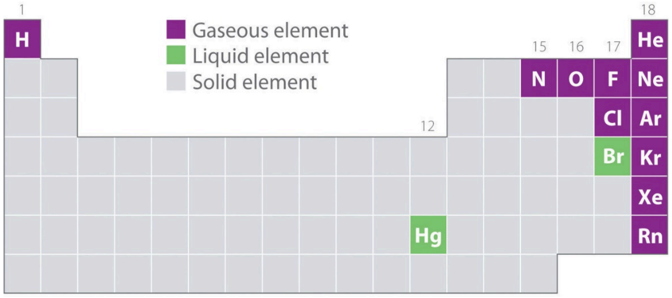


Figure 2.2.1. Elements that occur naturally as gases, liquids, and solids at 25 °C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

All of the gaseous elements (other than the monatomic noble gases) are molecules. Within the same group (1, 15, 16 and 17), the lightest elements are gases. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms. When referring to nongaseous elements, we use the term **vapour**. The term vapour refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are referred to as gases, but gaseous water in the atmosphere is called *water vapour*.

Questions

★ Questions

1. Neon, a gas at room temperature, condenses into a liquid at 25 K. Which chemical properties of neon are affected by this phase change?

2. Like oxygen, carbon also exists in multiple naturally-occurring allotropes. Are any of them in the gaseous state under normal conditions?

Answers

1. None, the inherent chemical properties of an element remain unchanged when there is a change in phase.

2. No. The three major allotropes of carbon – graphite, diamond, and fullerenes – are all solids under normal conditions.

2.3 – MEASURING VARIABLES OF GASES

Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased **pressure (*P*)** of the gas, the force (*F*) per unit area (*A*) of surface:

$$P = \frac{Force}{Area} = \frac{F}{A}$$

Equation 2.3.1. The pressure force area relation.

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from the equation relating force, area, and pressure that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. The SI unit for pressure, derived from the SI units for force (newtons) and area (square metres), is the newton per square metre (N/m^2), which is called the **Pascal (Pa)**, after the French mathematician Blaise Pascal (1623 – 1662):

$$1\ \text{Pa} = 1\ \text{N/m}^2$$

One pascal is a very small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or **bar** (1 bar = 100 000 Pa).

Example 2.3.1 – Pressure Exerted by a Paperback Book

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is:

(a) lying flat?

(b) standing on edge in a bookcase?

Solution

The force exerted by the book does *not* depend on its orientation. Recall that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity ($9.8067\ m/s^2$ at Earth's surface). In SI units, the force exerted by the book is therefore:

$$F = ma = 2.00\ kg \times 9.8067\ \frac{m}{s^2} = 19.6\ \frac{kg \cdot m}{s^2} = 19.6\ N$$

(a) We calculated the force as 19.6 N. When the book is lying flat, the area is:

$$A = 0.270\ \text{m} \times 0.210\ \text{m} = 0.0567\ \text{m}^2$$

If the book is standing on its end, the force remains the same, but the area decreases:

$$A = 21.0\ \text{cm} \times 4.5\ \text{cm} = 0.210\ \text{m} \times 0.045\ \text{m} = 9.5 \times 10^{-3}\ \text{m}^2$$

(b) The pressure exerted by the text lying flat is thus:

$$P = \frac{F}{A} = \frac{19.6\ N}{0.0567\ m^2} = 3.46 \times 10^2\ Pa$$

The pressure exerted by the text standing on its end is thus:

$$P = \frac{19.6\ N}{9.5 \times 10^{-3}\ m^2} = 2.06 \times 10^3\ Pa$$

Check Your Learning 2.3.1 – Pressure Exerted by a Paperback Book

What pressure does a 60.0 kg student exert on the floor:

(a) when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?

(b) as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer

(a) 3.27×10^4 Pa

(b) 5.9×10^6 Pa

Atmospheric Pressure

The air surrounding the earth is pulled toward the surface by gravity in the same way as the paperback book in the example above. Consequently, the air also exerts a pressure on the surface. This is called **atmospheric pressure**.

The following video shows the 'power' of atmospheric pressure. A metal can full of water is heated until the water inside boils, creating a high internal pressure. The can is then put upside down into a bowl of cold ice water, causing the formerly hot water vapour to cool and decrease in volume. This cooling causes a decrease in the internal pressure of the can. The lower pressure exerts less force on the can and can no longer counter the atmospheric pressure coming from the outside of the can, which pushes inward, crushing the can. This can also be seen in Figure 2.3.1 on a much larger scale.

Figure 2.3.1. Thomas the railroad tank car is crushed by the difference in pressure.

Because winds may add more air or take some away from the vertical column above a given area on the surface, atmospheric pressure will vary. Pressure also decreases as one moves to higher altitudes. The tops of the Himalayas, the highest mountains in the world at about 8000 m (almost 5 miles), are above more than half the atmosphere. The lower pressure at such heights makes breathing very difficult—even the slightest exertion leaves one panting and weak. For this reason, jet aircraft, which routinely fly at altitudes of 8 to 10 km, have equipment to maintain air pressure in their cabins artificially.

It is often convenient to express pressure using a unit which is about the same as the average atmospheric pressure at sea level. Atmospheric pressure is about 101 kPa, and the **standard atmosphere (atm)** is defined as exactly 101.325 kPa. Since this unit is often used, it is useful to remember that:

$$1\text{ atm} = 101.325\text{ kPa} = 1.01325\text{ bar}$$

Example 2.3.2 – Atmospheric Pressure

The total mass of air directly above a 30 cm by 140 cm section of the Atlantic Ocean was 4.34×10^3 kg on July 27, 1977. Calculate the pressure exerted on the surface of the water by the atmosphere.

Solution

First calculate the force of gravitational attraction on the air:

$$F = ma = (4.34 \times 10^3\text{ kg}) \times (9.81\text{ m}\cdot\text{s}^{-2}) = 4.26 \times 10^4\text{ kg}\cdot\text{m}\cdot\text{s}^{-2} = 4.26 \times 10^4\text{ N}$$

The area is:

$$A = 30\ cm \times 140\ cm = 4200\ cm^2 \times \left(\frac{1\ m}{100\ cm}\right)^2 = 0.42\ m^2$$

Thus the pressure is:

$$P = \frac{F}{A} = \frac{4.26 \times 10^4\ N}{0.42\ m^2} = 1.01 \times 10^5\ Pa = 101\ kPa$$

Barometric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface (Figure 2.3.2). Every point on Earth's surface experiences a net pressure called *barometric pressure*. The pressure exerted by the atmosphere is considerable: a 1 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10 000 kg, which gives a pressure of about 101 kPa. However, we typically do not perceive this pressure because we are physiologically adapted to it!

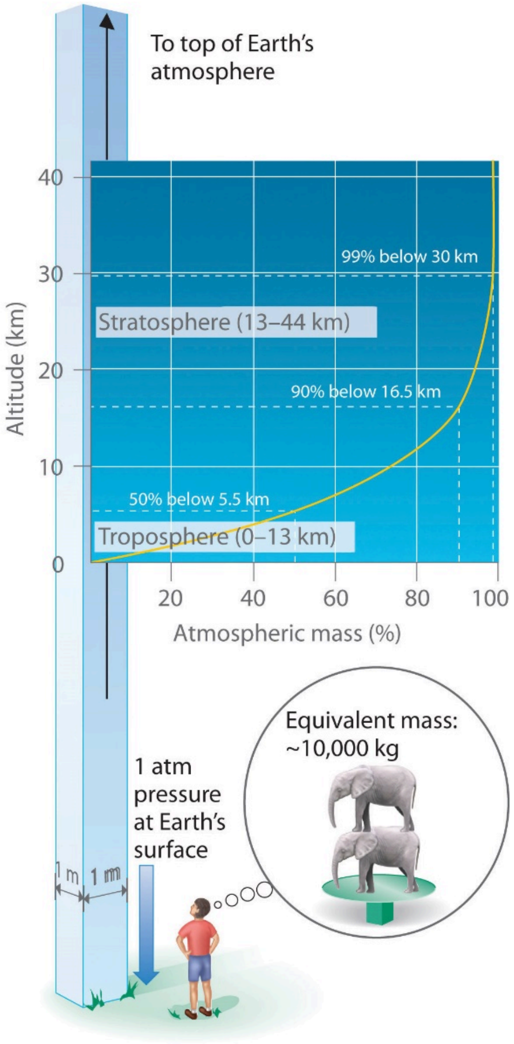


Figure 2.3.2. Barometric pressure. Each square metre of Earth's surface supports a column of air that is more than 200 km high and weighs about 10 000 kg at Earth's surface.

Barometric pressure can be measured using a **barometer**, a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). As shown in Figure 2.3.3, a barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside. Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a vacuum), there is no pressure pushing down on the column. Thus, the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. The pressure exerted by the mercury column can be expressed as:

$$P = \frac{F}{A}$$

$$P = \frac{mg}{A}$$

$$P = \frac{pV \cdot g}{A}$$

$$P = \frac{p \cdot Ah \cdot g}{A}$$

$$P = pgh$$

with g is the gravitational acceleration, m is the mass, ρ is the density, V is the volume, A is the bottom area, and h is the height of the mercury column.

Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 2.3.3. This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

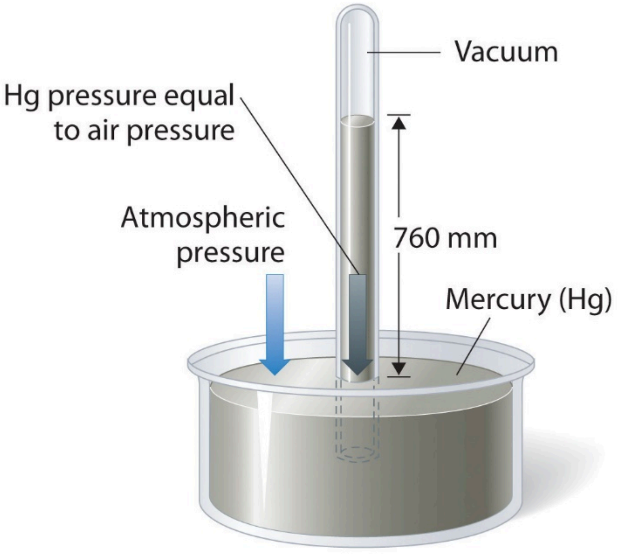


Figure 2.3.3. A mercury barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73 °C), there is negligible mercury vapour in the space above the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimetre of mercury (mmHg), often called the **Torr,** after Torricelli. Standard barometric pressure is the barometric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$\begin{aligned} 1\ \text{atm} &= 760\ \text{mmHg} \\ &= 760\ \text{Torr} \\ &= 1.01325 \times 10^{5}\ \text{Pa} \\ &= 101.325\ \text{kPa} \\ &= 1.01325\ \text{bar} \\ &= 14.6959\ \text{psi} \end{aligned}$$

Thus, a pressure of 1 atm equals 760 mmHg exactly.

We are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of barometric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The barometric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

To learn more about the barometer and its history, check out the following video.

Example 2.3.3 – Barometric Pressure

A general chemistry professor visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14 000 ft). He noticed that even slight exertion was very difficult at this altitude, where the barometric pressure is only 454 mmHg. Convert this pressure to:

(a) atmospheres (atm).

(b) bar.

Solution

(a) From the conversion factors, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus:

$$P = 454\ mmHg \times \frac{1\ atm}{760\ mmHg}$$

$$P = 0.597\ atm$$

(b) The pressure in bar is given by:

$$P = 0.597\ atm \times \frac{1.01325\ bar}{1\ atm}$$

$$P = 0.605\ bar$$

Check Your Learning 2.3.2 – Barometric Pressure

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to:

(a) Millimetres of mercury

(b) Bar

(c)Pascals

Answer

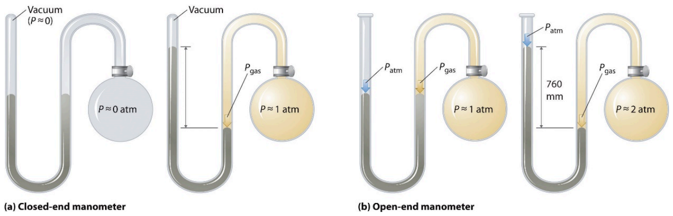
(a) 234 mmHg

(b) 0.312 bar

(c) 31 200 Pa

Manometers

Barometers measure barometric pressure, but **manometers** measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in Figure 2.3.4(a). When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury on either side of the U shape are identical because the space above the mercury on the left is also a near vacuum (it contains only traces of mercury vapour). If a gas is added to the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas. If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in Figure 2.3.4(b). then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the barometric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the barometric pressure minus the difference in the heights of the two columns.



(a) Closed-end manometer

(b) Open-end manometer

Figure 2.3.4. The two types of manometers. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1$ atm), and the difference in the heights of the two columns gives the *difference* between barometric pressure and the pressure of the gas in the bulb.

To learn more about manometers, check out the following video.

Example 2.3.4 – Applying Theories: Barometers and Manometers

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (The density of water is 1.00 g/cm^3; the density of mercury is 13.53 g/cm^3.)

Solution

In millimetres of mercury, a gas pressure of 0.200 atm is:

$$P = 0.200\ atm \times \frac{760\ mmHg}{1\ atm} = 152\ mmHg$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury to the density of water:

$$P = \rho_{wat} g h_{wat} = \rho_{Hg} g h_{Hg}$$

$$h_{wat} = h_{Hg} \times \frac{d_{Hg}}{d_{wat}} = 152\ mm \times \frac{13.53\ g/cm^3}{1.00\ g/cm^3} = 2070\ mm$$

The answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Check Your Learning 2.3.3 – Applying Theories: Barometers and Manometers

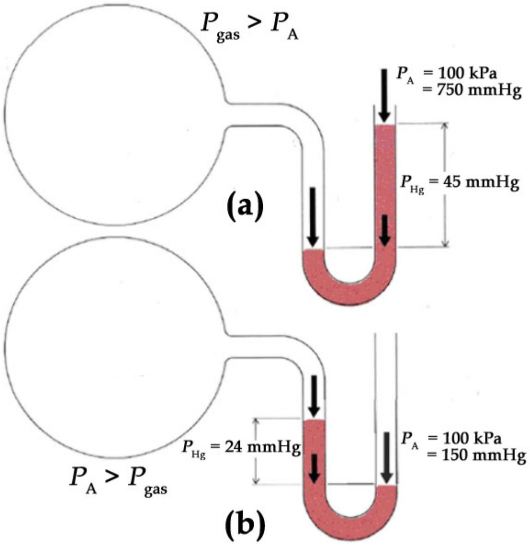
Suppose you want to design a barometer to measure barometric pressure in an environment that is always hotter than 30 °C. To avoid using mercury, you decide to use gallium, which melts at 29.76 °C; the density of liquid gallium at 25 °C is 6.114 g/cm^3. How tall a column of gallium do you need if $P = 1.00$ atm?

Answer

1.68 m

Check Your Learning 2.3.4 – Applying Theories: Barometers and Manometers

Consider the following open-end manometer. What can be concluded about the pressure of the gas within bulb (a)? Bulb (b)?



Answer

The pressure of the gas in bulb (a) is greater than that of the atmosphere. The pressure of the gas in bulb (b) is less than atmospheric.

The formula derived in Example 2.3.4 can also assist us in other areas, like hydrogeology. For example, consider the problem of building a well to obtain water from an underground aquifer. We can apply a similar method to determine the maximum depth of a well if a simple suction pump will be used to get the water out. A 1.00 atm external barometric pressure would therefore correspond to a maximum water column height of:

$$h_{wat} = h_{Hg} \times \frac{d_{Hg}}{d_{wat}}$$

$$h_{wat} = 760\ mmHg \times \frac{13.53\ g/cm^3}{1.00\ g/cm^3}$$

$$h_{wat} = 1.03 \times 10^4 mm$$

$$h_{wat} = 10.3\ m$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on barometric pressure to force the liquid up a tube. If 1.00 atm barometric pressure corresponds to a 10.3

m (33.8 ft) column of water, then it is physically impossible for barometric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

Volume

Volume is defined as length times width times height, so it has units of metre × metre × metre or metre^3 (m^3), sometimes spoken as 'cubic metres'. The cubic metre is a rather large unit, however, so another unit is defined that is somewhat more manageable: the litre (L). A litre is 1/1000th (1 x 10^{-3} m^3) of a cubic metre and is a little more than 1 quart in volume (Figure 2.3.5.). Prefixes can also be used with the litre unit, so we can speak of millilitres (1 mL = 1 x 10^{-3} L = 1 x 10^{-6} m^3), microlitres (1 µL = 1 x 10^{-6} L = 1 x 10^{-9} m^3), and so forth.

Another definition of a litre is one-tenth of a metre cubed. Because one-tenth of a metre is 10 cm, then a litre is equal to 1000 cm^3 (Figure 2.3.5). Because 1 L equals 1000 mL, we conclude that 1 mL equals 1 cm^3; thus, these units are interchangeable.

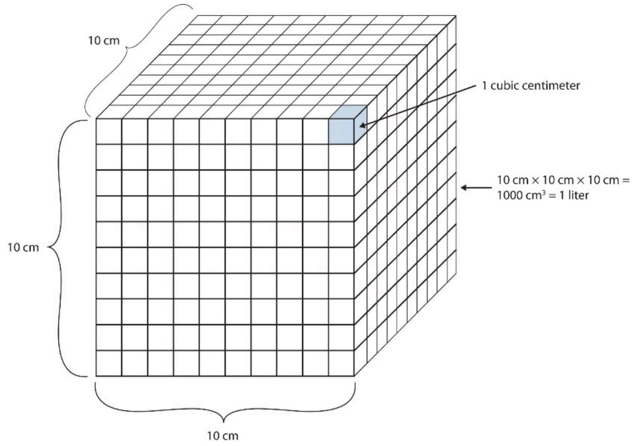


Figure 2.3.5. The size of 1 litre. One litre equals 1 000 cm^3, so 1 cm^3 is the same as 1 mL.

Temperature

One of the fundamental quantities in science is temperature, which is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees. There are three scales used for reporting temperatures. Figure 2.3.6. compares the three temperature scales.

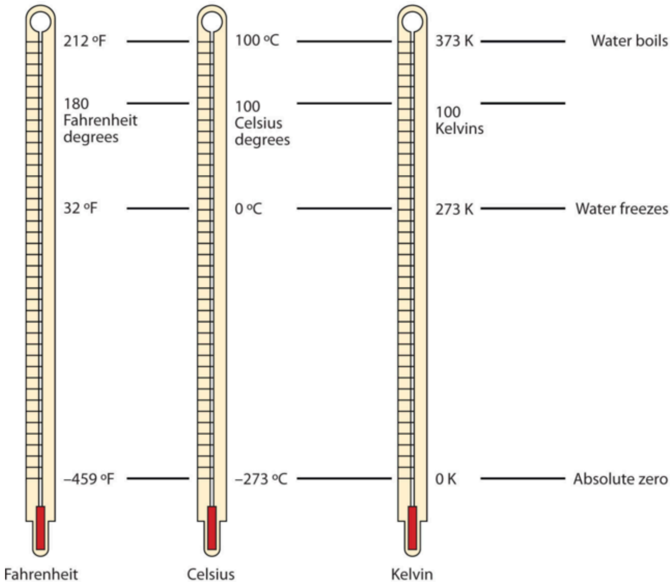


Figure 2.3.6. Fahrenheit, Celsius, and Kelvin temperatures. A comparison of the three temperature scales. These thermometers have a red-colored liquid which contains alcohol and food coloring. Silver-looking thermometers contain mercury, which is a neurotoxin.

In the United States, the commonly used temperature scale is the **Fahrenheit** scale (symbolized by °F and spoken as “degrees Fahrenheit”). On this scale, the freezing point of liquid water (the temperature at which liquid water turns to solid ice) is 32 °F, and the boiling point of water (the temperature at which liquid water turns to steam) is 212 °F.

Scientists use other scales to express temperature. For example, the Celsius scale (symbolized by °C and spoken as “degrees Celsius”) defines 0 °C as the freezing point of water and 100 °C as the boiling point of water. This scale is divided into 100 divisions between these two landmarks and extended higher and lower as well. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$°C = (°F - 32) \times \frac{5}{9}$$

$$°F = \left(°C \times \frac{9}{5}\right) + 32$$

Note that science uses the Celsius and Kelvin scales almost exclusively; virtually no practicing chemist expresses laboratory-measured temperatures with the Fahrenheit scale, but it is included here for the sake of completeness.

The fundamental unit of temperature in SI is the Kelvin (K). The Kelvin temperature scale (note that the name of the scale capitalizes the word *Kelvin*, but the unit itself is lowercase) uses degrees that are the same size as the Celsius degree, but the numerical scale is shifted up by 273.15 units. That is, the conversion between the Kelvin and Celsius scales is as follows:

$$K = {}^{\circ}C + 273.15$$

For most purposes, it is acceptable to use 273 instead of 273.15 when converting to Kelvin.

Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as “two hundred ninety-five kelvin” and not “two hundred ninety-five degrees kelvin.”

The reason that the Kelvin scale is defined this way is that there exists a minimum possible temperature called **absolute zero** (zero kelvin). The Kelvin temperature scale is set so that 0 K is absolute zero, and the temperature is counted upward from there. Normal room temperature is about 295 K, as seen in the following example.

Example 2.3.5 – Room Temperature

If the normal room temperature is 72.0 °F, what is room temperature in degrees Celsius and Kelvin?

Solution

First, we determine the temperature in degrees Celsius:

$$\begin{aligned} {}^{\circ}C &= (72.0 - 32) \times \frac{5}{9} \\ &= 40.0 \times \frac{5}{9} \\ &= 22.2\,{}^{\circ}C \end{aligned}$$

Then we determine the temperature in the Kelvin scale:

$$K = 22.2\,{}^{\circ}C + 273.15$$

$$K = 295.4\ K$$

So, the room temperature is about 295 K.

★ Questions

1. A scuba tank is filled before a dive with air until the pressure gauge reads 200.0 bar. Convert this pressure to:

(a) atm

(b) Pa and kPa

(c) mmHg

2. A round bottom flask with a diameter of 17.0 cm contains 1.00 mol of hydrogen gas at a pressure of 333 Torr. What is the force, in Newtons, exerted on the interior walls of the flask?

3. A cubic container measuring 40.0 cm x 40.0 cm x 40.0 cm weighs 255.0 g when evacuated (empty). When filled with some xenon gas, the pressure generated by the weight of the container on its bottom face is measured to be 21.65 kPa. What amount of xenon gas, in moles, is in the container?

4. Barometric pressure is directly related to meteorological conditions: a stable, high barometric pressure indicates good weather, whereas a falling pressure warns that a low pressure system, bringing poor weather, is

approaching. Over the course of an afternoon, the barometric pressure above Ottawa drops from 102.27 kPa to 99.85 kPa. What is the change in the amount of applied force (in Newtons) on the surface of a 1.5 m x 2.5 m picnic table, as the atmospheric pressure drops?

5. On the Canadian Red Cross website, you can find the following advice for what to do if you fall through the ice on a frozen body of water:

"Reach forward onto the broken ice without pushing down. Kick your legs to try to get your body into a horizontal position. Continue kicking your legs, and crawl onto the ice. When you are back on the ice, crawl on your stomach or roll away from the open area with your arms and legs spread out as far as possible. Do not stand up! Look for shore and make sure you are crawling in the right direction."

Why is it important to crawl or roll away from the open area, instead of standing up and walking away quickly?

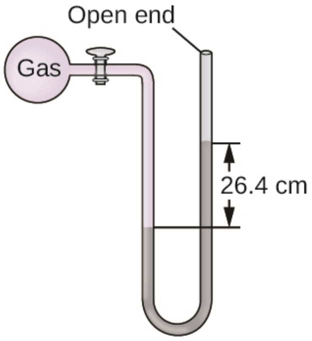
6. Barometers and manometers are always fabricated using non-volatile liquids to measure pressure. Give one reason why volatile liquids would be inappropriate.

7. The pressure of a sample of gas is measured at sea level with a closed-end manometer. The liquid in the manometer is mercury. Determine the pressure of the gas in:

(a) Torr

(b) Pa

(c) bar

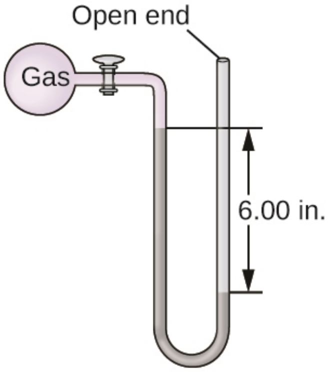


8. The pressure of a sample of gas is measured with an open-end manometer, partially shown to the right. The liquid in the manometer is mercury. Assuming atmospheric pressure is 1.010 atm, determine the pressure of the gas in:

(a) Torr

(b) Pa

(c) bar



9. When you ride an elevator to the top floor of a skyscraper, you may notice the sensation of your ears "popping". What physiological change are you experiencing?

Answers

1. (a) 197.4 atm

(b) 2.000×10^4 kPa

(c) 1.50×10^5 mmHg

2. $d = 0.17$ m, $r = 0.085$ m, Area of a sphere = 0.0908 m^2, P (in Pa) = 4.44×10^4 $N{\cdot}m^{-2}$, F (in N) = $P \times A$ = 4.03×10^3 N

3. 0.75 mol Xe

4. 9075 N

5. By spreading out your weight over a larger surface area, you decrease the pressure applied to the ice, decreasing your risk of falling through the ice again.

6. If a volatile liquid was used, it would produce a vapour, which would exert its own partial pressure against the surface of the liquid, resulting in false measurements.

7. (a) 264 Torr

(b) 35 200 Pa

(c) 0.352 bar

8. (a) P_{gas} = 615.2 Torr

(b) *P (in Pa)* = 8.20×10^4 Pa

(c) *P (in bar)* = 0.820 bar

9. As you ascend in altitude, the atmospheric pressure outside your body decreases. Air trapped inside your body in your Eustachian tubes expands, building up pressure in your middle ear, until the tubes suddenly open. When they open, the pressure is equalized and your eardrums move, creating the "popping" sensation.

2.4 – GAS LAWS

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure 2.4.1), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.

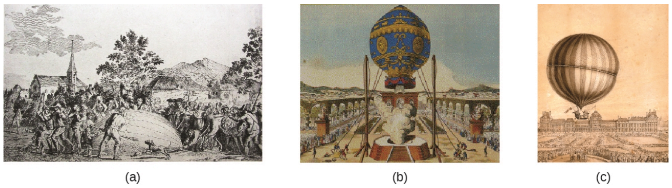


Figure 2.4.1. In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400 000 people in Paris.

Pressure and Temperature: Amontons's/Gay-Lussac's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure 2.4.2) and the pressure increases.

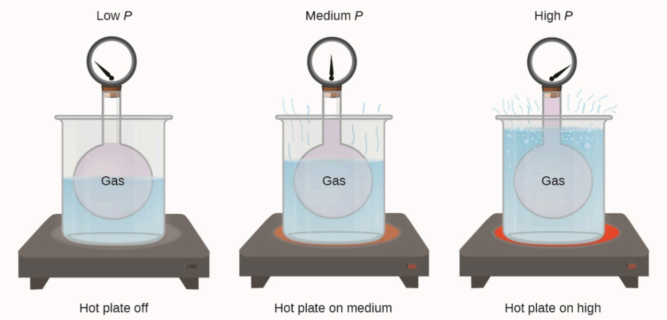


Figure 2.4.2. The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature graph is shown for a sample of air under these conditions in Figure 2.4.3. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then P and T are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

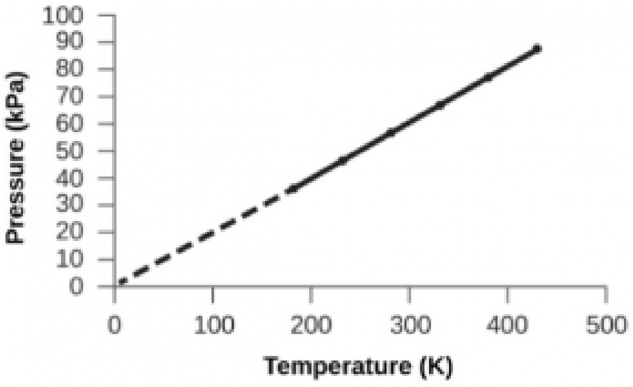


Figure 2.4.3. For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the Kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the $P – T$ relationship for gases is known as either **Amontons's law** or **Gay-Lussac's law**. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the Kelvin scale when the volume is held constant*. Mathematically, this can be written:

$$P \propto T \quad \text{or} \quad P = \text{constant} \times T \quad \text{or} \quad P = k \times T$$

where ∝ means "is proportional to," and k is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $^{P}/_{T}$ is therefore constant (i.e., $PT = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $^{P1}/_{T1} = k$ and $^{P2}/_{T2} = k$, which reduces to $^{P1}/_{T1} = {}^{P2}/_{T2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be in kelvin for any gas law calculations (0 on the Kelvin scale and the lowest possible temperature known as absolute zero). Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: we can use a table of values, a graph, or a mathematical equation.

Example 2.4.1 – Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

(a) On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?

(b) The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

(a) The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)

(b) We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{360\ kPa}{297\ K} = \frac{P_2}{323\ K}$$

Rearranging and solving gives:

$$P_2 = \frac{360\ kPa\ \times\ 323\ K}{297\ K} = 390\ kPa$$

Check Your Learning 2.4.1– Predicting Change in Pressure with Temperature

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 Torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer

400 Torr

To see Amonton's/Gay-Lussac's law in action, check out this video.

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up. Check out this video to see it in action.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are graphed in Figure 2.4.4.

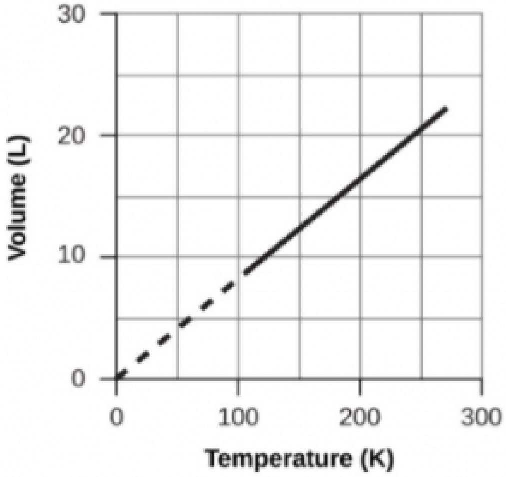


Figure 2.4.4. The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. **Charles's law** states that *the volume of a given amount of gas is directly proportional to its temperature on the Kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \propto T \quad \text{or} \quad V = \text{constant} \times T \quad \text{or} \quad V = k \times T \quad \text{or} \quad {}^{V1}/_{T1} = {}^{V2}/_{T2}$$

with k being a proportionality constant that depends on the amount and pressure of the gas. For a confined, constant pressure gas sample, ${}^{V}/_{T}$, is constant (*i.e.*, the ratio = k), and as seen with the $P – T$ relationship, this leads to another form of Charles's law: ${}^{V1}/_{T1} = {}^{V2}/_{T2}$.

Example 2.4.2 – Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 Torr. What volume will the gas have at 30 °C and 750 Torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300\ L}{283\ K} = \frac{V_2}{303\ K}$$

Rearranging and solving gives:

$$V_2 = \frac{0.300\ L \times 303\ K}{283\ K} = 0.321\ L$$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Check Your Learning 2.4.2 – Predicting Change in Volume with Temperature

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 Torr. What volume will it occupy at –70 °C and the same pressure?

Answer

21.6 mL

Example 2.4.3 – Measuring Temperature with a Volume Change

Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{150.0\ cm^3}{273.15\ K} = \frac{131.7\ cm^3}{T_2}$$

Rearrangement gives:

$$T_2 = \frac{131.7\ cm^3\ \times\ 273.15\ K}{150.0\ cm^3} = 239\ K$$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

Check Your Learning 2.4.3 – Measuring Temperature with a Volume Change

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer

635 mL

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure 2.4.5.

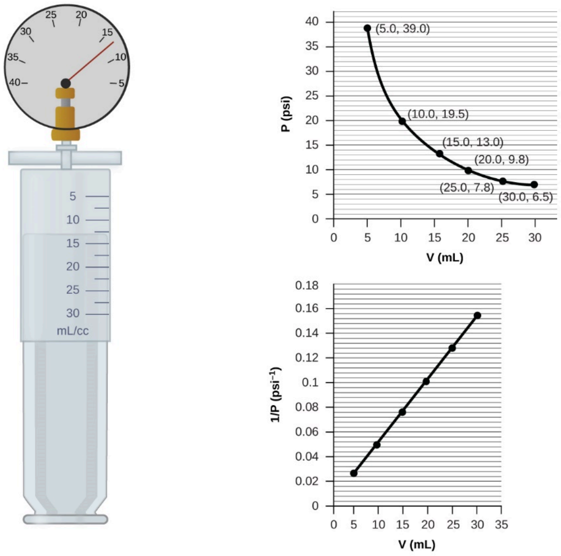
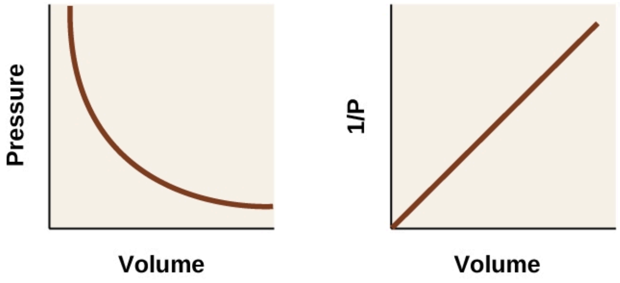


Figure 2.4.5. When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since *P* and *V* are inversely proportional, a graph of $^{1}/_{P}$ vs. V is linear.

Unlike the P– *T* and *V* – *T* relationships, pressure and volume are not directly proportional to each other. Instead, *P* and *V* exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto {}^{1}/_{V} \quad \text{or} \quad P = k\cdot{}^{1}/_{V} \quad \text{or} \quad P\cdot V = k \quad \text{or} \quad P_1V_1 = P_2V_2$$

with *k* being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure ($^{1}/_{P}$) versus the volume (*V*), or the inverse of volume ($^{1}/_{V}$) versus the pressure (*P*). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to "linearize" their data. If we plot *P* versus *V*, we obtain a hyperbola (see Figure 2.4.6).



(a)

(b)

Figure 2.4.6. The relationship between pressure and volume is inversely proportional. (a) The graph of *P* vs. *V* is a hyperbola, whereas (b) the graph of ($^{1}/_{P}$) vs. *V* is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.* Check out this experiment to learn more about Boyle's law.

Example 2.4.4 – Volume of a Gas Sample

The sample of gas in Figure 2.4.5. has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

(a) the *P*–*V* graph in Figure 2.4.5.

(b) the ($^1/_\text{P}$) vs. *V* graph in Figure 2.4.5.

(c) the Boyle's law equation.

Comment on the likely accuracy of each method.

Solution

(a) Estimating from the *P*–*V* graph gives a value for *P* somewhere around 27 psi.

(b) Estimating from the $^1/_\text{P}$ versus *V* graph gives a value of about 26 psi.

(c) From Boyle's law, we know that the product of pressure and volume (*PV*) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$. Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1V_1 = P_2V_2$$
$$13.0\ psi \times 15.0\ mL = P_2 \times 7.5\ mL$$

Solving:

$$P_2 = \frac{13.0\ psi\ \times\ 15.0\ mL}{7.5\ mL} = 26\ psi$$

It was more difficult to estimate accurately from the *P*–*V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Check Your Learning 2.4.4 – Volume of a Gas Sample

The sample of gas in Figure 2.4.5. has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

(a) the *P*–*V* graph in Figure 2.4.5.

(b) the $^1/_\text{P}$ vs *V* graph in Figure 2.4.5.

(c) the Boyle's law equation

Answer

(a) about 17–18 mL; (b) ~18 mL; (c) 17.7 mL

Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 2.4.7.).

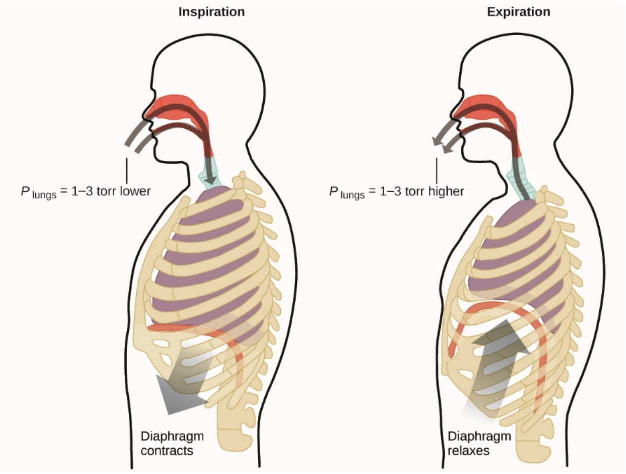


Figure 2.4.7. Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

Check out Chris Hadfield's demonstration in a submarine to learn more about Boyle's law.

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by **Avogadro's law**: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

$$V \propto n \quad or \quad V = k \times n \quad or \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as P versus n, and n versus T. Check out the following animation to see how the gas laws are affected by changes in pressure, temperature, moles of gas, and volume.

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's/Gay-Lussac's law: $^{P}/_{T}$ = constant at constant V and n
- Charles's law: $^{V}/_{T}$ = constant at constant P and n
- Avogadro's law: $^{V}/_{n}$ = constant at constant P and T

Combining these four laws yields the **ideal gas law**, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the Kelvin scale, and R is a constant called the **ideal gas constant** or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.314 kPa L mol^{-1} K^{-1}. To see the gas constant expressed in different units, visit this site.

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an **ideal gas**. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 2.4.5 – Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 Torr?

Solution

We must rearrange $PV = nRT$ to solve for V:

$$V = \frac{nRT}{P}$$

If we choose to use R = 0.08206 L atm mol^{-1} K^{-1}, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the correct units and solving:

$$n = 655\ g\ CH_4 \times \frac{1\ mol}{16.043\ g\ CH_3} = 40.8\ mol$$

$$T = 25\,^{\circ}C + 273 = 298\ K$$

$$V = \frac{nRT}{P} = \frac{(40.8\ mol)(0.08206\ L \cdot atm \cdot mol^{-1} \cdot K^{-1})(298\ K)}{0.980\ atm} = 1.02 \times 10^3\ L$$

It would require 1020 L of gaseous methane at about 1 atm of pressure to replace 1 gallon of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Check Your Learning 2.4.5 – Using the Ideal Gas Law

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $^{P1(V1)}/_{T1} = {}^{P2(V2)}/_{T2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law constant).

Example 2.4.6 – Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 2.4.8.). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 21 m in the ocean where the pressure is 3.13 atm?

Figure 2.4.8. Scuba divers use compressed air to breathe while underwater. (credit: KS Focsaneanu)

Solution

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}\rightarrow\frac{(153\ atm)(13.2\ L)}{300\ K}=\frac{(3.13\ atm)(V_2)}{310\ K}$$

Solving for V_2:

$$V_2=\frac{(153\ atm)(13.2\ L)(310\ K)}{(300\ K)(3.13\ atm)}=667\ L$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

Check Your Learning 2.4.6 – Using the Combined Gas Law

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

The Interdependence Between Ocean Depth and Pressure in SCUBA Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 2.4.9) or in the Caribbean, divers must un
how pressure affects a number of issues related to their comfort and safety.

Figure 2.4.9. Scuba divers must be constantly aware of buoyancy, pressure equalization, and the amount of time they
underwater, to avoid the risks associated with pressurized gases in the body. (credit: KS Focsaneanu)

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a
experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are give
of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 10 m of salt water represen
of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressur
the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to
potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body
on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears an
by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equaliz
Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If
ascending, the air in his BCD expands because of lower pressure according to Boyle’s law (decreasing the pressure of gase
the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent
the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air
BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled des
facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater befor
ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver
m, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available
fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a standard temperature and pressure (STP) for reporting properties of gases: 273.15 K and 1 bar (100 kPa). At STP, one mole of an ideal gas has a volume of about 22.7 L—this is referred to as the **standard molar volume** (Figure 2.4.10).

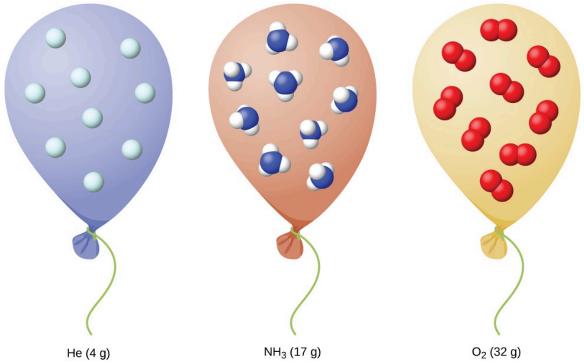


Figure 2.4.10. Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 bar or 100 kPa) to report properties of gases.

CHM1311 Laboratory | Experiment #1: Verification of Gas Laws

Purpose

Before you get started with your first experiment of the course, you'll first organize yourself by getting a lab partner, meeting your TA (lab demonstrator), and performing a locker examination of laboratory equipment at your disposal. You'll also be familiarizing yourself with the laboratory component of the general chemistry course and all logistical matters pertaining to it. This information will be presented to you briefly on your first day and is all available on Brightspace in the CHM1311 General Chemistry Laboratory course platform.

For the actual experiment, you'll be validating two of the gas laws you saw in this section:

Boyle's Law: at a given constant temperature, the pressure of a certain amount of gas is inversely proportional to its volume

$$P \propto {}^{1}/_{V}$$

Charles' Law: under constant pressure conditions, the volume of a particular amount of gas is directly proportional to its temperature

$$V \propto T$$

Principles

Charles' Law

Boyle's Law

Ideal gas behaviour

Determination of experimental parameters

Validation of experimental results

Safety Precautions

Wear appropriate personal protective equipment (PPE) at all times in the laboratory setting – this includes your lab coat and safety goggles/glasses.

You'll be working with hot objects, including the hot plate, boiling water bath, and heated Erlenmeyer flask during the first part of validating Charles' Law. Please take extra precaution when handling such objects and avoid direct contact with them. Equipment such as tongs and clamps are at your disposal to use.

Things to Consider

The notion and properties of an ideal gas differ from those of a real gas (see sections 2.6 and 2.8 on the differing properties of ideal and real gases). Note that the two gas laws you'll be investigating assume that air behaves as an ideal gas, since these two laws constitute the *ideal gas* law. Keep this assumption in mind when you perform your data analysis and discuss your findings in your report.

When thinking about sources of error for validating gas laws, consider the existence of other gas variables, what they are, and how they may or may not have affected your results.

Charles' Law

Why was it important to start every trial with a *dry* Erlenmeyer flask?

Why did the experiment have to be restarted if air bubbles escaped the flask when its mouth was submerged in the ice bath?

If you recall playing in water as a child, you might know that if you invert a container, like a toy bucket, and submerge it in the water with the opening facing downwards, the air occupying the inside remains trapped inside the container. So can you explain why, in this experiment, water entered the flask?

What was the purpose of matching the level of water in the flask to the level of water in the ice bath?

Boyle's Law

What are the independent and dependent variables of your experiment? How will you measure these variables? What are their units of measurement? Recall that the independent variable is typically the one that you handle first and that you can manipulate, whereas the dependent variable usually involves measurements that *depend* on your independent variable.

How many measurements do you need?

Why did you measured the initial volume twice? Think about why it's important to take multiple readings of the dependent variable for the same value of the independent variable

Which volume reading did you choose and why? Make sure you explain your choice in your report.

Be aware of correcting all measured volumes by adding 0.8 mL to reach reading; this will account for the space inside the pressure sensor itself.

Reference

Venkateswaran, R. General Chemistry – Laboratory Manual – CHM 1301/1311.

Questions

★ Questions

1. Determine the volume of 1 mol of CH_4 gas at 150 K and 1 atm, using Figure 2.4.4.

2. Determine the pressure of the gas in the syringe shown in Figure 2.4.5. when its volume is 12.5 mL, using:

(a) the appropriate graph

(b) Boyle's law

3. A spray can is used until it is empty except for the propellant gas, which has a pressure of 1344 Torr at 23 °C. If the can is thrown into a fire (T = 475 °C), what will be the pressure in the hot can?

4. A 2.50 L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

5. A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?

6. Iodine, I_2, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3 mL bulb that contains 0.292 g of I_2 vapor at a pressure of 0.462 atm?

7. How many grams of gas are present in each of the following cases?

(a) 0.100 L of CO_2 at 307 Torr and 26 °C

(b) 8.75 L of C_2H_4, at 378.3 kPa and 483 K

(c) 221 mL of Ar at 0.23 Torr and –54 °C

★★ Questions

8. A high altitude balloon is filled with 1.41×10^4 L of hydrogen at a temperature of 21 °C and a pressure of 745 Torr. What is the volume of the balloon at a height of 20 km, where the temperature is –48 °C and the pressure is 63.1 Torr?

9. A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

10. A 20.0 L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

11. For a given amount of gas showing ideal behavior, draw labeled graphs of:

(a) the variation of P with V

(b) the variation of V with T

(c) the variation of P with T

(d.) the variation of $^{1}/_{P}$ with V

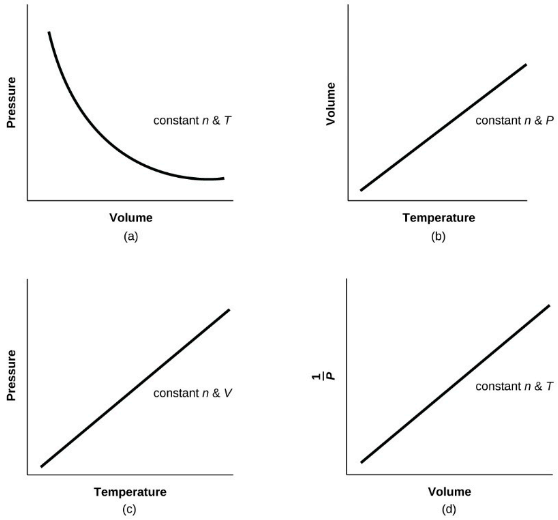
12. A liter of methane gas, CH_4, at STP contains more atoms of hydrogen than does a liter of pure hydrogen gas, H_2, at STP. Using Avogadro's law as a starting point, explain why.

13. If the temperature of a fixed amount of a gas is doubled at constant volume, what happens to the pressure?

14. If the volume of a fixed amount of a gas is tripled at constant temperature, what happens to the pressure?

Answers

1. About 12.2 L
2. (a) 15.38 psi, (b) 15.6 psi
3. 3.40×10^{3} Torr
4. 12.1 L
5. 217 L
6. 358.5 K
7. (a) 7.24×10^{-2} g; (b) 23.1 g; (c) 1.5×10^{-4} g
8. 1.274×10^{5} L
9. 5561 L
10. 46.4 g
11.



12. One mole of gas is equivalent to 22.4 Liters at STP. Hence there are twice as many H atoms in CH_4 than there are in H_2, and as a result there are more H atoms in the CH_4 sample.

13. ${}^{P1}/_{T1} = {}^{P2}/_{T2}$, hence $P1 = {}^{T1(P2)}/_{2(T1)}$, $2 \times P_1 = P_2$, hence the pressure doubles.

14. The pressure decreases by a factor of 3.

2.5 – GAS MIXTURES AND PARTIAL PRESSURES

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

The Pressure of a Mixture of Gases: Dalton's Law

In gas mixtures, each component in the gas phase can be treated separately. Each component of the mixture shares the same temperature and volume. (Remember that gases expand to fill the volume of their container; gases in a mixture do that as well.) However, each gas has its own pressure. Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure 2.5.1). The pressure exerted by each individual gas in a mixture is called its **partial pressure**, denoted P_i. This observation is summarized by **Dalton's law of partial pressures**: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{\text{Total}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \ldots = \Sigma_{\text{i}} P_{\text{i}}$$

Equation 2.5.1. Dalton's law of partial pressures.

In the equation, P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

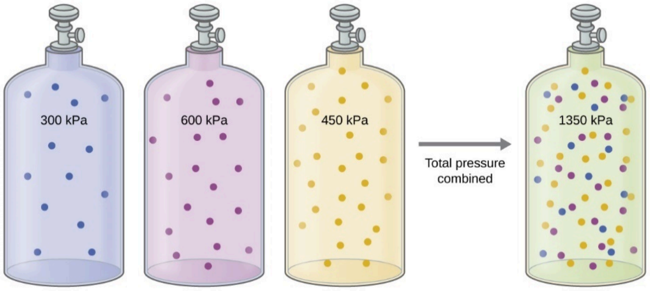


Figure 2.5.1. If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

In this scenario of gas mixtures, volume and temperature are held constant because the gas are mixed together in one container (same fixed volume) in the same surroundings (same temperature). In that case, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times constant$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

Hence, if we have, for example, a mixture of two ideal gases, *A* and *B*, we can write an expression for the total pressure as:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right)$$

More generally, for a mixture of *n* component gases, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \ldots + P_n)\left(\frac{RT}{V}\right)$$

$$P_{tot} = \sum_{i=1}^{n} n_i\left(\frac{RT}{V}\right)$$

Mole Fractions of Gas Mixtures

The partial pressure of gas A is related to the total pressure of the gas mixture via its **mole fraction (*X*)**, a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

Example 2.5.1 – The Pressure of a Mixture of Gases

A 10.0 L vessel contains 2.50 × 10^{-3} mol of H_2, 1.00 × 10^{-3} mol of He, and 3.00 × 10^{-4} mol of Ne at 35 °C.

(a) What are the partial pressures of each of the gases?

(b) What is the total pressure in atmospheres?

Solution

(a) The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = {}^{\text{nRT}}/V$:

$$P_{H_2} = \frac{(2.50\ \times\ 10^{-3}\ mol)(0.08206\ L \cdot atm \cdot mol^{-1} \cdot K^{-1})(308\ K)}{10.0\ L} = 6.32 \times 10^{-3}\ atm$$

$$P_{He} = \frac{(1.00\ \times\ 10^{-3}\ mol)(0.08206\ L \cdot atm \cdot mol^{-1} \cdot K^{-1})(308\ K)}{10.0\ L} = 2.53 \times 10^{-3}\ atm$$

$$P_{Ne} = \frac{(3.00\ \times\ 10^{-4}\ mol)(0.08206\ L \cdot atm \cdot mol^{-1} \cdot K^{-1})(308\ K)}{10.0\ L} = 7.58 \times 10^{-4}\ atm$$

(b) The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076)\ atm = 9.61 \times 10^{-3}\ atm$$

Check Your Learning 2.5.1 – The Pressure of a Mixture of Gases

A 5.73 L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer

1.14 atm

Here is another example of this concept, but dealing with mole fraction calculations.

Example 2.5.2 – The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O_2, and 8.41 mol nitrous oxide, N_2O. The total pressure of the mixture is 192 kPa.

(a) What are the mole fractions of O_2 and N_2O? What are the partial pressures of O_2 and N_2O?

Solution

The mole fraction is given by $X_A = \frac{n_A}{n_{Total}}$ and the partial pressure is $P_A = X_A \times P_{Total}$.

For O_2,

$$X_{O_2} = \frac{n_{O_2}}{n_{total}} = \frac{2.83\ mol}{(3.83\ +\ 8.41)\ mol} = 0.252$$

and:

$$P_{O_2} = X_{O_2} \times P_{total} = 0.252 \times 192\ kPa = 48.4\ kPa$$

For N_2O,

$$X_{N_2} = \frac{n_{N_2}}{n_{Total}} = \frac{8.41\ mol}{(2.83\ +\ 8.41)\ mol} = 0.748$$

and:

$$P_{N_2} = X_{N_2} \times P_{total} = 0.748 \times 192\ kPa = 143.6\ kPa$$

Check Your Learning 2.5.2 – The Pressure of a Mixture of Gases

What is the pressure of a mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar in a container with a volume of 2.00 L at 20°C?

Answer

1.87 atm

Collection of Gases over Water

The collection of gases over water by bubbling through it is one of the main reasons why we have to learn and understand Dalton's law of partial pressures. This simple way of collecting gases that do not react with water involves capturing them in a bottle that has been filled with water and inverting into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 2.5.2), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

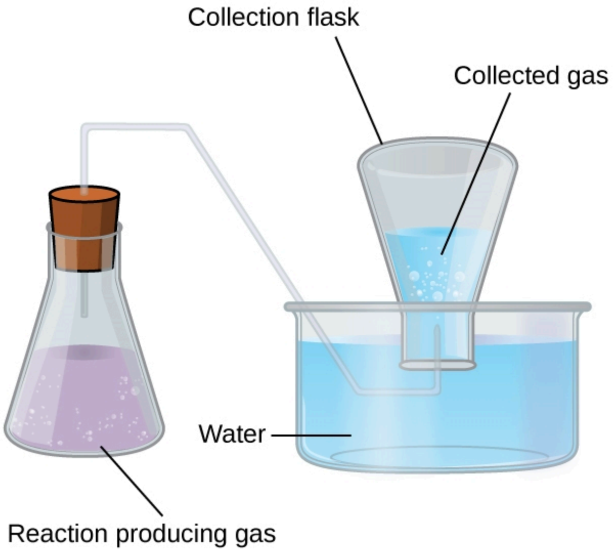


Figure 2.5.2. When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapour. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Liquids, including water, have a property of constantly evaporating into a vapour until the vapour achieves a partial pressure characteristic of the substance and the temperature. This partial pressure is called a vapour pressure. Water evaporates and there is always gaseous water (water vapour) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapour and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapour. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapour—this is referred to as the "dry" gas pressure, that is, the pressure of the gas only, without water vapour. The **vapour pressure of water**, which is the pressure exerted by water vapour in equilibrium with liquid water in a closed container, depends on the temperature (Figure 2.5.3); more detailed information on the temperature dependence of water vapour can be found in Table 2.5.1 below Figure 2.5.3.

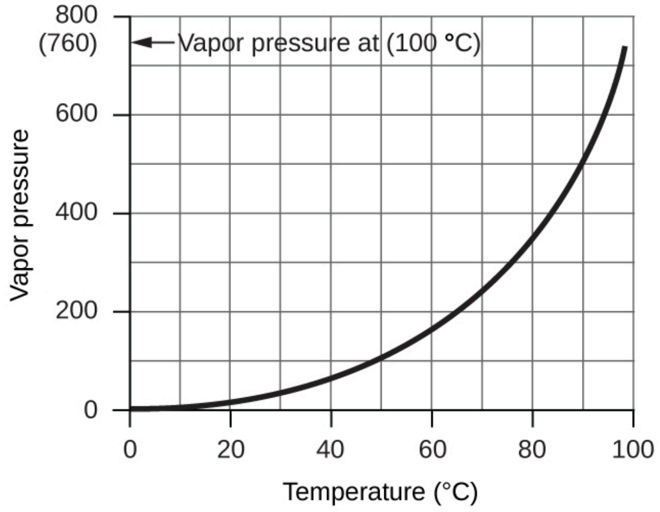


Figure 2.5.3. The vapour pressure of water at sea level as a function of temperature.

Table 2.5.1. Vapour pressure of ice and water in various temperatures at sea level.

Temperature (°C)	**Pressure (Torr)**	**Temperature (°C)**	**Pressure (Torr)**	**Temperature (°C)**	**Pressure (Torr)**
-10	1.95	18	15.48	30	31.82
-5	3.01	19	16.48	35	41.18
-2	3.88	20	17.54	40	55.32
0	4.58	21	18.65	50	92.51
2	5.29	22	19.83	60	149.38
4	6.10	23	21.07	70	233.7
6	7.01	24	22.38	80	355.1
8	8.04	25	23.76	90	525.76
10	9.21	26	25.21	95	633.90
12	10.52	27	26.74	99	733.24
14	11.99	28	28.35	100.0	760.00
16	13.63	29	30.04	101.0	787.57

***** CRC Handbook of Chemistry and Physics, 65th Edition. Cleveland, Ohio: CRC Press, 1984.

Example 2.5.3 – Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 Torr in a system like that shown in Figure 2.5.2, what is the partial pressure of argon?

Solution

According to Dalton's law, the total pressure in the bottle (750 Torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_T = P_{Ar} + P_{H2O}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{Ar} = P_T - P_{H2O}$$

The pressure of water vapour above a sample of liquid water at 26 °C is about 25.2 Torr (Appendix F), so:

$$P_{\mathrm{Ar}} = 750\ \mathrm{Torr} - 25.2\ \mathrm{Torr} = 725\ \mathrm{Torr}$$

Check Your Learning 2.5.3 – Pressure of a Gas Collected Over Water

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 Torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

Answer:

0.583 L

Food/Drink Application – Carbonated Beverages

Carbonated beverages—sodas, beer, sparkling wines—have one thing in common: they have CO_2 gas dissolved in them in such sufficient quantities that it affects the drinking experience. Most people find the drinking experience pleasant—indeed, in Canada alone in 2016, about 1/4 of those 5 to 19 years of age reported daily consumption of sugary drinks. Research shows that soda, energy and sports drinks are the top calorie source among North Americans ages 12 to 50.

All carbonated beverages are made in one of two ways. First, the flat beverage is subjected to a high pressure of CO_2 gas, which forces the gas into solution. The carbonated beverage is then packaged in a tightly sealed package (usually a bottle or a can) and sold. When the container is opened, the CO_2 pressure is released, resulting in the well-known *hiss*, and CO_2 bubbles come out of solution (Figure 2.5.4). This must be done with care: if the CO_2 comes out too violently, a mess can occur!

Figure 2.5.4. If you are not careful opening a container of a carbonated beverage, you can make a mess as the CO_2 comes out of solution suddenly. Source: "Champagne uncorking" by Niels Noordhoek is licensed under the Creative Commons Attribution-Share Alike 3.0 Unported license.

The second way a beverage can become carbonated is by the ingestion of sugar by yeast, which then generates CO_2 as a digestion product. This process is called *fermentation*. The overall reaction is:

$$C_6H_{12}O_6\,(aq) \rightarrow 2\,C_2H_5OH\,(aq) + 2\,CO_2\,(aq)$$

When this process occurs in a closed container, the CO_2 produced dissolves in the liquid, only to be released from solution when the container is opened. Most fine sparkling wines and champagnes are turned into carbonated beverages this way. Less-expensive sparkling wines are made like sodas and beer, with exposure to high pressures of CO_2 gas.

Source: Heart and Stroke Foundation.

Questions

★ Questions

1. A cylinder of $O_2\,(g)$ used in breathing by emphysema patients has a volume of 3.00 L at a pressure of 10.0 atm. If the temperature of the cylinder is 28.0 °C, what mass (in grams) of oxygen is in the cylinder?

2. What is the molar mass (in $g{\cdot}mol^{-1}$) of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 Torr?

3. How could you show experimentally that the molecular formula of propene is C_3H_6, not CH_2?

4. The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at STP (where $P = 1.00$ bar, $T = 273.15$ K, 1 mole = 22.7 L). Calculate the molar mass (in g•mol^{-1}) of this fluoride and determine its molecular formula.

5. What is the molecular formula of a compound that contains 39% C, 45% N, and 16% H if 0.157 g of the compound occupies 125 mL with a pressure of 99.5 kPa at 22 °C?

6. A cylinder of a gas mixture used for calibration of blood gas analyzers in medical laboratories contains 5.0% CO_2, 12.0% O_2, and the remainder N_2 at a total pressure of 146 atm. What is the partial pressure (in bars) of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

7. A sample of gas isolated from unrefined petroleum contains 90.0% CH_4, 8.9% C_2H_6, and 1.1% C_3H_8 at a total pressure of 307.2 kPa. What is the partial pressure (in bars) of each component of this gas? (The percentages given indicate the percent of the total pressure that is due to each component.)

8. A mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar is stored in a closed container at STP (where $P = 1.00$ bar, $T = 273.15$ K, 1 mole = 22.7 L). Find the volume of the container (in litres), assuming that the gases exhibit ideal behavior.

9. Calculate the volume (in litres) of oxygen required to burn 12.00 L of ethane gas, C_2H_6, to produce carbon dioxide and water, if the volumes of C_2H_6 and O_2 are measured under the same conditions of temperature and pressure.

10. Methanol, CH_3OH, is produced industrially by the following reaction:

$$CO\,(g) + 2\,H_2\,(g) \rightarrow CH_3OH\,(g) \text{ (using a copper catalyst 300 °C, 300 atm)}$$

Assuming that the gases behave as ideal gases, find the ratio of the total volume of the reactants to the final volume.

11. A 2.50-L sample of a colorless gas at STP decomposed to give 2.50 L of N_2 and 1.25 L of O_2 at STP. What is the colorless gas?

★★ Questions

12. Ethanol, C_2H_5OH, is produced industrially from ethylene, C_2H_4, by the following sequence of reactions:

$$3\,C_2H_4 + 2\,H_2SO_4 \rightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4$$

$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + 3\,H_2O \rightarrow 3\,C_2H_5OH + 2\,H_2SO_4$$

What volume (in litres) of ethylene at STP (where P = 1.00 bar, T = 273.15 K, 1 mole = 22.7 L) is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%?

★★★ Questions

13. A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 Torr. Hydrogen was added to the bulb until the pressure was 72 Torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 Torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.)

Answers

1. 38.8 g

2. 30.0 g mol^{-1}

3. By doing an elevation in boiling point and a depression of freezing point as an experiment, one can find the exact molecular mass. As a result of that, the difference between propene and CH_2 can be determined.

4. 88.1 g mol^{-1}; PF_3

5. (a) With the given percent compositions, one can assume a mass of 40 g C, 45 g N and 16 g H. Using this information, the empirical formula can be obtained by finding the moles of each atom making up the compound. From there, divide each mole value by the smallest amount of moles to get the makeup of the empirical formula. Calculate the molecular mass of the empirical formula based on its makeup as well as the molecular mass for the molecular formula with the given values in the question. Divide the molecular formula's molecular mass by one of the one from the empirical formula. That ratio will determine if the makeup must be multiplied by that factor in order to determine the molecular formula.; (b) CNH_5

6. CO_2 = 7 atm, O_2 = 18 atm, N_2 = 120 atm

7. CH_4: 276 kPa; C_2H_6: 27 kPa; C_3H_8: 3.4 kPa

8. 1.87 atm

9. 42.00 L

10. 3 : 1, if stoichiometric amounts are used

11. N_2O

12. 5.40×10^5 L

13. XeF_2

2.6 – KINETIC-MOLECULAR THEORY OF GASES (IDEAL GAS BEHAVIOURS)

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at lower pressures (*i.e.* less than 1 or 2 atm). Although the gas laws describe relationships that have been verified by many experiments, they do not tell us *why* gases follow these relationships.

The **kinetic molecular theory** (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

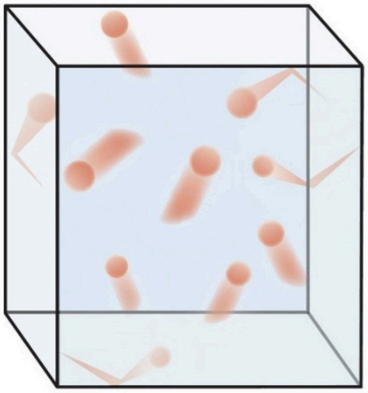


Figure 2.6.1. Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's/Gay-Lussac's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure 2.6.2(a)).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas (Figure 2.6.2(b)).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure 2.6.2(c)).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

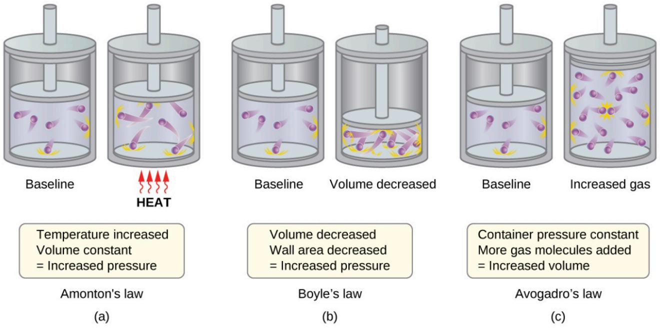


Figure 2.6.2. (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a *Maxwell-Boltzmann distribution*, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 2.6.3.).

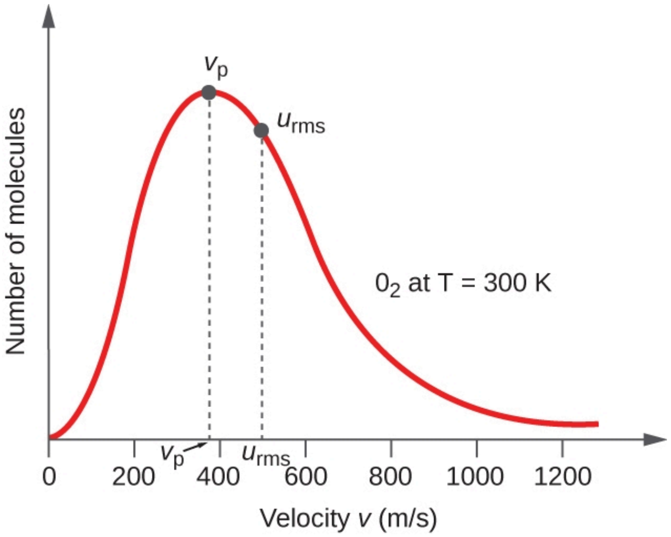


Figure 2.6.3. The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases

rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, ν_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s.

The kinetic energy (E_k) of a particle of mass (m) and speed (u) is given by:

$$E_k = \frac{1}{2}mu^2$$

Equation 2.6.1 Kinetic Energy to velocity and mass

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m^2 s^{-2}). To deal with a large population of gas molecules, we use *averages* for both speed and kinetic energy. In the KMT, the **root mean square speed** of a particle, $\boldsymbol{u_{rms}}$, is defined as the square root of the average of the squares of the velocities with n = the number of particles:

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

Equation 2.6.2 Root mean square of a particle

Note that this value is mathematically different from the gas population's arithmetic mean, and also does *not* correspond to the most probable molecular speed (ν_p).

The average kinetic energy for a mole of particles, $E_{k\ avg}$, is then equal to (where M is the average mass of the particles, expressed in kilograms):

$$E_{k\ avg} = \frac{1}{2}Mu_{rms}^2$$

Equation 2.6.3 Average kinetic energy fo a mole of particles

The E_{kavg} of a mole of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation (to extend your learning, check out the derivation for E_{kavg} here):

$$E_{k\ avg} = \frac{3}{2}RT$$

Equation 2.6.4 Average Kinetic Energy to temperature

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J/mol·K (8.314 kg $m^2 s^{-2} mol^{-1} K^{-1}$). These two separate equations for E_{kavg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2}Mu_{rms}^2 = \frac{3}{2}RT$$

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

Equation 2.6.5 Molecular Speed vs Temperature

Example 2.6.1 – Calculation of u_{rms}

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30^{\circ}\text{C} + 273 = 303\text{ K}$$

Determine the molar mass of nitrogen in kilograms:

$$\frac{28.0\ g}{1\ mol} = \frac{1\ kg}{1000\ g} = 0.028\ kg/mol$$

Replace the variables and constants in the root-mean-square velocity equation, replacing Joules with the equivalent kg m^2s^{-2}:

$$u_{rms} = \sqrt{\frac{3RT}{m}}$$

$$u_{rms} = \sqrt{\frac{3(8.314\ J/mol{\cdot}K)(303\ K)}{(0.028\ kg/mol)}} = \sqrt{2.70 \times 10^5 m^2 s^{-2}} = 519\ m/s$$

Check Your Learning 2.6.1 – Calculation of u_{rms}

Calculate the root-mean-square velocity for a mole of oxygen molecules at –23 °C.

Answer

441 m/s

If the temperature of a gas increases, its E_{kavg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution spreads out toward higher speeds overall, that is, to the right (note that the curve always passes through the origin, meaning there are always some slow-moving particles). If temperature decreases, E_{kavg} decreases, more molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behaviour is illustrated for nitrogen gas in Figure 2.6.4.

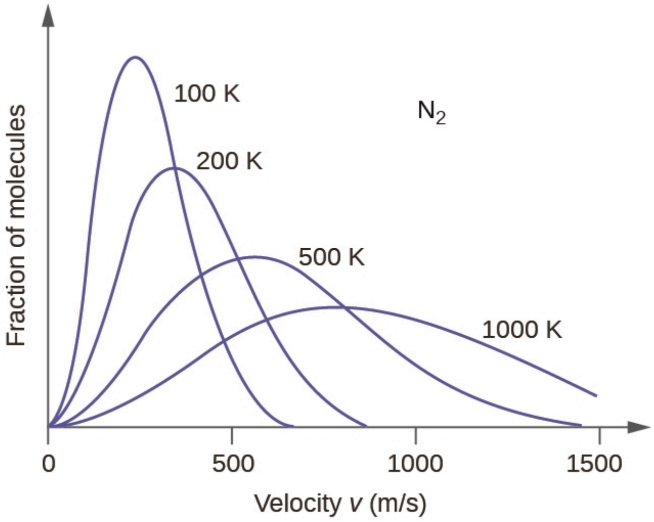


Figure 2.6.4. The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same E_{kavg} for their molecules. Gases composed of lighter molecules have more high-speed particles and thus a greater u_{rms}, with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in Figure 2.6.5.

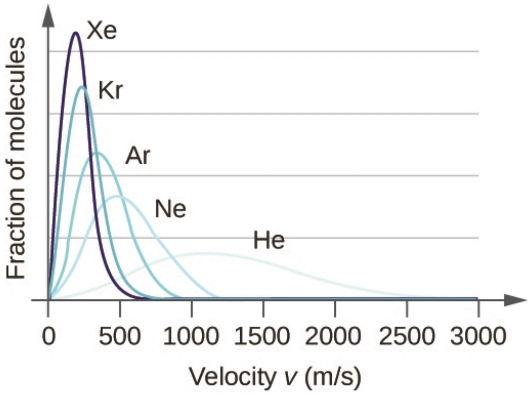


Figure 2.6.5. Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

The gas simulator may be used to examine the effect of temperature on molecular velocities. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.

Questions

★ Questions

1. Using the postulates of the kinetic molecular theory, explain why a gas uniformly fills a container of any shape.

2. Can the speed of a given molecule in a gas double at constant temperature? Explain your answer.

3. Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

    a. The pressure of the gas is increased by reducing the volume at constant temperature.

    b. The pressure of the gas is increased by increasing the temperature at constant volume.

    c. The average velocity of the molecules is increased by a factor of 2.

4. What is the ratio of the average kinetic energy of a SO_2 molecule to that of an O_2 molecule in a mixture of two gases? What is the ratio of the root mean square speeds, u_{rms}, of the two gases?

5. A 1-L sample of CO initially at STP is heated to 546 K, and its volume is increased to 2 L.

    a. What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?

    b. What is the effect on the average kinetic energy of the molecules?

    c. What is the effect on the root mean square speed of the molecules?

6. The root mean square speed of H_2 molecules at 25 °C is about 1.6 km/s. What is the root mean square speed of a N_2 molecule at 25 °C?

★★ Questions

7. Answer the following questions about a hot air balloon:

    a. Is the pressure of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

    b. Is the density of the gas in the hot air balloon shown at the opening of this chapter greater than, less than, or equal to that of the atmosphere outside the balloon?

    c. At a pressure of 1 atm and a temperature of 20 °C, dry air has a density of 1.2256 g/L. What is the (average) molar mass of dry air?

    d. The average temperature of the gas in a hot air balloon is 1.30×10^2 °F. Calculate its density, assuming the molar mass equals that of dry air.

    e. The lifting capacity of a hot air balloon is equal to the difference in the mass of the cool air displaced by the balloon and the mass of the gas in the balloon. What is the difference in the mass of 1.00 L of the cool air in part (c) and the hot air in part (d)?

    f. An average balloon has a diameter of 60 feet and a volume of 1.1×10^5 ft^3. What is the lifting power of such a balloon? If the weight of the balloon and its rigging is 500 pounds, what is its capacity for carrying passengers and cargo?

    g. A balloon carries 40.0 gallons of liquid propane (density 0.5005 g/L). What volume of CO_2 and H_2O gas is produced by the combustion of this propane?

    h. A balloon flight can last about 90 minutes. If all of the fuel is burned during this time, what is the approximate rate of heat loss (in kJ/min) from the hot air in the bag during the flight?

8. Show that the ratio of the rate of diffusion of Gas 1 to the rate of diffusion of Gas 2, $^{R1}/_{R2}$, is the same at 0 °C and 100 °C.

Answers

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines only deviating once colliding with other molecules. The pressure exerted by a gas in a container results from collisions between the gas molecules and the walls. The gas molecules are negligibly small in comparison to the distances between them.

2. Yes. At any given instant, there are a range of values of molecular speeds in a sample of gas. Any single molecule can speed up or slow down as it collides with other molecules. The average velocity of all the molecules is constant at constant temperature.

3. (a) Average kinetic energy remains unchanged, (b) P increase leads to average kinetic energy increase, (c) velocity doubled leads to a quadruple in kinetic energy

4. (a) The ratio of average kinetic energies is 1, (b) 0.71

5. (a) The number of collisions per unit area of the container wall is constant. (b) The average kinetic energy doubles. (c) The root mean square speed increases to sqrt(2) times its initial value; u_{rms} is proportional to sqrt(E_{kavg}).

6. (a) 1.92 km/s

7. (a) equal; (b) less than; (c) 29.48 g mol^{-1}; (d) 1.0966 g L^{-1}; (e) 0.129 g/L; (f) 4.01 × 10^{5} g; net lifting capacity = 384 lb; (g) 270 L; (h) 39.1 kJ min^{-1}

8. $\alpha = \frac{1}{\sqrt{m}}$, assume a system of Gas 1 and Gas 2 with masses m_1 and m_2, rate of diffusion is dependent on only mass and not temperature. Hence the rate of diffusion will remain constant at different temperatures.

2.7 – DIFFUSION AND EFFUSION

You're hanging out with your friends waiting for a pizza to arrive. The doorbell rings, and one of your friends gets up to open the door and receive the piping hot goodness. Just several seconds after and perhaps even before the door opens, you can already smell its amazing aroma. The quick speed at which the aroma propagates from the door to your nose is due to the nature of gases – gaseous molecules can quickly spread throughout a room. In this section, we discuss the process of diffusion and effusion of gases as an application of the KMT.

Diffusion

Although gaseous molecules travel at tremendous speeds (hundreds of meters per second), they collide with other gaseous molecules and travel in many different directions before reaching the desired target. At room temperature, a gaseous molecule will experience billions of collisions per second. The **mean free path** is the average distance a molecule travels between collisions. The mean free path increases with decreasing pressure; in general, the mean free path for a gaseous molecule will be hundreds of times the diameter of the molecule.

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called **diffusion** (shown in Figure 2.7.1). The gaseous atoms or molecules are, of course, unaware of any concentration gradient, they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in Figure 2.7.1. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no *net* transfer of molecules occurs).

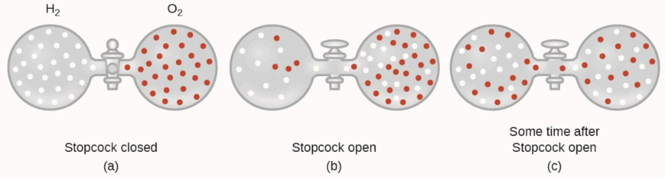


Figure 2.7.1. (a) Two gases, H_2 and O_2, are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas, H_2, passes through the opening faster than O_2, so just after the stopcock is opened, more H_2 molecules move to the O_2 side than O_2 molecules move to the H_2 side. (c) After a short time, both the slower-moving O_2 molecules and the faster-moving H_2 molecules have distributed themselves evenly on both sides of the vessel.

We are often interested in the **rate of diffusion**, the amount of gas passing through some area per unit time:

$$rate\ of\ diffusion = \frac{amount\ of\ gas\ passing\ through\ an\ area}{unit\ of\ time}$$

Equation 2.7.1 Rate of Diffusion

The diffusion rate depends on several factors: the concentration gradient (the increase or decrease in concentration from one point to another); the amount of surface area available for diffusion; and the distance the gas particles must travel. Note also that the time required for diffusion to occur is inversely proportional to the rate of diffusion, as shown in the rate of diffusion equation.

Effusion

A process involving movement of gaseous species similar to diffusion is **effusion**, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (Figure 2.7.2). Although diffusion and effusion rates both depend on the molar mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.

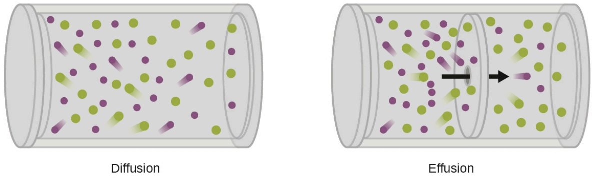


Figure 2.7.2. Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance traveled between collisions. Effectively, this means that only one particle passes through at a time.

If two gases of differing particle masses are placed into separate enclosed chambers, each with a wall containing a single pinhole, both gases will gradually effuse through the small opening in the wall. However, the lighter gas passes through the small opening more rapidly (at a higher rate) than the heavier one (Figure 2.7.3). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated **Graham's law of effusion**: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*:

$$rate\ of\ effusion \propto \frac{1}{\sqrt{M}}$$

Equation 2.7.2 Rate of effusion

This means that if two gases A and B are at the same temperature and pressure, the ratio of their effusion rates is inversely proportional to the ratio of the square roots of the masses of their particles:

$$\frac{rate\ of\ effusion\ of\ A}{rate\ of\ effusion\ of\ B} = \frac{\sqrt{M_B}}{\sqrt{M_A}}$$

Note that, when Graham's Law is used in this form, you can use molar masses expressed in either kg/mol or g/mol, as the units will cancel one another. Similarly, other units which are directly proportional to the gas's mass, such as density, can also be used.

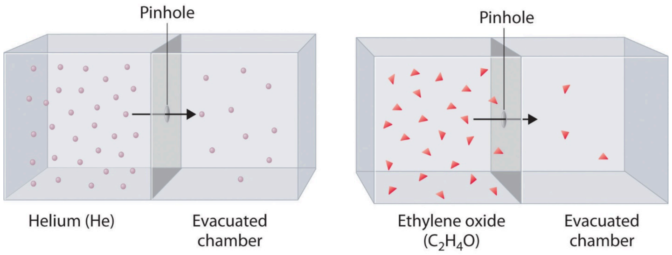


Figure 2.7.3. The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law (discussed next in this section), the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates. The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion} \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$M = \frac{3RT}{u_{rms}^2} = \frac{3RT}{\underline{u^2}}$$

$$\frac{effusion\ rate\ A}{effusion\ rate\ B} = \frac{u_{rms\ A}}{u_{rms\ B}} = \frac{\sqrt{\frac{3RT}{M}}}{\sqrt{\frac{3RT}{M}}} = \sqrt{\frac{M_B}{M_A}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law. Check out this video to better visualize rates of effusion.

Example 2.7.1 – Applying Graham's Law to Rates of Effusion

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen, using a) molar masses; and b) gas densities.

Solution

Using Graham's Law and applying molar masses:

$$\frac{rate\ of\ effusion\ of\ hydrogen}{rate\ of\ effusion\ of\ oxygen} = \frac{\sqrt{32\ g \cdot mol^{-1}}}{\sqrt{2\ g \cdot mol^{-1}}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

The densities of oxygen and hydrogen at STP are 1.43 g/L and 0.0899 g/L, respectively. Recalculating Graham's Law with densities gives the identical numerical result:

$$\frac{rate\ of\ effusion\ of\ hydrogen}{rate\ of\ effusion\ of\ oxygen} = \frac{\sqrt{1.43\ g \cdot L^{-1}}}{\sqrt{0.0899\ g \cdot L^{-1}}} = \frac{1.20}{0.300} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

Check Your Learning 2.7.1 – Applying Graham's Law to Rates of Effusion

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Using the same apparatus at the same temperature and pressure, at what rate will sulfur dioxide effuse?

Answer:

52 mL/s

Here's another example, making the point about how determining times differs from determining rates.

Example 2.7.2 – Effusion Time Calculations

It takes 243 s for 4.46×10^{-5} mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take 4.46×10^{-5} mol Ne to effuse?

Solution

It is important to resist the temptation to use the times directly, and to remember how rate relates to time as well as how it relates to mass. Recall the definition of rate of effusion:

$$rate\ of\ effusion = \frac{amount\ of\ gas\ transferred}{time}$$

and combine it with Graham's law:

$$\frac{rate\ of\ effusion\ of\ gas\ Xe}{rate\ of\ effusion\ of\ gas\ Ne} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

To get:

$$\frac{\frac{amount\ of\ Xe\ transferred}{time\ for\ Xe}}{\frac{amount\ of\ Ne\ transferred}{time\ for\ Ne}} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

Noting that *amount of A* = *amount of B*, and solving for *time for Ne*:

$$\frac{\frac{amount\ of\ Xe\ transferred}{time\ for\ Xe}}{\frac{amount\ of\ Ne\ transferred}{time\ for\ Ne}} = \frac{time\ for\ Ne}{Time\ for\ Xe} = \frac{\sqrt{M_{Ne}}}{\sqrt{M_{Xe}}}$$

and substitute values:

$$\frac{time\ for\ Ne}{243\ s} = \sqrt{\frac{20.2\ g \cdot mol^{-1}}{131.3\ g \cdot mol^{-1}}} = 0.392$$

Finally, solve for the desired quantity:

$$\frac{rate\ of\ effusion\ of\ unknown}{rate\ of\ effusion\ of\ CO_2} = \frac{\sqrt{M_{CO_2}}}{\sqrt{M_{unknown}}}$$

Note that this answer is reasonable: Since Ne is lighter than Xe, the effusion rate for Ne will be larger than that for Xe, which means the time of effusion for Ne will be smaller than that for Xe.

Check Your Learning 2.7.2 – Effusion Time Calculations

A party balloon filled with helium deflates to $^{2}/_{3}$ of its original volume in 8.0 hours. How long will it take an identical balloon filled with the same number of moles of air (M_m = 28.2 g/mol) to deflate to $^{1}/_{2}$ of its original volume?

Answer:

32 h

Finally, here is one more example showing how to calculate molar mass from effusion rate data.

Example 2.7.3 – Determining Molar Mass Using Graham's Law

An unknown gas effuses about 1.21 times more rapidly than CO_2. What is the molar mass of the unknown gas? Of the following 5 gases, which best fits the identity of the unknown gas??

Ne NO CH_4 C_3H_8 SO_2

Solution

From Graham's law, we have:

$$\frac{rate\ of\ effusion\ of\ unknown}{rate\ of\ effusion\ of\ CO_2} = \frac{\sqrt{M_{CO_2}}}{\sqrt{M_{unknown}}}$$

Plug in known data:

$$\frac{1.21}{1} = \frac{\sqrt{M_{CO_2}}}{\sqrt{M_{unknown}}}$$

Solve:

$$M_{unknown} = \frac{44.0\ g/mol}{(1.21)^2} = 30.0\ g/mol$$

The molar masses of the five gaseous compounds listed are:

Ne	CH_4	NO	C_3H_8	SO_2
20.18 g/mol	16.04 g/mol	30.01 g/mol	44.09 g/mol	64.06 g/mol

Of the five compounds, NO, also known as nitric oxide, has a molar mass of 30.01 g/mol. Hence, from the choices provided, the gas is NO.

Check Your Learning 2.7.3 – Determining Molar Mass Using Graham's Law

Hydrogen gas effuses through a porous container 8.97-times faster than an unknown gas. Estimate the molar mass of the unknown gas.

Answer

163 g/mol

In Case You're Interested... Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of ^{235}U, the kind of uranium that is "fissile," that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5% ^{235}U, and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham's law. In a gaseous diffusion enrichment plant, uranium hexafluoride (UF_6, the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The $^{235}UF_6$ molecules have a higher average speed and diffuse through the barrier a little faster than the heavier $^{238}UF_6$ molecules. The gas that has passed through the barrier is thus slightly enriched in $^{235}UF_6$ and the residual gas is slightly depleted. The small difference in molecular weights between $^{235}UF_6$ and $^{238}UF_6$ results in only about 0.4% enrichment per diffuser (Figure 2.7.4). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.

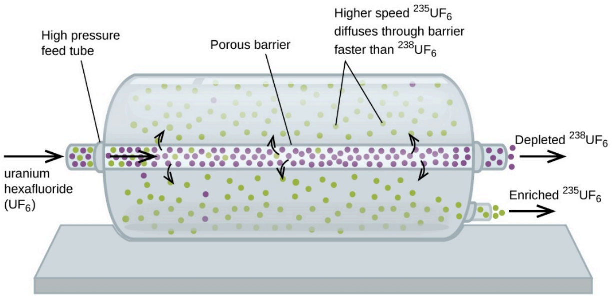


Figure 2.7.4. In a diffuser, gaseous UF_6 is pumped through a porous barrier, which partially separates $^{235}UF_6$ from $^{238}UF_6$ The UF_6 must pass through many large diffuser units to achieve sufficient enrichment in ^{235}U.

The large-scale separation of gaseous $^{235}UF_6$ from $^{238}UF_6$ was first done during World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about 10^{-6} cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive UF_6.

Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now being replaced by gas centrifuge technology, which requires far less energy.

Questions

★ Questions

1. A balloon filled with helium gas is found to take 6 hours to deflate to 50% of its original volume. How long will it take (time) for an identical balloon filled with the same volume of hydrogen gas (instead of helium) to decrease its volume by 50% (in hours)?

2. Explain why the numbers of molecules are not identical in the left- and right-hand bulbs shown in the center illustration of Figure 2.7.1.

3. Starting with the definition of rate of effusion and Graham's finding relating rate and molar mass, show

how to derive the Graham's law equation, relating the relative rates of effusion for two gases to their molecular masses.

4. Heavy water, D_2O (molar mass = 20.03 g mol^{-1}), can be separated from ordinary water, H_2O (molar mass = 18.01), as a result of the difference in the relative rates of diffusion of the molecules in the gas phase. Calculate the relative rates of diffusion of H_2O and D_2O.

5. Which of the following gases diffuse more slowly than oxygen? F_2, Ne, N_2O, C_2H_2, NO, Cl_2, H_2S

★★ Questions

6. During the discussion of gaseous diffusion for enriching uranium, it was claimed that $^{235}UF_6$ diffuses 0.4% faster than $^{238}UF_6$. Show the calculation that supports this value. The molar mass of $^{235}UF_6$ = 235.043930 + 6 × 18.998403 = 349.034348 g/mol, and the molar mass of $^{238}UF_6$ = 238.050788 + 6 × 18.998403 = 352.041206 g/mol.

7. Calculate the relative rate of diffusion of $^1H_2$ (molar mass 2.0 g/mol) compared to that of $^2H_2$ (molar mass 4.0 g/mol) and the relative rate of diffusion of O_2 (molar mass 32 g/mol) compared to that of O_3 (molar mass 48 g/mol).

8. A gas of unknown identity diffuses at a rate of 83.3 mL/s in a diffusion apparatus in which carbon dioxide diffuses at the rate of 102 mL/s. Calculate the molecular mass (g·mol^{-1}) of the unknown gas.

9. When two cotton plugs, one moistened with ammonia and the other with hydrochloric acid, are simultaneously inserted into opposite ends of a glass tube that is 87.0 cm long, a white ring of NH_4Cl forms where gaseous NH_3 and gaseous HCl first come into contact.

$$NH_3\,(g) + HCl\,(g)\ ?\ NH_4Cl\,(s)$$

At approximately what distance from the ammonia moistened plug does this occur? (Hint: Calculate the rates of diffusion for both NH_3 and HCl, and find out how much faster NH_3 diffuses than HCl.)

Answers

1. 4.2 hours

2. In the centre figure, it is seen that there is more H_2 present on the right side versus the left side. The reason for this is the rate of effusion. H_2 has a faster rate of effusion in comparison to O_2 as H_2 has a smaller molecular mass. This means that H_2 will pass through the hole at a faster rate than O_2 which creates that unequal particle distribution seen in Figure 2.7.1.

3. Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B: $\left(\frac{rate\ A}{rate\ B}\right) = \left(\frac{molar\ mass\ of\ B}{molar\ mass\ of\ A}\right)^{\frac{1}{2}}$. Both A and B are in the same container at the same temperature and therefore will have the same kinetic energy:

$$E_{k,A} = E_{k,B} \quad E_k = \frac{1}{2}mv^2$$

Therefore,

$$\frac{1}{2}m_Av_A^2 = \frac{1}{2}m_Bv_B^2$$

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_a}$$

$$(\frac{v_A^2}{v_B^2})^{\frac{1}{2}} = (\frac{m_B}{m_a})^{\frac{1}{2}}$$

$$\frac{v_A}{v_B} = (\frac{m_B}{m_a})^{\frac{1}{2}}$$

4. $\frac{r_1}{r_2} = 1.05$

5. F_2, N_2O, Cl_2, H_2S

6.

$$\frac{r_1 of\ ^{235}UF_6}{r_2\ of\ ^{236}UF_6} = \sqrt{\frac{MM\ of\ ^{236}UF_6}{MM\ of\ ^{235}UF_6}}$$

$$\frac{r_1 of\ \ ^{235}UF_6}{r_2\ of\ \ ^{236}UF_6} = \sqrt{\frac{352.041206\ g{\cdot}mol{-}1}{349.034348\ g{\cdot}mol{-}1}}$$

$$r_1\ of\ \ ^{235}UF_6 = 1.004 \cdot r_2\ of\ \ ^{236}UF_6$$

7. 1.4; 1.2

8. 65.99 g mol^{-1}

9. 51.7 cm

2.8 – REAL/NON-IDEAL GAS BEHAVIOURS

Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of $PV = nRT$ can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, V_m) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the **compressibility factor (Z)** with:

$$Z = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT}\right)_{measured}$$

Equation 2.8.1 Compressibility Factor

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. Figure 2.8.1. shows plots of Z over a large pressure range for several common gases.

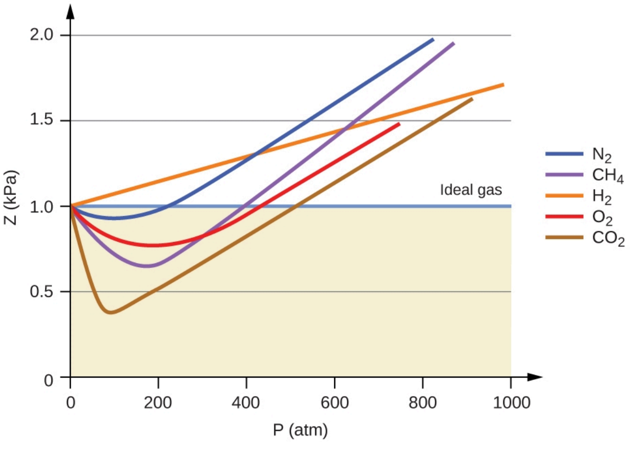


Figure 2.8.1. A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. To examine this behaviour closer to the origin, check out page 3 of the following lecture notes.

As is apparent from Figure 2.8.1., the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have no significant volume and do not attract or repel each other. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the particles of a gas are crowded closer together, and the amount of empty space between the particles is reduced. At these higher pressures, the volume of the gas particles themselves becomes appreciable relative to the total volume occupied by the gas (Figure 2.8.2.). The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

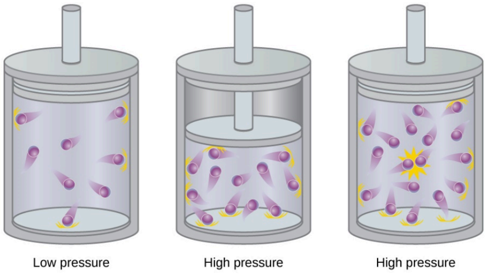


Figure 2.8.2. Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas particles and makes the gas less compressible. Here, the increase in pressure is achieved by either (b) decreasing the volume of the container or (c) increasing the amount of gas in the container. In both cases, deviations from ideal behaviour may appear.

At relatively low pressures, gas particles have practically no attraction for one another because they are (on average) so far apart, and they tend to behave like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the particles a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (if the pressure is constant) (Figure 2.8.3.). This change is more pronounced at low temperatures because the particles have lower E_k relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

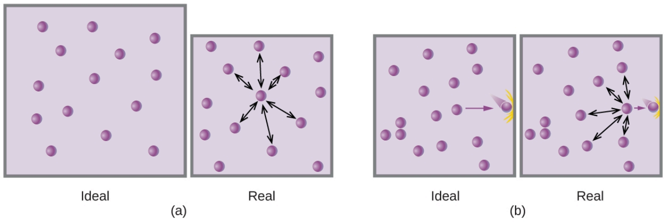


Figure 2.8.3. (a) Attractions between gas particles serve to decrease the gas volume at constant pressure compared to an ideal gas whose particles experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the particles and container walls, therefore reducing the pressure exerted compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law.

The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The **van der Waals equation** improves upon the ideal gas law by adding two terms: one correction factor to account for the volume of the gas particles and another for the attractive forces between them.

$$PV = nRT \longrightarrow \underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{Correction for molecular attraction}} (V - \underbrace{nb}_{\text{Correction for volume of molecules}}) = nRT$$

Equation 2.8.2 Van der Waals

The constant *a* corresponds to the strength of the attraction between particles of a particular gas, and the constant *b* corresponds to the size of the particles of a particular gas. The correction to the pressure term in the ideal gas law is $\frac{n^2a}{V^2}$, and the correction to the volume is *nb*. Note that when *V* is relatively large and *n* is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, $PV = nRT$. Such a condition corresponds to a gas in which a relatively low number of particles is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in Table 2.8.1.

Values of van der Waals Constants for Some Common Gases

Gas	*a* (L^2 atm/mol^2)	*b* (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

Table 2.8.1 Van der Waals constants. For more van der Waals constants, follow the following link.

At low pressures, the correction for intermolecular attraction, *a*, is more important than the one for molecular volume, *b*. At high pressures and small volumes, the correction for the volume of the particles becomes important because the particles themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by $PV = nRT$ over a small range of pressures. This behavior is reflected by the "dips" in several of the compressibility curves shown in Figure 2.8.4. The attractive force between particles initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing P). At very high pressures, the gas becomes less compressible (Z increases with P), as the gas particles begin to occupy an increasingly significant fraction of the total gas volume.

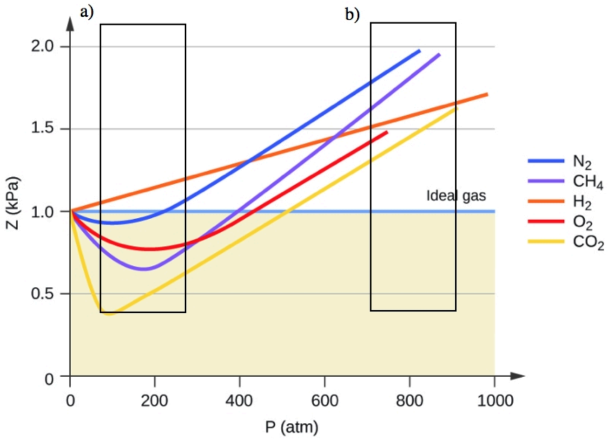


Figure 2.8.4. A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law. a) shows where intermolecular attraction (a) most impacts the ideal gas equation, and b) shows where particle volume (b) most impacts the ideal gas equation

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas particles are negligible and the gas particles themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Example 2.8.1 – Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO_2 at 229 °C. Calculate the pressure of this sample of CO_2:

(a) from the ideal gas law

(b) from the van der Waals equation

(c) Explain the reason(s) for the difference.

Solution

(a) From the ideal gas law:

$$P = \frac{nRT}{V} = \frac{(3.46\ mol)(0.08206\ L \cdot atm \cdot mol^{-1} \cdot K^{-1})(502\ K)}{4.25\ L} = 33.5\ atm$$

(b) From the van der Waals equation:

$$\left(P + \frac{n^2a}{V^2}\right) \times (V - nb) = nRT \rightarrow P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

$$P = \frac{(3.46\ \text{mol})(0.08206\ L \cdot \text{atm} \cdot \text{mol}^{-1} \cdot K^{-1})(502\ K)}{(4.25\ L - 3.46\ \text{mol} \times 0.0427\ L \cdot \text{mol}^{-1})} - \frac{(3.46\ \text{mol})^2 \times 3.59\ L^2 \cdot \text{atm} \cdot \text{mol}^2}{(4.25\ L)^2}$$

This finally yields $P = 32.4$ atm.

(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO_2 particles do have some volume and attractions between particles, and the ideal gas law assumes they do not have volume or attractions.

Check your Learning 2.8.1 – Comparison of Ideal Gas Law and van der Waals Equation

A 560-mL flask contains 21.3 g N_2 at 145 °C. Calculate the pressure of N_2:

(a) from the ideal gas law

(b) from the van der Waals equation

(c) Explain the reason(s) for the difference.

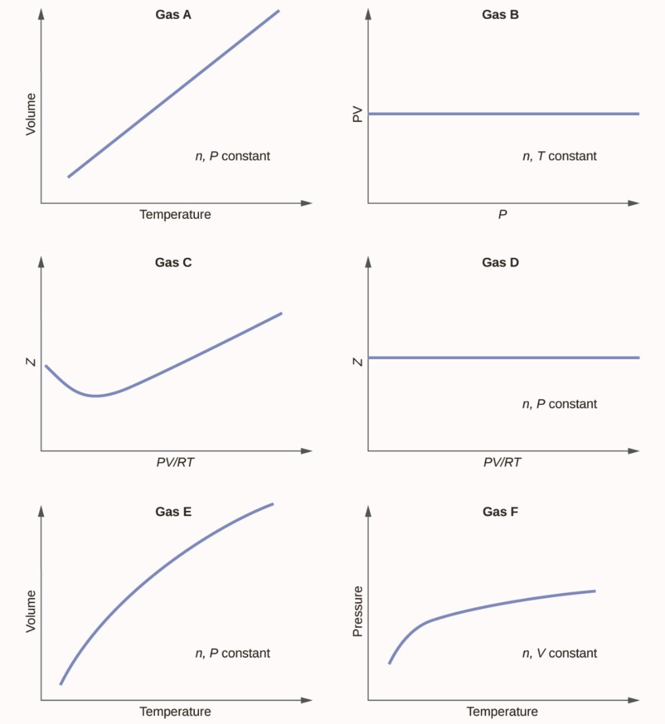
Answer

(a) 46.562 atm; (b) 46.594 atm; (c) The van der Waals equation takes into account the volume of the gas particles themselves as well as intermolecular attractions.

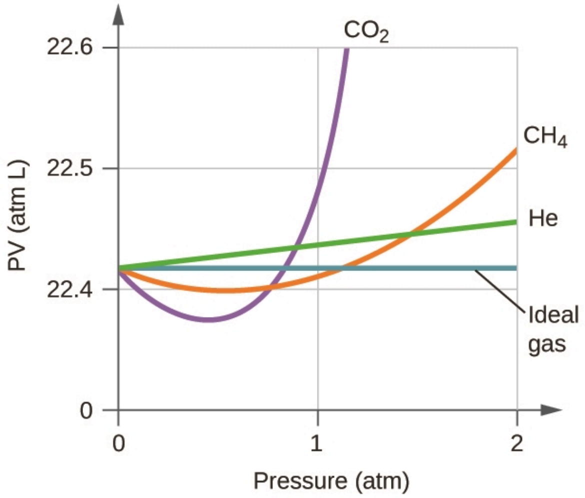
Questions

★ Questions

1. Graphs showing the behavior of several different gases follow. Which of these gases exhibit behavior significantly different from that expected for ideal gases?



Explain why the plot of *PV* for CO_2 differs from that of an ideal gas.



3. Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

   a. high pressure, small volume
   b. high temperature, low pressure
   c. low temperature, high pressure

4. Describe the factors responsible for the deviation of the behavior of real gases from that of an ideal gas.

5. For which of the following gases should the correction for the molecular volume be largest: CO, CO_2, H_2, He, NH_3, SF_6?

6. A 0.245-L flask contains 0.467 mol CO2 at 159 °C. Calculate the pressure:

   a. using the ideal gas law
   b. using the van der Waals equation
   c. Explain the reason for the difference.
   d. Identify which correction (that for *P* or *V*) is dominant and why.

★★ Questions

7. Answer the following questions:

   a. If XX behaved as an ideal gas, what would its graph of *Z* vs. *P* look like?
   b. For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
   c. What is the effect of the volume of gas molecules on *Z*? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
   d. What is the effect of intermolecular attractions on the value of *Z*? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
   e. In general, under what temperature conditions would you expect *Z* to have the largest deviations from the *Z* for an ideal gas?

Answers

1. Gases C, E, and F

2. CO_2 interacts intermolecularly with other molecules, and occupies a volume in space. Hence the CO_2 molecules repel other molecules and create pressure through collisions, leading to a non linear relationship between PV and P.

3. The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collisions; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

4. An ideal gas is assumed to have no volume or intermolecular interaction. Molecules that portray real gas behaviour show attraction between other molecules resulting in a deviation in ideal gas behaviour. Real gases only show ideal behaviour at high temperatures and low pressures.

5. SF_6

6. (a) 66.2 atm, (b) 60.5 atm, (c) van der Waals accounts for non ideal gas factors (repulsive forces and volume occupation) that the ideal gas law does not account for, (d) The factor for pressure correction used in the van der Waals is dominant in low pressure cases. At higher volumes, the pressure is higher as well.

7. (a) A straight horizontal line at 1.0; (b) When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the ideal gas equation (c) The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (d) Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. (e) low temperatures

CHAPTER 3

3.1 – INTRODUCTION TO THERMOCHEMISTRY

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and non-polluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called **thermochemistry**. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavour to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles are essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

What is Energy?

Energy can be defined as the capacity to produce heat or do work. One type of **work (*W*)** is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 3.1. 1). A battery has potential energy because the chemicals within it can produce electricity that can do work.

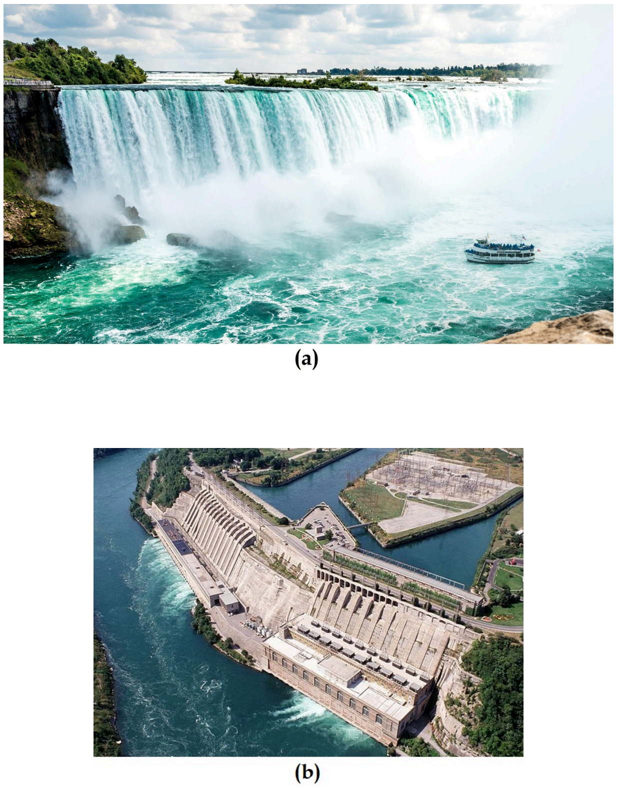


Figure 3.1.1. (a) Water that is higher in elevation, for example, at the top of Niagara Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Sir Adam Beck Hydroelectric Generating Stations in Niagara Falls, Ontario, shown here, its kinetic energy is converted into electrical energy. (credit a: Photo by Ivan Torres from Pexels ; credit b: Adam Beck Complex by Ontario Power Generation has been modified (cropped) and is used under a CC BY 2.0 license.)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in sugar molecules like sucrose. When the sugar molecules react with O_2 with the help of a reducing agent (e.g. potassium chlorate, $KClO_3$), the chemical reaction causes the chemical energy stored in the molecular bonds to be released and converted into other forms of energy including heat (the combustion being an exothermic process) and light (see the box "Gummy Bear Combustion").

Gummy Bear Combustion

Check out this experimental demonstration video* where a gummy bear is combusted using molten potassium chlorate as a reducing agent. The potassium chlorate is added and heated until it becomes molten (observed at 1:07). Notice what happens when the green gummy bear is added to the molten potassium chlorate at around 1:18.

* [C for Chemistry]. (2010, February 13). *"Gummy Bear Experiment" with molten Potassium chlorate* [Video file]. Retrieved from https://www.youtube.com/watch?v=7Xu2YZzufTM

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Units of Energy

Historically, energy was measured in units of **calories (cal)**. A calorie is the amount of energy required to raise one gram of water by 1°C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large/nutritional calorie, commonly used in quantifying food energy content, is a kilocalorie (1 kcal), or 1000 cal (see the box "Measuring Nutritional Calories if you're interested). The SI unit of heat, work, and energy is the joule. A **joule (J)** is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honour of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

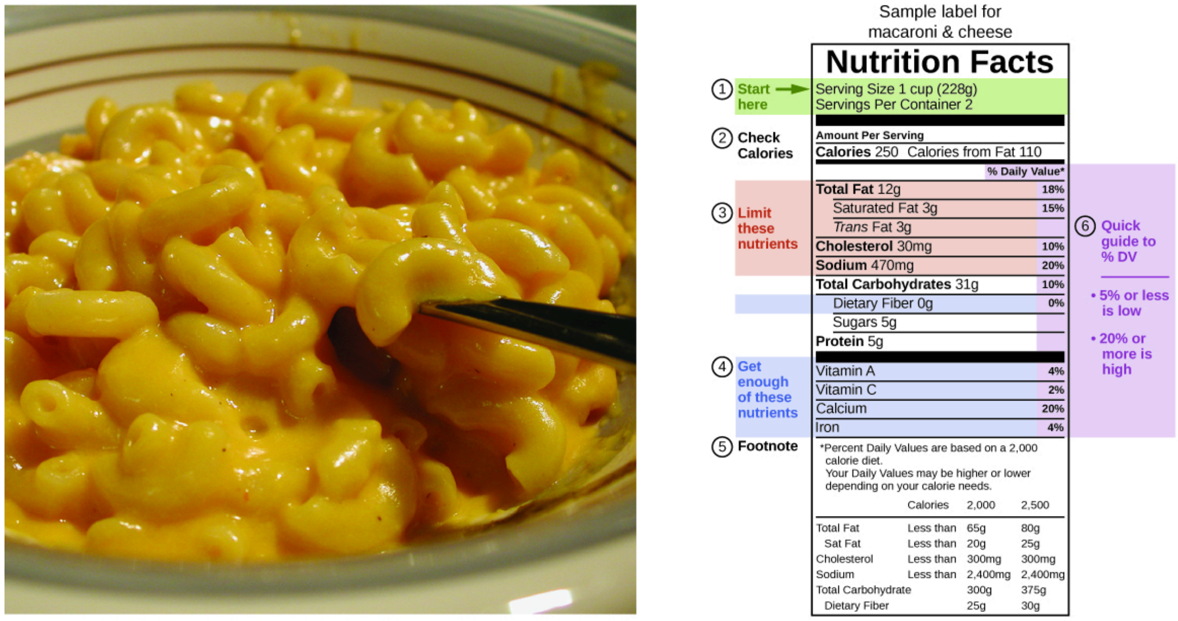
$$1 \text{ calorie} = 4.184 \text{ J}$$

A great deal of the problems you'll be dealing with in this unit will express energy in joules, however, it's very important to remember how to convert between joules and calories. Despite the joule predominating over time as the official SI unit for energy, the calorie unit is still extensively used in the industrial sector today and a lot of tabulated data for compounds still expresses values in terms of calories. So be aware of what units of energy you're working with and have the ability to perform unit conversions when necessary.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1°C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure 3.1. 2).



Sample label for macaroni & cheese

Nutrition Facts

Serving Size 1 cup (228g)
Servings Per Container 2

Amount Per Serving
Calories 250 Calories from Fat 110

	% Daily Value*
Total Fat 12g	18%
Saturated Fat 3g	15%
Trans Fat 3g	
Cholesterol 30mg	10%
Sodium 470mg	20%
Total Carbohydrates 31g	10%
Dietary Fiber 0g	0%
Sugars 5g	
Protein 5g	
Vitamin A	4%
Vitamin C	2%
Calcium	20%
Iron	4%

*Percent Daily Values are based on a 2,000 calorie diet.
Your Daily Values may be higher or lower depending on your calorie needs.

	Calories	2,000	2,500
Total Fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2,400mg	2,400mg
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

(a) (b)

Figure 3.1.2 (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In Canada (and the US), the energy content is given in Calories; the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

(5 g protein × 4 Calories/g) + (31 g carb × 4 Calories/g) + (12 g fat × 9 Calories/g) = 252 Calories

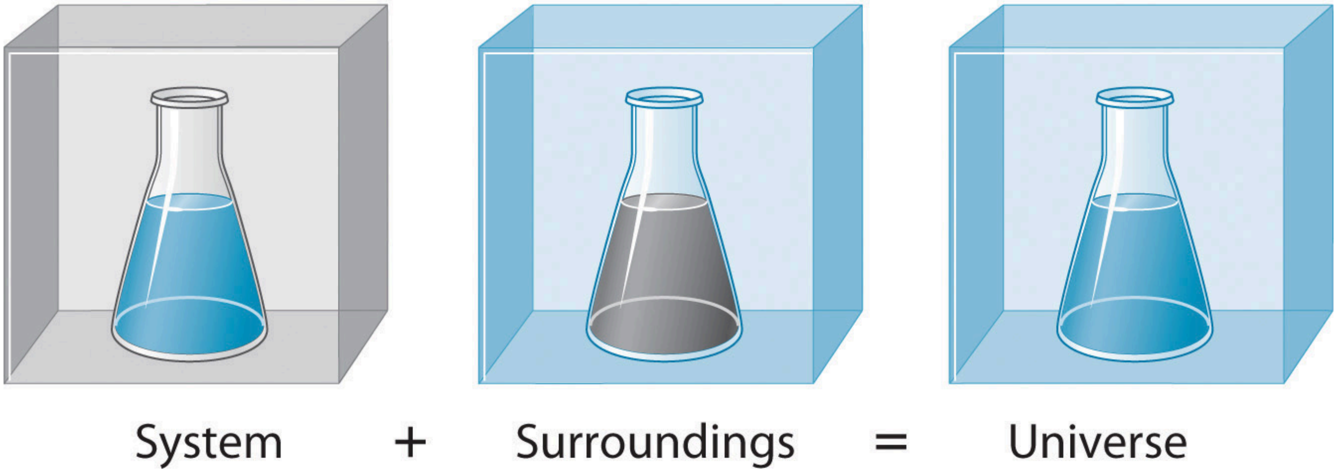
So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food (bomb calorimetry is covered in much more detail in the section "Calorimetry").

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fibre content, which is an indigestible carbohydrate. To determine the energy content of food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Energy in the Universe

Before we can begin to study and understand the flow of energy in the context of a chemical reaction, we need to distinguish between a **system**, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its **surroundings**, which is the environment immediately around it (such as the reaction vessel, the lab bench etc.). The universe is defined as everything, both the surroundings and the system (Figure 3.1.3). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

Figure 3.1.3. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.



Three kinds of systems are important in chemistry. An **open system** can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapour is lost as the water boils. A **closed system** can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An **isolated system** exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually, the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. In other words, just like it was said previously in our introduction to energy: *the total energy of a system plus its surroundings (i.e. the universe) is constant/fixed*, which must be true if *energy is conserved*.

Questions

★ Questions

Newton's cradle, a desk ornament that consists of 5 metal spheres suspended on wires that can freely swing into each other, demonstrates conservation of energy by showing that energy can be transferred through each sphere to make one several centimetres away move. This should be able to repeat forever, but it does stop eventually. Is this in violation of the law of conservation of energy? If not, where has the energy gone?

The idea of perpetual motion machines (theoretical machines that continue to do work forever by recycling all of its energy) has been fascinating humans for centuries. Why is this not possible in practice?

A cup of strawberries contains 53 Cal (nutritional calories). How much energy is this in Joules?

You've just baked a cake in your oven. Identify the system, surroundings, and the universe.

Answers

This does not violate the law of conservation of energy because the energy is transferred to different kinds rather than remaining in the form the system strictly needs. In this case, it can transform into sound, thermal, and more. This prevents it from going on forever.

The perpetual motion machine is a similar case to question 1. It is impossible to isolate a system to ensure that the transfer of energies remain what they are intended to be. The machine will eventually stop as it involves energies transforming into others that are not needed for this system, such as sound, thermal, etc.

1.3×10^4 J

System = cake, surroundings = oven, universe = cake and oven

3.2 – TYPES OF ENERGY

Thermochemistry is a branch of **chemical thermodynamics**, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the **internal energy (*U*)**, sometimes symbolized as E.

Internal energy

The internal energy of a system is identified with the random, disordered motion of molecules; the total (internal) energy in a system includes potential and kinetic energy. This is in contrast to external energy which is a function of the sample with respect to the outside environment (e.g. kinetic energy if the sample is moving or potential energy if the sample is at a height from the ground etc). The symbol for Internal Energy Change is ΔU and may be calculated using the following equation where U_1 is the initial internal energy of the system and U_2 is the system's final internal energy:

$$\Delta U = U_2 - U_1$$

Heat

Thermal energy is the kinetic energy associated with the random motion of atoms and molecules. **Temperature** is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating more quickly, they have a higher average kinetic energy (E_k), and we say that the object is "hot." When the atoms and molecules are moving more slowly, they have lower E_k, and we say that the object is "cold" (Figure 3.2.1.). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

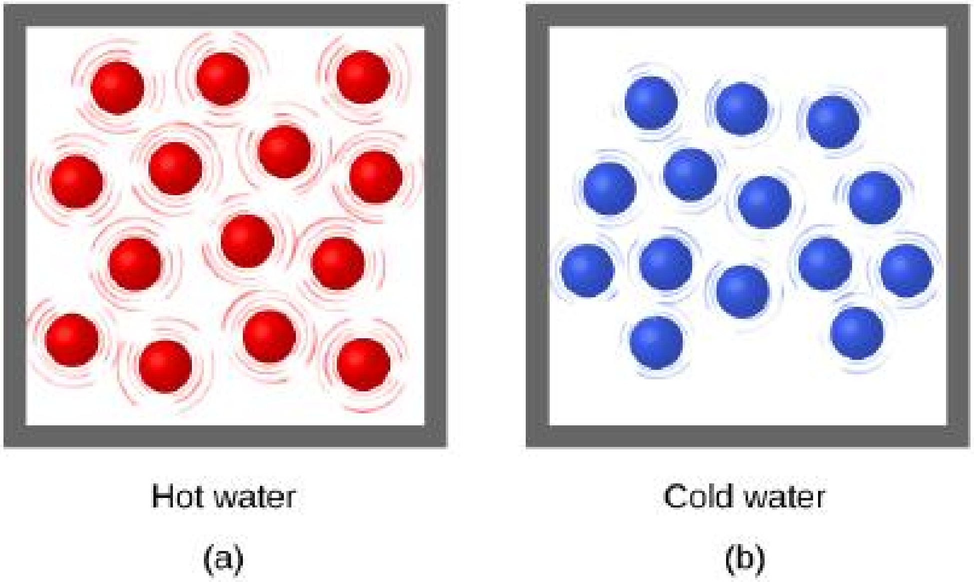


Figure 3.2.1. (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Heat (*q*) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average E_k than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average E_k of its molecules; the temperature of substance L will increase, along with the average E_k of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 3.2.2.).

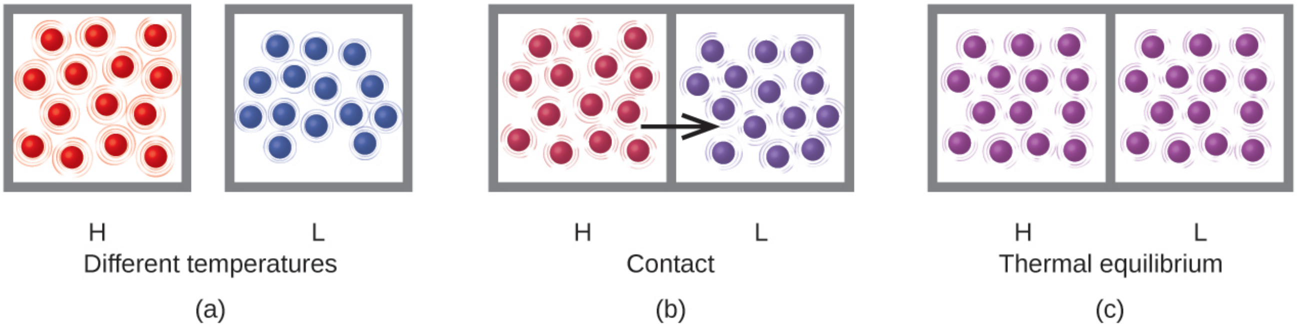


Figure 3.2.2. (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 3.2.3. a). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

Figure 3.2.3. (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons).

Heat Can do More than Increase Temperature

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 3.2.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

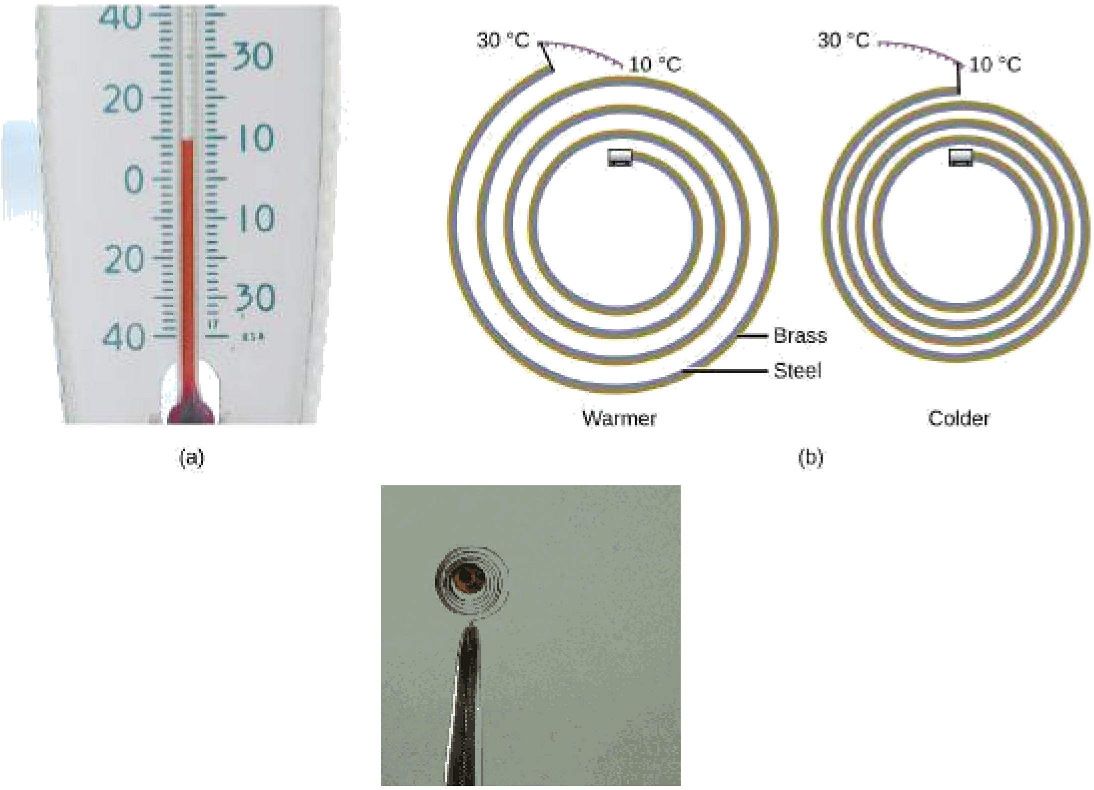


Figure 3.2.4. (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip. A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)

Direction of Heat Flow: Endothermic vs. Exothermic Processes

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel. The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al}\,(s) + \mathrm{Fe_2O_3}\,(s) \rightarrow 2\,\mathrm{Fe}\,(s) + \mathrm{Al_2O_3}\,(s)$$

We can also write this chemical equation as:

$$2\,\mathrm{Al}\,(s) + \mathrm{Fe_2O_3}\,(s) \rightarrow 2\,\mathrm{Fe}\,(s) + \mathrm{Al_2O_3}\,(s) + heat$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction. Check out this video to see the above reaction in action.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$heat + H_2O\ (s) \rightarrow H_2O\ (l)$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

In summary, by convention, q < 0 for an exothermic reaction and q > 0 for an endothermic reaction.

Example 3.2.1 – Exothermic vs. Endothermic Reactions

a. Decide whether the following are endothermic or exothermic processes
water evaporates off a shower door
b. an acid tablet being added to a pool and the surrounding water heats up
c. NH_4Cl is dissolved in water and the solution cools
d. the burning of a log in a campfire

Solution

a. Endothermic
b. Exothermic
c. Endothermic
d. Exothermic

Technically, it is poor form to have heat in the chemical reaction like in the equations depicted above since it is not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

Work

In chemistry, work is often defined in terms of a change in volume against pressure. (Pressure is force divided by area, so convince yourself that P x V has the same units as F x d.) For instance, atmospheric pressure is constant at 1 bar. If you have a sample of gas at higher pressure, and you let it come to mechanical equilibrium with the atmosphere, it will expand to some new volume. The work done by expanding against atmospheric pressure is (1 bar)(ΔV), where ΔV is (final volume – initial volume). In general, the work done by gases expanding is called PV work, and is expressed:

$$w = -P\Delta V$$

where P is the constant pressure and ΔV is the change in volume of the system. The negative sign associated with PV work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

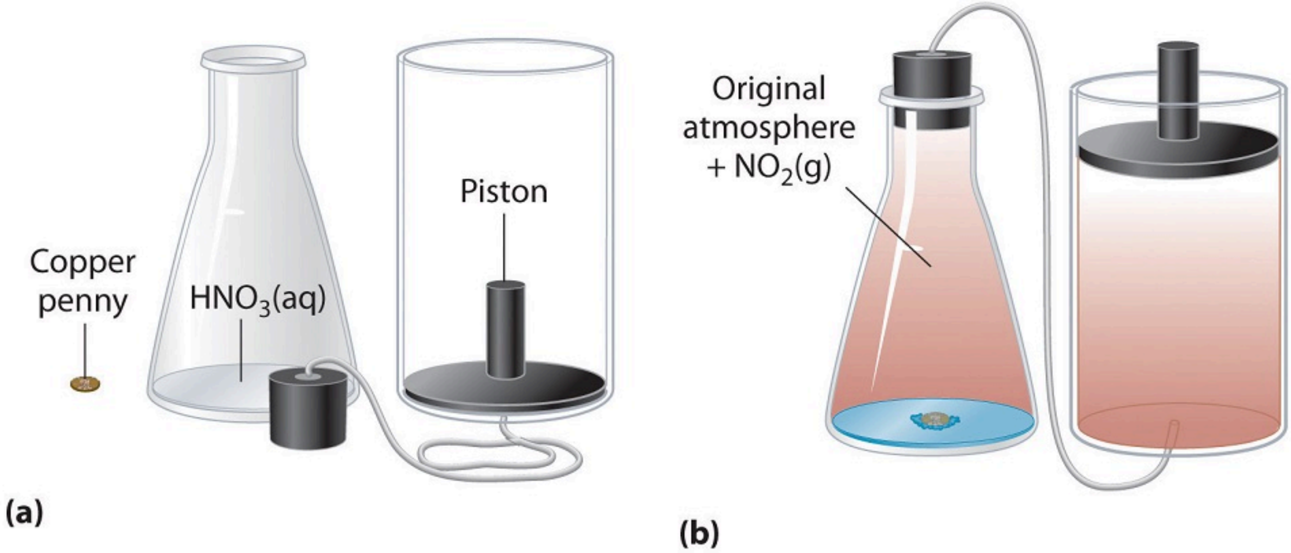


Figure 3.2.5. An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

Chemical reactions can carry out work by electrochemistry (this involves redox reactions and will be covered next year), and the pressure-volume work of gases.

Example 3.2.2 – Work Calculations with Gases

What is the work performed by a gas if it expands from 3.44 L to 6.19 L against a constant external pressure of 1.26 atm? Express the final answer in joules.

Solution

First, we need to determine the change in volume, ΔV. A change is always the final value minus the initial value:

$\Delta V = V_{final} - V_{initial}$

$\Delta V = 6.19\ L - 3.44\ L$

$\Delta V = 2.75\ L$

Now we can use the definition of work to determine the work done:

$w = -P_{external} \times \Delta V$

$w = -(1.26\ atm) \times (2.75\ L)$

$w = -3.47\ L \cdot atm$

Now we construct a conversion factor from the relationship between liter·atmospheres and joules:

$$-3.47\ L \cdot atm \times \frac{101.32 J}{1\ L \cdot atm} = -351\ J$$

Check Your Learning 3.2.1 – Work Calculations with Gases

What is the work performed when a gas expands from 0.66 L to 1.33 L against an external pressure of 0.775 atm?

Answer

-53 J

Heat and work are the ways that energy can move between objects. When you think about the molecules, the difference between work and heat is very simple. Work involves an orderly motion of molecules, like all the molecules in an object moving the same direction. Heat involves disorderly or random motions of molecules.

Questions

★Questions

1. A system of molecules has an original internal energy of 8700000 J. You cooled this system by 99 K and its internal energy is now 4501 kJ. Calculate the change in internal energy (ΔU).
2. You allow two iron cubes to come into contact. One cube is at 800 K and the other is at 323.15°C. Predict the temperature of these two cubes once they reach thermal equilibrium. State your answer in Kelvin.
3. Calculate how many calories are in 71 kJ.
4. Classify each reaction as exothermic or endothermic:

$$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(l) + \textit{heat}$$

   a. Ice melts into water
   b. TNT explodes
   c. Nuclear fission breaks uranium atoms into atoms with smaller nuclei

★★Questions

5. You have a balloon initially filled with 400 mL of air. What is the final volume of the balloon if you do -885.13 J of work to expand it? Atmospheric pressure is 1.12 atm.

Answers

1. – 4199 kJ
2. 698.15 K
3. 16.96 kilocalories
4. (a) Exothermic, (b) Endothermic, (c) Exothermic, (d) Exothermic
5. 1190.29 mL

3.3 – FIRST LAW OF THERMODYNAMICS

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w$$

This is one version of the **first law of thermodynamics** which states that "energy is neither created nor destroyed, only transferred", and it shows that the internal energy of a system changes through heat flow into or out of the system (positive *q* is heat flow in; negative *q* is heat flow out) or work is done on or by the system. The work, *w*, is positive if it is done on the system and negative if it is done by the system. In the case of *PV* work, we can consider work done on the system as contraction, while work done by the system is expansion.

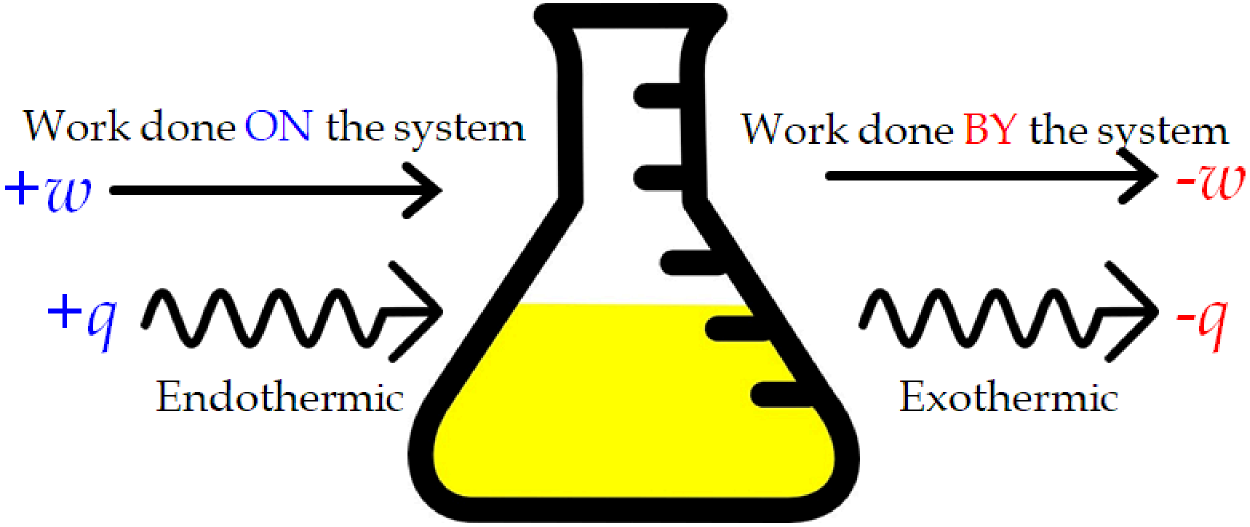


Figure 3.3.1. Sign conventions for heat and work. Work done on the system or heat absorbed by the system are positive. Work done by the system or heat produced by the system are negative. These can happen in **any** combination..

As we discussed in section 3.1, energy in the universe is constant/fixed. We can relate this to internal energy by saying that, while energy can be transferred between the system and the surroundings, the change in internal energy of the universe is equal to zero.

$$\Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0$$

There are many forms of work such as electrical and mechanical, but in this course, the relevant type of work is called **expansion work** (or pressure-volume work). Expansion work occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

This view of an internal combustion engine illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion. To learn more about the first law of thermodynamics, check out this video.

State Functions

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a **state function**, whereas heat and work are not state functions (typically referred to as **path functions**). The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you travelled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 3.3.2.). The distances travelled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

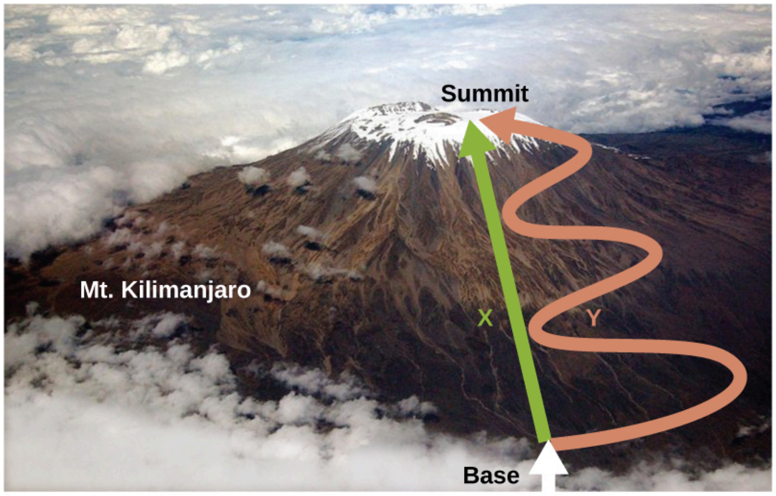
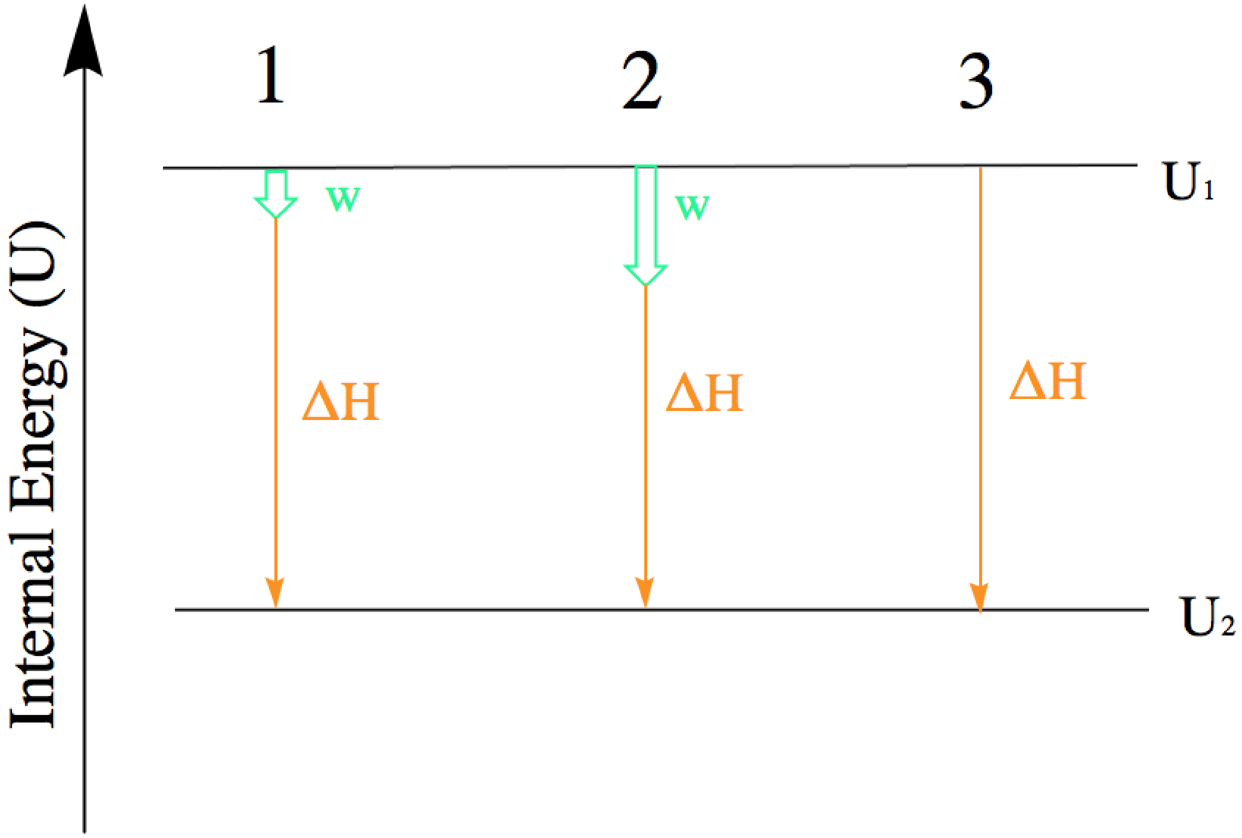


Figure 3.3.2. Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances travelled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Regarding energy, work and heat are both path functions, but internal energy is not. This means the path taken to get to the results matters when calculating w or q, but need not be taken into account when solving for ΔU.

Energy Diagrams

When working with systems involving both heat and work, it is often useful to visualize the transition from the initial to the final energy states using a diagram (Figure 3.3.3.).


Internal Energy (U)
1
2
3
U1
U2
w
w
ΔH
ΔH
ΔH

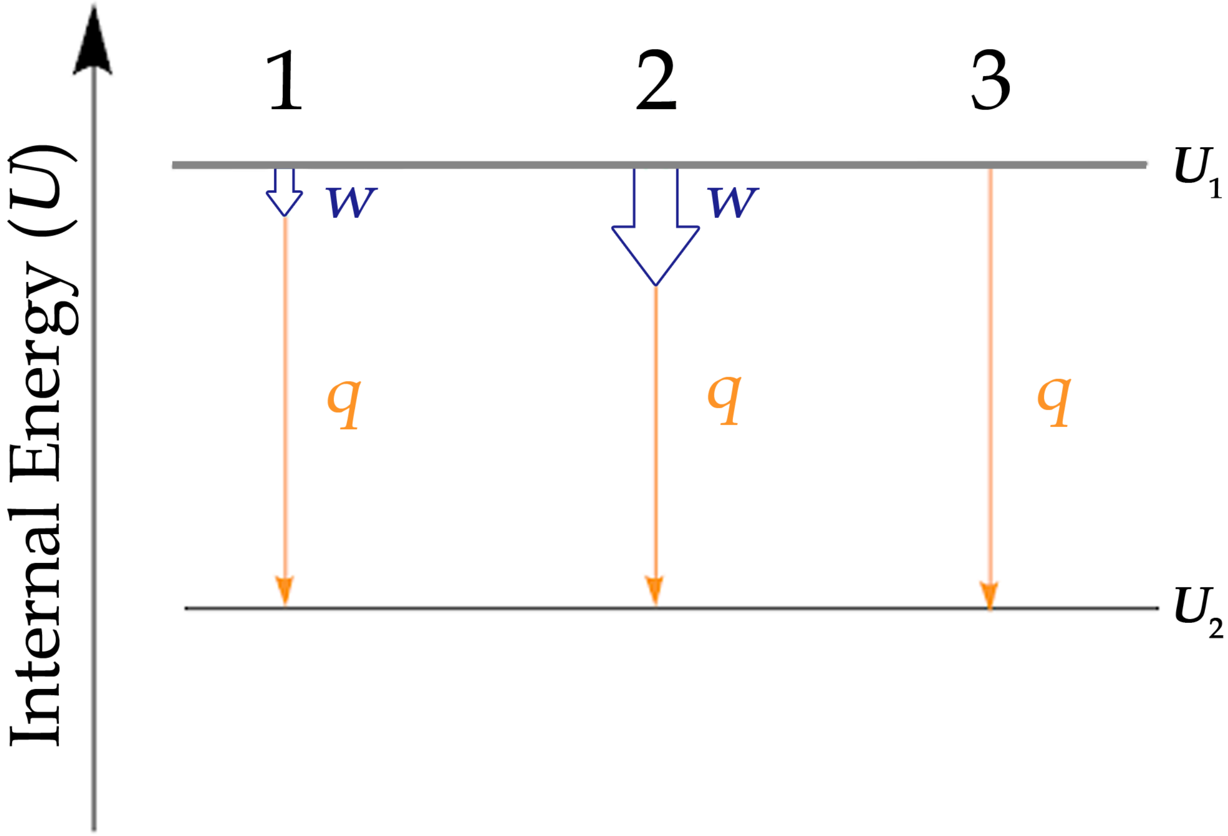


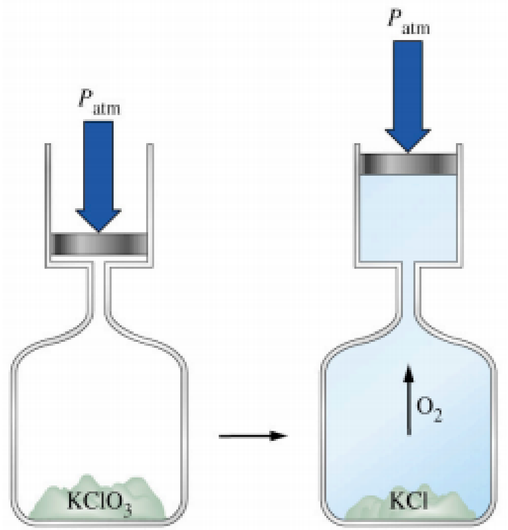
Figure 3.3.3. The internal energy of three processes from which the system loses energy. 1: Depiction of the change in internal energy essentially equal to the heat transfer. Mathematically: $\Delta U \approx q$. 2: Depiction of the change in internal energy where both work is done and heat is lost. Mathematically: $\Delta U = q + w$. 3: Depiction of the change in internal energy when no work is done but heat is lost. Mathematically: $\Delta U = q$

Although Figure 3.3.3. only shows processes for which a system loses energy, this tactic should be used whenever possible and can be modified for instances in which work and heat have different signs. This will be covered more in Hess' law.

Questions

★ Questions

1. A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?



2. When potassium chlorate decomposes it produces oxygen gas. From the system's point of view (which is the convention), *w* is:

A. Positive

B. Negative

C. Zero

3. What is the work when a gas contracts from 3.45 L to 0.97 L under an external pressure of 0.985 atm?

★★ Questions

4. The volume of a gas changes from 264 mL to 971 mL at constant temperature. Calculate the amount of work done by the gas (in joules) if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

5. For the following reactions, indicate if work will increase, decrease or remain constant. *Hint: remember that work is based on PV – so how is the volume changing in each reaction?*

a. $2\,H_2O\,(l) \rightarrow 2\,H_2\,(g) + O_2\,(g)$

b. $NO_2\,(g) + O_3\,(g) \rightarrow NO_3\,(g) + O_2\,(g)$

c. $CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)$

Answers

1. -216 J

2. B

3. 248 J

4. (a) 0 J, no work is done; (b) -287 J

5. (a) w increases because the moles of gas increase which would increase the volume of gas. (b) there is no change due to both sides of the reaction having the same number of moles. (c) decrease due to the

different amounts of gases on both sides of the reaction, the reactant side has a larger number of moles of gas.

3.4 – ENTHALPY

What is Enthalpy?

Chemists ordinarily use a property known as **enthalpy (*H*)** to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (*U*) and the mathematical product of its pressure (*P*) and volume (*V*):

$$H = U + PV$$

Equation 3.4.1 Enthalpy

Since it is derived from three state functions (*U*, *P*, and *V*), enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the **enthalpy change (Δ*H*)** is:

$$\Delta H = \Delta U + P\Delta V$$

Equation 3.4.2 Enthalpy Change

When pressure is constant, the mathematical product $P\Delta V$ represents work (*w*), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and *w* will always be opposite:

$$P\Delta V = -w$$

Equation 3.4.3 Work

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

$$\Delta H = \Delta U + P\Delta V$$

$$\Delta H = (q_P + w) - w$$

$$\Delta H = q_P$$

Equation 3.4.4 Substituted Enthalpy Change

where q_P is the heat of reaction under conditions of constant pressure. Thus, *enthalpy is defined as the quantity of heat transferred under constant pressure conditions.*

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_P) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter ([link]) is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

Comparing ΔH and ΔU

If ΔH for a reaction is known, we can use the change in the enthalpy of the system to calculate its change in internal energy:

$$\Delta H = \Delta U + P\Delta V$$

When a reaction *does not involve gases* (i.e. involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably ($\Delta V \approx 0$). Under these conditions, we can simplify the equation above where $P\Delta V$ gets cancelled out:

$$\text{Reaction with no gases} \rightarrow \Delta H \approx \Delta U$$

When a reaction *does involve gases*, however, ΔH and ΔU can differ significantly. We can calculate ΔU from the measured value of ΔH by modifying the right side of the equation, $P\Delta V$, with the ideal gas law, $PV = nRT$. P and T remain constant, so we recognize that

$$P\Delta V = (\Delta n_{gas})RT$$

Where

$$\Delta n_{gas} = n_{products} - n_{reactants}$$

We can rewrite the equation for the change in enthalpy as follows:

$$\text{Reaction with gases} \rightarrow \Delta H = \Delta U + \Delta n_{gas}RT$$

Where

$$\Delta n_{gas} = n_{products} - nr_{eactants}$$

This equation applies if

$$\Delta n_{gas} \neq 0$$

. However, if

$$\Delta n_{gas} = 0$$

:

$$\Delta H = \Delta U$$

Equation 3.4.5 Enthalpy Change, Potential Change

Enthalpy Changes in Reactions

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example,

consider this equation:

$$H_2\,(g) + 1/2\,O_2\,(g) \rightarrow H_2O\,(l) \qquad \Delta H = -\,286\text{ kJ}$$

This equation indicates that when 1 mole of hydrogen gas and 1/2 moles of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

(two-fold increase in amounts)

$$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(l) \qquad \Delta H = 2 \times (-\,286\text{ kJ}) = -\,572\text{ kJ}$$

(two-fold decrease in amounts)

$$1/2\,H_2\,(g) + 1/4\,O_2\,(g) \rightarrow 1/2\,H_2O\,(l) \qquad \Delta H = 1/2 \times (-\,286\text{ kJ}) = -143\text{ kJ}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 1/2 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$H_2\,(g) + 1/2\,O_2\,(g) \rightarrow H_2O\,(l) \qquad \Delta H = -\,286\text{ kJ}$$

A negative value of an enthalpy change, ΔH, indicates an exothermic reaction; a positive value of ΔH indicates an endothermic reaction (Figure 3.4.1). If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

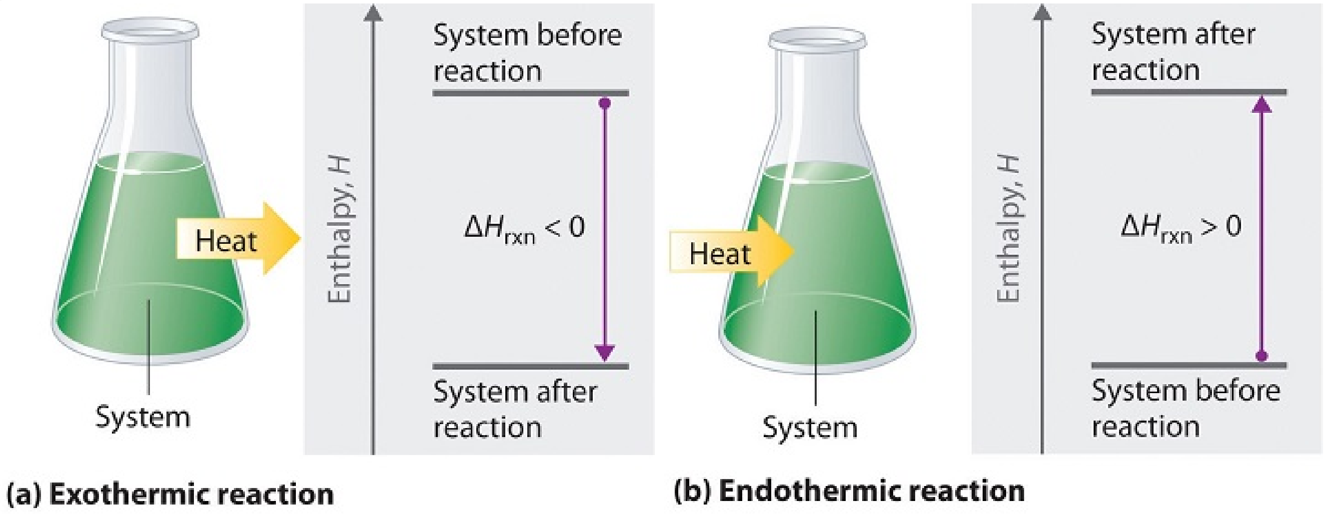


Figure 3.4.1. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the

reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.

Example 3.4.1 – Measurement of an Enthalpy Change

When 0.0500 mol of HCl (*aq*) reacts with 0.0500 mol of NaOH (*aq*) to form 0.0500 mol of NaCl (*aq*), 2.9 kJ of heat is produced. What is Δ*H*, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described in [link]?

$$\text{HCl}\,(aq) + \text{NaOH}\,(aq) \rightarrow \text{NaCl}\,(aq) + \text{H}_2\text{O}\,(l)$$

Solution

For the reaction of 0.0500 mol acid (HCl), $q = -2.9$ kJ. This ratio $\frac{-2.9\ kJ}{0.0500\ mol\ HCl}$, can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

$$\Delta H = 1\ mol\ HCl \times \frac{-2.9\ kJ}{0.0500\ mol\ HCl} = -58\ kJ$$

The enthalpy change when 1 mole of HCl reacts is −58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

$$\text{HCl}\,(aq) + \text{NaOH}\,(aq) \rightarrow \text{NaCl}\,(aq) + \text{H}_2\text{O}\,(l) \qquad \Delta\text{H} = -\,58\ \text{kJ}$$

Check Your Learning 3.4.1 – Measurement of an Enthalpy Change

When 1.34 g Zn (*s*) reacts with 60.0 mL of 0.750 M HCl (*aq*), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

$$\text{Zn}\,(s) + 2\ \text{HCl}\,(aq) \rightarrow \text{ZnCl}_2\,(aq) + \text{H}_2\,(g)$$

Answer

$\Delta H = -\,153$ kJ

Be sure to take both stoichiometry and limiting reactants into account when determining the Δ*H* for a chemical reaction.

Example 3.4.2 – Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11}\,(aq) + 8\ \text{KClO}_3\,(aq) \rightarrow 12\ \text{CO}_2\,(g) + 11\ \text{H}_2\text{O}\,(l) + 8\ \text{KCl}\,(aq)$$

Solution

We have:

$$2.67\ g \times \frac{1\ mol}{342.3\ g} = 0.00780\ mol\ \text{C}_{12}\text{H}_{22}\text{O}_{11}\ (aq)$$

available, and

$$7.19\ g \times \frac{1\ mol}{122.5\ g} = 0.0587\ mol\ \mathrm{KClO_3}$$

available. Since

$$0.0587\ mol\ KClO_3 \times \frac{1\ mol\ C_{12}H_{22}O_{11(aq)}}{8\ mol\ KClO_3} = 0.00734\ mol\ \mathrm{C_{12}H_{22}O_{11}}\ (aq)$$

is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant. The reaction uses 8 mol $KClO_3$, and the conversion factor is

$$\frac{}{0.0587\ mol\ KClO_3}$$

so we have

$$\Delta H = 8\ mol \times \frac{-43.7\ kJ}{0.0587\ mol\ KClO_3} = -5960\ kJ$$

The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$C_{12}H_{22}O_{11}\ (aq) + 8\ KClO_3\ (aq) \rightarrow 12\ CO_2\ (g) + 11\ H_2O\ (l) + 8\ KCl\ (aq)$$

$$\Delta H = -\ 5960\ kJ$$

Check Your Learning 3.4.2 – Another Example of the Measurement of an Enthalpy Change

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_2\ (s)$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2\ (s)$ is produced?

Answer

$\Delta H = -\ 338$ kJ

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A **standard state** is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 bar. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscript "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature (note: this differs from the STP for gases, don't confuse them!). Thus, the symbol (ΔH°_{298}) is used to indicate an enthalpy change for a process occurring under these conditions.

(The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often “normalized” to a per-mole basis. (Note that this is similar to determining the intensive property-specific heat from the extensive property heat capacity, which we will see in the next topic).

Questions

★ Questions

1. When 100 mL of 0.200 M NaCl (*aq*) and 100 mL of 0.200 M $AgNO_3$ (*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter (we will discover what these are used for in the next topic), the temperature increases to 23.5 °C as solid AgCl forms. Calculate ΔH in kJ/mol of $AgNO_3$ (*aq*) for the reaction:

$$NaCl\,(aq) + AgNO_3\,(aq) \rightarrow AgCl\,(s) + NaNO_3\,(aq)$$

2. When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack”. When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C. Calculate the enthalpy of solution (ΔH for the dissolution) per mole of NH_4NO_3.

3. Qualitatively compare ΔH and ΔU for each of the following reactions:
    a. $AgNO_3\,(aq) + NaCl\,(aq) \rightarrow AgCl\,(s) + NaNO_3\,(aq)$
    b. $H_2\,(g) + F_2\,(g) \rightarrow 2\,HF\,(g)$
    c. $C_3H_8\,(g) + 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$

4. Calculate ΔH for the reaction described by the equation. (*Hint*: use the value for the approximate amount of heat absorbed by the reaction that you calculated in a previous exercise.)

$$Ba(OH)_2 \cdot 8H_2O\,(s) + 2\,NH_4SCN\,(aq) \rightarrow Ba(SCN)_2\,(aq) + 2\,NH_3\,(aq) + 10\,H_2O\,(l)$$

5. How much heat is produced by combustion of 125 g of methanol under standard state conditions?

6. How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

7. What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

8. When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

Answers

1. 1.34 x 10^3 kJ/mol
2. We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{rxn} = -\ q_{soln}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$q_{rxn} = -\ q_{soln} = -\ (c \times m \times \Delta T)_{soln}$$
$$=[(4.184\ J/g^{\circ}\ C) \times (53.2\ g) \times (20.3^{\circ}\ C - 24.9^{\circ}\ C)]$$
$$=[(4.184\ J/g^{\circ}\ C) \times (53.2\ g) \times (-\ 4.6^{\circ}\ C)]$$
$$+1.0 \times 10^3\ J = +\ 1.0\ kJ$$

The positive sign for q indicates that the dissolution is an endothermic process.

3. (a) $\Delta U \approx \Delta H$: since there are no gases the volume change is negligible (basically equal to 0) meaning that $\Delta U \approx q_P$ and since $\Delta H = q_P$ then $\Delta U \approx \Delta H$; (b) $\Delta U = \Delta H$: Δn = 0 mol which means there is no work done, therefore $\Delta U = \Delta H$; (c) $\Delta U > \Delta H$: Δn = 1 mol resulting in $w = -\ RT$. $-\ RT$ will always be negative therefore, under constant pressure, $\Delta U = \Delta H - RT$ demonstrating $\Delta U > \Delta H$.

4. 95.72 kJ/mol
5. 2836.3 kJ
6. 1.83 × 10^{-2} mol
7. 17.3 g
8. 802 kJ/mol

3.5 – CALORIMETRY

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as **calorimetry**. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The measurement of heat transfer using this approach requires knowledge and understanding of a system and its surroundings (see "Introduction to Thermochemistry" to review the terminology of system and surroundings). As we saw in previous sections, energy in the universe is neither created nor destroyed, only transferred. This implies that the change in internal energy of the universe must be zero – it is all conserved where there is no gain of energy or loss of it:

$$\Delta U_{\text{universe}} = 0$$

In addition to this, we also need to understand a few other concepts that we'll go over in this section to grasp the concept of calorimetry.

Heat Capacities

We now introduce two concepts useful in describing heat flow and temperature change. The **heat capacity (*C*)** of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):

$$C = q/\Delta T$$

Equation 3.5.1 Heat Capacity

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18 150 J of energy to raise the temperature of the pan by 50.0 °C:

$$C_{\text{small pan}} = \frac{18\,140\ J}{50.0^\circ C} = 363\ \ J/^\circ C$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{large\ pan} = \frac{90\ 700\ J}{50.0^{\circ}C} = 1814\ \ J/^{\circ}C$$

The **specific heat capacity (*c*)** of a substance, commonly called its “specific heat,” is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m\Delta T}$$

Equation 3.5.2 Specific heat capacity

Note the important difference in units between *C* and *c*: the heat capacity, *C*, is expressed in energy per temperature change, whereas the specific heat capacity, *c*, is expressed in energy per temperature change as well, but this time *per mass*. In other words, the specific heat capacity takes it a step further by taking mass into account.

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is, therefore:

$$c_{iron} = \frac{90\ 700\ J}{(4040\ g)(50.0^{\circ}C)} = 0.449\ J/g^{\circ}C$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{iron} = \frac{90\ 700\ J}{(4040\ g)(50.0^{\circ}C)} = 0.449\ J/g^{\circ}C$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 3.5.1).

In real-life applications, we typically use *C* for larger-scale applications like *objects* where the exact mass isn’t important and differences in mass can be seen qualitatively (object is larger, feels significantly heavier), or when working with different-sized objects of the same composition. The specific heat capacity, *c*, applies to more smaller-scale applications like *substances* where the mass becomes something important to consider to meet specific requirements (e.g. determining the most appropriate mass of NH_4NO_3 to use in an ice pack that is convenient in terms of mass and delivers a temperature change that is just right).

Figure 3.5.1. Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in the table below.

Specific Heats of Common Substances at 25°C and 1 bar*		
Substance	**Symbol (*state*)**	**Specific Heat (J/g °C)**
helium	He *(g)*	5.193
water	H_2O *(l)*	4.184
ethanol	C_2H_6O *(l)*	2.438
ice	H_2O *(s)*	2.02 (at -10°C)
water vapour	H_2O *(g)*	1.864
nitrogen	N_2 *(g)*	1.040
Air		1.007
oxygen	O_2 *(g)*	0.918
aluminum	Al *(s)*	0.897
carbon dioxide	CO_2 *(g)*	0.853
argon	Ar *(g)*	0.520
iron	Fe (*s*)	0.449
copper	Cu (*s*)	0.385
lead	Pb (*s*)	0.130
gold	Au (*s*)	0.129
silicon	Si (*s*)	0.712

* CRC Handbook of Chemistry and Physics 100th Edition (Online) (Electronic ed.). (2019). Boca Raton, Fla: CRC Press.

Table 3.5.1 Specific Heats of Common Substances at 25°C and 1 bar*

If we know the mass of a substance and its specific heat, we can determine the amount of heat, *q*, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$

$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

In this equation, *c* is the specific heat of the substance, *m* is its mass, and ΔT (which is read "delta T") is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. Since *c* and *m* are both always positive values, the only variable that determines whether heat is absorbed or released is the temperature change. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of *q* is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of *q* is negative. If you try the math out using the equation $q = mc\Delta T$, you'll see that this reasoning checks out:

ΔT is (-) → $T_{\text{initial}} > T_{\text{final}}$ → heat release $q=mc\Delta T$ $q=(+)(+)(-)$ ∴ heat released √	ΔT is (+) → $T_{\text{initial}} < T_{\text{final}}$ → heat absorbed $q=mc\Delta T$ $q=(+)(+)(+)$ ∴ heat absorbed √

Example 3.5.1 – Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 8.0×10^2 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 8.0×10^2 g of water by 1 °C. Finally, we observe that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned} q &= c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J/g}^{\circ}\ \text{C}) \times (8.0 \times 10^{2}\ \text{g}) \times (85 - 21)^{\circ}\ \text{C} \\ &= (4.184\ \text{J/g}^{\circ}\ \text{C}) \times (8.0 \times 10^{2}\ \text{g}) \times (64)^{\circ}\ \text{C} \\ &= 210{,}000\ \text{J}\ \ (= 2.1 \times 10^{2}\ \text{kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and *q* is positive.

Check Your Learning 3.5.1 – Measuring Heat

How much heat, in joules, must be added to a 5.07 × 10^4 J iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

Answer

5.07 × 10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 3.5.2 – Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4°C to 43.6°C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

$$6640\ \text{J} = c \times (348\ \text{g}) \times (43.6 - 22.4)^{\circ}\ \text{C}$$

Solving:

$$c = \frac{6640\ J}{(348\ g) \times (21.2^{\circ}C)} = 0.900\ J/g^{\circ}C$$

Comparing this value with the values in the table for specific heats of common substances (at 25°C & 1 bar), this value matches the specific heat of aluminum, which suggests that the unknown metal is aluminum.

Check Your Learning 3.5.2 – Determining Other Quantities

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer:

c = 0.451 J/g °C; the metal is likely to be iron

Measuring Heat Flow – Calorimeters

A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 3.5.2). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

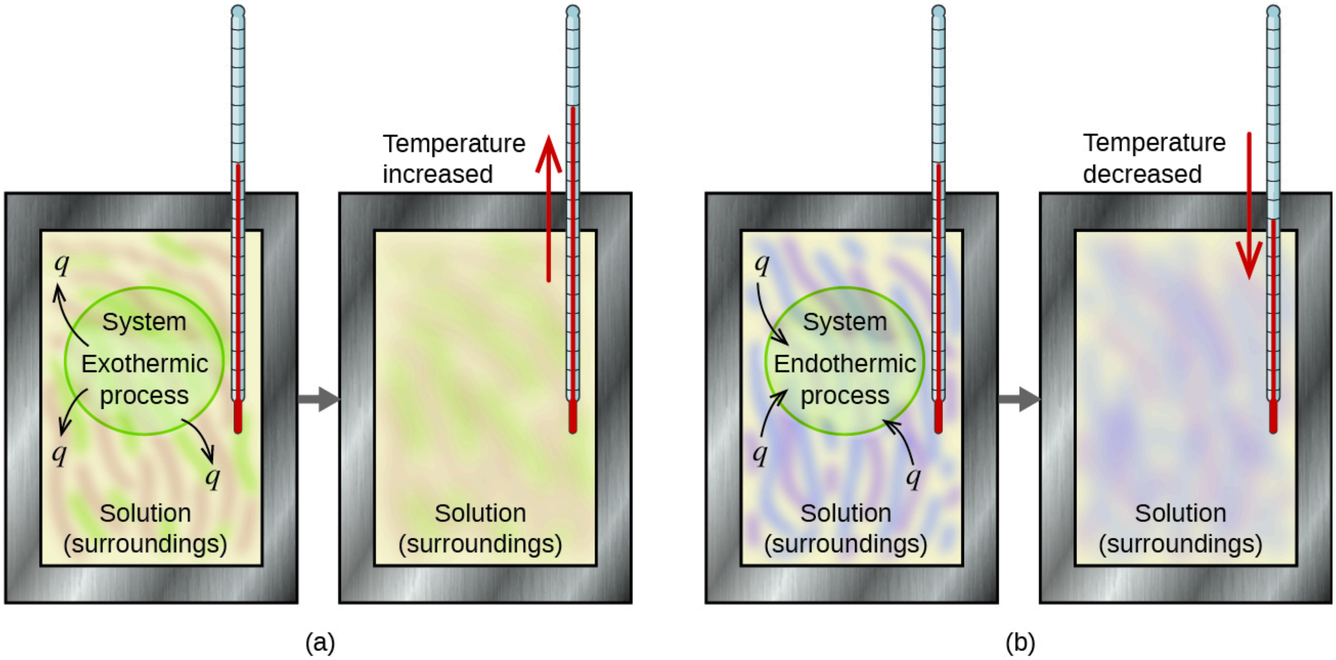


Figure 3.5.2. In a calorimetric determination, either (a) an exothermic process occurs and heat, *q*, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, *q*, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on.

Consider a simple example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase until the two substances have the same temperature— when they reach thermal equilibrium (Figure 3.5.3). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}}$$

Recall the first law of thermodynamics: energy is neither gained nor destroyed, only *transferred*. For calorimetry problems, keep in mind that heat flows in only one direction – always from hot to cold. So while one substance emits heat, the other substance will absorb that heat. The magnitude of the heat (change) is, therefore, the same for both substances, and the negative sign merely shows that $q_{\text{substance M}}$ and $q_{\text{substance W}}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{\text{substance M}}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

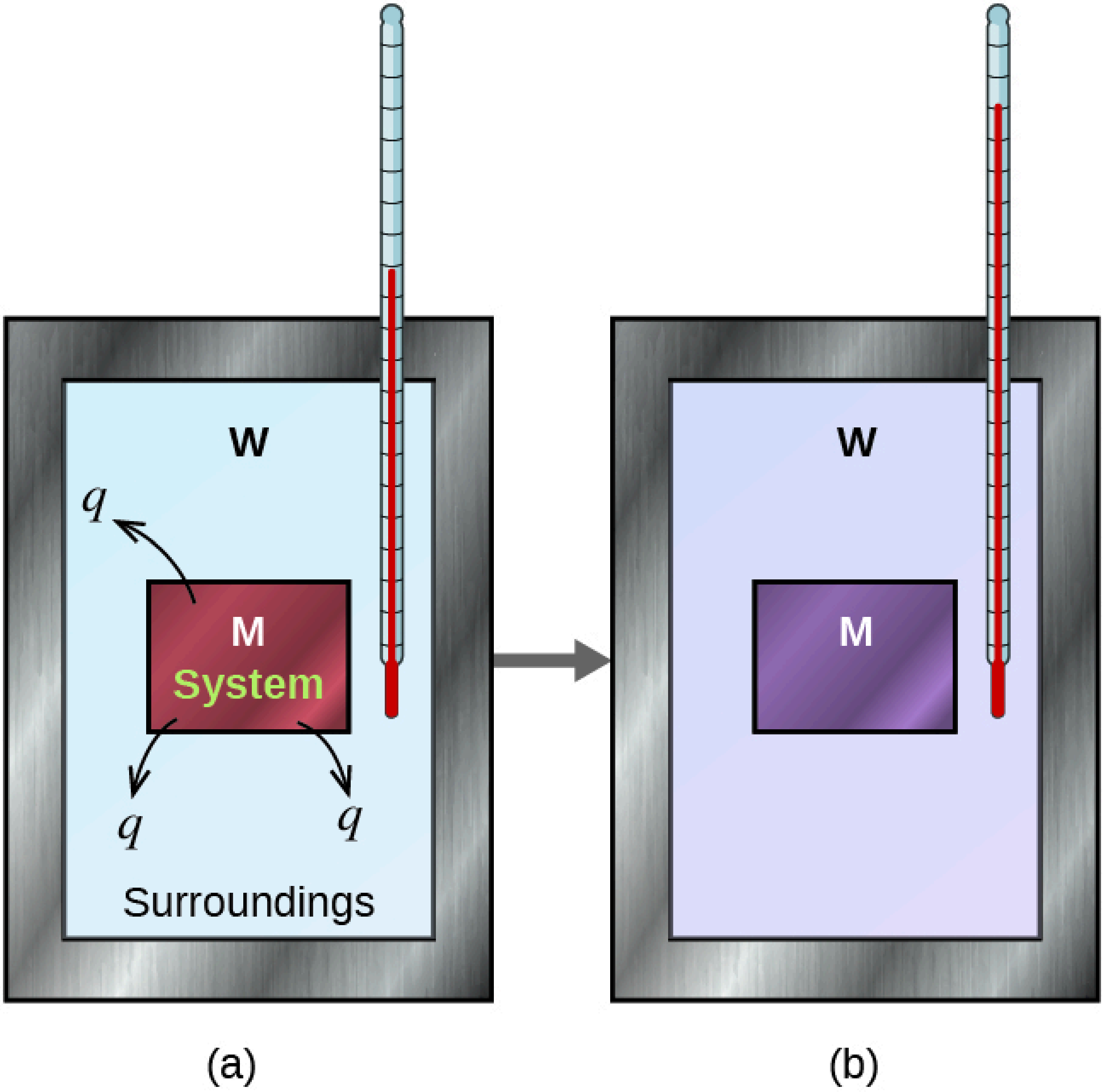


Figure 3.5.3. In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Here, we'll talk about two types of calorimeters – "coffee-cup" calorimeters and bomb calorimeters.

"Coffee-Cup" (or Constant Pressure) Calorimetry

General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure 3.5.4). These easy-to-use "coffee cup" calorimeters operate at constant pressure to allow more heat exchange with the outside environment and therefore produce less accurate energy values. In terms of real applications, these calorimeters are most appropriate for endothermic and *mildly* exothermic processes. Highly exothermic reactions, such as combustion reactions, are typically carried out using bomb calorimeters (which we discuss later).

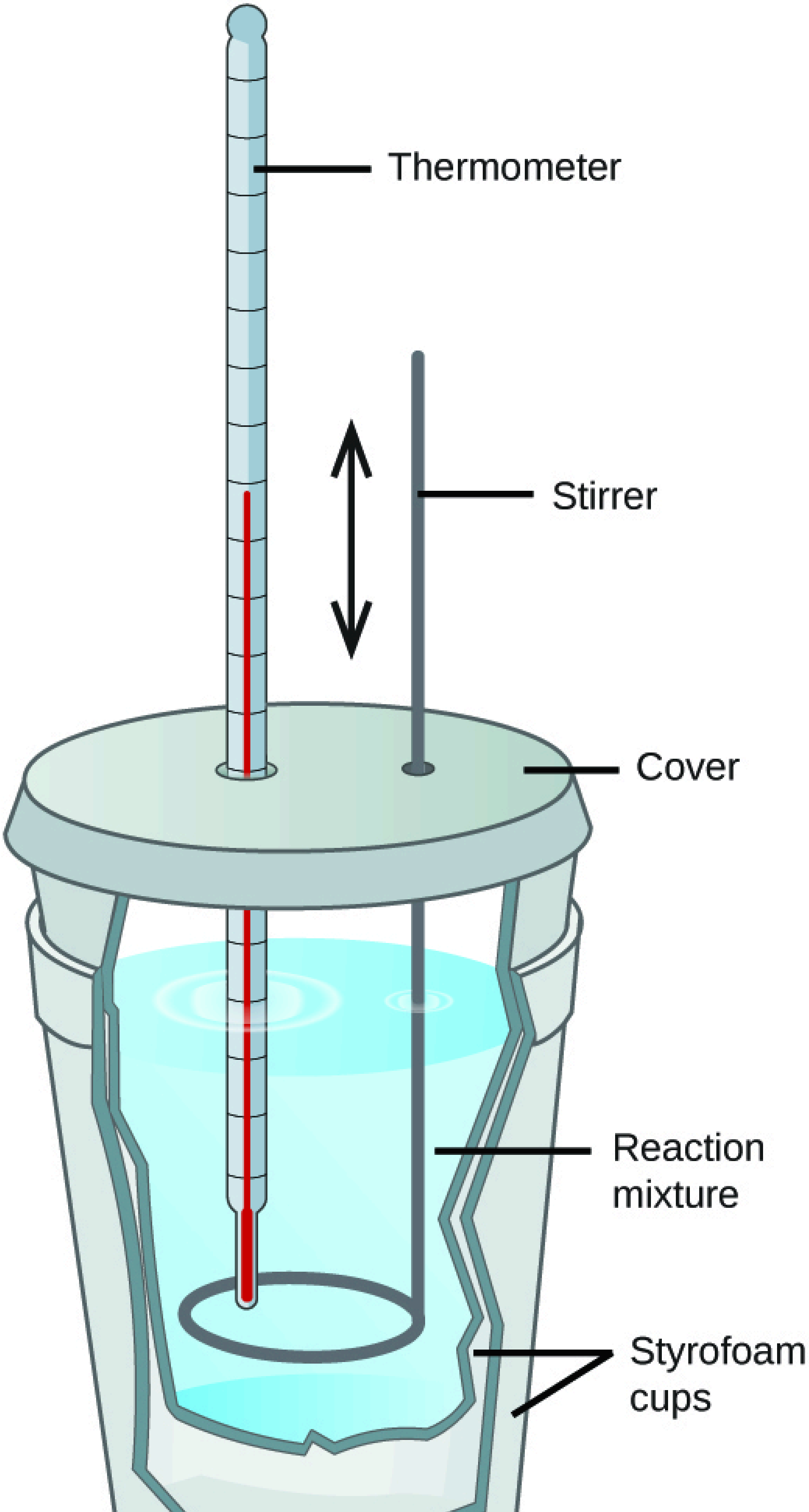

Thermometer
Stirrer
Cover
Reaction mixture
Styrofoam cups

Figure 3.5.4. A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure 3.5.5).

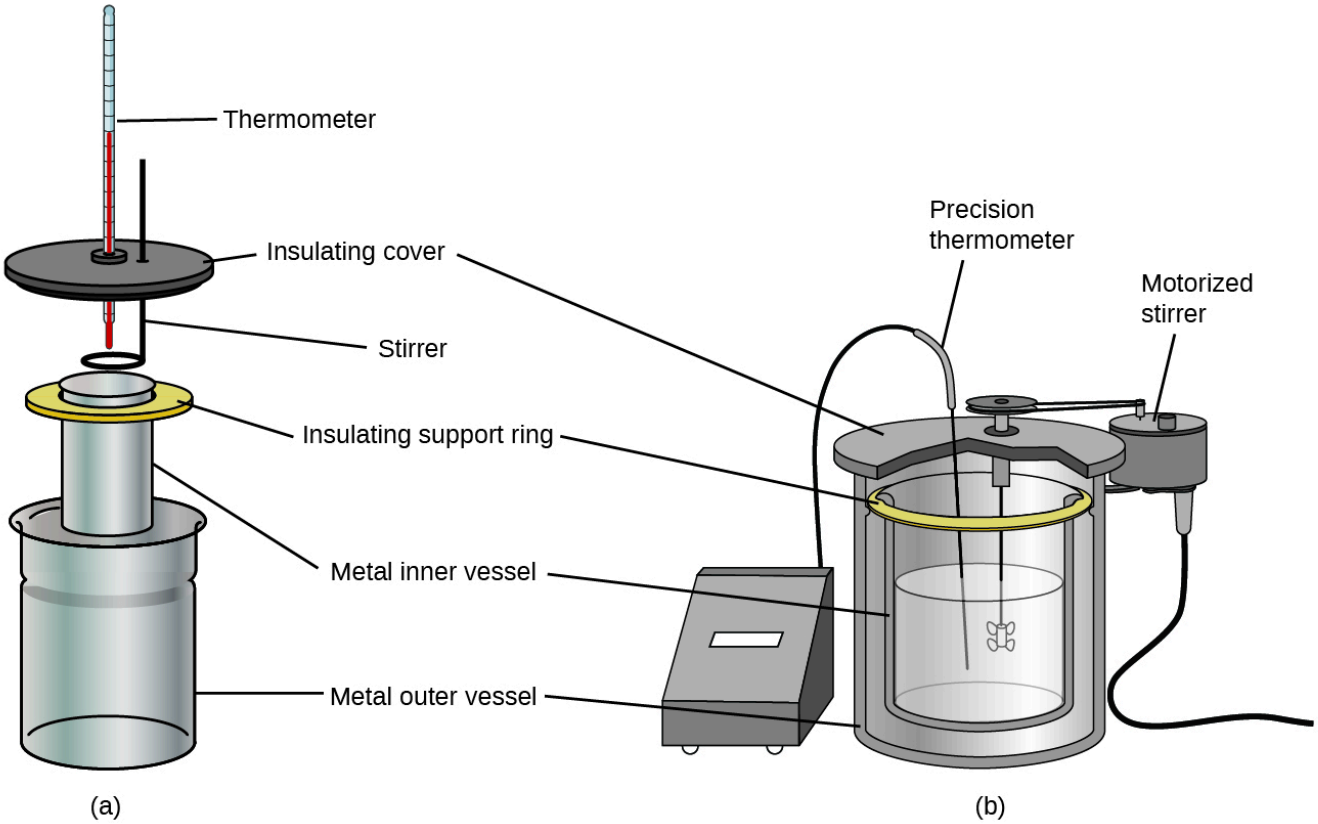


Figure 3.5.5. Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Example 3.5.3 – Heat Transfer between Substances at Different Temperatures

A 360.0-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0°C. The final temperature of the water was measured as 42.7°C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (see the Table 3.5.1) of specific heats for common substances), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0°C to 42.7°C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat “lost” to the outside environment, then *heat given off by rebar* = −*heat taken in by water*, or:

$$q_{\text{rebar}} = -\, q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -\,(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -\, c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7°C, substituting known values yields:

$$(0.449\ J/g^{\circ}C)(360.0\ g)(42.7^{\circ}C - T_{i,rebar}) = -(4.184\ J/g^{\circ}C)(425\ g)(42.7^{\circ}C - 24.0^{\circ}C)$$

$$T_{i,rebar} = \frac{(4.184\ J/g^{\circ}C)(425\ g)(42.7^{\circ}C - 24.0^{\circ}C)}{(0.449\ J/g^{\circ}C)(360.0\ g)} + 42.7^{\circ}C$$

Solving this gives $T_{\text{i,rebar}}$= 248°C, so the initial temperature of the rebar was 248°C.

Check Your Learning 3.5.3 – Heat Transfer between Substances at Different Temperatures

A 248-g piece of copper is dropped into 390 mL of water at 22.6°C. The final temperature of the water was measured as 39.9°C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer

The initial temperature of the copper was 335.6°C.

Check Your Learning 3.5.4 – Heat Transfer between Substances at Different Temperatures

A 248-g piece of copper initially at 314°C is dropped into 390 mL of water initially at 22.6°C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer

The final temperature (reached by both copper and water) is 38.7°C.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example 3.5.4 – Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0°C. The final temperature is 28.5°C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, *heat given off by metal* = −*heat taken in by water*, or:

$$q_{\text{metal}} = -\, q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -\, c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0°C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\ \text{g})(28.5^{\circ}\ \ \text{C} - 100^{\circ}\ \ \text{C}) = -\,(4.18\ \text{J/g}^{\circ}\ \ \text{C})(60.0\ \text{g})(28.5^{\circ}\ \ \text{C} - 22.0^{\circ}\ \ \text{C})$$

Comparing this with values in the table (Table 3.5.1) of specific heats of common substances, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as likely copper.

Check Your Learning 3.5.5 – Identifying a Metal by Measuring Specific Heat

A 92.9-g piece of a silver/gray metal is heated to 178.0°C, and then quickly transferred into 75.0 mL of water initially at 24.0°C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7°C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer

$c_{\text{metal}} = 0.13\ \text{J/g °C}$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the outside environment. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the “system”), q_{reaction}, plus the heat absorbed or lost by the solution (the “surroundings”), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -\, q_{\text{solution}}$$

This concept lies at the heart of all calorimetry problems and calculations. If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

Example 3.5.5 – Heat Produced by an Exothermic Reaction

When 50.0 mL of 1.00 M HCl (*aq*) and 50.0 mL of 1.00 M NaOH (*aq*), both at 22.0°C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9°C. What is the approximate amount of heat produced by this reaction?

$$HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0°C, and hence it will be that whole solution of 100.0 mL that will absorb the heat given off by the reaction. The HCl and NaOH then react until the solution temperature reaches 28.9°C.

The heat given off by the reaction is equal to that taken in by the solution.

Therefore:

$$q_{reaction} = -\,q_{solution}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and the outside environment.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{solution} = (c \times m \times \Delta T)_{solution}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{solution} = (4.184\ \text{J/g}^\circ\ \text{C})(1.0 \times 10^2\ \text{g})(28.9^\circ\ \text{C} - 22.0^\circ\ \text{C}) = 2.9 \times 10^3\ \text{J}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{reaction} = -\,q_{solution} = -2.9 \times 10^3\ \text{J}$$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat.

Check Your Learning 3.5.6 – Heat Produced by an Exothermic Reaction

When 100 mL of 0.200 M NaCl (*aq*) and 100 mL of 0.200 M $AgNO_3$ (*aq*), both at 21.9°C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5°C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer

1.34×10^3 J; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

As seen in the previous example, we assumed that the specific heat capacity of the solution mixture of

HCl *(aq)* and NaOH *(aq)* was equal to that for water. Therefore, in calorimetry problems (unless otherwise mentioned), you can set the value of *c* for solutions as 4.184 J/g °C if the assumption is reasonable (for example, the reactants used are all aqueous solutions).

Example 3.5.6 – Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an "instant ice pack" (Figure 3.5.6). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9°C in a calorimeter, the temperature decreases to 20.3°C.

Calculate the value of *q* for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.

Figure 3.5.6. An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{rxn} = -q_{soln}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Note: We're saying here that it's the *solution* that is losing heat, and not the solvent. In your calculations, when you consider the value for mass, *m*, you have to use the mass of the *solution*, NOT the solvent! When the reaction begins, the amount of salt is already dissolved and added to the amount of water present, so the solution is present and will be the one that emits heat. By the law of conservation of mass, the total mass of the solution *must* be the sum of masses for salt and water, hence it is this total mass of solution that loses heat.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned} q_{rxn} &= -q_{soln} = -(c \times m \times \Delta T)_{soln} \\ &= -[(4.184\ \text{J/g}^\circ\text{C}) \times (53.2\ \text{g}) \times (20.3^\circ\text{C} - 24.9^\circ\text{C})] \\ &= -[(4.184\ \text{J/g}^\circ\text{C}) \times (53.2\ \text{g}) \times (-4.6^\circ\text{C})] \\ &+ 1.0 \times 10^3\ \text{J} = +1.0\text{kJ} \end{aligned}$$

The positive sign for *q* indicates that the dissolution is an endothermic process.

Check Your Learning 3.5.7 – Heat Flow in an Instant Ice Pack

When a 3.00-g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05°C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Answer

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water

In Case You're Interested...Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 3.5.7). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes.

The process $NaC_2H_3O_2\,(aq) \rightarrow NaC_2H_3O_2\,(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused.

Figure 3.5.7. Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is $2\ Fe\,(s) + 3/2\ O_2\,(g) \rightarrow Fe_2O_3\,(s)$. Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

This link shows the precipitation reaction that occurs when the disk in a chemical hand warmer is flexed.

Bomb (or Constant Volume) Calorimetry

The coffee-cup calorimeters previously described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, a **bomb calorimeter**, is used to measure the energy produced by reactions that are very exothermic and yield large amounts of heat and gaseous products, such as combustion reactions. This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure 3.5.8). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is absorbed by the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.

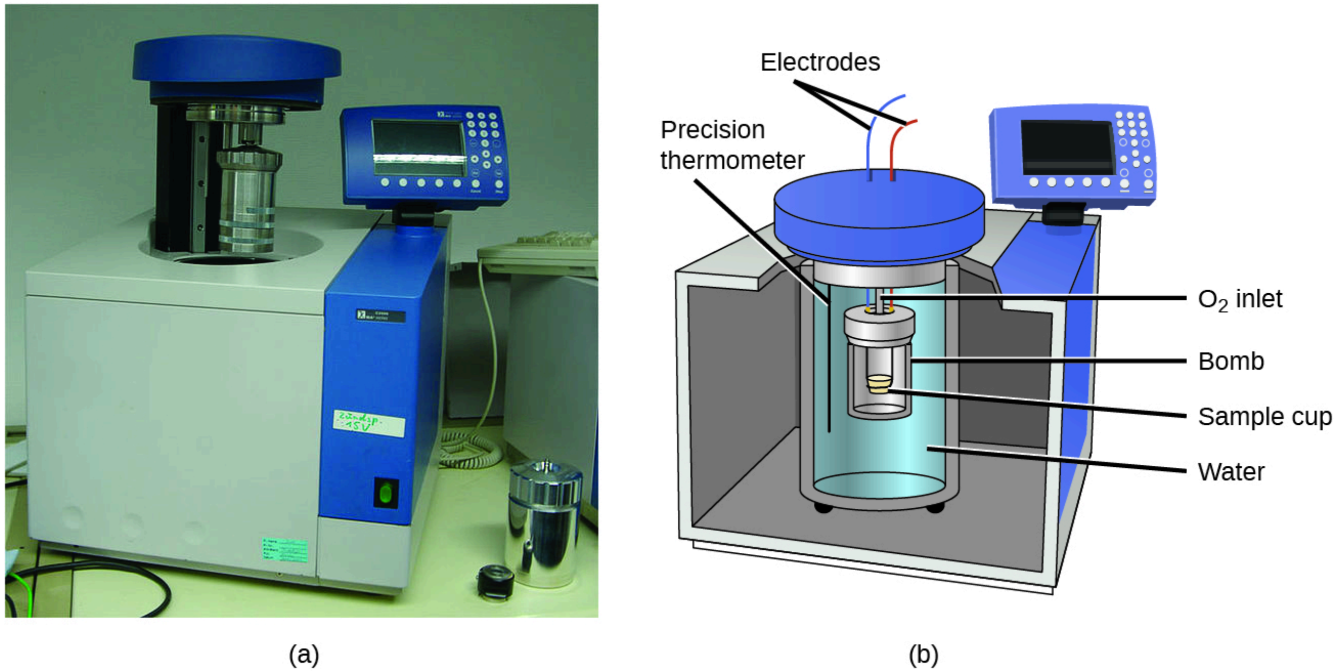


Figure 3.5.8. (a) A bomb calorimeter is used to measure the heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

Bomb Calorimetry – Video

See this link to learn more about how a bomb calorimeter is prepared for action.

Example 3.5.7 – Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8°C to 35.6°C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C.

(a) How much heat was produced by the combustion of the glucose sample?

(b) The metabolic breakdown of glucose is quite similar to its combustion – it requires oxygen (O_2) for its oxidation, except the energy harvested from glucose is primarily used to carry out cellular processes. Assuming the same amount of energy from part (a) was harnessed from consuming the same glucose sample and metabolizing it, how much nutritional calories (Cal) would this correspond to?

Solution

(a) The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$q_{rxn} = -(q_{water} + q_{bomb}) = -\{[m_{water} \times c_{water} \times (T_f - T_i)] + [C_{cal} \times (T_f - T_i)]\}$

$= -[(4{,}184\ J/g^\circ\ C) \times (775\ g) \times (35.6^\circ\ C - 23.8^\circ\ C) + 893\ J/^\circ\ C \times (35.6^\circ\ C - 23.8^\circ\ C)]$

$= -(38300\ J + 10500\ J)$

$= -48800\ J = -48.8\ kJ$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

(b) The energy produced, expressed in kilojoules, can easily be expressed in calories and furthermore in Calories by performing a unit conversion:

$$Calories = 48.7\ kJ \times \frac{1000\ J}{1\ kJ} \times \frac{1\ cal}{4.184\ J} \times \frac{1\ kcal}{1000\ cal} \times \frac{1\ Cal}{1\ kcal} = 11.6\ Calories$$

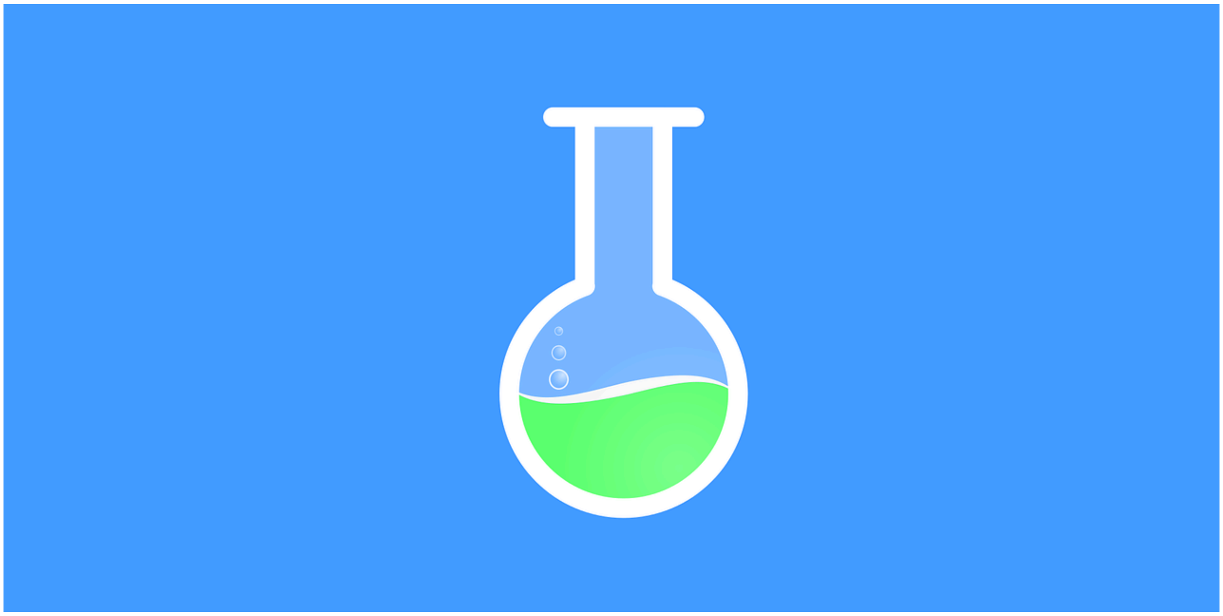
Therefore, a person consuming 3.12 g of glucose would get roughly 11.6 Calories.

Check Your Learning 3.5.8 – Bomb Calorimetry

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39°C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Answer

39.0 kJ



CHM1311 Laboratory | Experiment #2: Enthalpy of Various Reactions

Purpose

Using your knowledge of calorimetry in the context of thermochemistry, the goal of this experiment is to accomplish the following task: to design a drinks container that can be activated to cool 100 cm^3 of drinkable water by 5°C in no more than 5 minutes.

You have a choice between using either ammonium chloride (NH_4Cl) or ammonium nitrate (NH_4NO_3) as one of your main chemicals for the cooling process.

Principles

Calorimetry
Enthalpy of different reactions
Hess' Law
Graphical extrapolation

Safety Precautions

Wear appropriate personal protective equipment (PPE) at all times in the laboratory setting – this includes your lab coat and safety goggles/glasses.

Be sure to consult the MSDS for NH_4Cl and NH_4NO_3 for relevant health and safety, first aid, handling, and waste disposal information.

As you plan your procedure, always make sure that all steps are safe and follow lab safety guidelines. Your TA will verify your procedure before you conduct your experiment.

Things to Consider

Make sure you go through the pre-lab exercise for the experiment – it will allow you to better understand your task and make it much easier for you to plan your procedure. Some of the questions allow you to acquire information that you'll need for the experiment, such as the enthalpy of solution for NH_4Cl and NH_4NO_3.

In your report, make sure you explain your choice of chemical (NH_4Cl or NH_4NO_3) in terms of various factors such as cost, enthalpy of solution, solubility in water, and relevant health and safety information to pass Canada Health & Safety inspection.

You'll be responsible for reporting full details of the cooling process, the theoretical (*Hint:* $q = mc\Delta T$) and experimental quantities of chemicals used and the time periods required to achieve the -5°C temperature change.

Reference

Venkateswaran, R. General Chemistry – Laboratory Manual – CHM 1301/1311.

Questions

★ Questions

1. A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, four students gave the following answers,

a. Both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature.
b. The 2-L bottle of water lost more heat because there was more water.
c. The 500-mL bottle of water lost more heat because it cooled more quickly.

d. It's not possible to tell because we do not know the initial temperature and the final temperature of the water.

Indicate which of these answers is correct and describe the error in each of the other answers.

2. Would the amount of heat measured in an exothermic reaction be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

3. Would the amount of heat absorbed by the dissolution in Example 6. (heat flow in an instant ice pack) appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

★★ Questions

4. How many millilitres of water (volume) at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

5. How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

6. When 50.0 g of 0.200 M $NaCl(aq)$ at 24.1 °C is added to 100.0 g of 0.100 M $AgNO_3(aq)$ at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as $AgCl(s)$ forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.

7. The addition of 3.15 g of $Ba(OH)_2{\cdot}8H_2O$ to a solution of 1.52 g of NH_4SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat absorbed by the reaction (in kilojoules), which can be represented by the following equation:

$$Ba(OH)_2 \cdot 8H_2O\,(s) + 2\,NH_4SCN\,(aq) \rightarrow Ba(SCN)_2\,(aq) + 2\,NH_3\,(aq) + 10\,H_2O\,(l)$$

8. When 1.0 g of fructose, $C_6H_{12}O_6(s)$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is q for this combustion (in kilojoules)?

9. When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample (in kilojoules)?

10. The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g?

11. A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose (in grams) if the average number of Calories for carbohydrates is 4.1 Calories/g?

12. A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1×10^3 Calories if the average number of Calories for fat is 9.1 Calories/g?

13. Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs $4.23, or a litre of isooctane (density, 0.6919 g/mL) that costs $0.45? Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

Answers

1. Student 2 is correct. The error in the first student's answer is having ignored the mass of water. For the third student, the answer opposed the question asked. He needed to state that the 2-L bottle took longer to reach the refrigerator's temperature therefore it lost more heat. The error in the fourth student's answer ignored that the change in temperature of both water bottles are the same and both initial and final temperature are not needed.

2. Lesser; in a poorer insulator more of the heat produced by the reaction will escape, which would appear as a smaller value for q.

3. Greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings": $q_{\text{rxn}} = -(q_{\text{solution}} + q_{\text{calorimeter}})$; since both q_{solution} and $q_{\text{calorimeter}}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

4. 170.27 mL

5. The temperature of the coffee will drop 1 degree.

6. 693 J

7. 1.4 kJ

8. 15.64 kJ

9. 11.7 kJ

10. 30%

11. 3.90 g

12. 120.87 g, 0.055 lbs

13. Buying a dollar of isooctane it would give you 7.349×10^4 kJ. A dollar worth of cereal would only fuel 4.12 kJ of energy. Therefore, with one dollar it is best to invest in isooctane to obtain more energy.

3.6 – HESS' LAW

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law, which we'll discuss in this chapter, allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}): The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of formation (ΔH_f): The change in enthalpy due to the formation of a molecule from its elements in their natural state at standard conditions (ie. the state they are most stable at 25 C and 1 bar). As they are based on their elements, the enthalpy of formation for elements in their natural state is always equal to zero.
- Enthalpy of fusion (ΔH_{fus}): The enthalpy change that accompanies the melting (fusion) of a mole of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization (ΔH_{vap}): The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln}): The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.
- Enthalpy change can be visualized using the following energy diagram. The change in energy represents the enthalpy change after a chemical reaction has occurred.

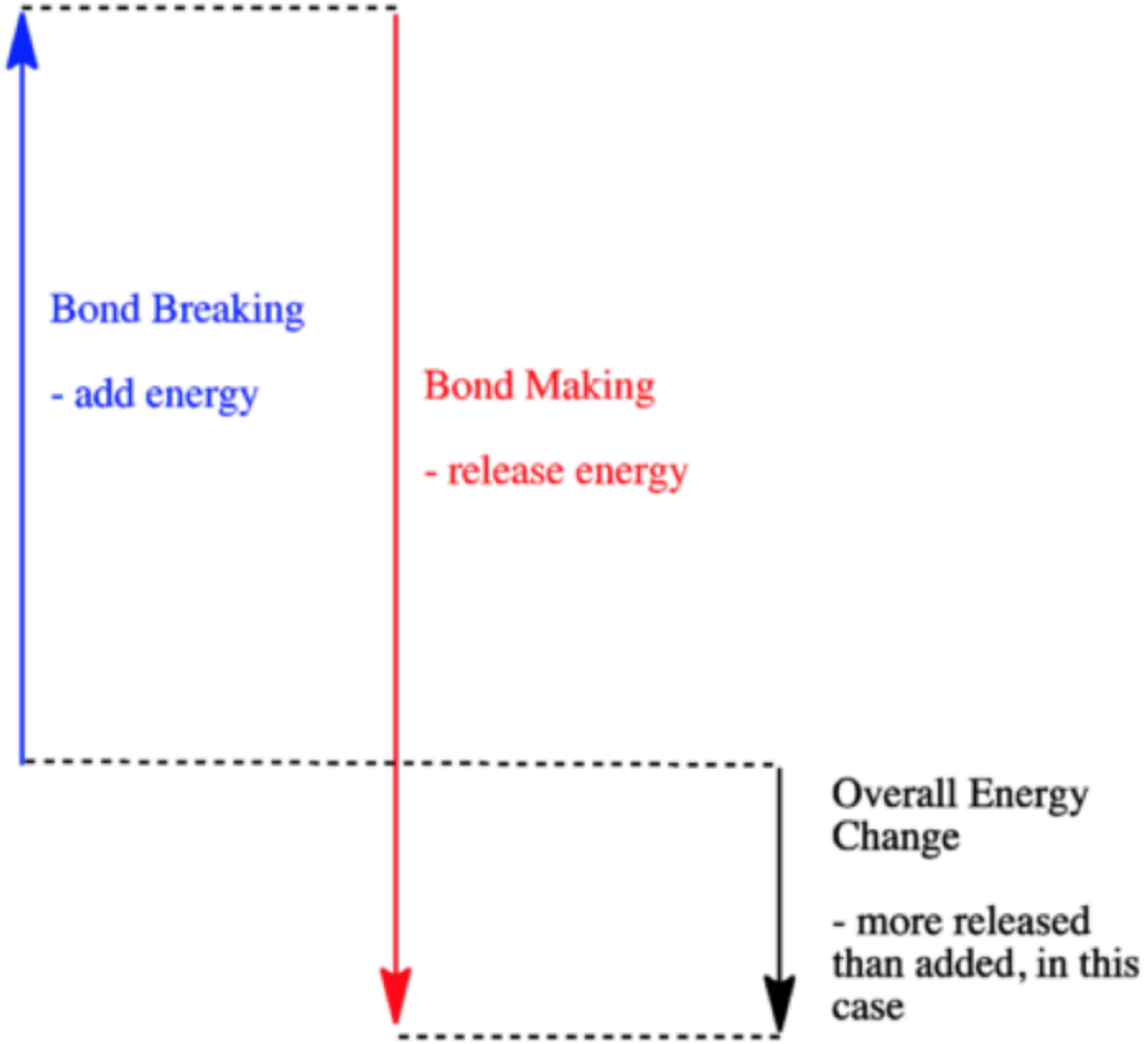


Figure 3.6.1. Bond energy diagram showing the change in energy of an exothermic reaction.

Enthalpy of Combustion

Standard enthalpy of combustion (ΔH°_C) is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, −1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 bar pressure, yielding products also at 25 °C and 1 bar.

$$C_2H_5OH\,(l) + 3\,O_2\,(g) \rightarrow 2\,CO_2 + 3\,H_2O\,(l) \quad \Delta H^\circ_{298} = -\,1366.8\ \text{kJ}$$

It should be noted that, historically, the unit of standard pressure was 1 atmosphere (101.325 kPa) but this was changed by IUPAC in 1982 to 1 bar (100 kPa). Be aware that both of these values are still commonly used as standard pressure.

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table

3.6.1. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and **hydrocarbons** (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table 3.6.1 Standard Molar Enthalpies of Combustion

Standard Molar Enthalpies of Combustion

Substance	**Combustion Reaction**	**Enthalpy of Combustion,** ΔH°_{C} (kJ at 25°C)
carbon	$C(s) + O_2(g) \rightarrow CO_2(g)$	−393.5
hydrogen	$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$	−285.8
magnesium	$Mg(s) + 1/2\ O_2(g) \rightarrow MgO(s)$	−601.6
sulfur	$S(s) + O_2(g) \rightarrow SO_2(g)$	−296.8
carbon monoxide	$CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$	−283.0
methane	$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$	−890.8
acetylene	$C_2H_2(g) + 5/2\ O_2(g) \rightarrow 2\ CO_2(g) + H_2O(l)$	−1301.1
ethanol	$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$	−1366.8
methanol	$CH_3OH(l) + 3/2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(l)$	−5461

Example 3.6.1 – Using Enthalpy of Combustion

As illustrated in Figure 3.6.2., the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.

Figure 3.6.2. The combustion of gasoline is very exothermic. (credit: modification of work by "AlexEagle"/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. The table above gives this value as −5460 kJ per one mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ L\ C_8H_{18} \times \frac{1000\ mL\ C_8H_{18}}{1\ L\ C_8H_{18}} \times \frac{0.692\ g\ C_8H_{18}}{1\ mL\ C_8H_{18}} \times \frac{1\ mol\ C_8H_{18}}{114\ g\ C_8H_{18}} \times \frac{-5460\ kJ}{1\ mol\ C_8H_{18}} = -3.31 \times 10^4\ kJ$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$\begin{aligned}
1.00\ L\ C_8H_{18} \times \frac{1000\ mL\ C_8H_{18}}{1\ L\ C_8H_{18}} &= 1.00 \times 10^3 mL\ C_8H_{18} \\
1.00 \times 10^3 mL\ C_8H_{18} \times \frac{0.692\ g\ C_8H_{18}}{1\ mL\ C_8H_{18}} &= 692\ g\ C_8H_{18} \\
692\ g\ C_8H_{18} \times \frac{1\ mol\ C_8H_{18}}{114\ g\ C_8H_{18}} &= 6.07\ mol\ C_8H_{18} \\
692\ g\ C_8H_{18} \times \frac{-5460\ kJ}{1\ mol\ C_8H_{18}} &= -3.31 \times 10^4\ kJ
\end{aligned}$$

Check Your Learning 3.6.1 – Using Enthalpy of Combustion

How much heat is produced by the combustion of 125 g of acetylene?

Answer

6.25×10^3 kJ

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 3.6.3.). The species of algae used are nontoxic, biodegradable, and among the world's fastest-growing organisms. About 50% of the algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.

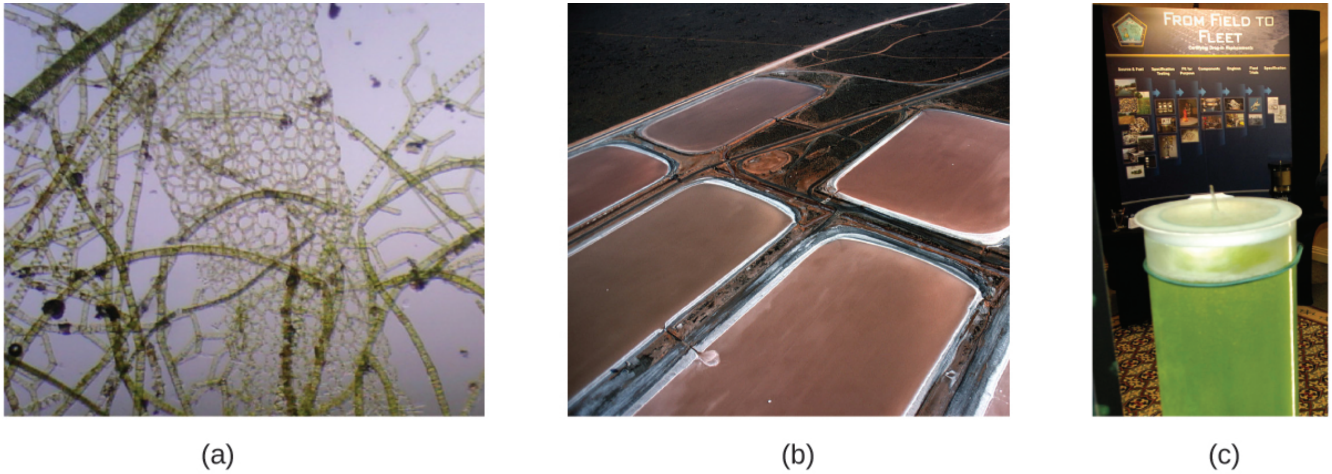


Figure 3.6.3. (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometres (about 0.4% of the landmass of the US or less than 1/7 of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 USD per gallon. The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify, and distribute (Figure 3.6.3.).

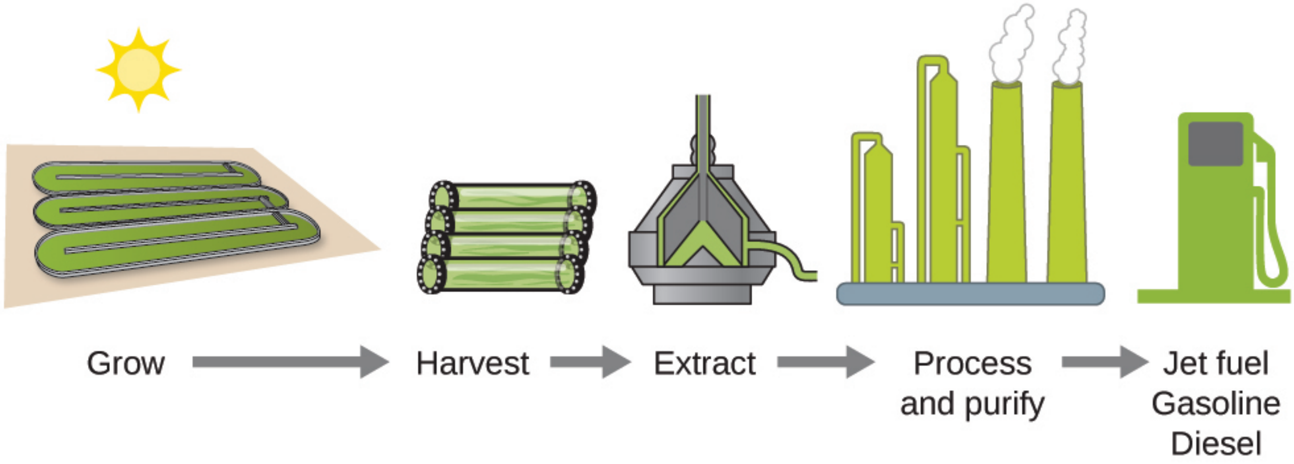


Figure 3.6.4. Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Click here to learn more about the process of creating algae biofuel.

Standard Enthalpy of Formation

Standard enthalpy of formation ΔH_f° is an enthalpy change for a reaction in which exactly one mole of a pure substance is formed from free elements in their most stable states under standard conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice here in this section.

The standard enthalpy of formation of $CO_{2(g)}$ is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_f^\circ = \Delta H_{298}^\circ = -\,393.5\text{ kJ}$$

starting with the reactants at a pressure of 1 bar and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 bar and 25 °C. For nitrogen dioxide, $NO_2\,(g)$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$1/2\,N_2\,(g) + O_2\,(g) \rightarrow NO_2\,(g) \qquad \Delta H_f^\circ = \Delta H_{298}^\circ = +\,33.2\text{ kJ}$$

A reaction equation with 1/2 mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_{2(g)}$.

You will find a table of standard enthalpies of formation of many common substances in Appendix G. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 bar for gases and 1 M for solutions. The reference forms used for most elements are simply the element itself (for example silver: Ag *(s)*), however, some are more unusual. These exceptions are summarized in the table below.

Element Reference Forms

Element	Reference Form
hydrogen	$H_2\,(g)$
nitrogen	$N_2\,(g)$
oxygen	$O_2\,(g)$
fluorine	$F_2\,(g)$
chlorine	$Cl_2\,(g)$
bromine	$Br_2\,(l)$
iodine	$I_2\,(s)$
carbon	C *(graphite, s)*
phosphorus	P *(white, s)*
sulfur	$S_8\,(s)$

Table 3.6.2 Unusual Element Reference Forms

Example 3.6.2 – Evaluating an Enthalpy of Formation

Ozone, $O_{3(g)}$, forms from oxygen, $O_{2(g)}$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f° of ozone from the following information:

$$3\,O_2\,(g) \rightarrow 2\,O_3\,(g) \quad \Delta H_{298}^\circ = +286\text{ kJ}$$

Solution

ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for $O_{3(g)}$ is the enthalpy change for the reaction:

$$3/2\,O_2\,(g) \rightarrow O_3\,(g)$$

For the formation of 2 mol of $O_{3(g)}$, ΔH°_{298}=+286 kJ. This ratio, $\left(\frac{286\ kJ}{2\ mol\ O_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_{3(g)}$ is formed, which is the enthalpy of formation for $O_{3(g)}$:

$$\Delta H^\circ\ for\ 1\ mole\ of\ O_{3(g)} = 1\ mol\ O_3 \times \frac{286\ kJ}{2\ mol\ O_3} = 143\ kJ$$

Therefore, $\Delta H_f^\circ [O_3\,(g)] = +\,143$ kJ/mol.

Check Your Learning 3.6.2 – Evaluating an Enthalpy of Formation

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, $HCl_{(g)}$. What is the enthalpy change for the reaction of 1 mole of $H_{2(g)}$ with 1 mole of $Cl_{2(g)}$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $HCl_{(g)}$ is −92.3 kJ/mol.

Answer

$H_2\,(g) + Cl_2\,(g) \rightarrow 2\,HCl\,(g) \quad \Delta H^\circ_{298} = -\,184.6$ kJ

Example 3.6.3 – Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

(a) $C_2H_5OH\,(l)$

(b) $Ca_3(PO_4)_2\,(s)$

Solution

Remembering that ΔH_f° reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $2\,C\,(s, graphite) + 3\,H_2\,(g) + 1/2\,O_2\,(g) \rightarrow C_2H_5OH\,(l)$

b. $3\,Ca\,(s) + 1/2\,P_4\,(s) + 4\,O_2\,(g) \rightarrow Ca_3(PO_4)_2\,(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Check Your Learning 3.6.3 – Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

(a) $C_2H_5OC_2H_5\,(l)$

(b) $Na_2CO_3\,(s)$

Answer

a. $4\,C\,(s, graphite) + 5\,H_2\,(g) + 1/2\,O_2\,(g) \rightarrow C_2H_5OC_2H\,(l)$

b. $2\,Na\,(s) + C\,(s, graphite) + 3/2\,O_2\,(g) \rightarrow Na_3CO_3\,(s)$

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of **Hess's law**, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps*. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_{298}^{\circ} = -\,394\text{ kJ}$$

In the two-step process, first carbon monoxide is formed:

$$C\,(s) + 1/2\,O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_{298}^{\circ} = -\,111\text{ kJ}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO\,(g) + 1/2\,O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_{298}^{\circ} = -\,283\text{ kJ}$$

The equation describing the overall reaction is the sum of these two chemical changes:

Step 1: $C\,(s) + 1/2\,O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_{298}^{\circ} = -\,111\text{ kJ}$

Step 2: $CO\,(g) + 1/2\,O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_{298}^{\circ} = -\,283\text{ kJ}$

Sum: $C\,(s) + O_2\,(g) + CO\,(g) \rightarrow CO\,(g) + CO_2\,(g)$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H_{298}^{\circ} = -\,394\text{ kJ}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table 3.6.1 to find the enthalpy change of the entire reaction from its two steps:

$$C\,(s) + 1/2\,O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H298^{\circ} = -\,111\text{ kJ}$$

$$\begin{array}{ll} CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} & \Delta H_{298}^{\circ} = \;\; -283\ kJ \\ \hline C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} & \Delta H_{298}^{\circ} = \;\; -394\ kJ \end{array}$$

The result is shown in Figure 3.6.5. We see that Δ*H* of the overall reaction is the same whether it occurs in one step or two (i.e. it is a state function). This finding (overall Δ*H* for the reaction = sum of Δ*H* values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

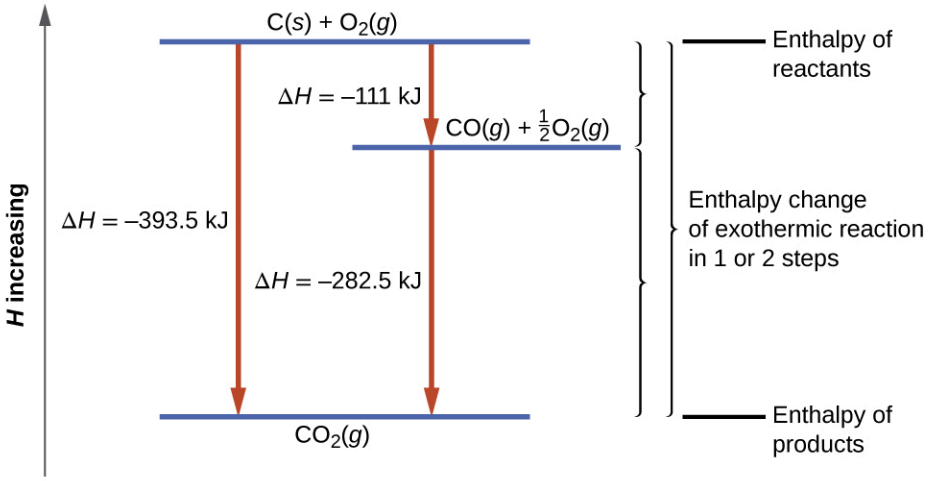


Figure 3.6.5. The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_{2(g)}$ is +33.2 kJ:

$$1/2\ N_2\ (g) + O_2\ (g) \rightarrow NO_2\ (g) \quad \Delta H = +33.2\ kJ$$

When 2 moles of NO_2 (twice as much) are formed, the ΔH will be twice as large:

$$N_2\ (g) + 2O_2\ (g) \rightarrow 2\ NO_2\ (g) \quad \Delta H = +66.4\ kJ$$

In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

ΔH for a reaction in one direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction. For example, given that:

$$H_2\ (g) + Cl_2\ (g) \rightarrow 2\ HCl\ (g) \quad \Delta H = -184.6\ kJ$$

Then, for the "reverse" reaction, the enthalpy change is also "reversed":

$$2\ HCl\ (g) \rightarrow H_2\ (g) + Cl_2\ (g) \quad \Delta H = +184.6 kJ$$

Example 3.6.4 – Stepwise Calculation of ΔH_f° Using Hess's Law

Determine the enthalpy of formation, ΔH_f°, of $FeCl_{3(s)}$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$Fe\ (s) + Cl_2\ (g) \rightarrow FeCl_2\ (s) \quad \Delta H = -341.8 kJ$$

$$FeCl_2\ (s) + 1/2\ Cl_2\ (g) \rightarrow FeCl_3\ (s) \quad \Delta H = -57.7\ kJ$$

Solution

We are trying to find the standard enthalpy of formation of $FeCl_3(s)$, which is equal to ΔH° for the reaction:

$$Fe\ (s) + 3/2\ Cl_2\ (g) \rightarrow FeCl_3\ (s) \quad \Delta H^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their enthalpies:

$$Fe\,(s) + Cl_2\,(g) \rightarrow FeCl_2\,(s) \quad \Delta H^\circ = -341.8\text{ kJ}$$

$$\begin{array}{ll} FeCl_{2(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow FeCl_{3(s)} & \Delta H^\circ = -57.7\text{ kJ} \\ \hline Fe_{(s)} + \frac{3}{2}Cl_{2(g)} \rightarrow FeCl_{3(s)} & \Delta H^\circ = -399.5\text{ kJ} \end{array}$$

The enthalpy of formation, ΔH_f°, of $FeCl_3(s)$ is – 399.5 kJ/mol.

Check Your Learning 3.6.4 – Stepwise Calculation of ΔH_f° Using Hess's Law

Calculate ΔH for the process:

$$N_2\,(g) + 2\,O_2\,(g) \rightarrow 2\,NO_2\,(g)$$

from the following information:

$$N_2\,(g) + 2\,O_2\,(g) \rightarrow 2\,NO_2\,(g) \quad \Delta H = 180.5\text{ kJ}$$

$$NO\,(g) + 1/2\,O_2\,(g) \rightarrow NO_2\,(g) \quad \Delta H = -57.06\text{ kJ}$$

Answer

66.4 kJ

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of ΔH) if they are difficult to determine experimentally.

Example 3.6.5 – A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$(i)\ ClF\,(g) + F_2\,(g) \rightarrow ClF_3\,(g) \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH° for reaction *(i)*:

(ii) $2\,OF_2\,(g) \rightarrow O_2\,(g) + 2\,F_2\,(g) \quad \Delta H^\circ_{(ii)} = -49.4$ kJ

(iii) $2\,ClF_2\,(g) + O_2\,(g) \rightarrow Cl_2O\,(g) + OF_2\,(g) \quad \Delta H^\circ_{(iii)} = +205.6$ kJ

(iv) $ClF_3\,(g) + O_2\,(g) \rightarrow 1/2\,Cl_2O\,(g) + 3/2\,OF_2\,(g) \quad \Delta H^\circ_{(iv)} = +266.7$ kJ

Solution

Our goal is to manipulate and combine reactions *(ii)*, *(iii)*, and *(iv)* such that they add up to reaction *(i)*. Going from left to right in *(i)*, we first see that $ClF(g)$ is needed as a reactant. This can be obtained by multiplying reaction *(iii)* by 1/2, which means that the ΔH° change is also multiplied by 1/2:

$$ClF\,(g) + 1/2\,O_2\,(g) \rightarrow 1/2\,Cl_2O\,(g) + 1/2\,OF_2\,(g)$$

$$\Delta H^\circ_{(iii)} = 12(+205.6\text{ kJ}) = +102.8\text{ kJ}$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction *(ii)*, which means that the ΔH° changes sign and is halved:

$$12\,O_2\,(g) + F_2\,(g) \rightarrow OF_2\,(g)$$

$$\Delta H^\circ_{(ii)} = +24.7\text{ kJ}$$

To get ClF_3 as a product, reverse *(iv)*, changing the sign of $\Delta H°$:

$$1/2\ Cl_2O\ (g) + 3/2\ OF_2\ (g) \rightarrow ClF_3\ (g) + O_2\ (g)$$

$$\Delta H^\circ_{(iv)} = -\ 266.7\ \text{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$ClF\ (g) + 1/2\ O_2\ (g) \rightarrow 1/2\ Cl_2O\ (g) + 1/2\ OF_2\ (g)$$

$$\Delta H^\circ_{(iii)} = 1/2(+\ 205.6\ \text{kJ}) = +\ 102.8\ \text{kJ}$$

$$1/2\ O_2\ (g) + F_2\ (g) \rightarrow OF_2\ (g)$$

$$\Delta H^\circ_{(ii)} = +\ 24.7\ \text{kJ}$$

$$\frac{\frac{1}{2}Cl_2O_{(g)} + \frac{3}{2}OF_{2(g)} \rightarrow ClF_{3(g)} + O_{2(g)}}{ClF_{(g)} + F_{2(g)} \rightarrow ClF_{3(g)}}$$

$$\frac{\Delta H^\circ_{(iv)} = \ -266.7\ kJ}{\Delta H^\circ = \ -139.2\ kJ}$$

Reactants 1/2 O_2 and 1/2 O_2 cancel out product O_2; product 1/2 Cl_2O cancels reactant 1/2 Cl_2O;, and reactant 3/2 OF_2 is cancelled by products 1/2 OF_2 and OF_2. This leaves only reactants $ClF_{(g)}$ and $F_{2(g)}$ and product $ClF_{3(g)}$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified $\Delta H°$ values will give the desired $\Delta H°$:

$$\Delta H^\circ = (+\ 102.8\ \text{kJ}) + (24.7\ \text{kJ}) + (-\ 266.7\ \text{kJ}) = -\ 139.2\ \text{kJ}$$

Check Your Learning 3.6.6 – A More Challenging Problem Using Hess's Law

Aluminum chloride can be formed from its elements:

$$(i)\ 2\ Al\ (s) + 3\ Cl_2\ (g) \rightarrow 2\ AlCl_3\ (s) \quad \Delta H^\circ = ?$$

Use the reactions here to determine the $\Delta H°$ for reaction *(i)*:

(ii) $HCl\ (g) \rightarrow HCl\ (aq) \quad \Delta H^\circ_{(ii)} = -\ 74.8$ kJ

(iii) $H_2\ (g) + Cl_2\ (g) \rightarrow 2\ HCl\ (g) \quad \Delta H^\circ_{(iii)} = -\ 185$ kJ

(iv) $AlCl_3\ (aq) \rightarrow AlCl_3\ (s) \quad \Delta H^\circ_{(iv)} = +\ 323$ kJ/mol

(v) $2\ Al\ (s) + 6\ HCl\ (aq) \rightarrow 2\ AlCl_3\ (aq) + 3\ H_2\ (g) \quad \Delta H^\circ_{(v)} = +\ 1049$ kJ

Answer

−1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with Σ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H_{\text{reaction}}^{\circ} = \Sigma n \times \Delta H_{f}^{\circ}\ (\text{products}) - \Sigma n \times \Delta H_{f}^{\circ}\ (\text{reactants})$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 3.6.7 – Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\ NO_2\ (g) + H_2O\ (l) \rightarrow 2\ HNO_3\ (aq) + NO\ (g) \quad \Delta H^{\circ} = ?$$

Solution:

Using the Equation

Use the special form of Hess's law given previously:

$$\Delta H_{\text{reaction}}^{\circ} = \Sigma n \times \Delta H_{f}^{\circ}\ (\text{products}) - \Sigma n \times \Delta H_{f}^{\circ}\ (\text{reactants})$$

$$\begin{aligned} &= \left[2\ mol\ HNO_{3(aq)} \times \frac{-207.4\ kJ}{mol\ HNO_{3(aq)}} + 1\ mol\ NO_{(g)} \times \frac{+90.2\ kJ}{mol\ NO_{(g)}}\right] \\ &\quad - \left[3\ mol\ NO_{2(g)} \times \frac{+33.2\ kJ}{mol\ NO_{2(g)}} + 1\ mol\ H_2O_{(l)} \times \frac{-285.8\ kJ}{mol\ H_2O_{(l)}}\right] \\ &= 2(-207.4\ kJ) + 1(+90.2\ kJ) - 3(+33.2\ kJ) - 1(-285.8\ kJ) \\ &= -138.4\ kJ \end{aligned}$$

Supporting Why the General Equation Is Valid

Alternatively, we can write this reaction as the sum of the decompositions of 3 $NO_2(g)$ and 1 $H_2O(l)$ into their constituent elements, and the formation of 2 $HNO_3(aq)$ and 1 $NO(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH_f° values for these compounds (from Appendix G), we have:

$$\begin{aligned} &3NO_2\ (g) \rightarrow \frac{3}{2}N_2\ (g) + 3O_2\ (g)\ \Delta H_1^{\circ} = -99.6\ kJ \\ &H_2O\ (l) \rightarrow H_2\ (g) + \frac{1}{2}O_2\ (g)\ \Delta H_2^{\circ} = +285.8\ kJ\ [-1 \times \Delta H_f^{\circ}(H_2O)] \\ &H_2\ (g) + N_2\ (g) + \frac{1}{2}O_2\ (g) \rightarrow 2HNO_3\ (aq)\ \Delta H_3^{\circ} = -414.8\ kJ\ [-1 \times \Delta H_f^{\circ}(HNO_3)] \\ &\frac{1}{2}N_2\ (g) + \frac{1}{2}O_2\ (g) \rightarrow NO\ (g)\ \Delta H_4^{\circ} = +90.2\ kJ\ [1 \times (NO)] \end{aligned}$$

Summing these reaction equations gives the reaction we are interested in:

$$3\ NO_2\ (g) + H_2O\ (l) \rightarrow 2\ HNO_3\ (aq) + NO\ (g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ} + \Delta H_4^{\circ} = (-\ 99.6\ \text{kJ}) + (+\ 285.8\ \text{kJ}) + (-\ 414.8\ \text{kJ}) + (+\ 90.2\ \text{kJ})$$

$$= -138.4 \text{kJ}$$

So the standard enthalpy change for this reaction is $\Delta H^{\circ} = -138.4$ kJ.

Note that this result was obtained by (1) multiplying the ΔH_f° of each product by its stoichiometric coefficient and summing those values, (2) multiplying the ΔH_f° of each reactant by its stoichiometric coefficient and summing those values, and then (3) subtracting the result found in (2) from the result found in (1). This is also the procedure in using the general equation, as shown.

For a more in-depth explanation of this approach, check out the following video.

Check Your Learning 3.6.7 – Using Hess's Law

Calculate the heat of combustion of 1 mole of ethanol, C_2H_5OH (*l*), when H_2O (*l*) and CO_2 (*g*) are formed. Use the following enthalpies of formation: C_2H_5OH (*l*), −278 kJ/mol; H_2O (*l*), −286 kJ/mol; and CO_2 (*g*), −394 kJ/mol.

Answer

−1368 kJ/mol

Questions

★ Questions

1. How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?

$$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (l) \quad \Delta H^\circ_{298} = -58\ kJ$$

If both solutions are at the same temperature and the heat capacity of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?

2. Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl_2F_2 (enthalpy of vaporization is 17.4 kJ/mol)? The vaporization reactions for SO_2 and CCl_2F_2 are $SO_2\ (l)$? $SO_2\ (g)$ and $CCl_2F\ (l)$? $CCl_2F_2\ (g)$, respectively.

3. Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

4. Does the standard enthalpy of formation of $H_2O\ (g)$ differ from ΔH° for the reaction $2\ H_2\ (g) + O_2\ (g)$? $2\ H_2O\ (g)$?

5. Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red $HgO(s)$ to $Hg(l)$ and $O_2(g)$ under standard conditions?

6. How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $Mn_3O_4(s)$ at standard state conditions?

★★ Questions

7. The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

$$4\ NH_3\ (g) + 5\ O_2\ (g) \rightarrow 4\ NO\ (g) + 6\ H_2O\ (l) \quad \Delta H = -907\ kJ$$

$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$ $\Delta H = -113$ kJ

$3\ NO_2 + H_2O\ (l) \rightarrow 2\ HNO_3\ (aq) + NO\ (g)$ $\Delta H = -139$ kJ

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

8. Both graphite and diamond burn.

$C\ (s,\ diamond) + O_2\ (g) \rightarrow CO_2\ (g)$

For the conversion of graphite to diamond:

$C\ (s,\ diamond) \rightarrow CO_2\ (g)$ $\Delta H_{298}^{\circ} = 1.90$ kJ

Which produces more heat, the combustion of graphite or the combustion of diamond?

9. From the molar heats of formation in Appendix G, determine how much heat is required to evaporate one mole of water:

$H_2O\ (l) \rightarrow H_2O\ (g)$

10. Calculate $\Delta H_{298}°$ for the process

$Sb\ (s) + 5/2\ Cl_2\ (g) \rightarrow SbCl_5\ (g)$

from the following information:

$$Sb\ (s) + \frac{3}{2}Cl_2\ (g)\ \rightarrow SbCl_5\ (g) \Delta H_{298}^{\circ} = -314\ kJ$$

$$SbCl_3\ (s) + Cl_2\ (g)\ \rightarrow SbCl_5\ (g)\ \Delta H_{298}^{\circ} = -80\ kJ$$

11. Calculate $\Delta H_{298}°$ for the process

$Zn\ (s) + S\ (s) + 2O_2\ (g) \rightarrow ZnSO_4\ (s)$

from the following information:

$Zn\ (s) + S\ (s) \rightarrow ZnS\ (s)$ $\Delta H_{298}^{\circ} = -206.0$ kJ

$ZnS\ (s) + 2\ O_2\ (g) \rightarrow ZnSO_4\ (s)$ $\Delta H_{298}^{\circ} = -776.8$ kJ

12. Calculate the standard molar enthalpy of formation of NO(*g*) from the following data:

$N_2\ (g) + 2\ O_2 \rightarrow 2\ NO_2\ (g)$ $\Delta H_{298}^{\circ} = 66.4$ kJ

$2\ NO\ (g) + O_2 \rightarrow 2\ NO_2\ (g)$ $\Delta H_{298}^{\circ} = -114.1$ kJ

13. Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

a. $N_2\ (g) + O_2\ (g) \rightarrow 2\ NO\ (g)$

b. $Si\ (s) + 2\ Cl_2\ (g) \rightarrow SiCl_4\ (g)$

c. $Fe_2O_3\ (s) + 3\ H_2\ (g) \rightarrow 2\ Fe\ (s) + 3\ H_2O\ (l)$

d. $2\ LiOH\ (s) + Co_2\ (g) \rightarrow Li_2CO_3\ (s) + H_2O\ (g)$

14. The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.

a. $2\ Ag_2O\ (s) \rightarrow 4\ Ag\ (s) + O_2\ (g)$

b. $SnO\ (s) + CO\ (g) \rightarrow Sn\ (s) + CO_2\ (g)$

c. $Cr_2O_3\ (s) + 3\ H_2\ (g) \rightarrow 2\ Cr\ (s) + 3\ H_2O\ (l)$

d. $2\ Al\ (s) + Fe_2O_3\ (s) \rightarrow Al_2O_3\ (s) + 2\ Fe\ (s)$

15. Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is −104 kJ/mol.

16. Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?

★★★ Questions

17. Ethanol, C_2H_5OH, is used as a fuel for motor vehicles, particularly in Brazil.

a. Write the balanced equation for the combustion of ethanol to $CO_2\ (g)$ and $H_2O\ (g)$, and, using the data in Appendix G, calculate the enthalpy of combustion of 1 mole of ethanol.

b. The density of ethanol is 0.7893 g/mL. Calculate the enthalpy of combustion of exactly 1 L of ethanol.

c. Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n−octane, C_8H_{18} ($\Delta H_f^\circ = -\ 208.4$ kJ/mol; density = 0.7025 g/mL).

18. Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B_2H_6, produces $B_2O_3(s)$ and $H_2O(g)$], methane [CH_4, produces $CO_2(g)$ and $H_2O(g)$], and hydrazine [N_2H_4, produces $N_2(g)$ and $H_2O(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The ΔH_f° of $B_2H_6(g)$, $CH_4(g)$, and $N_2H_4(l)$ may be found in Appendix G.

19. The oxidation of the sugar glucose, $C_6H_{12}O_6$, is described by the following equation:

$$C_6H_{12}O_6\ (s) + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (l) \quad \Delta H = -\ 2816\ kJ$$

The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.

a. How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?

b. How many Calories can be produced by the metabolism of 1.0 g of glucose?

20. During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).

a. Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.

b. How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8: density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $CO_2(g)$ and $H_2O(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.

c. What mass of carbon dioxide is produced by combustion of the methane used to heat the house?

d. What mass of water is produced by combustion of the methane used to heat the house?

e. What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.

f. How many kilowatt-hours (1 kWh = 3.6×10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.

g. Although electricity is 100% efficient in producing heat inside a house, the production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

Answers

1. ΔH_{298}° = – 1450 J; We assume that the heat is fully transferred and not lost to the solvent; temperature increase by 1.154 degrees

2. 367.12 g
3. 7.43 g
4. No.
5. 90.8 kJ
6. 459.6 kJ
7. −495 kJ/mol
8. Combustion of diamond produces more heat
9. 44.01 kJ/mol
10. −394 kJ
11. – 207 kJ
12. 90.3 mol^{-1} of NO
13. (a) 90.4 kJ/mol, (b) 105 kJ/mol, (c) -538.37 kJ/mol, (d) 94.49 kJ/mol
14. (a) 62.2 kJ/mol, (b) 3.2 kJ/mol, (c) 271 kJ/mol, (d) -847.6 kJ/mol
15. – 2044 kJ
16. Propane
17. (a) $C_2H_5OH + 3O_2$ *(g)* → $2CO_2$ *(g)* + $3H_2O$ *(g)*, -1234.8 kJ/mol, (b) -21187.56 kJ, (c) 44% Farther
18. On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.
19. (a) 15.63 kJ/g, (b) 3.74 cal/g

20. (a) 13260 cubic feet, (b) 141.2 gallons, (c) 701.52 kg, (d) 574.32 kg, (e) 3635637.26 L, (f) 3500 kWh, (g) 1756.34 kg

CHAPTER 4

4.1 – INTRODUCTION TO CHEMICAL EQUILIBRIUM

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions – this is the notion of chemical equilibrium which we will discuss here in this chapter.

Dynamic Equilibrium

In a chemical **equilibrium**, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is *at equilibrium*. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the following reaction:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

The color becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Figure 4.1.1).

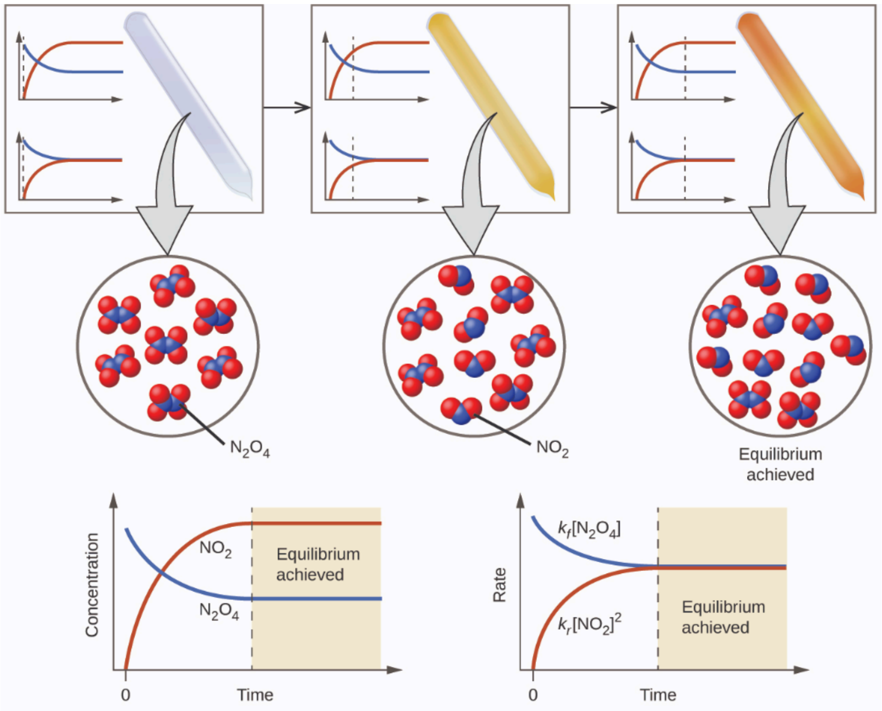


Figure 4.1.1. A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2. (Chem Libre, From: https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/15%3A_Principles_of_Chemical_Equilibrium/15.1%3A_Dynamic_Equilibrium, Creative Commons)

The formation of NO_2 from N_2O_4 is a **reversible reaction**, which is identified by the equilibrium arrows ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in the forward direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. Hence we get to a key idea: Chemical equilibrium is a *dynamic process.* For example, if two jugglers are each tossing clubs at the other at the same rate at which each receives clubs from the other, the numbers of clubs each will have at any point in time will remain roughly constant, yet there is always a flux back and forth between them (Figure 4.1.2).

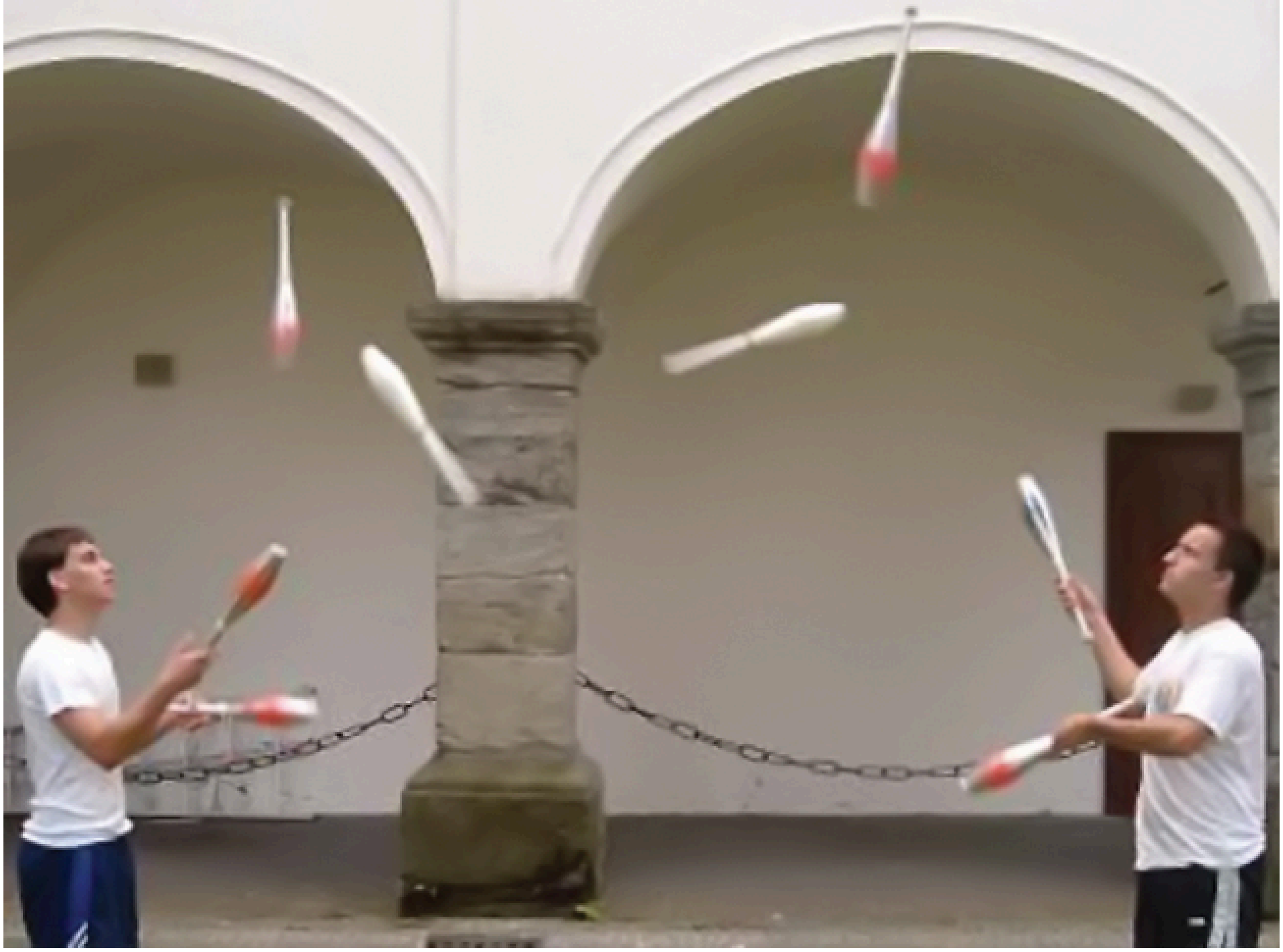


Figure 4.1.2. These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 4.1.1.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 4.1.1 shows the reaction:

$$\underset{\text{colorless}}{N_2O_4\,(g)} \quad \underset{\text{kr}}{\overset{\text{kf}}{\rightleftharpoons}} \quad \underset{\text{red-brown}}{2\,NO_2\,(g)}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 4.1.1, the rate of the forward reaction with rate constant k_f

$$\underset{\text{colorless}}{N_2O_4\,(g)} \quad \overset{\text{kf}}{\rightleftharpoons} \quad \underset{\text{red-brown}}{2\,NO_2\,(g)}$$

is equal to the rate of the backward reaction with rate constant k_r

$$\underset{\text{colorless}}{N_2O_4\,(g)} \quad \overset{\text{kr}}{\rightleftharpoons} \quad \underset{\text{red-brown}}{2\,NO_2\,(g)}$$

We'll talk more about rate constants in Chapter 7: Chemical Kinetics; for now, all you need to know is that each rate constant is unique to a particular reaction that helps mathematically define its rate of reaction.

Equilibrium & Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled "Impregnating Water with Fixed Air." The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: "oil of vitriol" literally means "liquid nastiness") onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$H_2SO_4\,(l) + CaCO_3\,(s) \rightleftharpoons CO_2\,(g) + H_2O\,(l) + CaSO_4\,(aq)$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can ionize into hydronium ions (H_3O^+) and hydrogen carbonate ions (HCO_3^-).

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$$

$$H_2O\,(l) + H_2CO_3\,(aq) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq)$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure 4.1.3). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."

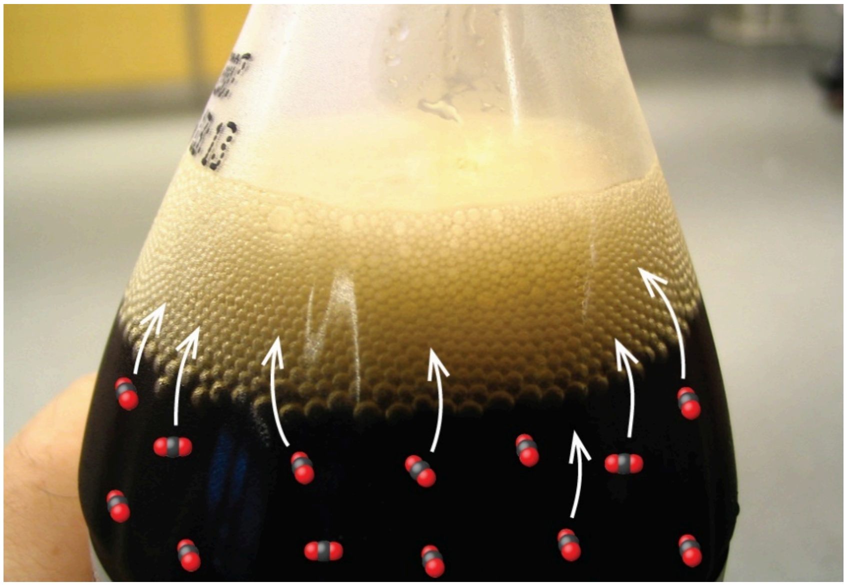


Figure 4.1.3. When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

The equilibrium between N_2O_4 and NO_2 consists of a chemical equilibrium – one which involves two or more substances through a chemical reaction. However, an equilibrium consisting of a single substance, known as a physical equilibrium, can be established for a physical change—like a liquid to gas transition—as well as for a chemical reaction. Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2\,(l) \rightleftharpoons Br_2\,(g)$$

Figure 4.1.4 shows a sample of liquid bromine at equilibrium with bromine vapour in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapour, some liquid evaporates, the amount of liquid decreases, and the amount of vapour increases. If we cap the bottle so no vapour escapes, the amount of liquid and vapour will eventually stop changing and an equilibrium between the liquid and the vapour will be established. If the bottle were not capped, the bromine vapour would escape and no equilibrium would be reached.

Figure 4.1.4. An equilibrium is pictured between liquid bromine, $Br_2\,(l)$, the dark liquid, and bromine vapour, $Br_2\,(g)$, the reddish-brown gas. Because the container is sealed, bromine vapour cannot escape and equilibrium is maintained. (credit: http://images-of-elements.com/bromine.php)

Deriving a Constant for Chemical Equilibria

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). Let's continue using the example of the decomposition of N_2O_4 to NO_2 to demonstrate this. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_2]$$

and

$$\text{reverse rate} = k_r[NO_2]^2$$

Note: You'll learn all about rate expressions and expressing reaction rates in the chapter on kinetics, but for now, we'll briefly explain these expressions. As previously mentioned, the rate constant, *k,* is unique to a particular reaction and helps mathematically define the rate of reaction. The concentration of reactant also determines the rate; the reason why NO_2 is squared in the expression for the reverse rate is because 2 molecules of NO_2 are required to form N_2O_4, as indicated in the chemical equilibrium equation. Note that the value of the exponent is based on the number of molecules of reactant *only for elementary reactions*; again don't worry about understanding what this means right now, since it will be properly covered later on.

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_2] = k_r[NO_2]^2$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_2]}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (*K*), which is defined as follows:

$$K = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_2]}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions. In other words, this equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Measure of Reaction Extent

Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants, when $k_f \gg k_r$, K has a large value, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K has a very small value, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have a value of K close to 1 and significant concentrations of both reactants and products at equilibrium.

Consider an equilibrium between substances A and B: A ⇌ B. The table below shows the percentage of moles of A and B that would be present at equilibrium for different values of *K*. At *K* values of 10^{-5} and 10^{5}, the mole percent of A and B are very nearly 100%, respectively. Hence, keep the following as a rule of thumb for this course: for $K < 10^{-5}$, the reaction is said to be "reactant-favoured" and consists of mostly reactant(s) with minimal product(s), whereas for $K > 10^{5}$, the reaction practically proceeds to completion with little to no reactant(s) remaining.

Table 4.1.1 Relationship between the magnitude of *K* and mole percent of reactant and product.

$A \rightleftharpoons B$		
K	**mol% A**	**mol% B**
100 000	0.001	99.999
10 000	0.01	99.99
1 000	0.10	99.90
100	0.99	99.01
10	9.09	90.91
1	50.00	50.00
0.1	90.91	9.09
0.01	99.01	0.99
0.001	99.90	0.10
0.0001	99.99	0.01
0.00001	99.999	0.001

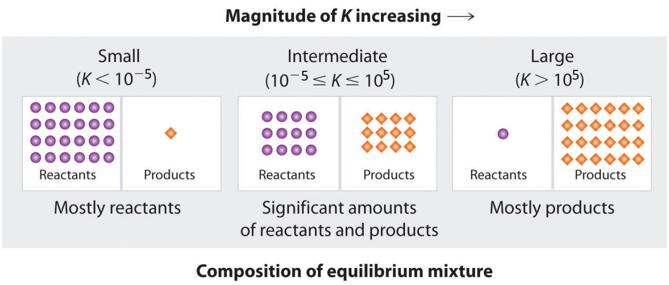


Figure 4.1.5. The larger the value of K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

Let's look at a few examples of reactions to understand this: the reaction between H_2 and Cl_2 to produce HCl has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the value of K is extremely large and the reaction proceeds essentially to completion. On the other hand, the reaction at 500 K between F_2 and two F atoms in the gas phase has an equilibrium constant of 7.4×10^{-13}. This K value is extremely small, indicating that the reactants don't tend to form products readily – the formation and presence of reactants is heavily favoured.

When Should You Use a One-Sided Arrow?

You may have noticed so far that in some reactions, equilibrium (two-direction) arrows are used, while in others only forward arrows are employed. The deciding factor on which arrow format is appropriate is the equilibrium constant (K) value. From Table 4.1.1, we see that if the value of K is 10^5, when equilibrium is reached, the system will contain about 0.001% of original reactant. This remainder is essentially negligible, and so we state that this product-favoured reaction therefore 'goes to completion', indicating ~100% expected formation of products. Thus, when encountering reactions with values of $K \geq 10^5$, we tend to use one-sided, forward direction arrows only. In all other scenarios, the forward *and* reverse directions must be considered, and therefore it is more appropriate to use the two-directional equilibrium arrows.

Example 4.1.1 – Composition of Reactants/Products at Equilibrium

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

(a) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \quad K_{(700\,K)} = 54$

(b) $2\,CO_2\,(g) \rightleftharpoons 2\,CO\,(g) + O_2\,(g) \quad K_{(1200\,K)} = 3.1 \times 10^{-18}$

(c) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g) \quad K_{(613\,K)} = 97$

(d) $2\,O_3\,(g) \rightleftharpoons 3\,O_2\,(g) \quad K_{(298\,K)} = 5.9 \times 10^{55}$

Solution

(a) K is closer to 1 ($10^{-5} < K < 10^5$), so the equilibrium mixture will contain appreciable amounts of both products and reactants..

(b) $K << 1$ ($K < 10^{-5}$), so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.

(c) K is closer to 1 ($10^{-5} < K < 10^5$), so the equilibrium mixture will contain appreciable amounts of both products and reactants.

(d) $K >> 1$ ($K > 10^5$), so at equilibrium it will consist of essentially only products.

Check Your Learning 4.1.1 – Composition of Reactants/Products at Equilibrium

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

Values of the equilibrium constant at various temperatures were reported as

$K_{25°C} = 3.3 \times 10^8$

$K_{177°C} = 2.6 \times 10^3$

$K_{327°C} = 4.1$

(a) At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?

(b) Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer

(a) 327°C, where K is smallest; (b) 25°C, where K is largest

Questions

★ Questions

1. What does it mean to describe a reaction as “reversible”?

2. When writing an equation, how is a reversible reaction distinguished from a non reversible reaction?
3. If a reaction is reversible, when can it be said to have reached equilibrium?
4. Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?
5. If the concentrations of products and reactants are equal, is the system at equilibrium?

Answers

1. The reaction can proceed in both the forward and reverse directions.

2. Between the two types of reactions, they are distinguished by the arrows used in the equation. In a reversible reaction “⇌” is appropriate, whereas in a non-reversible reaction “→” is used.

3. When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the forward and reverse reactions continue to occur, but at equivalent rates.

4. Not necessarily; equivalent values of k_f and k_r (for the forward and reverse directions) yield an equilibrium constant value of 1 (since $K = k_f/k_r$). However, this does not mean that the system is *at* equilibrium. Only *constant concentrations* of the reactant and products mean the reactions are at equilibrium. This does not mean that their concentrations have to be equal, but in some cases they can be.

5. The concept of equilibrium does not imply equal concentrations, though it is possible.

4.2 – THE EQUILIBRIUM CONSTANT & REACTION QUOTIENT

In the last section, we began deriving a constant for chemical equilibria based on the kinetics of the forward and reverse reactions. We established that the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions, or more specifically, that the equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction. Here, we'll develop an equilibrium constant expression for K applicable to any equilibrium reaction and look at how we can also predict the direction of net change given a set amount of reactants & products.

The Equilibrium Constant (*K*)

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$m\,\mathrm{A} + n\,\mathrm{B} \rightleftharpoons x\,\mathrm{C} + y\,\mathrm{D}$$

where A and B are reactants, C and D are products, and m, n, x, and y are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium quantities of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship was eventually summarized as follows:

$$K = \frac{(a_c)^x (a_D)^y}{(a_A)^m (a_B)^n}$$

Equation 4.2.1 Equilibrium Constant

where ***K*** is the **equilibrium constant** for the reaction, equivalent to the value defined in Section 4.1, and a_X represents the **activity** of each species participating in the equilibrium. The chemical equilibrium equation represented with reactants A & B and products C & D is called the equilibrium equation, and the right side of the mathematical equation above is called the *equilibrium constant expression*. The relationship shown in the expression for K is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

An important fact to note is that equilibrium constants are dimensionless (they have no units) but the temperature at which this value is valid must always be listed (since K is temperature dependent). This is due to computing K values using the *activities* of the reactants and products in the equilibrium system. The activity of a substance is a measure of its *effective concentration* under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (unitless) quantities and are in essence “adjusted” quantities of reactants and products.
- For relatively dilute solutions, a solute’s activity and its molar concentration are roughly equal (*i.e.* for a solute X, $a_X \approx [X]$ **in *mol/L or M***). Note that this approximation does not hold for highly concentrated solutes.
- For gases, a substance’s activity is equal to its partial pressure (*i.e.* $a_X = P_X$ **in *bar***)
- Activities for pure condensed phases (solids and liquids) are equal to 1 (*i.e.* $a_X = 1$), hence their activities do not appear in the expression for *K*

Further discussion about activities can be found here.

We categorize equilibria into two types: homogeneous and heterogeneous. A **homogeneous equilibrium** is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. A **heterogeneous equilibrium** is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (as we’ve mentioned above, the activities of pure solids, pure liquids, and solvents are 1).

NOTE:

The equilibrium constant, *K*, is temperature-dependent. When reporting its value for an equilibrium reaction (like in scientific literature), the temperature at which *K* was determined must always be included (*e.g.* $K = 2.0 \times 10^{-25}$ @ 100°C)

Example 4.2.1 – Writing Equilibrium Constant Expressions

Write the equilibrium constant expression for each reaction.

(a) $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

(b) $CO\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightleftharpoons CO_2\,(g)$

(c) $2\,CO_2\,(g) \rightleftharpoons 2\,CO\,(g) + O_2\,(g)$

(d) $H_2O\,(l) + H_2CO_3\,(aq) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq)$

(e) $Fe_3O_4\,(s) + 4\,H_2\,(g) \rightleftharpoons 3\,Fe\,(s) + 4\,H_2O\,(g)$

Solution

(a) The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. All species are gases, and so their activities are equal to their partial pressures. The equilibrium constant expression is as follows:

$$\frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

(b) The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of ½. Since all species are gases, the equilibrium constant expression is as follows:

$$\frac{(CO_2)}{(CO)(O_2)^2}$$

(c) This reaction is the reverse of the reaction in part (b), with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part (b), with all exponents multiplied by 2:

$$\frac{(CO_2)^2\left(O_2\right)}{(CO_2)^2}$$

(d) This reaction contains a pure liquid (H_2O), its activity is equal to 1 and thus does not appear in the equilibrium constant expression. The other three species are solutes, and their activities can be approximated using their molar concentrations:

$$\frac{1}{Cl_2}$$

(e) This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$\frac{(H_2O)^4}{(H_2)^4}$$

Check Your Learning 4.2.1 – Writing Equilibrium Constant Expressions

Write the equilibrium constant expression for each reaction.

(a) $N_2O\ (g) \rightleftharpoons N_2\ (g) + 12\ O_2\ (g)$

(b) $2\ C_8H_{18}\ (g) + 25\ O_2\ (g) \rightleftharpoons 16\ CO_2\ (g) + 18\ H_2O\ (g)$

(c) $H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g)$

(d) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

(e) $C_6H_{12}O_6\ (s) + 6\ O_2\ (g) \rightleftharpoons 6\ CO_2\ (g) + 6\ H_2O\ (g)$

Answer:

1. $K = \frac{(N_2)(O_2)^{\frac{1}{2}}}{(N_2O)}$
2. $K = \frac{(CO_2)^{16}(H_2O)^{18}}{(C_8H_{18})^2(O_2)^{25}}$
3. $K = \frac{(HI)^2}{(H_2)(I_2)}$
4. $K = (CO_2)$
5. $K = \frac{(CO_2)^6(H_2O)^6}{(O_2)^6}$

Manipulating Equilibrium Constants

Reversing the Equilibrium Equation

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the generic equilibrium reaction equation in reverse, we obtain the following:

$$c\,\mathrm{C} + d\,\mathrm{D} \rightleftharpoons a\,\mathrm{A} + b\,\mathrm{B}$$

If all species are solutes, then the corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Equation 4.2.2 Reverse Equilibrium Constant

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. Below is an example:

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g) \qquad K = \frac{(NO_2)^2}{(N_2O_4)}$$

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g) \qquad K' = \frac{(N_2O_4)}{(NO_2)^2}$$

Consider another example, the formation of water: $2\,H_2\,(g) + O_2\,(g) \rightleftharpoons 2\,H_2O\,(g)$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, the dynamic equilibrium always very heavily favours the formation of water molecules. This is related to the fact that the decomposition of water into O_2 and H_2 requires a substantial amount of activation energy; a concept we will return to in our study of Chemical Kinetics (Chapter 7).

Altering Species Coefficients

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, going back to our inverse equilibrium equation with an equilibrium constant *K*, we could write the equation for that reaction

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

as

$$NO_2\,(g) \rightleftharpoons ½\,N_2O_4\,(g)$$

with the equilibrium constant *K*” ’as follows:

$$K'' = \frac{(N_2O_4)^{\frac{1}{2}}}{(NO_2)}$$

The values for *K′* and *K″* are related as follows:

$$K'' = (K')^{\frac{1}{2}} = \sqrt{K'}$$

Equation 4.2.3 K’ and K” relation

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by *n*, then the new equilibrium constant is the original equilibrium constant raised to the *n*th power.

Combining Chemical Equilibrium Equations

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let’s consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \quad K_1 = 2.0 \times 10^{-25}$$

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \quad K_2 = 6.4 \times 10^{9}$$

Addition of reactions (1) and (2) gives the overall reaction of N_2 with O_2:

$$N_2\,(g) + 2\,O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \quad K_3 = ?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{(NO)^2}{(N_2)(O_2)} \qquad K_2 = \frac{(NO_2)^2}{(NO)^2\left(O_2\right)} \qquad K_3 = \frac{(NO_2)^2}{(N_2)(O_2)^2}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{(NO)^2}{(N_2)(O_2)} \times \frac{(NO_2)^2}{(NO)^2\left(O_2\right)} = \frac{(NO_2)^2}{(N_2)(O_2)^2} = K_3$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = \left(2.0 \times 10^{-25}\right)\left(6.4 \times 10^{9}\right) = 1.3 \times 10^{-15}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law (seen in the previous chapter on thermochemistry), ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

Summary

It is important to remember that an equilibrium constant is always tied to a specific chemical equation, and if you manipulate the equation in any way, the value of *K* will change. Fortunately, the rules are very simple:

- Writing the equation in reverse will invert the equilibrium expression (i.e. $K' = 1/K$)
- Multiplying the coefficients by a common factor *n* will raise *K* to the corresponding power of *n* (i.e. $K' = K^n$ where *n* is a common factor)
- The equilibrium constant for a reaction that is the sum of several chemical equilibrium equations is the product of the equilibrium constants for each of the steps (i.e. $K' = K_1K_2K_3$...)

Example 4.2.2 – Manipulating Equilibrium Constants – 1

At 745 K, *K* is 0.118 for the following reaction:

$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

What is the equilibrium constant for each related reaction at 745 K?

(a) $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$

(b) $12\,N_2(g) + 32\,H_2(g) \rightleftharpoons NH_3(g)$

Solution

The equilibrium constant expression for the given reaction of $N_2(g)$ with $H_2(g)$ to produce $NH_3(g)$ at 745 K is as follows:

$$K = \frac{(NH_3)^2}{(N_2)(H_2)^3} = 0.118$$

(a) This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{(N_2)(H_2)^3}{(NH_3)^2} = \frac{1}{0.118} = 8.47$$

(b) In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{(NH_3)}{(N_2)^{\frac{1}{2}}(H_2)^{\frac{3}{2}}} = K^{\frac{1}{2}} = \sqrt{K} = \sqrt{0.118} = 0.344$$

Check Your Learning 4.2.2 – Manipulating Equilibrium Constants – 1

At 527°C, the equilibrium constant for the reaction below is 7.9×10^4.

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_3\,(g) \rightleftharpoons SO_2\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

Answer:

3.6×10^{-3}

Example 4.2.3 – Manipulating Equilibrium Constants – 2

The following reactions occur at 1200°C:

$$CO\,(g) + 3\,H_2\,(g) \rightleftharpoons CH_4\,(g) + H_2O\,(g) \quad K_1 = 9.17 \times 10^{-2}$$

$$CH_4\,(g) + 2\,H_2S\,(g) \rightleftharpoons CS_2\,(g) + 4\,H_2\,(g) \quad K_2 = 3.3 \times 10^4$$

Calculate the equilibrium constant for the following reaction at the same temperature.

$$CO\,(g) + 2\,H_2S\,(g) \rightleftharpoons CS_2\,(g) + H_2O\,(g) + H_2\,(g) \quad K_3 = ?$$

Solution

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO\,(g) + \cancel{3\,H_2}\,(g) \rightleftharpoons \cancel{CH_4}(g) + H_2O\,(g)$$

$$\cancel{CH_4}(g) + 2\,H_2S\,(g) \rightleftharpoons CS_2\,(g) + \cancel{4}\,H_2\,(g)$$

$$CO\,(g) + 2\,H_2S\,(g) \rightleftharpoons CS_2\,(g) + H_2O\,(g) + H_2\,(g)$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3$$

Check Your Learning 4.2.3 – Manipulating Equilibrium Constants – 2

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. 1/8 S_8 *(s)* + O_2 *(g)* $\rightleftharpoons$ SO_2 *(g)* $K_1 = 4.4 \text{ x } 10^{53}$
2. SO_2 *(g)* + 12 O_2 *(g)* $\rightleftharpoons$ SO_3 *(g)* $K_2 = 2.6 \text{ x } 10^{12}$
3. 18 S_8 *(s)* + 32 O_2 *(g)* $\rightleftharpoons$ SO_3 *(g)* $K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

Equilibria Involving Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are molarities, expressed in moles/litre. For gases, however, the activities of each reaction component are expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. Occasionally, the symbol K_P is used to highlight equilibrium constants calculated from partial pressures. For the general reaction aA + bB $\rightleftharpoons$ cC + dD, in which all the components are gases, the equilibrium constant expression *must* be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_P = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Equation 4.2.4 Gas Equilibrium Constant

Thus K_P for the decomposition of N_2O_4 is as follows:

$$K_P = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

K_P is a unitless quantity because the quantity that is actually used to calculate it is an "effective pressure," the ratio of the measured pressure to a standard state of 1 bar, which produces a unitless quantity. But what if we need to describe a gas-phase equilibrium in concentration units?

Because partial pressures are usually expressed in bars, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, if we were to recalculate K using molar concentrations (like solutes) instead of partial pressures, we would obtain a new equilibrium constant, known as K_C. The resulting numerical value of K_C would very likely differ from K_P. They are, however, related by the ideal gas constant (R) and the absolute temperature (T) – this is because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where M is the molar concentration of gas, nV.

$$PV = nRT$$

$$P = (n/V)RT$$

$$P = MRT$$

Equation 4.2.5 Gas Pressure Proportionality

Thus, at constant temperature, the pressure of a gas is directly proportional to its concentration.

Hence, the equation relating K_C and K_P is derived as follows. For the gas-phase reaction mA + nB ⇌ xC + yD:

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n}$$

$$= \frac{([C] \times RT)^x ([D] \times RT)^y}{([A] \times RT)^m ([B] \times RT)^n}$$

$$= \frac{[C]^x [D]^y}{[A]^m [B]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}}$$

$$= K_C (RT)^{(x+y)-(m+n)}$$

$$= K_C (RT)^{n}$$

Therefore, relationship between K_C and K_P is

$$K_P = K_C (RT)^{n}$$

Equation 4.2.6 K_C and K_P Relation

where K_C is the equilibrium constant expressed in units of concentration (mol/L), K_P is the equilibrium constant expressed in units of pressure (bars), the temperature is expressed as the absolute temperature in Kelvin, R is the ideal gas constant in the appropriate units (R = 0.083145 bar•L/(mol•K)) and Δn is the difference between the sum of the coefficients of the gaseous products and the sum of the coefficients of the gaseous reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction mA + nB ⇌ xC + yD, we have

$$\Delta n = (x + y) – (m + n)$$

Equation 4.2.7 Change in Moles of a Reaction

If all the components of an equilibrium reaction are gaseous, the equilibrium constant must be K_P because its expression is derived solely from partial pressures and hence is in pressure units. Only in cases where gas concentrations are available will the calculation of K_C be appropriate. When solving equilibrium problems, be aware of the data provided and thus whether you'll need to use K_C or K_P in your solution.

NOTE:

According to the equation

$$\Delta n = (x + y) - (m + n)$$

$K_P = K_C$ only if the moles of gaseous products and gaseous reactants are the same (i.e. $\Delta n = 0$):

$$K_P = K_C(RT)^{n}$$

$$K_P = K_C(RT)^0$$

$$K_P = K_C$$

According to the equation above, $K_P = K_C$ *only* if the moles of gaseous products and gaseous reactants are the same (*i.e.*, $\Delta n = 0$).

For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_P = K_C(RT)^1 = K_CRT$$

Example 4.2.4 – Calculation of K_P

Write the equations for the conversion of K_C to K_P for each of the following reactions:

(a) $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

(b) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

(c) $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$K_P = K_C(RT)^{\Delta n} = K_C(RT)^1 = K_C(RT)$

(b) $\Delta n = (2) - (2) = 0$

$K_P = K_C(RT)^{\Delta n} = K_C(RT)^0 = K_C$

(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_C(RT)^{\Delta n} = K_C(RT)^{-2} = \frac{K_C}{(RT)^2}$$

Check Your Learning 4.2.4 – Calculation of K_P

Write the equations for the conversion of K_C to K_P for each of the following reactions, which occur in the gas phase:

(a) $2\ SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\ SO_3\,(g)$

(b) $N_2O_4\,(g) \rightleftharpoons 2\ NO_2\,(g)$

(c) $C_3H_8\,(g) + 5\ O_2\,(g) \rightleftharpoons 3\ CO_2\,(g) + 4\ H_2O\,(g)$

What would be the value of K_P at this temperature?

Answer

(a) $K_P = K_C(RT)^{-1}$; (b) $K_P = K_C(RT)$; (c) $K_P = K_C(RT)$

Example 4.2.5 – Calculation of K_P

Write the equation for the conversion of K_C to K_P for the following reaction, which occurs in the gas phase:

$$CS_2\,(g) + 4\ H_2\,(g) \rightleftharpoons CH_4\,(g) + 2\ H_2S\,(g)$$

K_C is equal to 0.28 for the following reaction at 900°C, what is K_P at this temperature?

Solution:

$K_P = K_C(RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

Check Your Learning 4.2.5 – Calculation of K_P

Write the equation for the conversion of K_C to K_P for the following reaction, which occurs in the gas phase:

$$CH_3OH\,(g) \rightleftharpoons CO\,(g) + 2\ H_2\,(g)$$

At 227°C, the following reaction has $K_C = 0.0952$, What would be the value of K_P at this temperature?

Answer:

160 or 1.6×10^{2}

Example 4.2.6 – Calculation of K_P – The Haber Process

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_2\,(g) + 3\ H_2\,(g) \rightleftharpoons 2\ NH_3\,(g)$$

What is K_P for this reaction at the same temperature?

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745$ K. Thus, we have the following:

$$K_P = K_C(RT)^{-2} = \frac{K}{(RT)^2} = \frac{0.118}{\left\{\left[0.08206\frac{L \cdot atm}{mol \cdot K}\right]\left[745\ K\right]\right\}} = 3.16 \times 10^{-5}$$

Because K_P is a unitless quantity, the answer is $K_P = 3.16 \times 10^{-5}$.

Check Your Learning 4.2.6 – Calculation of K_P – The Haber Process

Calculate K_P for the reaction

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer:

$K_P = 1.2 \times 10^3$

Heterogeneous Equilibria

The Reaction Quotient, *Q*

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time.

To determine whether a system has reached equilibrium, chemists use a quantity called the **reaction quotient (*Q*)**. The expression for the reaction quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$m\,A + n\,B \rightleftharpoons x\,C + y\,D$$

the reaction quotient is defined as follows:

$$Q = \frac{(a_c)^x (a_D)^y}{(a_A)^m (a_B)^n}$$

Equation 4.2.7 Reaction Quotient

Similarly to the equilibrium constant, the reaction quotient is dimensionless (no units) – this stems from using the species activities as its effective concentrations. As before, the activity of each species participating in the equilibrium can be represented as follows:

- For a solute X, $a_X \approx [X]$ in mol/L (note that again, this does not apply to highly concentrated solutions)
- For gases, $a_X = P_X$ in bar
- For pure solids and liquids, $a_X = 1$

CHM1311 Pointers

To reiterate, the expressions for the reaction quotient, *Q*, and the equilibrium constant, *K*, are constructed in the exact same way, but are used in different circumstances:

Concentrations/partial pressures **initially** → ***Q***
Concentration/partial pressures **at equilibrium** → ***K***

Example 4.2.6 – Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

(a) $3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)$

(b) $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$

(c) $HCl\,(g) + NaOH\,(aq) \rightleftharpoons NaCl\,(aq) + H_2O\,(l)$

Solution

1. $Q_C = \frac{(O_3)^2}{(O_2)^3}$
2. $Q_C = \frac{(NH_3)^2}{(N_2)(H_2)^3}$
3. $Q_C = \frac{[NaCl]}{(HCl)[NaOH]}$

Check Your Learning 4.2.7 – Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

(a) $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$

(b) $C_4H_8\,(g) \rightleftharpoons 2\,C_2H_4\,(g)$

(c) $Cd^{2+}\,(aq) + 4\,Cl^{-}\,(aq) \rightleftharpoons CdCl_4^{2-}\,(aq)$

Answer

a. $Q_C = \frac{(SO_3)^2}{(SO_2)^2\left(O_2\right)}$

b. $Q_C = \frac{(C_4H_4)^2}{(C_4H_8)}$

c. $Q_C = \frac{\left(CdCl_4^{2-}\right)}{(Cd^{2+})(Cl^{-})}$

Example 4.2.8 – Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25°C, the concentration changes so that at equilibrium, $[NO_2] = 0.016$ mol/L and $[N_2O_4] = 0.042$ mol/L.

(a) What is the value of the reaction quotient in concentration units, Q_C, before any reaction occurs?

(b) What is the value of the equilibrium constant in concentration units, K_C, for the reaction?

Solution

(a) Before any product is formed, $[NO_2] = \frac{0.10\,mol}{1.0\,L} = 0.10$ mol/L, and $[N_2O_4] = 0$ mol/L. Thus,

$$Q_C = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_C = Q_C = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2$$

The equilibrium constant is 1.6 × 10^2.

Note that dimensional analysis would suggest the unit for this K_C value should be $(mol/L)^{-1}$. However, as mentioned previously, it is common practice to omit units for K_C values, since it is the *magnitude* of an equilibrium constant that relays useful information.

Check Your Learning 4.2.8 – Evaluating a Reaction Quotient

For the reaction $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$, the concentrations at equilibrium are $[SO_2]$ = 0.90 mol/L, $[O_2]$ = 0.35 mol/L, and $[SO_3]$ = 1.1 mol/L. What is the value of the equilibrium constant, K_C?

Answer

$K_C = 4.3$

Predicting the Direction of Net Change Using *Q*

To understand how information is obtained using a reaction quotient, consider once again the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q_C for this reaction as follows:

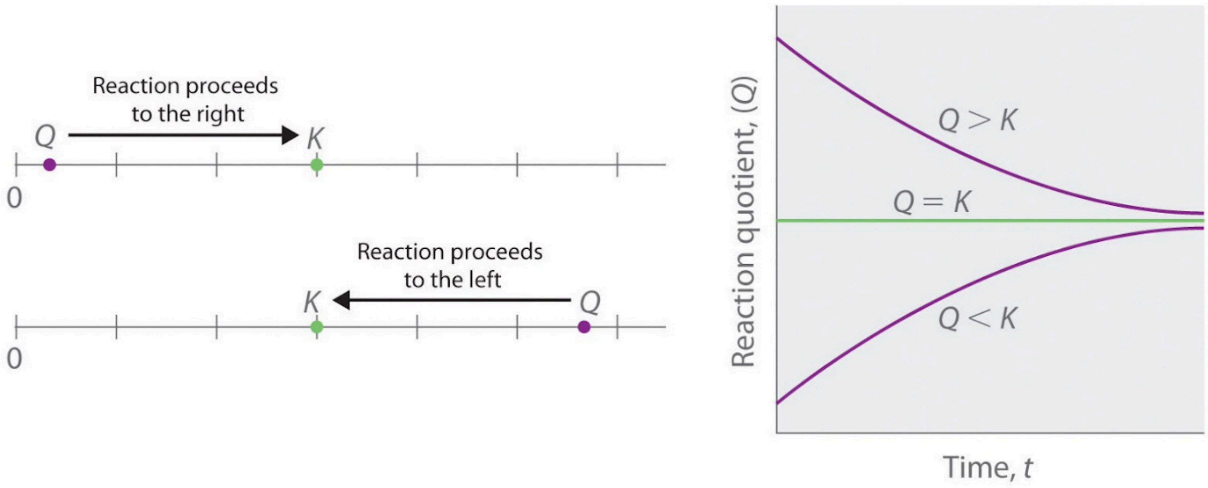
$$Q_2 = \frac{[NO_2]^2}{[N_2O_4]}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of *Q* were calculated for each. Each experiment begins with different proportions of product and reactant:

Experiment	$[NO_2]$ (mol/L)	$[N_2O_4]$ (mol/L)	$Q = \frac{[NO_2]^2}{[N_2O_4]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = undefined$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, *Q* can have any numerical value between 0 and infinity (undefined); that is, *Q* can be greater than, less than, or equal to *K*. Comparing the magnitudes of *Q* and *K* enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (*i.e.*, whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K:

- If $\boldsymbol{Q = K}$, for example, then the system is **already at equilibrium**, and no further change in the composition of the system will occur unless the conditions are changed.
- If $\boldsymbol{Q < K}$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, **the reaction will proceed to the right** as written, forming products at the expense of reactants
- If $\boldsymbol{Q > K}$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so **the reaction will proceed to the left** as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 4.2.1.



(a) Q versus *K*, t_0 to *t*

(b) Q versus *K*, t_0 to t_∞

Figure 4.2.1. (a) Both *Q* and *K* are plotted as points along a number line: the system will always react in the way that causes *Q* to approach *K*. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

Example 4.2.9 – Predicting the Direction of Reaction

Given here are the initial concentrations of reactants and products for three experiments involving this reaction:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

$$K_C = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Ex 2
$[CO]_i$	0.0203 mol/L	0.0
$[H_2O]_i$	0.0203 mol/L	0.0
$[CO_2]_i$	0.0203 mol/L	0.0
$[H_2]_i$	0.0203 mol/L	0.0

Solution

Experiment 1:

$$Q_C = \frac{[CO_2][H_2]}{[CO]H_2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

Check Your Learning 4.2.9 – Predicting the Direction of Reaction

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO *(g)*, 0.0155 mol of Cl_2 *(g)*, and 0.500 mol of NOCl:

$$2\,NO\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NOCl\,(g) \qquad Kc = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \qquad Kc = 0.060$$

(c) A 2.00-L flask containing 230 g of $SO_3(g)$:

$$2\,SO_3\,(g) \rightleftharpoons 2\,SO_2\,(g) + O_2\,(g) \qquad Kc = 0.230$$

Answer

(a) $Q_c = 6.45 \times 10^3$, shifts right. (b) $Q_c = 0.23$, shifts left. (c) $Q_c = 0$, shifts right

Questions

★ Questions

1. Explain why an equilibrium between Br_2 (*l*) and Br_2 (*g*) would not be established if the container were not a closed vessel.
2. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

3. Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation $CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$. Is $K_c > 1, < 1,$ or ≈ 1? Explain your answer.

b. Write the expression for the equilibrium constant for the reaction represented by the equation $3\,Ba^{2+}\,(aq) + 2\,PO_4^{3-}\,(aq) \rightleftharpoons Ba_3(PO_4)_2\,(s)$. Is $K_c > 1, < 1,$ or ≈ 1? Explain your answer.

4. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3\ C_2H_2\,(g)$? $C_6H_6\,(g)$. Which value of K_C would make this reaction most useful commercially? $K_C \approx 0.01$, $K_C \approx 1$, or $K_C \approx 10$. Explain your answer.

5. Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI\,(aq) + I_2\,(aq) \rightleftharpoons KI_3\,(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I^{3-}.

6. For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_C > 1, < 1,$ or ≈ 1 for a titration reaction?

7. Write the mathematical expression for the reaction quotient, Q_C, for each of the following reactions:

a. $CH_4\,(g) + Cl_2\,(g) \rightleftharpoons CH_3Cl\,(g) + HCl\,(g)$

b. $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$

c. $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$

d. $BaSO_3\,(s) \rightleftharpoons BaO\,(s) + SO_2\,(g)$

e. $P_4\,(g) + 5\,O_2\,(g) \rightleftharpoons P_4O_{10}\,(s)$

f. $Br_2\,(g) \rightleftharpoons 2Br\,(g)$

g. $CH_4\,(g) + 2\,O_2\,(g) \rightleftharpoons CO_2\,(g) + 2\,H_2O\,(l)$

h. $CuSO_4 \cdot 5H_2O\,(s) \rightleftharpoons CuSO_4\,(s) + 5\,H_2O\,(g)$

8. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$ Kc = 17; [NH3] = 0.20 mol/L, [N2] = 1.00 mol/L, [H2] = 1.00 mol/L

b. $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$ $K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 2.00 atm, N_2 = 10.00 atm, H_2 = 10.00 atm

c. $2\,SO_3\,(g) \rightleftharpoons 2\,SO_2\,(g) + O_2\,(g)$ Kc = 0.230; $[SO_3]$ = 2.00 mol/L, $[SO_2]$ = 2.00 mol/L, $[O_2]$ = 2.00 mol/L

d. $2\,SO_3\,(g) \rightleftharpoons 2\,SO_2\,(g) + O_2\,(g)$ K_P = 6.5 atm; initial pressures: SO_2 = 1.00 atm, O_2 = 1.130 atm, SO_3 = 0 atm

e. $2\,NO\,(g) + Cl_2\,(g) \rightleftharpoons 2\,NOCl\,(g)$ $K_P = 2.5 \times 10^3$; initial pressures: NO = 1.00 atm, Cl_2 = 1.00 atm, NOCl = 0 atm

f. $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$ Kc = 0.050; $[N_2]$ = 0.100 mol/L, $[O_2]$ = 0.200 mol/L, [NO] = 1.00 mol/L

★★ Questions

9. The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52

10. Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$

$[SO_2Cl_2]$ = 0.12 *mol/L*, $[Cl_2]$ = 0.16 *mol/L* and $[SO_2]$ = 0.050 *mol/l*. K_c for the reaction is 0.078.

11. Which of the systems described in question 8 give homogeneous equilibria? Which give heterogeneous equilibria?

12. For which of the reactions in question 8 does K_C (calculated using concentrations) equal K_P (calculated using pressures)?

13. Convert the values of K_C to values of K_P or the values of K_P to values of K_C.

a. N_2 *(g)* + 3 H_2 *(g)* ⇌ 2 NH_3 *(g)* $K_C = 0.50$ at 400°C

b. H_2 *(g)* + I_2 *(g)* ⇌ 2 HI *(g)* $K_C = 50.2$ at 448°C

c. $Na_2SO_4 \cdot 10H_2O$ *(s)* ⇌ Na_2SO_4 *(s)* + 10 H_2O *(g)* $K_P = 4.08 \times 10^{-25}$ at 25°C

d. H_2O *(l)* ⇌ H_2O *(g)* $K_P = 0.122$ at 50°C

14. What is the value of the equilibrium constant expression for the change H_2O *(l)* ⇌ H_2O *(g)* at 30 °C? (See Appendix F.)

15. Write the expression of the reaction quotient for the ionization of HOCN in water.

16. Write the reaction quotient expression for the ionization of NH_3 in water.

17. What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5$ *(l)* ⇌ $C_2H_5OC_2H_5$ *(g)* at 25 °C. (Vapor pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

Answers

1. Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

2. Yes, based on the changing of colours in the reaction it is possible to determine the direction of the reaction.

3. (a) $K_C = [Ca^{2+}][CO_3^{2-}]$, $K_C < 1$;(b) $K_C = 1 / [Ba^{2+}]^3[PO_4^{3-}]^2$, $K_C > 1$

4. Since $K_C = \frac{[C_6H_6]}{[C_2H_2]}$, a value of $K_C \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

5. Total Ionic: K^+ *(aq)* + I^- *(aq)* + I_2 *(aq)* ⇌ K^+ *(aq)* + I_3^- *(aq)*, Net Ionic: I^- *(aq)* + I_2 *(aq)* ⇌ I_3^- *(aq)*

6. $K_C > 1$

7.

a) $Q_C = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$

b) $Q_C = \frac{[NO]^2}{[N_2][O_2]}$

c) $Q_C = \frac{[SO_3]^2}{[SO_2]^2\left[O_2\right]}$

d) $Q_C = [SO_2]$

e) $Q_C = \frac{1}{[P_4][O_2]^5}$

f) $Q_C = \frac{[Br]^2}{[Br_2]}$

g) $Q_2 = \frac{[CO_2]}{[CH_4][O_2]^2}$

h) $Q_C = [H_2O]^5$

8. (a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

9. The system will shift toward the reactants to reach equilibrium.

10. The system is not at equilibrium since Q < K, therefore the reaction will shift towards the right.

11. (a) Homogeneous, (b) Homogeneous, (c) Homogeneous, (d) Homogeneous, (e) Homogeneous, (f) Homogeneous

12. F is the only one where $K_c = K_P$

13. (a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

14. $K_P = P_{H2O} = 0.042$.

15. $Q_C = \frac{[H^+][OCN^-]}{[HOCN]}$

16. $Q_C = \frac{[NH_4^+][OH^-]}{[HN_3]}$

17. 0.717 atm

4.3 – SOLVING EQUILIBRIUM PROBLEMS

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for *Q* to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Relative Changes in Concentration

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

$$2\ NH_3\ (g) \rightleftharpoons N_2\ (g) + 3\ H_2\ (g)$$

If a sample of ammonia decomposes in a closed system and the concentration of N_2 increases by 0.11 mol/L, the change in the N_2 concentration, $\Delta[N_2] = [N_2]_f - [N_2]_i$, is 0.11 M. The change is *positive* because the concentration of N_2 *increases*.

The change in the H_2 concentration, $\Delta[H_2]$, is also positive—the concentration of H_2 increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of H_2 is three times the change in the concentration of N_2 because for each mole of N_2 produced, 3 moles of H_2 are produced.

$$H_2 = 3 \times [N_2]$$

$$= 3 \times 0.11\ mol/L = 0.33\ mol/L$$

The change in concentration of NH_3, $\Delta[NH_3]$, is twice that of $\Delta[N_2]$; the equation indicates that 2 moles of NH_3 must decompose for each mole of N_2 formed. However, the change in the NH_3 concentration is *negative* because the concentration of ammonia *decreases* as it decomposes.

$$\Delta[NH_3] = -\ 2 \times \Delta[N_2] = -\ 2 \times 0.11\ mol/L = -\ 0.22\ mol/L$$

We can relate these relationships directly to the coefficients in the equation

$$\begin{array}{ccccc} 2\ NH_3\ (g) & \rightleftharpoons & N_2\ (g) & + & 3\ H_2\ (g) \\ \Delta[NH_3] = -2 \times \Delta[N_2] & & \Delta[N_2] = 0.11\ mol/L & & \Delta[H_2] = 3 \times \Delta[N_2] \end{array}$$

Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of N_2, we could represent it by the symbol +*x*.

$$\Delta[N_2] = +x$$

The changes in the other concentrations would then be represented as:

$$\Delta[H_2] = 3 \times \Delta[N_2] = +3x$$

$$\Delta[NH_3] = -2 \times \Delta[N_2] = -2x$$

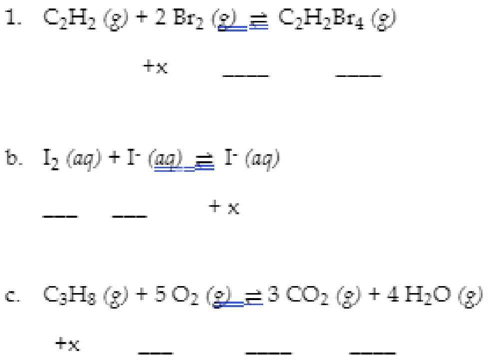
The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$2\ NH_3\ (g)$ $\rightleftharpoons$	$N_2\ (g)$ +	$3\ H_2\ (g)$
$-2x$	$+x$	$+3x$

The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example 4.3.1 – Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.



1. $C_2H_2\ (g) + 2\ Br_2\ (g) \rightleftharpoons C_2H_2Br_4\ (g)$

+x ____ ____

b. $I_2\ (aq) + I^-\ (aq) \rightleftharpoons I^-\ (aq)$

___ ___ + x

c. $C_3H_8\ (g) + 5\ O_2\ (g) \rightleftharpoons 3\ CO_2\ (g) + 4\ H_2O\ (g)$

+x ___ ____ ____

Solution

a. $C_2H_2\ (g) + 2\ Br_2\ (g) \rightleftharpoons C_2H_2Br_4\ (g)$

+ x - 2x - x

b. $I_2\ (aq) + I^-\ (aq) \rightleftharpoons I^-\ (aq)$

- x - x + x

c. $C_3H_8\ (g) + 5\ O_2\ (g) \rightleftharpoons 3\ CO_2\ (g) + 4\ H_2O\ (g)$

+ x + 5x - 3x - 4x

Check Your Learning 4.3.1 – Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions:

a. $2\ SO_2\ (g) + O_2\ (g) \rightleftharpoons 2\ SO_3\ (g)$

____ +x ____

b. $C_4H_8\ (g) \rightleftharpoons 2\ C_2H_4\ (g)$

____ -2x

c. $4\ NH_3\ (g) + 7\ H_2O\ (g) \rightleftharpoons 4\ NO_2\ (g) + 6\ H_2O\ (g)$

____ ____ ____ ____

Answer

(a) + 2*x*, + *x*, – 2*x*; (b) + *x*, – 2*x*; (c) + 4*x*, + 7*x*, – 4*x*, – 6*x* or – 4*x*, – 7*x*, + 4*x*, + 6*x*

Calculations Involving Equilibrium Concentrations or Pressures

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q = K$ (at equilibrium) in all of these situations and that there are only two basic types of equilibrium problems:

1. Calculation of an equilibrium constant. If concentrations/partial pressures of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. Calculation of equilibrium concentrations/partial pressures. If the value of the equilibrium constant and all of the equilibrium concentrations/pressures, except one, are known, the remaining unknown can be calculated. In addition, if the value of the equilibrium constant and a set of concentrations or

pressures of reactants and products that are not at equilibrium are known, the quantity at equilibrium can be calculated.

In the following discussion, we will examine examples of equilibrium calculations involving solutes and values of K in concentration units (K_C). However, please note that the problem-solving procedures equally hold for reactions involving gases and values of K in pressure units (K_P).

Calculation of an Equilibrium Constant

In order to calculate an equilibrium constant, enough information must be available to determine the equilibrium concentrations of all reactants and products. Armed with the concentrations, we can solve the equation for K, as it will be the only unknown.

In the previous section, we learned how to determine the equilibrium constant of a reaction if we know the concentrations of reactants and products at equilibrium. The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE chart – for Initial, Change, and Equilibrium – will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. The initial concentrations of the reactants and products are provided in the first row of the ICE table (these essentially time-zero concentrations that assume no reaction has taken place). The next row of the table contains the changes in concentrations that result when the reaction proceeds toward equilibrium (don't forget to account for the reaction stoichiometry). The last row contains the concentrations once equilibrium has been reached.

Example 4.3.2 – Calculation of an Equilibrium Constant – 1

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3^-\,(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} mol/L before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} mol/L, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of I_2.

$$I_2 + I^- \rightleftharpoons I_3^-$$

Initial Concentration (mol/L)	1.000 x 10^{-3}	1.000 x 10^{-3}	0
Change (mol/L)	– x	– x	+ x
Equilibrium concentration (mol/L)	1.000 x 10^{-3} – x	1.000 x 10^{-3} – x	+ x

Since the equilibrium concentration of I_2 is given, we can solve for *x*. At equilibrium the concentration of I_2 is 6.61×10^{-4} M, therefore:

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

$$x = 3.39 \times 10^{-4} \text{ mol/L}$$

Now we can fill in the table with the concentrations at equilibrium.

$$I_2 + I^- \rightleftharpoons I_3^-$$

Initial Concentration (mol/L)	1.000 x 10^{-3}	1.000 x 10^{-3}	0
Change (mol/L)	– x = -3.39 x 10^{-4}	– x	+ x
Equilibrium concentration (mol/L)	6.61 x 10^{-4}	6.61 x 10^{-4}	3.39 x 10^{-4}

We now calculate the value of the equilibrium constant.

$$K = Q = \frac{[I_3^-]}{[I_2][I^-]}$$

$$= \frac{3.39 \times 10^{-4}\,\frac{\text{mol}}{\text{L}}}{\left(6.61 \times 10^{-4}\,\frac{\text{mol}}{\text{L}}\right)\left(6.61 \times 10^{-4}\,\frac{\text{mol}}{\text{L}}\right)} = 776$$

This value for K makes sense – it is close to 1, indicating that, at equilibrium, the system will contain comparable amounts of reactants and products. This is true when we look at the equilibrium concentration in the ICE table, or even visualize the close proximity of concentration curves (in a graph) of species when equilibrium is reached (Figure 4.3.1).

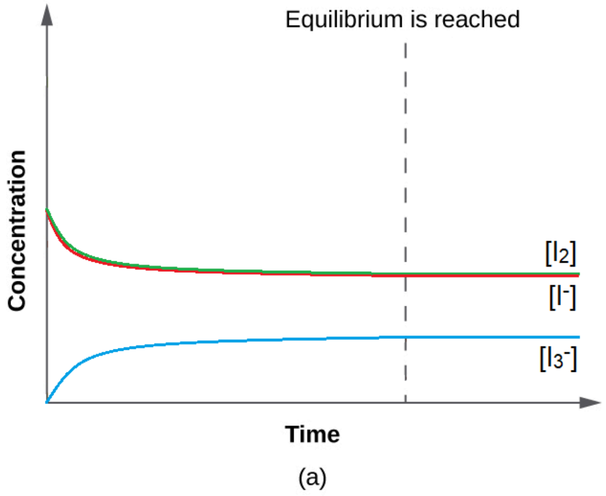


Figure 4.3.1. With a value of K relatively close to 1, the concentrations of reactants and products approach each other when the system moves towards equilibrium.

Check Your Learning 4.3.2 – Calculation of an Equilibrium Constant – 1

Ethanol and acetic acid react to form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers:

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1.00 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when 0.13 mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Answer

$K_C = 45$

Example 4.3.3 – Calculation of an Equilibrium Constant – 2

A 1.00 mol sample of NOCl was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K_C at this temperature. The equation for the decomposition of NOCl to NO and Cl_2 is as follows:

$$2\ NOCl\ (g) \rightleftharpoons 2\ NO\ (g) + Cl_2\ (g)$$

Solution

The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K_C = \frac{[NO]^2\left[Cl_2\right]}{[NOCl]^2}$$

Initially, the system contains 1.00 mol of NOCl in a 2.00 L container. Thus $[NOCl]_i$ = 1.00 mol/2.00 L = 0.500 mol/L. The initial concentrations of NO and Cl_2 are 0 mol/L because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f$ = 0.056 mol/2.00 L = 0.028 mol/L. We insert these values into the following table:

	$2\ NOCl\ (g) \rightleftharpoons 2\ NO\ (g) + Cl_2$		
	[NOCl]	**[NO]**	**[Cl_2]**
Initial concentration (mol/L)	0.500	0	0
Change (mol/L)			
Equilibrium concentration (mol/L)			0.028

We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = [0.028\text{ mol/L (final)} - 0.00\text{ mol/L (initial)}] = +\,0.028\text{ mol/L}$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ mol\ Cl_2}{L}\right)\left(\frac{2\ mol\ NO}{1\ mol\ Cl_2}\right) = 0.056\frac{mol}{L}$$

Similarly, 2 mol of NOCl are consumed for every 1 mol of Cl_2 produced, so the change in the NOCl concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ mol\ Cl_2}{L}\right)\left(\frac{-2\ mol\ NO}{1\ mol\ Cl_2}\right) = -0.056\frac{mol}{L}$$

We insert these values into our table:

	$2\ NOCl\ (g) \rightleftharpoons 2\ NO\ (g) + Cl_2$		
	[NOCl]	**[NO]**	**[Cl_2]**
Initial concentration (M)	0.500	0	0
Change (M)	– 0.056	+ 0.056	+ 0.028
Equilibrium concentration (M)			0.028

We sum the numbers in the [NOCl] and [NO] columns to obtain the final concentrations of NO and NOCl:

$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$

$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444\ M$

We can now complete the table:

2 NOCl (*g*) ⇌ 2 NO (*g*) + Cl_2

	[NOCl]	[NO]	$[Cl_2]$
Initial concentration (M)	0.500	0	0
Change (M)	– 0.056	+ 0.056	+ 0.028
Equilibrium concentration (M)	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K_C = \frac{[NO_2]^2\left[Cl_2\right]}{[NOCl]^2} = \frac{(0.056)^2(0.028)^2}{0.444} = 4.5 \times 10^{-4}$$

Check Your Learning 4.3.3 – Calculation of an Equilibrium Constant – 2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting 0.1248 M H_2 and 0.0416 M N_2 at about 500°C (Figure 4.3.2). At equilibrium, the mixture contained 0.00272 M NH_3. What is K_C for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at this temperature? What is the value of K_P?

Figure 4.3.2. The original laboratory apparatus designed by Fritz Haber and Robert Le Rossignol in 1908 for synthesizing ammonia from its elements. A metal catalyst bed, where ammonia was produced, is in the large cylinder at the left. The Haber-Bosch process used for the industrial production of ammonia uses essentially the same process and components but on a much larger scale. Unfortunately, Haber's process enabled Germany to prolong World War I when German supplies of nitrogen compounds, which were used for explosives, had been exhausted in 1914.

Answer

$K_C = 0.105$; $K_P = 2.61 \times 10^{-5}$

Calculation of Equilibrium Concentration(s)

In these types of equilibrium problems, if we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

Example 4.3.4 – Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000°C, the value of the equilibrium constant K_C for the reaction, $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\ NO\,(g)$, is 4.1×10^{-4}. Calculate the equilibrium concentration of NO *(g)* in air at

1.00 atm pressure and 2000°C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

$$[NO]^2 = K_C[N_2]\left[O_2\right]$$

$$[NO] = \sqrt{K_C[N_2][O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient, Q_C, to see whether it is equal to the equilibrium constant, and thus confirm that the system is indeed at equilibrium.

$$Q_C = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$

$$Q_C = 4.0 \times 10^{-4} = K_C$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

Check Your Learning 4.3.4 – Calculation of a Missing Equilibrium Concentration

The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 M and 2.09 M, respectively.

Answer

1.53 mol/L

In another scenario, if we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
    a. Write a balanced chemical equation for the reaction.
    b. If the direction in which the reaction must proceed to reach equilibrium is not readily obvious, calculate *Q* from the initial values and compare it to *K* to determine the direction of change.
2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
    a. Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol x and express the other changes in terms of the smallest change.
    b. Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
    a. Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for x, and check any assumptions used to find x.
    b. Calculate the equilibrium concentrations.
4. Check the arithmetic.
5. Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant.

Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps.

In solving equilibrium problems that involve changes in concentration, it is again very convenient to set up an ICE table.

Example 4.3.5 – Calculation of Concentration Changes as a Reaction Goes to Equilibrium

Under certain conditions, the equilibrium constant K_C for the decomposition of PCl_5 *(g)* into PCl_3 *(g)* and Cl_2 *(g)* is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 if the initial concentration of PCl_5 was 1.00 M?

Solution

Use the stepwise process described earlier.

1. *Determine the direction the reaction proceeds.*

The balanced equation for the decomposition of PCl_5 is

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

Because we have no products initially, $Q = 0$ and the reaction must proceed to the right (towards products).

2. *Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.*

Let us represent the increase in concentration of PCl_3 by the symbol x. The other changes may be written in terms of x by considering the coefficients in the chemical equation.

$$\begin{array}{ccc} PCl_5\,(g) \rightleftharpoons & PCl_3\,(g) + & Cl_2\,(g) \\ -x & +x & +x \end{array}$$

The changes in concentration and the expressions for the equilibrium concentrations are:

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initial Concentration (M)	1.00	0	0
Change (M)	− x	+ x	+ x
Equilibrium concentration (M)	1.00 − x	0 + x = x	0 + x = x

3. *Solve for the change and the equilibrium concentrations.*

Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.0211$$
$$= \frac{(x)(x)}{(1.00 - x)}$$

This equation contains only one variable, x, the change in concentration. We can write the equation as a quadratic equation and solve for x using the quadratic formula.

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211\,(1.00 - x) = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

Appendix C shows us an equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for a, b, and c yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4\left(1\right)\left(-0.0211\right)}}{2(1)}$$

$$x = \frac{-0.0211 \pm \sqrt{\left(4.45 \times 10^{-4}\right) + \left(8.44 \times 10^{2}\right)}}{2}$$

$$x = \frac{-0.0211 \pm 0.291}{2}$$

Hence

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

or

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

NOTE:

Quadratic equations often have two different solutions: one that is physically **possible** and one that is physically **impossible** (an extraneous root).

An extraneous root could be, for example, a negative value or one that is physically insignificant (e.g. if the "Change" in an ICE table is 0.100 – x, and one possible value for x is 0.300, then that value can't be physically possible because that would yield a negative value for equilibrium concentration).

In this case, the second solution (−0.156) is physically impossible because we know the change must be a positive number (otherwise we would end up with negative values for concentrations of the products). Thus, $x = 0.135$ M.

The equilibrium concentrations are

$$[PCl_5] = 1.00 - 0.135 = 0.87\ \text{M}$$

$$[PCl_3] = x = 0.135\text{ M}$$
$$[Cl_2] = x = 0.135\text{ M}$$

4. *Check the arithmetic.*

Substitution into the expression for K_c (to check the calculation) gives

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures). Thus, the calculated equilibrium concentrations are confirmed.

Check Your Learning 4.3.5 – Calculation of Concentration Changes as a Reaction Goes to Equilibrium

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The equilibrium constant for this reaction at a certain temperature, using dioxane as a solvent, is 4.0. What are the equilibrium concentrations when 0.15 mol CH_3CO_2H, 0.15 mol C_2H_5OH, 0.40 mol $CH_3CO_2C_2H_5$, and 0.40 mol H_2O are mixed in enough dioxane solvent to make 1.0 L of solution?

Answer

$[CH_3CO_2H]$ = 0.36 M, $[C_2H_5OH]$ = 0.36 M, $[CH_3CO_2C_2H_5]$ = 0.17 M, $[H_2O]$ = 0.17 M

Check Your Learning 4.3.6 – Calculation of Concentration Changes as a Reaction Goes to Equilibrium

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2. The value of the equilibrium constant K_C for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

Answer

$[H_2]$ = 0.06 M, $[I_2]$ = 1.06 M, [HI] = 1.88 M

Now let's consider another example where we can utilize a square root shortcut method to facilitate problem-solving. If we find that the fractional term consisting of reactants (denominator) and products (numerator) has perfect squares, we can take the square root of both sides when solving for x.

Example 4.3.6 – Concentration Changes as a Reaction Goes to Equilibrium – Square Root Shortcut

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)$$

K_C = 0.106 at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Solution

The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150$ M. Just as before, we will focus on the *change* in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

	$H_2\,(g) + CO_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)$		
	$[H_2]$	**$[CO_2]$**	**$[H_2O]$**
Initial concentration (M)	0.0150	0.0150	0
Change (M)	$-x$	$-x$	$+x$
Equilibrium concentration (M)	$(0.0150 - x)$	$(0.0150 - x)$	$+x$

We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.150 - x)(0.150 - x)} = \frac{x^2}{(0.150 - x)^2} = 0.160$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\left(\frac{x}{0.0150-x}\right)^2 = 0.106$$

Taking the square root of both sides of this equation yields,

$$\left(\frac{x}{0.0150-x}\right) = (0.106)^{\frac{1}{2}}$$

$$\frac{x}{0.0150-x} = 0.326$$

$$x = (0.326)(0.0150-x)$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

The final concentrations of all species in the reaction mixture are as follows:

$$\begin{gathered}[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)M = 0.0113\ M \\ [CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)M = 0.0113\ M \\ [H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)M = 0.00369\ M \\ [CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)M = 0.00369\ M\end{gathered}$$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K_C = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K_C is the same as the value given in the problem, so our answer is confirmed.

Check Your Learning 4.3.7 – Concentration Changes as a Reaction Goes to Equilibrium – Square Root Shortcut

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

K_C = 54.0 at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

$[HI]_f = 0.270$ M; $[H_2]_f = [I_2]_f = 0.037$ M

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products .

Consider the ionization of 0.150 M HA, a weak acid.

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq) \qquad K_C = 6.80 \times 10^{-4}$$

The most obvious way to determine the equilibrium concentrations would be to start in a system containing only reactants. This could be called the "all reactant" starting point. Using *x* for the amount of acid ionized at equilibrium, this is the ICE table and solution.

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$

Initial Concentration (M)	0.150	—	0	0
Change (M)	− x	—	+x	+x
Equilibrium concentration (M)	0.150 − x	—	+x	+x

Setting up and solving the quadratic equation gives

$$K_C = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.150 - x)} = 6.80 \times 10^{-4}$$

Using the positive (physical) root, the equilibrium concentrations are

$$[HA] = 0.150 - x = 0.140 \text{ M}$$

$$[H_3O^+] = [A^-] = x = 0.00977 \text{ M}$$

A less obvious way to solve the problem would be to assume *all* the HA ionizes first, *then* the system comes to equilibrium. This could be called the "all product" starting point. Assuming all of the HA ionizes gives

$$[HA] = 0.150 - 0.150 = 0\ M$$
$$[H_3O^+] = 0 + 0.150 = 0.150\ M$$
$$[A^-] = 0 + 0.150 = 0.150\ M$$

Using these as initial concentrations and "*y*" to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$

Initial Concentration (M)	0	—	0.150	0.150
Change (M)	+y	—	– y	– y
Equilibrium concentration (M)	+y	—	0.150 – y	0.150 – y

Setting up and solving the quadratic equation gives

$$K_C = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(0.150 - y)(0.150 - y)}{(y)} = 6.80 \times 10^{-4}$$
$$6.80 \times 10^{-4} y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

$$y^2 - 0.30068y + 0.022500 = 0$$
$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)\left(0.022500\right)}}{(2)(1)}$$
$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

$y = 0.160\ M$ or $y = 0.140\ M$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

$$[HA] = y = 0.140\ M$$
$$[H_3O^+] = 0.150 - y = 0.010\ M$$
$$[A^-] = 0.150 - y = 0.010\ M$$

Thus, the two approaches give the same results (to three *decimal places*), and show that *both* starting points lead to the same equilibrium conditions (Figure 4.3.3). The "all reactant" starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the "all product" starting point had a relatively large change (y) that was nearly the size of the initial concentrations. Notice that the graph in part (a) of Figure 4.3.3 experiences little change in concentration; hence, it can be said that a system that starts "close" to equilibrium will require only a "small" change in conditions (x) to reach equilibrium.

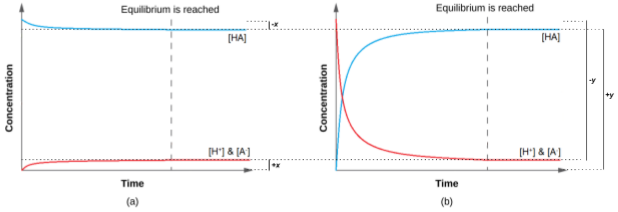


Figure 4.3.3. Regardless of wherever you start, whether it be with 100% reactants in (a) or 100% products in (b), we end up at the same equilibrium point regardless. (a) The change in the concentrations of reactants and products is depicted as the $HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$ reaction approaches equilibrium, when going from an "all reactant" starting point. (b) The change in concentrations of reactants and products is depicted as the reaction $HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$ approaches equilibrium, when going from an "all product" starting point.

Recall that a small value of K means that very little of the reactants form products and a large K means that most of the reactants form products. If the system can be arranged so it starts "close" to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. The following two examples demonstrate this.

NOTE:

For equilibrium problems in CHM1311, *"x is small"* is officially defined as resulting in an error of **less than 5%**.

Example 4.3.7 – Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$HCN\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CN^-\ (aq) \qquad K = 4.9 \times 10^{-10}$$

Solution

Using "x" to represent the concentration of each product at equilibrium gives this ICE table.

HCN *(aq)* + H_2O *(l)* ⇌ H_3O^+ *(aq)* + CN^- *(aq)*

Initial Concentration (M)	0.15	—	0	0
Change (M)	-x	—	+x	+x
Equilibrium concentration (M)	0.15 – x	—	+x	+x

The exact solution may be obtained using the quadratic formula with

$$K = \frac{(x)(x)}{(0.15 - x)}$$

solving

$$x^2 + (4.9 \times 10^{-10}) - (7.35 \times 10^{-11}) = 0$$
$$x = 8.56 \times 10^{-6}\ M\ (3\ sig.\ figs.) = 8.6 \times 10^{-6}\ M\ (2\ sig.\ figs.)$$

Thus $[H_3O^+] = [CN^-] = x = 8.6 \times 10^{-6}$ M and $[HCN] = 0.15 - x = 0.15$ M.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, x must be small compared to 0.15 M. More formally, if $x \ll 0.15$, then $0.15 - x \approx 0.15$ (Figure 4.3.4 visually demonstrates this).

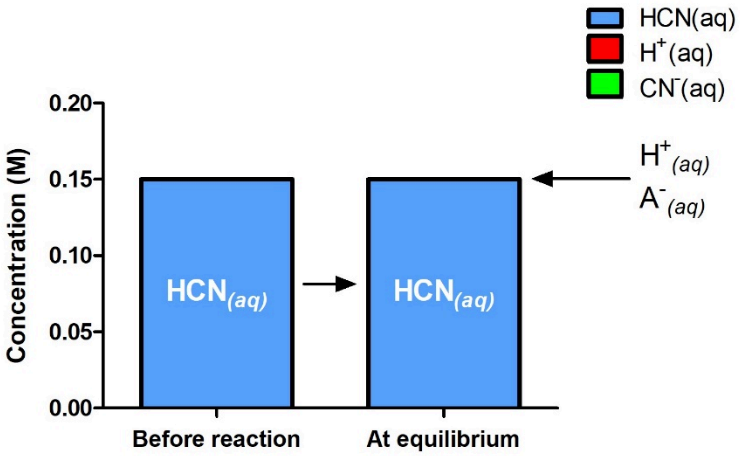


Figure 4.3.4. Concentrations of the reactant and products are shown initially and at equilibrium for the following reaction: HCN *(aq)* +H_2O *(l)* ⇌ H_3O^+ *(aq)* + CN^- *(aq)*. The reaction starts with only HCN*(aq)*, but even at equilibrium, you can tell that the relative amounts of H^+ and CN^- are so little that they are negligible – there is practically still only reagent which demonstrates the extremely small *K* value of the reaction and confirms the validity of the assumption that $0.15 - x \approx 0.15$.

If this assumption is true, then it simplifies obtaining *x*

$$K_C = \frac{(x)(x)}{(0.15 - x)} \approx \frac{x^2}{0.15}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)\left(4.9 \times 10^{-10}\right) = 7.4 \times 10^{-11}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to $(0.15 - x) \approx 0.15$ M, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\%$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

Check Your Learning 4.3.8 – Approximate Solution Starting Close to Equilibrium

What are the equilibrium concentrations in a 0.25 M NH_3 solution?

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \qquad K = 1.8 \text{ x } 10^{-5}$$

Assume that x is much less than 0.25 M and calculate the error in your assumption.

Answer

$[OH^-] = [NH_4^+] = 0.0021$ M; $[NH_3] = 0.25$ M, error = 0.84%

Whenever you make the assumption that [*initial*] ≈ [*equilibrium*] because the error is less than 5%, you MUST actually make the calculations and check to see if the error is indeed less than 5% and hence that the assumption is valid.

The second example requires that the original information be processed a bit, but it still can be solved using a small x approximation.

Example 4.3.8 – Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

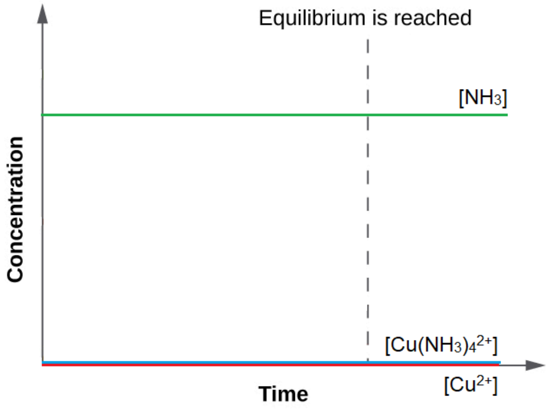
$$Cu^{2+}\,(aq) + 4\,NH_3\,(aq) \rightleftharpoons Cu(NH_3)_4^{2+}\,(aq) \qquad K = 5.0 \times 10^{13} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 M NH_3 what are the concentrations when the system comes to equilibrium?

Solution:

The initial concentration of copper(II) is 0.010 M. The equilibrium constant is very large so it would be better to start with as much product as possible because "all products" is much closer to equilibrium than "all reactants" (Figure 4.3.5). Therefore, to simplify our calculations, let us assume that the reaction goes 100% to completion. Note that Cu^{2+} is the limiting reactant; if all 0.010 M of it reacts to form product the concentrations would be

$$[Cu^{2+}] = 0.010 - 0.010 = 0 \text{ M}$$
$$[Cu(NH_3)_4^{2+}] = 0.010 \text{ M}$$
$$[NH_3] = 1.00 - 4 \text{ x } 0.010 = 0.96 \text{ M}$$



(a)

Figure 4.3.5. The *K* value is very large for the equilibrium reaction $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$, so products are very heavily favoured. The *change* in concentration of both products and reactants is almost minimal since as it stands, the relative concentration of all species initially almost already corresponds to the relative amounts at equilibrium, where the product is close to its maximum possible concentration.

Using these "shifted" values as initial concentrations with *x* as the free copper(II) ion concentration at equilibrium gives this ICE table.

$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$

Initial Concentration (M)	0	0.96	0.010
Change (M)	+x	+4x	-x
Equilibrium concentration (M)	+x	0.96 + 4x	0.010 − x

Since we are starting close to equilibrium, *x* should be small so that

$$0.96 + 4x \approx 0.96\ M$$

$$0.010 - x \approx 0.010\ M$$

$$K_C = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$

$$x = \frac{(0.010 - x)}{K_C(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule – dividing a value by the smallest value possible will yield the largest possible error to really put the 5% rule to the test.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[Cu^{2+}] = x = 2.4 \text{ x } 10^{-16}\ M$$

$$[NH_3] = 0.96 - 4x = 0.96\ M$$

$$[Cu(NH_3)_4{}^{2+}] = 0.010 - x = 0.010\ M$$

If we subtract *x* from 0.010 M, for example, we end up with 0.00999999… M which, when counting significant figures, rounds back up to 0.010 M anyway.

Overall, we started with a much higher concentration of reactant compared to product – note that we use up Cu^{2+} so initially we have the highest possible concentration of products. But since *K* is very large, the *change* in concentration is kept minimal since this reaction mixture almost practically corresponds to what is expected at equilibrium.

By starting with the maximum amount of product, this system was near equilibrium and the change (*x*) was very small – this very small change was particularly driven by the complete absence of Cu^{2+} initially (we discuss this in the context of Le Châtelier's Principle in the next section). With only a small change required to get to equilibrium, the equation for *x* was greatly simplified and gave a valid result well within the 5% error maximum.

Check Your Learning 4.3.9 – Approximate Solution After Shifting Starting Concentration

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 M NH_3 solution?

$$Ni^{2+}\,(aq) + 6\,NH_3\,(aq) \rightleftharpoons Ni(NH_3)_6{}^{2+}\,(aq) \qquad K_C = 5.5 \text{ x } 10^8$$

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (*x*) of the product shifts left. Calculate the error in your assumption.

Answer

$[Ni(NH_3)_6{}^{2+}] = 0.25$ M, $[NH_3] = 0.50$ M, $[Ni^{2+}] = 2.9 \times 10^{-8}$ M, error = 1.2×10^{-5} %

Questions

★ Questions

1. In the equilibrium reaction A + B ⇌ C, what happens to *K* if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction A ⇌ B + C?

2. The following table shows the reported values of the equilibrium P{O2} at three temperatures for the reaction Ag_2O *(s)* ⇌ 2 Ag *(s)* + 1/2 O_2 *(g)* for which $\Delta H° = 31$ kJ/mol. Are these data consistent with what you would expect to occur? Why or why not?

T (°C)	**P (O_2) mm Hg**
150	182
184	143
191	126

3. Given the equilibrium system N_2O_4 *(g)* ⇌ 2 NO_2 *(g)*, what happens to K_P if the initial pressure of N_2O_4 is doubled? If K_P is 1.7×10^{-1} at 2300°C, and the system initially contains 100% N_2O_4 at a pressure of 2.6×10^{2} bar, what is the equilibrium pressure of each component?

4. At 430°C, 4.20 mol of HI in a 9.60 L reaction vessel reaches equilibrium according to the following equation: H_2 *(g)* + I_2 *(g)* ⇌ 2 HI *(g)*. At equilibrium, [H_2] = 0.047 M and [HI] = 0.345 M. What are *K* and K_P for this reaction?

5. Methanol, a liquid used as an automobile fuel additive, is commercially produced from carbon monoxide and hydrogen at 300°C according to the following reaction: CO *(g)* + 2 H_2 *(g)* ⇌ CH_3OH *(g)* and $K_P = 1.3 \times 10^{-4}$. If 56.0 g of CO is mixed with excess hydrogen in a 250 mL flask at this temperature, and the hydrogen pressure is continuously maintained at 100 bar, what would be the maximum percent yield of methanol? What pressure of hydrogen would be required to obtain a minimum yield of methanol of 95% under these conditions?

★★ Questions

6. Starting with pure A, if the total equilibrium pressure is 0.969 atm for the reaction A *(s)* ⇌ 2 B *(g)* + C *(g)*, what is K_P (hint: must use the unit "bar" when working with K_P)?

7. The decomposition of ammonium carbamate to NH_3 and CO_2 at 40°C is written as $NH_4CO_2NH_2$ *(s)* ⇌ 2 NH_3 *(g)* + CO_2 If the partial pressure of NH_3 at equilibrium is 0.242 atm, what is the equilibrium

partial pressure (in atm) of CO_2? What is the total gas pressure of the system (in atm)? What is K_P(hint: must use the unit "bar" when working with K_p)?

8. At 375 K, K_P for the reaction $SO_2Cl_2\ (g) \rightleftharpoons SO_2\ (g) + Cl_2\ (g)$ is 2.4, with pressures expressed in atmospheres. At 303 K, K_P is 2.9×10^{-2}.

a. What is K for the reaction at each temperature?

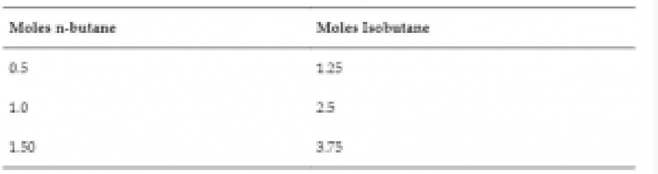
b. If a sample at 375 K has 0.100 M Cl_2 and 0.200 M SO_2 at equilibrium, what is the concentration of SO_2Cl_2?

c. If the sample given in part b is cooled to 303 K, what is the pressure inside the bulb (in atm)?

9. Experimental data on the system $Br_2\ (l) \rightleftharpoons Br_2\ (aq)$ are given in the following table. Graph [Br_2] versus moles of $Br_2\ (l)$ present; then write the equilibrium constant expression and determine K.

Grams Br_2 in 100 mL Water	**[Br_2] (M)**
1.0	0.0626
2.5	0.156
3.0	0.188
4.0	0.219
4.5	0.219

10. Data accumulated for the reaction n-butane $(g) \rightleftharpoons$ isobutane (g) at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of *n*-butane is allowed to equilibrate under the same reaction conditions, what is the final number of moles of *n*-butane and isobutane?



Moles n-butane	Moles Isobutane
0.5	1.25
1.0	2.5
1.50	3.75

11. Solid ammonium carbamate ($NH_4CO_2NH_2$) dissociates completely to ammonia and carbon dioxide when it vaporizes:

$$NH_4CO_2NH_2\ (s) \rightleftharpoons 2\ NH_3\ (g) + CO_2\ (g)$$

At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium partial pressure of each gas (in atm)? What is K_p(hint: must use the unit "bar" when working with K_P)? If the concentration of CO_2 is doubled and then equilibrates to its initial equilibrium partial pressure +*x* atm, what change in the NH_3 concentration is necessary for the system to restore equilibrium?

12. The equilibrium constant for the reaction $COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$ is $K_P = 2.2 \times 10^{-10}$ at 100°C. If the initial concentration of $COCl_2$ is 3.05×10^{-3} M, what is the partial pressure of each gas at equilibrium at 100°C (in bar)? What assumption can be made to simplify your calculations?

13. Aqueous dilution of $IO4^{-}$ results in the following reaction:

$$IO_4^{-}\ (aq) + 2\ H_2O\ (l) \rightleftharpoons H_4IO_6^{-}\ (aq)$$

and $K = 3.5 \times 10^{-2}$. If you begin with 50 mL of a 0.896 M solution of IO_4^{-} that is diluted to 250 mL with water, how many moles of $H_4IO_6^{-}$ are formed at equilibrium?

★★★ Questions

14. Iodine and bromine react to form IBr, which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation:

$$I_2\ (g) + Br_2\ (g) \rightleftharpoons 2\ IBr\ (g)$$

$K_P = 1.2 \times 10^2$ (Hint: assumed to have used "bar" as a unit while calculating K_P). If you begin the reaction with 7.4 g of I_2 vapor and 6.3 g of Br_2 vapor in a 1.00 L container, what is the concentration of IBr (g) at equilibrium (gmol-1)? What is the partial pressure of each gas at equilibrium (in bar)? What is the total pressure of the system (in bar)?

15. For the reaction

$$C\ (s) + 12\ N_2\ (g) + 5/2\ H_2\ (g) \rightleftharpoons CH_3NH_2\ (g)$$

$K = 1.8 \times 10^{-6}$. If you begin the reaction with 1.0 mol of N_2, 2.0 mol of H_2, and sufficient C(s) in a 2.00 L container, what are the concentrations of N_2 and CH_3NH_2 at equilibrium (gmol-1)? What happens to *K* if the concentration of H_2 is doubled?

Answers

1. The K value is now raised to the respected factor. When it is doubled K is now K^2 and when it is tripled, K is K^3

2. These results are not expected, as with an increase in temperature an increase in pressure should occur. $\Delta H°$ is a positive value in this case (31 kJ/mol) indicating that it is an endothermic reaction. This being said, with an increase in temperature the reaction will shift forward meaning that more product will be produced. If more product is produced, more oxygen gas is present, therefore increasing its pressure.

3. Kp would remain the same, $P_{N2O2} = 2.3 \times 10^2$ bar, $P_{NO2} = 6.6$ bar

4. K = 53.88; Kp = 53.88

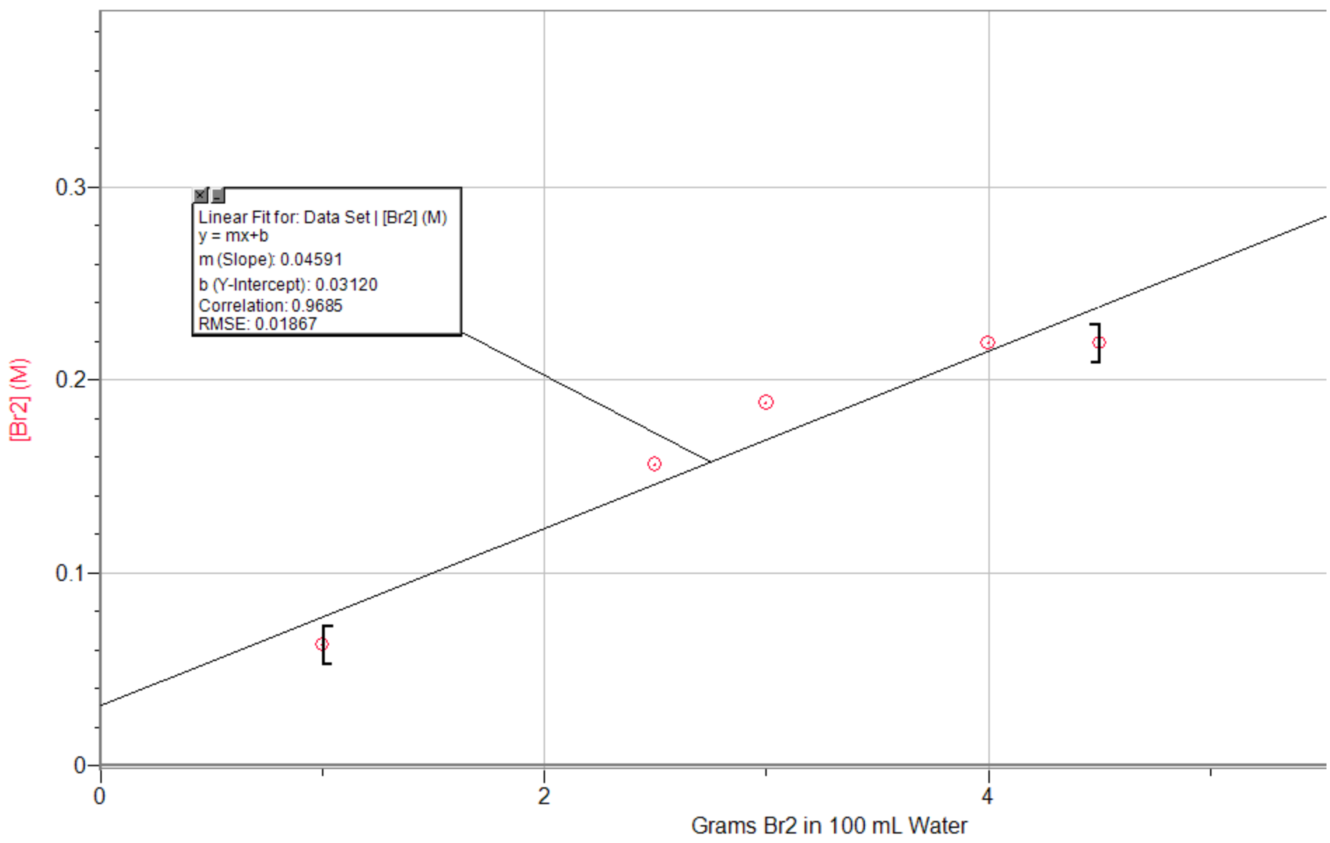
5. 215 bar MeOH; 383 bar H_2

6. Kp = 0.140

7. Partial Pressure of CO_2 = 0.121 atm; total gas pressure of the system = 0.363 atm; Kp = 7.37×10^{-3}

8. (a) K = 7.8×10^{-2} at 375K, K = 1.2×10^{-3} at 303K ; (b) 0.256 M; (c) 14.13 atm

9.



K = 0.046 (based on the slope of the line of best fit)

10. K = 2.5; the final moles will be 0.3 mol of n-butane and 0.7 mol of isobutane.

11. P_{NH_3}= 0.0773 atm, P_{CO_2} = 0.0387 atm; $K_p = 2.411 \times 10^{-4}$; the concentration of NH_3 will drop in order for the equilibrium to restore.

12. P_{COCl_2} = 0.042 bar, $P_{CO} = 4.59 \times 10^{-6}$ bar, $P_{Cl_2} = 4.59 \times 10^{-6}$ bar; An assumption to be made is that the total volume is 1L.

13. $H_4IO_6^{-} = 9.09 \times 10^{-3}$ mol

14. P_{I_2} = 7.7 bar, P_{Br_2} = 47 bar, $P_{IBr} = 2.1 \times 10^{2}$ bar = 0.054 M, $P_T = 2.6 \times 10^{2}$ bar

15. $[N_2] \approx 0.99$ M, $[H_2] \approx 2$ M, $[CH_3NH_2] = 1.02 \times 10^{-5}$ M; if the $[H_2]$ doubles, K remains unchanged (only temperature can alter a K value)

4.4 – LE CHÂTELIER'S PRINCIPLE

As you already know by now about equilibrium reactions, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (*Q*) is equal to the equilibrium constant (*K*). We next address what happens when a system at equilibrium is disturbed so that *Q* is no longer equal to *K*. If a system at equilibrium is subjected to a perturbation or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of *Q* will no longer equal the value of *K*. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until *Q* returns to the same value as *K*.

This process is described by **Le Châtelier's principle**: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in *Q*; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Châtelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of *Q* and *K* for the system to predict the changes.

Effect of Change in Concentration on Equilibrium

A chemical system at equilibrium can be temporarily shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure 4.4.1 is the reduction of the equilibrium concentration of SCN^-: lowering the concentration of this reactant would cause *Q* to be larger than *K*. As a consequence, Le Châtelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.

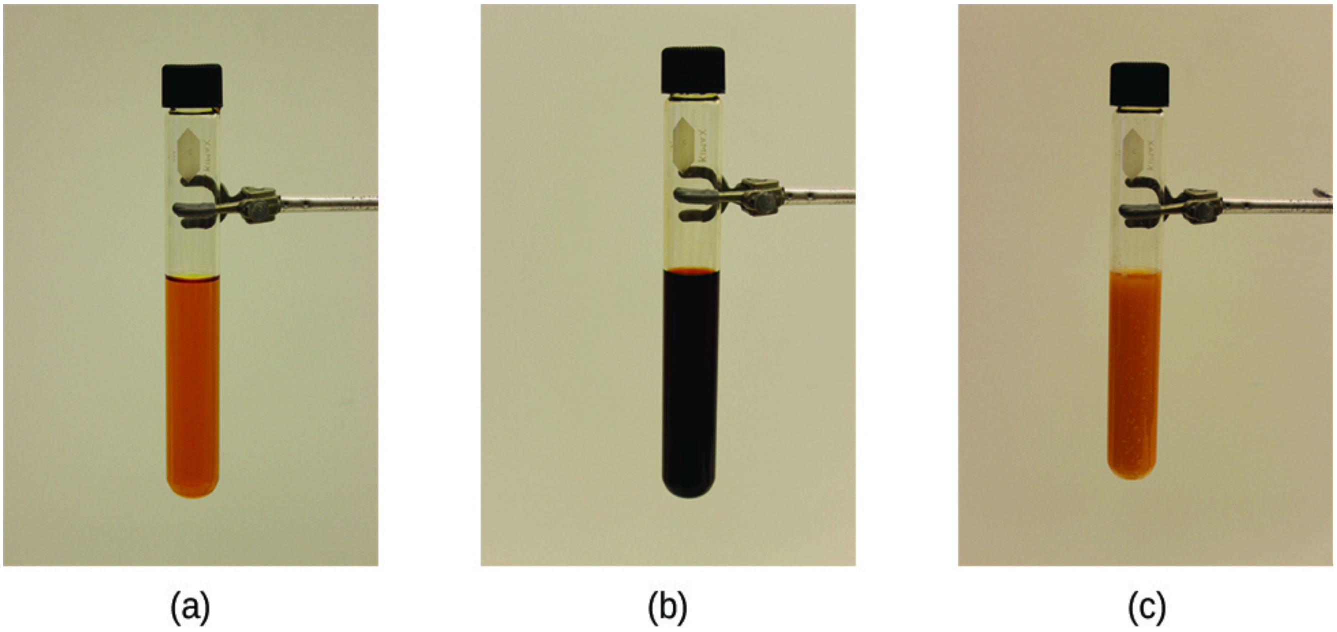


Figure 4.4.1. a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion, according to the chemical equilibrium: $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN^{-} as the white solid AgSCN, according to: $Ag^{+}(aq) + SCN^{-}(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN^{-} concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott)

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \qquad K_C = 50.0 \text{ at } 400°C$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400°C with $[H_2] = [I_2] = 0.221$ M and $[HI] = 1.563$ M is at equilibrium; for this mixture, $Q_c = K_C = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles instantaneously (new $[H_2] = 0.442$ M), the reaction will shift so that a new equilibrium is reached, at which $[H_2] = 0.374$ M, $[I_2] = 0.153$ M, and $[HI] = 1.692$ M. This gives:

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_C$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure/Volume on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_C) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the individual gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Châtelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of reactants (NO and O_2) are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Pressure on Equilibrium – Video Demonstration

Check out this cool video to observe the colour change that happens when pressure is applied to an equilibrium mixture of NO_2 (brown) and N_2O_4 (colourless).

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

Notice how sometime after the pressure is applied, the colour of the mixture lightens – if we think about this using Le Châtelier's Principle, the increase of pressure is the stress that needs to be offset by decreasing the pressure in the system – this can be achieved by reducing the number of moles of gas in the system. This means that the reaction to the left is driven forward, where molecules of NO_2 react to form more N_2O_4 which is colourless and hence gives the mixture a lighter colour (i.e. increased extent of colourlessness).

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Châtelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved/released.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \qquad \Delta H = -9.4\text{ kJ (exothermic)}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) + \text{heat}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favours the production of heat, and favours the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C. Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g) \qquad \Delta H = 57.20\text{ kJ}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{Heat} + N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

Temperature Dependence of K

As we've just recently noted, temperature is special in that it actually affects the value of the equilibrium constant for a reaction. Hence, equilibrium constants are temperature dependent. This relationship, which also relates *K* and the standard enthalpies and entropies, is known as the **Van't Hoff equation**. It is expressed as

$$lnK = -\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R} \qquad 4.4.1$$

where

- *K* is the equilibrium constant
- *ΔH°* is the standard enthalpy change, in units of energy (*e.g.* J)

- R is the gas constant (as seen in the gases unit) expressed in units of energy per Kelvin (*e.g.* J/K)
- T is the temperature in Kelvin

ΔS^o is a thermodynamic property just like enthalpy (ΔH^o), known as the standard change in **entropy (*S*)**, expressed in units of energy per Kelvin (*e.g.* J/K). This topic is beyond the scope of this course (instead, you will learn about entropy in detail in your 2nd-year physical chemistry course), but for now, all you need to know is that it is a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the "disorder" of the system. The greater the disorder in a system, the greater the entropy. For example, the entropy of a gas is greater than that of a liquid, and the entropy of a liquid is greater than that of a solid. In addition, heating substances increases the disorder of its constituent particles and hence increases their entropy.

Looking at the equation above, notice how it can be formatted in the form $y = mx + b$. This gives us a linear relationship between $\ln K$ (y) and $1/T$ (x). Consequently, the thermodynamic enthalpy and entropy changes (ΔH^o and ΔS^o) for a reversible reaction can be determined from plotting $\ln K$ vs. $1/T$ data without the aid of calorimetry. The plot of $\ln K$ vs. $1/T$ shows that it should be a line with slope $-\Delta H^o/R$ (this represents m) and intercept $\Delta S^o/R$ (this represents b). Of course, the main assumption here is that only K is dependent on T; ΔH^o and ΔS^o are only very weakly dependent on T, which is usually valid over a narrow temperature range.

Assuming ΔH° and ΔS° are temperature independent, for an **exothermic** reaction ($\Delta H^\circ < 0$), the slope of the graph is **positive** and the magnitude of $\ln K$ increases with increasing temperature, whereas for an **endothermic** reaction ($\Delta H^\circ > 0$), the slope of the graph is **negative** and the magnitude of $\ln K$ decreases with increasing temperature (Figure 4.4.2).

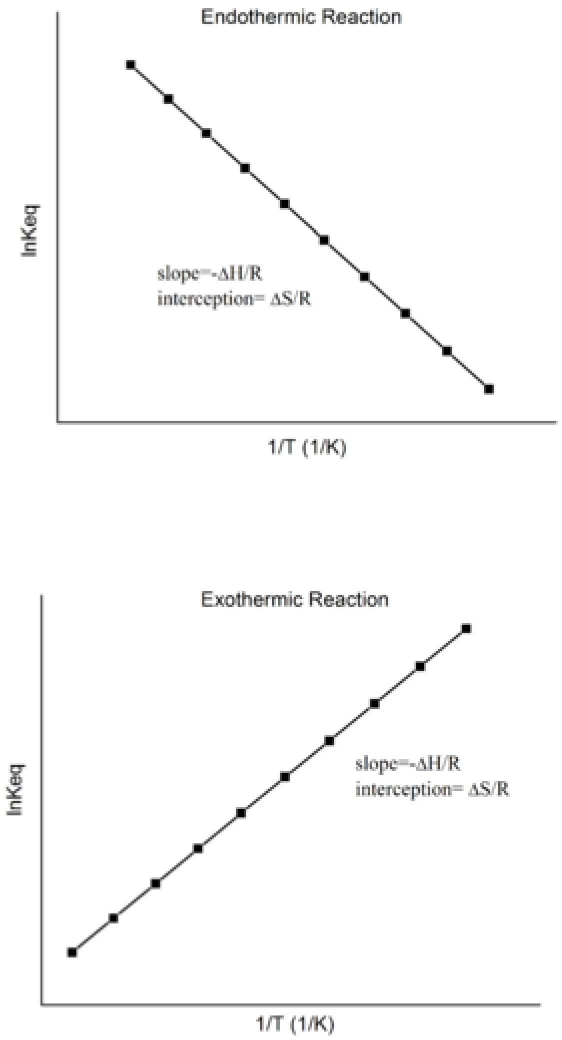


Figure 4.4.2. Endothermic reaction (left) and exothermic reaction van't Hoff plots (right). (CC BY-SA 3.0)

The quantitative relationship expressed in the van't Hoff equation agrees with the qualitative predictions made by applying Le Châtelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. The van't Hoff equation also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS°. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying the van't Hoff equation gives the following relationship at each temperature:

$$lnK_1 = -\left(\frac{\Delta H^\circ}{RT_1}\right) + \frac{\Delta S^\circ}{R}$$
$$lnK_2 = -\left(\frac{\Delta H^\circ}{RT_2}\right) + \frac{\Delta S^\circ}{R}$$

Subtracting ln K_1 from ln K_2 we get:

$$lnK_1 = lnK_2 = ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This modified van't Hoff equation is one we'll call the "two-point van't Hoff equation." Hence, by calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1), we can calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature. There are also a few other points to consider when using the two-point van't Hoff equation – see the note below.

NOTE:

To determine the most accurate values for ΔH° and ΔS° for a particular reaction in an experimental setting, a good scientist would measure multiple values of K at different temperatures to collect many data points. This allows them to visualize a more accurate relationship between ln K and $1/T$ in a van't Hoff plot.

If the scientist is in a hurry, collecting just two data points and using the two-point version of the van't Hoff equation should still suffice in most cases. In order to work, however, we must assume that the relationship between ln K and $1/T$ is perfectly linear between the two temperatures T_1 and T_2. This linearity is usually the case when both temperatures are relatively close to one another, but it breaks down the further apart the two temperatures are.

Example 4.4.1 – Using the van't Hoff Equation

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C is $K_P = 5.4 \times 10^5$. What is K_P at 500°C? ($\Delta H^\circ = -91.8$ kJ)

Solution:

If we set T_1 = 25°C = 298 K and T_2 = 500°C = 773 K, then using van't Hoff's equation we obtain the following:

$$ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Check Your Learning 4.4.1 – Using the van't Hoff Equation

You calculate $K_P = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH_f° values provided in Appendix G to calculate K_P for this reaction at 1000°C.

Answer:

5.6×10^{-4}

Effect of Catalysts on Equilibrium

As we'll learn later on and in greater depth during our study of kinetics, a catalyst accelerates the rate of a reaction and is regenerated in the process. Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. Note the definition of activation energy: it is the minimum amount of energy required for a chemical reaction to proceed either in the forward direction from reactants to products, or in the reverse direction for products to reactants.

This lowered activation energy by a catalyst results in an increase in rate as described by the Arrhenius equation (which we'll cover in detail in Chapter 7: Chemical Kinetics). Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant.

Catalysts DO NOT affect the equilibrium position in any way – it only relates to the time it takes to reach the final "destination." For example, if a reaction mixture at equilibrium has a ratio of products:reactants of 1:4, then the reaction will always proceed towards that equilibrium position of 1:4, regardless of starting conditions. Adding a catalyst will make the reaction proceed faster, but you'll still get the 1:4 product:reactant ratio. Even if the uncatalyzed reaction proceeds for days, weeks, or even months, *eventually*, the reaction mixture will reach equilibrium, the concentrations of species remain constant, but you'd again encounter the same product:reaction ratio of 1:4.

An Application of Equilibrium Concepts – The Haber Process

The interplay of changes in concentration or pressure, temperature, and the presence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \qquad \Delta H^{\circ} = -92.2\text{ kJ}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favour the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure 4.4.3).

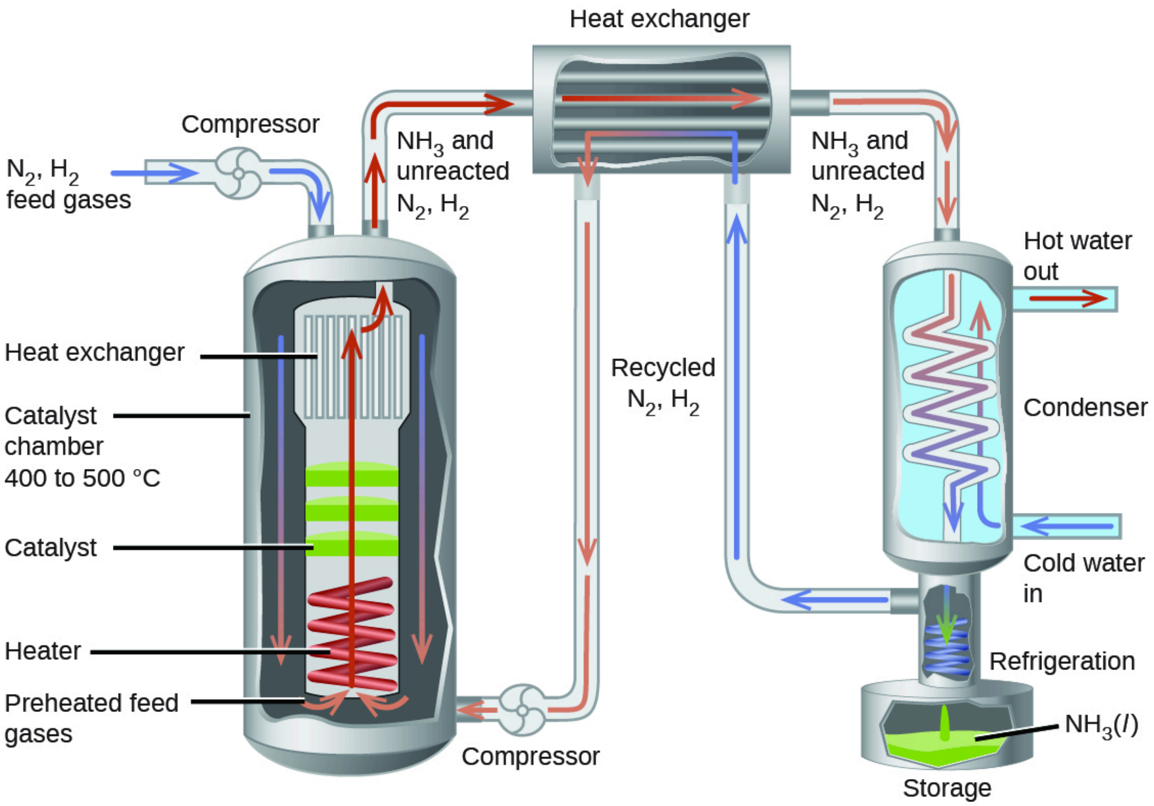


Figure 4.4.3. Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Summary – Le Châtelier's Principle

The following table summarizes how each disturbance will restore equilibrium in the system and its effect (if applicable) on *K*.

Table 4.4.1 Effects of Disturbances of Equilibrium and K

Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/ increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/ decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Example 4.4.2 – Qualitative Predictions of Equilibrium Shifts – 1

Consider the following reaction:

$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g) \Delta H^o < 0$

Explain how each of the following will affect the amount of $SO_3\,(g)$:

(a) Increase in pressure

(b) Increase in temperature

(c) Increase in the amount of $O_2\,(g)$

Solution

(a) There are three moles of gas on the reactants side and only two moles of gas on the products side. The equilibrium position will shift to decrease the total pressure exerted by the system and counteract the stress of the increase in pressure. Having fewer moles of gas present decreases the pressure. Therefore, the forward reaction is favoured, and the amount of $SO_3\,(g)$ will increase.

(b) $\Delta H^o < 0$, so the reaction is exothermic and hence produces heat and we can rewrite the chemical equilibrium equation as follows:

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g) + \textit{heat}$$

The equilibrium position will shift to counteract the increase in temperature by removing heat from the system. Therefore, the reverse reaction is favoured to yield more reactants, and correspondingly the amount of $SO_3(g)$ will decrease.

(c) The equilibrium position will shift to decrease the amount of $O_2(g)$ present to counteract the increase in $O_2(g)$. Using up excess $O_2(g)$ is favoured to decrease its amount in the system. Therefore, the forward reaction is favoured to yield more product, and the amount of $SO_3(g)$ will increase.

Check Your Learning 4.4.2 – Qualitative Predictions of Equilibrium Shifts – 1

Given the following situations, determine what will happen to the amount of H_2 that will be present in an equilibrium mixture in the reaction

$$3\,Fe\,(s) + 4\,H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4\,H_2\,(g) \quad \Delta H° = -150\text{ kJ}$$

(a) Decreasing the temperature of the mixture

(b) Introducing more $Fe(s)$

(c) Halving the volume of the container

(d) Adding a catalyst

Answer

(a) amount of $H_2(g)$ will increase; (b) no change in the amount of $H_2(g)$ (recall that solids and pure liquids have activities equal to 1 and thus have no influence on an equilibrium's position!); (c) no change in the amount of $H_2(g)$; (d) no change in the amount of $H_2(g)$

Check Your Learning 4.4.3 – Qualitative Predictions of Equilibrium Shifts – 1

Consider the equilibrium reaction

$$A\,(g) + \tfrac{1}{2}\,B\,(g) \rightleftharpoons 2\,C\,(g) \Delta H° = -52\text{ kJ}$$

Which of the following options would be most effective at encouraging the forward reaction?

(a) Remove C + add heat

(b) Increase volume + add heat

(c) Add C + remove heat

(d) Decrease volume + add heat

(e) Increase volume + add A

(f) Remove B + remove heat

Answer

(e) Increase volume + add A

In Case You're Interested...Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?

Figure 4.4.4. This species of hydrangea has flowers that can be either red or blue. Why the color difference? Source: "Hydrangea" by Janne Moren is Licensed under the Creative Commons Attribution-NonCommercial-ShareAlike 2.0 Generic.

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H_3O^+ or OH^- ions themselves that affect the color of the flowers. Rather, it is the presence of aluminum ions that causes the color change.

The solubility of various aluminum salts in soil—and thus the ability of plants to absorb the Al^{3+} ions —is dependent on the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

We will examine the effect of pH on salt solubility in more detail in Chapter 6.

Questions

★ Questions

1. The following equation represents a reversible decomposition:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

2. Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.

3. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

4. What would happen to the color of the solution in part (b) of Figure 4.4.1. if a small amount of NaOH were added and $Fe(OH)_3$ precipitated? Explain your answer.

5. The following reaction occurs when a burner on a gas stove is lit:

$$CH_4\,(g) + 2\,O_2\,(g) \rightleftharpoons CO_2\,(g) + 2\,H_2O\,(g)$$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

6. A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

$$SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

a. Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

b. Is the reaction endothermic or exothermic?

7. Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

$$N_2\,(g) + 2\,H_2\,(g) \rightleftharpoons N_2H_4\,(g) \qquad \Delta H = 95\text{ kJ}$$

8. Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4\,(g) + 6\,H_2\,(g) \rightleftharpoons 4\,PH_3\,(g) \qquad \Delta H = 110.5\text{ kJ}$$

9. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,H_2O\,(g) \rightleftharpoons 2\,H_2\,(g) + O_2\,(g) \qquad \Delta H = 484\text{ kJ}$

b. $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \qquad \Delta H = -92.2\text{ kJ}$

c. $2\,Br\,(g) \rightleftharpoons Br_2\,(g) \qquad \Delta H = -224\text{ kJ}$

d. $H_2\,(g) + I_2\,(s) \rightleftharpoons 2\,HI\,(g) \qquad \Delta H = 53\text{ kJ}$

★★ Questions

10. Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction: $H_2O\,(g) + C\,(s) \rightleftharpoons H_2\,(g) + CO\,(g)$. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

a. Write the expression for the equilibrium constant (K_C) for the reversible reaction

$$2\,H_2\,(g) + CO\,(g) \rightleftharpoons CH_3OH\,(g) \qquad \Delta H = -90.2\text{ kJ}$$

b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

c. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

e. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

f. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

11. Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

a. Write the expression for the equilibrium constant (K_C) for the reversible reaction

$$Fe_2O_3\,(s) + 3\,H_2\,(g) \rightleftharpoons 2\,Fe\,(s) + 3\,H_2O\,(g) \qquad \Delta H = 98.7\text{ kJ}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

d. What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?

e. What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?

f. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

12. Acetic acid is a weak acid that reacts with water according to this equation:

$$CH_3CO_2H\,(aq) + H_2O\,(aq) \rightleftharpoons H_3O^-\,(aq) + CH_3CO_2\,(aq)$$

Will any of the following increase the percent of acetic acid that reacts and produces CH_3CO^{2-} ion?

a. Addition of HCl

b. Addition of NaOH

c. Addition of $NaCH_3CO_2$

13. Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

$$Na^+\,(aq) + Cl^-\,(aq) + Ag^+\,(aq) + NO_3^-\,(aq) \rightleftharpoons AgCl\,(s) + Na^+\,(aq) + NO_3^-\,(aq)$$

$$\Delta H = -\,65.9\text{ kJ}$$

14. How can the pressure of water vapor be increased in the following equilibrium?

$$H_2O\,(l) \rightleftharpoons H_2O\,(g) \qquad \Delta H = 41\text{ kJ}$$

15. Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.

$$2\,Ag^+\,(aq) + SO_4^{2-}\,(aq) \rightleftharpoons Ag_2SO_4\,(s)$$

Which of the following will occur?

a. Ag^+ or SO_4^{2-} concentrations will not change.

b. The added silver sulfate will dissolve.

c. Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine.

d. The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

16. The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization ($HX \rightleftharpoons H^+ + X^-$)?

Answers

1. The amount of $CaCO_3$ must be so small that PCO_2 is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full PCO_2 required for equilibrium.

2. When there is an unequal amount of gases in the products compared to the reactants would have an effect on the system at equilibrium.

3. The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

4. The SCN^- would start being removed from reaction, and the system would shift towards the reactants. Solution will begin to look like solution (a).

5. No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

6. (a) As the temperature increase, $P \propto T$, pressure increases and the reaction shifts towards the products decreasing the equilibrium constant, (b) Exothermic

7. Add N_2; add H_2; decrease the container volume; heat the mixture.

8. Increase temperature, Increase pressure, Introduce more hydrogen gas, Decrease Volume, removal of PH_3

9. (a) (i) shift to the right, (ii) shift to the left, (b) (i)shift to the left, (ii) shift to the right, (c) (i) shift to the left, (ii) shift to the right, (d) (i) shift to the right, (ii) shift to the left

10.

a.
$$K_C = \frac{[CH_3OH]}{[H_2]^2 [CO]}$$

b. $[H_2]$ increases, $[CO]$ decreases, $[CH_3OH]$ increases

c. $[H_2]$ increases, $[CO]$ decreases, $[CH_3OH]$ decreases

d. $[H_2]$ increases, [CO] increases, $[CH_3OH]$ increases

e. $[H_2]$ increases, [CO] increases, $[CH_3OH]$ decreases

f. no changes

11. (a) $K_C = [H_2O]^3 / [H_2]^3$, (b) no effect, (c) shift towards the products, (d) shift towards the products, (e) reaction is not affected by pressure, (f) shift towards the products

12. B

13. Add NaCl or some other salt that produces Cl– to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl (*s*).

14. Decrease the temperature

15. A

16. α-alanine

CHAPTER 5

5.1 – ACID-BASE DEFINITIONS & CONJUGATE ACID-BASE PAIRS

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the colour of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. They have opposing chemical properties and are able to neutralize one another to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations in the table below.

Table 5.1.1. General Properties of Acids and Bases.

Acids	**Bases**
Produce a piercing pain in a wound	Give a slippery feel
Taste sour	Taste bitter
Are colourless when placed in phenolphthalein (an indicator)	Are pink when placed in phenolphthalein (an indicator)
Are red on blue litmus paper (a pH indicator)	Are blue on red litmus paper (a pH indicator)
Have a pH < 7	Have a pH > 7
Produce hydrogen gas when reacted with metals	
Produce carbon dioxide when reacted with carbonates	
Common examples: lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common examples: soap, toothpaste, bleach, cleaning age limewater, ammonia water, sodium hydroxide

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are electrolytes, with strong acids and bases behaving as strong electrolytes *versus* weak acids and bases behaving as weak electrolytes.

In chemistry, acids and bases have been defined differently by three sets of theories: First is the Arrhenius definition, which relies on the idea that acids are substances that dissociate (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide ($OH^−$) ions in solution. The other two definitions, discussed in detail in this chapter, include the Brønsted-Lowry definition, which defines acids as proton (H^+) donors and bases as proton acceptors, and the Lewis Theory of acids and bases, which states that acids are electron pair acceptors while bases are electron pair donors. As shown in Figure 5.1.1, as the level of theory expands to include more substances covered under each definition, the closer the theory comes to accurately describing actual acid-base chemistry.

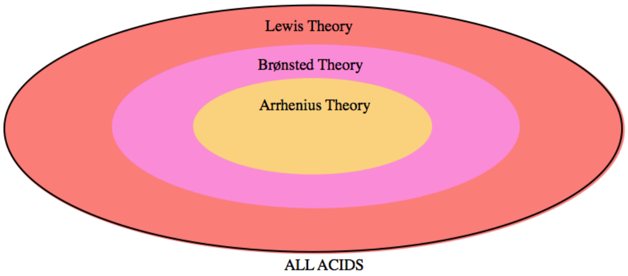


Figure 5.1.1. A Venn diagram representing the three levels of acid classification theory. Arrhenius Theory

is the least accurate, and covers only a small subset of substances. Brønsted-Lowry expands upon Arrhenius' definitions and thus is slightly broader. Lewis Theory, the most extensive explanation, most accurately describes all acid-base behaviour.

Arrhenius Definition of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

According to this theory, an **Arrhenius acid** is a compound that increases the concentration of H^+ ions when added to water. This process is represented in what is known as a dissociation reaction in a chemical equation. For example:

$$HCl\,(aq) \rightarrow H^+\,(aq) + Cl^-\,(aq)$$

In this reaction, hydrochloric acid (HCl) *dissociates* (breaks apart) into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution.

An **Arrhenius base** is a compound that increases the concentration of hydroxide ions, OH^-, when added to water. For example:

$$NaOH\,(aq) \rightarrow Na^+\,(aq) + OH^-\,(aq)$$

In this reaction, an aqueous solution of sodium hydroxide (NaOH) dissociates into sodium ions (Na^+) and hydroxide ions (OH^-) when dissolved in water.

As you can imagine, this Arrhenius level of theory is quite limited. The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, a solution of pure H_2SO_4 or HCl dissolved in toluene would not be considered to be acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment, and the Arrhenius theory excludes many substances known to display acid-base character.

Another flaw in Arrhenius's theory is its reliance on the concept of *dissociation* of acids, *i.e.* an acid "HX" breaking apart in water to form H^+ and X^- ions. We now know that the H^+ cation does not actually exist in this form in aqueous solution; it is more accurately depicted as the hydronium ion, H_3O^+.

Therefore, since the Arrhenius level of theory can *only* describe acids and bases in an aqueous environment, relies on the flawed concept of acid dissociation, and excludes many substances based on its restrictive definitions, this theory can generally be disregarded moving forward in our discussion.

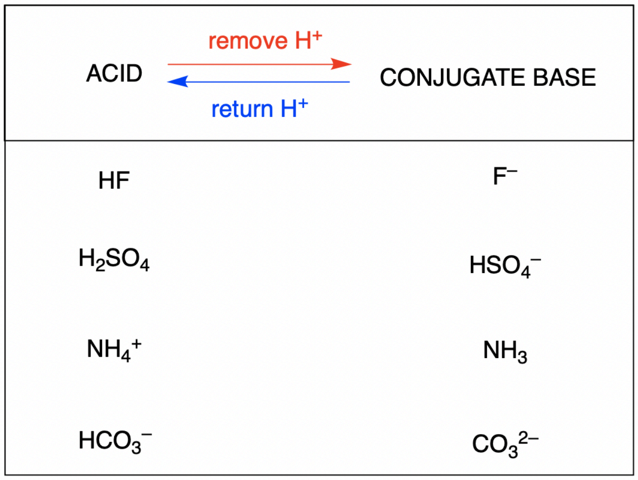
Brønsted-Lowry Definition of Acids and Bases

In 1923, the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry expanded upon Arrhenius's ideas by broadening the definitions of acids and bases. The Brønsted-Lowry theory centers on the proton, H^+. A proton is what remains when the most common isotope of hydrogen, ^{1}H, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is thus defined as the *transfer of a proton* from a proton donor (acid) to a proton acceptor (base).

Using these very simple definitions, the Brønsted-Lowry level of theory covers the large majority of known acid-base behaviour, and thus this theory can be successfully applied for most of this chapter (and this course). However, to be inclusive to *all* acids and bases, an even more general theory is required. In Section 5.6 of this text, we will introduce the final and most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

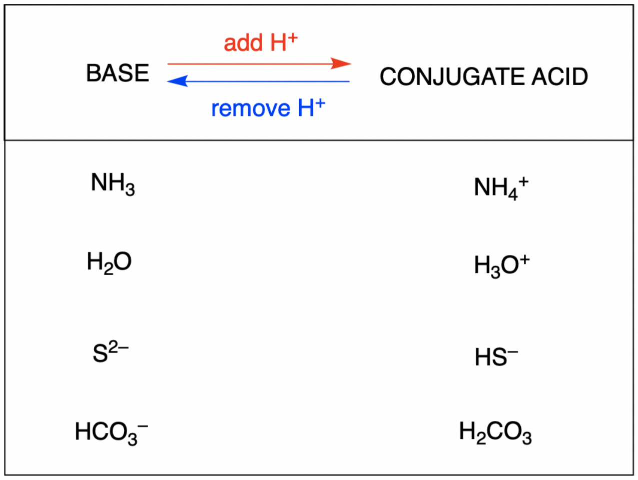
Acids may be inorganic or organic substances (*e.g.* HCl *vs* acetic acid, CH_3COOH), neutral substances or ions (*e.g.* H_2O *vs* HSO_4^-). Each of these species contains at least one hydrogen atom; to be defined as a Brønsted-Lowry acid, the substance must be able to donate this atom to another substance in the form of a proton, H^+. Bases may also be inorganic or organic substances (*e.g.* NaOH *vs* methyl amine, CH_3NH_2), neutral substances or ions (*e.g.* NH_3 *vs* $[Al(H_2O)_5OH]^{2+}$). Each of these examples are capable of accepting a proton and may therefore be classified as Brønsted-Lowry bases. The most familiar and recognizable bases tend to be inorganic ionic compounds which contain the hydroxide ion, such as NaOH and $Ca(OH)_2$.

The **conjugate base** of an acid is what remains after the acid has donated a proton. This species is a base because it can accept a proton to re-form the original acid:



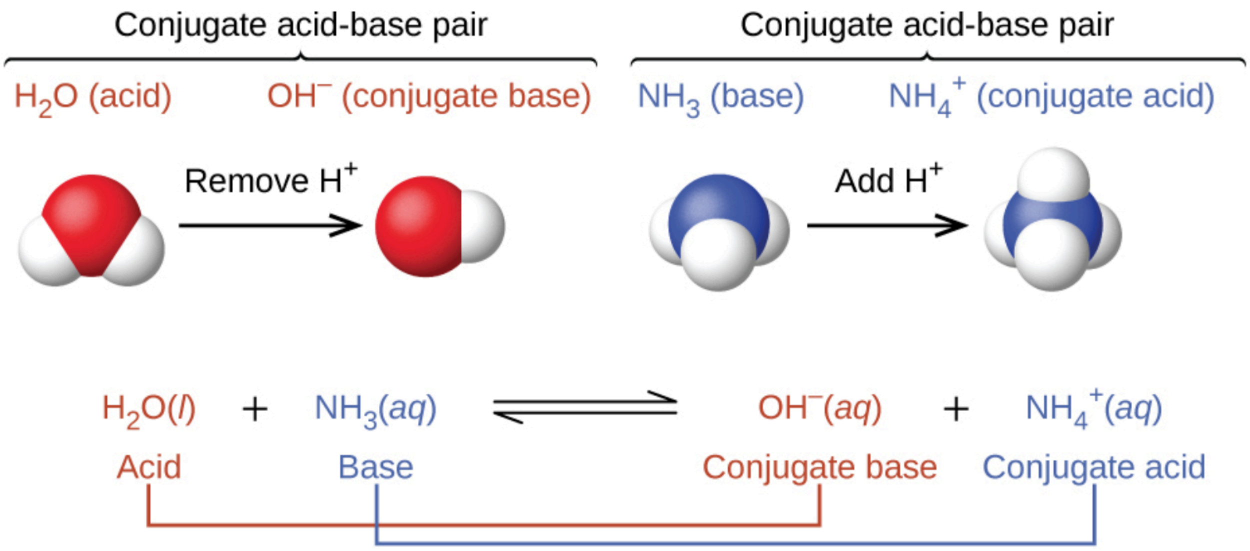
ACID	$\xrightleftharpoons[\text{return } H^+]{\text{remove } H^+}$	CONJUGATE BASE
HF		F^-
H_2SO_4		HSO_4^-
NH_4^+		NH_3
HCO_3^-		CO_3^{2-}

The **conjugate acid** of a base is what results after the base has accepted a proton. This species is an acid because it can give up a proton to re-form the original base:

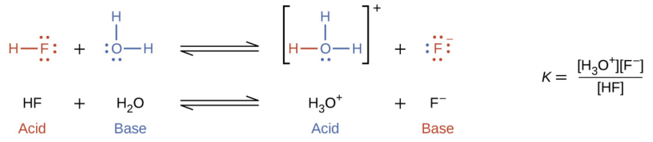


BASE	$\underset{\text{remove } H^+}{\overset{\text{add } H^+}{\rightleftarrows}}$	CONJUGATE ACID
NH_3		NH_4^+
H_2O		H_3O^+
S^{2-}		HS^-
HCO_3^-		H_2CO_3

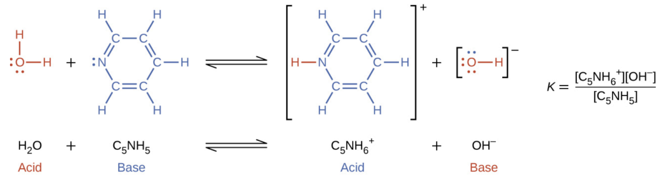
In the two schemes above, the behaviour of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the *transfer* of protons between acids and bases. This is quite useful when tasked with exercises asking you to classify reactions, such as those done in Section 1.4 – Solution Stoichiometry when we discussed the three types of chemical reactions covered in CHM 1311: acid-base, redox and precipitation reactions. If you can identify all four terms in a proton-transfer reaction (an acid, a base, a conjugate acid, and a conjugate base), you can be certain that it is a Brønsted-Lowry acid-base reaction. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



The reaction between a Brønsted-Lowry acid and base is called **ionization** (note how this differs slightly from the term *dissociation* defined previously). More specifically, when we add an acid to water, an **acid ionization** occurs, in which protons are transferred from the acid molecules to the water molecules. For example, when hydrogen fluoride dissolves in water and *ionizes*, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



When we add a base to water, a **base ionization** reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter.

All acid-base reactions *must* have four terms in the chemical equation: an acid, a base, a conjugate acid, and conjugate base. If this is the case, then it can only be an acid-base reaction and not any other reaction type.

Since an acid-base reaction starts with two species and finishes two species, we should not use the term "*dissociation*" in the context of acids and bases (e.g. the dissociation of an acid in solution). The reason is because the term implies that one species dissociates into two, while in reality the acid-base reaction involves a proton transfer between two species.

Often when describing an acid-base reaction, we can refer to the portion of acid or base that does not ionize in solution (*i.e.* it remains in its neutral form) as either *non*ionized or *un*ionized. In this text, we will use the latter term, but be prepared to recognize both adjectives when studying chemistry.

How can you spot the difference between a chemist and a plumber? Ask them to pronounce the word UNIONIZED!

Questions

★ Questions

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.
2. Write equations that show $H_2PO_4^-$ acting both as an acid and as a base.
3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) H_3O^+

(b) HCl

(c) NH_3

(d) CH_3CO_2H

(e) NH_4^+

(f) HSO_4^-

4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3

(b) PH_4^+

(c) H_2S

(d) CH_3CH_2COOH

(e) $H_2PO_4^-$

(f) HS^-

5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) HS^-

(b) PO_4^{3-}

(c) NH_2^-

(d) C_2H_5OH

(e) O^{2-}

(f) $H_2PO_4^-$

6. What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) H_2S

(b) $H_2PO_4^-$

(c) PH_3

(d) HS^-

(e) HSO_3^-

(f) $H_3O_2^+$

(g) H_4N_2

(h) CH_3OH

7. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

(b) $CN^- + H_2O \rightarrow HCN + OH^-$

(c) $H_2SO_4 + Cl^- \rightarrow HCl + HSO_4^-$

(d) $HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$

(e) $O_2^- + H_2O \rightarrow 2\ OH^-$

(f) $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \rightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $H_2S + NH_2^- \rightarrow HS^- + NH_3$

Answers

1. One example for NH_3 as a conjugate acid: $NH_2^- + H^+ \rightarrow NH_3$; as a conjugate base: NH_4^+ *(aq)* + OH^- *(aq)* → NH_3 *(aq)* + H_2O *(l)*

2. As an acid: $H_2PO_4^- + H^+ \rightarrow H_3PO_4$; as a base: $H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2$

3. (a) H_3O^+ *(aq)* → H^+ *(aq)* + H_2O *(l)*

(b) HCl *(l)* → H^+ *(aq)* + Cl^- *(aq)*

(c) $NH_3 \rightarrow NH_2^- + H^+$

(d) CH_3CO_2H *(aq)* → H^+ *(aq)* + $CH_3CO_2^-$ *(aq)*

(e) NH_4^+ *(aq)* → NH_3 *(aq)* + H^+ *(aq)*

(f) HSO_4^- *(aq)* → H^+ *(aq)* + SO_4^{2-} *(aq)*

4. (a) $HNO_3 \rightarrow H^+ + NO_3^-$

(b) $PH_4^+ \rightarrow H^+ + PH_3$

(c) $H_2S \rightarrow H^+ + HS^-$

(d) $CH_3CH_2COOH \rightarrow H^+ + CH_3CH_2COO^-$

(e) $H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$

(f) $HS^- \rightarrow H^+ + S^{2-}$

5. (a) H_2O *(l)* + H^+ *(aq)* → H_3O^+ *(aq)*

(b) OH^- *(aq)* + H^+ *(aq)* → H_2O *(l)*

(c) NH_3 *(aq)* + H^+ *(aq)* → NH_4^+ *(aq)*

(d) CN^- *(aq)* + H^+ *(aq)* → HCN *(aq)*

(e) S^{2-} *(aq)* + H^+ *(aq)* → HS^- *(aq)*

(f) $H_2PO_4^-$ *(aq)* + H^+ *(aq)* → H_3PO_4 *(aq)*

6. (a) Conjugate acid: H_3S^+ ; Conjugate base: HS^-

(b) Conjugate acid: H_3PO_4 ; Conjugate base: HPO_4^{2-}

(c) Conjugate acid: PH_4^+ ; Conjugate base: PH_2^-

(d) Conjugate acid: H_2S ; Conjugate base: S^{2-}

(e) Conjugate acid: H_2SO_3 ; Conjugate base: SO_3^{2-}

(f) Conjugate acid: $H_4O_2^{2+}$; Conjugate base: H_2O_2

(g) Conjugate acid: $H_5N_2^+$; Conjugate base: $H_3N_2^-$

(h) Conjugate acid: $CH_3OH_2^+$; Conjugate base: CH_3O^-

7. The labels are Bronsted-Lowry acid = BA; its conjugate base = CB; Bronsted-Lowry Base = BB; its conjugate acid = CA.

(a) HNO_3 (BA), H_2O (BB), H_3O^+ (CA), NO_3^- (CB)

(b) CN^- (BB), H_2O (BA), HCN (CA), OH^- (CB)

(c) H_2SO_4 (BA), Cl^- (BB), HCl (CA), HSO_4^- (CB)

(d) HSO_4^- (BA), OH^- (BB), SO_4^{2-} (CB), H_2O (CA)

(e) O^{2-} (BB), H_2O (BA), OH^- (CA *and* CB)

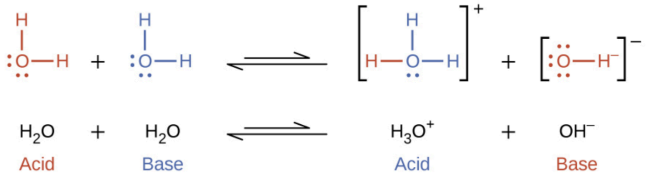
(f) $[Cu(H_2O)_3(OH)]^+$ (BB), $[Al(H_2O)_6]^{3+}$ (BA), $[Cu(H_2O)_4]^{2+}$ (CA), $[Al(H_2O)_5(OH)]^{2+}$ (CB)

(g) NH_2^- (BB), HS^- (CB), NH_3 (CA)

5.2 – AUTOIONIZATION OF WATER & PH/POH

The Autoionization of Water

In the preceding section we saw examples where water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or indeed any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**.

Pure water undergoes autoionization to a very slight extent. Only about two out of every billion (10^9) molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the **ion-product constant for water (K_w)**:

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq) \quad K_w = [H_3O^+][OH^-]$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 5.2.1 – Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0\times10^{-14}$$

So:

$$[H_3O^+] = [OH\text{-}] = \text{sqrt}(\ 1.0\times10^{-14}\ ) = 1.0\times10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal 1.0×10^{-7} M.

Check Your Learning 5.2.1 – Ion Concentrations in Pure Water

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}$ M

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. The following example demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 5.2.2 – The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water at equilibrium has a hydronium ion concentration of 2.0×10^{-6} M. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-] = 1.0\times10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = K_w/[H_3O^+] = (1.0\times10^{-14})/(2.0\times10^{-6}\ M) = 5.0\times10^{-9}\ M$$

The hydroxide ion concentration in water is reduced to 5.0×10^{-9} M as the hydronium ion concentration increases to 2.0×10^{-6} M. This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water. This is best visualized with a seesaw analogy, as shown in Figure 5.2.1.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0\times10^{-6}\ M)(5.0\times10^{-9}\ M) = 1.0\times10^{-14}$$

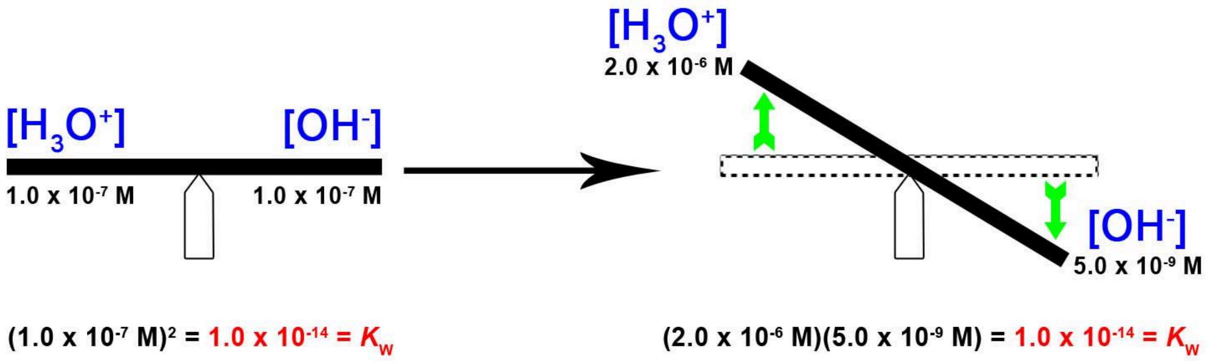


Figure 5.2.1. The ion-product constant is $K_W = 1.0 \times 10^{-14}$ the whole time at 25°C. In pure water, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$. When we increase $[H_3O^+]$, like a seesaw, this is balanced and counteracted by a decrease in $[OH^-]$ – this keeps K_W constant.

Check Your Learning 5.2.2 – The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$[H_3O^+] = 1 \times 10^{-11}$ M

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be **amphiprotic**. Another term used to describe such species is **amphoteric**, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)$$

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq)$$

Example 5.2.3 – Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

(a) acting as an acid with OH^-

(b) acting as a base with HI

Solution

$$HSO_3^-(aq) + OH^-\,(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O\,(l)$$

$$HSO_3^-(aq) + HI\,(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$$

Check Your Learning 5.2.3 – Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $H_2PO_4^-$

(a) as a base with HBr

(b) as an acid with OH^-

Answer

$$H_2PO_4^-(aq) + HBr\,(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$$

$$H_2PO_4^-(aq) + OH^-\,(aq) \rightleftharpoons HPO_4^{2-}\,(aq) + H_2O\,(l)$$

pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$pX = -\log(X)$$

The **pH** of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$pH = -\log[H_3O^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[H_3O^+] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH**:

$$pOH = -\log[OH^-]$$

or

$$[OH^-] = 10^{-pOH}$$

NOTE:

The p-function is not an entirely different concept – it simply serves as a logarithmic shortcut to express very large/small numbers in numbers that are more "tangible" and easier to work with. For example, for a particular solution of H_2SO_4*(aq)*, to say: "Its pH is two" is significantly easier than saying: "Its hydronium ion concentration is point zero one molar." Remember that both phrases have the exact same correct meaning; hence, the p-function (in this case pH) is much more convenient to use.

Finally, the relation between these two ion concentrations expressed as p-functions is easily derived from the K_w expression:

$$K_w = [H_3O^+][OH^-]$$

$$-\log(K_w) = -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + -\log[OH^-]$$

$$pK_w = pH + pOH$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = pH + pOH$$

As was shown in the reaction of a Brønsted-Lowry acid with water, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} M at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00$$

$$pOH = -\log[OH-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0 × 10^{-7} M and hydroxide ion molarities less than 1.0 × 10^{-7} M (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than 1.0 × 10^{-7} M and hydroxide ion molarities greater than 1.0 × 10^{-7} M (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C (Figure 5.2.2). For example, the "Check Your Learning" exercise from the previous topic showed the hydronium molarity of pure water at 80 °C is 4.9 × 10^{-7} M, which corresponds to pH and pOH values of:

$$\text{pH} = \text{-log}[H_3O^+] = \text{-log}(4.9\times10^{-7}) = 6.31$$

$$\text{pOH}\text{=-log}[OH^-] = \text{-log}(4.9\times10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at non standard temperatures, such as enzyme reactions in warm-blooded organisms.

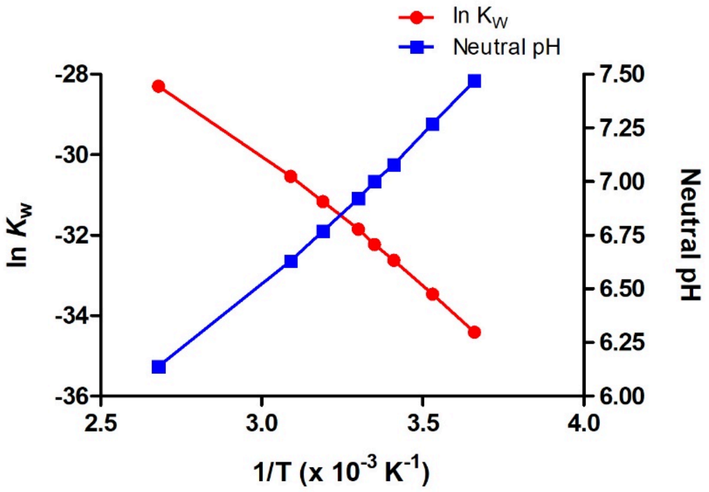


Figure 5.2.2. Like any other equilibrium constant, the autoionization constant, K_W, is temperature-dependent. Hence, a van't Hoff plot can be constructed to see the variation of K_W over *T*. The graph also plots the variation of the pH of neutral pure water over varying temperatures.

Unless otherwise noted, references to pH values, such as those in Table 5.2.1 below, are presumed to be those at standard temperature (25 °C).

Table 5.2.1 Summary of Relations for Acidic, Basic, and Neutral Solutions

Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	$pH < 7$
neutral	$[H_3O^+] = [OH^-]$	$pH = 7$
basic	$[H_3O^+] < [OH^-]$	$pH > 7$

NOTE:

Keep in mind that pH is simply shorthand and a reference of the $[H_3O^+]$ concentration. Therefore, *negative pH values are possible* and fall under the acidic solutions of $pH < 7$. Substances with a $pH > 14$ are also possible and fall under the category of basic solutions ($pH > 7$).

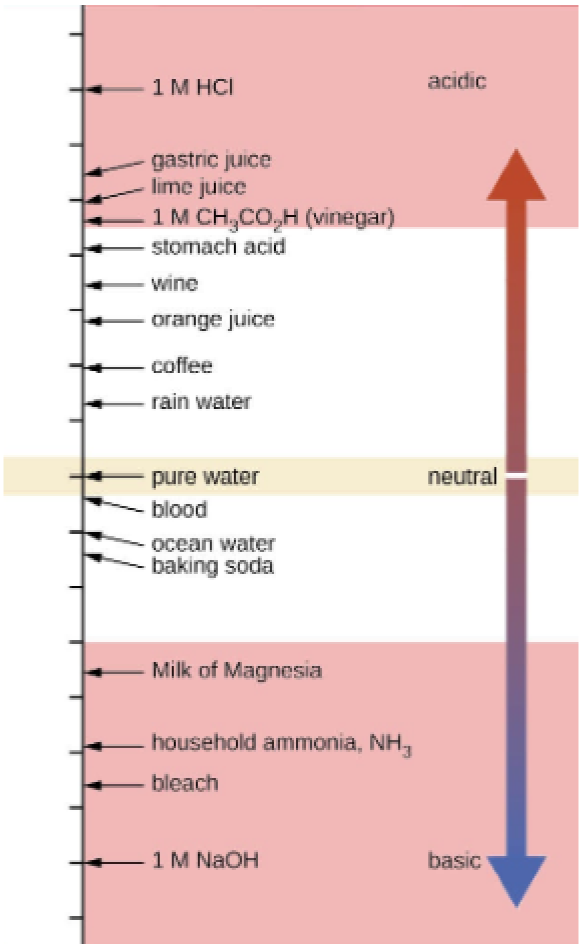
$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH	Sample Solution
10^{1}	10^{-15}	-1	15	
10^{0} or 1	10^{-14}	0	14	
10^{-1}	10^{-13}	1	13	
10^{-2}	10^{-12}	2	12	
10^{-3}	10^{-11}	3	11	
10^{-4}	10^{-10}	4	10	
10^{-5}	10^{-9}	5	9	
10^{-6}	10^{-8}	6	8	
10^{-7}	10^{-7}	7	7	
10^{-8}	10^{-6}	8	6	
10^{-9}	10^{-5}	9	5	
10^{-10}	10^{-4}	10	4	
10^{-11}	10^{-3}	11	3	
10^{-12}	10^{-2}	12	2	
10^{-13}	10^{-1}	13	1	
10^{-14}	10^{0} or 1	14	0	
10^{-15}	10^{1}	15	-1	

Figure 5.2.2. The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example 5.2.4 – Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} M?

Solution

$$pH = -\log[H_3O^+]$$
$$pH = -\log(1.2\times10^{-3})$$
$$pH = -(-2.92) = 2.92$$

(The use of logarithms is explained in Appendix C. Recall that, as we have done here, when taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Check Your Learning 5.2.4 – Calculation of pH from $[H_3O^+]$

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of 2.0×10^{-6} M, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 5.2.4 – Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$\text{pH} = -\log[H_3O^+] = 7.3$$
$$\log[H_3O^+] = -7.3$$
$$[H_3O^+] = 10^{-7.3} \text{ or} [H3O+] = \text{antilog of } -7.3$$
$$[H_3O^+] = 5 \times 10^{-8}\ \text{M}$$

(On a calculator take the antilog, or the “inverse” log, of −7.3, or calculate $10^{-7.3}$.)

Check Your Learning 5.2.5 – Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \rightleftharpoons H_2CO_3\,(aq)$$
$$H_2CO_3\,(aq) + H_2O(l) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$$
$$H_2SO_4(aq) + H_2O(aq) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 5.2.3.). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

If you’re interested in this subject and want to learn more about this topic and/or other environmental topics and their relation to chemistry, the Department of Chemistry and Biomolecular Sciences of the Faculty of Science offers the course CHM 2313: Environmental Chemistry in the winter semester.

Figure 5.2.3. (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)

Example 5.2.5 – Calculation of pOH

What are the pOH and the pH of a 0.0125 M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely ionizes when dissolved in dilute solution,

yielding $[OH^-] = 0.0125$ M:

$$pOH = -\log[OH^-] = -\log(0.0125)$$

$$= -(-1.903)=1.903$$

The pH can be found from the pOH:

$$\text{pH}+\text{pOH} = 14.00$$

$$\text{pH}= 14.00-\text{pOH} = 14.00-1.903 =12.10$$

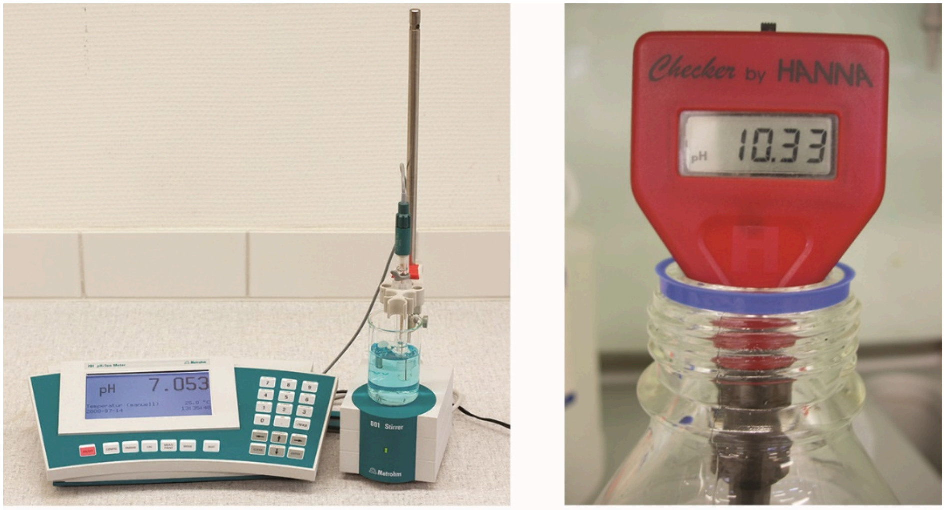
Check Your Learning 5.2.6 – Calculation of pOH

The hydronium ion concentration of vinegar is approximately 4×10^{-3} M. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6, pH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The most accurate way of ascertaining the pH of an acidic solution is by titration. The second most effective tool is by directly measuring using a pH meter (Figure 5.2.4.).



(a) (b)

Figure 5.2.4. (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using coloured indicators (Figure 5.2.5.), which give the least accuracy in pH determination.

Figure 5.2.5. (a) A universal indicator assumes a different colour in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1 M solutions of progressively weaker acids: HCl (pH = 1), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1 M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colours in solutions of differing pH values. (credit: modification of work by Sahar Atwa)

Questions

★ Questions

1. What is the relationship between $[H^+]$ and K_w? Write a mathematical expression that relates them.

2. Write the chemical equation for the autoionization of water and label the conjugate acid-base pairs.

3. If HNO_2 is ionized only to an extent of 0.445%, what are $[H^+]$ and $[OH^-]$ in a 0.307 M solution of HNO_2?

4. Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+]$ = 1.7 × 10–7 M. K_w is 2.9×10^{-14} at 40 °C.

5. The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

6. The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

7. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 M HCl

(b) 0.0143 M NaOH

(c) 3.0 M HNO_3

(d) 0.0031 M $Ca(OH)_2$

8. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.000259 M $HClO_4$

(b) 0.21 M NaOH

(c) 0.000071 M $Ba(OH)_2$

(d) 2.5 M KOH

9. What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

10. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

11. Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 5.2.2. for useful information.

12. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 5.2.2. for useful information.

13. The hydronium ion concentration in a sample of rainwater is found to be 1.7×10^{-6} M at 25 °C. What is the concentration of hydroxide ions in the rainwater?

14. The hydroxide ion concentration in household ammonia is 3.2×10^{-3} M at 25 °C. What is the concentration of hydronium ions in the solution?

Answers

1. $[H^+] = K_w[OH^-]$

2. $H_2O + H_2O \rightarrow H_3O^+ + OH^-$; H_2O/H_3O^+ and H_2O/OH^-

3. $[H^+] = 0.00137$ M; $[OH^-] = 7.32 \times 10^{-12}$ M

4. In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C, $[H_3O^+] = [OH^-] = (2.910–14)*(1/2) = 1.7 \times 10^{-7}$ M

5. $[H_3O^+] = [OH^-] = 1.703 \text{ x } 10^{-7}$ M, pOH = pH = 6.77

6. $x = 3.051 \times 10^{-7}$ M $= [H_3O^+] = [OH^-]$, pH = −log(3.051) × 10^{-7} = −(−6.5156) = 6.5156, pOH = pH = 6.5156

7. (a) pH = 0.699, pOH = 13.3, (b) pH = 12.15, pOH = 1.85, (c) pH = -0.477, pOH = 14.5, (d) pH = 12.8, pOH = 1.2

8. (a) pH = 3.587; pOH = 10.413; (b) pH = 0.68; pOH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pH = −0.40; pOH = 14.4

9. pOH = 14.301, pH = -0.301

10. $[H_3O^+]= 3.0 \times 10^{-7}$ M; $[OH^-] = 3.3 \times 10^{-8}$ M

11. $[H_3O^+]= 3.162 \text{ x } 10^{-4}$ M; $[OH^-] = 3.162 \text{ x } 10^{-11}$ M

12. $[H_3O^+]= 1 \times 10^{-2}$ M; $[OH^-] = 1 \times 10^{-12}$ M

13. $[OH^-] = 5.9 \times 10^{-9}$ M

14. $[OH^-] = 3.1 \times 10–12$ M

5.3 – ACID-BASE STRENGTH

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$HA\ (aq) + H_2O\ (aq) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$

Water is the base that reacts with the acid HA, A^- is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A **strong acid** yields 100% of H_3O^+ and A^- when the acid ionizes in water; Figure 5.3.1 lists several strong acids. If we start with 0.1 M HCl, at equilibrium we get 0.1 M H_3O^+ and 0.1 M Cl^-. Based on the Brønsted-Lowry definition, as a strong acid, HCl is a very good proton donor. For a reaction of a *strong* acid with water, the general chemical equation above applies, except the equilibrium symbol is usually replaced with a one-way arrow to indicate that the reaction goes entirely to completion:

$$HA\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + A^-\ (aq)$$

A **weak acid** gives amounts of H_3O^+ and A^- that represent *much less* than 100% ionization. Hence, referring back to the Brønsted-Lowry definition, we can say that weak acids are poor proton donors.

For a reaction of a *weak* acid with water, the general chemical equation first indicated in this section applies – we use an equilibrium arrow to indicate that the reaction isn't to completion and that at equilibrium both reactants are products are present:

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$

Strong Acids	**Strong Bases**
$HClO_4$ perchloric acid	LiOH lithium hydroxide
HCl hydrochloric acid	NaOH sodium hydroxide
HBr hydrobromic acid	KOH potassium hydroxide
HI hydroiodic acid	$Ca(OH)_2$ calcium hydroxide
HNO_3 nitric acid	$Sr(OH)_2$ strontium hydroxide
H_2SO_4 sulfuric acid	$Ba(OH)_2$ barium hydroxide

Figure 5.3.1. Some of the common strong acids and bases are listed here.

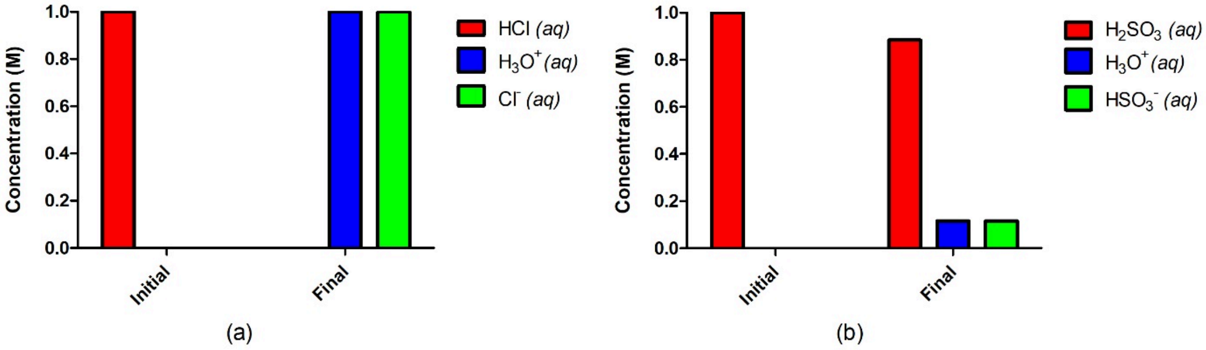


Figure 5.3.2. A strong acid such as HCl in water (a) will completely ionize and go to completion with no reactant remaining, where 1.0 M of HCl will yield 1.0 M H_3O^+ and 1.0 M Cl^-. A weak acid such as H_2SO_3 (b), on the other hand, will only partially ionize in water, giving us an equilibrium mixture of reactants and products.

If you recall back to the previous chapter on chemical equilibria, you'll notice that this notion of ratio of products to reactants is exactly how we express equilibrium constants! Therefore, we can use this knowledge to determine the relative strengths of acids by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize completely, and so yield higher concentrations of hydronium ions than do weaker acids. When writing an equation for the ionization of a strong acid, a one-way arrow is used in order to show that it is a complete reaction. While any acid with less than 100% ionization is technically classified as a 'weak acid', for most weak acids, at equilibrium only a very small fraction of the acid will ionize. The equilibrium constant for an acid is called the **acid-ionization constant, K_a**. For the reaction of an acid HA:

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

we write the equation for the ionization constant as:

$$K_a = ([H_3O^+][A^-])/[HA]$$

where the concentrations are those at equilibrium. Recall from Chapter 4 that although water is a reactant in the reaction, it is a liquid, its activity is equal to 1, and thus it does not appear in the K_a expression. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the neutral, unionized acid, HA. Thus a stronger acid has a larger ionization constant than a weaker acid, and the ionization constants increase as the strengths of the acids increase. Table 5.3.1, found later in this section, lists values of ionization constants of a few common weak acids; a more complete table of K_a values can be found in Appendix H.

To illustrate, consider the three acid equilibria below: the acid-ionization constants indicate that the order of acid strength for these acids is: $CH_3CO_2H < HNO_2 < HSO_4^-$.

$$CH_3CO_2H\,(aq) + H_2O\,(aq) \rightarrow H_3O^+\,(aq) + CH_3CO_2^-\,(aq)\ K_a = 1.8 \times 10^{-5}$$

$$HNO_2\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + NO_2^-\,(aq)\ K_a = 4.6 \times 10^{-4}$$

$$HSO_4^-\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + SO_4^{2-}\,(aq)\ K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\text{ionization} = ([H_3O^+]_{eq}/[HA]_0) \times 100\%$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually *decreases with increasing acid concentration*...but why?

Let's take a look back at the equilibrium for acid ionization, again using HA as our generic weak acid with a K_a value of 1.00×10^{-5}:

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq) \quad K_a = 1.00 \text{ x } 10^{-5}$$

Imagine we have 1 L of water and we add exactly 0.100 mol of this weak acid, giving an initial value of $[HA]_0$ = 0.100 M. Following the ICE table method shown in Chapter 4, we find that, at equilibrium, the solution contains 0.00100 M H_3O^+, resulting in a percent ionization of exactly 1.0% (take a moment to confirm this calculation for yourself). Now imagine we increase the amount of initial acid, by adding another 0.100 mol to the existing solution, giving a total of 0.200 mol HA in 1 L of water, thus $[HA]_0$ = 0.200 M. This *second* addition of 0.100 mol HA is trying to ionize in a solution that *already contains* 0.00100 M H_3O^+ produced from the *first* 0.100 mol of HA added. According to Le Chatelier's Principle, increasing the amount of a product shifts the equilibrium towards reactants. Therefore, *trying to produce H_3O^+ in a solution that already contains some H_3O^+ is disfavoured.* In other words, the presence of some H_3O^+ from the first addition of 0.100 mol HA inhibits the ionization of the second addition of 0.100 mol HA. We can confirm this by redoing our ICE table calculation: a value of $[HA]_0$ = 0.200 M yields an equilibrium concentration of 0.00141 M H_3O^+ and a percent ionization of 0.71% (again, you should confirm these values yourself). Notice how the *total amount* of H_3O^+ at equilibrium has indeed increased (because we added more HA), but the *fraction that ionized* has gotten smaller: this is Le Chatelier's Principle in action!

This is a very important concept, so it is prudent to emphasize it again, as illustrated in Figure 5.3.3 below. This figure shows the percent ionization and the equilibrium concentration of H_3O^+ for the ionization of nitrous acid, HNO_2:

$$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq) \quad K_a = 5.6 \text{ x } 10^{-4}$$

Increasing the initial concentration of HNO_2 *will increase* the amount of H_3O^+ produced at equilibrium. However, as we add more and more nitrous acid, we *further inhibit* the ionization, instead favouring the reverse reaction. Therefore, what is being directly affected isn't the final equilibrium concentration of H_3O^+ (which keeps increasing) but rather the actual *extent of acid ionization* – what fraction of the acid actually ionizes successfully in solution. So, in conclusion, as $[HNO_2]_0$ increases, $[H_3O^+]_{eq}$ increases, but the *percent ionization* of HNO_2 decreases.

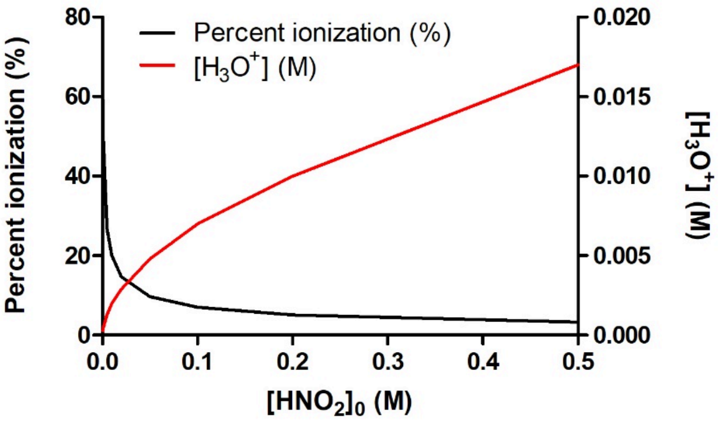


Figure 5.3.3. As the concentration of HNO_2 increases in aqueous solution, the concentration of H_3O^+ produced increases as well; however, the fraction of the original concentration that is ionizing is decreasing, as indicated by the decrease in percent ionization.

Try it For Yourself – Percent Ionization and $[H_3O^+]_{eq}$ against Initial Acid Concentration

The K_a value for benzoic acid is approximately 6.25 × 10^{-5}. The equilibrium equation for the ionization of benzoic acid is as follows:

$$C_6H_5COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons C_6H_5COO^-{}_{(aq)} + H_3O^+{}_{(aq)}$$

Assume that K_a is constant and that you only initially start with reactant (i.e. benzoic acid). Using a spreadsheet software (*e.g.* Microsoft Excel, Google Sheets):

Determine $[H_3O^+]_{eq}$ and the percent ionization at the following initial concentrations of benzoic acid: 0.005 M, 0.010 M, 0.020 M, 0.025 M, 0.050 M, 0.075 M, 0.10 M, 0.25 M, 0.5 M, 1.0 M. (*Hint*: Recall that acid ionization is an equilibrium reaction…use equilibrium-reaction problem solving to assist you).

Using this data, plot a graph of $[C_6H_5COOH]_0$ (initial concentration of benzoic acid) versus $[H_3O^+]_{eq}$ on one *y*-axis and percent ionization on another *y*-axis.

Do you notice any trends? Can you explain them?

Example 5.3.1 – Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125 M solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$([H_3O^+]_{eq}/[HNO_2]_0)\times100\%$$

The chemical equation for the ionization of the nitrous acid is:

$$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq)\;K_a = 5.6 \text{ x } 10^{-4}$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}$ M, so that percent ionization is:

$$8.1\times10^{-30.125}\times100\%=6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Check Your Learning 5.3.1 – Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.10 M solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The general reaction of a Brønsted-Lowry base with water is given by:

$$\text{B}\ (aq) + \text{H}_2\text{O}\ (l) \rightarrow \text{HB}^+\ (aq) + \text{OH}^-\ (aq)$$

Water is the acid that reacts with the base, HB^+ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A **strong base** yields 100% (or very nearly so) of OH^- and HB^+ when it reacts with water; Figure 5.3.1. lists several strong bases. Based on the Brønsted-Lowry definition, we could characterize strong bases as being very good proton acceptors (*i.e.* they have a high tendency to accept protons from acids). A **weak base** yields a small proportion of hydroxide ions and is thus a poor proton acceptor. Soluble ionic hydroxides such as NaOH are considered strong bases because they ionize completely when dissolved in water. You can view a PhET simulation of strong and weak acids and bases at the molecular level by clicking here.

As we did with acids, we can measure the relative strengths of bases by measuring their **base-ionization constant (K_b)** in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\text{B}\ (aq) + \text{H}_2\text{O}\ (l) \rightarrow \text{HB}^+\ (aq) + \text{OH}^-\ (aq)$$

we write the equation for the ionization constant as:

$$K_\text{b} = ([\text{HB}^+][\text{OH}^-])/[\text{B}]$$

where the concentrations are those at equilibrium. Again, we do not include H_2O in the equation because water is a liquid with an activity equal to 1. Like K_a values, there is a wide range of known K_b values, as shown in the three examples below:

$$\text{NO}_2^-\ (aq) + \text{H}_2\text{O}\ (l) \rightleftharpoons \text{HNO}_2\ (aq) + \text{HO}^-\ (aq)\ K_\text{b} = 2.22 \text{ x } 10^{-11}$$

$$\text{CH}_3\text{CO}_2^-\ (aq) + \text{H}_2\text{O}\ (l) \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}\ (aq) + \text{OH}^-\ (aq)\ K_\text{b} = 5.6 \text{ x } 10^{-10}$$

$$\text{NH}_3\ (aq) + \text{H}_2\text{O}\ (l) \rightleftharpoons \text{NH}_4^+\ (aq) + \text{OH}^-\ (aq)\ K_\text{b} = 1.8 \text{ x } 10^{-5}$$

Table 5.3.1, found later in this section, lists values of ionization constants of a few common weak bases; a more complete table of K_b values can be found in AppendixI.

As with acids, percent ionization can be measured for basic solutions, but, as explained above, this value will vary depending on the base ionization constant *and* the initial concentration of the solution.

Equilibrium Constants and Conjugate Pairs

Consider the ionization reactions for a conjugate acid-base pair, HA and A^-:

$$\text{HA}\ (aq) + \text{H}_2\text{O}\ (l) \rightleftharpoons \text{H}_3\text{O}^+\ (aq) + \text{A}^-\ (aq)$$

$K_a = ([H_3O^+][A^-])/[HA]$

$$A^- \,(aq) + H_2O\,(l) \rightleftharpoons OH^- \,(aq) + HA\,(aq)$$

$K_b = ([HA][OH^-])/[A^-]$

Adding these two chemical equations yields the equation for the autoionization for water:

$$HA\,(aq) + H_2O\,(l) + A^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq) + OH^-\,(aq) + HA\,(aq)$$

$$HA\,(aq) + H_2O\,(l) + A^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq) + OH^-\,(aq) + HA\,(aq)$$

$$\text{Simplifies to : } 2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

As discussed in Chapter 4, the *K* expression for any chemical equation that is derived by adding together two or more other equations is equal to the *mathematical product* of the individual *K* expressions. Multiplying the equilibrium constants together and canceling common terms, we see that:

$$K_a \times K_b = ([H_3O^+][A^-]/[HA]) \times ([HA][OH^-]/[A^-]) = [H_3O^+][OH^-] = K_w$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8\times10^{-5})\times(5.6\times10^{-10}) = 1.0\times10^{-14} = K_w$$

NOTE:

Make sure you fully understand the relationship between conjugate acids and bases:

The conjugate base of an acid, HA, is what remains after it has donated a single proton, A^-.

The conjugate acid of a base, B, is what is produced after it has accepted a single proton, HB^+.

Note that in both cases, the two species in a conjugate acid-base pair differ by only one proton. This will be very important to remember and understand once we start discussing multiple K_a and K_b values for polyprotic acids – *only the product of K_a and K_b between a conjugate acid-base pair will equal K_w.*

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base (a good proton acceptor), any protons that are donated to water molecules to form hydronium ions are easily recaptured by A^- to regenerate HA. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base (poor proton acceptor), it remains in its deprotonated form, and the solution contains primarily A^- and H_3O^+, and correspondingly the acid is strong. Hence, we derive the following important conclusion:

Strong acids form very weak conjugate bases, and strong bases form very weak conjugate acids.

This is illustrated in Figure 5.3.4: as the relative acid strength increases from right to left in the top bar, you can see that the strength of the corresponding conjugate bases decreases from right to left in the bottom bar.

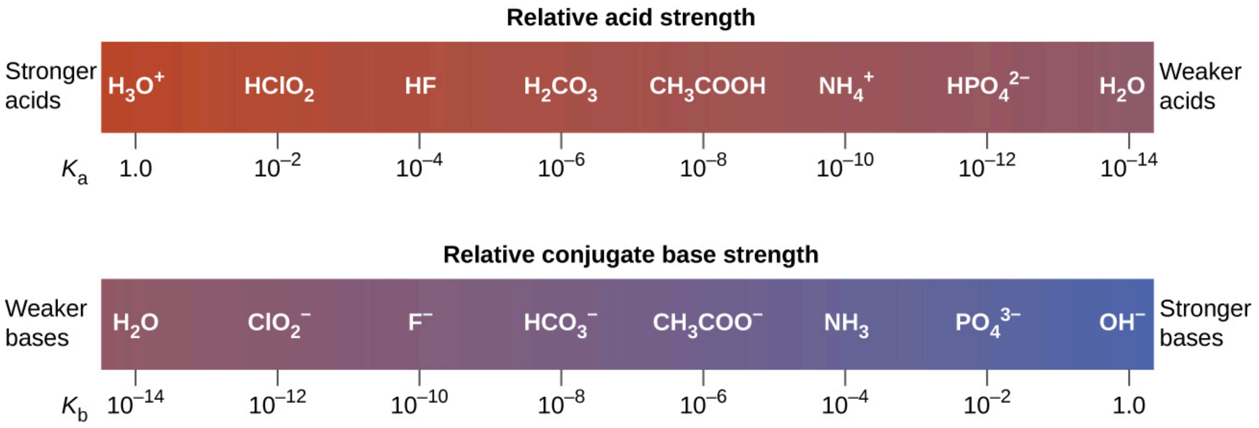
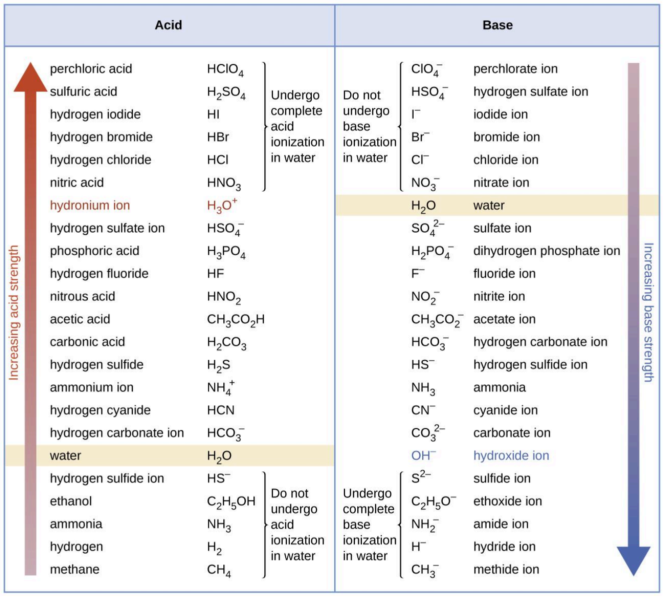


Figure 5.3.4. This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.



Acid			Base		
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			NH_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Figure 5.3.5. The chart shows the relative strengths of conjugate acid-base pairs.

Figure 5.3.5 also demonstrates this concept: the first six acids listed on the left are the most common strong acids. These acids are completely ionized in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 5.3.5 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and unionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 5.3.5 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion; if any conjugate base were formed, it would react with water to form the hydroxide ion.

The extent to which a base forms hydroxide ions in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 5.3.5. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Example 5.3.2 – the Product $K_a \times K_b = K_w$

Using a K_b value of 1.8×10^{-11} for the nitrite ion, NO_2^-, calculate the K_a for its conjugate acid.

Solution

The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = K_w/K_b = 1.0 \times 10^{-14}/1.8 \times 10^{-11} = 5.6 \times 10^{-4}$$

This answer matches the K_a for HNO_2 found in Table 5.3.1 and in Appendix H.

Check Your Learning 5.3.2 – the Product $K_a \times K_b = K_w$

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Appendix H as 6.2×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

HCN is the slightly stronger acid (K_a for $NH_4^+ = 5.6 \times 10^{-10}$).

Recall what we discussed earlier concerning the relationship between conjugate acids and bases: strong acids and bases will yield very weak conjugate bases and acids, respectively. We can use this fact to predict the direction of net change on an acid-base equilibrium reaction – the favoured direction of the reaction will be from the stronger to the weaker species of a conjugate pair. This relative strength can be assessed either qualitatively using a chart that shows the relative strengths of conjugate acid-base pairs (as in Figure 5.3.5) or quantitatively using K_a & K_b values, knowing that higher K_a and K_b values indicate stronger acids and bases, respectively. An example is shown below to illustrate this.

Example 5.3.3 – Predicting Products and Direction of Net Change – Acid-Base Equilibria

For the following acid-base reaction, predict the products and determine the preferred direction of change (i.e. the forward reaction, $K > 1$, or the reverse reaction, $K < 1$):

$$H_3PO_4 + HS^-$$

Solution

(a) H_3PO_4 is found much farther up in the chart (Figure 5.3.5) compared to HS^- in the acids column, meaning that it is the species that will preferentially donate its proton. Hence, it is our proton-donating acid and the bisulfide ion is our proton-accepting base. This gives us the following equilibrium reaction:

$$H_3PO_4 + HS^- \rightleftharpoons H_2PO_4^- + H_2S$$

$$\text{Acid} + \text{Base} \rightleftharpoons \text{Conj. Base} + \text{Conj. Acid}$$

To determine the preferred reaction direction, we must compare the relative strengths of the acid (in this case, H_3PO_4) and conjugate acid (H_2S) in this equilibrium: the stronger acid is the better proton donor, and thus will be more successful at donating its proton. *As a result, the preferred equilibrium direction is always from the stronger acid to the weaker acid.* Looking at the conjugate acid-base pairs in the chart, we find that H_3PO_4 is the relatively stronger acid compared to H_2S (likewise, HS^- is the relatively stronger base compared to $H_2PO_4^-$). Therefore, the reactants are the stronger species and hence the reaction preferentially proceeds to the right, *i.e.* towards products ($K > 1$).

We can verify our conclusion using K_a & K_b values as well (Appendices H & I). First, let's look at the K_a values of the *reactants* to confirm the choice of products: the K_a values for H_3PO_4 and HS^- are 6.9×10^{-3} and 1×10^{-19}, respectively. Of the two, phosphoric acid has a higher K_a value, so it is the better proton donor and hence will behave as the acid in this reaction. By consequence, that makes HS^- the base, the proton acceptor, and therefore the predicted products, $H_2PO_4^-$ and H_2S, are correct.

Next, let's use the K_a values of the *acid* and *conjugate acid* to confirm the predicted preferred reaction direction. Comparing these K_a values, we find that H_3PO_4 is indeed the better proton donor ($K_a = 6.9 \times 10^{-3}$) than H_2S ($K_a = 8.9 \times 10^{-8}$). Furthermore, if we calculate and compare K_b values between bases, HS^- is stronger ($K_b = 1.1 \times 10^{-7}$) than $H_2PO_4^-$ ($K_b = 1.4 \times 10^{-12}$). Therefore, we confirm that the reactants are the stronger species and that the direction of net change is to the right.

Check Your Learning 5.3.3

Predict the products and determine the preferred direction of change for the following acid-base reaction:

$$HCO_3^- + HSO_3^-$$

Answer

The products are SO_3^{2-} and H_2CO_3. The direction of net change will be towards the left (*i.e.* the reactants HCO_3^- and HSO_3^-).

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the unionized acid, hydronium ion, and the conjugate base of the acid, with the unionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid, CH_3CO_2H, is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2^-\,(aq)$$

giving an equilibrium mixture with most of the acid present in the unionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 5.3.4.). The remaining weak acid is present in the unionized form.

For acetic acid, at equilibrium:

$$K_a = ([H_3O(aq)+][CH_3CO_2(aq)^-]/[CH_3CO_2H(aq)]) = 1.8\times10^{-5}$$

Figure 5.3.4. pH paper indicates that a 0.1 M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+] = 0.1$ M. A 0.1 M solution of CH_3CO_2H (beaker on right) is a pH of 3 ($[H_3O^+] = 0.001$ M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

Table 5.3.1. Ionization Constants and pH (0.1 M) of Some Weak Acids.

Ionization Reaction	**K_a at 25 °C**	**pH of 0.1 M sol'n**
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	5.10
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}	4.78
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	4.0×10^{-8}	4.20
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.75×10^{-5}	2.88
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}	2.38
$HCNO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	3.5×10^{-4}	2.24
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	5.6×10^{-4}	2.14
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.3×10^{-4}	2.12
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.0×10^{-2}	1.57

The above table gives the ionization constants for several weak acids, including the pH for a 0.1 M solution of each acid; additional ionization constants can be found in Appendix H.

Looking at the pH of each 0.1 M solution of each weak acid, it's important to appreciate the tremendous magnitude in the difference of acidity between various weak acids. For example, the K_a values for HCO_2H and CH_3COOH do not seem to be very different, and their pH values differ only by 0.5 units. However, we must appreciate that the K_a of HCO_2H is in fact 10 times larger than that of CH_3COOH, and that in terms of difference in acidity (difference in $[H_3O^+]$), it is about 3 times more acidic. Now consider the difference between HCO_2H and HBrO – a pH difference of about 2.4 units. Doesn't seem like much, but if we translate this in terms of acidity…a 0.1 M solution of HCO_2H is about 250 times more acidic than 0.1 M HBrO! Therefore, when you come across these seemingly small differences in pH, keep in mind that it is a logarithmic scale and their acidity actually differs significantly.

At equilibrium, a solution of a weak base in water is a mixture of the unionized base, the conjugate acid of the weak base, and hydroxide ion with the unionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N\ (aq) + H_2O\ (l) \rightleftharpoons (CH_3)_3NH^+\ (aq) + OH^-\ (aq)$$

giving an equilibrium mixture with most of the base present as the unionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 5.3.5.). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the ionization constant of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$Kb=([(CH_3)_3NH(aq)^+][OH^-(aq)]/[(CH_3)_3N(aq)])$$

Figure 5.3.5. pH paper indicates that a 0.1 M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-] = 0.001$ M) because the weak base NH_3 only partially reacts with water. A 0.1 M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base. (credit: modification of work by Sahar Atwa)

The ionization constants of several weak bases are given in table below and in Appendix I.

Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 5.3.4 – Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 5.3.6.) resulting in its sour taste. At equilibrium, a solution contains $[CH_3CO_2H] = 0.0787$ M and $[H_3O^+] = [CH_3CO_2^-] = 0.00118$ M. What is the value of K_a for acetic acid?

Figure 5.3.6. Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2^-\,(aq)$$

$$Ka= ([H_3O(aq)+][CH_3CO_2(aq)-]/[CH_3CO_2H(aq)]) = ((0.00118)(0.00118))/0.0787$$
$$=1.77\times10^{-5}$$

Check Your Learning 5.3.4 – Determination of K_a from Equilibrium Concentrations

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + SO_4^{2-}\,(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 M; $[HSO_4^-]$ = 0.29 M; and $[SO_4^{2-}]$ = 0.13 M.

Answer

K_a for HSO_4^- = 1.2×10^{-2}

Example 5.3.5 – Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 M, $[C_8H_{10}N_4O_2H^+]$ = 5.0×10^{-3} M, and $[OH^-]$ = 2.5×10^{-3} M?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2\,(aq) + H_2O\,(l) \rightleftharpoons C_8H_{10}N_4O_2^+\,(aq) + OH^-\,(aq)$$

$$K_b= ([C_8H_{10}N_4O_2H(aq)+][OH(aq)-]/[C_8H_{10}N_4O_2(aq)]) = ((5.0\times10^{-3})(2.5\times10^{-3}))/0.050$$
$$= 2.5\times10^{-4}$$

Check Your Learning 5.3.5 – Determination of K_b from Equilibrium Concentrations

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}\,(aq) + H_2O\,(l) \rightleftharpoons H_2PO_4^-\,(aq) + OH^-\,(aq)$$

in a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium, $[OH^-]$ = 1.3×10^{-6} M; $[H_2PO_4^-]$=0.042 M; and $[HPO_4^{2-}]$=0.341 M.

Answer

K_b for HPO_4^{2-} = 1.6×10^{-7}

Example 5.3.6 – Determination of K_a or K_b from pH

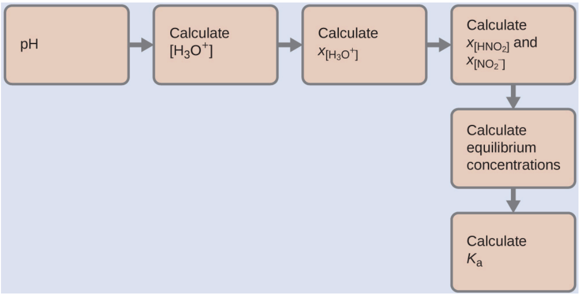
The pH of a 0.0516 M solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the hydronium ion concentration). Notice how this type of problem falls under one of the two types of chemical equilibrium problems covered in the previous unit (4.3 – Solving Equilibrium Problems) – we're calculating an equilibrium constant given that we know/determine the concentration of reactants and products at equilibrium.

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+]=10^{-2.34}=0.0046\text{ M}$$

The change in concentration of H_3O^+, $X_{[H3O+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, 1 x 10^{-7} M, which is so much less than the final concentration that we can approximate it as zero (~0) in order to simplify our calculations.

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$: the stoichiometry of the reaction dictates that for each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

Initial Concentration (M)	0.0516	/	~0	0
Change (M)	$-x$	/	$x =$ 0.0046	$x =$ 0.0046
Equilibrium concentration (M)	0.0470	/	0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a=([H_3O^+][NO_2(aq)^-])/[HNO_2(aq)] = ((0.0046)(0.0046)/(0.0470) = 4.5\times10^{-4}$$

Check Your Learning 5.3.6 – Determination of K_a or K_b from pH

The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$K_b = 1.8 \times 10^{-5}$

Example 5.3.7 – Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings (Figure 5.3.7).

Figure 5.3.7. The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534 M solution of formic acid?

$$HCO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_2^-\,(aq) K_a = 1.8 \text{ x } 10^{-4}$$

Solution

Determine x and equilibrium concentrations. The equilibrium expression is:

$$HCO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_2^-\,(aq)$$

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in colour):

$HCO_2H + H_2O \rightleftharpoons H_3O^+ + NO_2^-$

Initial Concentration (M)	0.534	/	~0	0
Change (M)	– x	/	x	x
Equilibrium concentration (M)	0.534 + (-x)	/	0 + x = x	0 + x = x

Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a=1.8\times10^{-4}=([H_3O^+(aq)][HCO_2^-(aq)])/[HCO_2H(aq)]$$
$$=x^2/(0.534-x)=1.8\times10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we make the assumption that $x << 0.534$, which allows us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a=1.8\times10^{-4}=x^2/0.534$$

Solve for x as follows:

$$x^2=(0.534)(1.8\times10^{-4})=9.6\times10^{-5}$$
$$x=\text{sqrt}(9.6\times10^{-5})$$
$$=9.8\times10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$(x/0.534)(100\%)=1.8\%$$

x is less than 5% of the initial concentration and so the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[H3O+]=\sim0+x=0+9.8\times10^{-3}M$$
$$=9.8\times10^{-3}M$$

The pH of the solution is thus:

$$\text{pH}=-\log(9.8\times10^{-3})=2.01$$

Check Your Learning 5.3.7 – Equilibrium Concentrations in a Solution of a Weak Acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100 M solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2^-\,(aq) \qquad K_a = 1.8 \text{ x } 10^{-5}$$

(Hint: Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or:

$$([CH_3CO_2^-(aq)]_{eq}/[CH_3CO_2H(aq)]_{initial})\times100\%$$

Answer

Percent Ionization = 1.3%

The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

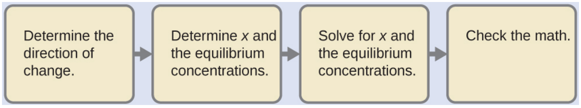
Example 5.3.8 – Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25 M solution of trimethylamine, a weak base:

$$(CH_3)_3N\,(aq) + H_2O\,(l) \rightleftharpoons (CH_3)_3NH^+\,(aq) + OH^-\,(aq) K_b = 6.3 \text{ x } 10^{-5}$$

Solution

This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in the previous example. The reactants and products will be different and the numbers will be different, but the logic will be the same:



Determine x and equilibrium concentrations. The table shows the changes and concentrations:

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Initial Concentration (M)	0.25	/	0	~0
Change (M)	– x	/	x	x
Equilibrium concentration (M)	0.25 + (-x)	/	0 + x	~0 + x

Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b=([(CH_3)_3NH(aq)][OH^-(aq)]/[(CH_3)_3N(aq)])=x^2/(0.25-x)=6.3\times10^{-5}$$

If we assume that x is small relative to 0.25, then we can replace $(0.25 - x)$ in the preceding equation with 0.25. Solving the simplified equation gives:

$$x=4.0\times10^{-3}$$

This change is less than 5% of the initial concentration (0.25 M), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$[OH\text{-}]=\sim0+x,\ x=4.0\times10^{-3}\ M$$

$$[OH\text{-}]=4.0\times10^{-3}$$

Then calculate pOH as follows:

$$pOH=-\log(4.0\times10^{-3})=2.40$$

Using the relation introduced in the previous section of this chapter:

$$pH+pOH=pK_w=14.00$$

This allows us to determine the pH:

$$pH=14.00-pOH=14.00-2.40=11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

Check Your Learning 5.3.8 – Equilibrium Concentrations in a Solution of a Weak Base

(a) Show that the calculation in Step 2 of this example gives an x of 4.0×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

(b) Find the concentration of hydroxide ion in a 0.0325 M solution of ammonia, a weak base with a K_b of 1.76×10^{-5}. Calculate the percent ionization of ammonia, the fraction ionized × 100%, or:

$$([NH_4^+]_{eq}/[NH_3]_i)\times100\%$$

Answer

7.56×10^{-4} M, 2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that *x* is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

Example 5.3.9 – Equilibrium Concentrations in a Solution of a Weak Acid

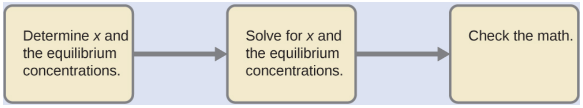
Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50 M solution of HSO_4^-?

$$HSO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + SO_4^{2-}\,(aq) K_a = 1.2 \text{ x } 10^{-2}$$

Solution

One question that may come up is why we aren't considering the case of HSO_4^- acting as a proton acceptor since it is an amphiprotic species. There are 2 reasons: 1) HSO_4^- is relatively much more acidic than water (Figure 5.3.5), so in this acid-base reaction, it will be most inclined to be the proton donor, and 2) if HSO_4^- was the proton acceptor (and H_2O was the proton donor), we would get H_2SO_4 and OH^-. These are *very strong* acid and base products, so ultimately, the reaction would proceed to completion to the left; in other words, the forward reaction would essentially not proceed at all, which is why we can disregard this possibility.

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



Determine x and equilibrium concentrations. This table shows the changes and concentrations:

$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

Initial Concentration (M)	0.50	/	~0	0
Change (M)	− x	/	x	x
Equilibrium concentration (M)	0.50 + (-x) = 0.50 − x	/	0 + x = x	0 + x = x

Solve for x and the concentrations. As we begin solving for *x*, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of *x*.

At equilibrium:

$$K_a=1.2\times10^{-2}=([H_3O^+][SO_4^{2-}])/[HSO_4^-]=x^2/(0.50-x)$$

If we assume that x is small and approximate $(0.50 - x)$ as 0.50, we find:

$$x=7.7\times10^{-2}$$

When we check the assumption, we calculate:

$$x_{eq}/[HSO_4^-]_i$$

$$x_{eq}/0.50=7.7\times10^{-2}/0.50=0.15,\ 15\%$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a=1.2\times10^{-2}=x^2/(0.50-x)$$

Gives

$$6.0\times10^{-3}-1.2\times10^{-2}x=x^2$$

Or

$$x^2+1.2\times10^{-2}x-6.0\times10^{-3}=0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^2+bx+c=0$$

x is given by the equation:

$$x=(-b\pm \mathrm{sqrt}(b^2-4ac))/2a$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root and a positive root. Since the negative root cannot possibly be correct (a concentration cannot be negative), we will continue our solution using the positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$[H_3O^+] = {\sim}0 + x,\ x = 7.2 \times 10^{-2}\ M$$

$$[H_3O^+] = 7.2 \times 10^{-2}\ M$$

The pH of this solution is:

$$pH = -\log[H_3O^+] = -\log(7.2 \times 10^{-2}) = 1.14$$

Check Your Learning 5.3.9 – Equilibrium Concentrations in a Solution of a Weak Acid

(a) Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.

(b) Calculate the pH in a 0.010 M solution of caffeine, a weak base:

$C_8H_{10}N_4O_2\,(aq) + H_2O\,(l) \rightleftharpoons C_8H_{10}N_4O_2H^+\,(aq) + OH^-\,(aq) K_b = 2.5 \times 10^{-4}$

(Hint: It will be necessary to convert $[OH^-]$ to $[H_3O^+]$ or pOH to pH toward the end of the calculation.)

Answer

pH = 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a better proton acceptor when compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order HCl < HBr < HI, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the **leveling effect of water.**

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, NH_2^-, are such strong bases that they react completely with water:

$$O^{2-}\,(aq) + H_2O\,(l) \rightarrow OH^-\,(aq) + OH^-\,(aq)$$

$$NH_2^-\,(aq) + H_2O\,(l) \rightarrow NH_3\,(aq) + OH^-\,(aq)$$

Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion. Consequently, this signifies that O^{2-} and NH_2^- as species do not exist in aqueous solutions.

Effect of Molecular Structure on Acid-Base Strength

NOTE: This topic is briefly covered to understand acid-base strength due to molecular structure. However, this is emphasized to a much greater extent and discussed in greater detail in the Winter semester course CHM1321: Organic Chemistry I.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is HF < HCl < HBr < HI. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases (note: if you are unfamiliar with the concept of electronegativity, it is discussed in Section 9.1). Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 5.3.8).

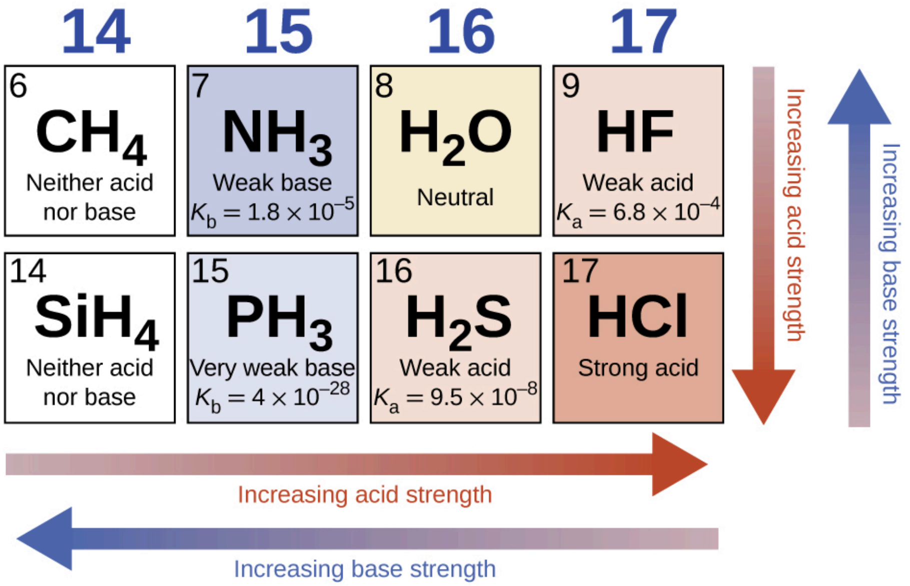
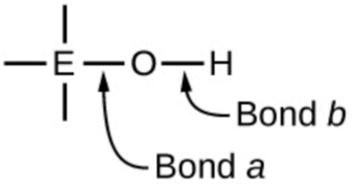


Figure 5.3.8. As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



Atom electronegativity and its relationship to bond character is discussed in detail in Section 9.1, but briefly: electronegativity is a measure of the ability of an atom to attract bonding electrons towards its nucleus. The nature of the chemical bond between two atoms (X–Y) is directly correlated to the difference in electronegativity between the two atoms, i.e. $\Delta EN_{XY} = |EN_X - EN_Y|$. A low value of ΔEN_{XY} results in a chemical bond that is mostly covalent – the electrons are being equally shared by both atoms. A high value of ΔEN_{XY} results in a chemical bond that is mostly ionic in character – the electron density is not equally distributed and cleavage of the bond will likely create one cation and one anion.

Referring back to the scheme above, the O atom has a high EN value. If the central atom, E, has a low electronegativity, then ΔEN_{EO} is large and the central atom tends to form a bond with greater ionic character with the oxygen atom. Consequently, bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the E atom has a relatively high electronegativity, ΔEN_{EO} is low, and the E atom shares the bonding electrons equally with the oxygen atom, making bond *a* relatively strongly covalent. Comparatively, the oxygen-hydrogen bond, bond *b*, has greater ionic character and is much more polar. As a consequence, the O-H bond is more readily broken and releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic –OH groups, known as oxoacids.

Increasing the oxidation state of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen. This polarization of electron density weakens the O-H bond, resulting in easier ionization. For example, sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 5.3.9.).

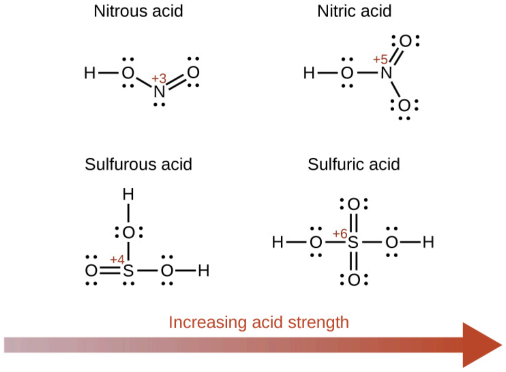


Figure 5.3.9. As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$Al(H_2O)_3(OH)_3\,(aq) + OH^-\,(aq) \rightleftharpoons H_2O\,(l) + [Al(H_2O)_2(OH)_4]^-\,(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3H_3O^+\,(aq) + Al(H_2O)_3(OH)_3\,(aq) \rightleftharpoons Al(H_2O)_6^{3+}\,(aq) + 3H_2O\,(l)$$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

Questions

★ Questions

1. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

2. Use this list of important industrial compounds (and Figure 5.3.3.) to answer the following questions regarding: CaO, $Ca(OH)_2$, CH_3CO_2H, CO_2, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, $NaOH$, Na_2CO_3. Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.

(a) List those compounds in (a) that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.

(b) List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

(c) The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1 M aqueous solution of this acid.

3. Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1 M aqueous solution of this base.

4. Explain why the ionization constant, Ka, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

5. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

6. Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

7. What is the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-11}$?

8. Which is the stronger acid, NH_4^+ or HBrO?

9. Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$?

10. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a) HSO_4^- or $HSeO_4^-$

(b) NH_3 or H_2O

(c) PH_3 or HI

(d) NH_3 or PH_3

(e) H_2S or HBr

11. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl, HBr, HI

(b) basicity: H_2O, OH^-, H^-, Cl^-

(c) basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$).

(d) acidity: HF, H_2O, NH_3, CH_4

12. Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base? See the ionization constants of weak acids to solve this problem.

13. The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001 M aqueous solution of $C_6H_4OH(CO_2H)$.

14. What do we represent when we write:

$$CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2^-\,(aq)$$

15. Explain why equilibrium calculations are not necessary to determine ionic concentrations in solutions of certain strong electrolytes such as NaOH and HCl. Under what conditions are equilibrium calculations necessary as part of the determination of the concentrations of all ions of some other strong electrolytes in solution?

16. Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

17. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

18. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?

19. Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water (Hint: Use LeChâtelier's principle.)?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NH_4Cl

20. Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NaF

21. What is the effect on the concentrations of NO_2^-, HNO_2, and OH– when the following are added to a solution of KNO_2 in water:

(a) HCl

(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

22. The equation for the equilibrium is:

$$NO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HNO_2\,(aq) + OH^-\,(aq)$$

Why is the hydronium ion concentration in a solution that is 0.10 M in HCl and 0.10 M in HCOOH determined by the concentration of HCl?

23. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) NH_3:$[OH^-]=3.1\times10^{-3}$ M;
$[NH_4^+]=3.1\times10^{-3}$ M

(b) $[NH_3]=0.533$ M
HNO_2:$[H_3O^+]=0.011$ M

(c) $[NO_2^-]=0.0438$ M
$[HNO_2]=1.07$ M

(d) $(CH_3)_3N$:$[(CH_3)_3N]=0.25$ M
$[(CH_3)_3NH^+]=4.3\times10^{-3}$ M

(e) $[OH^-]=4.3\times10^{-3}$ M
NH_4^+:$[NH_4^+]=0.100$ M

(f) $[NH_3]=7.5\times10^{-6}$ M
$[H_3O^+]=7.5\times10^{-6}$ M

★★ Questions

24. Determine K_b for the nitrite ion, NO_2^-. In a 0.10 M solution this base is 0.0015% ionized.

25. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10 M solution the acid is 29% ionized.

26. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) HTe^- (as a base)
(b) $(CH_3)_3NH^+$
(c) $HAsO_4^{3-}$ (as a base)
(d) HO_2^- (as a base)
(e) $C_6H_5NH_3^+$
(f) HSO_3^- (as a base)

27. For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?

(a) 3×10^{-8} M HNO_3
(b) 0.10 g HCl in 1.0 L of solution
(c) 0.00080 g NaOH in 0.50 L of solution
(d) 1×10^{-7} M $Ca(OH)_2$
(e) 0.0245 M KNO_3

28. Calculate the equilibrium concentration of the unionized acids and all ions in a solution that is 0.134 M in HNO_2 and 0.120 M in HBrO.

29. Calculate the equilibrium concentration of the unionized bases and all ions in a solution that is 0.115 M in NH_3 and 0.100 M in $C_6H_5NH_2$.

30. Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the hydronium ion concentration in a 0.698 M solution of $C_2H_5CO_2H$?

31. The pH of a 0.15 M solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

32. The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

Answers

1. The conjugate acid of the weak base used causes the slightly acidic solution.he salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

2. (a) $Ca(OH)_2$, NH_3, NaOH, Na_2CO_3 ; (b) CH_3COOH, H_2CO_3, HF, HNO_2, H_3PO_4 ; (c) NH_3, Na_2CO_3 $[H_2O]>[CH_3CO_2H]>[H_3O^+]\approx[CH_3CO_2^-]>[OH^-]$

3. Moles of

$H_2O>[NH_3]>[NH_4^+]\approx[OH^-]>[H_3O^+]$

4. The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

5. $Mg(OH)_2\ (s) + 2HCl\ (aq) \rightleftharpoons Mg^{2+}\ (aq) + 2Cl^-\ (aq) + 2H_2O\ (l)$

Brønsted Base + Brønsted Acid ⇌ Conjugate Base + Conjugate Acid

6. $CuO\ (s) + 2HNO_2\ (l) \rightleftharpoons Cu(NO_3)_2\ (l) + H_2O\ (l)$

7. $K_a=2.3\times10^{-11}$

8. HBrO

9. Triethylamine

10. (a) HSO_4^- ; (b) H_2O; (c) HI; (d) PH_3 ;(e) HBr

11. (a) HCl < HBr < HI; (b) $H_2O < Cl^- < H^- < OH^-$; (c) $ClO_3(OH) < Si(OH)_4 < Mg(OH)_2$; (d) $CH_4 < NH_3 < H_2O < HF$

12. CN^- is the stronger base.

13, $[H_2O]>[C_6H_4OH(CO_2H)]>[H^+]0>[C_6H_4OH(CO_2)\text{-}]>>[C_6H_4OH(CO_2)H)^-]>[OH^-]$

14. It is the equilibrium expression for the acid-base reaction between acetic acid and water to form acetate (conjugate base) and hydronium (conjugate acid), and vice-versa.

15. Strong electrolytes are 100% ionized, and, as long as the component ions are neither weak acids nor weak bases, the ionic species present result from the ionization of the strong electrolyte. Equilibrium calculations are necessary when one (or more) of the ions is a weak acid or a weak base.

16. Inversely proportional; As one concentration increases the other must decrease because $K_w= [H+]\cdot[OH-]=1.00\times10^{-14}$ must remain as a true statement.

17. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

18. The [H+] before the addition of acid or base (1.00×10^{-7}) is negligible.

19. The quantity of weak acid or base that ionizes is negligible.

20. (a) The addition of HCl

(b) The addition of NaOH

21. (a) Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2 and decreasing the concentration of NO_2^- ions.

(b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentration of OH^- ions.

(c) Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentration of HNO_2

(d) Adding NaCl has no effect on the concentrations of the ions.

(e) Adding KNO_2 adds NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentration.

22. This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

23. (a) $K_b=1.8\times10^{-5}$

(b) $K_a=4.5\times10^{-4}$

(c) $K_b=7.4\times10^{-5}$

(d) $K_a=5.6\times10^{-10}$

24. $K_b = 4.44\times10^{-4}$

25. $K_a = 1.2 \times 10^{-2}$

26. (a) $K_b=4.3\times10^{-12}$

(b) $K_a=1.6\times10^{-8}$

(c) $K_b=5.9\times10^{-7}$

(d) $K_b=4.2\times10^{-3}$

(e) $K_b=2.3\times10^{-3}$

(f) $K_b=6.3\times10^{-13}$

27. A and D

28. $[H_3O^+] = 7.5 \times 10^{-3}$ M, $[HNO_2] = 0.127$, $[OH^-] = 1.3 \times 10^{-12}$ M, $[BrO^-] = 4.5 \times 10^{-8}$ M, $[HBrO] = 0.120$ M

$[OH^-]=NO_4^+]=0.0014$ M

29. $[NH_3]=0.144$ M

$[H_3O^+]=6.9\times10^{-12}$ M

$[C_6H_5NH_3^+]=3.9\times10^{-8}$ M

$[C_6H_5NH_2]=0.100$ M

30. pH = 2.51

31. $K_a = 1.2\times10^{-2}$

32. $K_b = 1.77\times10^{-5}$

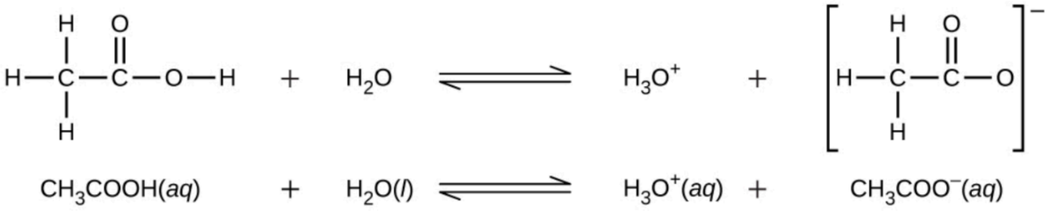
5.4 – POLYPROTIC ACIDS

We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

$$HCl\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + Cl^-\ (aq)$$
$$HNO_3\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + NO_3^-\ (aq)$$
$$HCN\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CN^-\ (aq)$$

Note: the K_a of HCN is 6.2 x 10^{-10}. This means that the acid does not fully ionize in water and necessitates the equilibrium arrow.

Even though it contains four hydrogen atoms, acetic acid, CH_3CO_2H, is also monoprotic because only the hydrogen atom from the carboxylic acid functional group (COOH) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

NOTE: Ionizable (also known as acidic) protons are typically written at the beginning of a condensed chemical formula. Examples of this include H_2SO_4, which is diprotic, and H_3PO_4, which is triprotic. Occasionally, some chemical formulae *do not* follow this pattern. This is usually due to historical reasons where the chemical formula has been written a certain way for several years. For example, acetic acid can be written $HC_2H_3O_2$, CH_3CO_2H, or CH_3COOH. When in doubt, check the literature for the correct formula.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

$$\text{First ionization: } H_2SO_4\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HSO_4^-\ (aq)$$

For this reaction, $K_{a1} > 10^2$, indicating ~100% complete ionization of the first proton.

$$\text{Second ionization: } HSO_4^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + SO_4^{2-}\ (aq)$$

For this reaction, $K_{a2} = 1.0 \times 10^{-2}$, indicating that the second ionization is only partial.

This **stepwise ionization** process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, H_2CO_3, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

$$\text{First ionization: } H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq)$$
$$K_{H2CO3}=([H_3O^+][HCO_3^-])/[H_2CO_3]=4.5\times10^{-7}$$

$$\text{Second ionization: } HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq)$$
$$K_{HCO3-}=([H_3O+][CO_3^{2-}])/[HCO_3^-]=4.7\times10^{-11}$$

K_{H2CO3} is larger than K_{HCO3-} by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that *very little* of the HCO_3^- (formed by the ionization of H_2CO_3) ionizes a *second* time to give more hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

Let's confirm this very important concept mathematically. The ICE tables below display both ionization reactions, starting with a 10.0 M solution of H_2CO_3. Notice that with the first ionization reaction, we generate a small concentration of H_3O^+ and HCO_3^- (even starting with 10.0 M of H_2CO_3!) – this is again due to the relatively small K_{a1} value. Afterwards, the second ionization reaction which has an even smaller K_{a2} value practically causes no change in the concentration of HCO_3^- and H_3O^+ and generates a negligible amount of CO_3^{2-}.

1ST IONIZATION: $H_2CO_3(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$

	$[H_2CO_3]$	**$[H_3O^+]$**	**$[HCO_3^-]$**
Initial concentration (M)	10.0	0.0	0.0
	x = 0.0021 M		
Change (M)	10.0 – 0.0021	0.0 + 0.0021	0.0 + 0.0021
Equilibrium concentration (M)	9.9979	0.0021	0.0021

2ND IONIZATION: $HCO_3^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

	$[HCO_3^-]$	$[H_3O^+]$	$[CO_3^{2-}]$
Initial concentration (M)	0.0021	0.0021	0.0
	$x = 4.7 \times 10^{-11}$ M		
Change (M)	$0.0021 - 4.7 \times 10^{-11}$	$0.0021 + 4.7 \times 10^{-11}$	$0.0 + 4.7 \times 10^{-11}$
Equilibrium concentration (M)	~0.0021	~0.0021	~0.0

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 5.4.1 – Ionization of a Diprotic Acid

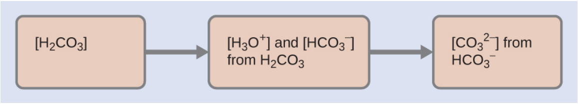
When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033$ M?

$$H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) K_{a1} = 4.5 \text{ x } 10^{-7}$$

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq) K_{a2} = 4.7 \text{ x } 10^{-11}$$

Solution

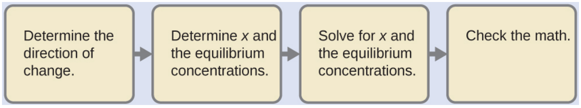
As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ions in solution. Thus there are two parts in the solution of this problem: (1) Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3. (2) Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1). To summarize:



Determine the concentrations of H_3O^+ *and* HCO_3^-.

$$H_2CO_3\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) \qquad K_{a1} = 4.5 \text{ x } 10^{-7}$$

As for the ionization of any other weak acid:



An abbreviated table of changes and concentrations shows:

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

Initial Concentration (M)	0.033	/	~0	0
Change (M)	– x	/	x	x
Equilibrium concentration (M)	0.033 – x	/	x	x

Substituting the equilibrium concentrations into the equilibrium gives us:

$$K_{H2CO3}=([H_3O^+][HCO_3^-])/[H_2CO_3]=x^2/(0.033\text{-}x)=4.5\times10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x=1.2\times10^{-4}$$

Thus:

$$[H_2CO_3]=0.033\text{ M}$$

$$[H_3O^+]=[HCO_3^-]=1.2\times10^{-4}\text{ M}$$

Determine the concentration of CO_3^{2-} *in a solution at equilibrium with* $[H_3O^+]$ *and* $[HCO_3^-]$ *both equal to 1.2 × 10*$^{-4}$ M.

$$HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq)$$

$$K_{HCO3-}=([H_3O+][CO_3^{2-}])/[HCO_3^-]=((1.2\times10^{-4})[CO_3^{2-}])/1.2\times10^{-4}$$

$$[CO_3^{2-}]=((4.7\times10^{-11})(1.2\times10^{-4}))/1.2\times10^{-4}=4.7\times10^{-11}$$

To summarize: In part 1 of this example, we found that the H_2CO_3 in a 0.033 M solution ionizes slightly and at equilibrium $[H_2CO_3]$ = 0.033 M; $[H_3O^+]$ = 1.2 × 10^{-4} M; and $[HCO_3^-]$ = 1.2×10^{-4} M. In part 2, we determined that $[CO_3^{2-}]$ = 4.7×10^{-11} M.

Check Your Learning 5.4.1 – Ionization of a Diprotic Acid

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HS^-\ (aq) \quad K_{a1} = 8.9 \text{ x } 10^{-8}$$

$$HS^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + S^{2-}\ (aq) \quad K_{a2} = 1.0 \text{ x } 10^{-19}$$

Answer

$$[H_2S] = 0.1\text{ M};\ [H_3O^+] = [HS^-] = 0.000094\text{ M};\ [S^{2-}] = 1 \times 10^{-19}\text{ M} \approx 0\text{ M}$$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent ionization of a polyprotic acid occurs to a lesser degree.

Triprotic Acids

A **triprotic acid** is an acid that has three ionizable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

First ionization: $H_3PO_4\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + H_2PO_4^-\ (aq) \quad K_{a1} = 7.5 \text{ x } 10^{-3}$

Second ionization: $H_2PO_4^-\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + HPO_4^{2-}\ (aq) \quad K_{a2} = 6.2 \text{ x } 10^{-5}$

Third ionization: $HPO_4^{2-}\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + PO_4^{3-}\ (aq) \quad K_{a3} = 4.2 \text{ x } 10^{-13}$

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6.

This set of three ionization reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic Bases

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a **diprotic base**, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

First protonation: $H_2O\ (l) + CO_3^{2-}\ (aq) \rightleftharpoons HCO_3^-\ (aq) + OH^-\ (aq) \quad K_{b1} = K_W/K_{a2} = 2.1 \times 10^{-4}$

Second protonation: $H_2O\ (l) + HCO_3^-\ (aq) \rightleftharpoons H_2CO_3\ (aq) + OH^-\ (aq) \quad K_{b2} = K_W/K_{a1} = 2.2 \times 10^{-8}$

Example 5.4.2 – Converting Between K_a and K_b – Polyprotic Acids-Bases

Given the following chemical equilibrium reaction, which of the following expressions correctly describes its equilibrium constant, K:

$$PO_4^{3-} + H_2O \rightleftharpoons OH^- + HPO_4^-$$

(a) $1/K_{a2}$

(b) K_w/K_{a3}

(c) $1/K_{a3}$

(d) K_w/K_{a2}

Solution

Notice how in this reaction, the main species PO_4^{3-} accepts a proton as it reacts with water – this means that it is the base in this reaction and hence, K is more specifically K_b. Recall that, for any conjugate acid-base pair, the relationship between K_a and K_b is: $K_w = K_a \times K_b$. We can already rule out options (a) and (c) since they do not include K_w in the expression for K.

The reaction indicated starts with a phosphate ion (which is non-protonated) that is converted into its conjugate monoprotic acid HPO_4^-. PO_4^{3-} is in its most deprotonated form (no protons), so this reaction is K_{b1} – the first reaction in which PO_4^{3-} picks up its very first proton. With that in mind, we can say that this reaction corresponds to K_{a3}. Since we're working with HPO_4^- as the acid and PO_4^{3-} as its conjugate base, this equilibrium can be seen in one of two ways: either we have PO_4^{3-} as the base reacting with water to pick it up its very *first* proton and become HPO_4^{3-} (which is K_{b1}), or we have HPO_4^{3-} as the acid reacting with water to lose its *last* proton and become PO_4^{3-} (which is K_{a3}). We can see that both (b) and (d) both have the expression arranged correctly such that $K_w/K_a = K_b$, however, only (b) uses K_{a3} to correctly convert to K_{b1}.

Therefore, the correct answer is (b).

Check Your Learning 5.4.2 – Converting Between K_a and K_b – Polyprotic Acids-Bases

Given the information below, give the balanced chemical equations and calculate the equilibrium constants for the 3 successive protonation reactions of the hypothetical base, A^{3-} *(aq)*.

$H_3A\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + H_2A^-\,(aq)\ K_{a1} = 1.5 \text{ x } 10^{-4}$
$H_2A^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HA^{2-}\,(aq)\ K_{a2} = 2.7 \text{ x } 10^{-9}$
$HA^{2-}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^{3-}\,(aq)\ K_{a3} = 8.8 \text{ x } 10^{-12}$

Answer:

$A^{3-}\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + HA^{2-}\,(aq)\ K_{b1} = K_W/K_{a3} = 1.1 \text{ x } 10^{-3}$
$HA^{2-}\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + H_2A^-\,(aq)\ K_{b2} = K_W/K_{a2} = 3.7 \text{ x } 10^{-6}$
$H_2A^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + H_3A\,(aq)\ K_{b3} = K_W/K_{a1} = 6.7 \text{ x } 10^{-11}$

Questions

★ Questions

1. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134 M solution of H_2CO_3, a diprotic acid: $[H_3O^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$, $[CO_3^{2-}]$? No calculations are needed to answer this question.

2. Calculate the concentration of each species present in a 0.050 M solution of H_2S.

3. Calculate the concentration of each species present in a 0.010 M solution of phthalic acid, $C_6H_4(CO_2H)_2$.

$C_6H_4(CO_2H)_2(aq)+H_2O(l)\leftrightarrow H_3O(aq)^++C_6H_4(CO_2H)(CO_2)(aq)^-\ \ K_a=1.1\times10^{-3}$
$C_6H_4(CO_2H(CO_2)(aq)\text{-}+H_2O(l)\leftrightarrow H_3O(aq)^++C_6H_4(CO_2)_2(aq)^{2-}\ \ K_a=3.9\times10^{-6}$

★★ Questions

4. Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the $-OH$ group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, $Ka = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

(c) Under some conditions, aspirin reacts with water and forms a solution of salicylic acid and acetic acid:

$$CH_3CO_2C_6H_4CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons HOC_6H_4CO_2H\,(aq) + CH_3CO_2H\,(aq)$$

(i) Which of the acids, salicylic acid or acetic acid, produces more hydronium ions in such a solution?

(ii) What are the concentrations of molecules and ions in a solution produced by the hydrolysis of 0.50 g of aspirin dissolved in enough water to give 75 mL of solution?

5. The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O?

(b) What is K_b for the reaction in which HTe^- functions as a base in water?

(c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

Answers

1. $[H_3O^+]$ and $[HCO_3^-]$ are practically equal.

2. $[HS] = 7.1 \text{ x } 10^{-5}$ M, $[H_3O^+] = 7.1 \text{ x } 10^{-5}$ M, $[S^{-2}] = 1.29 \text{ x } 10^{-13}$ M, $[H_2S] = 0.0499$ M

3. $[C_6H_4(CO_2H)_2(aq)]=7.2\times10^{-3}M,[C_6H_4(CO_2H)(CO_2)(aq)\text{-}]=[H_3O^+(aq)]=2.8\times10^{-3}\,M,$

$[C_6H_4(CO_2)_2{}^{2-}(aq)]=3.9\times10^{-6}\,M,\ [OH\text{-}]=3.6\times10^{-12}\,M$

4. (a) pH = 2.44, (b) pH = 2.70, (c) (i) salicylic acid (ii) The concentration of aspirin and acetic acid is $2.1 \text{ x } 10^{-4}$ M

5. (a) $K_{a2}=1.5\times10^{-11}$

(b) $K_b=4.3\times10^{-12}$

(c) $([Te^{2-}][H_3O^+(aq)])/[HTe^-]=((x)(0.0141+x))/(0.0141-x)\approx((x)(0.0141))/(0.0141)=1.5\times10^{-11}$

Solving for x gives 1.5×10^{-11} M. Therefore, compared with 0.014 M, this values is negligible (1.1×10^{-7}%)

5.5 – HYDROLYSIS OF SALT SOLUTIONS

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word "neutralization" seems to imply that a stoichiometrically equivalent solution of an acid and a base would have a neutral pH. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

Acid-Base Neutralization

When we mix solutions of an acid and a base, an acid-base **neutralization reaction** occurs. All acid-base neutralization reactions are assumed to be 100% complete for stoichiometric purposes. For example, consider the following acid-base reaction:

$$HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)$$

Note the one-way arrow, indicating that this is a heavily product-favoured reaction. Why do we not use an equilibrium arrow instead? Let's breakdown the above reaction into its individual steps to explain:

HCl ionizes completely in water. This means there is no actual HCl in the solution, it completely dissolves into H_3O^+ and $Cl^−$:

$$HCl\,(aq) \rightarrow H_3O^+\,(aq) + Cl^-(aq)$$

NaOH also ionizes completely in water and leaves only Na^+ and $OH^−$ in solution:

$$NaOH\,(aq) \rightarrow Na^+\,(aq) + OH^-(aq)$$

In the acid-base neutralization, the products of Step 1 react with the products of Step 2, to yield the following full ionic equation:

$$H_3O^+\,(aq) + Cl^-(aq) + Na^+\,(aq) + OH^-(aq) \rightarrow 2H_2O\,(l) + Cl^-(aq) + Na^+(aq)$$

Once the spectator ions are removed, you get the net ionic equation:

$$H_3O^+\,(aq) + OH^-(aq) \rightarrow 2H_2O\,(l)$$

Notice that this is the reverse of the autoionization of water, meaning $K = 1/K_w = 10^{14}$. This K value is so large that the reaction is assumed to go to completion, allowing for a one way arrow to be drawn.

Application of Acid-Base Neutralization 1: Stomach Antacids

Our stomachs contain a solution of roughly 0.03 M HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO3\,(aq) + 2HCl\,(aq) \rightarrow CaCl2\,(aq) + H2O\,(l) + CO2\,(g)$$

not only neutralizes stomach acid, it also produces $CO_{2(g)}$, which may result in a satisfying belch.

Application of Acid-Base Neutralization 2: Culinary Aspects of Chemistry

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 5.5.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odour of the fish, and also adds a "sour" taste that we seem to enjoy.

$$\begin{array}{ccccccc} CH_3COOH & + & NH_2CH_2CH_2CH_2CH_2NH_2 & \longrightarrow & CH_3COO^- & + & NH_3^+CH_2CH_2CH_2CH_2NH_2 \\ \text{Acetic acid} & + & \text{Putrescine} & \longrightarrow & \text{Acetate ion} & + & \text{Putrescinium ion} \end{array}$$

Figure 5.5.1. A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favours the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavour of the vegetables with the acid making them taste sour.

Acid-base neutralization reactions can be summarized by the following general chemical equation:

$$\text{acid}\,(aq) + \text{base}\,(aq) \rightarrow \text{salt}\,(aq) + \text{water}$$

where the driving force of the reaction (why we use a one-way arrow) is the formation of water. Again, the term *neutralization* implies that the product, an aqueous solution of an ionic salt, has a neutral pH. However, even if we mix stoichiometrically equivalent quantities, we sometimes may find that the resulting solution is *not* neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic.

Example 5.5.1 – Predicting the salts formed in acid-base neutralizations

Predict the salt produced when the following neutralizations go to completion:

(a) HCOOH and NaOH

(b) HCN and NH_3

(c) HCl and CH_3NH_2

Solution

(a) HCOOH is a weak acid and NaOH is a strong base. The resulting salt will be HCOONa.

(b) HCN is a weak acid and NH_3 is a weak base. The resulting salt will be NH_4CN.

(c) HCl is a strong acid and CH_3NH_2 is a weak base. The resulting salt will be CH_3NH_2Cl.

Check Your Learning 5.5.1 – Predicting the salts formed in acid-base neutralizations

Predict the salt produced when the following neutralizations go to completion.

(a) RbOH and HCl

(b) HNO_2 and NaOH

(c) CH_3COOH and NH_3

(d) NH_3 and HCl

(e) HI and CH_3NH_2

Answer

(a) RbCl

(b) $NaNO_2$

(c) NH_4CH_3COO

(d) NH_4Cl

(e) CH_3NH_3I

Hydrolysis of Salts

As a general term in chemistry, the word hydrolysis refers to cleavage of a bond (*-lysis*) by the action of water (*hydro-*). In the context of ionic salts, they may hydrolyze in water to produce either acidic or basic aqueous solutions, depending on the nature of the salt. Consider a generic ionic compound, XY *(s)*. This salt is dissolved in water and ionizes to form a cation, X^+ *(aq)* and an anion, Y^- *(aq)*. By looking at the charges on the ions, we see that, if hydrolysis occurs, the cation produces H_3O^+ ion and the anion produces OH^- ion (Figure 5.5.2).

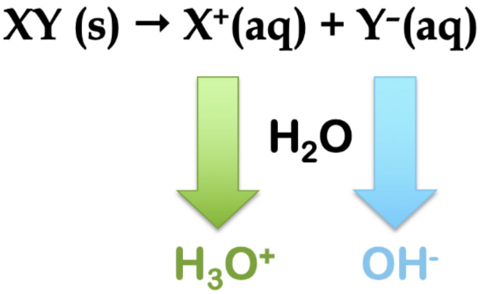


Figure 5.5.2. The general reaction scheme for the hydrolysis of a salt, XY. If reaction with water occurs, the cation produces hydronium ion and the anion produces hydroxide ion.

Therefore, we can envision 4 possible scenarios for the hydrolysis of any salt, XY:

If X^+ hydrolyzes but Y^- doesn't, then H_3O^+ is produced and the solution is ACIDIC.

If Y^- hydrolyzes but X^+ doesn't, then OH^- is produced and the solution is BASIC.

If neither X^+ nor Y^- hydrolyzes, then there is NO CHANGE to the solution's pH.

If both X^+ and Y^- hydrolyze, then the change to the solution's pH cannot immediately be determined (we will need to perform further calculations).

Let us examine first how and when salts ionize, and then look at examples of salts from each of the above 4 scenarios.

Conjugate Acid-Base Pairs and Hydrolysis

As discussed in previous sections, in conjugate acid-base pairs, if one species is strong, the other is comparatively weak; for example, a strong acid (very good proton donor) has a weak conjugate base (very poor proton acceptor). As we saw, this leads to acid-base equilibria proceeding in preferred directions, from the stronger acid and base to the weaker acid and base. Let's use HCl again as an example: it is a very strong acid and ionizes completely in water:

$$HCl\ (aq) + H_2O\ (aq) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

In this reaction, HCl is a strong acid (an excellent proton donor), making its conjugate base, Cl^-, a very poor proton acceptor. This means that, if we were to add the conjugate base, Cl^- to water instead, we would NOT expect it to behave as a Brønsted-Lowry base: it would NOT react with water to pick up a proton to produce OH^-:

$$Cl^-\ (aq) + H_2O\ (aq) \rightleftharpoons HCl\ (aq) + OH^-\ (aq)$$

The above reaction is pure nonsense: we know that HCl is a powerful proton donor and thus would not remain in solution (it would immediately react with the generated OH^- to return to the reactants). In other words, since Cl^- is the weak conjugate base of a strong acid, it does not hydrolyze (react with water).

Let's now compare this result to that of acetic acid, CH_3COOH, a weak acid that only partially ionizes in solution:

$$CH_3COOH\ (aq) + H_2O\ (aq) \leftrightarrows H_3O^+\ (aq) + CH_3COO^-\ (aq)$$

As we have seen, this is reactant-favoured, meaning that at equilibrium, the majority of the acid prefers to be in its neutral, unionized form. Since CH_3COOH is a weak acid (poor proton donor) we must conclude that its conjugate base, CH_3COO^-, must be a good base (good proton acceptor). Therefore, if we were to add acetate ion directly to water instead, we WOULD expect it to behave as a Brønsted-Lowry base: it would react with water to pick up a proton to produce OH^-:

$$CH_3COO^- (aq) + H_2O (aq) \leftrightarrows CH_3COOH (aq) + OH^- (aq)$$

Since we know that acetic acid prefers to be in its neutral, unionized form, we can expect that the above reaction occurs appreciably and forms a non-negligible amount of hydroxide ion at equilibrium. In other words, the acetate ion does hydrolyze in water, producing OH^- and thus yielding a basic aqueous solution.

While the above discussion compared a strong acid and a weak acid, we can extend the same arguments to a strong base and a weak base, and come to the following conclusions about ion hydrolysis:

Conjugate bases of strong acids do NOT hydrolyze.

Conjugate bases of weak acids DO hydrolyze.

Conjugate acids of strong bases do NOT hydrolyze.

Conjugate acids of weak bases DO hydrolyze.

Rules for Hydrolysis

Armed with the above understanding of the relative strength of conjugate acid-base pairs, we can now return to our discussion of salts (XY) and the 4 possible scenarios for ion hydrolysis. To determine the effect of a salt on solution pH, we must follow these steps:

Determine the cation and anion produced when the salt is dissolved.

Determine if the cation hydrolyzes or not. The cation X^+ will hydrolyze in two situations:

It is the conjugate acid of a weak base, and will generate H_3O^+ directly via the donation of a proton to water.

It is a small, highly charged, metal cation, and will generate H_3O^+ indirectly via a different mechanism *(note: this situation is not as common and is discussed in further detail at the end of this section).*

Determine if the anion hydrolyzes or not. The anion Y^- will hydrolyze if it is the conjugate base of a weak acid, and will generate OH^- directly via the acceptance of a proton from water.

If both hydrolyze, perform additional analysis to find the overall effect on pH.

Hydrolysis of Salts: Qualitative Prediction of pH Changes

Let's look at several examples and apply the above procedure to determine the acid-base character of different salts.

Example 1: NaCl

Sodium chloride dissolves in water to produce sodium cations and chloride anions:

$$NaCl (s) \rightarrow Na^+ (aq) + Cl^- (aq)$$

The cation, Na^+, *does not hydrolyze*: it is not the conjugate acid of a weak base (it cannot act as a proton donor!) and it is not a small, highly charged metal ion:

$$Na^+ (aq) + H_2O (l) \rightarrow \text{no hydrolysis}$$

As seen already, the anion, Cl^-, is the conjugate base of a strong acid (HCl), and so it also *does not hydrolyze*:

$$\mathrm{Cl^-}\,(aq) + \mathrm{H_2O}\,(l) \rightarrow \text{no hydrolysis}$$

Therefore, since neither the cation nor the anion hydrolyze, neither H_3O^+ nor OH^- is produced, and so overall, adding NaCl to an aqueous solution will have no effect on the pH. NaCl is thus called a NEUTRAL salt.

Example 2: NH_4Br

Ammonium bromide dissolves in water to produce ammonium cations and bromide anions:

$$\mathrm{NH_4Br}\,(s) \rightarrow \mathrm{NH_4^+}\,(aq) + \mathrm{Br^-}\,(aq)$$

The cation, NH_4^+, *does hydrolyze*: it is the conjugate acid of a weak base, NH_3, and so will react with water in an equilibrium to produce some H_3O^+:

$$\mathrm{NH_4^+}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{NH_3}\,(aq) + \mathrm{H_3O^+}\,(aq)$$

The anion, Br^-, is the conjugate base of a strong acid (HBr), and so it *does not hydrolyze*:

$$\mathrm{Br^-}\,(aq) + \mathrm{H_2O}\,(l) \rightarrow \text{no hydrolysis}$$

Therefore, since the cation hydrolyzes but the anion does not, overall, adding NH_4Br to an aqueous solution will produce some H_3O^+ and the pH will decrease. NH_4Br is thus called an ACIDIC salt.

Example 3: KCN

Potassium cyanide dissolves in water to produce potassium cations and cyanide anions:

$$\mathrm{KCN}\,(s) \rightarrow \mathrm{K^+}\,(aq) + \mathrm{CN^-}\,(aq)$$

The cation, K^+, *does not hydrolyze*: it is not the conjugate acid of a weak base, and it is not a small, highly charged metal ion:

$$\mathrm{K^+}\,(aq) + \mathrm{H_2O}\,(l) \rightarrow \text{no hydrolysis}$$

The anion, CN^-, *does hydrolyze:* it is the conjugate base of a weak acid (HCN), and so will react with water in an equilibrium to produce some OH^-:

$$\mathrm{CN^-}\,(aq) + \mathrm{H_2O}\,(aq) \leftrightarrows \mathrm{HCN}\,(aq) + \mathrm{OH^-}\,(aq)$$

Therefore, since the anion hydrolyzes but the cation does not, overall, adding KCN to an aqueous solution will produce some OH^- and the pH will increase. KCN is thus called a BASIC salt.

Example 4: NH_4CN

Ammonium cyanide dissolves in water to produce ammonium cations and cyanide anions:

$$\mathrm{NH_4CN}\,(s) \rightarrow \mathrm{NH_4^+}\,(aq) + \mathrm{CN^-}\,(aq)$$

As seen above, the cation, NH_4^+, *does hydrolyze*:

$$\mathrm{NH_4^+}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{NH_3}\,(aq) + \mathrm{H_3O^+}\,(aq)$$

Also seen above, the anion, CN^-, *also hydrolyzes:*

$$\mathrm{CN^-}\,(aq) + \mathrm{H_2O}\,(aq) \leftrightarrows \mathrm{HCN}\,(aq) + \mathrm{OH^-}\,(aq)$$

Therefore, since BOTH the cation AND anion hydrolyze with water, we must now determine the extent of the two equilibria above. In other words, does the ammonium cation produce more H_3O^+ than the OH^- produced by the cyanide anion or vice-versa? Which of these two equilibria is more *product-favoured*? To answer this, we simply need to calculate and compare the equilibrium constants of the two reactions above:

$$\mathrm{NH_4^+}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{NH_3}\,(aq) + \mathrm{H_3O^+}\,(aq)$$

$$K_a(\text{for } NH_4^+)=K_w/K_b(\text{for } NH_3)=(1.0\times10^{-14})/(1.8\times10^{-5})=5.6\times10^{-10}$$

$$CN^-\ (aq) + H_2O\ (aq) \leftrightarrows HCN\ (aq) + OH^-\ (aq)$$
$$K_b(\text{for } CN^-)=K_w/K_a(\text{for HCN})=(1.0\times10^{-14})/(6.2\times10^{-10})=1.6\times10^{-5}$$

Comparing the two K values, we see that the K_b of the anion is greater than the K_a of the cation. The second equilibrium is more product-favoured than the first, and overall, more OH^- than H_3O^+ is produced in solution as a result of the hydrolysis of both ions. Therefore, adding NH_4CN to an aqueous solution will cause the pH to increase and it is thus classified as a BASIC salt.

Example 5.5.2 – Qualitative Prediction of pH Changes

Predict whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) KBr
(b) $NaHCO_3$
(c) NH_4Cl
(d) Na_2HPO_4
(e) NH_4F

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

(a) The K^+ cation and the Br^- anion do not hydrolyze, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral.

(b) The Na^+ cation does not hydrolyze, and will not affect the pH of the solution, while the HCO_3^- anion is amphiprotic. The K_a of HCO_3^- is 4.7×10^{-11}, and its K_b is:

$$1.0\times10\text{-}^{14}/4.3\times10^{-7}=2.3\times10^{-8}$$

Since $K_b >> K_a$, this species is better at *accepting* protons than *donating* protons. Therefore, the bicarbonate anion will behave as a base and the solution is basic.

(c) The NH_4^+ ion is acidic and the Cl^- ion does not hydrolyze. The solution will be acidic.

(d) The Na^+ cation does not hydrolyze, and will not affect the pH of the solution, while the HPO_4^{2-} anion is amphiprotic. The K_a of HPO_4^{2-} is 4.2×10^{-13}, and its K_b is:

$$1.0\times10^{-14}/6.2\times10^{-8}=1.6\times10^{-7}$$

Because $K_b >> K_a$, the solution is basic.

(e) The NH_4^+ ion is listed as being acidic, and the F^- ion is listed as a base, so we must directly compare the K_a and the K_b of the two ions. K_a of NH_4^+ is 5.6×10^{-10}, which seems very small, yet the K_b of F^- is 1.4×10^{-11}, so the solution is acidic, since $K_a > K_b$.

Check Your Learning 5.5.2 – Qualitative Prediction of pH Changes

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) K_2CO_3
(b) $CaCl_2$

(c) KH_2PO_4
(d) $(NH_4)_2CO_3$
(e) $Mg(NO_3)_2$

Answer

(a) basic; (b) neutral; (c) acidic; (d) basic; (e) neutral

Hydrolysis of Salts: Quantitative Prediction of pH Changes

The examples above provide an excellent illustration of how we can quickly determine the acid-base properties of ionic salts in aqueous solutions. But what if we need to calculate the exact effect on a solution's pH? Below is an example to show how we can combine the described procedure with the equilibrium problem-solving steps used previously to find the final pH of salt solutions.

Example 5.5.3 – Quantitative Prediction of pH Changes

Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride, $C_6H_5NH_3Cl$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 M solution of aniline hydrochloride?

Solution

Aniline hydrochloride dissolves in water to produce $C_6H_5NH_3^+$ cations and chloride anions:

$$C_6H_5NH_3Cl\ (s) \rightarrow C_6H_5NH_3^+\ (aq) + Cl^-\ (aq)$$

We know the anion, Cl^-, *does not hydrolyze*:

$$Cl^-\ (aq) + H_2O\ (l) \rightarrow \text{no hydrolysis}$$

However, the cation, $C_6H_5NH_3^+$, is the conjugate acid of a weak base, $C_6H_5NH_2$, and so it *does hydrolyze*:

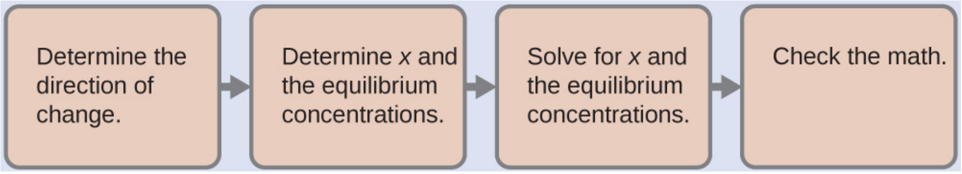
$$C_6H_5NH_3^+\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + C_6H_5NH_2\ (aq)$$

Thus, following our previous procedure, at this point we predict an ACIDIC pH for this salt. However, to find the *exact* pH of the 0.233 M solution, our next step in this example is to determine K_a for the $C_6H_5NH_3^+$ ion. The value of K_a for this acid is not listed in Appendix H, but we can determine it from the value of K_b for aniline, $C_6H_5NH_2$, which is given as 4.3×10^{-10} (Appendix I):

$$K_a(\text{for } C_6H_5NH_3^+) \times K_b(\text{for } C_6H_5NH_2) = K_w = 1.0 \times 10^{-14}$$

$$K_a(\text{for } C_6H_5NH_3^+) = K_w / K_b(\text{for } C_6H_5NH_2) = (1.0 \times 10^{-14})/(4.3 \times 10^{-10}) = 2.3 \times 10^{-5}$$

Now we have the ionization constant and the initial concentration of the weak acid, all the information necessary to determine the equilibrium concentration of H_3O^+, and the pH:



With these steps we find $[H_3O^+] = 2.3 \times 10^{-3}$ M and pH = 2.64, matching with the acidic pH we predicted qualitatively at the beginning. You should perform the calculations yourself to confirm these values.

Check Your Learning 5.5.3 – Quantitative Prediction of pH Changes

You are given a 0.100 M solution of ammonium nitrate, NH_4NO_3.

(a) Predict qualitatively: is this a neutral, acidic, or basic salt?

(b) Use the data in Appendix I to determine K_a for the ammonium ion.

(c) What is the hydronium ion concentration of the solution?

(d) What is the pH of the solution?

Answer

Acidic; (b) K_a (for NH_4^+) = 5.6×10^{-10}; (c) $[H_3O^+] = 7.5 \times 10^{-6}$ M; (d) pH = 5.13

Example 5.5.4 – Quantitative Prediction of pH Changes

What is the pH of a 0.100 M solution of calcium hypochlorite, $Ca(OCl)_2$?

Solution

Calcium hypochlorite dissolves in water to produce calcium cations and hypochlorite anions (note the stoichiometry):

$$Ca(OCl)_2\,(s) \rightarrow Ca^{2+}\,(aq) + 2\,OCl^-\,(aq)$$

The cation, Ca^{2+}, *does not hydrolyze*: it is not the conjugate acid of a weak base, and it is not a small, highly charged metal ion:

$$Ca^{2+}\,(aq) + H_2O\,(l) \rightarrow \text{no hydrolysis}$$

The anion, OCl^-, *does hydrolyze:* it is the conjugate base of a weak acid (HOCl), and so will react with water in an equilibrium to produce some OH^-:

$$OCl^-\,(aq) + H_2O\,(aq) \leftrightarrows HOCl\,(aq) + OH^-\,(aq)$$

Therefore, at this point, we predict a BASIC pH for the solution. The next step is to find the K_b for the OCl^- ion using the K_a for HOCl from Appendix H:

$$K_b(\text{for } OCl^-)=K_w/K_a(\text{for HOCl})=(1.0\times10^{-14})/(4.0\times10^{-8})=2.5\times10^{-7}$$

Combining this value along with the initial concentration of hypochlorite anion ($[OCl^-]_i$ = 0.200 M, due to stoichiometry) we can use an ICE table to find that, at equilibrium, $[OH^-]$ = $2.2 \text{ x } 10^{-4}$ M and pH = 10.35, matching our original prediction.

Check Your Learning 5.5.4 – Quantitative Prediction of pH Changes

What is the pH of a 0.083 M solution of LiCN?

Answer

11.06

The Ionization of Hydrated Metal Ions

As mentioned earlier in this Section, certain metal ions do hydrolyze, but via an indirect, alternate mechanism (i.e. *not* direct proton transfer to water molecules). If we measure the pH of the solutions of a variety of metal ions we will find that occasionally, these ions act as weak acids when in solution. The aluminum ion is an example. When aluminum nitrate dissolves in water, the aluminum ion reacts with water to give a hydrated aluminum ion, $Al(H_2O)_6{}^{3+}$, dissolved in bulk water. What this means is that the aluminum ion has the strongest interactions with the six closest water molecules (the so-called first solvation shell), even though it does interact with the other water molecules surrounding this $Al(H_2O)_6{}^{3+}$ cluster as well:

$$Al(NO_3)_3\,(s) + 6H_2O\,(l) \rightleftharpoons Al(H_3O^+)_6{}^{3+}\,(aq) + 3NO_3{}^-\,(aq)$$

Note: we frequently see the formula of this ion written simply as "$Al^{3+}{}_{(aq)}$", without explicitly noting that six water molecules are bonded to the aluminum ion (similar to how, in older textbooks, the formula of the hydronium ion, H_3O^+, was simplified to $H^+(aq)$).

Hydrated metal ions can behave as Brønsted-Lowry acids via an indirect proton transfer with water. Clearly, the aluminum atom itself cannot donate a proton – doing so would change the identity of the nucleus, transforming it into magnesium! Therefore, to act as Brønsted-Lowry acid, instead one of the bound water molecules acts as the proton donor to another external water molecule, becoming an OH^- group and generating one equivalent of H_3O^+ in the process. This is depicted in Figure 5.5.3 below – note that the charge on the complex ion has reduced from +3 to +2, due to the loss of one positive charge.

$$Al(H_2O)_6{}^{3+}(aq)+H2O(l)\leftrightarrow H_3O^+(aq)+Al(H_2O)_5(OH)^{2+}(aq)\quad K_a=1.4\times10^{-5}$$

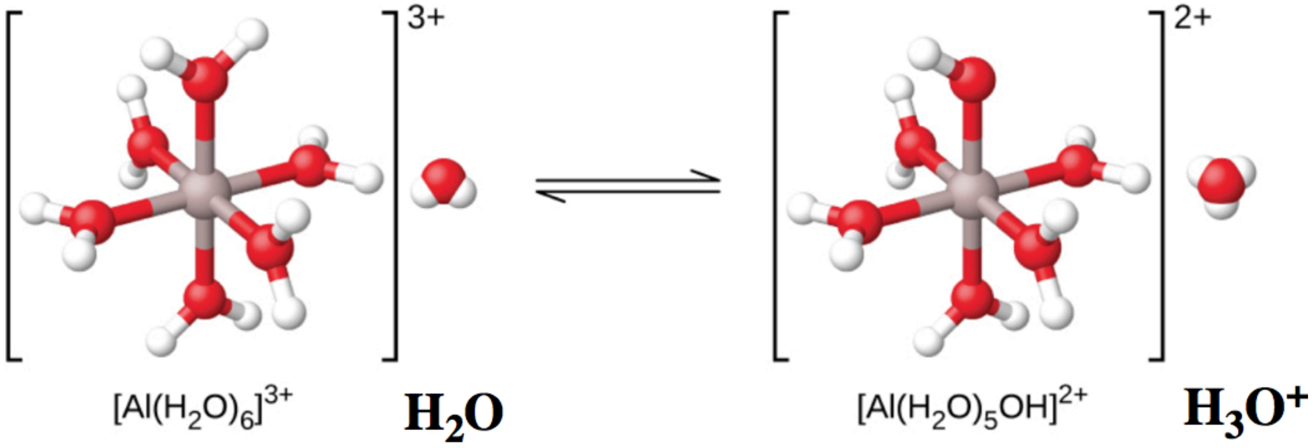


Figure 5.5.3. When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid. Note the top H_2O ligand changes to an OH^-. Additionally, the overall charge on the complex has decreased.

So, what other metal cations are capable of displaying similar acid behaviour? It is difficult to know for certain if a metal cation is acidic or not without experimental evidence. However, in general, a good rule of thumb is that metal cations with high charge densities tend to be significantly acidic. As the name implies, the charge density of an ion is the ratio of the charge of the ion to the volume of the ion, Equation 5.5.1:

$$\text{Charge Density} = \text{Charge of Ion}/\text{Volume of Ion}$$

Equation 5.5.1. Charge Density.

Metal cations with high charges (*e.g.* ≥ +2) and small ionic radii will overall have high charge densities, and thus often display acidic character. Additional examples of acidic hydrated metal ions are:

$$Fe(H_2O)_6{}^{3+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Fe(H_2O)_5(OH)^{2+}\,(aq)\quad pK_a = 2.74$$

$$Cu(H_2O)_6^{2+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Cu(H_2O)_5(OH)^+\,(aq) \quad pK_a = \text{~}6.3$$
$$Zn(H_2O)_4^{2+}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Zn(H_2O)_5(OH)^+\,(aq) \quad pK_a = 9.6$$

To further illustrate the acidity of these hydrated metal ions, the pH value of a 0.10 M solution of each are the following:

$$Fe(H_2O)_6^{3+}(aq)\ pH = 1.89$$
$$Cu(H_2O)_6^{2+}(aq)\ pH = 3.66$$
$$Zn(H_2O)_4^{2+}(aq)\ pH = 5.30$$

Note to CHM1311 Students:

Predicting the acid-base properties of a salt containing a metal cation can be somewhat tricky. We can determine the charge on the metal cation very easily, simply from the formula of the compound. However, whether it hydrolyzes or not depends on the *charge density*, and that relies on also knowing the size of the ion, which is not always readily apparent. In general, the Group 1 metal cations (Li^+, Na^+, K^+, *etc.*) have charges too low to ever hydrolyze using the mechanism described above. Of the Group 2 metal cations, only Be^{2+} is acidic due to its very small size. Transition metals with multiple oxidation states tend to be more acidic when they are in the higher oxidation state; for example, the Co^{2+} ion is acidic, whereas the Co^+ ion is not.

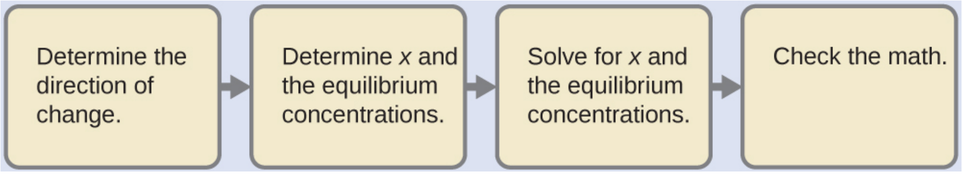
So, ask your professor if you will be solving problems involving acidic metal ions, and if necessary, a table of relevant K_a values will be provided to you.

Example 5.5.5 – Hydrolysis of $[Al(H_2O)_6]^{3+}$

Calculate the pH of a 0.10 M solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion $[Al(H_2O)_6]^{3+}$ in solution.

Solution

In spite of the unusual appearance of the acid, this is a typical acid ionization problem.



Determine the direction of change. The equation for the reaction and K_a are:

$$Al(H_2O)_6^{3+}(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + Al(H_2O)_5(OH)^{2+}(aq) \quad K_a = 1.4 \times 10^{-5}$$

The reaction shifts to the right to reach equilibrium.

Determine x and equilibrium concentrations. Use the table:

$$Al(H_2O)_6 + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)$$

Initial Concentration (M)	0.10		~0	0
Change (M)	$-x$		x	x
Equilibrium concentration (M)	$0.10 - x$		x	x

Solve for x and the equilibrium concentrations. Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a=([H_3O^+][Al(H_2O)_5(OH)^{2+}(aq)])/[Al(H_2O)_6{}^{3+}(aq)]=x^2/(0.10\text{-}x)=1.4\times10^{-5}$$

Solving this equation gives:

$$x=1.2\times10^{-3}\ \text{M}$$

From this we find:

$$[H_3O^+]=0+x=1.2\times10^{-3}\ \text{M}$$

$$\text{pH}=-\log[H_3O^+]=2.92\ \text{(an acidic solution)}$$

Check the work. The arithmetic checks; when 1.2×10^{-3} M is substituted for x, the result = K_a.

Check Your Learning 5.5.5 – Hydrolysis of $[Al(H_2O)_6]^{3+}$

What is $[Al(H_2O)_5(OH)^{2+}]$ in a 0.15 M solution of $Al(NO_3)_3$ that also contains enough of the strong acid HNO_3 to bring $[H_3O^+]$ to 0.10 M?

Answer

2.1×10^{-5} M

Questions

★ Questions

1. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $Al(NO_3)_3$
(b) RbI
(c) $KHCO_2$
(d) CH_3NH_3Br

2. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $FeCl_3$
(b) K_2CO_3
(c) NH_4Br

(d) $KClO_4$

★★ Questions

3. Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

Answers

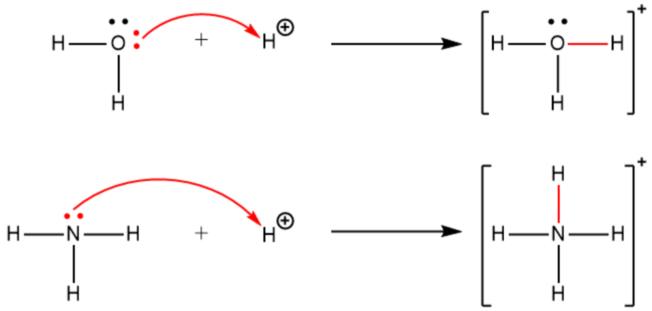
1. (a) acidic, (b) neutral, (c) basic, (d) acidic
2. (a) acidic; (b) basic; (c) acidic; (d) neutral
3. Acidic, $[H_3O^+] = 3.2 \text{ x } 10^{-5}$ M, $[OH^-] = 3.1 \text{ x } 10^{-10}$ M, pH = 4.50

5.6 – LEWIS ACIDS & BASES

Note: The Brønsted-Lowry Theory is sufficiently accurate enough to cover the acid-base concepts introduced in CHM1311. However, in the context of organic chemistry, the Lewis Theory of acid-base behaviour is much more appropriate, and thus it will be further discussed in detail in CHM 1321. The description of the theory is included here for completion, as supplementary material.

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

A **coordinate covalent bond** (or **dative bond**) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a proton to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a proton to form an ammonium ion. Both of these equations are shown here, with the coordinate covalent bonds consisting of two electrons each indicated in red.



Reactions involving the formation of coordinate covalent bonds are classified as **Lewis acid-base chemistry**.

A **Lewis acid** is any species (molecule or ion) that can accept a pair of electrons, and a **Lewis base** is any species (molecule or ion) that can donate a pair of electrons.

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid. In many Lewis acid-base reactions, a **Lewis acid-base adduct**, a compound that contains a coordinate covalent bond between the Lewis acid and the Lewis base, is formed.

Example 5.6.1 – Identifying Lewis Acids & Bases

Identify the acid and the base in each Lewis acid–base reaction.

(a) $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$

(b) $CaO + CO_2 \rightarrow CaCO_3$

(c) $BeCl_2 + 2\,Cl^- \rightarrow BeCl_4^{2-}$

Solution

(a) In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3.

(b) The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.

(c) The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

Check Your Learning 5.6.1 – Identifying Lewis Acids & Bases

Identify the acid and the base in each Lewis acid–base reaction.

(a) $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$

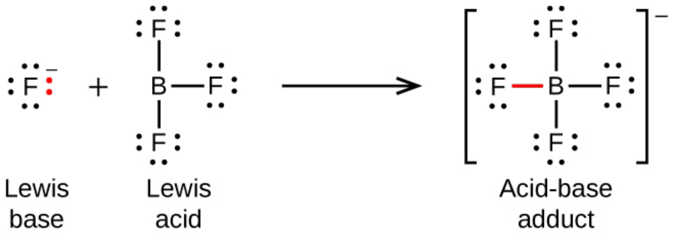
(b) $H_2O + SO_3 \rightarrow H_2SO_4$

Answer

(a) Lewis base: $(CH_3)_2O$; Lewis acid: BF_3; (b) Lewis base: H_2O; Lewis acid: SO_3

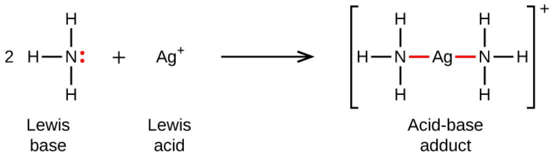
The following equations illustrate the general application of the Lewis concept and Lewis structures. Lewis Structures are covered in detail in the section on molecular bonding, Section 9.1, but for now, all you need to know is that atoms are indicated by their elemental symbol, with the lines connecting them within molecules representing covalent bonds. The dots surrounding the elemental symbols represent lone pairs of electrons – we'll visually display the dative bonds and the electrons that form them with a red colour to assist you with your understanding.

The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Since the boron atom has an incomplete octet, it can behave as an electron pair acceptor. As a result, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:

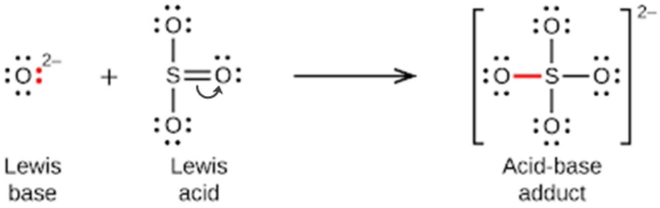


Note the negative charge on the adduct – since the sum of charges on the left hand side of the equation is -1, the sum of charges on the right hand side must also be -1.

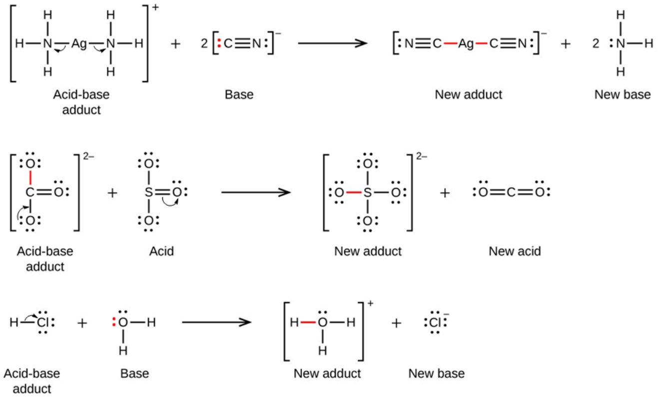
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a positively charged silver ion, the Lewis acid. Note once again that the sum of charges on the left side is +1, so the acid-base adduct on the right hand side must carry a charge of +1:



Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:

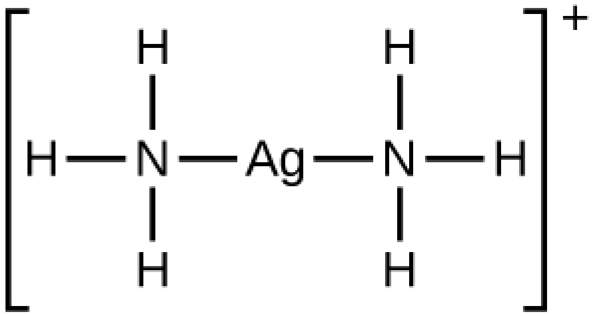


Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:



The last displacement reaction shows how the reaction of a Brønsted-Lowry acid with a base fits into the Lewis concept. A Brønsted-Lowry acid such as HCl is an acid-base adduct according to the Lewis concept, and proton transfer occurs because a more stable acid-base adduct is formed. Thus, although the definitions of acids and bases in the two theories are quite different, the theories overlap considerably.

Many slightly soluble ionic solids dissolve when the concentration of the metal ion in solution is decreased through the formation of complex (polyatomic) ions in a Lewis acid-base reaction. For example, silver chloride dissolves in a solution of ammonia because the silver ion reacts with ammonia to form the complex ion $Ag(NH_3)_2^+$. The Lewis structure of the $Ag(NH_3)_2^+$ ion is:



The equations for the dissolution of AgCl in a solution of NH_3 are:

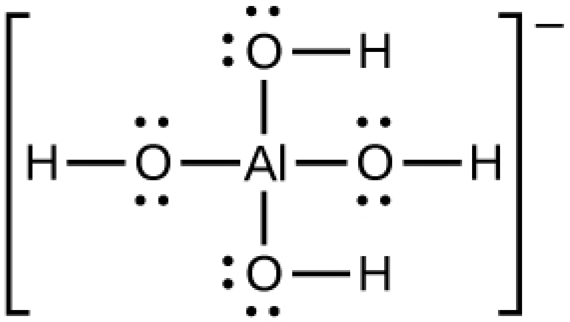
$$AgCl\ (s) \rightleftharpoons Ag^{+}\ (aq) + Cl^{-}\ (aq)$$

$$Ag^{+}\ (aq) + 2NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^{-}\ (aq)$$

$$\text{Net: } AgCl\ (s) + Ag^{+}\ (aq) + 2NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^{+}\ (aq) + Ag^{+}\ (aq) + Cl^{-}\ (aq)$$

$$\text{Net: } AgCl\ (s) + 2NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^{+}\ (aq) + Cl^{-}\ (aq)$$

Aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion $Al(OH)^{4-}$. The Lewis structure of the $Al(OH)^{4-}$ ion is:



The equations for the dissolution are:

$$Al(OH)_3\ (s) \rightleftharpoons Al^{3+}\ (aq) + 3OH^{-}\ (aq)$$

$$Al^{3+}\ (aq) + 4OH^{-}\ (aq) \rightleftharpoons Al(OH)_4^{-}\ (aq)$$

$$\text{Net: } Al(OH)_3\ (s) + Al^{3+}\ (aq) + 3OH^{-}\ (aq) + OH^{-}\ (aq) \rightleftharpoons Al(OH)_4^{-}\ (aq) + Al^{3+}\ (aq) + 3OH^{-}\ (aq)$$

$$\text{Net: } Al(OH)_3\ (s) + OH^{-}\ (aq) \rightleftharpoons Al(OH)_4^{-}\ (aq)$$

Mercury(II) sulfide dissolves in a solution of sodium sulfide because HgS reacts with the S^{2-} ion:

$$HgS\ (s) \rightleftharpoons Hg^{2+}\ (aq) + S^{2-}\ (aq)$$

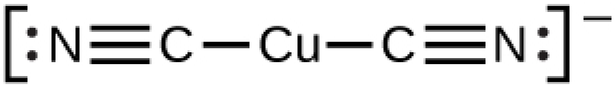
$$Hg^{2+}\ (aq) + 2S^{2-}\ (aq) \rightleftharpoons HgS_2^{2-}\ (aq)$$

$$\text{Net: } HgS\ (s) + S^{2-}\ (aq) + S^{2-}\ (aq) + Hg^{2+} \rightleftharpoons HgS_2^{2-}\ (aq) + S^{2-}\ (aq) + Hg^{2+}$$

$$\text{Net: } HgS\ (s) + S^{2-}\ (aq) \rightleftharpoons HgS_2^{2-}\ (aq)$$

A complex ion consists of a central atom, typically a transition metal cation, surrounded by ions, or molecules called **ligands**. These ligands can be neutral molecules like H_2O or NH_3, or ions such as CN^{-} or OH^{-}. Uusally, the ligands act as Lewis bases, donating a pair of electrons to the central atom. The ligands form bonds with the central atom or ion, creating a new ion with a charge equal to the sum of the charges of the ligands and the central atom or ion. This more complex arrangement is why the resulting ion is called a *complex ion*. The complex ion formed in these reactions cannot be predicted; it must be determined experimentally. The types of bonds formed in complex ions are coordinate covalent bonds, as electrons from the ligands are being shared with the central atom. Because of this, complex ions are sometimes referred to as *coordination complexes*.

The equilibrium constant for the reaction of the components of a complex ion to form the complex ion in solution is called a **formation constant (K_f)** (sometimes called a stability constant). For example, the complex ion $Cu(CN)_2^-$ is shown here:



It forms by the reaction:

$$Cu^+ (aq) + 2CN^- (aq) \rightleftharpoons Cu(CN)_2^- (aq)$$

At equilibrium:

$$K_f=[Cu(CN)^{2-}]/([Cu^+][CN^-]^2)$$

The inverse of the formation constant is the **dissociation constant (K_d),** the equilibrium constant for the *decomposition* of a complex ion into its components in solution. AppendixJ and Table 5.6.1 show a range of formation constants. In general, the larger the formation constant, the more stable the complex.

Table 5.6.1. Common Complex Ions by Decreasing Formation Constants

Substance	**K_f at 25°C**
AlF_6^{3-}	7×10^{19}
$Ag(NH_3)_2^+$	1.7×10^7
$Cd(CN)_4^{2-}$	3×10^{18}

As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[Ag^+] = 1.3 \times 10^{-5}$ M):

$$AgCl (s) \rightleftharpoons Ag^+ (aq) + Cl^- (aq)$$

However, if NH_3 is present in the water, the complex ion, $Ag(NH_3)_2^+$, can form according to the equation:

$$Ag^+ \textit{(aq)} + 2NH_3 \textit{(aq)} \rightleftharpoons Ag(NH_3)_2^+ \textit{(aq)}$$

with

$$K_f = [Ag(NH_3)_2^+(aq)]/([Ag^+][NH_3]^2) = 1.7 \times 10^7$$

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of AgCl combine with NH_3 to form $Ag(NH_3)_2^+$. As a consequence, the concentration of silver ions, $[Ag^+]$, is reduced, and the reaction quotient for the dissolution of silver chloride, $[Ag^+][Cl^-]$, falls below the solubility product of AgCl:

$$Q = [Ag^+][Cl^-] < K_{sp}$$

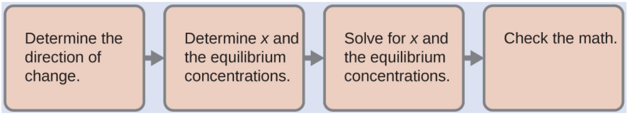
More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

Example 5.6.2 – Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that is initially 0.10 M $Ag(NH_3)_2^+$.

Solution

We use the familiar path to solve this problem:



1. *Determine the direction of change.* The complex ion $Ag(NH_3)_2^+$ is in equilibrium with its components, as represented by the equation:

$$Ag^+ \textit{(aq)} + 2NH_3 \textit{(aq)} \rightleftharpoons Ag(NH_3)_2^+ \textit{(aq)} \quad K_f = 1.7 \times 10^7$$

We write the equilibrium as a formation reaction because Appendix J lists formation constants for complex ions. Initially, only the complex ion is present ($[Ag^+] = 0$ and $[NH_3] = 0$), $Q > K_f$, and so the reaction shifts to the left (towards reactants) to reach equilibrium.

2. Determine x and equilibrium concentrations. We let the change in concentration of Ag^+ be x. Dissociation of 1 mol of $Ag(NH_3)_2^+$ gives 1 mol of Ag^+ and 2 mol of NH_3, so the change in $[NH_3]$ is $2x$ and that of $Ag(NH_3)_2^+$ is $-x$. In summary:

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

Initial Concentration (M)	0	0	0.10
Change (M)	$+x$	$+2x$	$-x$
Equilibrium concentration (M)	$0 + x$	$0 + 2x$	$0.10 - x$

---

3. *Solve for x and the equilibrium concentrations.* At equilibrium:

$$K_f=[Ag(NH_3)_2^{+}(aq)]/([Ag+][NH3]^2)$$
$$1.7\times10^7 = (0.10-x)/((x)(2x)^2)$$

Since K_f is very large, we know that this is a heavily product-favoured reaction, and therefore very little of the complex will dissociate into the separate ions. Therefore, let us assume that the changes in concentrations needed to reach equilibrium are small. Thus 0.10 – x is approximated as 0.10 to simplify our calculations:

$$1.7\times10^7= (0.10-x)/((x)(2x)^2)$$
$$x^3 = 0.104(1.7\times10^7)=1.5\times10^{-9}$$
$$x= \text{cbrt}(1.5\times10^{-9})=1.1\times10^{-3}$$

Checking the assumption we made, we find that only 1.1% of the $Ag(NH_3)_2^+$ dissociates into Ag^+ and NH_3, and therefore the assumption that x is small is justified.

Now we determine the equilibrium concentrations:

$$[Ag+]=0+x=1.1\times10^{-3}\ M$$
$$[NH_3]=0+2x=2.2\times10^{-3}\ M$$
$$[Ag(NH_3)_2^+]=0.10-x=0.10-0.0011=0.099$$

The concentration of free silver ion in the solution is 0.0011 M.

4. *Check the work.* The value of Q calculated using the equilibrium concentrations is equal to K_f within the error associated with the significant figures in the calculation.

Check Your Learning 5.6.2 – Dissociation of a Complex Ion

Calculate the silver ion concentration, $[Ag^+]$, of a solution prepared by dissolving 1.00 g of $AgNO_3$ and 10.0 g of KCN in sufficient water to make 1.00 L of solution. (Hint: Because $Q < K_f$, assume the reaction goes to completion then calculate the $[Ag^+]$ produced by dissociation of the complex.)

Answer

2.5×10^{-22} M

Questions

★ Questions

1. Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?
2. Explain why the addition of NH_3 or HNO_3 to a saturated solution of Ag_2CO_3 in contact with solid Ag_2CO_3 increases the solubility of the solid.
3. Calculate the cadmium ion concentration (g·mol^{-1}), $[Cd^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 M $Cd(NO_3)_2$ with 1.150 L of 0.100 M $NH_3(aq)$.
4. Explain why addition of NH_3 or HNO_3 to a saturated solution of $Cu(OH)_2$ in contact with solid $Cu(OH)_2$ increases the solubility of the solid.
5. Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d. For the complex ion AlF_6^{3-} the dissociation reaction is:

$$AlF_6^{3-} \rightleftharpoons Al^{3+} + 6F^{-} \text{ and } K_d=([Al^{3+}][F^{-}]^6)/[AlF_6^{3-}]=2\times10^{-24}$$

Calculate the value of the formation constant, K_f, for AlF_6^{3-}.

6. Using the dissociation constant, $K_d = 7.8 \times 10^{-18}$, calculate the equilibrium concentrations (g·mol^{-1}) of Cd^{2+} and CN^{-} in a 0.250 M solution of $Cd(CN)_4^{2-}$.

7. Using the dissociation constant, $K_d = 2.2 \times 10^{-34}$, calculate the equilibrium concentrations (g·mol^{-1}) of Co^{3+} and NH_3 in a 0.500 M solution of $Co(NH_3)_6^{3+}$.

8. Calculate the mass of potassium cyanide ion (in grams) that must be added to 100 mL of solution to dissolve 2.0×10^{-2} mol of silver cyanide, AgCN.

★★ Questions

9. A roll of 35 mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass (in grams) of $Na_2S_2O_3{\cdot}5H_2O$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as $Ag(S_2O_3)_2^{3-}$ ($K_f = 4.7 \times 10^{13}$)?

10. We have seen an introductory definition of an acid: An acid is a compound that reacts with water and increases the amount of hydronium ion present. In the chapter on acids and bases, we saw two more definitions of acids: a compound that donates a proton (a hydrogen ion, H^+) to another compound is called a Brønsted-Lowry acid, and a Lewis acid is any species that can accept a pair of electrons. Explain why the introductory definition is a macroscopic definition, while the Brønsted-Lowry definition and the Lewis definition are microscopic definitions.

11. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

(a) $CO_2 + OH^- \rightarrow HCO_3^-$

(b) $B(OH)_3 + OH^- \rightarrow B(OH)_4^-$

(c) $I^- + I_2 \rightarrow I_3^-$

(d) $AlCl_3 + Cl^- \rightarrow AlCl_4^-$ (use Al – Cl single bonds)

(e) $O^{2-} + SO_3 \rightarrow SO_4^{2-}$

12. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

(a) $CS_2 + SH^- \rightarrow HCS_3^-$

(b) $BF_3 + F^- \rightarrow BF_4^-$

(c) $I^- + SnI_2 \rightarrow SnI_3^-$

(d) $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$

(e) $F^- + SO_3 \rightarrow SFO_3^-$

13. Using Lewis structures, write balanced equations for the following reactions:

(a) $HCl\,(g) + PH_3\,(g) \rightarrow$

(b) $H_3O^+ + CH_3^- \rightarrow$

(c) $CaO + SO_3 \rightarrow$

(d) $NH_4^+ + C_2H_5O^- \rightarrow$

14. In a titration of cyanide ion, 28.72 mL of 0.0100 M $AgNO_3$ is added before precipitation begins. [The reaction of Ag^+ with CN–goes to completion, producing the $Ag(CN)_2^-$ complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of $Ag(CN)_2^-$. How many grams (mass) of NaCN were in the original sample?

15. In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides that are Lewis acids and accept F^- ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3.

16. Boric acid, H_3BO_3, is not a Brønsted-Lowry acid but a Lewis acid.

(a) Write an equation for its reaction with water.

(b) Predict the shape of the anion thus formed.

(c) What is the hybridization on the boron consistent with the shape you have predicted?

Answers

1. When the amount of solid is so small that a saturated solution is not produced.
2. CO_3 is a conjugate base of a weak acid meaning it hydrolyzes pushing the equilibrium to the right, therefore increasing solubility.
3. 8×10^{-5} M
4. OH- is removed from the solution by reacting with either NH_3 or HNO_3 pushing the equilibrium to the right, therefore increasing solubility.
5. 5×10^{23}
6. $[Cd(CN)_4^{2-}] + [CN^-] \rightleftharpoons [Cd^{2+}]$

Initial Concentration (M)	0.250	0	0
Equilibrium concentration (M)	0.250 – x	$4x$	x

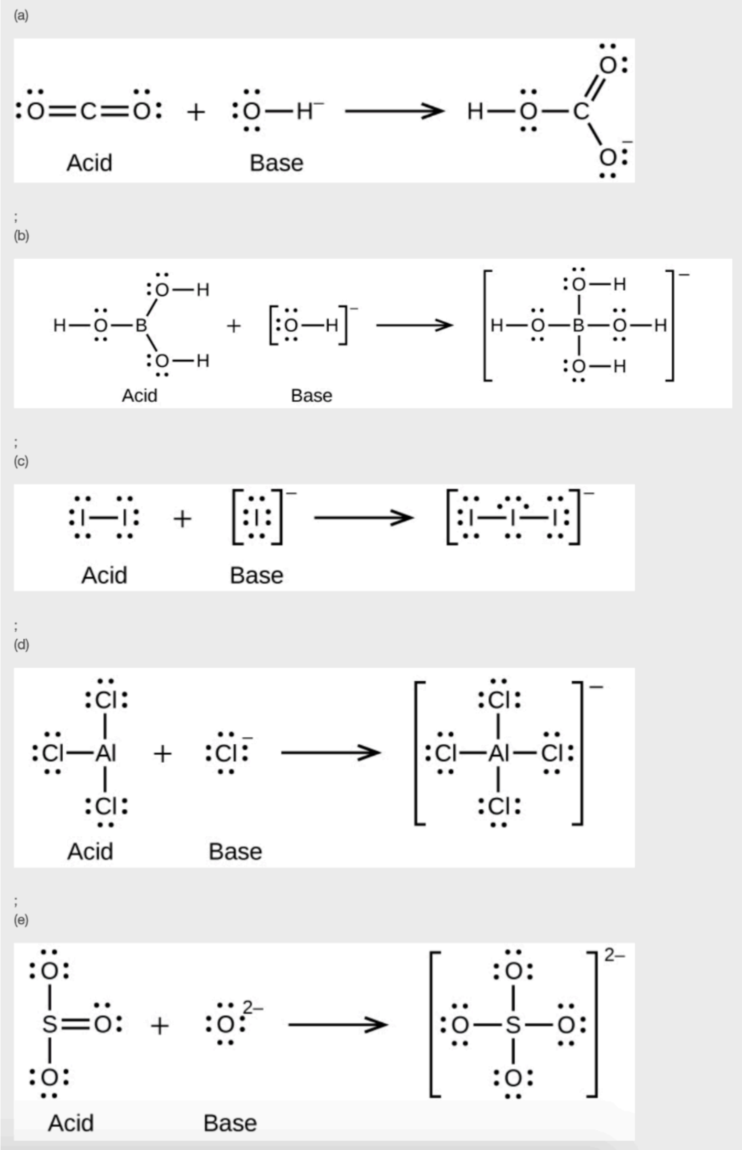
7. [Co_3^{+}] = 3.0 × 10–6 M; [NH_3] = 1.8 × 10^{-5} M

8. 1.3 g

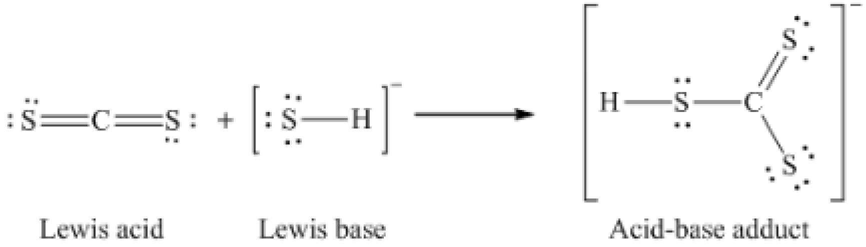
9. 0.79 g

10. Since almost all acids (whether Lewis or Brønsted-Lowry) increase the concentration of hydronium in the solution by reacting with water, the introductory definition of acids encompasses the behaviour of such compounds, and is therefore a macroscopic definition of an acid. Since the Lewis or Brønsted-Lowry definitions explain the mechanisms behind the (i.e Brønsted-Lowry acids release H^+) hydronium ion concentration increase, they are considered a microscopic definition.

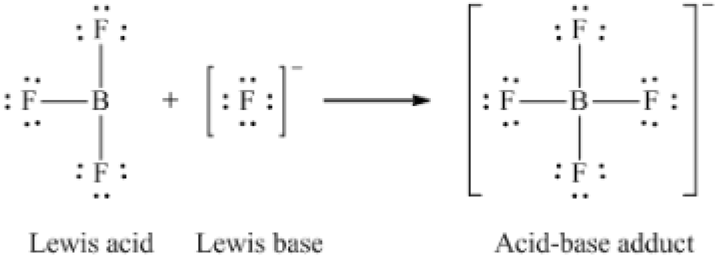
11.


(a)
Acid
Base
;
(b)
Acid
Base
;
(c)
Acid
Base
;
(d)
Acid
Base
;
(e)
Acid
Base

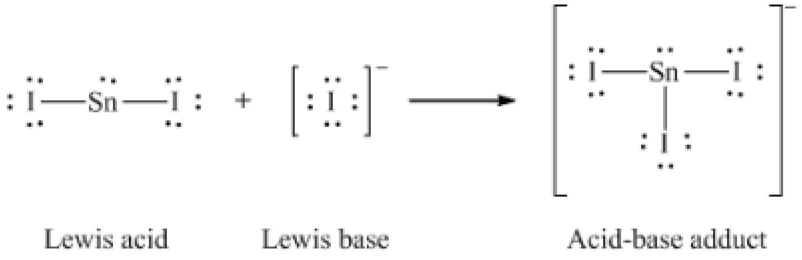
12.


Lewis acid
Lewis base
Acid-base adduct

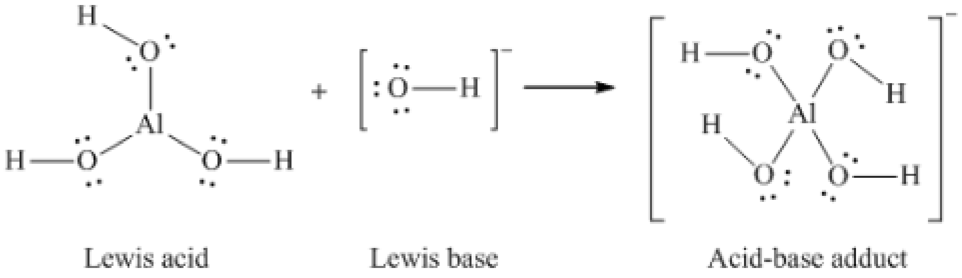
(a)


Lewis acid
Lewis base
Acid-base adduct

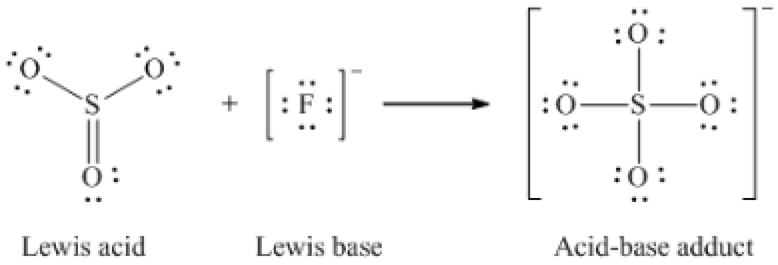
(b)


Lewis acid
Lewis base
Acid-base adduct

(c)


Lewis acid
Lewis base
Acid-base adduct

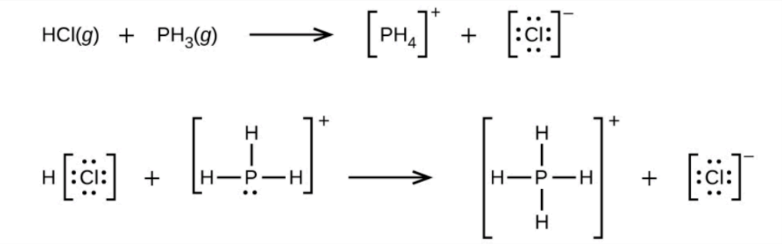
(d)


Lewis acid
Lewis base
Acid-base adduct

(e)

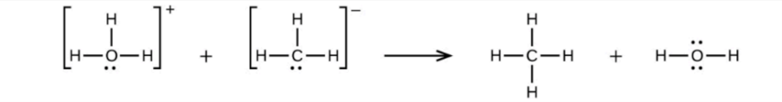
13.

(a)



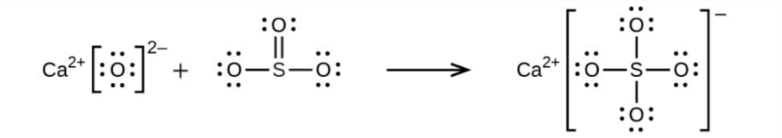
;

(b) $H_3O^+ + CH_3^- \longrightarrow CH_4 + H_2O$



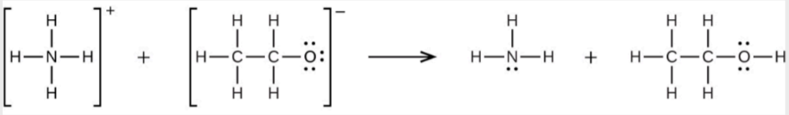
;

(c) $CaO + SO_3 \longrightarrow CaSO4$



;

(d) $NH_4{}^+ + C_2H_5O^- \longrightarrow C_2H_5OH + NH_3$



14. 0.0281 g

15. $HNO_3\,(l) + HF\,(l) \rightarrow H_2NO_3{}^+ + F^-$; $HF\,(l) + BF_3\,(g) \rightarrow H^+ + BF_4$

16. (a) $H_3BO_3 + H_2O \rightarrow H_4BO_4{}^- + H^+$; (b) The electronic and molecular shapes are the same – both tetrahedral. (c) The tetrahedral structure is consistent with sp^3 hybridization.

CHAPTER 6

6.1 – COMMON-ION EFFECT

The **common ion effect** is used to describe the effect on an existing equilibrium by the addition of a second substance that contains an ion common to the equilibrium. If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion.

Common Ions

When NaCl and KCl, both very soluble salts, are dissolved in the same solution, the Cl^- ions are *common* to both salts. In a system containing NaCl and KCl, the Cl^- ions are common ions.

$$NaCl\,(s) \rightarrow Na^+\,(aq) + Cl^-\,(aq)$$

$$KCl\,(s) \rightarrow K^+\,(aq) + Cl^-\,(aq)$$

Since both salts ionize completely in solution, we can use stoichiometry to express the concentrations of the dissolved ions in solution in the following equation:

$$[Na^+] + [K^+] = [Cl^-]$$

You may recognize the above equivalence as an application of the concepts of *charge balance* and *mass balance*.

Example 6.1.1 – Concentrations of Common Ions

What are $[Na^+]$, $[Cl^-]$, $[Ca^{2+}]$, and $[H^+]$ in a solution containing 0.10 M each of NaCl, $CaCl_2$, and HCl?

Solution

All three species ionize completely in water:

$$NaCl\,(s) \rightarrow Na^+\,(aq) + Cl^-\,(aq)$$

$$KCl\,(s) \rightarrow K^+\,(aq) + Cl^-\,(aq)$$

$$CaCl_2\,(s) \rightarrow Ca^{2+}\,(aq) + 2Cl^-\,(aq)$$

Using stoichiometry, we see that each mol of dissolved compound produces a mol of cations. Therefore, due to the conservation of ions, we have:

$$[Na^+] = [Ca^{2+}] = [H_3O^+] = 0.10\text{ M}$$

Each compound produces chloride ions; however, we note that calcium chloride produces 2 mol of Cl^- ions for every mol of $CaCl_2$ dissolved. Therefore, the total amount of chloride ion in solution is:

$$[Cl^-] = 0.10\text{ M(due to NaCl)} + 0.20\text{ M(due to CaCl}_2\text{)} + 0.10\text{ M(due to HCl)}$$

$$[Cl^-] = 0.40\text{ M}$$

Example 6.1.2 – Common Ion Calculations

John poured 10.0 mL of 0.10 M NaCl, 10.0 mL of 0.10 M KOH, and 5.0 mL of 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is $[Cl^-]$ in the final solution?

Solution

$$[Cl^-] = (0.1\ M \times 10\ mL + 0.2\ M \times 5.0\ mL)/100.0\ mL = 0.020\ M$$

Common Ion Effect and Equilibria

In the above examples, since all of the compounds undergo 100% ionization, we could use simple stoichiometry to find the concentrations of the common ion. But what happens if we involve substances that only *partially* ionize in solution? What effect would a common ion have on an equilibrium?

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift in order to restore the balance. Consider the following chemical equation, representing the ionization of a generic weak acid:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

If we were to add a second substance, for example, the sodium salt of the conjugate base (NaA) to this solution, then this soluble salt would increase the concentration of the A^- ion in solution:

$$NaA\ (s) \rightarrow Na^+\ (aq) + A^-\ (aq)$$

The A^- ion is the *common ion* to both chemical equations, but note their differences: the first is an equilibrium but the second goes to completion. Thus, the presence of the sodium salt increases the concentration of conjugate base. According to Le Chatelier's Principle, increased $[A^-]$ means that the weak acid equilibrium will shift towards the reactants.

In general, we can conclude that adding a common ion prevents a weak acid (or similarly, a weak base) from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium. *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.* The example below, involving the dissolution of a slightly soluble salt, illustrates this important concept.

Example 6.1.3 – Common Ion Added to a System at Equilibrium

Calcium hydroxide is a sparingly soluble salt that exists in equilibrium in aqueous solution with its ions. A solution of $Ca(OH)_2$ at equilibrium contains $[Ca^{2+}] = 0.0108$ M, $[OH^-] = 0.0216$ M, and some solid salt. To this solution, you add some solid calcium chloride, which ionizes completely into Ca^{2+} and Cl^- and allow the system to re-establish equilibrium. When you re-measure the ion concentrations, you find the solution now contains $[Ca^{2+}] = 0.0374$ M and $[OH^-] = 0.0116$ M. Calculate the equilibrium constant for the dissolution of calcium hydroxide before and after the addition of calcium chloride, rounding to 2 significant figures. What can you conclude when you compare these values?

Solution

First, write out the chemical equation for the dissolution of calcium hydroxide at equilibrium:

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2OH^{-}\,(aq)$$

The equilibrium constant expression for the above equilibrium is:

$$K = [Ca^{2+}][OH^{-}]^2$$

Substituting the concentrations of calcium and hydroxide ions present at equilibrium *before* the addition of calcium chloride, we obtain:

$$K = (0.0108)(0.0216)^2$$

$$K = 5.0\times10^{-6}$$

Now, we recalculate K using the concentrations *after* the addition of the salt containing the common ion:

$$K = (0.0374)(0.0116)^2$$

$$K = 5.0\times10^{-6}$$

Comparing these values, we can conclude that, while the equilibrium concentrations of ions change, the value of the equilibrium constant itself *does not change* with the addition of a common ion.

Returning to our discussion of weak acids, we now know that the presence of a common ion suppresses the ionization of the weak acid, decreasing the concentrations of the product ions, but does not affect the equilibrium constant, K_a. This is illustrated below in Figure 6.1.1: adding a strong acid, such as HCl, to a solution of a weak acid shifts the equilibrium towards the reactants. HCl ionizes completely, increasing the concentration of H_3O^+, which then suppresses the ionization of the weak acid present, acetic acid.

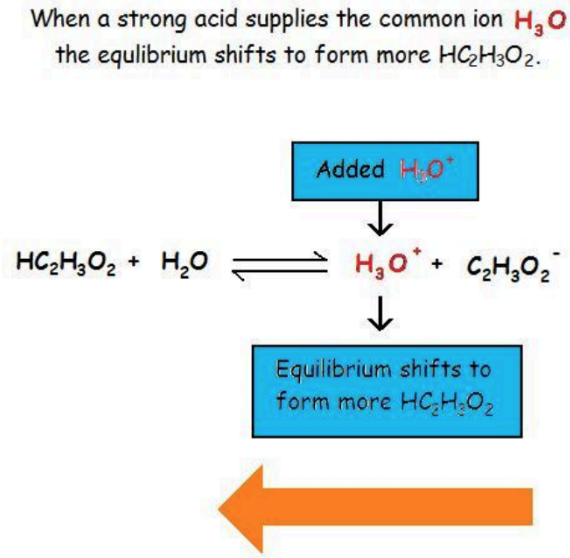


Figure 6.1.1. Adding a strong acid (e.g. HCl) to a solution of acetic acid (a weak acid) shifts the equilibrium towards reactants, thus inhibiting the ionization of the weak acid.

The common ion effect also suppresses the ionization of a weak base by again increasing the concentration of a product ion of the equilibrium. For example, Figure 6.1.2 shows the common ion effect of the addition of OH^- (from a strong base) on the ionization of ammonia, a weak base.

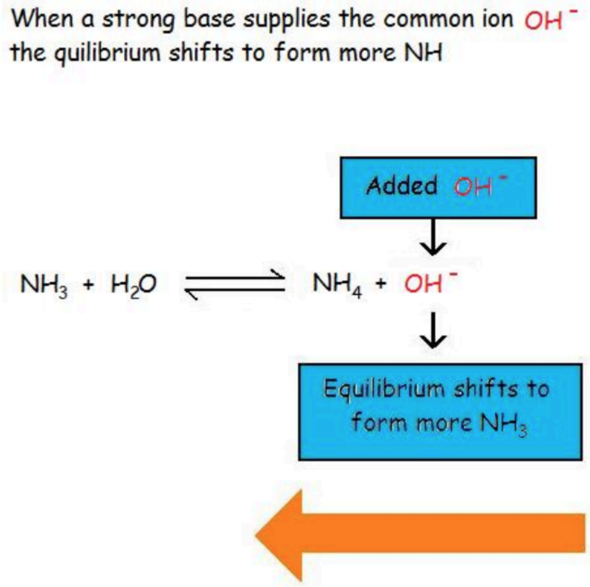


Figure 6.1.2. Adding a strong base (e.g. NaOH) to a solution of ammonia (a weak base) shifts the equilibrium towards reactants, thus inhibiting the ionization of the weak base.

Adding a strong base such as NaOH, causes the concentration of the common ion of hydroxide to increase, and thus increases the reaction quotient, Q:

$$Q = [NH4+][OH-][NH3]$$

$Q > K$, and thus the system is no longer at equilibrium. To re-establish equilibrium, the value of Q must be decreased by decreasing the amount of products and increasing the amount of reactant. Therefore, the reaction shifts to the left to counteract the imbalance (in accordance with Le Châtelier's Principle), forming more reactants. This decreases Q until it equals the equilibrium constant, K_b = 1.8 x 10^{-5}, and a new equilibrium point is reached.

Example 6.1.4 – Common Ion Added to a System at Equilibrium

What is the pH of a 0.100 M solution of HOCl? What is the pH of a solution that contains both 0.100 M HOCl and 0.010 HCl? What can you conclude by comparing these two values?

Solution

HOCl is a weak acid, with $K_a = 4.0 \times 10^{-8}$. We use an ICE table to find the hydronium ion concentration at equilibrium and then the pH:

$$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$$

Initial Concentration (M)	0.100	/	~0	0
Change (M)	$-x$	/	x	x
Equilibrium concentration (M)	$0.100 - x$	/	x	x

$$K_a = 4.0\times10^{-8} = ([H_3O^+(aq)][OCl^-])/[HOCl]$$
$$4.0\times10^{-8} = x^2/(0.100\text{-}x)$$
$$x = 6.3\times10^{-5}\ M = [H_3O^+]$$
$$pH = 4.20$$

Now, we repeat this calculation, but this time taking into account the 0.010 M H_3O^+ formed from the complete ionization of the strong acid, HCl:

$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$

Initial Concentration (M)	0.100	/	0.010	0
Change (M)	$-x$	/	x	x
Equilibrium concentration (M)	$0.100 - x$	/	$0.010 + x$	x

$$K_a = 4.0\times10^{-8} = ([H_3O^+(aq)][OCl^-])/[HOCl]$$
$$4.0\times10^{-8} = ((0.010+x)(x))/(0.100\text{-}x)$$
$$x = 4.0\times10^{-7}\ M$$
$$[H_3O^+] = 0.010 + x = 0.010\ M + 4.0\times10^{-7}\ M = 0.010\ M$$
$$pH = 2.00$$

In both cases, we made the assumption that "x is small" to simplify the calculation (verifying the result confirms that this assumption is valid). Comparing the two results, we see that in the second case, nearly 100% of the hydronium ion at equilibrium comes from the strong acid source, HCl. In the presence of the strong acid, very little of the HOCl ionizes, illustrating the common ion effect on this equilibrium.

Check Your Learning 6.1.4 – Common Ion Added to a System at Equilibrium

What is the pH of a solution of 0.150 M NH_3 and 0.045 M NH_4Cl?

Answer

pH = 9.78

★ Questions

1. The solubility product K_{sp} for bismuth sulfide Bi_2S_3 is 1.6 x 10^{-72} at 25°C. What is the molar solubility of bismuth sulfide in a solution that is 0.0010 M in sodium sulfide Na_2S?

2. John poured 1.0 mL of 0.10 M NaCl, 1.0 mL of 0.10 M KOH, and 1.0 mL 0.20 M HCl solutions together and then he made the total volume to be 100.0 mL. What is the [Cl^-] in the final solution (g·mol^{-1})?

3. The K_{sp} for AgCl is 1.0 x 10^{-10}. From which of the following solutions would silver chloride precipitate?

A. A solution 0.10 M Ag^+ and 1.00 M Cl^-

B. A solution 1.0 x 10^{-5} M in Ag^+ and 0.20 M in Cl^-

C. A solution 1.0 x 10^{-7} M in Ag^+ and 10^{-7} M in Cl^-

4. Addition of which of the following substances will cause the precipitation of a salt from one liter of a 1 x 10^{-4} M Mg^{2+} solution?

A. 1 x 10^{-4} mole NaOH

B. 1 x 10^{-1} mole nitric acid

C. 1 x 10^{-5} mole potassium acetate

D. 1 x 10^{-4} mole ammonium nitrate

E. 1 x 10^{-2} mole sodium fluoride

Substance	**K_{sp}**
Magnesium hydroxide	1.2 x 10^{-11}
Magnesium carbonate	1.6 x 10^{-5}
Magnesium fluoride	6.4 x 10^{-9}

5. The K_{sp} for strontium chromate is 3.5 x 10^{-5} and K_{sp} for barium chromate is 1.2 x 10^{-10}. What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.10 M solution of barium and strontium ions without precipitating the other?

6. Iron(II) hydroxide is only sparingly soluble in water at 25 °C; its K_{sp} is equal to 7.9 × 10^{-16}. Calculate the solubility (g·mol^{-1}) of iron(II) hydroxide in a solution of pH 6.0.

Answers

1. 1.08 x 10^{13}
2. 0.003 M
3. A and B
4. E
5. 3.6 x 10^{-4}
6. 7.9 M

6.2 – BUFFER SOLUTIONS

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or simply a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 6.2.1). A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a *weak acid and its conjugate base*, whereas a solution of ammonia and ammonium chloride (NH_3 + NH_4Cl) is an example of a buffer that consists of a *weak base and its conjugate acid*.

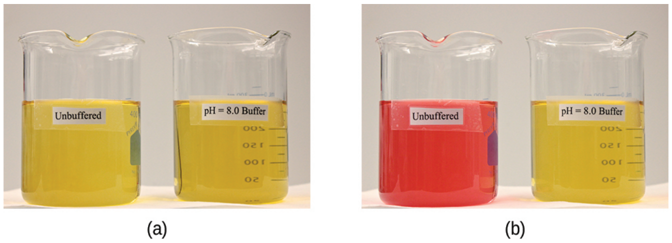


Figure 6.2.1. (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow colour of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01 M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in colour of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

Buffers are made from mixing a weak acid with its conjugate base or a weak base with its conjugate acid. It is vital that the acid and base form a conjugate pair; this way, the two species cannot neutralize one another. For example, if a buffer is formed from a weak acid HA and its conjugate base A^-, any proton transfer that occurs yields products that are identical to the reactants, a process known as an *identity reaction*:

$$HA + A^- \rightarrow A^- + HA$$

Instead, the acid and base conjugate pair function to neutralize *external* sources of base and acid, respectively, in the following reactions:

$$HA + OH^- \rightarrow A^- + H_2O$$

$$A^- + H_3O^- \rightarrow HA + H_2O$$

We will return to these neutralization reactions later, but first let us examine the differences between acidic and basic buffers.

Acidic Buffers: Aqueous Mixtures of HA + A^-

If we mix together acetic acid and sodium acetate in water, the resulting aqueous solution has a pH <

7. It is acidic because the K_a of acetic acid (1.8 x 10^{-5}) is greater than the K_b of the conjugate base acetate (5.6 x 10^{-10}):

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \; K_a = 1.8 \text{ x } 10^{-5}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \; K_b = 5.6 \text{ x } 10^{-10}$$

Comparing the K values, the first equilibrium lies further towards products than the second, thus there is more hydronium ion than hydroxide ion in the mixture, producing an overall pH for the mixture that is acidic.

This solution is a buffer because it contains the conjugate pair of a weak acid and its conjugate base, HA and A^-, and both species are present in significant concentrations. This acts to keep the hydronium ion concentration (the pH) almost constant even after the addition of a strong acid or a strong base. The conjugate acid/base pair is able to neutralize the strong acid or base added to the solution.

For example, if an external source of acid increases the amount of H_3O^+, the buffer counteracts this addition:

$$CH_3COO^- \,(aq) + H_3O^+ \,(aq) \rightarrow CH_3COOH \,(aq) + H_2O \,(l)$$

In this reaction, the conjugate base, CH_3COO^-, will neutralize the added acid, H_3O^+. This reaction goes to completion, because the reaction of CH_3COO^- with H_3O^+ has an equilibrium constant that is the inverse of the K_a for CH_3COOH: $1/K_a = 1/(1.8 \text{ x } 10^{-5}) = 5.5 \text{ x } 10^4$, indicating a heavily product-favoured reaction. So long as there is significantly more CH_3COO^- than H_3O^+, the externally added H_3O^+ will be consumed, increasing the concentration of CH_3COOH and decreasing the concentration of CH_3COO^- . But, since these two species are both present in large concentrations, the ratio of acid-to-conjugate base is nearly constant and there will be hardly any change in the amount of H_3O^+ present once equilibrium is re-established.

If a strong base were added such as sodium hydroxide (NaOH):

$$CH_3COOH + OH^- \,(aq) + OH^- \,(aq) \rightleftharpoons CH_3COO^- \,(aq) + H_2O \,(l)$$

In this reaction, the conjugate acid, CH_3COOH, will neutralize added amounts of base, OH^-, slightly increasing the concentration of CH_3COO^- in the solution and decreasing the amount of CH_3COOH. Again, since most of the OH^- is neutralized, little pH change will occur.

Basic Buffers: aqueous mixtures of B + HB^+

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the conjugate acid of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$NH_4^+ \,(aq) + OH^- \,(aq) \rightarrow NH_3 \,(aq) + H_2O \,(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$H_3O^+ \,(aq) + NH_3 \,(aq) \rightarrow NH_4^+ \,(aq) + H_2O \,(l)$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

Example 6.2.1 – pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

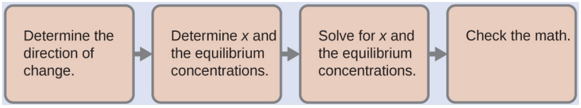
(a) Calculate the pH of an acetate buffer that is a mixture of 0.10 M acetic acid and 0.10 M sodium acetate.

(b) Calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of this buffer, giving a solution with a total volume of 101 mL.

(c) Calculate the pH after 1.0 mL of 0.10 M NaOH is added to an 100 mL of an unbuffered solution of 1.8×10^{-5} HCl.

Solution

(a) To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



Determine the direction of change. The equilibrium in a mixture of H_3O^+, $CH_3CO_2^-$, and CH_3CO_2H is:

$$CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2^-\,(aq)$$

The equilibrium constant for CH_3CO_2H is not given, so we look it up in Appendix H: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10$ M and $[H_3O^+] = {\sim}0$ M, the reaction shifts to the right to form H_3O^+.

Determine x and equilibrium concentrations. A table of changes and concentrations follows:

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Initial Concentration (M)	0.10	/
Change (M)	$-x$	/
Equilibrium concentration (M)	$0.10 - x$	/

Solve for x and the equilibrium concentrations. We find:

$$x = 1.8\times10^{-5}\ \text{M}$$

and

$$[H_3O^+] = 0+x = 1.8\times10^{-5}\ \text{M}$$

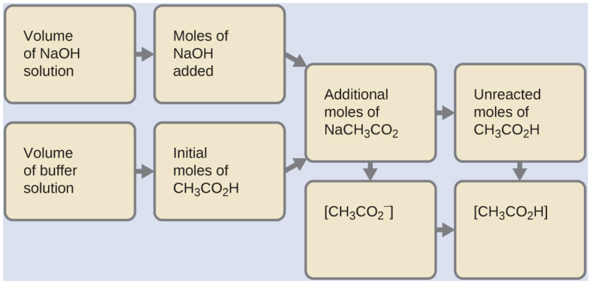
Thus:

$$\text{pH} = -\log[H_3O+] = -\log(1.8\times10^{-5}) = 4.74$$

Check the work. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

Note: Notice that when [HA] = [A-], pH = pK_a. Qualitatively, one would expect a decrease in pH as the [HA] increases since this increases the $[H_3O^+]$. Inversely, one would expect an increase in pH as the $[A^-]$ increases. Since A^- is the conjugate base of HA (see equation below), by increasing the concentration of A^-, the equilibrium will favour HA (based on Le Chatelier's Principle) thereby decreasing the $[H_3O^+]$ in solution and therefore increasing the pH. Later in this chapter, the *Henderson-Hasselbach equation* will be introduced and will mathematically demonstrate why pH = pK_a when [HA] = [A-].

(b) Since we are adding base, it will be neutralized by the acid of the buffer, acetic acid. First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



Determine the moles of NaOH. One milliliter (0.0010 L) of 0.10 M NaOH contains:

$$0.0010\ \text{L}\times(0.10\ \text{mol NaOH}/1\ \text{L}) = 1.0\times10^{-4}\ \text{mol NaOH}$$

Determine the moles of CH_2CO_2H. Before reaction, 0.100 L of the buffer solution contains:

$$0.100\ \text{L}\times(0.100\ \text{mol}\ CH_3CO_2H/1\text{L}) = 1.00\times10^{-2}\ \text{mol}\ CH_3CO_2H$$

Solve for the amount of $NaCH_3CO_2$ produced. The 1.0×10^{-4} mol of NaOH neutralizes 1.0×10^{-4} mol of CH_3CO_2H, leaving:

$$(1.0\times10^{-2})-(0.01\times10^{-2}) = 0.99\times10^{-2}\ \text{mol}\ CH_3CO_2H$$

and producing 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

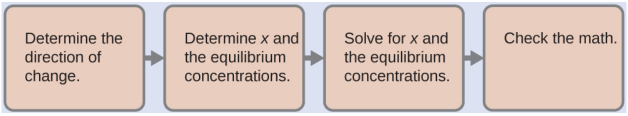
$$(1.0\times10^{-2})+(0.01\times10^{-2}) = 1.01\times10^{-2}\ \text{mol NaCH3CO2}$$

Find the molarity of the products. After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = (9.9\times10^{-3}\text{mol}/0.101\text{L}) = 0.098\text{ M}$$

$$[NaCH_3CO_2] = (1.01\times10^{-2}\text{ mol}/0.101\text{ L}) = 0.100\text{ M}$$

Now we calculate the pH after the intermediate solution, which is 0.098 M in CH_3CO_2H and 0.100 M in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base only slightly increased the pH of the solution from 4.74 to 4.75.

(c) The 1.8×10^{-5} M solution of HCl has the same hydronium ion concentration as the 0.10 M solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100\text{L} = (1.8\times10^{-5}\text{ mol HCl}/1\text{L}) = 1.8\times10^{-6}\text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 M NaOH contains 1.0×10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0\times10^{-4})\text{-}(1.8\times10^{-6}) = 9.8\times10^{-5}\text{ M}$$

The concentration of NaOH is:

$$9.8\times10^{-5}\text{ M NaOH}/0.101\text{L}= 9.7\times10^{-4}\text{ M}$$

The pOH of this solution is:

$$\text{pOH} = \text{-log}[\text{OH}^-] = \text{-log}(9.7\times10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00\text{-pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

Check Your Learning 6.2.1 – pH Changes in Buffered and Unbuffered Solutions

Show that adding 1.0 mL of 0.10 M HCl changes the pH of 100 mL of a 1.8×10^{-5} M HCl solution from 4.74 to 3.00.

Solution

Initial pH of 1.8×10^{-5} M HCl:

$$\text{pH} = -\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$$

Moles of H_3O^+ in 100 mL of 1.8×10^{-5} M HCl:

$$1.8 \times 10^{-5}\ \text{mol/L} \times 0.100\ \text{L} = 1.8 \times 10^{-6}\ \text{mol}$$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 M HCl:

$$0.10\ \text{mol/L} \times 0.0010\ \text{L} = 1.0 \times 10^{-4}\ \text{mol}$$

Final pH after addition of 1.0 mL of 0.10 M HCl:

$$\text{pH} = -\log[H_3O^+] = -\log(\text{total moles } H_3O^+/\text{total volume}) = -\log((1.0\times10^{-4} + 1.8\times10^{-6}\ \text{mol})/0.101\ \text{L}) = 3.00$$

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components.

2. A buffer solution has generally lost its usefulness when the amount of one component of the buffer pair is less than about 10% of the other. Figure 6.2.2 shows the effect on the pH of an acetic acid-acetate ion buffer as the amount of strong base is added. Initially, the buffer contains equal amounts of acetic acid and acetate, and the initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

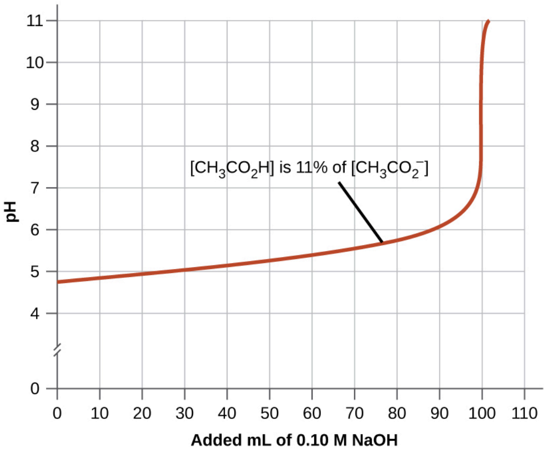


Figure 6.2.2. The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10 M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10$ M and $[CH_3CO_2^-] = 0.10$ M.

3. Weak acids and their conjugate bases are better as buffers for pHs less than 7; weak bases and their conjugate acids are better as buffers for pHs greater than 7.

Buffering Action Curves

Why do buffering action curves look the way they do? The key is to identify what happens at every part of the curve. Figure 6.2.2 shows an acetic acid-acetate ion buffer which begins at a pH of 4.74. As NaOH is slowly added the pH rises very little until about 90 mL NaOH is introduced. This is caused by the acetic acid reacting with the ionized OH^- anions and the conjugate acid/base pair achieving equilibrium. This uses up the OH^- in solution and keeps the pH fairly constant.

After this, the graph shows us that the pH rises very quickly with a very small addition of NaOH. This is because the NaOH has used up all of the acetic acid available for neutralization of its OH^- anion. Once there is no more neutralization possible, the excess OH^- in solution quickly makes the solution basic with excess OH^-. Although the graph cuts off, the end of the curve will plateau into a straight line. This occurs when sufficient NaOH has been added to bring the entire solution to a pH of approximately 13 (the pH of NaOH).

The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = ([H_3O^+][A^-])/[HA]$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = K_a \times ([HA]/[A^-])$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log(K_a) - \log([HA]/[A^-])$$

which can be written as:

$$pH = pK_a + \log([A^-]/[HA])$$

where pK_a is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log(K_a)$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its conjugate base in a buffered solution. Scientists often use this expression, called the **Henderson-Hasselbalch equation**, to calculate the pH of buffer solutions. It is important to note that the "x is small" assumption must be valid to use this equation.

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph **Henderson** (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert **Hasselbalch** (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

Medicine: the Buffer System in Blood

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, HCO_3^-. When an excess of hydrogen ion enters the bloodstream, it is removed primarily by the reaction:

$$H_3O^+ (aq) + HCO_3^- (aq) \rightarrow H_2CO_3 (aq) + H_2O (l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^- (aq) + H_2CO_3 (aq) \rightarrow HCO_3^- (aq) + H_2O (l)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 M, and the concentration of the hydrogen carbonate ion, HCO_3–, is around 0.024 M. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\text{pH} = \text{p}K_a + \log([\text{base}]/[\text{acid}]) = 6.4 + \log(0.024/0.0012) = 7.7$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Buffer Range and Buffer Capacity

Buffers are characterized by two parameters, buffer range and buffer capacity. **Buffer range** is the interval of pH values over which a buffer can reliably neutralize added external acids/bases. It is equal to pK_a ± 1, and is thus a function of the *identity* of the acid in the conjugate acid/base pair used to construct the buffer. For example, the pK_a of acetic acid is 4.74; therefore, buffers made by mixing acetic acid and acetate can have pH's ranging from 3.74 up to 5.74. This is a consequence of the second requirement for buffers mentioned above: one component cannot be present in an amount that is less than 10% of the other, or:

$$1/10 < [\text{base}]/[\text{acid}] < 10/1$$

In other words, the ratio of base-to-acid in the buffer, must be greater than 0.1 but less than 10. As soon as this ratio becomes too lopsided (*i.e.* outside the above interval), then the buffer range has been exceeded, and we no longer expect the mixture to neutralize external acids/bases effectively.

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 6.2.3). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.

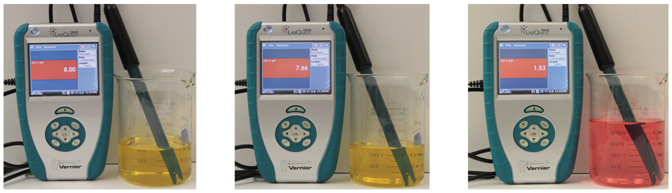


Figure 6.2.3. The indicator colour (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little effect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The **buffer capacity** therefore is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the *amounts* of the weak acid and its conjugate base that are in a buffer mixture.

The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 6.2.4, when NaOH is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

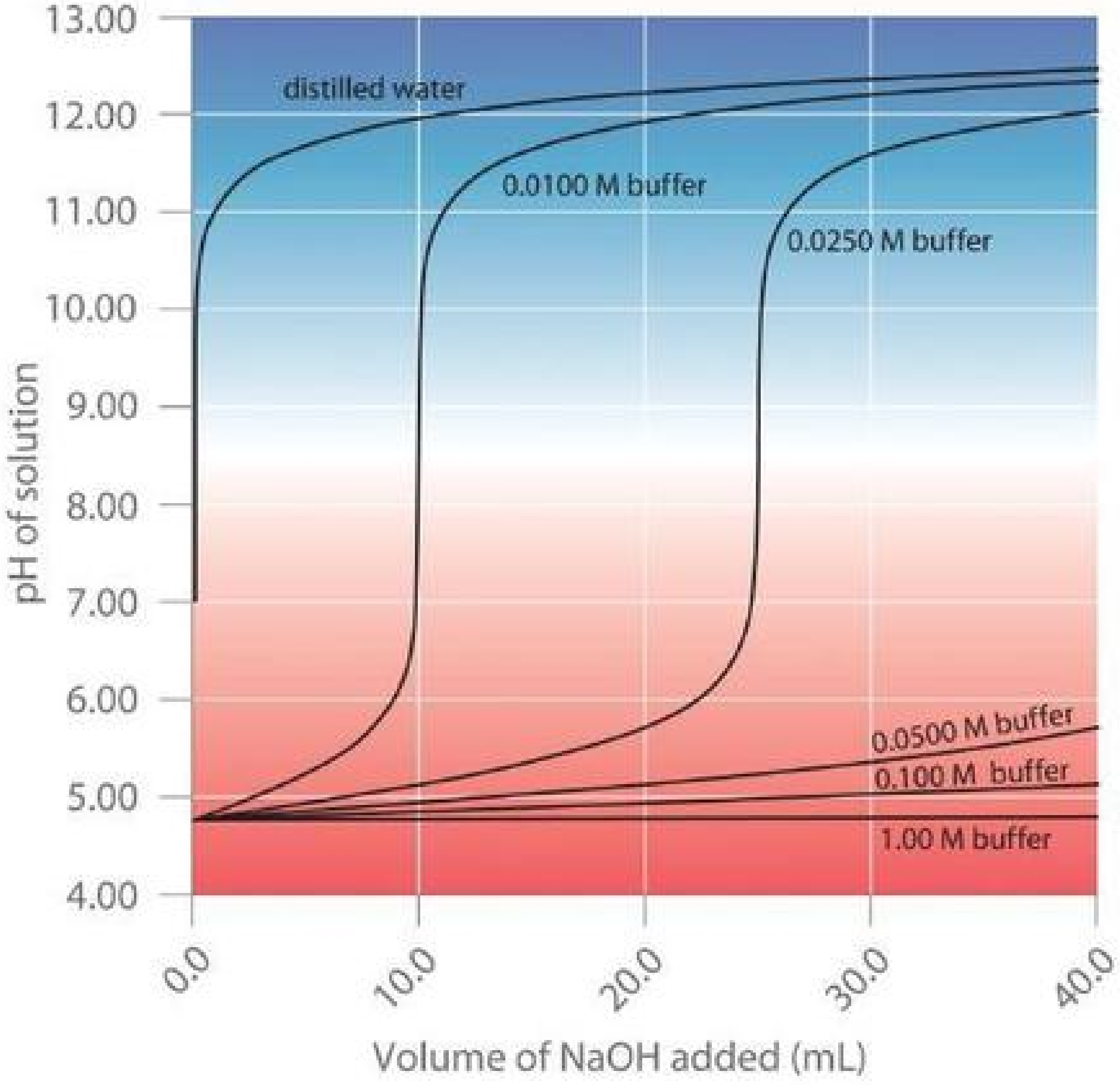
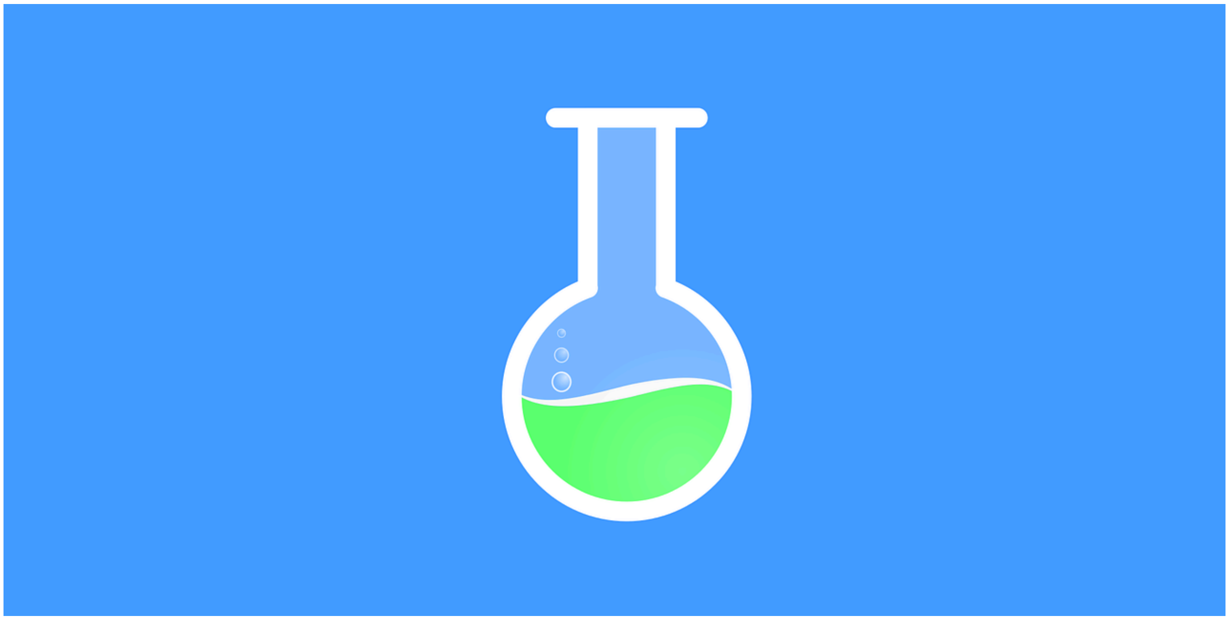


Figure 6.2.4. Effect of Buffer Concentration on the Capacity of a Buffer.



CHM1311 Laboratory | Experiment #3: Equilibria

Purpose

In this experiment, you'll need to refresh your memory of multiple concepts across various chapters (including this one): the core principles of equilibria and Le Châtelier's Principle (Chapter 4), strong/weak acids and bases, dissociation constants, pH, and indicators (Chapter 5), and the purpose and function of buffers that we cover in this section (Chapter 6). This experiment is split into three main parts. First, you'll be examining the effect of adding and consuming reactants on a $[Cu(H_2O)_4]^{2+}$ / $[Cu(NH_3)_4]^{2+}$ system at equilibrium in the context of Le Châtelier's Principle. Following this, you'll be establishing multiple equilibria using the Ag^+ ion and noting observations when you add various reagents. Finally, you'll prepare a buffer system that simulates the metabolic bicarbonate buffer system found in the blood of most animals, and determine what effects on the body are mimicked as you add acids and bases.

Principles

Equilibria
pH
Buffer systems
Common-ion effect
Temperature effect

Safety Precautions

Wear appropriate personal protective equipment (PPE) at all times in the laboratory setting – this includes your lab coat and safety goggles/glasses.

Be sure to consult the MSDS for the following compounds for relevant health and safety, first aid, handling, and waste disposal information:

$CuSO_4$ *(aq)*
Na_2S *(aq)*
NH_3 *(aq)*
$AgNO_3$ *(aq)*
HCl *(aq)*
$NaHCO_3$ *(aq)*
NH_4Cl *(s)*
HNO_3 *(aq)*
$C_3H_6O_3$ *(aq)* lactic acid
KI *(aq)*
CO_2 *(s)* dry ice

You'll be working with acids and bases in the lab. Note that even when diluted, they are still corrosive and should be handled with caution. In case of contact with skin or clothing, notify your TA and make sure you rinse thoroughly with water for at least 15 minutes. If you happen to spill an acid or base, make sure you clean it up immediately since it can easily be mistaken for water (given that both are colourless).

Handle silver nitrate with caution as it stains easily.

Avoid deeply inhaling ammonia and sodium sulfide; both substances have very strong odours.

You'll be working with a lot of chemicals in this experiment, many of which are similar in appearance (e.g. many acids and bases appear colourless and non-viscous). Make sure you don't confuse the reactants – check the label of each reagent you add when preparing the reaction mixture.

Things to Consider

As already emphasized in the experiment theory and instructions, all of the observations you'll be taking are qualitative in nature, so make sure you record as many observations as possible! These include physical properties (e.g. phase of matter, colour, viscosity, solubility) and chemical properties (e.g. pH, reactivity with other substances).

If needed, review your knowledge of acid/base equilibria, shifts in equilibrium systems and buffer systems. For practically all steps of this experiment, you add a reagent to a reaction mixture/system and you'll need to explain the chemistry behind each step. To do so, you'll need to 1) use the reaction equation provided in the instructions, and 2) *integrate* your knowledge of acid/base equilibria, equilibrium system and buffer systems.

Reference

Venkateswaran, R. General Chemistry – Laboratory Manual – CHM 1301/1311.

6.3 – ACID-BASE REACTIONS & TITRATIONS

In an acid–base titration, a **buret** is used to deliver measured volumes of an acid or a base solution of known concentration (the **titrant**) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown, or **analyte**). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a **titration curve**. The shape of the curve provides important information about what is occurring in solution during the titration.

Acid-Base Indicators

Certain organic substances change colour in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colourless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} M (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} M (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

Let's use methyl orange as an example of an acid-base indicator. Since this organic molecule is a weak acid, we will represent it using HIn (similar to using "HA" to represent a generic weak acid). Methyl orange, HIn, thus exists in equilibrium in aqueous solution with its ionized form, the conjugate base In^-, and we can describe this by the equilibrium constant K_{In}:

$$\underset{\text{red}}{HIn\,(aq)} + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + \underset{\text{yellow}}{In^-\,(aq)}$$

$$K_{In} = ([H_3O^+][In^-])/[HIn] = 4.0\times10^{-4}$$

The anion of methyl orange, In^-, is yellow, and the unionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the unionized red form, in accordance with Le Châtelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

An indicator's colour is the visible result of the ratio of the concentrations of the two species In^- and HIn. If most of the indicator (typically about 60−90% or more) is present as In^-, then we see the colour of the In^- ion, which would be yellow for methyl orange. If most is present as HIn, then we see the colour of the HIn molecule: red for methyl orange. For methyl orange, we can rearrange the equation for K_{In} and write:

$$[In^-]/[HIn] = [\text{substance with yellow colour}]/[\text{substance with red colour}] = K_{In}/[H_3O^+]$$

This shows us how the ratio of [In-]/[HIn] varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$[H_3O^+]/K_{In} = [HIn]/[In^-]$$
$$\log([H_3O^+]/K_{In}) = \log([HIn]/[In^-])$$
$$\log([H_3O^+])\text{-}\log(K_{In}) = \text{-}\log([In^-]/[HIn])$$
$$\text{-}pH+pK_{In} = \text{-}\log([In^-]/[HIn])$$
$$pH = pK_{In} + \log([In^-]/[HIn])$$

The last formula is the same as the Henderson-Hasselbalch equation, which means this equation can also be applied to describe the equilibrium of indicators.

When $[H_3O^+]$ has the same numerical value as K_{In}, the ratio of $[In^-]$ to [HIn] is equal to 1, meaning that 50% of the indicator is present in the red form (HIn) and 50% is in the yellow ionic form (In^-), and the solution appears orange in colour. When the hydronium ion concentration increases to 8×10^{-4} M (a pH of 3.1), the solution turns red. No change in colour is visible for any further increase in the hydronium ion concentration (decrease in pH). At a hydronium ion concentration of 4×10^{-5} M (a pH of 4.4), most of the indicator is in the yellow ionic form, and a further decrease in the hydronium ion concentration (increase in pH) does not produce a visible colour change. The pH range between 3.1 (red) and 4.4 (yellow) is the **colour-change interval** of methyl orange; the pronounced colour change takes place between these pH values.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, anthocyanins are a class of organic molecules found in fruits, vegetables, cereals, and flowers, and their colour is highly dependent on pH. Their colour gradually changes from red through yellow as the pH changes from 1 to 13 (see Table 6.3.1 below). In all cases, though, a good indicator must have the following properties:

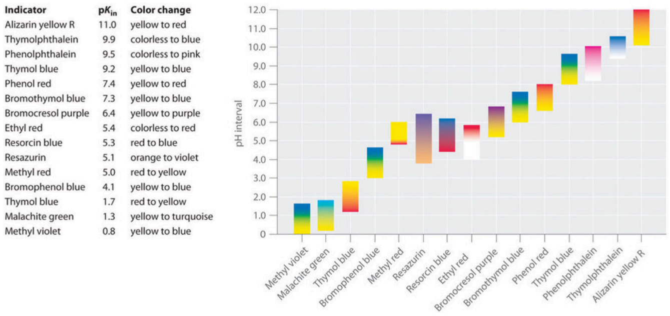
- The colour change must be easily detected.
- The colour change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{In} that is within one pH unit of the expected pH at the equivalence point of the titration.

Figure 6.3.1. Aqueous solutions of anthocyanins extracted from petunias.

Table 6.3.1 Colour and pH of Anthocyanins.

pH	Colour of Anthocyanins
1	Red
4	Blue-red
6	Purple
8	Blue
12	Green
13	Yellow

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure 6.3.2 shows the approximate pH range over which some common indicators change colour and their change in colour. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change colour twice at widely separated pH values.



Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

Figure 6.3.2. Some Common Acid–Base Indicators. Approximate colours are shown, along with pK_{In} values and the pH range over which the colour changes.

It is important to be aware that an indicator does not change colour abruptly at a particular pH value; instead, it actually undergoes a titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In^{-} increases, the colour of the solution slowly changes from the characteristic colour of HIn to that of In^{-}. As we will see later, the $[In^{-}]/[HIn]$ ratio changes from 0.1 at a pH one unit below pK_{In} to 10 at a pH one unit above pK_{In}. Thus most indicators change colour over a pH range of about two pH units.

We have stated that a good indicator should have a pK_{in} value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point (we will see this more later). In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors.

The importance of the choice of indicator is illustrated in Figure 6.3.3. This figure shows plots of pH *versus* volume of base added for two separate titration curves: a 0.100 M solution of NaOH is used to titrate a) 50.0 mL of a 0.100 M solution of a strong acid (HCl) and b) 50.0 mL of a 0.100 M solution of a weak acid (CH_3COOH). For both of these titrations, the number of moles of initial acid present is 0.00500 mol (0.100 mol•L^{-1} x 0.0500 L). The **equivalence point** of the titration occurs when the amount of added base is equal to the amount of initial acid. Since 0.00500 mol of acid is present in both titrations, in both cases the equivalence point will occur when exactly 50.0 mL of 0.100 M NaOH has been added. Note that, for both titrations, the curves become nearly vertical around 50.0 ml of added NaOH: because we are close to the equivalence point around this volume, each drop of NaOH causes a relatively sharp increase in the solution's pH.

In the Figure 6.3.3, the pH ranges over which two common indicators (methyl red, pK_{In} = 5.0, and phenolphthalein, pK_{In} = 9.5) change colour are also shown. The horizontal bars indicate the pH ranges over which both indicators change colour. Notice that for the HCl titration curve, both of the indicators have pH ranges that lie completely within the vertical portion of the titration curve. Hence both indicators change colour around the equivalence point, when about 50 mL of NaOH has been added. Therefore, both of these indicators could be used in the strong acid titration.

In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Phenolphthalein displays a pH range that lies within the vertical portion of the titration curve. Therefore, the colour change is expected close to the equivalence point and the solution will turn pink when about 50 mL of NaOH has been added. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of NaOH will therefore cause the methyl red indicator to change colour, resulting in a huge error.

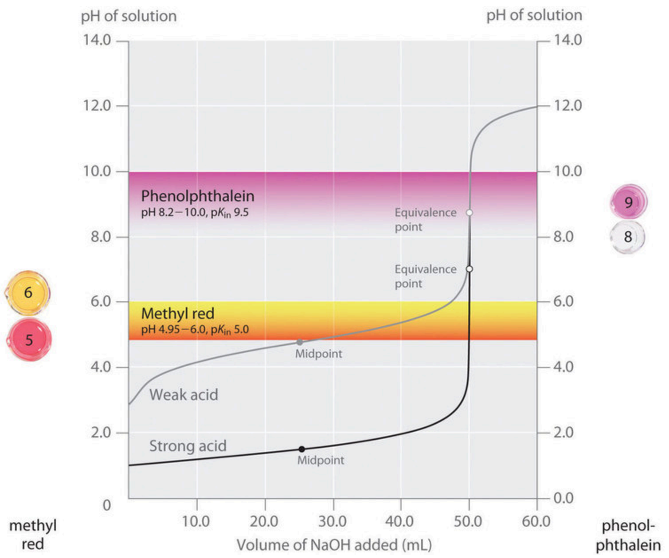


Figure 6.3.3. Choosing the Correct Indicator for an Acid–Base Titration.

Figure 6.3.3 shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M NaOH. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change colour at the equivalence point for the titration of the strong acid. In contrast, the pK_{in} for methyl red (5.0) is very close to the pK_{a} of acetic acid (4.76); the midpoint of the colour change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

When is a Titration Finished?

When an acid is titrated with a base, there is typically a sudden change in the pH of the solution at the *equivalence point* (where the amount of titrant added equals the amount of acid originally present). If a few drops of indicator solution have been added, this sharp increase in pH causes an abrupt change in colour, which is called the **endpoint** of the indicator. *The terms endpoint and equivalence point are not interchangeable.* The titration is over when the endpoint is reached and the indicator changes colour. This can vary with the indicator used. Where is the endpoint of methyl red in Figure 6.3.3? Of phenolphthalein? How accurate would the results of a titration with a weak acid and methyl red be? With phenolphthalein? Is this an underestimation or an overestimation?

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pK_{in} between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with p$K_{\text{In}} > 7.0$, is more appropriate. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with p$K_{\text{In}} < 7.0$, should be used.

The existence of many different indicators with different colours and pK_{In} values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting colour with the standards printed on the container (Figure 6.3.4).

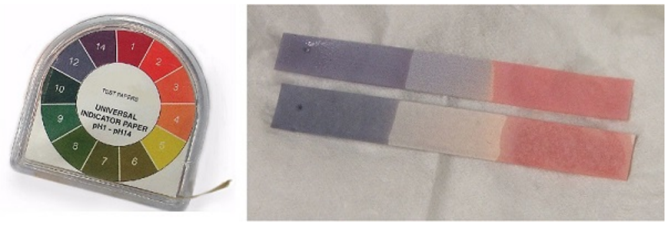
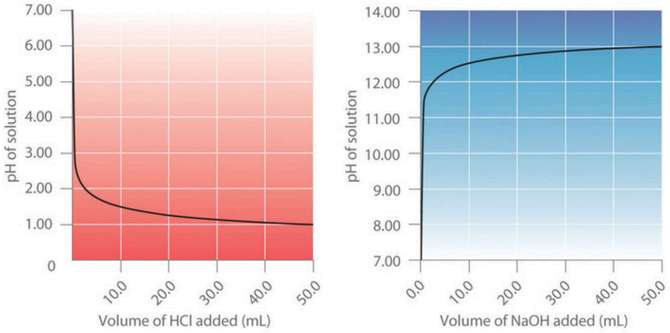


Figure 6.3.4. pH paper. pH paper contains a set of indicators that change colour at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the colour to the standards provided.

Titrations of Strong Acids and Bases

Figure 6.3.5 (a) shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH approaches a limit as the concentration of the sample approaches its maximum value (0.20 M HCl). In contrast, Figure 6.3.5 (b) show that when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of when the concentration of NaOH approaches its maximum. As you can see from these plots, the pH curve for adding a base is the mirror image of the curve for adding an acid.



(a) Water with strong acid added **(b) Water with strong base added**

Figure 6.3.5. Solution pH as a function of the volume of a strong acid or a strong base added to distilled water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum (the pH of 0.20 M HCl). (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum (the pH of 0.20 M NaOH).

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Figure 6.3.6 (a) shows the pH observed as a function of added NaOH. Because HCl is a strong acid that is completely ionized in water, the initial $[H_3O^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H_3O^+ because of the neutralization reaction:

$$OH^{-}\,(aq) + H_3O^{+}\,(aq) \rightarrow 2H_2O\,(l)$$

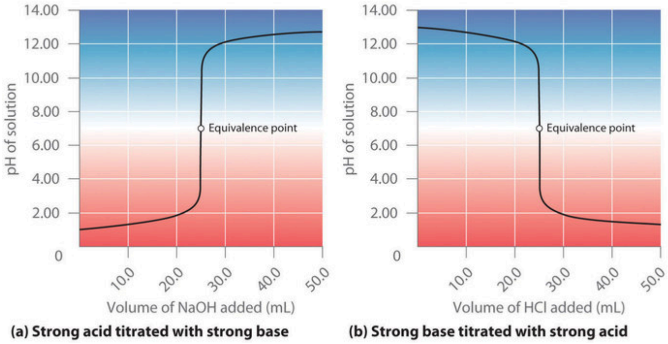
Thus, as NaOH is added, the HCl is consumed, and the pH of the solution increases gradually. Near the equivalence point, however, *only a small fraction* of the HCl initially present now remains, and so the pH increases much more rapidly as each individual drop of NaOH is added. For the titration of a monoprotic strong acid (HCl) with a monobasic strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$\text{moles of acid} = \text{moles of base}$$

$$C_{acid} \times V_{acid} = C_{base} \times V_{base}$$

In our titration, 50.0 mL of a 0.10 M solution of HCl, is being titrated with 0.20 M NaOH. Therefore, we can solve for V_{base}, the volume of base needed to reach the equivalence point:

$$V_{base} = (C_{acid} \times V_{acid}) / C_{base} = 0.0250\text{ L} = 25.0\text{ mL}$$



(a) Strong acid titrated with strong base

(b) Strong base titrated with strong acid

Figure 6.3.6. The titration of (a) a strong acid with a strong base and (b) a strong base with a strong acid. (a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M NaOH, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more.

At the equivalence point (when 25.0 mL of NaOH solution has been added), the neutralization is complete. Recall from Chapter 5 that all acid-base neutralization reactions follow the general equation:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

In the reaction of HCl + NaOH, the salt produced is NaCl, which does not hydrolyze and is thus a *neutral* salt. In general, titrations of a strong acid and strong base yield neutral salts, and hence the pH of the solution at the equivalence point is always 7.00. Past the equivalence point, adding more NaOH produces a rapid increase in pH, but eventually the pH levels off at the maximum value, the pH of 0.20 M NaOH.

As shown in Figure 6.3.6 (b), the titration of 50.0 mL of a 0.10 M solution of NaOH with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in Figure 6.3.6 (a). The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

In conclusion, titrations of strong acids with strong bases (or vice-versa) produce an S-shaped curve.

The curve is not quite perfectly symmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Since strong acids and strong bases ionize completely in water, the exact position and shape of the curve only depends on the *concentrations* of the acid and base used, not their *identities*. Finally, these titrations always produce neutral salts, and so the aqueous solution obtained at the equivalence point always has a pH of 7.

Example 6.3.1 – Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M NaOH has been added to 50.00 mL of 0.100 M HCl.

Solution

Calculate the number of millimoles of H_3O^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.

Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of H_3O^+ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$(50.00\text{ mL})(0.100\text{ mmol HCl/mL}) = 5.00\text{ mmol HCl} = 5.00\text{ mmol } H_3O^+$$

The number of millimoles of NaOH added is as follows:

$$(24.90\text{ mL})(0.200\text{ mmol NaOH/mL}) = 4.98\text{ mmol NaOH} = 4.98\text{ mmol OH-}$$

Thus H_3O^+ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of OH^- to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess H_3O^+ is:

$$5.00\text{ mmol} - 4.98\text{ mmol} = 0.02\text{ mmol of } H_3O^+$$

Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of H_3O^+ is as follows:

$$[H+] = 0.02\text{ mmol H+}/ 74.90\text{ mL} = 3\times10^{-4}\text{ M}$$

Hence,

$$pH \approx -\log[H_3O^+] = -\log(3\times10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

Check Your Learning 6.3.1 – Hydrochloric Acid

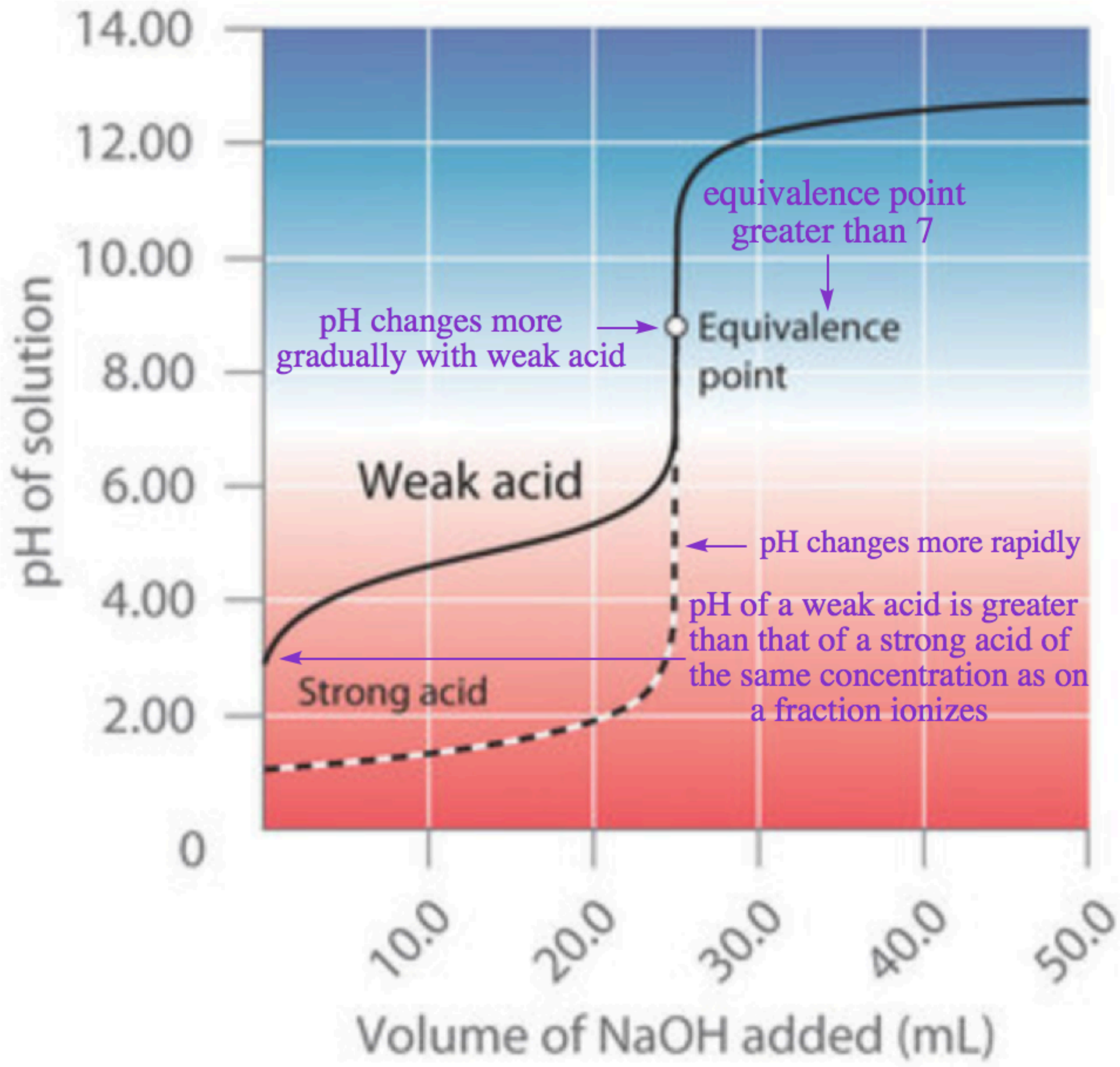
Calculate the pH of a solution prepared by adding 40.00 mL of 0.237 M HCl to 75.00 mL of a 0.133 M solution of NaOH.

Answer

pH = 11.6

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the half-equivalence point in the titration of a weak acid or a weak base. As you learned previously, $[H_3O^+]$ of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its K_a and its concentration. Because only a fraction of a weak acid dissociates, $[H_3O^+]$ is less than [HA]. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration. Figure 6.3.7 (a) shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure 6.3.6.



(a) Weak acid titrated with strong base

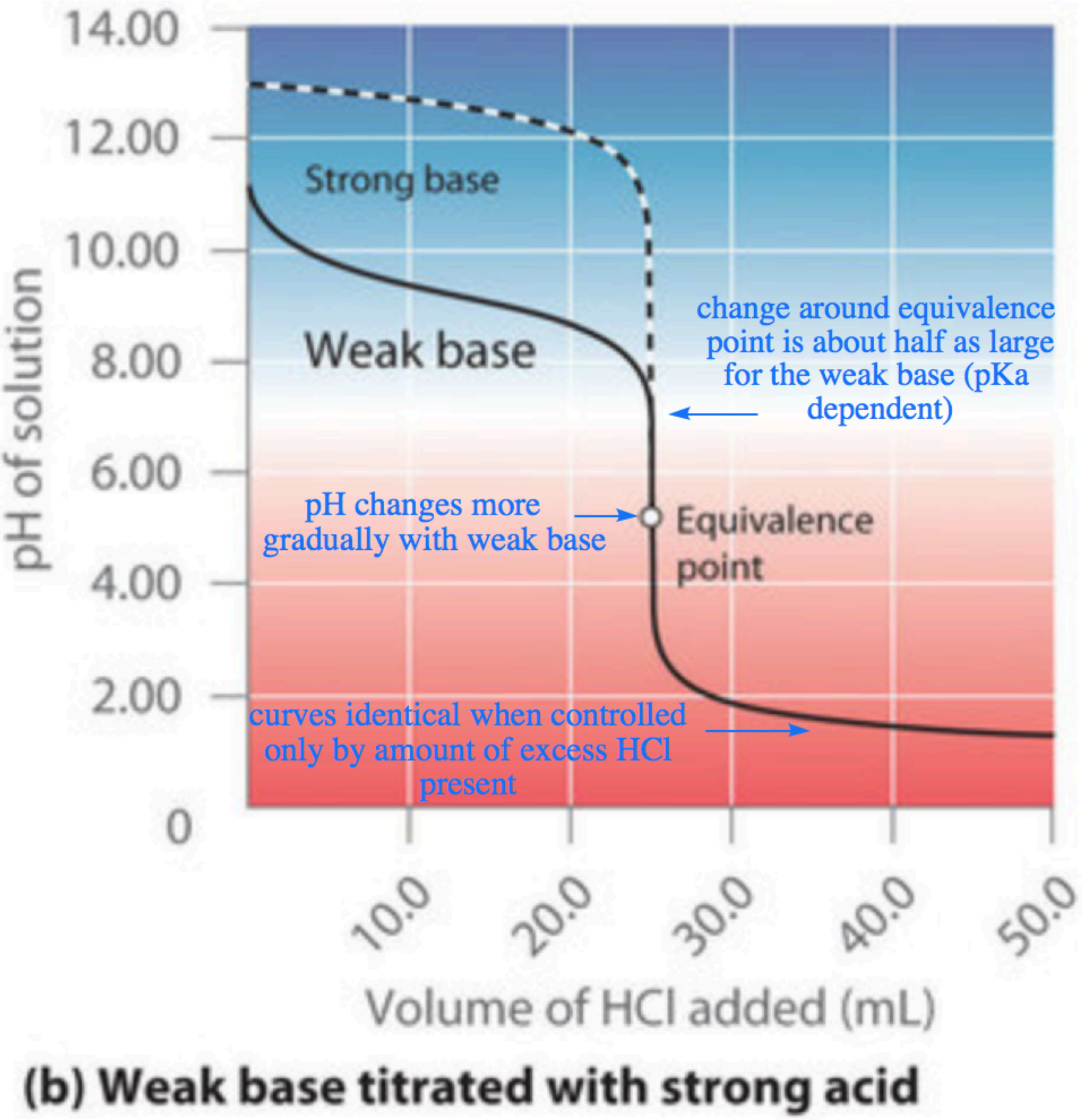


Figure 6.3.7. The titration of (a) a weak acid with a strong Base and (b) a weak base with a strong acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH_3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line.

Below the equivalence point, the two curves are very different. First, note that before any base is added, the initial pH of the acetic acid solution is greater than the initial pH of the HCl solution – this is because acetic acid is a weak acid and thus does not completely ionize in solution. Second, note that the shape of the curves in between the initial point and the equivalence point have different shapes: for the acetic acid titration, the pH changes more rapidly at first, levels off slightly, and then begins to increase again as we approach the equivalence point. Finally, note also that the pH of the solution at the equivalence point is greater than 7.00, i.e. the solution is basic. Past the equivalence point, however, the two curves are identical: once the acid has been neutralized, the pH of the solution is controlled only by the amount of *excess* NaOH present, regardless of whether the acid is weak or strong.

Let's now take a more quantitative look at the construction of titration curves. The curve in Figure 6.3.7 (a) was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of NaOH. In the next subsection, we'll go through these calculations for three points on the curve, using the pK_a of acetic acid (4.74 at 25°C).

Calculating the initial pH of a Titration

As discussed previously, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, respectively, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table. In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[H_3O^+]$, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2^-\,(aq)$$

Initial Concentration (M)	0.100	/	0*	0
Change (M)	$-x$	/	$+x$	$+x$
Equilibrium concentration (M)	0.100-x	/	x	x

*Note: In this and all subsequent examples, we will ignore any $[H_3O^+]$ and $[OH^-]$ due to the autoionization of water, as these quantities will be negligible.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = ([H_3O^+][CH_3CO^{2-}])/[CH_3CO_2H] = x^2/(0.100-x) \approx x^2/0.100 = 1.8\times10^{-5}$$

Solving this equation gives $x = [H_3O^+] = 1.32 \times 10^{-3}$ M. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32\times10^{-3}) = 2.879$$

This is the initial pH for our titration curve (*i.e.* the *y*-intercept, where the volume of added base is 0 mL).

Calculating the pH during the Titration

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M CH_3CO_2H (still following Figure 6.3.7 (a)). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H\,(aq) + OH^-\,(aq) \rightarrow CH_3CO_2^-\,(aq) + H_2O\,(l)$$

Equilibrium Arrows

Wondering why the above reaction has a one-way arrow instead of an equilibrium arrow? The above reaction is the reverse of the following:

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)$$

Recall from Chapter 5 that this equation corresponds to the hydrolysis of the conjugate base of acetic acid, and we can determine its equilibrium constant, K_b, as: $K_w/K_a = 5.6\times10^{-10}$.

Now recall from Chapter 4 that when an equilibrium is reversed, the value of the equilibrium constant must be the reciprocal value, $K' = 1/K$. Therefore, for the original, forward direction:

$$CH_3CO_2H\,(aq) + OH^-\,(aq) \rightarrow CH_3CO_2^-\,(aq) + H_2O\,(l)$$

$$K = 1/5.6\times10^{-10} = 1.8\times10^{9}$$

This value is enormous, indicating a strongly product-favoured reaction, and hence we may draw a one-way arrow and use simple stoichiometry to solve our calculations.

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[H_3O^+]$ of the resulting solution.

Step 1 – Stoichiometry first

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of CH_3CO_2H in the original solution and the amount of OH^- in the NaOH solution that was added. The acetic acid solution originally contained:

$$(50.00\text{mL})(0.100\text{ mmol }CH_3CO_2H/\text{mL}) = 5.00\text{ mmol }CH_3CO_2H$$

The NaOH solution added contained:

$$(5.00\text{ mL})(0.200\text{ mmol NaOH/mL}) = 1.00\text{ mmol NaOH}$$

Comparing these two amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

$$5.00\text{ mmol }CH_3CO_2H - 1.00\text{ mmol OH-} = 4.00\text{ mmol }CH_3CO_2H$$

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following table, often referred to as a

BAMA table or a stoichiometry table, which shows the numbers of moles of the various species and their resulting changes following a reaction that proceeds 100% to completion:

$$CH_3CO_2H\,(aq) + OH^-\,(aq) \rightarrow CH_3CO_2^-\,(aq) + H_2O\,(l)$$

	CH_3CO_2H *(aq)*	OH^- *(aq)*	$CH_3CO_2^-$ *(aq)*	H_2O *(l)*
Before (mmol)	5.00	/	0	/
Addition (mmol)		1.00		/
Modification (mmol)	-1.00	-1.00	+1.00	/
After (mmol)	4.00	0	1.00	/

Note: ICE tables help keep track of changing concentrations or pressures in an *equilibrium* problem. The above is distinctly *not* an ICE table, as this is a one-way reaction that goes 100% to products, and thus the calculation is a limiting-reagent type problem.

The BAMA table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is also insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2 – Now turn on the acid-base equilibrium

To calculate $[H_3O^+]$ at equilibrium following the addition of NaOH, we must first re-calculate $[CH_3CO_2H]$ and $[CH_3CO_2^-]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$\text{Total volume} = 50.00\text{ mL} + 5.00\text{ mL} = 55.00\text{ mL}$$

$$[CH_3CO_2H] = 4.00\text{ mmol } CH_3CO_2H / 55.00\text{ mL} = 7.27\times10^{-2}\text{ M}$$

$$[CH_3CO_2^-] = 1.00\text{mmol } CH_3CO_2^- / 55.00\text{ mL} = 1.82\times10^{-2}\text{ M}$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H_3O^+]$ at equilibrium:

$$K_a = ([CH_3CO_2^-][H_3O^+])/[CH_3CO_2H]$$

$$[H_3O^+] = (K_a \text{ x } [CH_3CO_2H])/[CH_3CO_2^-] = (1.72\times10^{-5})(7.27\times10^{-2})/(1.82\times10^{-2}) = 6.95\times10^{-5}\text{ M}$$

Calculating $-\log [H_3O^+]$ gives:

$$pH = -\log(6.95\times10^{-5}) = 4.158$$

Comparing the titration curves for HCl and acetic acid in Figure 6.3.7 (a), we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. Let's now repeat the above process for another point in the titration curve of acetic acid.

Example 6.3.2 – Calculating the pH at the Equivalence Point of the Titration

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

Solution

Ignoring the spectator ion (Na^+), the equation for the neutralization is still:

$$CH_3CO_2H\,(aq) + OH^-\,(aq) \rightarrow CH_3CO_2^-\,(aq) + H_2O\,(l)$$

The number of millimoles of OH^- added after 25.00 mL is:

$$(25.00\text{ mL})(0.200\text{ mmol }OH^-/\text{mL}) = 5.00\text{ mmol }OH^-$$

Since the titration began with exactly 5.00 mmol of CH_3CO_2H, the number of millimoles of OH^- added equals the number of millimoles of CH_3CO_2H, neither species is present in excess, and thus we have reached the *equivalence point*. Again, the results of the neutralization reaction can be summarized in a BAMA (stoichiometry) table:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO_2^-{}_{(aq)} + H_2O_{(l)}$$

	$CH_3CO_2H_{(aq)}$	$OH^-_{(aq)}$	$CH_3CO_2^-{}_{(aq)}$	$H_2O_{(l)}$
Before (mmol)	5.00		0	/
Addition (mmol)		5.00		/
Modification (mmol)	-5.00	-5.00	+5.00	/
After (mmol)	0	0	5.00	/

At the equivalence point, all 5.00 millimoles of CH_3CO_2H have been converted into its conjugate base, $CH_3CO_2^-$; however, the new total volume of the solution is 75.00 mL (50.00 + 25.00 mL), and so its concentration is:

$$[CH_3CO_2^-] = 5.00\text{ mmol }CH_3CO_2^- / (50.00+25.00)\text{ mL} = 6.67\times10^{-2}\text{ M}$$

What is the pH of this solution of acetate? Acetate is a base, and thus will hydrolyze in solution to reform some acetic acid, in the equilibrium:

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)$$

Therefore, we must consider the reaction of the conjugate base with water to calculate $[H_3O^+]$ at equilibrium and thus the final pH of the solution, using an ICE table:

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)$$

	$CH_3CO_2^-$ *(aq)*	H_2O *(l)*	CH_3CO_2H *(aq)*	OH^- *(aq)*
Initial (M)	0.0667	/	0	0
Change (M)	$-x$	/	$+x$	$+x$
Equilibrium (M)	$0.667 - x$	/	x	x

Substituting the values from this table into the K_b equation:

$$K_b = K_w/K_a = (1.01\times10^{-14})/(1.74\times10^{-5}) = 5.80\times10^{-10} = x^2/0.0667$$

$$5.80\times10^{-10} = x^2/0.0667\text{-}x$$

$$5.80\times10^{-10} = x^2/0.0667$$

$$x = 6.22 \times 10^{-6}$$

Thus, at equilibrium, $[OH^-] = 6.22 \times 10^{-6}$ M, and the pH of the final solution is 8.794 (Figure 6.3.7 (a)). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then hydrolyzes to produce OH^-.

Check Your Learning 6.3.2 – Calculating the pH at the Equivalence Point of the Titration

125.0 mL of a 0.150 M solution of ammonia is titrated with 45.0 mL of a 0.213 M HCl solution. (a) Is this titration *before*, *past*, or *at* the equivalence point? (b) Calculate the pH of the solution. The pK_b of ammonia is 4.75 at 25°C.

Answer

(a) Before the equivalence point; (b) pH = 9.23

As shown in Figure 6.3.7 (b), the titration curve for NH_3, a weak base, is the reverse of the titration curve for acetic acid. In particular, note the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

As we saw previously, the titration curves of strong acids and strong bases are nearly symmetrical S-shaped curves, where only the *concentration*, but not the *identity*, of the species is relevant. However, in titrations of weak acids or weak bases, identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

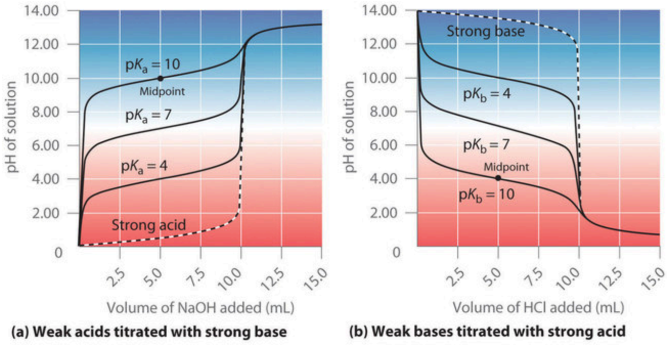


Figure 6.3.8. Effect of acid or base strength on the shape of titration curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10.

One point in the titration of a weak acid or a weak base is particularly important: the **midpoint** (or **half-equivalence point**) of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize *one-half* of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figure 6.3.8 for the two shallowest curves. By definition, at the midpoint of the titration of an acid, $[HA] = [A^-]$. Recall that the ionization constant for a weak acid is as follows:

Equation 6.3.1 Ionization Constant for Weak Acid

$$K_a = ([H_3O^+][A^-])/[HA]$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log(K_a) = -\log[H_3O^+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH$$

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid. In Figure 6.3.8 (a), we can see that the midpoint for the pK_a = 10 weak acid occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base).

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic proton is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pH units, then the overall titration curve shows well-resolved "steps" corresponding to the titration of each proton. For example, the titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 6.3.9 and shows two well-defined steps: the first midpoint corresponds to pK_{a1}, and the second midpoint corresponds to pK_{a2}. Because HPO_4^{2-} is a very weak acid, pK_{a3} has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

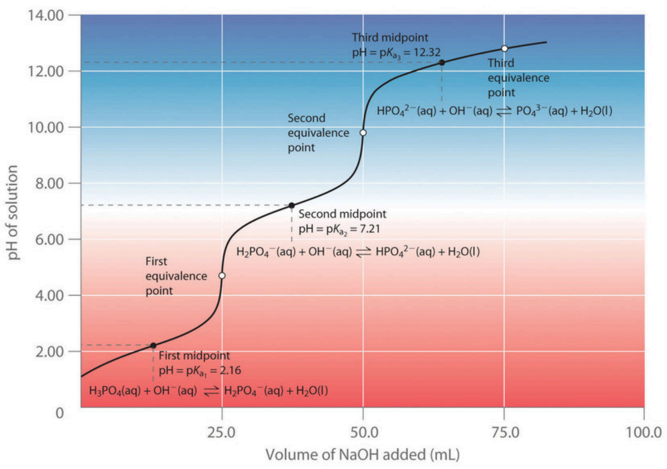
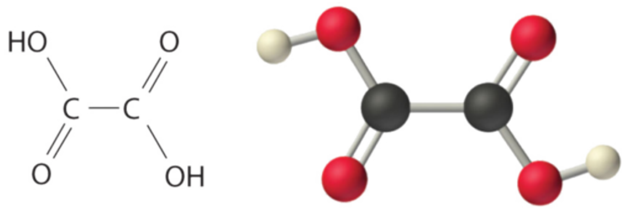


Figure 6.3.9. Titration curve for phosphoric acid (H_3PO_4), a typical polyprotic acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each pK_a is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined.

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 6.3.9. The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated.

Diprotic Acid Titration

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid (HO_2CCO_2H), a diprotic acid (abbreviated as H_2A). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($^-O_2CCO_2^-$, abbreviated A^{2-}). Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

The pK_a values of oxalic acid are 1.25 and 3.81. We proceed by determining the millimoles of acid and base initially present:

$$(100.00\text{ mL})(0.510\text{ mmol } H_2A / \text{mL}) = 5.10\text{ mmol } H_2A$$

$$(55.00\text{ mL})(0.120\text{ mmol NaOH} / \text{mL}) = 6.60\text{ mmol NaOH}$$

The strongest acid (H_2A) reacts with the base first. This leaves (6.60 – 5.10) = 1.50 mmol of OH^- to react with HA^-, forming A^{2-} and H_2O. The reactions can be written as follows:

$$H_2A + OH^- \rightarrow HA^- + H_2O$$

$$HA^- + OH^- \rightarrow A^{2-} + H_2O$$

Shown as two sequential stoichiometry tables:

	H_2A	OH^-	HA^-	H_2O
Before (mmol)	5.10		0	/
Addition (mmol)		6.60		/
Modification (mmol)	-5.10	-5.10	+5.10	/
After (mmol)	0	1.50	5.10	/

	HA^-	OH^-	A^{2-}	H_2O
Before (mmol)	5.10		0	/
Addition (mmol)		1.50		/
Modification (mmol)	-1.50	-1.50	+1.50	/
After (mmol)	3.60	0	1.50	/

The equilibrium between the weak acid (HA^-) and its conjugate base (A^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H_3O^+]$, which is determined by first finding concentrations of each species:

$$\text{Final volume of solution} = 100.0\text{ mL} + 55.0\text{ mL} = 155.0\text{ mL}$$

$$[HA^-] = 3.60\text{ mmol } HA^- / 155.0\text{ mL} = 2.32\times10^{-2}\text{ M}$$

$$[A^{2-}] = 1.50\text{ mmol} / 155.0\text{ mL} = 9.68\times10^{-3}\text{ M}$$

We can now calculate $[H_3O^+]$ at equilibrium using the K_{a2} expression:

$$K_{a2} = ([A^{2-}][H_3O^+])/[HA^-]$$

Rearranging this equation and substituting the values for the concentrations of HA^- and A^{2-},

$$[H_3O^+] = K_{a2}([HA^-]/[A^{2-}]) = (1.6\times10^{-4})((2.32\times10^{-2})/(9.68\times10^{-3})) = 3.7\times10^{-4}\text{ M}$$

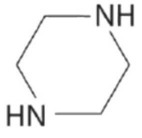
So:

$$pH = -\log[H_3O^+] = -\log(3.7\times10^{-4}) = 3.43$$

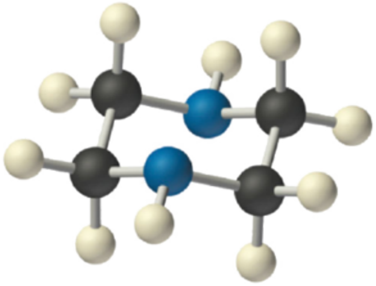
This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

Check Your Learning 6.3.3 – Piperazine

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.

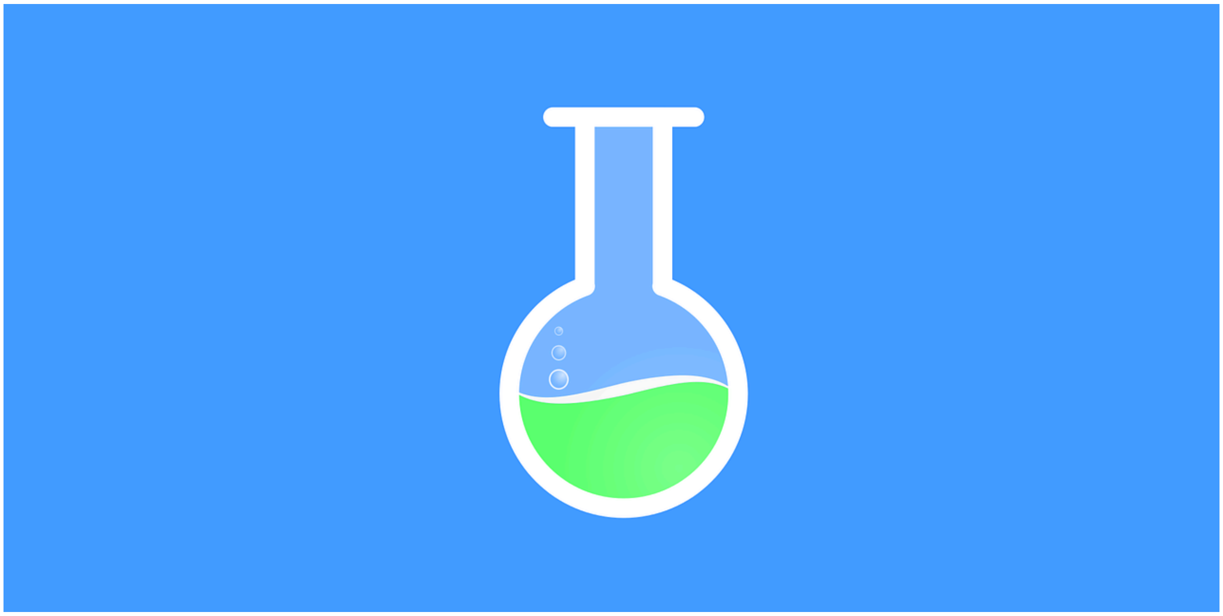


piperazine



Answer

pH = 4.9



CHM1311 Laboratory | Experiment #4: Acid Base Titrations

Purpose

This experiment involves performing titration procedures, like you may have done in high school, to determine the concentration of an unknown diprotic acid solution. The procedure involves three parts: 1) preparing a dilution from a concentrated NaOH solution, 2) determining the concentration of the diluted NaOH solution by standardizing it against a monoprotic acid solution of known concentration, and 3) titrating the unknown diprotic acid solution by volumetric titration using your standardized base solution.

Principles

Acidity/basicity
Concentration
Equivalence point, endpoint
Mass percent

Safety Precautions

Wear appropriate personal protective equipment (PPE) at all times in the laboratory setting – this includes your lab coat and safety goggles/glasses.

Be sure to consult the MSDS for NaOH*(aq)*, HCl*(aq)*, and maleic acid for relevant health and safety, first aid, handling, and waste disposal information.

You'll be working with acids and bases in the lab. The base stock solution you'll be working with is concentrated, so be extra careful when handling it since it is very corrosive. Note that even when diluted, acids and bases are still corrosive and should be handled with caution. In case of contact with skin or clothing, notify your TA and make sure you rinse thoroughly with water for at least 15 minutes. If you happen to spill an acid or base, make sure you clean it up immediately since it can easily be mistaken for water (given that both are colourless).

Things to Consider

The observations taken in this experiment are quantitative in nature and ultimately dictate how accurately you'll determine the concentration of your unknown acid. Ensure that you are as precise and accurate as possible when reading measurements; one example is reading the buret to two decimal places to try to get exact initial and final readings and minimize error.

Why is it so important to ensure that there are no air bubbles trapped in the tap of the buret when conducting the titration procedure?

Consider the whole purpose of diluting and standardizing the NaOH solution before performing the actual titration on the unknown acid solution. Why was it particularly important to determine the concentration of the dilute base solution before using it?

Be sure you can understand and explain the titration curves of both monoprotic and diprotic acids – this will help you when discussing your results in your report.

Reference

Venkateswaran, R. General Chemistry – Laboratory Manual – CHM 1301/1311.

6.4 – EQUILIBRIA OF SLIGHTLY SOLUBLE IONIC COMPOUNDS

Solubility

When a solid substance is mixed with a solvent in order to form a solution, there are several possible results. The determining factor for the result is the **solubility** of the substance, which is defined as the maximum possible concentration of the solute. The solubility rules help determine which substances are soluble, and to what extent.

Solubility Effects on Reactions

Depending on the solubility of a solute, there are three possible results: 1) if the solution has less solute than the maximum amount that it is able to dissolve (its solubility), it is a dilute **unsaturated** solution; 2) if the amount of solute is exactly the same amount as its solubility, it is **saturated**; 3) if there is more solute than is able to be dissolved, it is said to be **supersaturated** and the excess solute separates from the solution. If this separation process includes crystallization, it forms a **precipitate**. Precipitation lowers the concentration of the solute to the saturation in order to increase the stability of the solution.

We can use the following general rules for predicting the relative solubility of many ionic compounds:

Solubility Rules

1. Salts containing Group I elements (Li^+, Na^+, K^+, Cs^+, Rb^+) are soluble. There are few exceptions to this rule. Salts containing the ammonium ion (NH_4^+) are also soluble.

2. Salts containing nitrate ion (NO_3^-) are generally soluble.

3. Salts containing Cl^-, Br^-, or I^- are generally soluble. Important exceptions to this rule are halide salts of Ag^+, Pb^{2+}, and $(Hg_2)^{2+}$. Thus, AgCl, $PbBr_2$, and Hg_2Cl_2 are insoluble.

4. Most silver salts are insoluble. $AgNO_3$ and $Ag(C_2H_3O_2)$ are common soluble salts of silver; virtually all others are insoluble.

5. Most sulfate salts are soluble. Important exceptions to this rule include $CaSO_4$, $BaSO_4$, $PbSO_4$, Ag_2SO_4 and $SrSO_4$.

6. Most hydroxide salts are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$ are not soluble.

7. Most sulfides of transition metals are highly insoluble, including CdS, FeS, ZnS, and Ag_2S. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.

8. Carbonates are frequently insoluble. Group II carbonates ($CaCO_3$, $SrCO_3$, and $BaCO_3$) are insoluble, as are $FeCO_3$ and $PbCO_3$.

9. Chromates are frequently insoluble. Examples include $PbCrO_4$ and $BaCrO_4$.

10. Phosphates such as $Ca_3(PO_4)_2$ and Ag_3PO_4 are frequently insoluble.
11. Fluorides such as BaF_2, MgF_2 and PbF_2 are frequently insoluble.

Example 6.4.1 – Calculating the pH at the Equivalence Point of the Titration

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

(a) Potassium sulfate and barium nitrate

(b) Lithium chloride and silver acetate

(c) Lead nitrate and ammonium carbonate

Solution

The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is:

$$Ba^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow BaSO_4\,(s)$$

The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is:

$$Ag^{+}\,(aq) + Cl^{-}\,(aq) \rightarrow AgCl\,(s)$$

The two possible products for this combination are PbCO3 and NH4NO3. The solubility guidelines indicate PbCO3 is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is:

$$Pb^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow PbCO_3\,(s)$$

Check Your Learning 6.4.1 – Calculating the pH at the Equivalence Point of the Titration

Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:

(a) $BaSO_4$

(b) Ag_2SO_4

(c) $Al(OH)_3$

(d) Pb(OH)Cl

Answer

(a) $BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$
$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

(b) $Ag_2SO_4\,(s) \rightleftharpoons 2Ag^{+}\,(aq) + SO_4^{2-}\,(aq)$
$K_{sp} = [Ag^{+}]^2[SO_4^{2-}]$

(c) $Al(OH)_3\,(s) \rightleftharpoons Al^{3+}\,(aq) + 3OH^{-}\,(aq)$
$K_{sp} = [Al^{3+}][OH^{-}]^3$

(d) $Pb(OH)Cl\,(s) \rightleftharpoons Pb^{2+}\,(aq) + OH^-\,(aq) + Cl^-\,(aq)$
$K_{sp} = [Pb^{2+}][OH^-][Cl^-]$

The Solubility Product Constant

By applying the above solubility rules, we can make qualitative predictions about precipitation reactions. However, these precipitates still exist in a dynamic equilibrium with aqueous ions, since these are technically *sparingly* (or slightly) soluble compounds that dissolve partially in aqueous solutions. For example, according to the solubility rules, silver chloride, AgCl, is classified as a sparingly soluble ionic solid (Figure 6.4.1). However, when we add an excess of solid AgCl to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

This equilibrium, like other equilibria, is dynamic; some of the solid AgCl is continuously dissolving, but at the same time, Ag^+ and Cl^- ions in the solution combine to produce an equal amount of the solid. At equilibrium, *the opposing processes have equal rates,* and macroscopically, the concentrations of dissolved ions and mass of remaining solid appear constant.

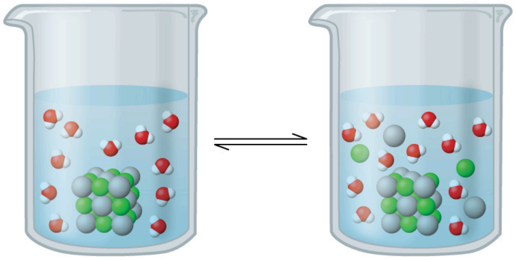


Figure 6.4.1. Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is the **solubility product (K_{sp})** of the solid. Recall from Chapter 4 that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$
$$K_{sp} = [Ag^+(aq)][Cl^-(aq)]$$

When looking at dissolution reactions such as this, the solid is listed as a reactant, whereas the ions are listed as products. The solubility product constant, as with every equilibrium constant expression, is written as the product of the concentrations of each of the ions, raised to the power of their stoichiometric coefficients. Here, the solubility product constant is equal to $[Ag^+] \times [Cl^-]$ when a solution of silver chloride is in equilibrium with undissolved AgCl. There is no denominator representing the reactants in this equilibrium expression since the reactant is a pure solid; therefore [AgCl] does not appear in the expression for K_{sp}.

Some common solubility products are listed in Table 6.4.1, according to their K_{sp} values, whereas a more extensive compilation of products appears in Appendix L. Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small K_{sp} represents a system in which the equilibrium lies to the left, so that relatively few hydrated ions would be present in a saturated solution.

Table 6.4.1 Common Solubility Products and their Equilibrium Constants

Substance	**K_{sp} at 25 °C**
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
AgI	1.5×10^{-16}
PbS	7×10^{-29}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}

Example 6.4.2 – Writing Equations and Solubility Products

Write the ionic equation for the dissolution and the solubility product expression for each of the following slightly soluble ionic compounds:

(a) AgI, silver iodide, a solid with antiseptic properties

(b) $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids

(c) $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia

(d) $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium

(e) $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

(Hint: When determining how to break (d) and (e) up into ions, refer to the list of polyatomic ions in the section on chemical nomenclature.)

Solution

(a) $AgI\ \mathit{(s)} \rightleftharpoons Ag^{+}\ \mathit{(aq)} + I^{-}\ \mathit{(aq)}$

$K_{sp} = [Ag^{+}][I^{-}]$

(b) $CaCO_3\ \mathit{(aq)} \rightleftharpoons Ca^{2+}\ \mathit{(aq)} + CO_3^{\ 2-}\ \mathit{(aq)}$

$K_{sp} = [Ca^{2+}][CO_3^{\ 2-}]$

(c) $Mg(OH)_2\ \mathit{(s)} \rightleftharpoons Mg^{2+}\ \mathit{(aq)} + 2OH^{-}\ \mathit{(aq)}$

$K_{sp} = [Mg^{2+}(aq)][OH^{-}]^2$

(d) $Mg(NH_4)PO_4\ \mathit{(s)} \rightleftharpoons Mg^{+}\ \mathit{(aq)} + NH_4^{\ +}\ \mathit{(aq)} + PO_4^{\ 3-}\ \mathit{(aq)}$

$K_{sp} = [Mg^{2+}][NH_4^{\ +}][PO_4^{\ 3-}]$

(e) $Ca_5(PO_4)_3OH\ \mathit{(s)} \rightleftharpoons 5Ca^{2+}\ \mathit{(aq)} + 3PO_4^{\ 3-}\ \mathit{(aq)} + OH^{-}\ \mathit{(aq)}$

$K_{sp} = [Ca^{2+}]^5[PO_4^{\ 3-}]^3[OH^{-}]$

Check Your Learning 6.4.1 – Writing Equations and Solubility Products

Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:

(a) $BaSO_4$

(b) Ag_2SO_4

(c) $Al(OH)_3$

(d) $Pb(OH)Cl$

Answer

(a) $BaSO_4\ \mathit{(s)} \rightleftharpoons Ba^{2+}\ \mathit{(aq)} + SO_4^{\ 2-}\ \mathit{(aq)}$

$K_{sp} = [Ba^{2+}][SO_4^{\ 2-}]$

(b) $Ag_2SO_4\ \mathit{(s)} \rightleftharpoons 2Ag^{+}\ \mathit{(aq)} + SO_4^{\ 2-}\ \mathit{(aq)}$

$K_{sp} = [Ag^{+}]^2[SO_4^{\ 2-}]$

(c) $Al(OH)_3\ \mathit{(s)} \rightleftharpoons Al^{3+}\ \mathit{(aq)} + 3OH^{-}\ \mathit{(aq)}$

$K_{sp} = [Al^{3+}][OH^{-}]^3$

(d) $Pb(OH)Cl\ \mathit{(s)} \rightleftharpoons Pb^{2+}\ \mathit{(aq)} + OH^{-}\ \mathit{(aq)} + Cl^{-}\ \mathit{(aq)}$

$K_{sp} = [Pb^{2+}][OH^{-}][Cl^{-}]$

Now we will extend the discussion of K_{sp} and show how the solubility product constant is determined from the solubility of its ions, as well as how K_{sp} can be used to determine the molar solubility of a substance.

The Ion Product

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) discussed for equilibria in Chapter 4. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

As summarized in Figure 6.4.2, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$ The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$ The solution is saturated and at equilibrium.
- $Q > K_{sp}$ The solution is supersaturated, and ionic solid will precipitate.

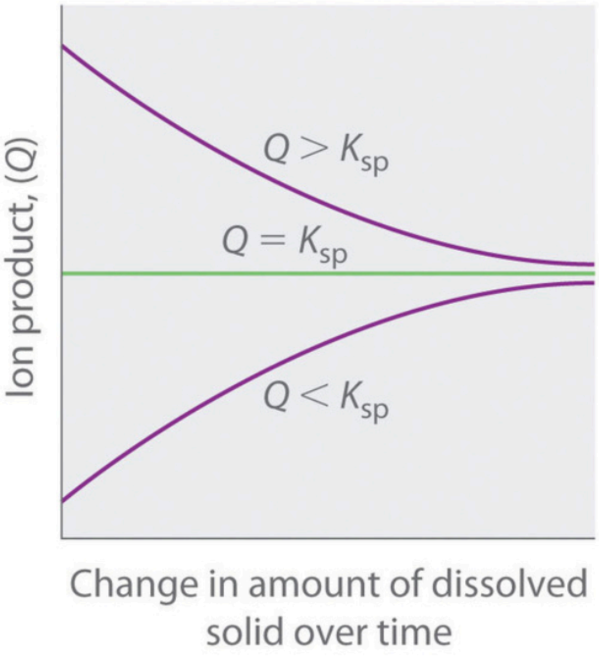


Figure 6.4.2. The relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

K_{sp} and Solubility

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$M_pX_q\,(s) \rightleftharpoons pM^{m+}\,(aq) + qX^{n-}\,(aq)$$

Equation 6.4.1 – Solubility product of slightly soluble solid.

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its **molar solubility.**

Example 6.4.3 – Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^-\,(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15×10^{-4} M; therefore, that of F^- is 4.30×10^{-4} M, that is, twice the concentration of Ca^{2+}. What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp}:

$$CaF_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2F^-\,(aq)$$

A saturated solution is a solution at equilibrium with the solid. Thus:

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2.1\times10^{-4})(4.2\times10^{-4})^2 = 3.7\times10^{-11}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Check Your Learning 6.4.2 – Calculation of K_{sp} from Equilibrium Concentrations

In a saturated solution that is in contact with solid $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31×10^{-4} M. What is the solubility product for $Mg(OH)_2$?

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2OH^-\,(aq)$$

Answer

$K_{sp} = 8.99 \times 10^{-12}$

Example 6.4.4 – Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3×10^{-9}.

The reaction is:

$$CuBr\,(s) \rightleftharpoons Cu^+\,(aq) + Br^-\,(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [Cu^+][Br^-]$$

Create an ICE table (as introduced in Chapter 4), leaving the CuBr column empty as it is a solid (its activity is equal to one) and thus does not appear in the K_{sp} expression:

$$CuBr\,(s) \rightleftharpoons Cu^+\,(aq) + Br^-\,(aq)$$

	$CuBr\,(s)$	$Cu^+\,(aq)$	$Br^-\,(aq)$
Initial (M)	/	0	0
Change (M)	/	$+x$	$+x$
Equilibrium (M)	/	x	x

At equilibrium:

$$K_{sp} = [Cu^{+}][Br^{-}]$$
$$6.3\times10^{-9} = (x)(x)=x^{2}$$
$$x = \mathrm{sqrt}(6.3\times10^{-9}) = 7.9\times10^{-5}$$

Therefore, the molar solubility of CuBr is 7.9×10^{-5} M.

Check Your Learning 6.4.3 – Determination of Molar Solubility from K_{sp}

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer

1.2×10^{-8} M

Example 6.4.5 – Determination of Molar Solubility from K_{sp}, Part II

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The solubility product constant of calcium hydroxide is 1.3×10^{-6}.

The reaction is:

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,OH^{-}\,(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [Ca^{2+}][OH^{-}]^{2}$$

Create an ICE table, leaving the $Ca(OH)_2$ column empty as it is a solid and does not contribute to the K_{sp}:

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2OH^{-}\,(aq)$$

	$Ca(OH)_2\,(s)$	$Ca^{2+}\,(aq)$	$2OH^{-}\,(aq)$
Initial (M)	/	0	0
Change (M)	/	$+x$	$+2x$
Equilibrium (M)	/	x	$2x$

At equilibrium:

$$K_{sp} = [Ca^{2+}][OH^{-}]^{2}$$
$$1.3\times10^{-6} = (x)(2x)^{2} = (x)(4x^{2}) = 4x^{3}$$
$$x = \mathrm{cbrt}(1.3\times10^{-6}/4) = 6.9\times10^{-3}$$

Therefore, the molar solubility of $Ca(OH)_2$ is 1.3×10^{-2} M.

Check Your Learning 6.4.4 – Determination of Molar Solubility from K_{sp}, Part II

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer

1.5×10^{-3} M

Note that solubility is not always given as a molar value. When the solubility of a compound is given in some unit other than moles per liter, we must convert the solubility into moles per liter (i.e., molarity) in order to use it in the solubility product constant expression. The following example shows how to perform those unit conversions before determining the solubility product equilibrium.

Example 6.4.6 – Determination of K_{sp} from Gram Solubility

Many of the pigments used by artists in oil-based paints (Figure 6.4.3) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product equilibrium constant for $PbCrO_4$.

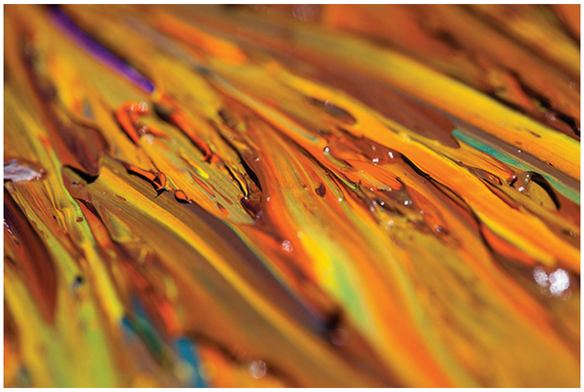
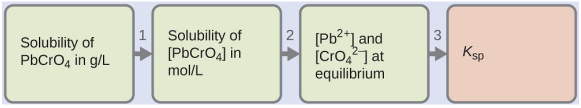


Figure 6.4.3. Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange colour vermilion (HgS), and green colour veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

We are given the solubility of $PbCrO_4$ in grams per litre. If we convert this solubility into moles per litre, we can find the equilibrium concentrations of Pb^{2+} and $CrO_4{}^{2-}$, then K_{sp}:



Use the molar mass of $PbCrO_4$ (323.2g/mol) to convert the solubility of $PbCrO_4$ in grams per litre into moles per litre:

$$[PbCrO_4] = (4.6\times10^{-6}\ \text{g}\ PbCrO_4 / 1\ \text{L}) \times (1\ \text{mol}\ PbCrO_4 /\ 323.2\ \text{g}\ PbCrO_4)$$

$$= 1.4\times10^{-8}\ \text{mol PbCrO4} / 1\ \text{L}$$

$$[PbCrO_4] = 1.4\times10^{-8}\ \text{M}$$

The chemical equation for the dissolution indicates that 1 mol of $PbCrO_4$ gives 1 mol of $Pb^{2+}{}_{(aq)}$ and 1 mol of $CrO_4{}^{2-}{}_{(aq)}$:

$$PbCrO_4\,(s) \rightleftharpoons Pb^{2+}\,(aq) + CrO_4{}^{2-}\,(aq)$$

Thus, at equilibrium, both $[Pb^{2+}]$ and $[CrO_4{}^{2-}]$ are equal to the molar solubility of $PbCrO_4$:

$$[Pb^{2+}(aq)] = [CrO_4^{2-}(aq)] = 1.4{\times}10^{-8}\,M$$

Solve.

$$K_{sp} = [Pb^{2+}][CrO_4^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$$

Check Your Learning 6.4.5 – Determination of K_{sp} from Gram Solubility

The solubility of thallium(I) chloride (TlCl), an intermediate formed when thallium is being isolated from ores, is 3.46 grams per litre at 20°C. What is its solubility product?

Answer

1.7×10^{-4}

Example 6.4.7 – Calculating the Solubility of Hg_2Cl_2

Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I), Hg_2^{2+}, and chloride ions, Cl^-. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel is quite insoluble:

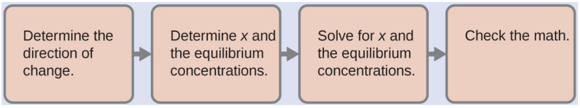
$$Hg_2Cl_2\,(s) \rightleftharpoons Hg_2^{2+}\,(aq) + 2Cl^-\,(aq)$$

$$K_{sp} = 1.1{\times}10^{-18}$$

Calculate the molar solubility of Hg_2Cl_2.

Solution

The molar solubility of Hg_2Cl_2 is equal to the concentration of Hg_2^{2+} ions because for each 1 mol of Hg_2Cl_2 that dissolves, 1 mol of Hg_2^{2+} forms:



Determine the direction of change. Before any Hg_2Cl_2 dissolves, Q is zero, and the reaction will shift to the right to reach equilibrium.

Determine x *and equilibrium concentrations.* Concentrations and changes are given in the following ICE table:

$$Hg_2Cl_2\,(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-\,(aq)$$

	$Hg_2Cl_2\,(s)$	$Hg_2^{2+}(aq)$	$2Cl^-\,(aq)$
Initial (M)	/	0	0
Change (M)	/	$+x$	$+2x$
Equilibrium (M)	/	x	$2x$

Note that the change in the concentration of Cl^- ($2x$) is twice as large as the change in the concentration of Hg_2^{2+} (x) because 2 mol of Cl^- forms for each 1 mol of Hg_2^{2+} that forms. Hg_2Cl_2 is a pure solid, so it does not appear in the calculation.

Solve for x and the equilibrium concentrations. We substitute the equilibrium concentrations into the expression for K_{sp} and calculate the value of x:

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

$$1.1\times10^{-18} = (x)(2x)^2$$

$$4x^3 = 1.1\times10^{-18}$$

$$x = \text{cbrt}(1.1\times10^{-18}/4) = 6.5\times10^{-7}\text{ M}$$

$$[Hg_2^{2+}] = 6.5\times10^{-7}\text{ M} = 6.5\times10^{-7}\text{ M}$$

$$[Cl^-] = 2x = 2(6.5\times10^{-7}\text{ M}) = 1.3\times10^{-6}\text{ M}$$

The molar solubility of Hg_2Cl_2 is equal to $[Hg_2^{2+}]$, or 6.5×10^{-7} M.

Check the work. At equilibrium, $Q = K_{sp}$:

$$Q = [Hg_2^{2+}][Cl^-]^2 = (6.5\times10^{-7})(1.3\times10^{-6})^2 = 1.1\times10^{-18}$$

The calculations check out.

Check Your Learning 6.4.6 – Calculating the Solubility of Hg_2Cl_2

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

Answer

1.2×10^{-3} M

Tabulated K_{sp} values can also be compared to reaction quotients calculated from experimental data to tell whether a solid will precipitate in a reaction under specific conditions: Q equals K_{sp} at equilibrium; if Q is less than K_{sp}, the solid will dissolve until Q equals K_{sp}; if Q is greater than K_{sp}, precipitation will occur at a given temperature until Q equals K_{sp}.

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnosis of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 1.1×10^{-10}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 6.4.4).

Figure 6.4.4. The suspension of barium sulfate coats the intestinal tract, which allows for

greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons)

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

You can visit this website for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

The Common Ion Effect and Solubility

What happens if we try to dissolve a sparingly soluble salt in an aqueous solution that already contains one of the salt's ions? Following Section 6.1, this would be an example of the *common ion effect*. According to Le Chatelier's Principle, the presence of product ion shifts the equilibrium towards the solid reactant, and we expect the solubility of the salt to be reduced.

Example 6.4.8 – The Common Ion Effect and Solubility

If we attempt to dissolve lead(II) chloride in a 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions, as compared to pure water?

First, let us determine the solubility of $PbCl_2$ in pure water. We can define x to be the concentration of the lead(II) ions at equilibrium, and use an ICE table:

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$$

	$PbCl_2\,(s)$	$Pb^{2+}(aq)$	$2Cl^{-}(aq)$
Initial (M)	/	0	0
Change (M)	/	$+x$	$+2x$
Equilibrium (M)	/	x	$2x$

We substitute the equilibrium concentrations into the expression for K_{sp} and calculate the value of x:

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2$$
$$1.7\times10^{-5} = (x)(2x)^2$$
$$4x^3 = 1.7\times10^{-5}$$
$$x = \text{cbrt}(1.7\times10^{-5}/4) = 0.016\text{ M}$$

Now, to find the solubility of lead (II) chloride in 0.100 M NaCl, we repeat this process, only we take into account the presence of the *common ion*. In this example, the common ion is the chloride ion. Since NaCl is a soluble salt, we assume 100% ionization and thus $[Cl^{-}]_i = 0.100$ M.

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$$

	$PbCl_2\,(s)$	$Pb^{2+}(aq)$	$2Cl^{-}(aq)$
Initial (M)	/	0	0.100
Change (M)	/	$+x$	$+2x$
Equilibrium (M)	/	x	$0.100{+}2x$

Again, we substitute the equilibrium concentrations into the expression for K_{sp} and calculate the value of x, and to simplify the calculation, we assume that the value of x is small:

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2$$

$$1.7\times10^{-5} = (x)(0.100+2x)^2$$

$$1.7\times10^{-5} = (x)(0.100)^2$$

$$x = 1.7\times10^{-3}\ M$$

Finally, let's compare the obtained values:

Original solution:

$$[Pb^{2+}] = 0.016\ M$$

In 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M$$

The concentration of the lead(II) ions has decreased by a factor of about 10, confirming that the common ion effect inhibits the solubility of a sparingly soluble salt. If more concentrated solutions of sodium chloride are used, the solubility decreases further.

Check Your Learning 6.4.7 – The Common Ion Effect and Solubility

$BaSO_4$ is a sparingly soluble salt that ionizes into Ba^{2+} and SO_4^{2-}:

$$BaSO_4\,(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = 1.1\times10^{-10}$$

Find the concentration of each ion at equilibrium for a saturated solution of barium sulfate. Next, lithium sulfate (Li_2SO_4) is added to the reaction vessel until its concentration is 0.500 M. What is the concentration of barium and sulfate ions after the addition of lithium sulfate?

Answer

Before addition of Li_2SO_4:

$$[Ba^{2+}] = 1.0 \text{ x } 10^{-5}\ M\,,\ [SO_4^{2-}] = 1.0 \text{ x } 10^{-5}\ M$$

After addition of Li_2SO_4:

$$[Ba^{2+}] = 2.2 \text{ x } 10^{-10}\ M\,,\ [SO_4^{2-}] = 0.500\ M$$

Check Your Learning 6.4.8 – The Common Ion Effect and Solubility

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The K_{sp} of silver carbonate is 8.46×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)

Effect of pH on solubility

For certain salts, hydronium and hydroxide ion concentrations can influence solubility, as a special case of the common ion effect. Taking the concept of hydrolysis, introduced in Chapter 5, and applying Le Chatelier's Principle to sparingly soluble salts, we can qualitatively predict that:

- ACIDIC salts will be less soluble in acid (pH < 7), and more soluble in base (pH > 7).
- BASIC salts will be less soluble in base (pH > 7), and more soluble in acid (pH < 7).
- NEUTRAL salts have solubilities unaffected by pH.

Consider the example of cobalt (II) hydroxide. It dissolves in the following equilibrium:

$$Co(OH)_2\,(s) \rightleftharpoons Co^{2+}\,(aq) + 2\,OH^-\,(aq)$$

$$K_{sp} = 2.5 \times 10^{-16} = [Co^{2+}][OH^-]^2$$

We can compare the solubility of this compound in pure water (where $[OH^-] = 1.0 \times 10^{-7}$) versus its solubility in a pH = 6 buffer solution (where $[OH^-] = 1.0 \times 10^{-8}$), using the following two ICE tables:

Pure water, $[OH^-] = 1 \times 10^{-7}$ M				**Buffer (pH = 6), $[OH^-] = 1 \times 10^{-8}$ M**			
$Co(OH)_2\,(s) \rightleftharpoons Co^{2+}\,(aq) + 2\,OH^-\,(aq)$				$Co(OH)_2\,(s) \rightleftharpoons Co^{2+}\,(aq) + 2\,OH^-\,(aq)$			
I	–	0	1×10^{-7}	**I**	–	0	1×10^{-8}
C	–	+x	+2x	**C**	–	+x	NO change
E	–	x	$1 \times 10^{-7} + 2x$	**E**	–	x	1×10^{-8}
$\mathbf{K_{sp} = (x)(1.0 \times 10^{-7} + 2x)^2}$ $\mathbf{s \approx (x)(2x)^2}$ **s = 1.1×10^{-5} M**				$\mathbf{K_{sp} = (x)(1.0 \times 10^{-8})^2}$ $\mathbf{s = (K_{sp})/(1.0 \times 10^{-8})^2}$ **s > 50 M (soluble!)**			

From the above calculations, we see that $Co(OH)_2$, originally only slightly soluble in neutral water, becomes much more soluble under acidic conditions. Why is this so? Complete the exercise below to illustrate the reason.

Check Your Learning 6.4.9 – The Common Ion Effect and Solubility

The equilibrium for the dissolution of cobalt (II) hydroxide is:

$$Co(OH)_2\,(s) \rightleftharpoons Co^{2+}\,(aq) + 2\,OH^-\,(aq)\ K_{sp} = 5.9 \times 10^{-15}$$

In acidic solution, each hydroxide ion produced is neutralized by a hydronium ion. As we saw in Chapter 5, the net ionic equation for the acid-base neutralization is the inverse of the autoionization of water:

$$OH^{-}\,(aq) + H_3O^{+}\,(aq) \leftrightharpoons 2H_2O(l)\ K = 1/K_w = 1.0 \text{ x } 10^{14}$$

Combine the two equilibria provided, taking note of stoichiometry, to find an overall chemical equation for the dissolution of cobalt (II) hydroxide in acidic solution, as well as the value of the equilibrium constant. (Recall the rules for manipulating equilibrium constants from Chapter 4).

Answer:

$$Co(OH)_2\,(s) + 2H_3O^{+}\,(aq) \leftrightharpoons Co^{2+}\,(aq) + 4H_2O\,(l),\ K = 5.9 \text{ x } 10^{13}$$

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$CaCO_3\,(aq) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ($Q = [Ca^{2+}][CO_3^{2-}]$) is equal to the solubility product ($K_{sp} = 8.7 \times 10^{-9}$). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains CO_3^{2-} ions, the slightly soluble ionic solid $CaCO_3$ will precipitate, provided that the concentrations of Ca^{2+} and CO_3^{2-} ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as the following example shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

Example 6.4.9 – Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^{-} ion:

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2OH^{-}\,(aq)$$
$$K_{sp} = 8.9{\times}10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 M. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^{-}]$ of 0.0010 M?

Solution

This problem asks whether the reaction:

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2OH^{-}\,(aq)$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}] = 0.0537$ M and $[OH^{-}] = 0.0010$ M. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$Q = [Mg^{2+}][OH^{-}]^2 = (0.0537)(0.0010)^2 = 5.4 \text{ x } 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2$ *(s)* forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

Check Your Learning 6.4.10 – Precipitation of $Mg(OH)_2$

Will $KClO_4$ precipitate when 20 mL of a 0.050 M solution of K^{+} is added to 80 mL of a 0.50 M solution of ClO_4^{-}? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Answer

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$

In the previous example, we have seen that a precipitate forms when Q is greater than K_{sp}. In general, according to Equation 6.4.1, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Example 6.4.10 – Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 6.4.5). At sufficiently high concentrations, the calcium and oxalate ions form solid calcium oxalate monohydrate, $CaC_2O_4•H_2O$. The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} M. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4•H_2O$ begins to precipitate?

Figure 6.4.5. Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$CaC_2O_4\,(s) \rightleftharpoons Ca^{2+}\,(aq) + C_2O_4^{2-}\,(aq)$$

For this reaction:

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96\times10^{-8} \text{ (see Appendix L)}$$

Solid CaC_2O_4 does not begin to form until Q equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of $C_2O_4^{2-}$ that is necessary to produce the first trace of solid precipitate:

$$Q = K_{sp} = [Ca^{2+}(aq)][C_2O_4^{2-}(aq)] = 1.96\times10^{-8}$$

$$(2.2\times10^{-3})[C_2O_4^{2-}(aq)] = 1.96\times10^{-8}$$

$$[C_2O_4^{2-}(aq)] = 1.96\times10^{-8}/2.2\times10^{-3} = 8.9\times10^{-6}\text{ M}$$

A concentration of $[C_2O_4^{2-}] = 8.9 \times 10^{-6}$ M is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Check Your Learning 6.4.11 – Precipitation of Calcium Oxalate

If a solution contains 0.0020 mol of CrO_4^{2-} per litre, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer

4.5×10^{-9} M

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in the previous example—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations *after* precipitation is complete, rather than at the *start* of precipitation.

Example 6.4.11 – Concentrations Following Precipitation

Clothing washed in water that has an aqueous manganese (II) ion (Mn^{2+}) concentration exceeding 0.1 mg/L (1.8×10^{-6} M) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep $[Mn^{2+}]$ equal to 1.8×10^{-6} M?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$Mn(OH)_2\,(s) \rightleftharpoons Mn^{2+}\,(aq) + 2OH^-\,(aq)$$

$$K_{sp} = 2\times10^{-3}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is 1.8×10^{-6} M. From that, we calculate the pH. At equilibrium:

$$K_{\text{sp}} = [Mn^{2+}][OH^-]^2$$

Or:

$$(1.8\times10^{-6})[OH^-]^2 = 2\times10^{-3}$$

So:

$$[OH^-] = 3.3\times10^{-4}\text{ M}$$

Now we calculate the pH from the pOH:

$$\text{pOH} = -\log[OH^-] = -\log(3.3\times10^{-4}) = 3.48$$

$$\text{pH} = 14.00\text{-pOH} = 14.00\text{-}3.80 = 10.52$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.52, the manganese ion will be reduced to a concentration of 1.8×10^{-6} M; at that concentration or less, the ion will not stain clothing.

Check Your Learning 6.4.12 – Concentrations Following Precipitation

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} M. Calculate the pH at which $[Mg^{2+}]$ is diminished to 1.0×10^{-5} M by the addition of $Ca(OH)_2$.

Answer

pH = 10.97

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and — before the advent of digital photography—in photographic film. Even though AgCl (K_{sp} = 1.6×10^{-10}), AgBr (K_{sp} = 5.0×10^{-13}), and AgI (K_{sp} = 1.5×10^{-16}) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its lower molar solubility. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (the compound with the smaller molar solubility) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the molar solubilities of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of **selective precipitation**, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 6.4.6). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{2-}) are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure 6.4.6. Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, known as lime, $Ca(OH)_2$. The lime is converted into calcium carbonate, a strong base, in the water. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO_4)_3(OH)$, which then precipitates out of the solution:

$$10Ca^{2+}(aq) + 6PO_4^{3-}(aq) + 2OH^{-}(aq) \rightleftharpoons Ca_{10}(PO_4)_6 \cdot (OH)_2(s)$$

The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this site for more information on how phosphorus is removed from wastewater.

Selective precipitation can also be used in qualitative analysis. In this method, reagents are added to an unknown chemical mixture in order to induce precipitation. Certain reagents cause specific ions to precipitate out; therefore, the addition of the reagent can be used to determine whether the ion is present in the solution.

View this simulation to study the process of salts dissolving and forming saturated solutions and precipitates for specific compounds, or compounds for which you select the charges on the ions and the K_{sp}.

Example 6.4.12 – Precipitation of Silver Halides

A solution contains 0.0010 mol of KI and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

Solution

The two equilibria involved are:

$$AgCl\,(s) \rightleftharpoons Ag^{+}\,(aq) + Cl^{-}\,(aq),\ K_{sp} = 1.6\times10^{-10}$$

$$AgI\,(s) \rightleftharpoons Ag^{+}\,(aq) + I^{-}\,(aq),\ K_{sp} = 1.5\times10^{-16}$$

In this example, both salts form the same number of ions (1 mol of dissolved solid produces 1 mol of cations and 1 mol of anions) and so in both cases, the K_{sp} value is calculated as the square of the molar solubility (*i.e.* if the molar solubility is x, $K_{sp} = x^2$). Consequently, we can compare these K_{sp} values directly to get a qualitative sense of the order of precipitation. Note that K_{sp} values may NOT be directly compared if the number of ions formed in the dissolution equilibrium is not identical (for example, it would not be appropriate to compare the K_{sp} value of AgCl to that of Ag_2SO_4).

Fortunately, in this case, since the K_{sp} values identically correlate to each solid's molar solubility ($K_{sp} = x^2$), that means we can deduce that if the solution contained about *equal* concentrations of Cl^- and I^-, then the silver salt with the smallest K_{sp} (AgI) would precipitate first. The concentrations are not equal, however, so we should find the $[Ag^+]$ at which AgCl begins to precipitate and the $[Ag^+]$ at which AgI begins to precipitate. The salt that forms at the lower $[Ag^+]$ precipitates first.

For AgI: AgI precipitates when Q equals K_{sp} for AgI (1.5×10^{-16}). When $[I^-] =$ 0.0010 M:

$$Q = [Ag^+][I^-] = [Ag^+](0.0010) = 1.5{\times}10^{-16}$$
$$[Ag^+] = (1.8{\times}10^{-10})(0.10) = 1.6{\times}10^{-9}\text{ M}$$

AgI begins to precipitate when $[Ag^+]$ is 1.5×10^{-13} M.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10^{-10}). When $[Cl^-] = 0.10$ M:

$$Q = [Ag^+][Cl^-] = [Ag^+](0.10) = 1.6{\times}10^{-10}$$
$$[Ag+] = 1.8{\times}10^{-10}(0.10) = 1.6{\times}10^{-9}\text{ M}$$

AgCl begins to precipitate when $[Ag^+]$ is 1.6×10^{-9} *M*.

AgI begins to precipitate at a lower $[Ag^+]$ than AgCl, so AgI begins to precipitate first.

Check Your Learning 6.4.13 – Precipitation of Silver Halides

If silver nitrate solution is added to a solution which is 0.050 M in both Cl^- and Br^- ions, at what $[Ag^+]$ would precipitation begin, and what would be the formula of the precipitate?

Answer

$[Ag^+] = 1.0 \times 10^{-11}$ M; AgBr precipitates first

Questions

★ Questions

1. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

(a) LaF_3

(b) $CaCO_3$

(c) Ag_2SO_4

(d) $Pb(OH)_2$

2. The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

(a) $BaSeO_4$, 0.0118 g/100 mL

(b) $Ba(BrO_3)_2{\cdot}H_2O$, 0.30 g/100 mL

(c) $NH_4MgAsO_4{\cdot}6H_2O$, 0.038 g/100 mL

(d) $La_2(MoO_4)_3$, 0.00179 g/100 mL

3. Use solubility products and predict which of the following salts is the most soluble, in terms of moles per liter, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.

4. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

(a) $KHC_4H_4O_6$

(b) PbI_2

(c) $Ag_4[Fe(CN)_6]$, a salt containing the $Fe(CN)_4^-$ ion

(d) Hg_2I_2

★★ Questions

5. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

(a) $AgCl(s)$ in 0.025 M NaCl

(b) $CaF_2(s)$ in 0.00133 M KF

(c) $Ag_2SO_4(s)$ in 0.500 L of a solution containing 19.50 g of K_2SO_4

(d) $Zn(OH)_2(s)$ in a solution buffered at a pH of 11.45

6. Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract (Figure 6.4.4). This use of $BaSO_4$ is possible because of its low solubility. Calculate the molar solubility of $BaSO_4$ and the mass of barium present in 1.00 L of water saturated with $BaSO_4$.

7. The solubility product of $CaSO_4{\cdot}2H_2O$ is 2.4×10^{-5}. What mass of this salt will dissolve in 1.0 L of 0.010 M SO_4^{2-}?

8. Which of the following carbonates will form first? Which of the following will form last? Explain.

(a) $MgCO_3$ $K_{sp} = 3.5 \times 10^{-8}$

(b) $CaCO_3$ $K_{sp} = 4.2 \times 10^{-7}$

(c) $SrCO_3$ $K_{sp} = 3.9 \times 10^{-9}$

(d) $BaCO_3$ $K_{sp} = 4.4 \times 10^{-5}$

(e) $MnCO_3$ $K_{sp} = 5.1 \times 10^{-9}$

9. How many grams of Milk of Magnesia, $Mg(OH)_2$ *(s)* (58.3 g/mol), would be soluble in 200 mL of water.

$K_{sp} = 7.1 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. ($K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$)

10. A volume of 0.800 L of a 2×10^{-4} M $Ba(NO_3)_2$ solution is added to 0.200 L of 5×10^{-4} M Li_2SO_4. Does $BaSO_4$ precipitate? Explain your answer.

11. Calculate the concentration of PO_4^{3-} when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 M in Ag^+.

Answers

1. (a) $LaF_3\,(s) \rightleftharpoons La^{3+}\,(aq) + 3F^-\,(aq)$ $K_{sp} = [La^{3+}][F^-]^3$

(b) $CaCO_3\,(s) \rightleftharpoons Ca^{3+}\,(aq) + CO_3^{2-}\,(aq)$ $K_{sp} = [Ca^{2+}][CO_3^{2-}]$

(c) $Ag_2SO_4\,(s) \rightleftharpoons 2Ag^+\,(aq) + SO_4^{2-}\,(aq)$ $K_{sp} = [Ag^+]^2[SO_4^{2-}]$

(d) $Pb(OH)_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2OH^-\,(aq)$ $K_{sp} = [Pb^{2+}][OH^-]^2$

2. (a) 1.77×10^{-7}; (b) 1.6×10^{-6}; (c) 2.2×10^{-9}; (d) 7.91×10^{-22}

3. PbI_2 is the most soluble.

4. (a) 2×10^{-2} M; (b) 1.5×10^{-3} M; (c) 2.27×10^{-9} M; (d) 2.2×10^{-10} M

5. (a) 6.4×10^{-9} M = $[Ag^+]$, [Cl-] = 0.025 M

Check: (6.4×10^{-9} M/0.025 M)×100% = 2.6×10^{-5}%, an insignificant change

(b) 2.2×10^{-5} M = $[Ca^{2+}]$, $[F^-]$ = 0.0013 M

Check: (2.26×10^{-5} M/0.00133 M)×100% = 1.70%, This value is less than 5% and can be ignored.

(c) 0.2238 M = $[SO_4^{2-}]$, $[Ag^+]$ = 7.4×10^{-3} M

Check: (3.7×10^{-3} M/0.2238 M)×100% = 1.64×10^{-2}%, the condition is satisfied

(d)$[OH^-]$ = 2.8×10^{-3} M, 5.7×10^{-12} M = $[Zn^{2+}]$

Check: (5.7×10^{-12} M/2.8×10^{-3} M)×100% = 2.0×10^{-7}%, x is less than 5% of $[OH^-]$ and is, therefore, negligible.

6. The molar solubility of $BaSO_4$ is 1.51×10^{-4} M and the mass of barium present in 1 L of water in 0.020 g.

7. Mass ($CaSO_4{\cdot}2H_2O$) = 0.72 g/L

8. $MnCO_3$ will form first, since it has the smallest K_{sp} value it is the least soluble. $MnCO_3$ will be the last to precipitate, it has the largest K_{sp} value.

9. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$ $K_{sp} = [Mg^{2+}][OH^-]^2$ 1.23×10^{-3} g $Mg(OH)_2$

10. No precipitation occurs because the value of the solubility product (2.3×10^{-8}) is greater than the ionic product (1.6×10^{-8}).

11. 9.2×10^{-13} M

CHAPTER 7

7.1 - INTRODUCTION TO REACTION RATES

In previous units, we've covered several different variables to describe a chemical reaction – in thermochemistry, we saw that we can use ΔH to tell if a reaction is energetically favourable, and in our discussion of chemical equilibria, we saw that we can use K, the equilibrium constant, to tell if a reaction favours products or reactants. However, we haven't yet discussed how we can describe how *fast* a reaction proceeds. This will be covered here when we talk about *kinetics* – the study of reaction rates and the mechanisms that explain how fast or slow a reaction proceeds.

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance travelled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more coloured substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution (the most common case), reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per litre per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in concentration per unit time.

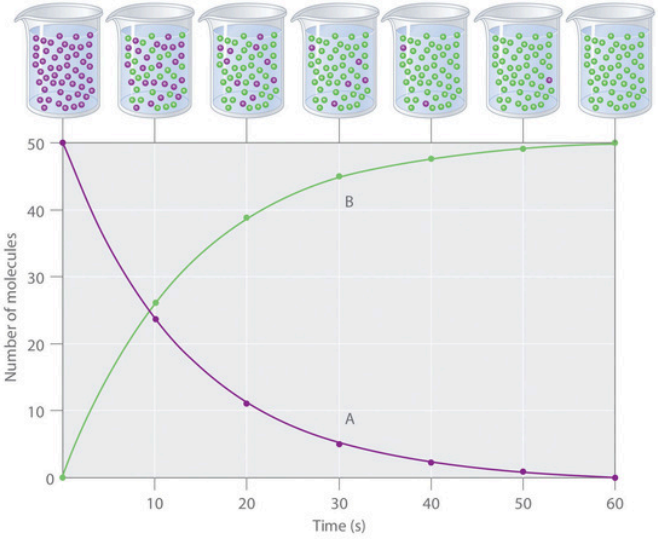


Figure 7.1.1. The progress of a simple reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 7.1.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 7.1.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \Delta[B]\Delta t = -\Delta[A]\Delta t$$

Equation 7.1.1 Rate Relation to Concentration of Reactants

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Due to it being a common practice among chemists to follow the convention of expressing all reaction rates as positive numbers, a negative sign is inserted in front of $\Delta[A]/\Delta t$ to convert the otherwise negative rate into a positive number. The reaction rate calculated for the reaction A → B using the equation above is different for each interval (this is not true for every reaction, as shown below). For example, a greater change occurs in [A] and [B] during the first 10 s interval than during the last, meaning that the reaction rate is greatest at first. Hence, an important thing to keep in mind is that reaction rates generally decrease with time as reactant concentrations decrease.

Let’s apply what we’ve just learned with an example of a reaction – if we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2\,(g)$$

The rate at which the hydrogen peroxide is consumed can be expressed in terms of the rate of change of its concentration, as shown here:

$$\text{rateofdecompositionof}H_2O_2=-\text{changeinconcentrationofreactanttimeinterval}$$
$$= -[H_2O_2]t_2 - [H_2O_2]t_2t_2 - t_1$$
$$= -\Delta[H_2O_2]\Delta t$$

Equation 7.1.2 Rate of Decomposition

$[H_2O_2]_1$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]_2$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). When dealing with rates of reaction, it is important to consider stoichiometric coefficients. For the decomposition of hydrogen peroxide, as H_2O and H_2O_2 have the same coefficients we can conclude the magnitude of their rate of formation and decomposition are identical. As for the O_2, using stoichiometric ratios we can conclude that the magnitude of its rate of formation is half of the other 2 molecules.

NOTE: Remember that (as previously mentioned) reaction rates are, by convention, positive. Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression to express the reaction rate as a positive quantity.

Factors Affecting Reaction Rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure 7.1.2). Large pieces of wood smoulder, smaller pieces burn rapidly, and sawdust burns explosively.

(a) (b)

Figure 7.1.2. (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total surface area: $2Fe(s) + 6HCl(aq)$? $2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly.

Reaction of Cesium with Water – Video Demonstration

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10°C will approximately double the rate of a reaction in a homogeneous system.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 7.1.3). An acidic oxide, sulfur dioxide combines with water vapour in the air to produce sulfurous acid in the following reaction:

$$SO_2\,(g) + H_2O\,(g) \rightarrow H_2SO_3\,(aq)$$

Calcium carbonate reacts with sulfurous acid as follows:

$$CaCO_3\,(s) + H_2SO_3\,(aq) \rightarrow CaSO_3\,(s) + CO_2\,(g) + H_2O\,(l)$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

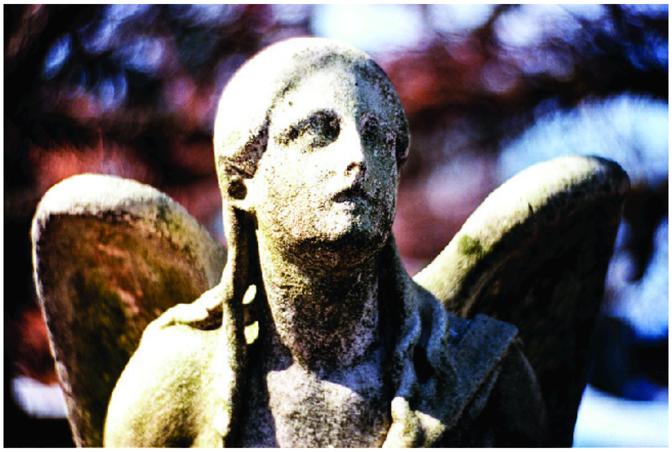


Figure 7.1.3. Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, the deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Phosphorus Burning in Air with Higher [O_2] – Video Demonstration

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow. Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

Factors Affecting Reaction Rates – Interactive Activity

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modelling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

Questions

★ Questions

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Explain why an egg cooks more slowly in boiling water in Lake Louise, AB(elevation 1.6km) than in Charlottetown, PEI(elevation 0-49m). (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

What is the difference between average rate, initial rate, and instantaneous rate?

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction Cl_2 *(g)* + $3F_2$ *(g)* ? $2ClF_3$ *(g)*. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

Answers

Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because a more reactive surface exists.

The boiling points in this question are dependent on the elevation of our two cities. The higher the elevation, the lower the air pressure; when we reduce the pressure over boiling water, it is able to boil at a lower temperature. This affects the rate at which our egg will cook because the lower temperature will decrease the rate of our reaction.

The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as the product just begins to form). The average rate is the average of the instantaneous rates over a time period.

$$\text{rate} = +12$$

$$\Delta[CIF_3]\Delta t$$

$$= -\Delta[CI_2]\Delta t = -13\Delta[F_2]\Delta t$$

7.2 - MEASURING & EXPRESSING REACTION RATES

The method for determining a reaction rate is relatively straightforward. Since a reaction rate is based on change over time, it must be determined from tabulated values or found experimentally. With the obtained data, it is possible to calculate the reaction rate either algebraically or graphically. What follows is general guidance and examples of measuring the rates of a reaction.

Measuring time change is easy; a stopwatch or any other time device is sufficient. However, determining the change in concentration of the reactants or products involves more complicated processes. The change of concentration in a system can generally be acquired in two ways:

By monitoring the depletion of reactant over time, or
By monitoring the formation of product over time

It does not matter whether an experimenter monitors the reagents or products because there is no effect on the overall reaction. However, since reagents decrease during the reaction, and products increase, there is a sign difference between the two rates. Reagent concentration decreases as the reaction proceeds, giving a negative number for the change in concentration. The products, on the other hand, increase concentration with time, giving a positive number. Graphically, the general shape of the curves of concentration versus time for reactants and products looks like this:

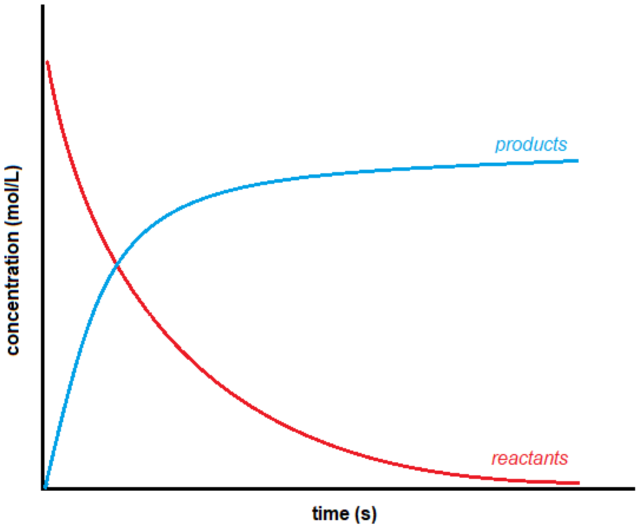


Figure 7.2.1 Concentration vs Time

Since the convention is to express the rate of reaction as a positive number, to solve a problem, set the overall rate of the reaction equal to the negative of a reagent's disappearing rate. The overall rate also depends on stoichiometric coefficients.

It is worth noting that the process of measuring the concentration can be greatly simplified by taking advantage of the different physical or chemical properties (ie: phase difference, reduction potential, etc.) of the reagents or products involved in the reaction by using the above methods. We have emphasized the importance of taking the sign of the reaction into account to get a positive reaction rate. Now, we will turn our attention to the importance of stoichiometric coefficients.

A reaction rate can be reported quite differently depending on which product or reagent selected to be monitored. Given a reaction:

$$aA + bB \rightarrow cC + dD$$

the general rate for this reaction is defined as

$$\text{rate} = -1a\Delta[A]\Delta t = \text{-}1b\Delta[B]\Delta t = \text{-}1c\Delta[C]\Delta t = 1d\Delta[D]\Delta t$$

Equation 7.2.1 General Rate of Reaction

Following the Course of a Reaction

There are two different ways you can follow the course of a reaction.

Samples of the mixture can be collected at intervals and titrated to determine how the concentration of one of the reagents is changing.

A physical property of the reaction which changes as the reaction continues can be measured: for example, the volume of gas produced.

These approaches must be considered separately.

Consider that bromoethane reacts with sodium hydroxide solution as follows:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

During the course of the reaction, both bromoethane and sodium hydroxide are consumed. However, it is relatively easy to measure the concentration of sodium hydroxide at any one time by performing a titration with a standard acid: for example, with hydrochloric acid of a known concentration. The process starts with known concentrations of sodium hydroxide and bromoethane, and it is often convenient for them to be equal. Because the reaction is 1:1, if the concentrations are equal at the start, they remain equal throughout the reaction. Samples are taken with a pipette at regular intervals during the reaction and titrated with standard hydrochloric acid in the presence of a suitable indicator.

The problem with this approach is that the reaction is still proceeding in the time required for the titration. In addition, only one titration attempt is possible because, by the time another sample is taken, the concentrations have changed. There are two ways around this problem:

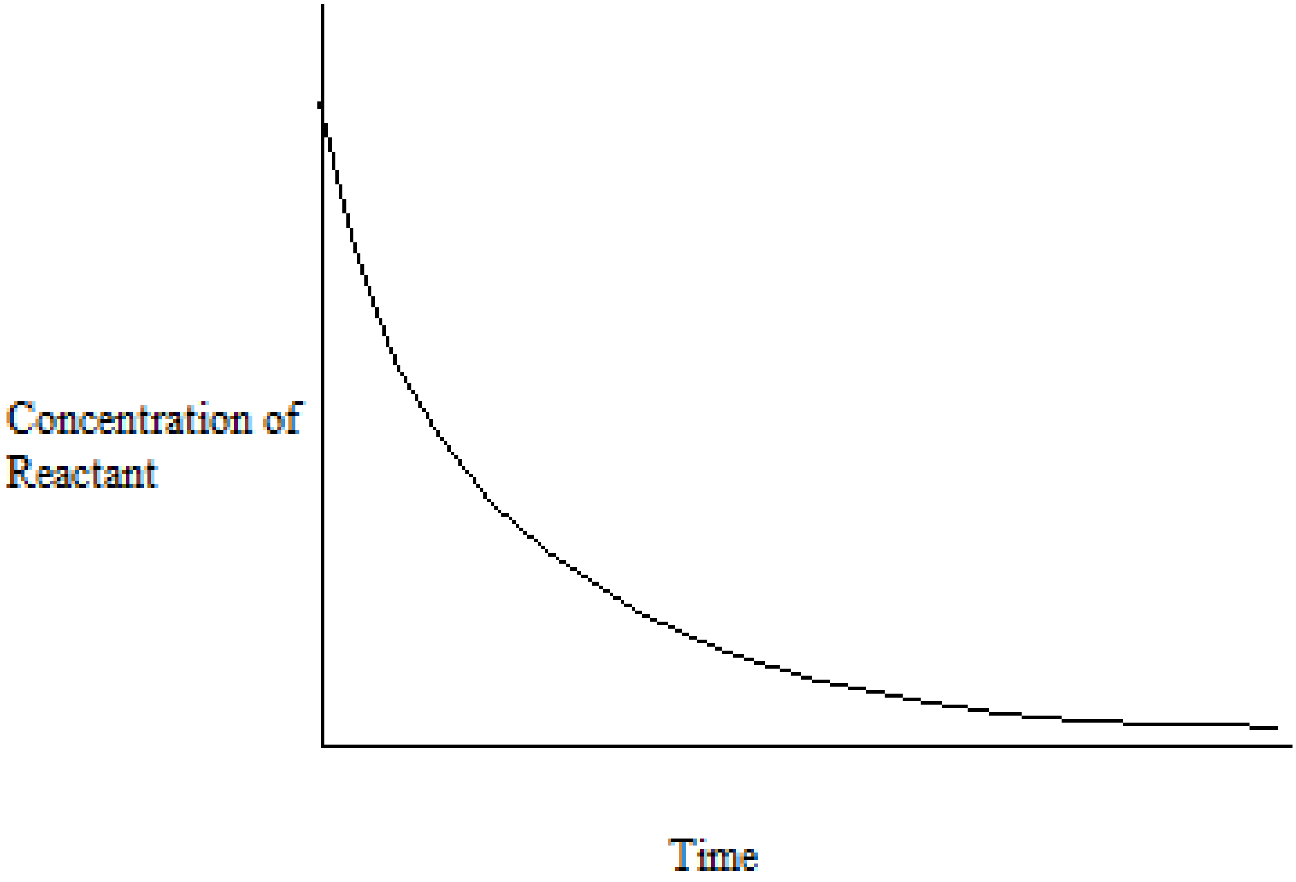
The reaction can be slowed by diluting it, adding the sample to a larger volume of cold water before the titration. Then the titration is performed as quickly as possible. This is most effective if the reaction is carried out above room temperature. Cooling it as well as diluting it slows it down even more.

If possible (and it is possible in this case) it is better to stop the reaction completely before titrating.

In this case, this can be accomplished by adding the sample to a known, excess volume of standard hydrochloric acid. This consumes all the sodium hydroxide in the mixture, stopping the reaction.

At this point, the resulting solution is titrated with standard sodium hydroxide solution to determine how much hydrochloric acid is left over in the mixture. This allows one to calculate how much acid was used, and thus how much sodium hydroxide must have been present in the original reaction mixture. This technique is known as back titration.

This process generates a tabulated set of values for the concentration of (in this example) sodium hydroxide over time. The concentrations of bromoethane are, of course, the same as those obtained if the same concentrations of each reagent were used. These values are plotted to give a concentration-time graph, such as that below:



With either the tabulated results or a graph like the one above, we can calculate different types of rates of reaction: average and instantaneous rates of reaction.

Average vs. Instantaneous Reaction Rates

Reaction rates have the general form of (change in concentration/change in time). There are two types of reaction rates(the third method using initial rates will be addressed separately). One is called the average rate of reaction, often denoted by (Δ[conc.] / Δt), while the other is referred to as the instantaneous rate of reaction, denoted as either:

$$\text{lim}\Delta\text{t}\rightarrow 0\ \Delta[\text{concentration}]\Delta\text{t}$$

or

$$\text{d}[\text{concentration}]\text{dt}$$

The **average rate of reaction**, as the name suggests, is an average rate, obtained by taking the change in concentration over a time period, for example: -0.3 M / 15 minutes. This is an approximation of the reaction rate in the interval; it does not necessarily mean that the reaction has this specific rate throughout the time interval or even at any instant during that time. The instantaneous rate of reaction, on the other hand, depicts a more accurate value. The **instantaneous rate of reaction** is defined as the change in concentration of an infinitely small time interval, expressed as the limit or derivative expression above. In simpler words, it is the rate at which a reaction is proceeding at any specific time.

Consider the analogy of a car slowing down as it approaches a stop sign. The reading on the speedometer at any one specific point in time—call it t_1—during the deceleration is an instantaneous rate. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance travelled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

Recall the example from the previous section for the breakdown of H_2O_2 into H_2O and O_2. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2\,(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned}\text{rateofdecompositionof}H_2O_2 &= -\text{changeinconcentrationofreactanttimeinterval}\\ &= -[H_2O_2]\text{t}_2 - [H_2O_2]\text{t}_1\text{t}_2 - \text{t}_1\\ &= -\Delta[H_2O_2]\Delta\text{t}\end{aligned}$$

Note: There isn't a ½ in front since we are not looking at the overall rate of the reaction. Here we are specifically looking at the rate of decomposition of H_2O_2 (aq).

Now imagine that at regular time intervals we experimentally determine the concentration of H_2O_2 present in the reaction mixture – Figure 7.2.2 below provides an example of data collected during the decomposition of H_2O_2.

Time (h)	**[H_2O_2] (mol L^{-1})**	**Δ[H_2O_2] (mol L^{-1})**	**Δt (h)**	**Rate of Decomposition (M/h)**
0.00	1.000	-0.500	6.00	0.0833
6.00	0.500	-0.500 ↔ -0.250	6.00	0.0833 ↔ 0.0417
12.00	0.250	-0.250 ↔ -0.125	6.00	0.0417 ↔ 0.0208
18.00	0.125	-0.125 ↔ -0.062	6.00	0.0208 ↔ 0.0103
24.00	0.0625	-0.062	6.00	0.0103

Figure 7.2.2. The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40°C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$-\Delta[H_2O_2]\Delta t = -(0.500\ \text{mol/L} - 1.000\text{mol/L})(6.00\text{h} - 0.00\text{h}) = 0.0833\ \text{molL}^{-1}\text{h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$-\Delta[H_2O_2]\Delta t = -(0.0625\ \text{mol/L} - 0.125\text{mol/L})(24.00\text{h} - 18.00\text{h}) = 0.0104\ \text{molL}^{-1}\text{h}^{-1}$$

Both calculations above involve determining an average rate of reaction since we look at concentration values at the beginning and end of a time period. Hence, these calculated values are an average rate of reaction over that particular time interval (e.g. the time period between 18.00 h and 24.00 h spanning the last 6 hour time interval).

Graphically, determining an average rate of reaction follows the same principle – a line is drawn between two points on the concentration versus time curve (Figure 7.2.3). These two points represent the two concentration values at two different instants in time. Calculating the slope of this line uses the same formula to calculate an average rate of reaction – Δ[conc.] / Δt.

$$\text{averagerate} = \text{slope}$$

$$\text{averagerate} = \Delta y \Delta x$$

$$\text{averagerate} = \Delta[\text{conc}]\Delta t$$

$$\text{averagerate} = ([\text{conc}]_2 - [\text{conc}]_1)(t_2 - t_1)$$

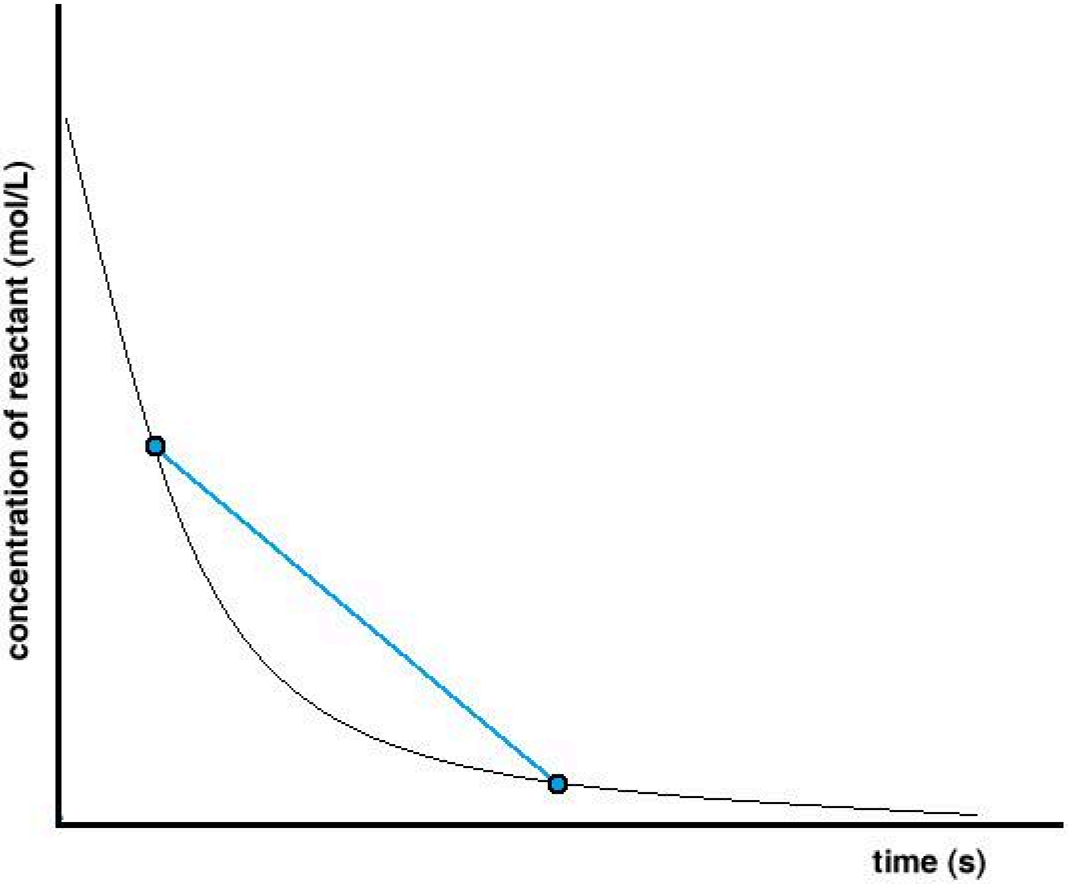


Figure 7.2.3. Determining the average rate of reaction from a concentration versus time graph.

The instantaneous rate of a reaction may be determined in one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible (Figure 7.2.4). Going back to our example for the decomposition of H_2O_2, if we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time *t* is given by the slope of a straight line that is tangent to the curve at that time (Figure 7.2.5). We can use calculus to evaluate the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

$$\text{instantaneousrateatt} = \text{slope}$$

$$\text{instantaneousrateatt} = \Delta y \Delta x$$

$$\text{instantaneousrateatt} = \Delta[\text{conc}]\Delta t$$

$$\text{instantaneousrateatt} = ([\text{conc}]_2 - [\text{conc}]_1)(t_2 - t_1)$$

Figure 7.2.4. Determining the instantaneous rate of reaction from a concentration versus time graph.

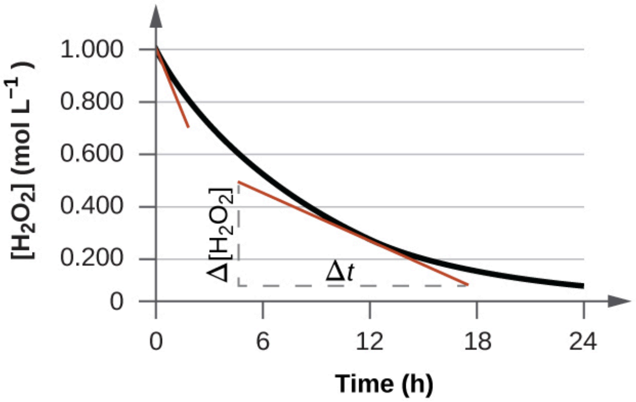


Figure 7.2.5. This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 10 h ("instantaneous rate" at that particular time).

Initial Rate of Reaction

The **initial rate of reaction** is the rate at which the reagents are first brought together. Recall the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0).

Like the instantaneous rate mentioned above, the initial rate can be obtained either experimentally or graphically. To experimentally determine the initial rate, scientists must bring the reagents together and measure the reaction rate as quickly as possible. If this is not possible, they can find the initial rate graphically. To do this, one must find the slope of the line tangent to the reaction curve when $t = 0$ (Figure 7.2.6).

$$\text{initialrate} = \text{slope}$$

$$\text{initialrate} = \Delta y \Delta x$$

$$\text{initialrate} = \Delta[\text{conc}]\Delta t$$

$$\text{initialrate} = ([\text{conc}]_2 - [\text{conc}]_1)(t_2 - t_1)$$

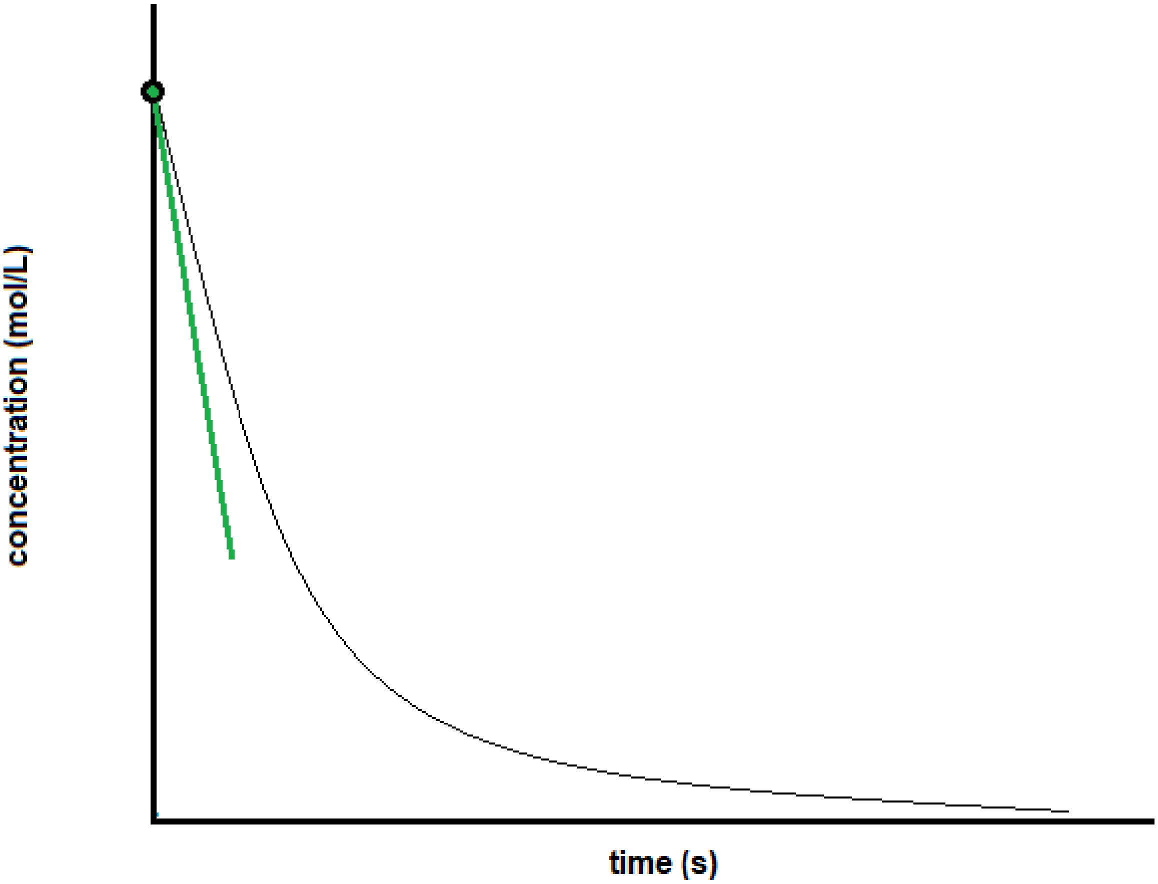


Figure 7.2.6. Determining the initial rate of reaction from a concentration versus time graph.

Reaction Rates in Analysis: Test Strips for Urinalysis

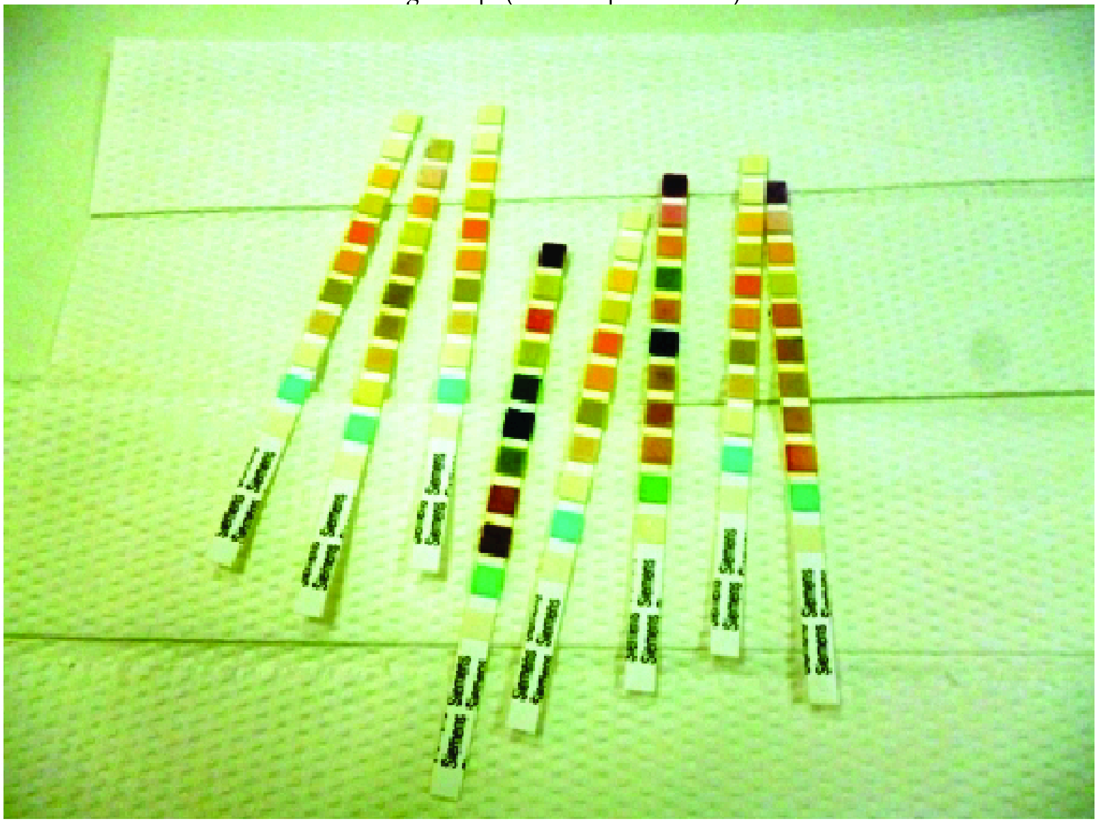
Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 7.2.7). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in colour upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colourless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct colour change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for the completion of the colour-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the colour change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ions by other substances found in urine.

Figure 7.2.6. Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)



7.3 - RATE LAWS

As described in the previous section, the rate of a reaction is affected by the concentrations of reactants. **Rate laws** or **rate equations** are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. In general, a rate law (or ***differential rate law***, as it is sometimes called) takes this form:

$$\text{rate}=k[A]^m[B]^n[C]^p....$$

in which [*A*], [*B*], and [*C*] represent the molar concentrations of reactants, and ***k*** is the **rate constant**, which is specific for a particular reaction at a particular temperature. The numerical value of the rate constant is specific for a particular reaction under a given set of conditions, including temperature, pressure, reactant phase, solvents, etc. We will see later how individual factors influence the numeric value of *k*. Note that the numeric value of the rate constant is independent of the concentrations of the reactants *A*, *B*, or *C*, but we will see in the next section how the units of *k* are affected by the exponents *m*, *n*, and *p*. The numerical value of *k*, however, does not change as the reaction progresses under a given set of conditions. The exponents *m*, *n*, and *p* are usually positive integers (although it is possible for them to be fractions or negative numbers). The rate constant *k* and the exponents *m*, *n*, and *p* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the **reaction order**. Consider a reaction for which the rate law is:

$$\text{rate} = k[A]^m[B]^n$$

If the exponent *m* is 1, the reaction is first order with respect to *A*. If *m* is 2, the reaction is second order with respect to *A*. If *n* is 1, the reaction is first order in *B*. If *n* is 2, the reaction is second order in *B*. If *m* or *n* is zero, the reaction is zero order in *A* or *B*, respectively, and the rate of the reaction is not affected by the concentration of that reactant. The **overall reaction order** is the sum of the orders with respect to each reactant. If $m = 1$ and $n = 1$, the overall order of the reaction is second-order ($m + n = 1 + 1 = 2$).

The rate law:

$$\text{rate} = k[H_2O_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[C_4H_6]^2$$

describes a reaction that is second order in C_4H_6 and second-order overall. The rate law:

$$\text{rate} = k[H^+][OH^-]$$

describes a reaction that is first order in H^+, first-order in OH^-, and second-order overall.

Reaction Order and Rate Constant Units

Sometimes, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2(g)$	Rate = $k[N_2O_5]$
$2NO_2\,(g) + F_2(g) \rightarrow 2NO_2F\,(g)$	Rate = $k[NO_2][F_2]$
$2H_2O_2(aq) \rightarrow 2H_2O\,(l) + O_2(g)$	Rate = $k[H_2O_2]$
$H_2\,(g) + Br_2\,(g) \rightarrow 2HBr\,(g)$	Rate = $k[H_2][Br_2]$
$O_3\,(g) + CI\,(g) \rightarrow O_2\,(g) + CIO\,(g)$	Rate = $k[O_3][CI]$

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

Reaction orders also play a role in determining the units for the rate constant *k*. For example, in a second-order reaction, the units for *k* are L mol^{-1} s^{-1}, whereas in a third-order reaction, the units for *k* are mol^{-2} L^{2}/s. This is because the rate must always be in the form of M/s or mol/L•s, hence the units of individual concentrations must work out to one of the aforementioned units. More generally speaking, the units for the rate constant for a reaction of order $(m + n)$ are mol$^{1-(m+n)}$ L$^{(m+n)-1}$ s^{-1}. The table below summarizes the rate constant units for common reaction orders.

Rate Constants for Common Reaction Orders

Reaction Order	**Units of *k***
$(m + n)$	$mol^{1-(m+n)}L^{(m+n)-1}s^{-1}$
zero	mol/L/s
first	s^{-1}
second	L/mol/s
third	$mol^{2-}L^{2}s^{-1}$

Table 7.3.1 Rate Constants for Common Reaction Orders

Note that the units in the table can also be expressed in terms of molarity (*M*) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

Example 7.3.1 – Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

is second order in NO_2 and zero-order in CO at 100°C. What is the rate law for the reaction? What are the units of *k*?

Solution

The reaction will have the form:

$$\text{rate} = k[NO_2]^m[CO]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

From this we know that the rate must be in M/s and the concentration (once squared) will be in M^2, hence our *k* value must be $M^{-1}s^{-1}$.

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Check Your Learning 7.3.1 – Writing Rate Laws from Reaction Orders

The rate law for the reaction:

$$H_2\,(g) + 2NO\,(g) \rightarrow N_2O\,(g) + H_2O\,(g)$$

has been determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

order in NO = 2; order in H_2 = 1; overall order = 3

Check Your Learning 7.3.2 – Writing Rate Laws from Reaction Orders

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$CH_3OH + CH_3CH_2OCOCH_3 \rightarrow CH_3OCOCH_3 + CH_3CH_2OH$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k[CH_3OH]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

order in CH_3OH = 1; order in $CH_3CH_2OCOCH_3$ = 0; overall order = 1

Example 7.3.2 – Interpreting Rate Laws

Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

$$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$

$$\text{rate} = -12(\Delta[HI]\Delta t) = k[HI]^2$$

$$2N_2O\,(g) \rightarrow 2N_2\,(g) + O_2\,(g)$$

$$\text{rate} = -12(\Delta[N_2O]\Delta t) = k$$

$$\text{cyclopropane}(g) \rightarrow \text{propane}(g)$$

$$\text{rate} = -\Delta[\text{cyclopropane}]\Delta t = k[\text{cyclopropane}]$$

Solution

(a) $[HI]^2$ will give units of (moles per litre)^2. For the reaction rate to have units of moles per litre per second, the rate constant must have reciprocal units [1/(M·s)]:

$$kM^2 = M{\cdot}sk = M / s{\cdot}M^2$$
$$= 1M{\cdot}s = M^{-1} \cdot s^{-1}$$

The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second-order overall.

If the concentration of HI is doubled, the reaction rate will increase from $k[HI]_0^2$ to $k(2[HI])_0^2 = 4k[HI]_0^2$. The reaction rate will therefore quadruple.

(b) Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth-order overall.

Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

(c) The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per litre per second for the reaction rate: $M{\cdot}s^{-1} = M/s$.

The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first-order overall.

Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

Check Your Learning 7.3.3 – Interpreting Rate Laws

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

$$CH_3N = NCH_3\,(g) \rightarrow C_2H_6\,(g) + N_2\,(g)$$

with

$$\text{rate} = -\Delta[CH_3N = NCH_3]\Delta T = K[CH_3N = NCH_3]$$

$$2NO_2\,(g) + F_2\,(g) \rightarrow 2NO_2F\,(g)$$

with

$$\text{rate} = -\Delta[F_2]\Delta t = -12(\Delta[NO_2]\Delta t) = k[NO_2][F_2]$$

Answer

(a) s^{-1}; first order in $CH_3N{=}NCH_3$; first-order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.

(b) $M^{-1}{\cdot}s^{-1}$; first order in NO_2, first-order in F_2; second-order overall; doubling $[NO_2]$ will double the reaction rate.

Experimental Kinetics – Method of Initial Rates

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding reaction mechanisms can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time.

For the reaction A + B → products, for example, we need to determine *k* and the exponents *m* and *n* in the following equation:

$$\text{rate} = k[A]^m[B]^n$$

Equation 7.3.1 Rate Law Equation

We can use an explicit algebraic method, often referred to as the **method of initial rates**, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After cancelling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient. Rate data for a hypothetical reaction of the type A + B → products are given in the table below.

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

Table 7.3.2 Initial Rate to Concentration

The general rate law for the reaction is

$$\mathrm{rate} = \mathrm{k}[\mathrm{A}]^{\mathrm{m}}[\mathrm{B}]^{\mathrm{n}}$$

Equation 7.3.2 General Rate Law

We can obtain *m* or *n* directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in the table above.

$$\mathrm{rate}_1\mathrm{rate}_3 = \mathrm{k}[\mathrm{A}_1]^{\mathrm{m}}[\mathrm{B}_1]^{\mathrm{n}}\mathrm{k}[\mathrm{A}_3]^{\mathrm{m}}[\mathrm{B}_3]^{\mathrm{n}}$$

Inserting the appropriate values from the table,

$$8.5 \times 10^{-3}\ \mathrm{M / min}\ 34{\times}10^{-3}\ \mathrm{M / min} = \mathrm{k}[0.50\mathrm{M}]^{\mathrm{m}}[0.50\mathrm{M}]^{\mathrm{n}}\mathrm{k}[1.00\mathrm{M}]^{\mathrm{m}}[0.50\mathrm{M}]^{\mathrm{n}}$$

Because 1.00 to any power is 1, $[1.00\ \mathrm{M}]^{m} = 1.00\ \mathrm{M}$. We can cancel like terms to give $0.25 = [0.50]^{m}$, which can also be written as $1/4 = [1/2]^{m}$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for m.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for n.

$$\mathrm{rate}_1\mathrm{rate}_5 = \mathrm{k}[\mathrm{A}_1]^{\mathrm{m}}[\mathrm{B}_1]^{\mathrm{n}}\mathrm{k}[\mathrm{A}_5]^{\mathrm{m}}[\mathrm{B}_5]^{\mathrm{n}}$$

Substituting the appropriate values from the table,

$$8.5 \times 10^{-3}\ \mathrm{M / min}\ 8.5 \times 10^{-3}\ \mathrm{M / min} = \mathrm{k}[0.50\mathrm{M}]^{\mathrm{m}}[0.50\mathrm{M}]^{\mathrm{n}}\mathrm{k}[0.50\mathrm{M}]^{\mathrm{m}}[1.00\mathrm{M}]^{\mathrm{n}}$$

Canceling leaves $1.0 = [0.50]^{n}$, which gives $n = 0$; that is, the reaction is zeroth-order in B. The experimentally determined rate law is therefore

$$\mathrm{rate} = k[\mathrm{A}]^2[\mathrm{B}]^0 = k[\mathrm{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of the table into the experimentally determined rate law and solving for k. Using Experiment 2, we obtain

$$19 \times 10^{-3}\ \mathrm{M/min} = k(0.75\ \mathrm{M})^2$$

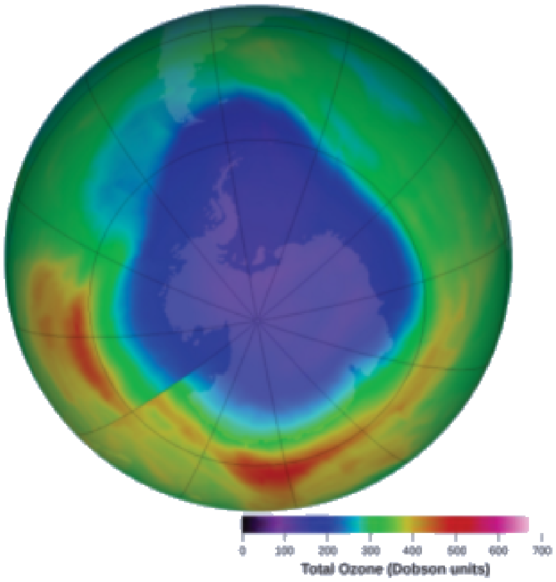
$$3.4 \times 10^{-2}\ \mathrm{M}^{-1}{\cdot}\mathrm{min}^{-1} = \mathrm{k}$$

You should verify that using data from any other row of the table gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

Example 7.3.3 – Determining a Rate Law from Initial Rates – 1

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 7.3.7). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

$$\mathrm{NO}\,(g) + \mathrm{O}_3\,(g) \rightarrow \mathrm{NO}_2\,(g) + \mathrm{O}_2\,(g)$$



(credit: modification of work by NASA)

Figure 7.3.1. Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area.

This reaction has been studied in the laboratory, and the following rate data were determined at 25°C.

Trial	[NO] (mol/L)	$[O_3]$ (mol/L)	$\Delta[NO2]\Delta t$ (mol L^{-1} s^{-1})
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25°C.

Solution

The rate law will have the form:

$$\text{rate} = k[NO]^m[O_3]^n$$

We can determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. *Determine the value of m from the data in which [NO] varies and $[O_3]$ is constant.* In the last three experiments, [NO] varies while $[O_3]$ remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.
2. *Determine the value of n from data in which $[O_3]$ varies and [NO] is constant.* In the first three experiments, [NO] is constant and $[O_3]$ varies. The reaction rate changes in direct proportion to the change in $[O_3]$. When $[O_3]$ doubles from trial 1 to 2, the rate doubles; when $[O_3]$ triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to $[O_3]$, and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[NO]^1[O_3]^1 = K[NO][O_3]$$

3. *Determine the value of k from one set of concentrations and the corresponding rate.*

$$k = \text{rate}[NO][O_3]$$

$$k = 6.60 \text{ x } 10^{-5}(1.00\times10^{-6})(3.00\times10^{-6}\text{ molL}^{-1})$$
$$k = 2.20\times10^{7}\text{ L mol}^{-1}\text{s}^{-1}$$

The large value of *k* tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Check Your Learning 7.3.4 – Determining a Rate Law from Initial Rates – 1

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$CH_3CHO\,(g) \rightarrow CH_4\,(g) + CO\,(g)$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	$[CH_3CHO]$ (mol/L)	$-\Delta[CH3CHO]\Delta t$ (mol L^{-1} s^{-1})
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

rate = $k[CH_3CHO]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

Example 7.3.4 – Determining a Rate Law from Initial Rates – 2

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O_2 to give NO_2, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2NO + O_2 \rightarrow 2NO_2$$
$$H_2O \rightarrow HNO_2 + HNO_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$$2NO\,(g) + O_2\,(g) \rightarrow 2NO_2\,(g)$$

Determine the rate law for the reaction and calculate the rate constant.

Experiment	**$[NO]_0$ (M)**	**$[O_2]$ (M)**	**Initial Rate (M/s)**
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Solution

Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

rate = $k[NO]^2[O_2]$. The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \text{rate}[NO]^2[O^2] = 7.98 \text{ x } 10^{-3} \text{ M / s } [0.0235\text{M}]^2[0.0125\text{M}] = 1.16 \text{ x } 10^3 \text{ M}^{-2} \cdot \text{s}^{-1}$$

Alternatively, using Experiment 2 gives

$$k = \text{rate}[NO]^2[O^2] = 15.9 \text{ x } 10^{-3} \text{ M / s } [0.0235\text{M}]^2[0.0250\text{M}] = 1.15 \text{ x } 10^3 \text{ M}^{-2} \cdot \text{s}^{-1}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m + n) = 3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

Check Your Learning 7.3.5 – Determining a Rate Law from Initial Rates – 2

The peroxydisulfate ion ($S_2O_8{}^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O_8^{2-}\,(aq) + 3I^{1-}\,(aq) \rightarrow 2SO_4^{2-}\,(aq) + I_3^{-}\,(aq)$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

Experiment	**$[S_2O_8^{2-}]_0$ (M)**	**$[I^{-}]_0$ (M)**	**Initial Rate (M/s)**
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer

rate = $k[S_2O_8^{2-}][I^{-}]$; k = 20 $M^{-1}{\cdot}s^{-1}$

Integrated Rate Laws

The rate laws we have seen thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for zero-, first-, second-order reactions.

In addition, we'll be looking at the case of half-life for these reactions of different orders. The **half-life of a reaction ($t_{1/2}$)** is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 M to 0.500 M. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 M to 0.250 M; during the third half-life, it decreases from 0.250 M to 0.125 M. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^0 = k$$

Equation 7.3.3 Zero Order Differential Rate Law

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactants.

$$[A] = -kt + [A]_0$$

$$y = mx + b$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.

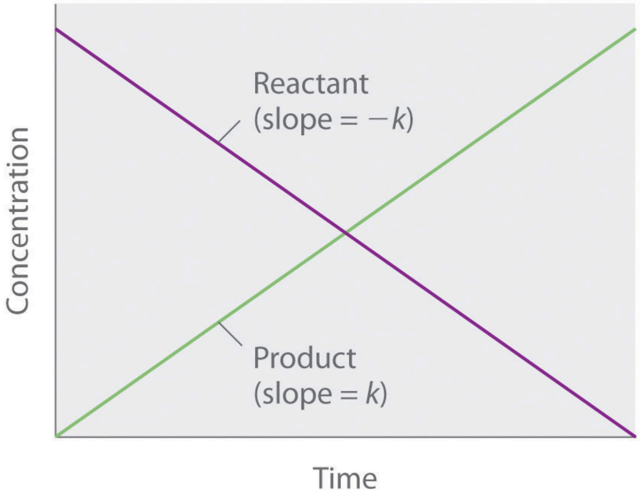


Figure 7.3.2. The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt$$

where $[A]_0$ is the initial concentration of reactant A. The equation above has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = [A]$, $mx = -kt$, and $b = [A]_0$.) In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per litre per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O\,(g)$$
$$\text{pt} \rightarrow 2N_2\,(g) + O_2\,(g)$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -12(\Delta[N_2O]\Delta t) = 12(\Delta[N_2]\Delta t) = \Delta[O_2]\Delta t = k[N_2O]_0 = k$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 7.3.3 below, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

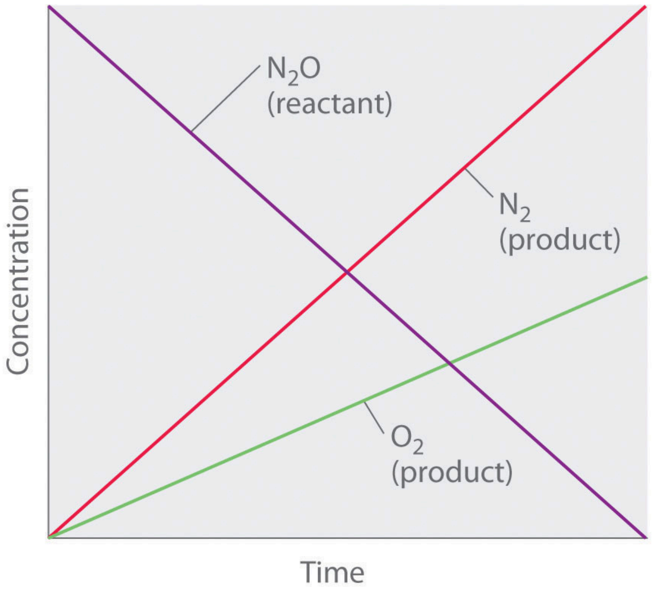


Figure 7.3.3. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the enzyme alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

$$CH_3CH_2OH + NAD^+$$
$$\text{alcoholdehydrogenase} \rightarrow CH_3COH + NADH + H^+$$

where NAD^+ (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (part (a) in Figure 7.3.4). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 7.3.4).

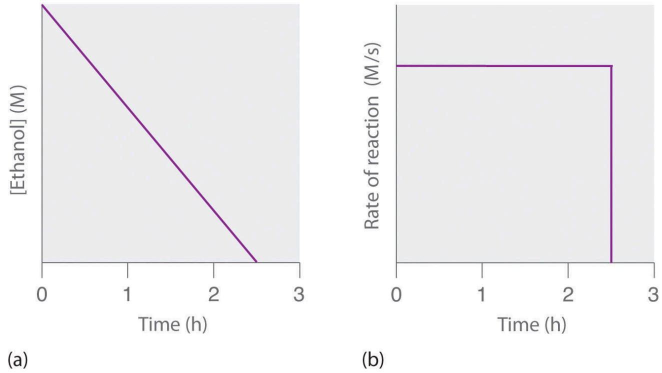


Figure 7.3.4. The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.

A linear change in concentration with time is a clear indication of a zeroth-order reaction.

Half-Life of Zero-Order Reactions

We can derive an equation for calculating the half-life of a zero-order reaction as follows:

$$[A] = -kt + [A]_0$$

When half of the initial amount of reactant has been consumed $t = t_{1/2}$ and $[A] = [A]_0^2$

Thus:

$$[A]_0^2 = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = [A]_0 - [A]_0^2 = [A]_0^2$$

and

$$t_{1/2} = [A]_0^2 k$$

The half-life of a zero-order reaction increases as the initial concentration increases; hence, its half-life is dependent on the concentration.

First-Order Reactions

In a first-order reaction, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\Delta[\text{A}]\Delta t = k[\text{A}]$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per litre per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[\text{A}] = [\text{A}]_0 e^{-kt}$$

where $[\text{A}]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. The equation above predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of the equation and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

Because this equation has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[\text{A}]$ and $b = \ln[\text{A}]_0$, a plot of ln [A] versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[\text{A}]_0$. Either the differential rate law or the integrated rate law can be used to determine whether a particular reaction is first order.

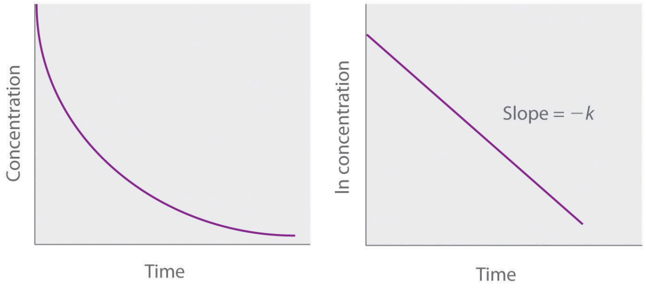
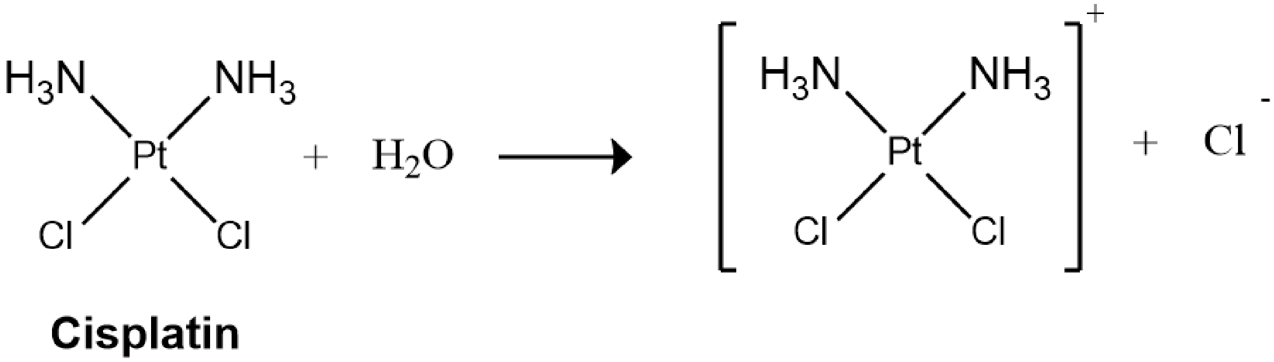


Figure 7.3.5. Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin.

Cisplatin, the first “inorganic” anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:



Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown above is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction have been studied extensively to find ways of maximizing the concentration of the active species.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in the table below. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin. Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in the table shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = $k[\text{cisplatin}]^1$. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of the table. For example, substituting the values for Experiment 3 into the differential rate law,

$$3.6 \times 10^{-5}\ \text{M/min} = k(0.024\ \text{M})$$
$$1.5 \times 10^{-3}\ \text{min}^{-1} = k$$

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 7.3.5 – The Integrated Rate Law for a First-Order Reaction – 1

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ($k = 1.6 \times 10^{-6}\ \text{s}^{-1}$)?

Solution

The exponential form of the integrated rate law for a first-order reaction is $[A] = [A]_0e^{-kt}$. Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6}\ \text{s}^{-1}$, we can use the rate law to calculate the concentration of the reactant at a given time *t*. Substituting the known values into the integrated rate law,

$$[CH_3CH_2Cl]_{10\text{ h}} = [CH_3CH_2Cl]_0e^{-kt}$$

$$= 0.0200\text{ M}(e^{-(1.6\text{ x }10\text{^-}6\text{ s^- }1)\ [(10\text{ h})(60\text{ min/h})(60\text{s/min})]})$$

$$= 0.0189\text{ M}$$

We could also have used the logarithmic form of the integrated rate law:

$$\ln[CH_3CH_2Cl]_{10\text{ h}} = \ln[CH_3CH_2Cl]_0 - kt$$

$$= \ln 0.0200 - (1.6\text{ x }10^{-6}\text{ s}^{-1})\ [(10\text{ h})(60\text{ min/h})(60\text{s/min})]$$

$$[CH_3CH_2Cl]_{10\text{ h}} = e^{-3.970}\text{ M}$$

$$= 0.0189\text{ M}$$

To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for *t*. Using the integrated rate law gives the following:

$$\ln[CH_3CH_2Cl]_t = \ln[CH_3CH_2Cl]_0 - kt$$

$$kt = \ln[CH_3CH_2Cl]_0 - \ln[CH_3CH_2Cl]_t = \ln[\text{CH3CH2Cl}]0[\text{CH3CH2Cl}]t$$

$$t = 1k(\ln[CH_3CH_2Cl]_0[\text{CH3CH2Cl}]_t) = 11.6{\times}10^{-6}\text{s}^{-1}\ (\ln 0.0200\text{ M }0.0050\text{ M}) = 8.7\text{ x }10^5\text{ s} = 240\text{h} = 2.4{\times}10^2\text{h}$$

Check Your Learning 7.3.6 – The Integrated Rate Law for a First-Order Reaction – 1

You find that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculate the rate constant at 320°C to be $2.2 \times 10^{-5}\ s^{-1}$. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C. The equation for the decomposition of SO_2Cl_2 is:

$$SO_2Cl_2\,(g) \rightarrow SO_2\,(g) + Cl_2\,(g)$$

How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer

0.0252 M; 29 h

Example 7.3.6 – The Integrated Rate Law for a First-Order Reaction – 2

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500°C is 9.2×10^{-3} s^{-1}:

$$C_4H_8 \rightarrow 2C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

We use the integrated form of the rate law to answer questions regarding time:

$$\ln([A]_0[A]) = kt$$

There are four variables in the rate law, so if we know three of them, we can determine the fourth. In this case we know $[A]_0$, $[A]$, and k, and need to find t.

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or $0.200x$. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$t=\ln|x||0.200x|x1k = \ln0.100\ \text{molL} – 10.020\ \text{molL} – 1\ \text{x}\ 19.2\ \text{x}\ 10^{-3}\text{s}^{-1} = \ln1.609\ \text{x}\ 19.2\ \text{x}\ 10^{-3}\text{s}^{-1} = \ln1.7\ \text{x}\ 10^{2}\text{s}$$

Check Your Learning 7.3.7 – The Integrated Rate Law for a First-Order Reaction – 2

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

I-131 → Xe-131 + electron

The decay is first-order with a rate constant of $0.138\ d^{-1}$. All radioactive decay is first order. How many days will it take for 90% of the iodine−131 in a 0.500 M solution of this substance to decay to Xe-131?

Answer

16.7 days

Example 7.3.7 – Determination of Reaction Order by Graphing

Show that the data below can be represented by a first-order rate law by graphing ln $[H_2O_2]$ versus time. Determine the rate constant for the rate of decomposition of H_2O_2 from this data.

Time (h)	$[H_2O_2]$ (molL^{1})	$\Delta[H_2O_2]$ (mol L^{1})	Δt (h)	Rat Decomp (mol/
0.00	1.000	-0.500	6.00	0.0833
6.00	0.500	-0.500 ↔ -0.250	6.00	0.0833 0.0417
12.00	0.250	-0.250 ↔ -0.125	6.00	0.0417 0.0208
18.00	0.125	-0.125 ↔ -0.062	6.00	0.0208 0.0103
24.00	0.0625	-0.062	6.00	0.0103

Solution

The data from above with the addition of values of ln$[H_2O_2]$ are given in Figure 7.3.6.

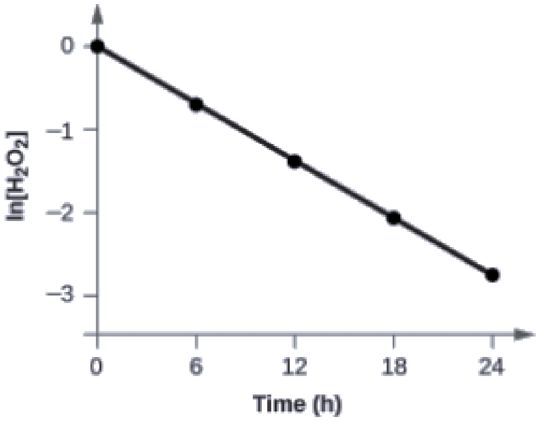


Figure 7.3.6. The linear relationship between the ln$[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

Trial	Time (h)	$[H_2O_2]$ (M)	$\ln[H_2O_2]$
1	0.00	1.000	0.0
2	6.00	0.500	-0.693
3	12.00	0.250	-1.386
4	18.00	0.125	-2.079
5	24.00	0.0625	-2.772

The plot of $\ln[H_2O_2]$ versus time is linear, thus we have verified that the reaction may be described by a first-order rate law.

The rate constant for a first-order reaction is equal to the negative of the slope of the plot of $\ln[H_2O_2]$ versus time where:

$$\text{slope} = \text{changeinychangeinx} = \Delta y\Delta x = \Delta\ln[H_2O_2]\Delta t$$

In order to determine the slope of the line, we need two values of $\ln[H_2O_2]$ at different values of *t* (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when *t* is 6.00 h is −0.693; the value when *t* = 12.00 h is −1.386:

$$\text{slope} = -1.386 - (-0.693)\ 12.00\text{ h} - 6.00\text{ h} = -0.693\ 6.00\text{ h} = -1.155\times10\text{-}1\text{ h-}1$$

$$k = -\text{slope} = -(-1.155\times10^{-1}\text{ h}^{-1}) = 1.155\times10^{-1}\text{ h}^{-1}$$

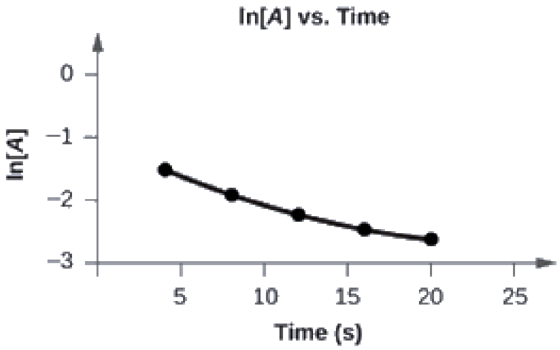
Check Your Learning 7.3.8 – Determination of Reaction Order by Graphing

Graph the following data to determine whether the reaction A → B + C is first order.

Trial	Time (s)	[A] (M)
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Answer

The plot of $\ln[A]$ vs. t is not a straight line. The equation is not first order:



Half-Life of First-Order Reactions

We can derive an equation for determining the half-life of a first-order reaction from the alternate form of the integrated rate law as follows:

$$\ln[A]_0[A] = kt$$

$$t = \ln[A]_0[A] \text{ x } 1k$$

If we set the time t equal to the half-life, $t_{1/2}$, the corresponding concentration of A at this time is equal to one-half of its initial concentration.

Hence, when $t = t_{1/2}$, $[A] = 12[A]_0$.

Therefore

$$t_{1/2} = \ln[A]_0 12[A]]_0 \text{ x } 1k = \ln 2 \text{ x } 1k = 0.693 \text{ x } 1k$$

Thus:

$$t_{1/2} = 0.693k$$

We can see that the half-life of a first-order reaction is inversely proportional to the rate constant *k* and entirely independent of the concentration. A fast reaction (shorter half-life) will have a larger *k*; a slow reaction (longer half-life) will have a smaller *k*.

Example 7.3.8 – Calculation of a First-Order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40°C, using the data given in Figure 7.3.7.

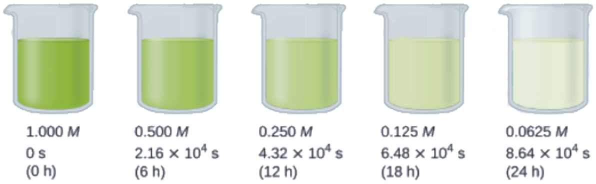


Figure 7.3.7. The decomposition of H_2O_2 ($2H_2O_2 \rightarrow 2H_2O + O_2$) at 40°C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

The half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$t_{1/2} = 0.693k$$

$$k = 0.693\ t_{1/2} = 0.693\ 2.16 \times 10^4\ s = 3.21 \text{ x } 10^{-5} s^{-1}$$

Check Your Learning 7.3.9 – Calculation of a First-Order Rate Constant using Half-Life

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer

5.02 d.

Second-Order Reactions

The simplest kind of second-order reaction is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form 2A → products. A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\Delta[A]^2 \Delta t = k[A]^2$$

Equation 7.3.4 Second-Order Differential Rate Law

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

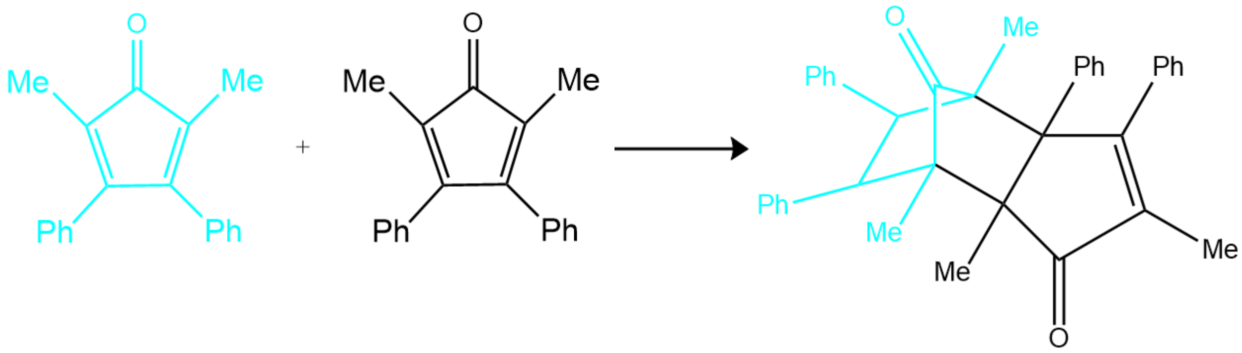
For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$1[A] = 1[A]_0 + kt$$

Because this equation has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of 1/[A] versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:



2 monomers
(red)

dimer
(colorless)

For simplicity, we will refer to this reactant and product as "monomer" and "dimer," respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by "dimer." Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law or the integrated rate law .

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

Table 7.3.3 Time to Rate to Concentration

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in the table above. From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$5.0\times10 = 5\ \mathrm{M / min}\ 1.8\times10^{-5}\ \mathrm{M / min} = 2.8$$

and

$$3.4 \text{ x } 10 = 3\ \mathrm{M/min}\ 2.0\times10^{-3}\ \mathrm{M/min} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using the differential rate law and the data from any row in the table, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[A]^2$$

$$8.0\times10^{-5}\ \mathrm{M/min} = k(4.4\times10\text{-}3\mathrm{M})^2 = 4.1\ \mathrm{M}^{-1} \cdot \mathrm{min}^{-1} = k$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in part (a) in Figure 7.3.8. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time.

According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in part (b) in Figure 7.3.8. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1\ M^{-1}{\cdot}min^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

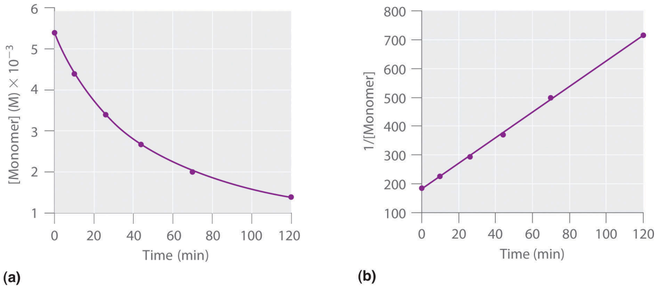


Figure 7.3.8. These plots correspond to dimerization of the monomer as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form A + B → products, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$rate = -\Delta[A]\Delta t = -\Delta[B]\Delta t = k[A][B]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Example 7.3.9 – The Integrated Rate Law for a Second-Order Reaction – 1

The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:

$$2C_4H_6\,(g) \rightarrow C_8H_{12}\,(g)$$

The reaction is second order with a rate constant equal to 5.76×10^{-2} L/mol/min under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration remaining after 10.0 min?

Solution

We use the integrated form of the rate law to answer questions regarding time. For a second-order reaction, we have:

$$1[A] = kt + 1[A]_0$$

We know three variables in this equation: $[A]_0 = 0.200$ mol/L, $k = 5.76 \times 10^{-2}$ L/mol/min, and $t = 10.0$ min. Therefore, we can solve for $[A]$, the fourth variable:

$$1[\mathrm{A}] = (5.76 \text{ x } 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1})\ (10 \text{ min}) + 10.200\text{mol}^{-1}$$

$$1[\mathrm{A}] = (5.76 \text{ x } 10^{-1} \text{ L mol}^{-1}) + 5.00 \text{ L mol}^{-1}$$

$$1[\mathrm{A}] = 5.58 \text{ L mol}^{-1}$$

$$[\mathrm{A}] = 1.79 \text{ x } 10^{-1} \text{ mol L}^{-1}$$

Therefore 0.179 mol/L of butadiene remains at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Check Your Learning 7.3.10 – The Integrated Rate Law for a Second-Order Reaction – 1

If the initial concentration of butadiene is 0.0200 M, what is the concentration remaining after 20.0 min?

Answer

0.0195 mol/L

Example 7.3.10 – The Integrated Rate Law for a Second-Order Reaction – 2

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2\mathrm{NO_2}\,(g) \rightarrow 2\mathrm{NO}\,(g) + \mathrm{O_2}\,(g)$$

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction and the rate constant $k = 0.54\ \mathrm{M^{-1}{\cdot}s^{-1}}$.

Solution

We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values,

$$1[\mathrm{NO_2}]_{3600} = 1[\mathrm{NO_2}]0 + \mathrm{kt} = 10.056 \text{ M}+[(0.54 \text{ M}^{-1} \cdot \text{s}^{-1})(3600 \text{ s})] = 2.0 \text{ x } 10^{3} \text{ M}^{-1}$$

$$\text{Thus } [\mathrm{NO_2}]_{3600} = 5.1 \times 10^{-4} \text{ M.}$$

I this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0$ = 0.1(0.056 M) = 0.0056 M. To do this, we solve the integrated rate law for t, using the concentrations given.

$$\mathrm{t} = (1/[\mathrm{NO_2}]) - (1/[\mathrm{NO_2}]^0)\mathrm{k} = (1/0.0056\mathrm{M}) - (1/0.056\mathrm{M})0.54\mathrm{M}\text{-}1 \cdot \mathrm{s}^{-1} = 3.0{\times}10^{2}\ \mathrm{s} = 5.0\text{minutes}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Check Your Learning 7.3.11 – The Integrated Rate Law for a Second-Order Reaction – 2

When the highly reactive species HO_2 forms in the atmosphere, one important second-order reaction that then removes it from the atmosphere is as follows:

$$2\mathrm{HO_2}\,(g) \rightarrow \mathrm{H_2O_2}\,(g) + \mathrm{O_2}\,(g)$$

You calculate the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^{9}\ \mathrm{M^{-1}{\cdot}s^{-1}}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction and the rate constant $k = 1.4 \times 10^{9}$ M^{-1}?s^{-1}.

Answer

2.0×10^{-13} M; 6.4×10^{-6} s

Example 7.3.11 – Determination of Reaction Order by Graphing

The data below are for the same reaction described in the example "The Integrated Rate Law for a Second-Order Reaction – 1". Test these data to confirm that this dimerization reaction is second-order.

Solution

Trial	Time (s)	$[C_4H_6]$ (M)
1	0	1.00×10^{-2}
2	1600	5.04×10^{-3}
3	3200	3.37×10^{-3}
4	4800	2.53×10^{-3}
5	6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, we plot ln $[C_4H_6]$ versus t and compare it with a plot of 1[C4H6] versus t. The values needed for these plots follow.

Time (s)	1[C4H6] **(M^{-1})**	**ln [C_4H_6]**
0	100	-4.605
1600	198	-5.289
3200	296	-5.692
4800	395	-5.978
6200	481	-6.175

The plots are shown in Figure 7.3.9. As you can see, the plot of ln [C_4H_6] versus *t* is not linear, therefore the reaction is not first order. The plot of 1[C4H6] versus *t* is linear, indicating that the reaction is second order.

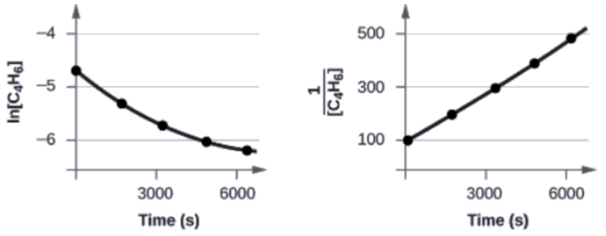


Figure 7.3.9. These two graphs show first- and second-order plots for the dimerization of C_4H_6. Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

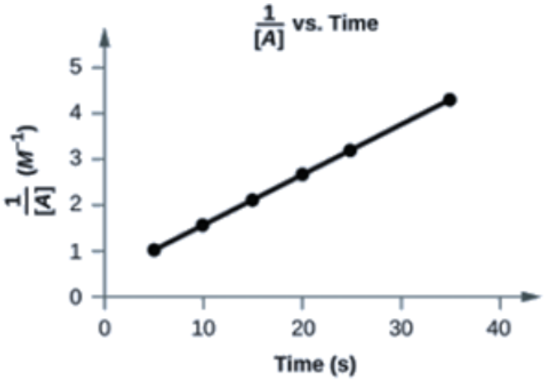
Check Your Learning 7.3.12 – Determination of Reaction Order by Graphing

Does the following data fit a second-order rate law?

Trial	Time (s)	[A] (M)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Answer

Yes. The plot of 1[A] vs. *t* is linear:



Half-Life of Second-Order Reactions

We can derive the equation for calculating the half-life of a second order as follows:

$$1[A] = kt+1[A]_0$$

or

$$1[A] - 1[A]_0 = kt$$

If

$t = t_{1/2}$

then

$$[A] = 12[A]_0$$

and we can write:

$$112[A]_0 - 1[A]_0 = kt_{1/2}$$

$$2[A]_0 - 1[A]_0 = kt_{1/2}$$

$$1[A]_0 = kt_{1/2}$$

Thus:

$$t_{1/2} = 1k[A]_0$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant (hence its half-life is dependent on the concentration), and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Consequently, we find the use of the half-life concept to be more complex for second-order reactions than for first-order reactions. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

Questions

★ Questions

Note: Reminder that the units used in rate law equations will differ from each other based on their order.

In the reaction $4A + 3B \rightarrow 2C + 3D$ reaction A is found to disappear at a rate of 5.1×10^{-5} Ms^{-1}

What is the rate of reaction?

What is the rate of disappearance of B?

What is the rate of formation of C?

In the reaction $3A + 2B \rightarrow C + 2D$ reaction A is found to disappear at a rate of 4.6×10^{-5} Ms^{-1}

What is the rate of reaction?

What is the rate of disappearance of reactant B?

What is the rate of appearance for product D?

In the reaction $A \rightarrow B$, [A] is found to be 0.750 M at t = 61.2s and 0.704 M at t = 73.5s. Determine the average rate of the reaction during this time interval.

What is the average rate of reaction over a time interval for [A] if it is 0.455 M at t = 80.25s and 0.474 M at t = 82.4s?

For the reaction $A + 2B \rightarrow 2C$, the rate of reaction is 1.75×10^{-5} Ms^{-1} at the time when [A] = 0.3575 M.

What is the rate of formation of C?

What will [A] be 1 minute later?

Assume the rate remains at 1.75 x 10-5M s-1. How long would it take for [A] to change from 0.3580 to 0.3500M?

The initial rate of the reaction $A + B \rightarrow C + D$ is determined for different initial conditions, with the results listed in the table.

Expt[A]	M[B]	MInitial Rate M s^{-1}
10.185	0.144	3.35 x 10-4
20.185	0.288	1.35 x 10-3
30.370	0.144	6.75 x 10-4
40.370	0.288	2.70 x 10-3

What is the order of reaction with respect to A and to B?
What is the overall reaction order?
What is the value of the rate constant, k?

The initial rate of the reaction A + B → C + D is determined for different initial conditions, with the results listed in the table:

Expt[A]	M[B]	MInitial Rate M s^{-1}
10.331	0.203	2.205 x 10-4
20.331	0.406	8.82 x 10-4
30.662	0.203	4.41 x 10-4
40.662	0.406	1.7 x 10-3

What is the order of reaction with respect to A and B?
What is the overall reaction order?
What is the value of the rate constant k?

The initial rate of the reaction A + B → C + D is determined for difference initial conditions, with the results listed in the table:

Expt[A]	M[B]	MInitial Rate M s^{-1}
10.241	0.153	1.261 x 10-4
20.241	0.306	5.044 x 10-4
30.482	0.153	2.522 x 10-4
40.482	0.306	6.741 x 10-4

What is the order of the reaction with respect of A and B? Write out respective rate laws for A and B

What is the overall reaction order?

What is the value of the k, the rate constant?

The first-order reaction A→products has $t_{1/2} = 300s$

What percent of sample A remains unreacted 1000 s after the reaction starts?

What is the rate of reaction when [A] = 0.25M?

A first order reaction A→products has a half life of 120 seconds calculate the following:

What percentage of A remains unreacted after 800 seconds of reaction?

What is the rate of reaction at [A] = 0.25M?

The first order reaction has $t_{1/2}$ of 250s.

What percent of a sample of A remains unreacted 1500s after a reaction starts?

What if the rate of the reaction is 1/2 the rate of disappearance of A?

★★ Questions

The reaction A→products is first order in A

If 4.2g A decomposes for 45 minutes, the undecomposed A is measured to be 1.05g. What is the half-life, $t_{1/2}$, of this reaction (in minutes)?

Starting with the same 4.2 g, what is the mass (in grams) of undecomposed A after 75 minutes?

Explain why

A reaction rate cannot be calculated from solely the collision frequency.

The rate of a chemical reaction may increase dramatically with temperature, whereas the collision frequency rises a lot more slowly.

Introducing a catalyst to a reaction mixture can have such a significant impact on the rate of the reaction, even if the temperature is held constant.

Answer the following:

What two factors does the rate of a reaction depend on other than the frequency of collisions?

Why does the rate of reaction increase dramatically with temperature?

What is the net effect of the addition of a catalyst?

Answers

$$-14(-\Delta[A]\Delta t) = 14(5.1\times10\text{-}5\ M\ s^{-1}) = 1.3\times10^{-5}\ M\ s^{-1}$$

Rate of disappearance of B = reaction rate X coefficient of B

$$(1.3 \times 10^{-5}\ M\ s^{-1})(3) = 3.9\times10^{-5}\ M\ s^{-1}$$

Rate of formation of C = reaction rate X coefficient of C

$$(1.3 \text{ x } 10^{-5}\text{ M s}^{-1})(2) = 2.6\times10^{-5}\text{ M s}^{-1}$$

$$-13((-\Delta[A]\Delta t) = 13(4.6\times10^{-5}\text{ M s}^{-1}) = 1.5\times10^{-5}\text{ M s}^{-1}$$

Rate of disappearance of B = (rate of reaction) X 2(coefficient of B)

$$(1.5 \text{ x } 10^{-5}\text{ M s}^{-1})(2) = 3.1\times10^{-5}\text{ M s}^{-1}$$

Same process as B) (multiply rate of reaction by 2) OR:

$$\text{Rate of appearance of D} = -13(2)(\Delta[A]\Delta t) = -23(4.6\times10^{-5}\text{ M s}^{-1}) = 3.1\times10^{-5}\text{ M s}^{-1}$$

$$-\Delta[A]\Delta t = 0.704\text{M} - 0.750\text{M } 61.2\text{ s} - 73.5\text{s} = 3.7\times10^{-3}\text{ M s}^{-1}$$

$$-\Delta[A]\Delta t = 0.474\text{M} - 0.455\text{M } 82.4\text{s} - 80.25\text{s} = 8.8\times10^{-3}\text{ M s}^{-1}$$

$$-14(-\Delta[A]\Delta t) = 14(5.1\times10^{-5}\text{ M s}^{-1}) = 1.3\times10^{-5}\text{ M s}^{-1}$$

Rate of disappearance of B = reaction rate X coefficient of B

$$(1.3 \text{ x } 10^{-5}\text{ M s}^{-1})(3) = 3.9\times10^{-5}\text{ M s}^{-1}$$

Rate of formation of C = reaction rate X coefficient of C

$$(1.3 \text{ x } 10^{-5}\text{ M s}^{-1})(2) = 2.6\times10^{-5}\text{ M s}^{-1}$$

(a) Order with respect to A = 1, Order with respect to B = 2; (b) overall order of reaction = 3; (c) 0.103 M s^{-1}

$$\text{Reaction1} = 2.205 \text{ x } 10^{-4} = \text{kx}[0.331]^m[0.203]^n$$

$$\text{Reaction2} = 8.82 \text{ x } 10^{-4} = \text{kx}[0.331]^m[0.406]^n$$

$$\text{Reaction3} = 4.41 \text{ x } 10^{-4} = \text{kx}[0.662]^m[0.203]^n$$

$$\text{Reaction4} = 1.7 \text{ x } 10^{-3} = \text{kx}[0.662]^m[406]^n$$

Order of Reaction with respect to B:

Find where A is constant and B changes (Reaction 1 and Reaction 2)

$$\text{Divide: Reaction2 / Reaction1} = 8.82\times10^{-4}\ 2.205\times10^{-4} = [0.331]^m[0.406]^n[0.331]^m[0.203]^n$$

$$\text{Reaction2 / Reaction1} = 4 = 2n \rightarrow n = 2$$

Thus the reaction is second order with respect to B.

Order of Reaction with respect to A:

Find where B is constant and A changes (Reaction 1 and Reaction 2)

$$\text{Divide: Reaction3 / Reaction1} = 4.41\times10^{-4}\ 2.205\times10^{-4} = [0.406]^m[0.662]^n[0.203]^m[0.662]^n$$

$$\text{Reaction3 / Reaction1} = 2 = 2m \rightarrow m = 1$$

Thus the reaction is second order with respect to A

b) Reaction order = reaction order of A + reaction order of B = 3rd order reaction

c) $2.205 \text{ x } 10^{-4} = \text{k x } [0.331][0.203]2\text{k} = 1.6 \text{ x } 10^{-2}$

Reaction is first order with respect to A

Overall reaction order = (reaction order of A + reaction order of B) = 1 + 2 = 3rd order overall

$k = 0.0224\ M^{-2}s^{-1}$
ln(%unreacted) = -kt
$k = \ln 2\ t_{1/2} = \ln 2300\ s = 0.0023\ s^{-1}$
ln(%unreacted) = -(0.0023 $^{s-1}$)(1000 s) = -2.3
$e^{-2.3}$=0.1 x 100% = 10%unreacted

Rate = k[A]
Rate = 0.0023 s^{-1}
[0.25 M] = 5.74 x 10^{-4} M s^{-1}
$t_{1/2}$ (first order) = ln2k
$k = \ln 2\ t_{1/2} = \ln 2\ 120\ s = 5.77\times10^{-3}$
percent unreacted defined by $[A]_t[A]_0$
$[A]_t[A]_0$ = e-kt = e(-5.77×10^{-3} x 800) x 100 = 0.98% remains unreacted.

For a first order reaction, rate = k[C] = 0.0046/s x 0.25 = 1.15 x 10^{-3} M/s
$k = \ln 2\ t_{1/2}$ = 0.693250s = 0.00277s-1
ln(%unreacted) = -kt = (-.00277 s^{-1})(1500 s) = -4.155
%unreacted = 0.0157 x 100% = 1.57% of the original quantity
Rate = k[A] = (0.00277 s^{-1})(0.5 M) = 0.00139 M/s
(4.2 g)(14) = 1.05 g → 2 halflives have passed → 45minutes / 2 = $t_{1/2}$ = 22.5 minutes
$\ln[A]_t \ln[A]_0=-kt$

$k = \ln 2\ t_{1/2}$ = ln2 22.5minutes = 0.0308 min^{-1}
$\ln[A]_t \ln[A]_0$ = (-0.0308 min^{-1})(75 min) = -2.31

$[A]_t = [A]_0\ e^{-2.31}$
$[A]_t$ = (4.2 g)(0.09926) = 0.417 g A

7.4 - REACTION KINETICS: SUMMARY

Collision Frequency does not solely determine the rate of the reaction because in order to overcome the activation energy to react, temperature and concentrations will also dictate the rate of the reaction.

A rise in temperature results in higher kinetic energies in the molecules thus increasing the % chance of colliding AND reacting rather than colliding and staying inert. Having a steady collision frequency with higher kinetic energy will result in spiked rates of reactions.

Catalysts induce reactants to react with one another by lowering the activation energy of the chemical reaction. This can be done without any sort of flux in the enthalpy of the system.

1) Whether or not the collisions occurring have enough energy to get over the activation energy and become products.
2) Whether or not the molecules involved in the collisions are situated properly for the reaction to occur.

Collision frequency does not increase dramatically with temperature; however, the percentage of molecules with enough energy to get over the activation energy and become products does.

The net effect of the addition of a catalyst is the decreasing of the energy barrier to products. The catalyst does so by enabling an alternative mechanism with a lower activation energy.

You learned that the integrated rate law for each common type of reaction (zeroth, first, or second order in a single reactant) can be plotted as a straight line. Using these plots offers an alternative to the methods described for showing how reactant concentration changes with time and determining reaction order.

We will illustrate the use of these graphs by considering the thermal decomposition of NO_2 gas at elevated temperatures, which occurs according to the following reaction:

$$2NO_2\,(g)\Delta \;\rightarrow\; 2NO\,(g) + O_2\,(g)$$

Experimental data for this reaction at 330°C are listed in the table below; they are provided as $[NO_2]$, $\ln[NO_2]$, and $1/[NO_2]$ versus time to correspond to the integrated rate laws for zeroth-, first-, and second-order reactions, respectively. The actual concentrations of NO_2 are plotted versus time in part (a) in Figure 7.4.1.

Time (s)	[NO_2] (M)	ln[NO_2]	1/[NO_2] (M-1)
0	1.00×10^{-2}	-4.605	100
60	6.83×10^{-3}	-4.986	146
120	5.18×10^{-3}	-5.263	193
180	4.18×10^{-3}	-5.477	239
240	3.50×10^{-3}	-5.655	286
300	3.01×10^{-3}	-5.806	332
360	2.64×10^{-3}	-5.937	379

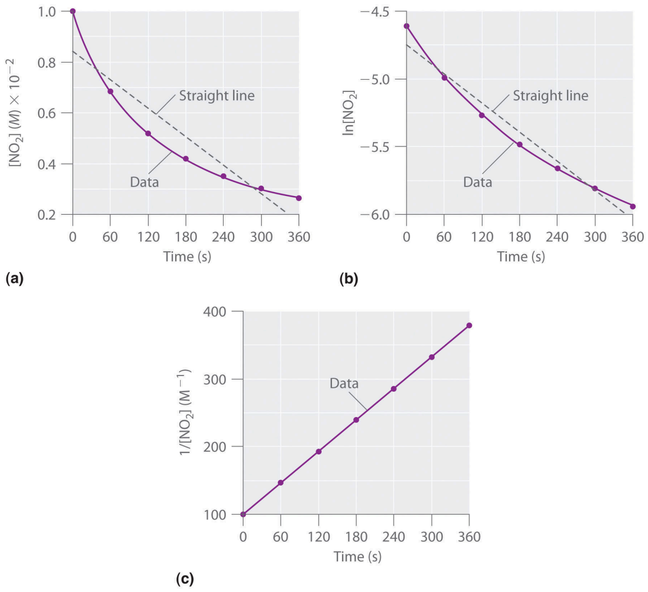


Figure 7.4.1. These plots show the decomposition of a sample of NO_2 at 330°C as (a) the concentration of NO_2 versus *t*, (b) the natural logarithm of [NO_2] versus *t*, and (c) 1/[NO_2] versus *t*.

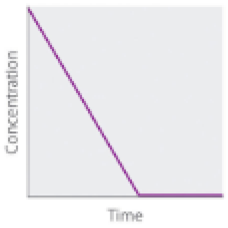
Because the plot of [NO_2] versus *t* is not a straight line, we know the reaction is not zeroth order in NO_2. A plot of ln[NO_2] versus *t* (part (b) in Figure 7.4.1) shows us that the reaction is not first order in NO_2 because a first-order reaction would give a straight line. Having eliminated zeroth-order and first-order behavior, we construct a plot of 1/[NO_2] versus *t* (part (c) in Figure 7.4.1). This plot is a straight line, indicating that the reaction is second order in NO_2.

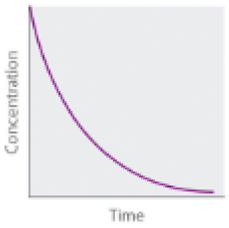
We have just determined the reaction order using data from a single experiment by plotting the concentration of the reactant as a function of time. Because of the characteristic shapes of the lines shown in Figure 7.4.2, the graphs can be used to determine the reaction order of an unknown reaction. In contrast, the method of initial rates required multiple experiments at different NO_2 concentrations as well as accurate initial rates of reaction, which can be difficult to obtain for rapid reactions.

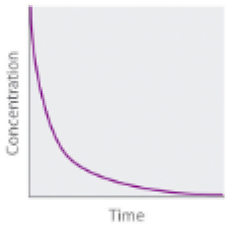
Zeroth Order First Order Second Order

Differential Rate = $-\Delta[A]\Delta t=k$

Rate = $-\Delta[A]\Delta t=k$
$[A]$ Rate = $-\Delta[A]\Delta t=k[A]^2$
rate law



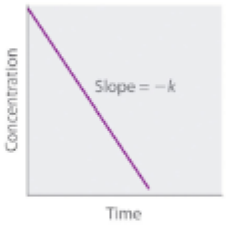




Concentration vs. time

Integrated $[A] = [A]_0 - kt$ $[A] = [A]_0\, e^{-kt1[A]} = 1[A]0 + kt$

rate law or $\ln[A] = \ln[A]_0 - kt$



Straight-line plot to determine rate constant

Relative rate vs. concentration

[A]	M Rate	M/s [A]	M Rate	M/s [A]	M Rate
1	1	1	1	1	1
2	1	2	2	2	4
3	1	3	3	3	9

Half-life

$t_{1/2} = [A]_0{}^2k$
$t_{1/2} = 0.693k$
$t_{1/2} = 1k[A]_0$

Units of k, M/s 1/s M^{-1} s^{-1}

rate constant

Figure 7.4.2. Properties of reactions that obey zero-, first-, and second-order rate laws.

Example 7.4.1 – Integrated Example – Describing the Reaction Kinetics for a Reaction

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

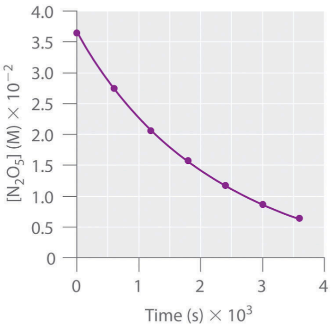
$$2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$$

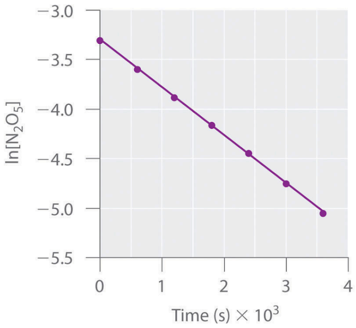
This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

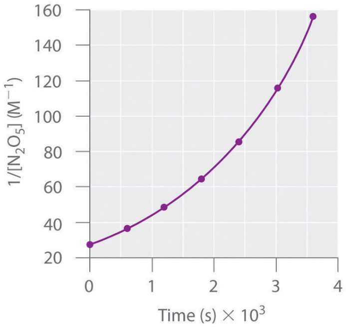
Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	-3.310	27.4
600	0.0274	-3.597	36.5
1200	0.0206	-3.882	48.5
1800	0.0157	-4.154	63.7
2400	0.0117	-4.448	85.5
3000	0.00860	-4.756	116
3600	0.00640	-5.051	156

Solution

Here are plots of $[N_2O_5]$ versus *t*, $\ln[N_2O_5]$ versus *t*, and $1/[N_2O_5]$ versus *t*:







The plot of ln[N_2O_5] versus *t* gives a straight line, whereas the plots of [N_2O_5] versus *t* and 1/[N_2O_5] versus *t* do not. This means that the decomposition of N_2O_5 is first order in [N_2O_5]. The rate law for the reaction is therefore

$$\text{rate} = k[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus *t* for a first-order reaction is −*k*. We can calculate the slope using any two points that lie on the line in the plot of ln[N_2O_5] versus *t*. Using the points for *t* = 0 and 3000 s,

$$\text{slope} = \text{In}[N_2O_5]_{3000} - \text{In}[N_2O_5]_{3000\text{s-0s}} = (-4.756)\text{-}(-3.310)\ 3000\text{s} = -4.820\times10^{-4}\text{s}$$

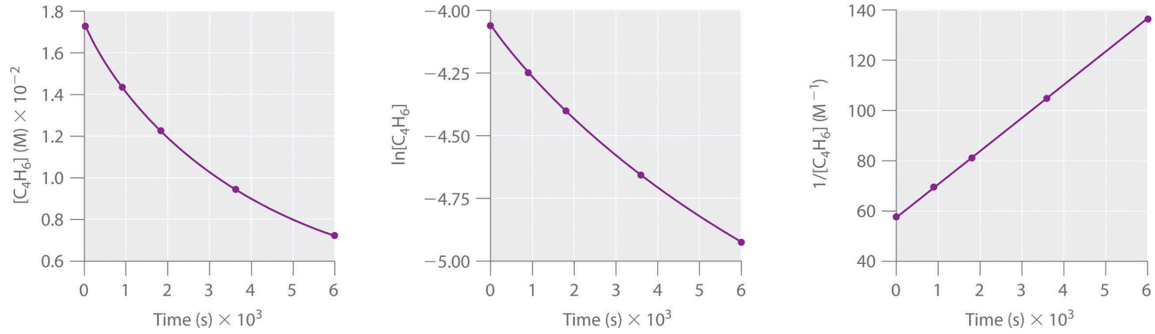
Thus $k = 4.820 \times 10^{-4}\ s^{-1}$.

Check Your Learning 7.4.1 – Integrated Example – Describing the Reaction Kinetics for a Reaction

1,3-Butadiene (CH_2=CH—CH=CH_2; C_4H_6) is a volatile and reactive organic molecule used in the production of rubber. Above room temperature, it reacts slowly to form products. Concentrations of C_4H_6 as a function of time at 326°C are listed in the following table along with ln[C_4H_6] and the reciprocal concentrations. Graph the data as concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t*. Then determine the reaction order in C_4H_6, the rate law, and the rate constant for the reaction.

Time (s)	**$[C_4H_6]$ (M)**	**$\ln[C_4H_6]$**	**$1/[C_4H_6]$ (M^{-1})**
0	1.72×10^{-2}	-4.063	58.1
900	1.43×10^{-2}	-4.247	69.9
1800	1.23×10^{-2}	-4.398	81.3
3600	9.52×10^{-3}	-4.654	105
6000	7.30×10^{-3}	-4.920	137

Answer



second order in C_4H_6; rate = $k[C_4H_6]^2$; $k = 1.3 \times 10^{-2}\ M^{-1}{\cdot}s^{-1}$

7.5 - COLLISION THEORY

We should not be surprised that atoms, molecules, or ions must collide prior to reacting. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates.

Collision theory is based on the following postulates:

1) The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reactionrate} \propto \text{\#collisionstime}$$

2) The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.

3) The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO\,(g) + O_2\,(g) \rightarrow CO_2\,(g) + O\,(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure 7.5.1. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (O=C=O). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

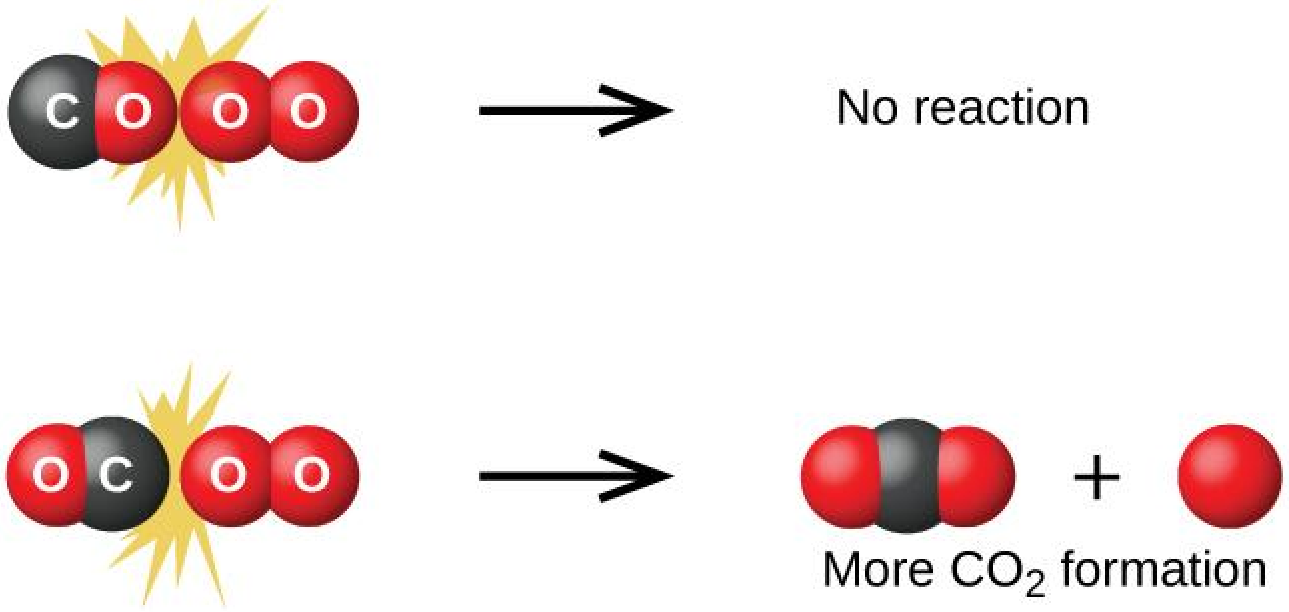


Figure 7.5.1. Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. Every reaction requires a certain amount of activation energy for it to proceed in the forward direction, yielding an appropriate activated complex along the way. As Figure 7.5.2. demonstrates, even a collision with the correct orientation can fail to form the reaction product. In the study of reaction mechanisms, each of these three arrangements of atoms is called a proposed **activated complex** or **transition state**.

$$\mathrm{O=C\cdots O=O}$$

$$\mathrm{O\cdots C\cdots O=O}$$

$$\mathrm{O=C\cdots O\cdots O}$$

Figure 7.5.2. Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as the product is formed. In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third "extra" oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the **activation energy (E_a)**. The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Figure 7.5.3. shows the energy relationships for the general reaction of a molecule of *A* with a molecule of *B* to form molecules of *C* and *D*:

$$A + B \rightarrow C + D$$

The figure shows that the energy of the transition state is higher than that of the reactants *A* and *B* by an amount equal to E_a, the activation energy. Thus, the sum of the kinetic energies of *A* and *B* must be equal to or greater than E_a to reach the transition state. After the transition state has been reached, and as *C* and *D* begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules *A* and *B*) therefore tends to take place readily once the reaction has started. In Figure 7.5.3., ΔH represents the difference in enthalpy between the reactants (*A* and *B*) and the products (*C* and *D*). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

$$C + D \rightarrow A + B$$

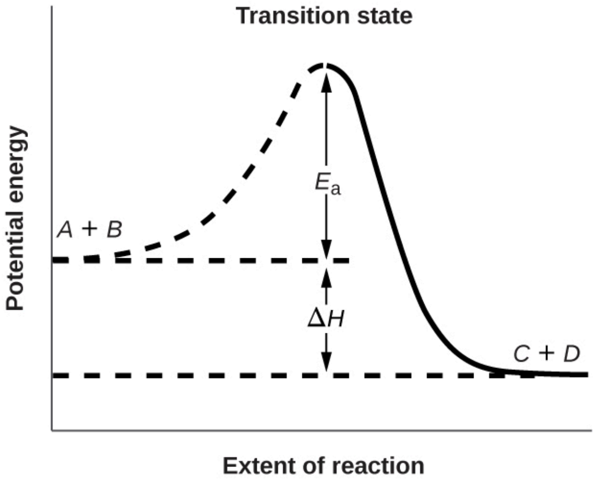


Figure 7.5.3. This graph shows the potential energy relationships for the reaction A + B ? C + D. The

dashed portion of the curve represents the energy of the system with a molecule of *A* and a molecule of *B* present, and the solid portion the energy of the system with a molecule of *C* and a molecule of *D* present. The activation energy for the forward reaction is represented by E_a. The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH. The curve's peak is represented the transition state.

We can use the **Arrhenius equation** to relate the activation energy and the rate constant, *k*, of a given reaction:

$$k=Ae^{-EaIRT}$$

Equation 7.5.1 Arrhenius Equation

In this equation, *R* is the ideal gas constant, which has a value 8.314 J/mol/K, T is temperature on the Kelvin scale, E_a is the activation energy in joules per mole, *e* is the natural exponential function with an approximate value 2.7183, and *A* is a constant called the **pre-exponential factor (A)**, which is related to the frequency of collisions and the orientation of the reacting molecules.

Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The pre-exponential factor *A* is related to the rate at which collisions having the correct *orientation* occur. The exponential term, $e^{-Ea/RT}$, is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-Ea/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-Ea/RT}$, a larger rate constant, and a faster rate for the reaction. An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure 7.5.4.), as indicated by an increase in the value of $e^{-Ea/RT}$. The rate constant is also directly proportional to the pre-exponential factor, *A*. Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in *A* and, consequently, an increase in *k*.

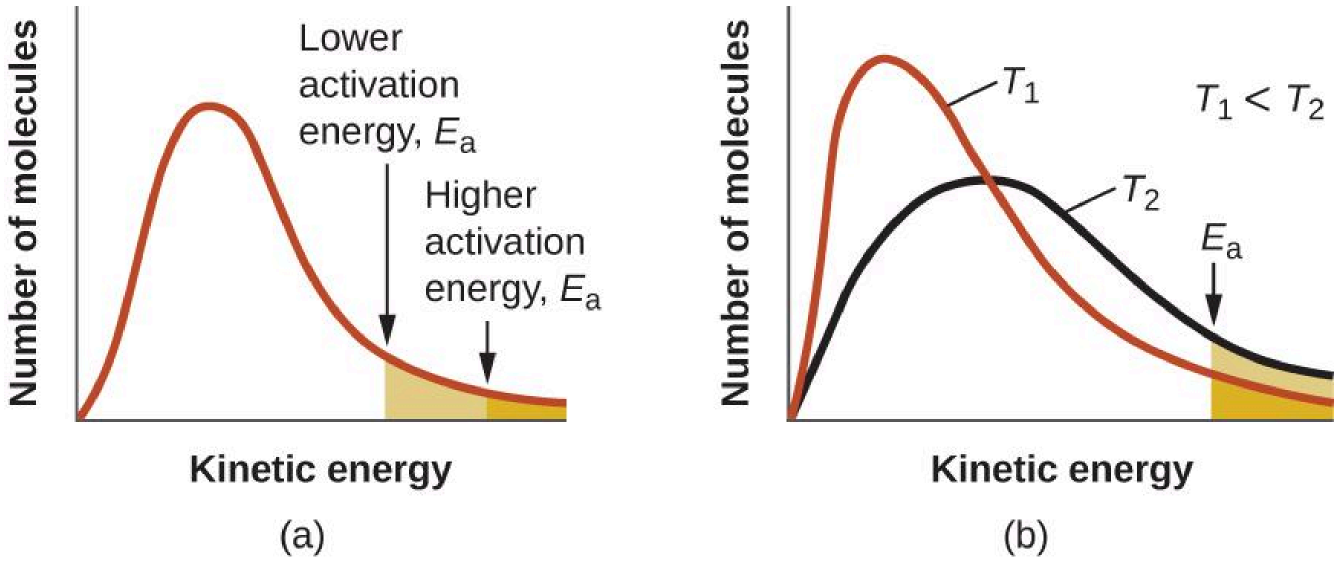


Figure 7.5.4. (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T_2, more molecules have kinetic energies greater than E_a, as shown by the yellow shaded area.

A convenient approach to determining E_a for a reaction involves the measurement of k at different temperatures and using of an alternate version of the Arrhenius equation that takes the form of a linear equation:

$$\text{Ink} = (\text{-EaR})(1\text{T}) + \text{InA}$$

$$\text{y} = \text{mx} + \text{b}$$

Thus, a plot of ln k versus 1T gives a straight line with the slope $\text{-E}_\text{a}\text{R}$, from which E_a may be determined. The intercept gives the value of ln A.

Example 7.5.1 – Determination of E_a

The variation of the rate constant with temperature for the decomposition of HI *(g)* to H_2 *(g)* and I_2 *(g)* is given here. What is the activation energy for the reaction?

$$2\text{HI}\,(g) \rightarrow \text{H}_2\,(g) + \text{I}_2\,(g)$$

T (K)	K (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Values of 1T and ln *k* are:

1T (K^{-1})	ln k
1.80 × 10−3	-14.860
1.74 × 10−3	-13.617
1.55 × 10−3	-9.362
1.43 × 10−3	-6.759
1.28 × 10−3	-3.231

Figure 7.5.5. is a graph of ln *k* versus 1T. To determine the slope of the line, we need two values of ln *k*, which are determined from the line at two values of 1T (one near each end of the line is preferable). For example, the value of ln *k* determined from the line when 1T = 1.25×10^{-3} is −2.593; the value when 1T = 1.78×10^{-3} is −14.447.

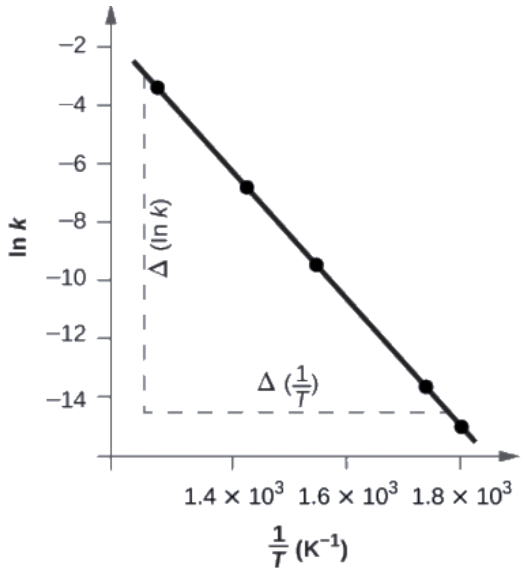


Figure 7.5.5. This graph shows the linear relationship between ln *k* and 1T for the reaction 2HI ? $H_2 + I_2$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

$$\text{Slope} = \Delta(\ln k)\Delta(1T) = (-14.447) - (-2.593)(1.78 \text{ x } 10^{-3}\text{K}^{-1}) = (-11.854)(0.53 \text{ x } 10^{-3}\text{K}^{-1})) = 2.2 \text{ x } 10^{4}\text{ K} = -E_aR$$

Thus:

$$E_a = \text{-slope} \times R = -(-2.2\times10^{4}\text{K} \times 8.314 \text{ Jmol}^{-1}\text{K}^{-1})$$
$$E_a = 1.8\times10^{5}\text{J}^{-1}\text{mol}$$

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

$$\ln k = (-E_aR)(1T) + \ln A$$

can be rearranged as shown to give:

$$\Delta(\ln k)\Delta(1T) = -E_aR \; \ln k_1k_2 = E_aR(1T_2 - 1T_1)$$

Or

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

$$E_a = -R\;(\ln k_2 - \ln k_1\;(1T_2 - 1T_1))$$

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

T (K)	k (L/mol/s)	1T (K^{-1})	ln k
555	$3{,}52 \times 10^{-7}$	$1{,}80 \times 10^{-3}$	$-14{,}860$
781	$3{,}95 \times 10^{-2}$	$1{,}28 \times 10^{-3}$	$-3{,}231$

After calculating 1T and ln k, we can substitute into the equation: $E_a = -8.314\ Jmol^{-1}K^{-1}\ (-3.231 - (-14.860)\ 1.28 \times 10^{-3}K^{-1}\ -1.80 \times 10^{-3}K^{-1})$ and the result is $E_a = 185{,}900$ J/mol.

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

Check Your Learning 7.5.2 – Determination of E_a

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\,N_2O_5\,(g) \rightarrow 4NO\,(g) + 3O_2\,(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer

113,000 J/mol

Questions

★ Questions

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

How does an increase in temperature affect the rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

The rate of a certain reaction doubles for every 10 °C rise in temperature.

How much faster does the reaction proceed at 45 °C than at 25 °C?

How much faster does the reaction proceed at 95 °C than at 25 °C?

★★ Questions

An elevated level of the enzyme alkaline phosphatase (ALP) in the serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy (in kJ/mol) for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H2, and iodine, I2. The value of the rate constant, *k*, for the reaction was measured at several different temperatures and the data are shown here. What is the value of the activation energy (in kJ/mol) for this reaction

Temperature (K)	**k (M^{-1} s^{-1})**
555	6,23 x 10 -7
575	2,42 x 10 -6
645	1,44 x 10 -4
700	2,01 x 10 -3

Answers

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

Order of reaction and concentration

After finding *k* at several different temperatures, a plot of ln *k* versus 1/T, gives a straight line with the slope −Ea/R from which *E*a may be determined.

When temperature is increased the overall average velocity of particles increases as well. As a result, the kinetic energy will increase allowing for particles to collide more frequently together. With more collisions, the rate of the reaction will also increase.

(a) 4-times faster (b) 128-times faster

43.0 kJ/mol

177 kJ/mol

7.6 - TRANSITION STATE THEORY

Transition state theory (TST) provides a more accurate alternative to the previously used Arrhenius equation and the collision theory. The transition state theory attempts to provide a greater understanding of activation energy, E_a, and the thermodynamic properties involving the transition state. Collision theory of reaction rate, although intuitive, lacks an accurate method to predict the probability factor for the reaction. The theory assumes that reactants are hard spheres rather than molecules with specific structures. In 1935, Henry Eyring helped develop a new theory called the **transition state theory** to provide a more accurate alternative to the previously used Arrhenius equation and the collision theory. The Eyring equation involves the statistical frequency factory, v, which is fundamental to the theory.

According to TST, between the state where molecules are reactants and the state where molecules are products, there is the transition state. In the transition state, the reactants are combined in a species called the activated complex. The theory suggests that there are three major factors that determine whether a reaction will occur:

The concentration of the activated complex

The rate at which the activated complex breaks apart

The way in which the activated complex breaks apart: whether it breaks apart to reform the reactants or whether it breaks apart to form a new complex, the products.

Collision theory proposes that not all reactants that combine undergo a reaction. However, assuming the stipulations of the collision theory are met and a successful collision occurs between the molecules, transition state theory allows one of two outcomes: a return to the reactants, or a rearranging of bonds to form the products.

Consider a bimolecular reaction:

$$A + B \rightarrow C$$

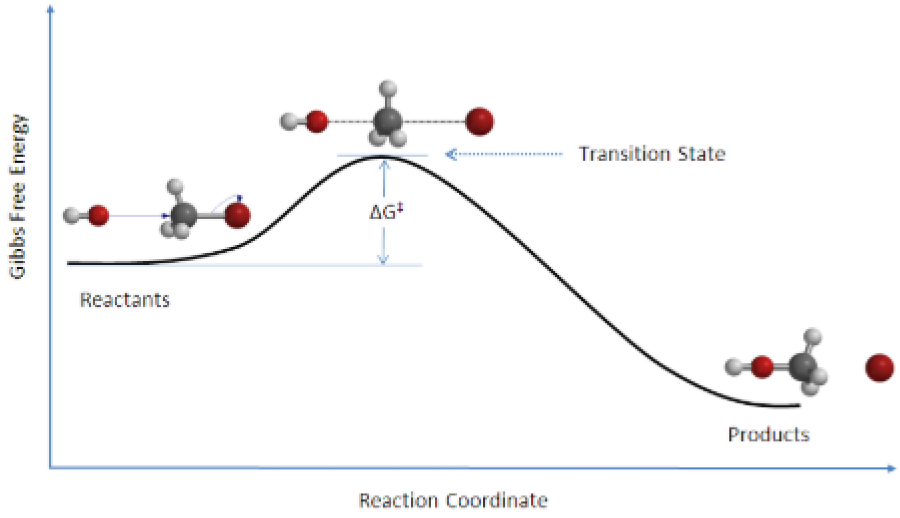
$$K = [C][A][B]$$

where K is the equilibrium constant. In the transition state model, the activated complex AB is formed:

$$A + B \rightleftharpoons AB^{\ddagger} \rightarrow C$$

$$K^{\ddagger}=[AB]^{\ddagger}[A][B]$$

There is an energy barrier, which is the activation energy, in the reaction pathway. A certain amount of energy is required for the reaction to occur. The transition state, $AB^{\ddagger}$, is formed at maximum energy. This high-energy complex represents an unstable intermediate. Once the energy barrier is overcome, the reaction is able to proceed and product formation occurs.



Reaction: $HO^{-} + CH_3Br \rightarrow [HO—CH_3—Br]^{\ddagger} \rightarrow CH_3OH + Br$

Figure 7.6.1. Reaction coordinate diagram for the bimolecular nucleophilic substitution (S_N2) reaction between bromomethane and the hydroxide anion. Image used with permission from Wikipedia.

The change in free energy, ΔG, is equal to the sum of the enthalpy plus the product of the temperature and entropy of the system and will be taught later in physical chemistry. Additionally, an S_N2 reaction denotes the addition of the nucleophile and the departure of the leaving group which will be covered in organic chemistry II.

The rate of a reaction is equal to the number of activated complexes decomposing to form products. Hence, it is the concentration of the high-energy complex multiplied by the frequency of it surmounting the barrier.

$$\text{rate} = v[AB]\ddagger = v[A][B]K^{\ddagger}$$

The rate can be rewritten:

$$\text{rate} = k[A][B]$$

Combining the above equations gives:

$$k[A][B] = v[A][B]K^{\ddagger}$$

$$k = vK^{\ddagger}$$

Equation 7.6.1 Thermodynamic Equilibrium Constant

where

v is the frequency of vibration,
k is the rate constant and
K‡ is the thermodynamic equilibrium constant.

Statistical mechanics (not shown) provides that the frequency, v, is equivalent to the thermal energy, k_BT, divided by Planck's constant, h.

$$v = k_BTh$$

where

k_B is the Boltzmann's constant (1.381 x 10^{-23} J/K),
T is the absolute temperature in Kelvin (K) and
h is Planck's constant (6.626 x 10^{-34} Js).

Substituting the equation for v into the equation for k:

$$k = k_B ThK^{\ddagger}$$

The equation for k is often tagged with another term (M^{1-m}) that makes the units equal with M is the molarity and m is the molecularly of the reaction.

It is important to note here that the equilibrium constant K‡ can be calculated by absolute, fundamental properties such as bond length, atomic mass, and vibration frequency. This gives the transition rate theory the alternative name **absolute rate theory**, because the rate constant, k, can be calculated from fundamental properties.

A balanced equation for a chemical reaction indicates what is reacting and what is produced, but it reveals nothing about how the reaction actually takes place. The **reaction mechanism** (or reaction path) is the process, or pathway, by which a reaction occurs.

A chemical reaction usually occurs in steps, although it may not always be obvious to an observer. The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$O_3(g) \rightarrow O_2(g) + O$$
$$O + O_3(g) \rightarrow 2O_2(g)$$

We call each step in a reaction mechanism an **elementary reaction**. Elementary reactions occur exactly as they are written and cannot be broken down into simpler steps. Elementary reactions add up to the overall reaction, which, for the decomposition, is:

$$2O_3(g) \rightarrow 3O_2(g)$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called **intermediates**.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction does not involve the collision and reaction of two ozone molecules. Rather, it involves a molecule of ozone decomposing to an oxygen molecule and an intermediate oxygen atom; the oxygen atom then reacts with a second ozone molecule to give two oxygen molecules. These two elementary reactions occur exactly as they are shown in the reaction mechanism.

7.7 - REACTION MECHANISMS

Unimolecular Elementary Reactions

The **molecularity** of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a **unimolecular reaction** involves the rearrangement of a *single* reactant species to produce one or more molecules of product:

$$\text{A} \rightarrow \text{products}$$

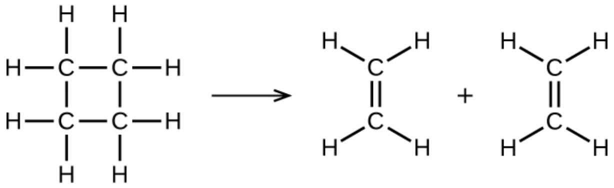
The rate equation for a unimolecular reaction is:

$$\text{rate} = k[\text{A}]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

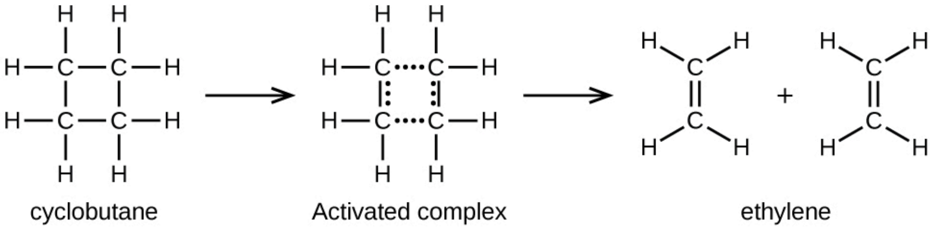
$$O_3 \rightarrow O_2 + O$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, occurs via a unimolecular, single-step mechanism:



For these unimolecular reactions to occur, all that is required is the separation of parts of single reactant molecules into products.

Chemical bonds do not simply fall apart during chemical reactions. Energy is required to break chemical bonds. The activation energy for the decomposition of C_4H_8, for example, is 261 kJ per mole. This means that it requires 261 kilojoules to distort one mole of these molecules into activated complexes that decompose into products:



In a sample of C_4H_8, a few of the rapidly moving C_4H_8 molecules collide with other rapidly moving molecules and pick up additional energy. When the C_4H_8 molecules gain enough energy, they can transform into an activated complex, and the formation of ethylene molecules can occur. In effect, a particularly energetic collision knocks a C_4H_8 molecule into the geometry of the activated complex. However, only a small fraction of gas molecules travel at sufficiently high speeds with large enough kinetic energies to accomplish this. Hence, at any given moment, only a few molecules pick up enough energy from collisions to react.

The rate of decomposition of C_4H_8 is directly proportional to its concentration. Doubling the concentration of C_4H_8 in a sample gives twice as many molecules per liter. Although the fraction of molecules with enough energy to react remains the same, the total number of such molecules is twice as great. Consequently, there is twice as much C_4H_8 per liter, and the reaction rate is twice as fast:

$$\text{rate} = -\Delta[C_4H_8]\Delta t = k[C_4H_8]$$

A similar relationship applies to any unimolecular elementary reaction; the reaction rate is directly proportional to the concentration of the reactant, and the reaction exhibits first-order behavior. The proportionality constant is the rate constant for the particular unimolecular reaction.

Bimolecular Elementary Reactions

The collision and combination of two molecules or atoms to form an activated complex in an elementary reaction is called a **bimolecular reaction**. There are two types of bimolecular elementary reactions:

$$A + B \rightarrow \text{products}$$

and

$$2A \rightarrow \text{products}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B*:

$$\text{rate} = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

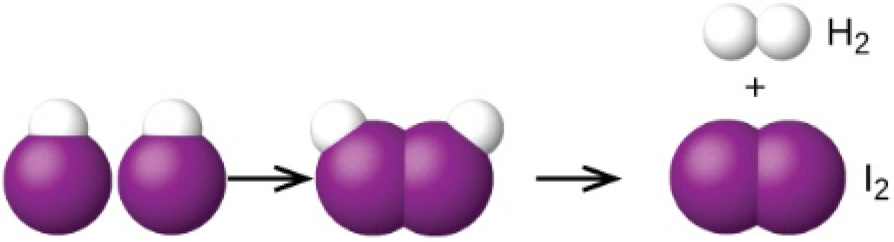
$$\text{rate} = k[A][A] = k[A]^2$$

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

Another is the decomposition of two hydrogen iodide molecules to produce hydrogen, H_2, and iodine, I_2 Figure 7.7.1.:

$$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$



Two HI molecules – Transition state – Hydrogen iodide molecules decompose to produce hydrogen H_2 and iodine I_2.

Figure 7.7.1. The probable mechanism for the dissociation of two HI molecules to produce one molecule of H_2 and one molecule of I_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is one example:

$$O\,(g) + O_3\,(g) \rightarrow 2O_2\,(g)$$

Termolecular Elementary Reactions

An elementary **termolecular reaction** involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$2NO + O_2 \rightarrow 2NO_2$$

$$\text{rate} = k[NO]^2\,[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2NO + Cl_2 \rightarrow 2NOCl$$

$$\text{rate} = k[NO]^2\,[Cl_2]$$

Relating Reaction Mechanisms to Rate Laws

It’s often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the **rate-limiting step** (or **rate-determining step**) of the reaction Figure 7.7.2.

Figure 7.7.2. A cattle chute is a non chemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, we must determine the overall rate law from experimental data and deduce the mechanism from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2\,(g) + CO\,(g) \rightarrow CO_2\,(g) + NO\,(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate} = k[NO_2][CO]$$

The reaction is first order with respect to NO_2 and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to NO_2:

$$\text{rate} = k[NO_2]^2$$

This is consistent with a mechanism that involves the following two elementary reactions, the first of which is slower and is therefore the rate-determining step:

$$NO_2\,(g) + NO_2\,(g) \rightarrow NO_3\,(g) + NO\,(g)\ \text{(slow)}$$

$$NO_3\,(g) + CO\,(g) \rightarrow NO_2\,(g) + CO_2\,(g)\ \text{(fast)}$$

The rate-determining step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an *equilibrium* reaction, the rate law for the overall reaction may be more difficult to derive. In order to solve this type of rate equation, the method used is called *pre-equilibrium*.

An elementary reaction is at equilibrium when it proceeds in both the forward and reverse directions at equal rates. Consider the dimerization of NO to N_2O_2, with k_1 used to represent the rate constant of the forward reaction and k_{-1} used to represent the rate constant of the reverse reaction:

$$NO + NO \rightleftharpoons N_2O_2$$

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$

$$k_1[NO]^2 = k_{-1}\,[N_2O_2]$$

If N_2O_2 was an intermediate in a mechanism, this expression could be rearranged to represent the concentration of N_2O_2 in the overall rate law expression using algebraic manipulation:

$$k_1[NO]^2\,k_{-1}=[\text{N2O2}]$$

However, once again, intermediates cannot be listed as part of the overall rate law expression, though they can be included in an individual elementary reaction of a mechanism. The following example will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example 7.7.2 (*using pre-equilibrium*) – Deriving the Overall Rate Law Expression for a Multistep Reaction Mechanism

Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism:

$2NO_2Cl\,(g) \rightleftharpoons ClO_2\,(g) + N_2O\,(g) + ClO\,(g)$ (fast, k_1 represents the rate constant for the forward reaction and k_{-1} the rate constant for the reverse reaction)

$N_2O\,(g) + ClO_2\,(g) \rightleftharpoons NO_2\,(g) + NOCl\,(g)$(fast, k_2 for the forward reaction, k_{-2} for the reverse reaction)

$NOCl + ClO \rightarrow NO_2 + Cl_2$ (slow, k_3 the rate constant for the forward reaction)

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Solution

For the overall reaction, simply sum the three steps, cancel intermediates, and combine like formulas:

$$2NO_2Cl\,(g) \rightarrow 2NO_2\,(g) + Cl_2\,(g)$$

Next, write the rate law expression for each elementary reaction. Remember that for elementary reactions that are part of a mechanism, the rate law expression can be derived directly from the stoichiometry:

$$k_1[NO_2Cl]_2 = k_{-1}\,[ClO_2][N_2O][ClO]$$

$$k_2[N_2O][ClO_2] = k_{-2}[NO_2][NOCl]$$

$$\text{Rate} = k_3\,[NOCl][ClO]$$

The third step, which is the slow step, is the rate-determining step. Therefore, the overall rate law expression could be written as Rate = k_3 [NOCl][ClO]. However, both NOCl and ClO are intermediates. Algebraic expressions must be used to represent [NOCl] and [ClO] such that no intermediates remain in the overall rate law expression.

Using elementary reaction 1,

$$[ClO] = k_1[NO_2Cl]^2\,k_{-1}[ClO_2][N_2O]$$

Using elementary reaction 2,

$$[NOCl] = k_2[N_2O][ClO_2]k_{-2}[NO_2]$$

Now substitute these algebraic expressions into the overall rate law expression and simplify:

$$\text{rate} = k_3\,(k_2[N_2O][ClO_2]k_{-2}[NO_2])\,(k_1[NO_2Cl]^2k_{-1}[ClO_2][N_2O])$$

$$\text{rate} = k_1k_2k_3[NO_2Cl]2k = 2k_{-1}[NO_2]$$

Notice that this rate law shows an *inverse* dependence on the concentration of one of the product species, consistent with the presence of an equilibrium step in the reaction mechanism.

Check Your Learning 7.7.1 (*using the steady-state approximation*) – Deriving the Overall Rate Law Expression for a Multistep Reaction Mechanism

Atomic chlorine in the atmosphere reacts with ozone in the following pair of elementary reactions:

$$Cl + O_3\,(g) \;\rightarrow\; ClO\,(g) + O_2\,(g)\ \text{(rate constant } k_1)$$

$$ClO\,(g) + O \;\rightarrow\; Cl\,(g) + O_2\,(g)\ \text{(rate constant } k_2)$$

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Answer

$$\text{overall reaction: } O_3\,(g) + O \rightarrow 2O_2\,(g)$$

$$\text{rate}_1 = k_1[O_3][Cl];\ \text{rate}_2 = k_2[ClO][O]$$

$$\text{intermediate: } ClO\,(g)$$

$$\text{overall rate} = k_2k_1[O_3][Cl][O]$$

Questions

★★ Questions

In an alternative mechanism for the reaction of NO_2 with CO, N_2O_4 appears as an intermediate. Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

step 1 $NO_2 + NO_2 \rightarrow N_2O_4$
step 2 $N_2O_4 + CO \rightarrow NO + NO_2 + CO_2$
sum $NO_2 + CO \rightarrow NO + CO_2$

Iodine monochloride (ICl) reacts with H2 as follows. $2ICl\ (l) + H_2\ (g) \rightarrow 2HCl\ (g) + I_2\ (s)$. The experimentally determined rate law is rate = $k[ICl][H_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Assume the reaction between NO and H_2 occurs via a three-step process. Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction: rate = $k[NO]^2[H_2]$?

Answers

The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$. If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

step 1 $ICl + H_2 \rightarrow HCl + HI$ rate = $k_1[ICl][H_2]$ (slow)
step 2 $HI + ICl \rightarrow HCl + I_2$ rate = $k_1[HI][ICl]$ (fast)
sum $2ICl + H_2 \rightarrow 2HCl + I_2$

Rate determining step = #2. Yes, because the rate of formation of $[N_2O_2] = k_1[NO]^2$. Substituting

$k_1[NO]^2$ for $[N_2O_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

- Step 1: $rate = k_1[NO]^2$
- Step 2: $rate = k_2[N_2O_2][H_2]$
- Step 3: $rate = k_2[N_2O_2][H_2]$

The overall reaction is then

$2NO\ (g) + 2H_2\ (g) \rightarrow N_2\ (g) + 2H_2O\ (g)$

7.8 - CATALYSIS

It was introduced in a previous section that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are thermodynamically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One such reaction is catalytic hydrogenation, the process by which hydrogen is added across an alkene C=C bond to afford the saturated alkane product. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed alkene hydrogenation is shown in Figure 7.8.1.

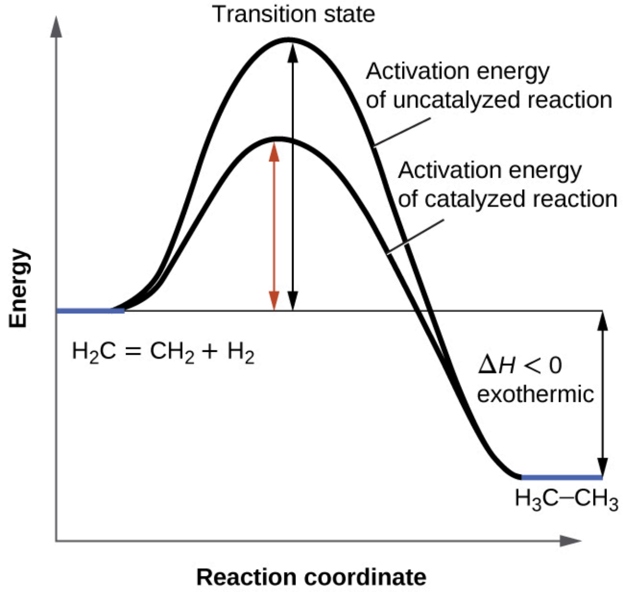


Figure 7.8.1. This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

Reaction coordinate diagrams (also known as **reaction profiles**) display how a reaction progresses from reactants to products in terms of energy. These diagrams consist of the following elements:

Reaction coordinate on the *X*-axis: the progression of a reaction from reactants (left) to products (right) for the forward reaction, and vice-versa for the reverse reaction

Energy on the *Y*-axis: the amount of potential energy present as the reaction proceeds; the lower the potential energy, the more stable the species

Reactants: indicated as the flat line on the far left

Products: indicated as the flat line on the far right

Transition state (activated complex): represents the complex found at the peak of the curve. It is a particular configuration of reactants at the moment of reaction collision(s) that gives a “structure” of maximum potential energy and hence of greatest instability. Note that the transition state is not a defined structure or intermediate.

Activation energy: represented by the difference and rise in potential energy between 1) reactants, products or an intermediate, and 2) the transition state (forward reaction) or between products and the transition state (reverse reaction). It represents the energy barrier that must be overcome to attain the transition state. The system must gain energy and become increasingly unstable to adopt the activated complex; once it is reached, an input of energy is no longer required, and the system decreases in energy and becomes more stable as the reaction proceeds.

Intermediate (not shown in Figure 7.8.1 but portrayed in the catalyzed pathway of Figure 7.8.2): represents the structure found at the trough of a curve. It is a species that temporarily exists as the product for one step of the reaction and as a reactant for the next step. It has a well-defined chemical structure and is hence more stable than a transition state, but it only persists momentarily so is less stable and higher in energy than both reactants and products.

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in Figure 7.8.2. This lower activation energy results in an increase in rate as described by the Arrhenius equation. Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the previous topic on chemical equilibrium).

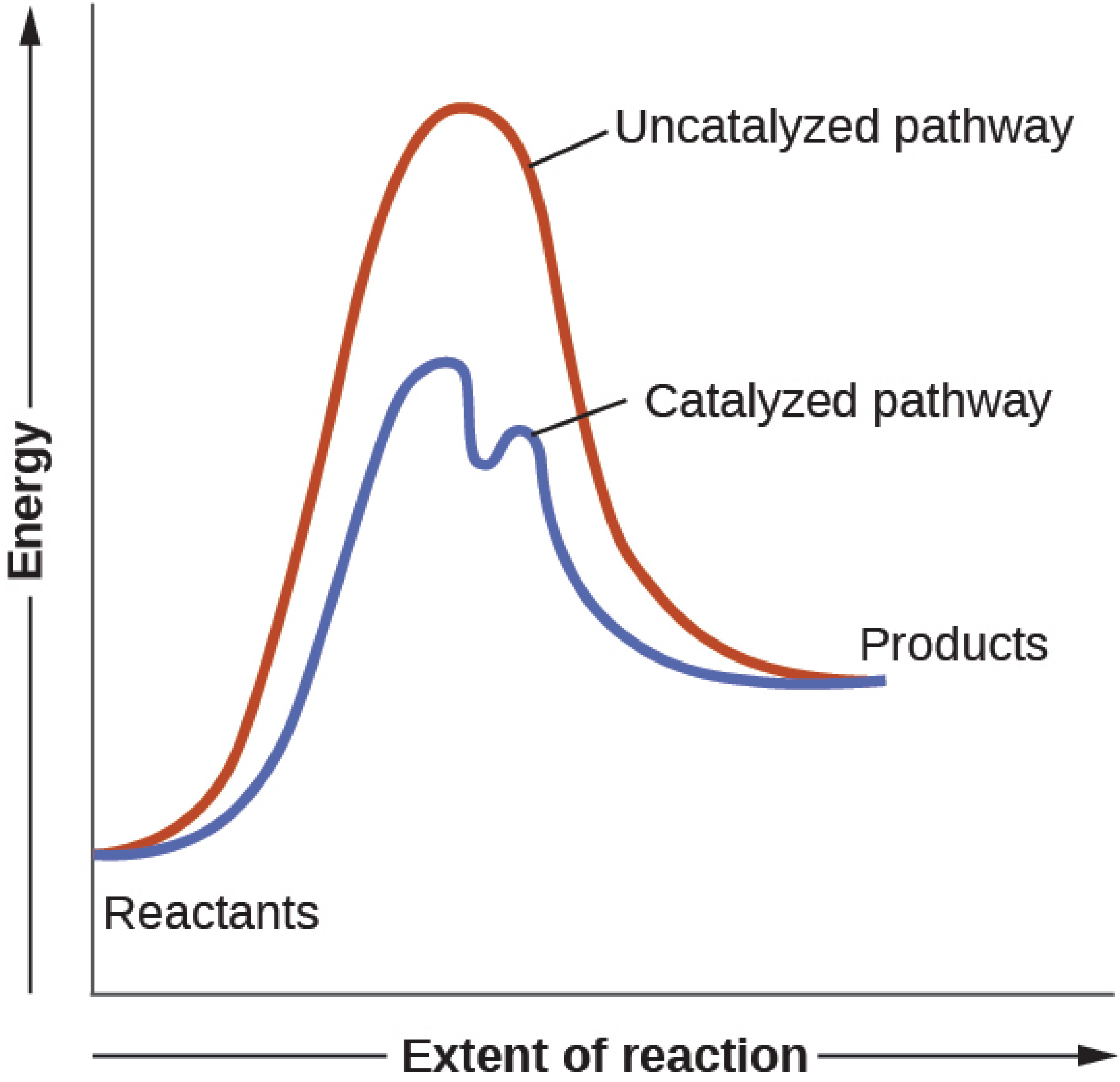
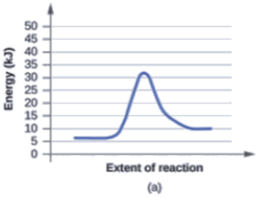
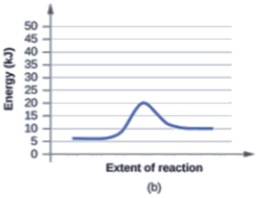


Figure 7.8.2. This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 7.8.1 – Using Reaction Diagrams to Compare Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:





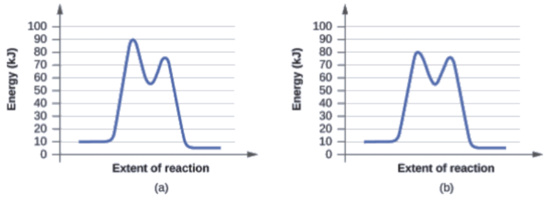
Solution

A catalyst does not affect the energy of the reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in energy in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

$$E_a = 20\text{ kJ} - 6\text{ kJ} = 14\text{ kJ}$$

Check Your Learning 7.8.1 – Using Reaction Diagrams to Compare Catalyzed Reactions

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:



Answer

Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

Homogeneous Catalysts

present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product.

As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3O_2(g)\ h\nu \rightarrow 2O_3(g)$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following mechanism:

$$O_3 \rightarrow O_2 + O$$

$$O + O_3 \rightarrow 2O_2$$

The presence of nitric oxide, NO, influences the rate of decomposition of ozone. Nitric oxide acts as a catalyst in the following mechanism:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

$$O_3(g) \rightarrow O_2(g) + O(g)$$

$$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$$

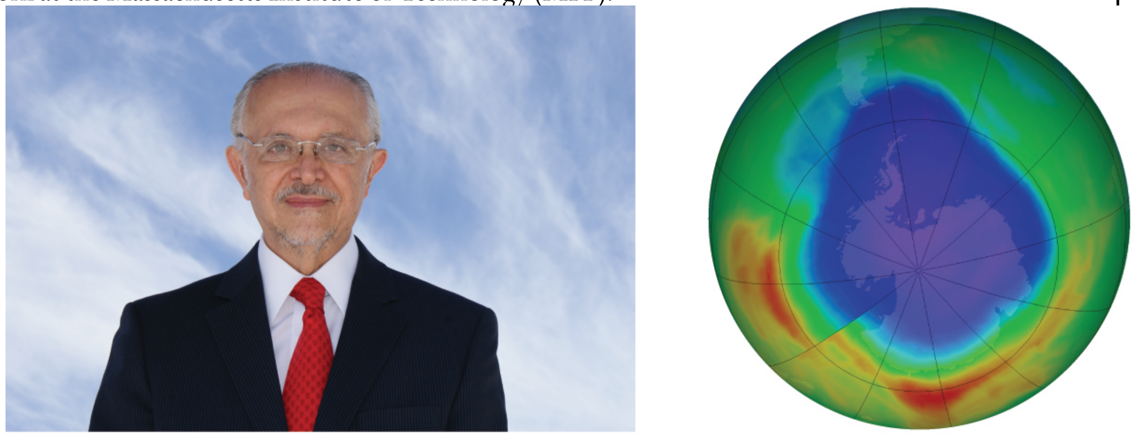
The overall chemical change for the catalyzed mechanism is the same as:

$$2O_3(g) \rightarrow 3O_2(g)$$

The nitric oxide reacts and is regenerated in these reactions. It is not permanently used up; thus, it acts as a catalyst. The rate of decomposition of ozone is greater in the presence of nitric oxide because of the catalytic activity of NO. Certain compounds that contain chlorine also catalyze the decomposition of ozone.

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 7.8.3.), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[1] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).



(a)

(b)

Figure 7.8.3. (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* (one of the major peer-reviewed publications in the field of science) detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

$$CH_3Cl + OH \rightarrow Cl + \text{other products}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

$$\text{overall Reaction: } O_3 + O \rightarrow 2O_2$$

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

[1] The Nobel Prize in Chemistry 1995. (n.d.). Retrieved from https://www.nobelprize.org/prizes/chemistry/1995/summary/

Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 7.8.4., is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure 7.8.4.).

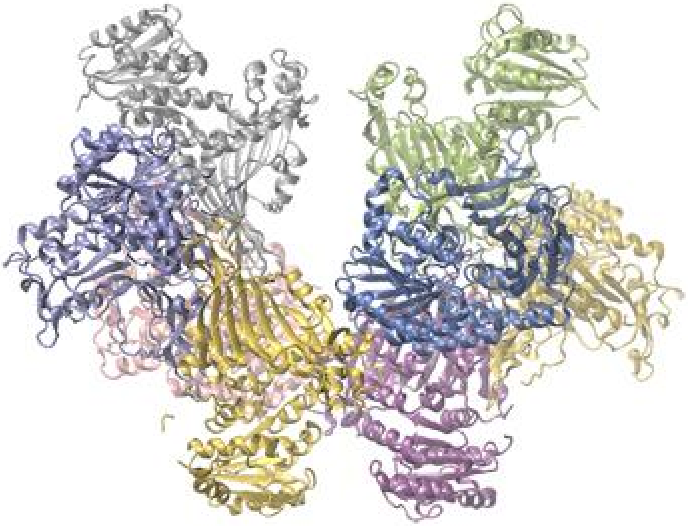


Figure 7.8.4. Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage to their glutathione-deficient red blood cells.

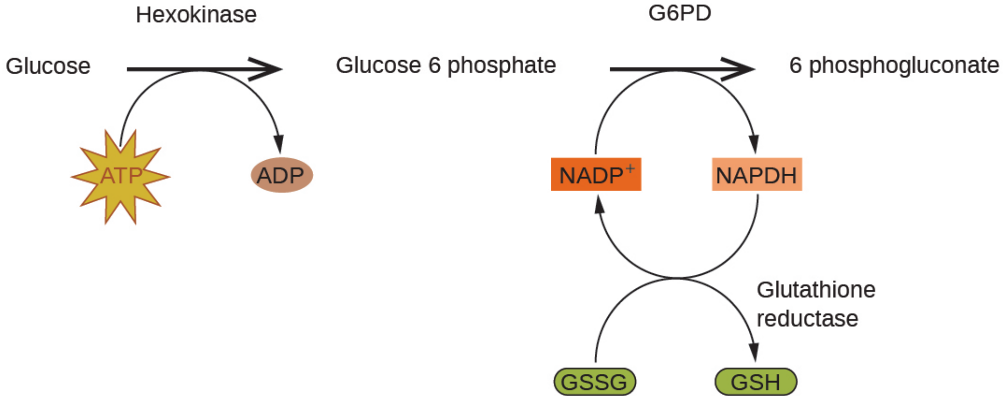


Figure 7.8.5. In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NAPDH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

Heterogeneous Catalysts

A **heterogeneous catalyst** is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur.

Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis has at least four steps:

Adsorption of the reactant onto the surface of the catalyst
Activation of the adsorbed reactant
Reaction of the adsorbed reactant
Diffusion of the product from the surface into the gas or liquid phase (desorption).

Any one of these steps may be slow and thus may serve as the rate determining step. In general, however, in the presence of the catalyst, the overall rate of the reaction is faster than it would be if the reactants were in the gas or liquid phase.

Figure 7.8.6. illustrates the steps that chemists believe to occur in the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

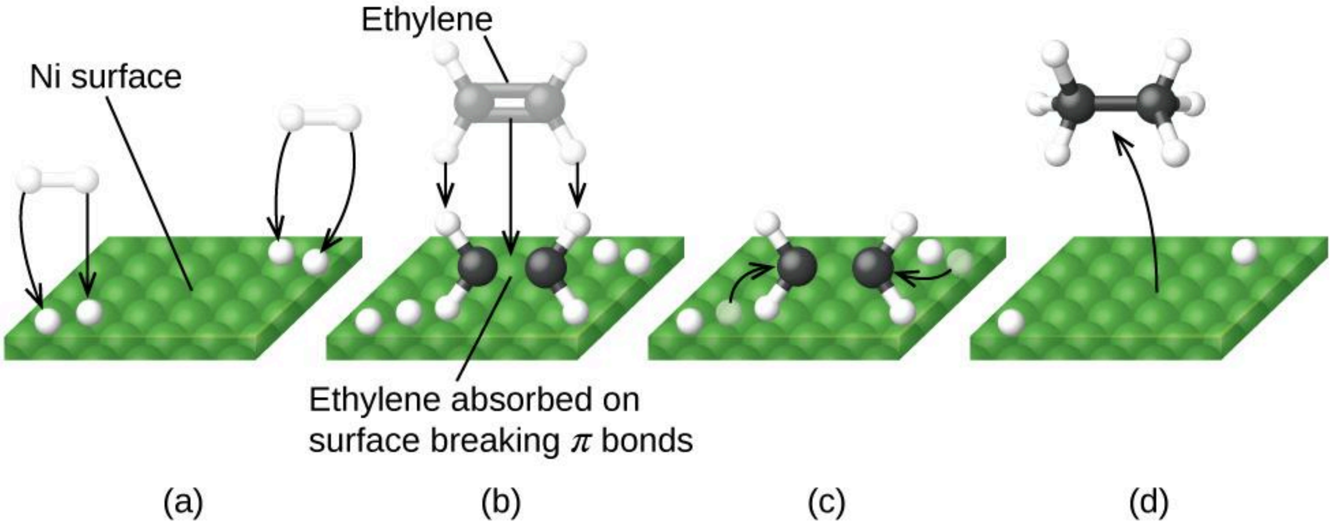


Figure 7.8.6. There are four steps in the catalysis of the reaction $C_dH_4 + H_2$? C_2H_6 by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules escape from the nickel surface, since they are not strongly attracted to nickel.

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 7.8.7.).

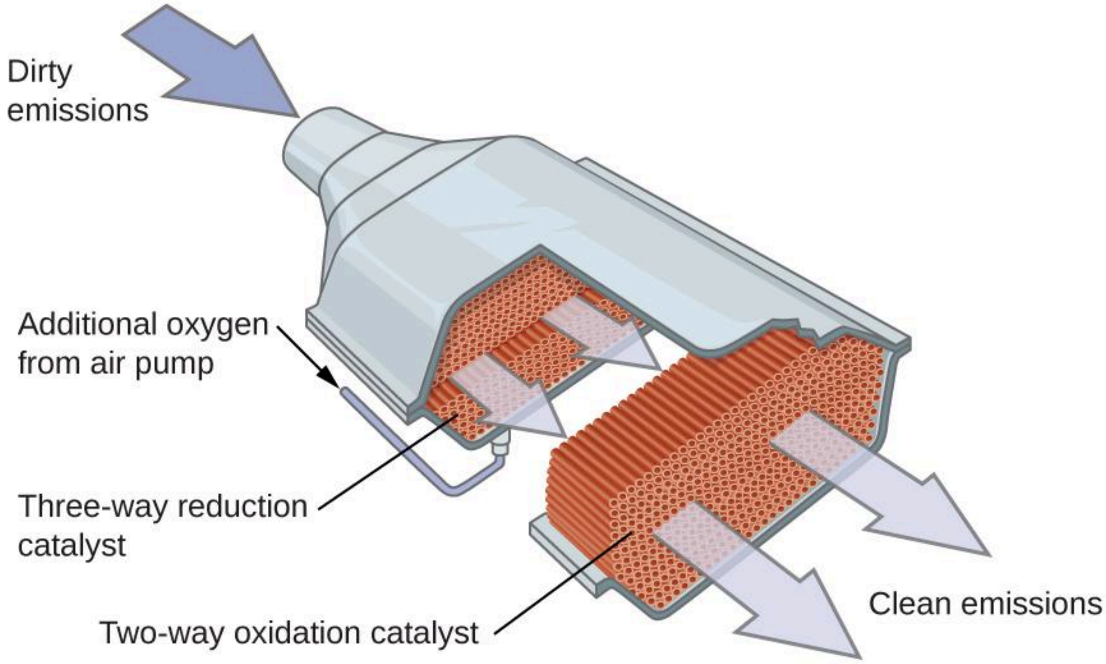


Figure 7.8.7. A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of nitric oxide into nitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2NO_2\,(g) \rightarrow N_2\,(g) + 2O_2\,(g)$$

$$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$$

$$2C_8H_{18}\,(g) + 25\,O_2\,(g) \rightarrow 16CO_2\,(g) + 18H_2O\,(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

The University of California at Davis' "ChemWiki" provides a thorough explanation of how catalytic converters work.

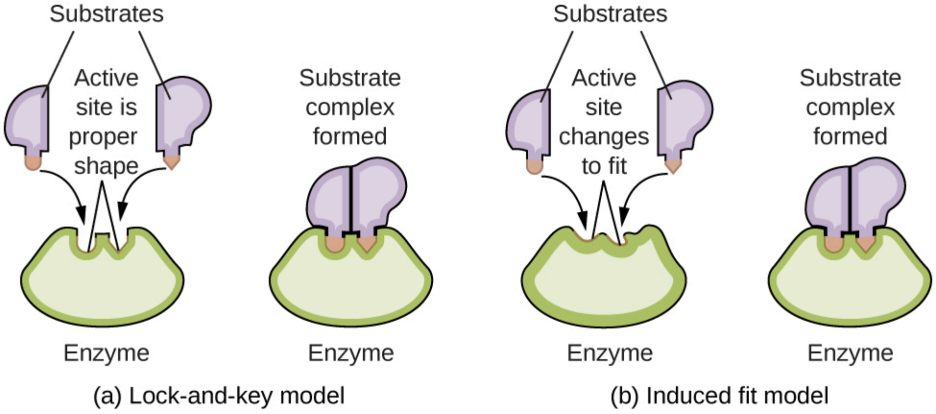
Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in the table below.

Classes of Enzymes and Their Functions

Class	Functions
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 7.8.8.).

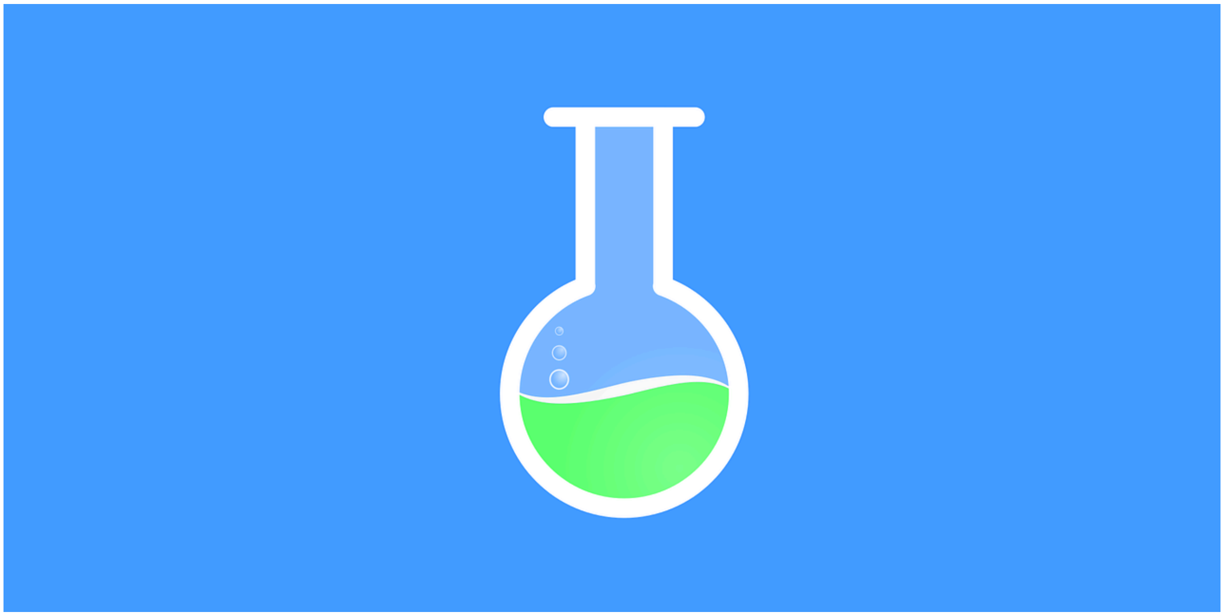


(a) Lock-and-key model

(b) Induced fit model

Figure 7.8.8. (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.



CHM1311 Laboratory | Experiment #5: A Kinetic Study: Catalase

Purpose

This experiment will look at the kinetics of reactions in the context of catalysts – substances that speed up the rate of reactions by lowering the activation energy. Some catalysts exist as compounds, such as potassium iodide (KI) while others are biological proteins which are found in living organisms – these biological catalysts are referred to as enzymes

In the first part of this experiment, you'll be investigating the catalyzed decomposition of hydrogen peroxide by the enzyme catalase in lettuce. Your job is to design and carry out experiments to determine the partial order with respect to hydrogen peroxide in the rate law:

$rate = k\,[H_2O_2]^x\,[\text{catalase}]^y$

In part two of your experiment, you'll again need to design and carry out an experimental procedure to determine and compare the activation energies of catalase-catalyzed and iodide-catalyzed (from potassium iodide) decomposition of hydrogen peroxide. With this information, you can deduce which of the two catalysts is more efficient in accelerating the rate of reaction.

Principles

Initial reaction rate
Order of the reaction
Activation energy

Safety Precautions

Wear appropriate personal protective equipment (PPE) at all times in the laboratory setting – this includes your lab coat and safety goggles/glasses.

Be sure to consult the MSDS for $H_2O_2(aq)$, KI and catalase for relevant health and safety, first aid, handling, and waste disposal information.

As you plan your procedure, always make sure that all steps are safe and follow lab safety guidelines. Your TA will verify your procedure before you conduct your experiment.

Make sure you don't confuse the reactants – check the label of each reagent you add when preparing the mixture.

Things to Consider

Make sure you go through the pre-lab exercise for the experiment – it will allow you to review your knowledge of chemical kinetics, better understand your task and give you a good idea of how to plan your experiment.

In your report, make sure you fully detail your experimental procedures. You'll need to provide the data you collected, analyze it and discuss your results. Make sure your conclusions respond to the two tasks asked of you.

The experimental instructions provided to you on Brightspace gives an extensive list of questions and things to consider as you plan your experiment and before you carry out your lab protocol. Make sure you go through and cover these points in your experimental procedure – this will help you better plan your experiment and allow you to be well-prepared before coming into the lab.

Reference

Venkateswaran, R. General Chemistry – Laboratory Manual – CHM 1301/1311.

CHAPTER 8

8.1 - THE NATURE OF LIGHT

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

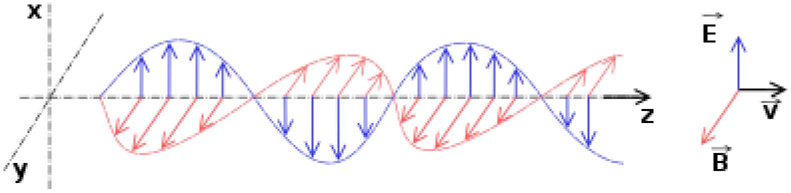


Figure 8.1.0. Electric and Magnetic fields oscillating perpendicular to the direction of propagation of the wave.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998 × 10^8 m/s, the speed of light (denoted by *c*).

All waves, including forms of electromagnetic radiation, are characterized by a **wavelength** (denoted by λ, the lowercase Greek letter lambda), a **frequency** (denoted by ν, the lowercase Greek letter nu), and an **amplitude**. As can be seen in Figure 8.1.1., the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range – wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz (Hz)**. Common multiples of this unit are megahertz, (1 MHz = 1 × 10^6 Hz) and gigahertz (1 GHz = 1 × 10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure 8.1.1., this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

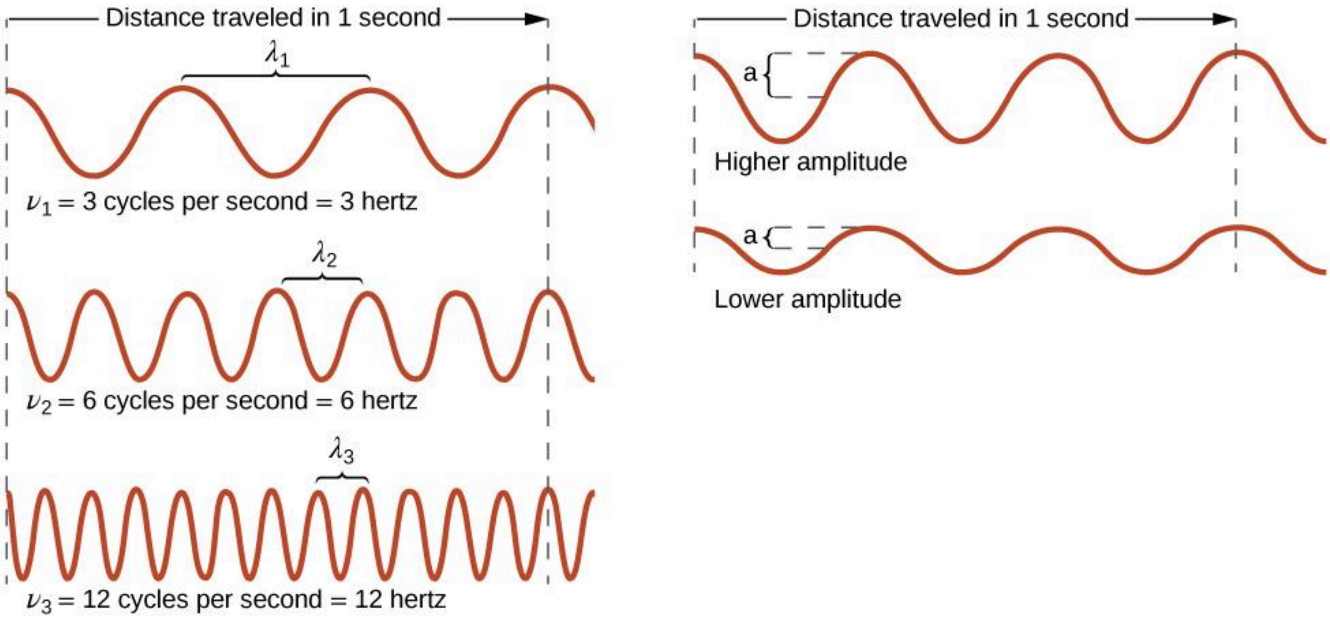


Figure 8.1.1. One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^{8}\ \mathrm{ms}^{-1} = \lambda v$$

Equation 8.1.1 Speed of Light Related to its Frequency and Wavelength

Wavelength and frequency are inversely proportional: as the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 8.1.2. This figure also shows the **electromagnetic spectrum**, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

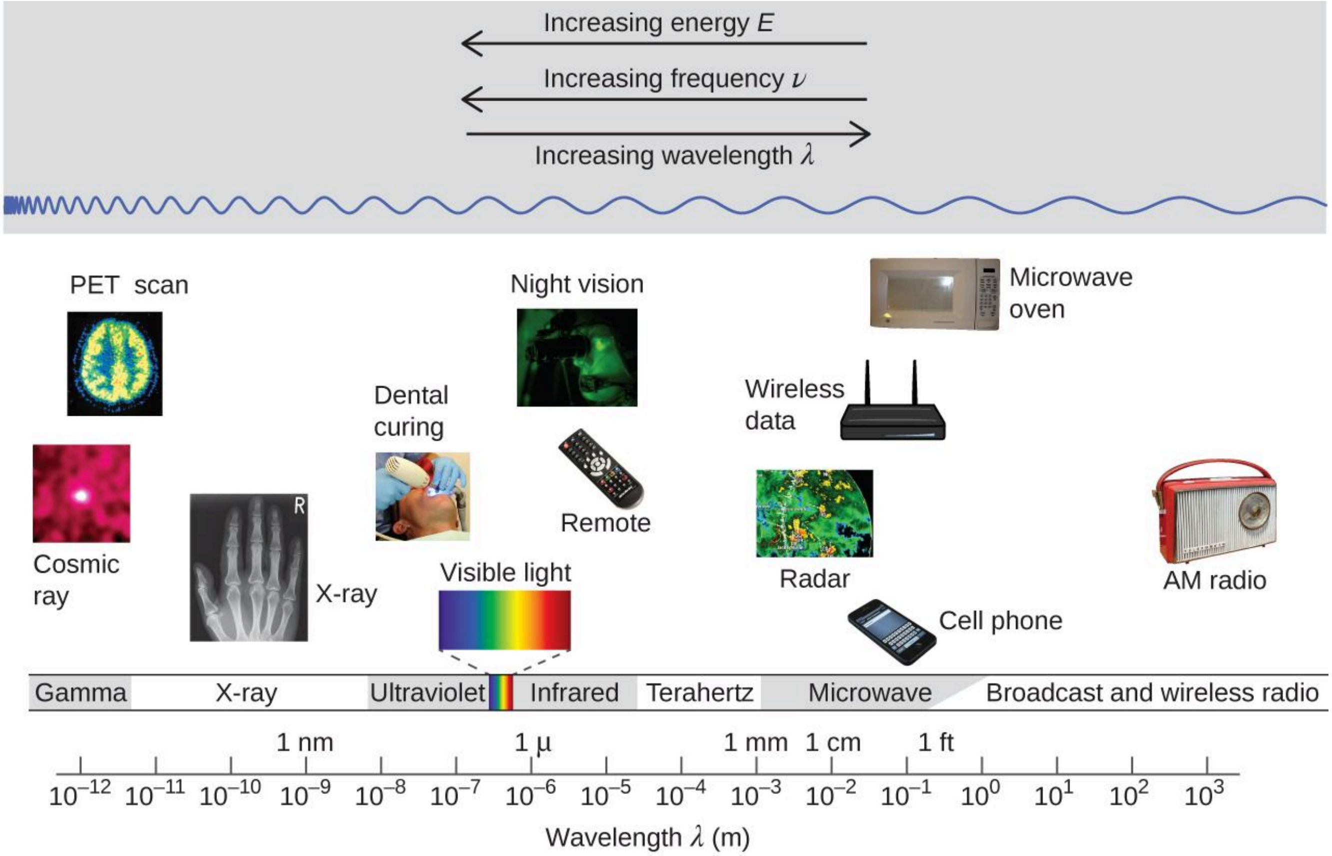


Figure 8.1.2. Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit "Cosmic ray": modification of work by NASA; credit "PET scan": modification of work by the National Institute of Health; credit "X-ray": modification of work by Dr. Jochen Lengerke; credit "Dental curing": modification of work by the Department of the Navy; credit "Night vision": modification of work by the Department of the Army; credit "Remote": modification of work by Emilian Robert Vicol; credit "Cell phone": modification of work by Brett Jordan; credit "Microwave oven": modification of work by Billy Mabray; credit "Ultrasound": modification of work by Jane Whitney; credit "AM radio": modification of work by Dave Clausen)

Example 8.1.1 – Determining the Frequency and Wavelength of Radiation

A sodium street light gives off yellow light that has a wavelength of 589 nm (1 nm = 1 × 10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the equation $c = \lambda\nu$ to solve for the frequency:

$$v = c\lambda$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$v = (2.998\times10^{8}\ \text{ms} - 1589\ \text{nm})\ (1 \times 10^{9}\ \text{nm x 1 m}) = 5.09 \times 10^{14}\ \text{s}^{-1}$$

Check Your Learning 8.1.1 – Determining the Frequency and Wavelength of Radiation

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer

0.353 m = 35.3 cm

Wireless Communication

Figure 8.1.3. Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 8.1.4.), whereas the frequency is kept constant. In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

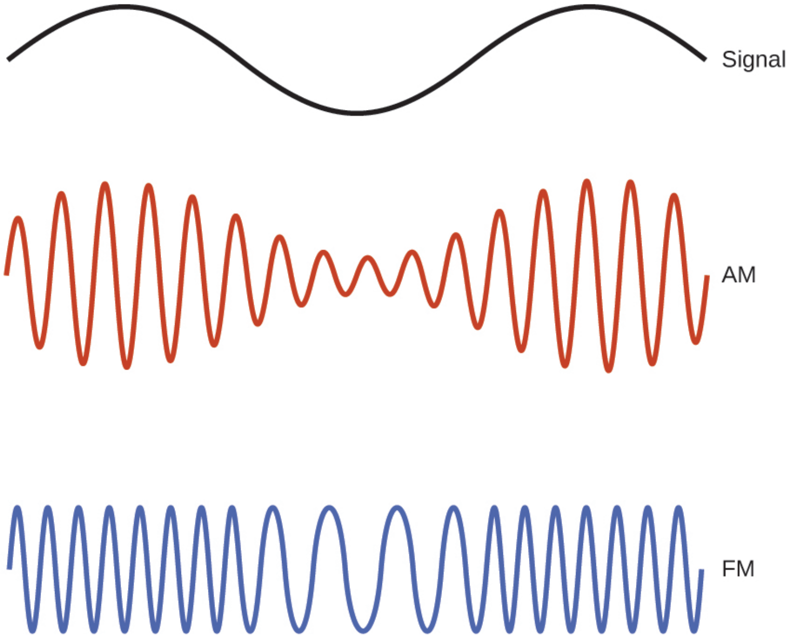


Figure 8.1.4. This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 8.1.5. shows the **interference patterns** that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 8.1.5. correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.

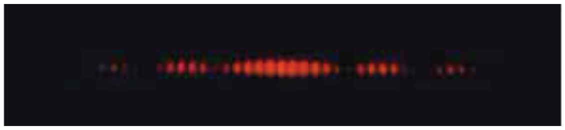


Figure 8.1.5. Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. A video demonstrating how this interference results can be found here (credit: PASCO)

Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules.

Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Not all waves are travelling waves. **Standing waves** (also known as **stationary waves**) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two endpoints. Figure 8.1.6. shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in Figure 8.1.6. The key observation from the figure is *that only those waves having an integer number, n, of half-wavelengths between the end points can form*. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of **quantization**, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are **nodes**. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths n. Since the number of nodes is $n - 1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.

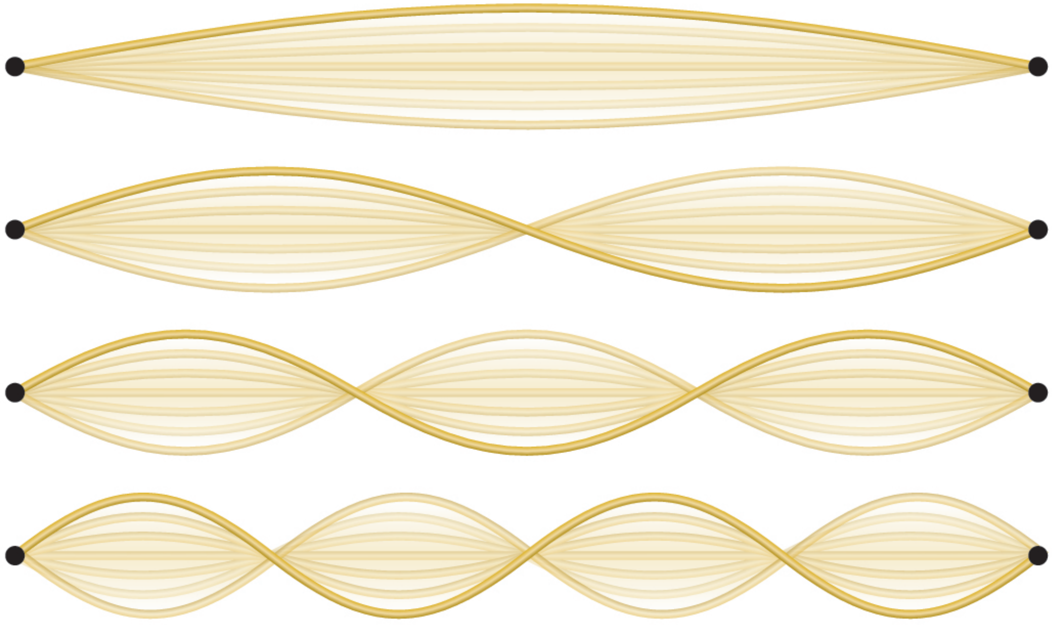


Figure 8.1.6. A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the endpoints that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 8.1.7., which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume).

Because of the circular symmetry of the drum surface, its boundary conditions (the drum surface being tightly constrained to the circumference of the drum) result in two types of nodes: radial nodes that sweep out all angles at constant radii and, thus, are seen as circles about the center, and angular nodes that sweep out all radii at constant angles and, thus, are seen as lines passing through the center. The upper left image in Figure 8.1.7. shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

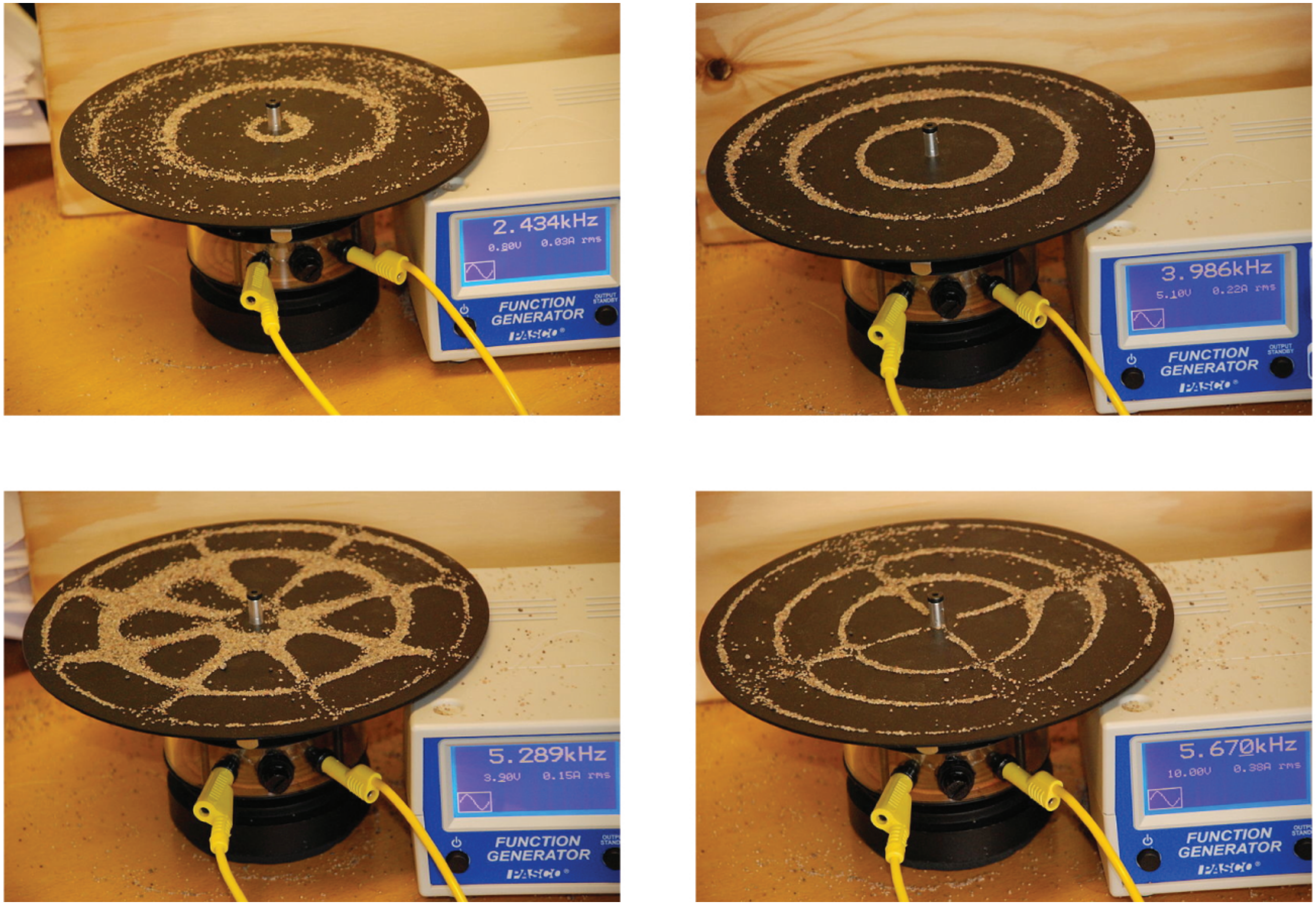


Figure 8.1.7. Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii).

You can watch the formation of various radial nodes here as singer Imogen Heap projects her voice across a kettle drum.

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a **continuous spectrum**. Figure 8.1.8. shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

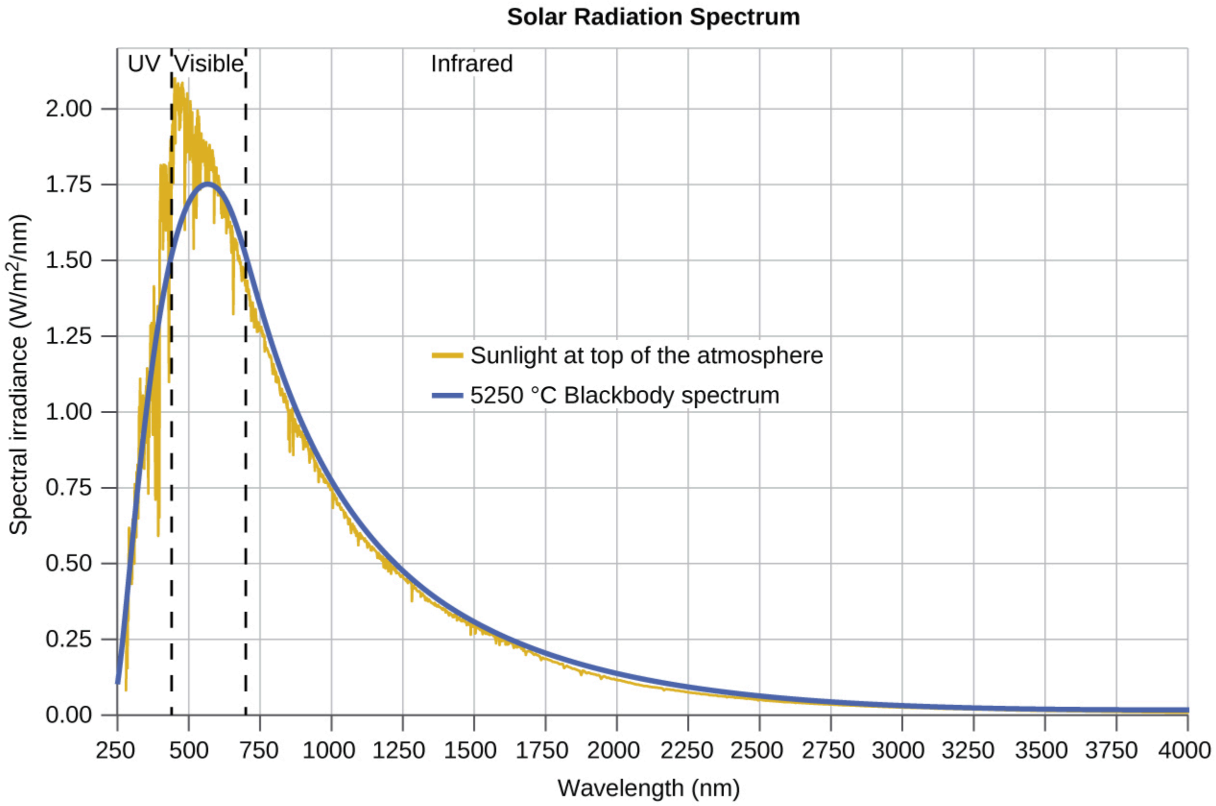


Figure 8.1.8. The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In Figure 8.1.9., the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A **blackbody** is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is "ideal" in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure 8.1.9. shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max}, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the "ultraviolet catastrophe" because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$E=nhv,n=1,2,3\ldots$

The quantity $\boldsymbol{h}$ is a constant now known as Planck's constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

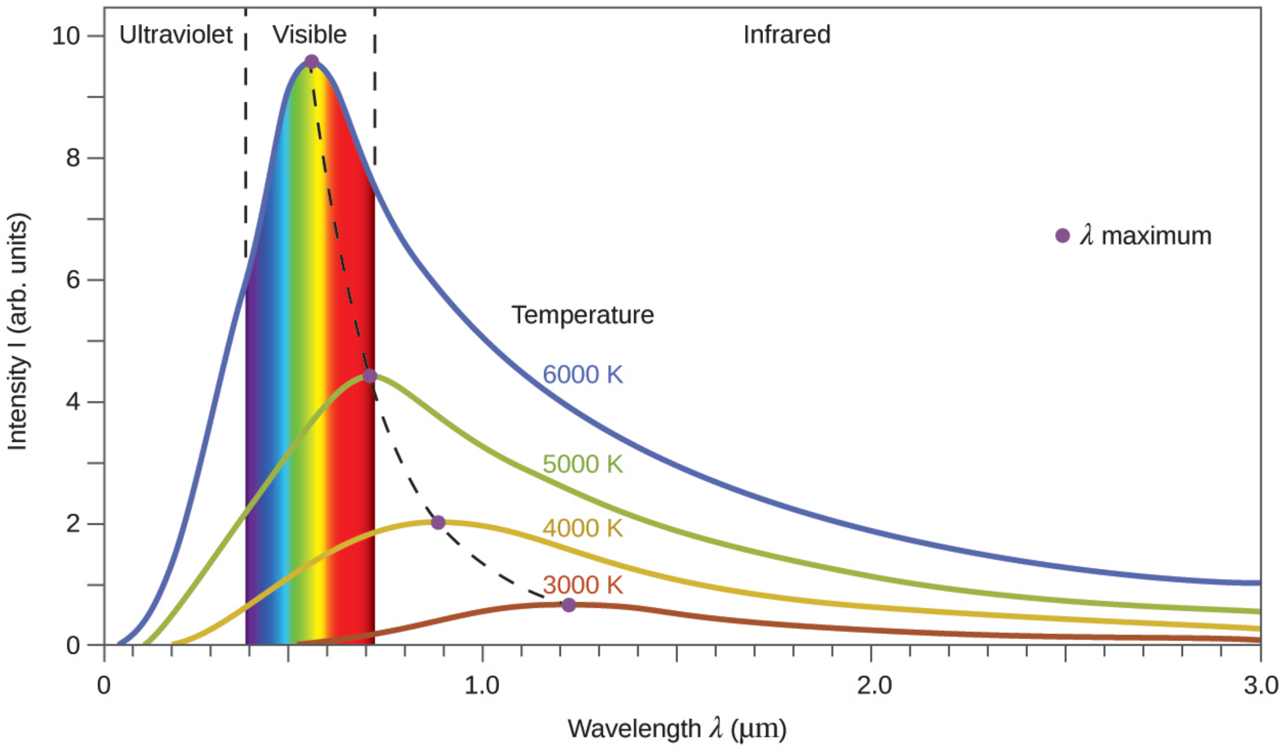


Figure 8.1.9. Blackbody spectral distribution curves are shown for some representative temperatures.

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 8.1.10.). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$,
E=hcλ

). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions.

Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein’s findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality**.

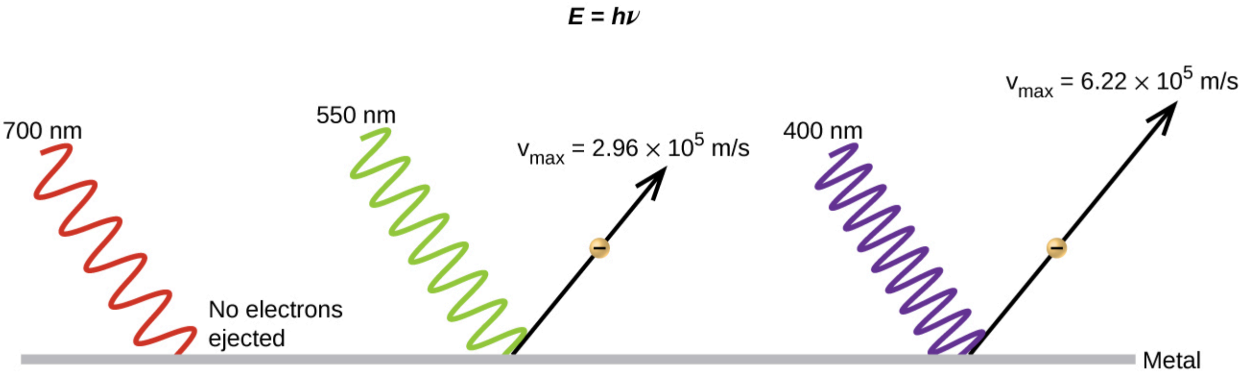


Figure 8.1.10. Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

Example 8.1.2 – Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck’s equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$E = hc / \lambda$$

$$E = (6.626 \times 10^{-19}\ \mathrm{Js})(2.998 \times 10^{8}\ \mathrm{ms}^{-1})(640\mathrm{nm})(1\mathrm{m} \text{ x } 10^{9}\ \mathrm{nm})$$

$$E = 3.10 \times 10^{-19}\ \mathrm{J}$$

Check Your Learning 8.1.2 – Calculating the Energy of Radiation

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3×10^{9} Hz. What is the energy of one photon in these microwaves?

Answer

2×10^{-24} J

Use this simulation program to experiment with the photoelectric effect to see how intensity, frequency, type of metal, and other factors influence the ejected photons.

Example 8.1.3 – Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

(a) Increasing the brightness of incoming light increases the kinetic energy of the ejected electrons.

(b) Increasing the wavelength of incoming light increases the kinetic energy of the ejected electrons.

(c) Increasing the brightness of incoming light increases the number of ejected electrons.

(d) Increasing the frequency of incoming light can increase the number of ejected electrons.

Solution

(a) False. Increasing the brightness of incoming light has no effect on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.

(b) False. Increasing the frequency of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.

(c) True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.

(d) True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Check Your Learning 8.1.3 – Photoelectric Effect

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is 9.87×10^{14} Hz.

Answer

394 kJ/mol

★ Questions

1. Describe the characteristics of a light wave.
2. What is the frequency (in s^{-1}) of light if its wavelength is 7.33×10^{-5} m?
3. What is the frequency (in s^{-1}) of light if its wavelength is 733 nm?
4. What is the wavelength (in meters) of light if its frequency is $8.19 \times 10^{14}\ s^{-1}$?
5. What is the wavelength (in meters) of light if its frequency is 1.009×10^{6} Hz?

6. What is the energy (in Joules) of a photon if its frequency is $5.55 \times 10^{13}\ \text{s}^{-1}$?

7. What is the energy (in Joules) of a photon if its wavelength is 5.88×10^{-4} m?

8. As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun (in millimeters)?

9. Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation (in meters)?

Answers

1. Light has a wavelength and a frequency.
2. $4.09 \times 10^{12}\ \text{s}^{-1}$
3. $4.09 \times 10^{14}\ \text{s}^{-1}$
4. 3.66×10^{-7} m
5. 297 m
6. 3.68×10^{-20} J
7. 3.38×10^{-22} J
8. 8.45 mm
9. 2.965 m

8.2 - ATOMIC SPECTRA

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 8.1.8 in the previous topic, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure 8.1.9 in the previous section.

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure 8.2.2. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure 8.2.1.). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.

Figure 8.2.1. Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure 8.2.2.

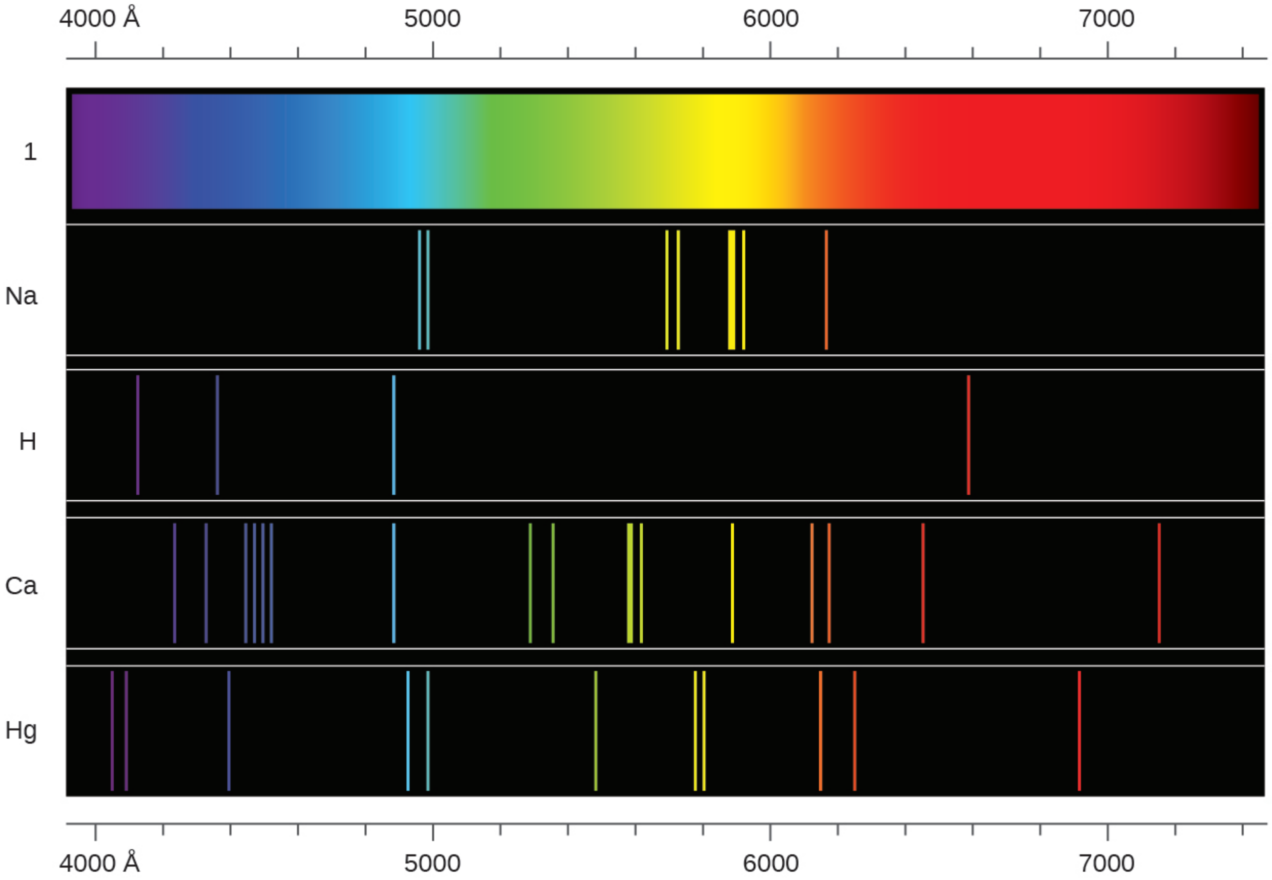


Figure 8.2.2. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which *k* is a constant:

$$1 / \lambda = k((1 / 4) - (1 / n_2)), n = 3,4,5,6$$

Other discrete lines for the hydrogen atom were subsequently found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, $n_1$and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant (1.097×10^7 m^{-1}).

$$1 / \lambda = R_\infty((1 / n_1^2)- (1 / n_2^2))$$

Equation 8.2.1 Rydberg Equation

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

The Bohr Model

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton in the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. The electrostatic force has the same form as the gravitational force between two mass particles except that the electrostatic force depends on the magnitudes of the charges on the particles (+1 for the proton and −1 for the electron) instead of the magnitudes of the particle masses that govern the gravitational force. Since forces can be derived from potentials, it is convenient to work with potentials instead, since they are forms of energy. The electrostatic potential is also called the Coulomb potential. Because the electrostatic potential has the same form as the gravitational potential, according to classical mechanics, the equations of motion should be similar, with the electron moving around the nucleus in circular or elliptical orbits (hence the label "planetary" model of the atom). Potentials of the form $V(r)$ that depend only on the radial distance r are known as central potentials. Central potentials have spherical symmetry, and so rather than specifying the position of the electron in the usual Cartesian coordinates (x, y, z), it is more convenient to use polar spherical coordinates centered at the nucleus, consisting of a linear coordinate r and two angular coordinates, usually specified by the Greek letters theta (θ) and phi (Φ). These coordinates are similar to the ones used in GPS devices and most smartphones that track positions on our (nearly) spherical earth, with the two angular coordinates specified by the latitude and longitude, and the linear coordinate specified by sea-level elevation. Because of the spherical symmetry of central potentials, the energy and angular momentum of the classical hydrogen atom are constants, and the orbits are constrained to lie in a plane like the planets orbiting the sun. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|?E| = |E_f - E_i| = hv = h(c / \lambda)$$

Equation 8.2.2 Orbital Energy Difference

In this equation, *h* is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values for the angular momentum, energy, and orbit radius, Bohr assumed that only discrete values for these could occur (actually, quantizing any one of these would imply that the other two are also quantized). Bohr's expression for the quantized energies is:

$$E_n = -kn_2, n = 1,2,3\ldots$$

In this expression, *k* is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

$$\Delta E = k((1 / n_1^2) - (1 / n_2^2)) = h(c / \lambda)$$

Or

$$1 / \lambda = khc((1 / n_1^2) - (1 / n_2^2))$$

which is identical to the Rydberg equation for

$$R_\infty = khc$$

. When Bohr calculated his theoretical value for the Rydberg constant, R_∞, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that **Bohr's model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

The lowest few energy levels are shown in Figure 8.2.3. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its **ground electronic state** (or simply **ground state**). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher *n* value and the atom is now in an **excited electronic state** (or simply an **excited state**) with a higher energy.

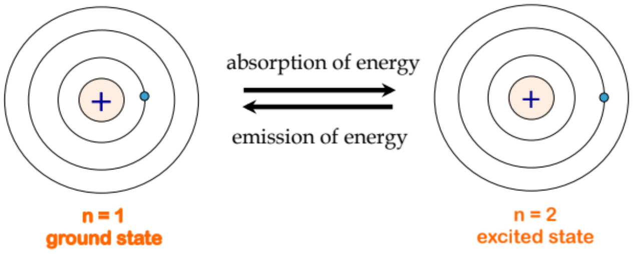


Figure 8.2.3. On the left, a hydrogen atom is shown in the lowest energy state, a.k.a. the ground state, where the electron is in the n = 1 orbit. When the atom absorbs energy, the electron is promoted to a higher orbit, resulting in a less stable, higher energy state shown on the right, known as an excited state. To return to the ground state, the atom must emit some energy.

When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 8.2.2.). In effect, an atom can "store" energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of energy, as the electron returns to its ground state (say, from $n = 5$ to $n = 1$), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from $n = 5$ to $n = 4$, emitting one quantum, then to $n = 1$, emitting a second quantum).

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^{+}, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and k has a value of 2.179×10^{-18} J.

$$E_n = -kZ^2n^2$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which a_0 is a constant called the Bohr radius, with a value of 5.292×10^{-11} m:

$$r = n^2 Z a_0$$

Equation 8.2.3 Orbital Radius

The equation also shows us that as the electron's energy increases (as n increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence on r in the Coulomb potential, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases, and it is held less tightly in the atom. Note that as n gets larger and the orbits get larger, their energies get closer to zero, and so the limits n ? ∞, and r ? ∞ imply that $E = 0$ corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state $n = 1$, the ionization energy would be:

$$\Delta E = E_n \rightarrow \infty - E_1 = 0 + k = k$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

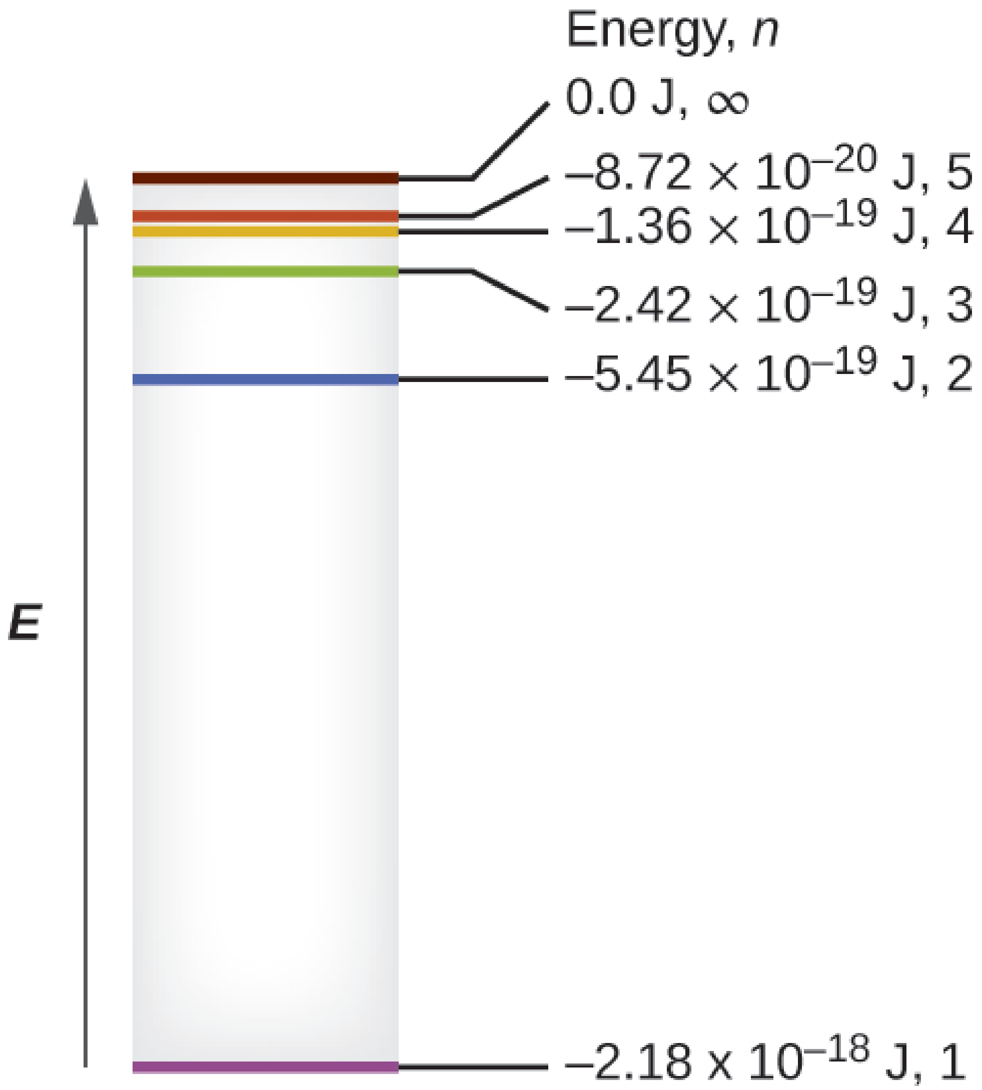


Figure 8.2.4. Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

Example 8.2.1 – Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with $n = 3$, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by this equation:

$$E = -kZ^2n^2$$

The atomic number, *Z*, of hydrogen is 1; *k* = 2.179 × 10^{-18} J; and the electron is characterized by an *n* value of 3. Thus,

$$E = -(2.179 \times 10^{-18}\,J) \times (1)^2(3)^2 = -2.421 \times 10^{-19}\,J$$

Check Your Learning 8.2.1 – Calculating the Energy of an Electron in a Bohr Orbit

The electron in Figure 8.2.4. is promoted even further to an orbit with *n* = 6. What is its new energy?

Answer

-6.053×10^{-20} J

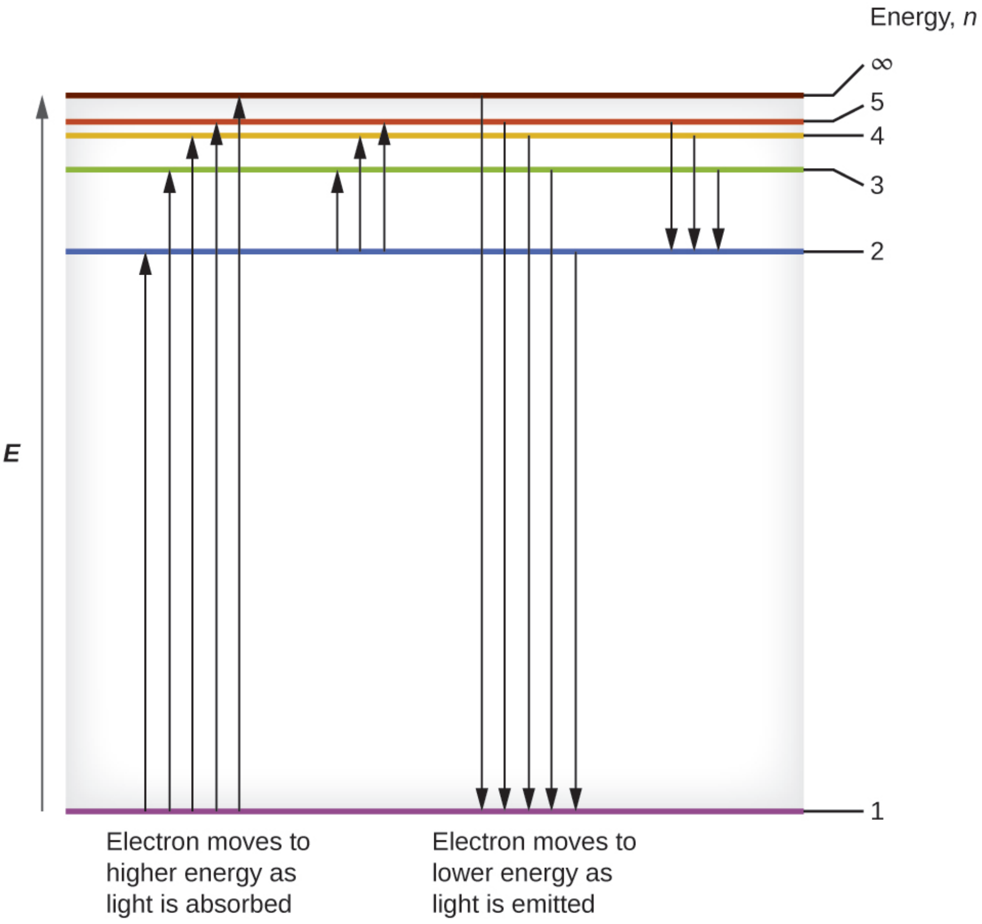


Figure 8.2.4. The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Example 8.2.2 – Calculating the Energy and Wavelength of Electron Transitions in a One–electron (Bohr) System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18} ((1 / n_1^2) \text{-} (1 / n_2^2))$$

$$\Delta E = 2.179 \times 10^{-18} ((1 / 4^2) - (1 / 6^2))\text{J}$$

$$\Delta E = 2.179 \times 10^{-18} ((1 / 1^6)\text{-}(1 / 3^6))\text{J}$$

$$\Delta E = 7.566 \times 10^{-20}\ \text{J}$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the $n = 4$ orbit up to the $n = 6$ orbit. The wavelength of a photon with this energy is found by the expression

$$E = h(c / \lambda)$$

Rearrangement gives:

$$\lambda = hcE$$

$$= (6.626 \times 10^{-34}\ \text{Js}) \times 2.998 \times 10^{8}\ \text{ms} - 17.566 \times 10^{-20}\ \text{J}$$

$$= 2.626 \times 10^{-6}\ \text{m}$$

From Figure 8.2.1. of the previous topic, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

Check Your Learning 8.2.2 – Calculating the Energy and Wavelength of Electron Transitions in a One–electron (Bohr) System

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a He^+ ion ($Z = 2$ for He^+)?

Answer

6.198×10^{-19} J; 3.205×10^{-7} m

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.

An electron's energy increases with increasing distance from the nucleus.

The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom.

As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

★ Questions

1. The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.
2. A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?
3. Light with a wavelength of 614.5 nm looks orange.
   a) What is the energy, in joules, per photon of this orange light?
   b) What is the energy in eV (1 eV = 1.602 × 10−19 J)?
4. A photon of light produced by a surgical laser has an energy of 3.027 × 10−19 J.
   a) Calculate the frequency and wavelength of the photon.
   b) What is the total energy in 1 mole of photons?
   c) What is the color of the emitted light?
5. The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45 × 1014 Hz and (b) 6.53×10^{14} Hz.
   a) What are the wavelengths and energies per photon of the two lines?
   b) What color are the lines?

★★ Questions

6. RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change.
   a) Using a spectrum of visible light, determine the approximate wavelength of each of these colors.
   b) What is the frequency and energy of a photon of each of these colors?
7.
   a)What is the threshold frequency for sodium metal if a photon with frequency 6.66 × 1014 s−1 ejects an electron with 7.74 × 10−20 J kinetic energy?
   b) Will the photoelectric effect be observed if sodium is exposed to orange light?
8. Heated lithium atoms emit photons of light with an energy of 2.961 × 10−19 J.
   a) What is the total energy in 1 mole of these photons?
   b) What is the color of the emitted light?
9. Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a

wavelength of 1.5 × 10−6 m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

10. The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15 × 10−14 J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

Answers

1. The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

2. $4.56 \text{ x } 10^{-19}$ J

3. a) 3.233×10^{-19} J; b) 2.018 eV

4. a) $v = 4.568 \times 10^{14}$ s; b) $\lambda = 656.3$ nm; c) Energy $\text{mol}^{-1} = 1.823 \times 10^{5}$ J mol^{-1}; red

5. a) $\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; (b) $\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; The color of (a) is red; (b) is blue.

6. Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

7. a) 5.49×10^{14} s^{-1}; b) no

8. a) Energy in 1 mole of photons: 178.3 kJ; b) color: red

9. $8.3 \text{ x } 10^{22}$ photons

10. $1.3 \text{ x } 10^{5}$ photons

8.3 - WAVE-PARTICLE DUALITY OF MATTER & ENERGY

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his *special theory of relativity*, which related energy and mass according to the following equation:

$$E = hv = h(c / \lambda) = mc^2$$

Equation 8.3.1 Energy Mass Relation

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = Ec^2 = hv / c^2 = h\lambda / c$$

Equation 8.3.2 Energy Mass Relation of Photon

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a principle that matter and energy have properties typical of both waves and particles). Depending on conditions, light could be viewed as either a wave or a particle.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ, given by this expression in which h is the familiar Planck's constant:

$$\lambda = hmv = hp$$

Equation 8.3.3 Wavelength Momentum Equation

This is called the *de Broglie wavelength*. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols appear nearly identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 8.3.1.).

$$2\pi r = n\lambda, n = 1, 2, 3, \ldots$$

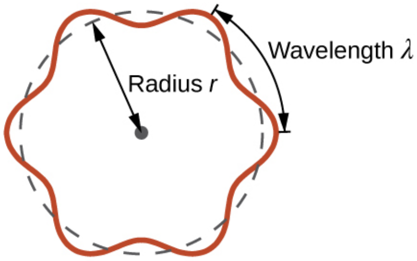


Figure 8.3.1. If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

For a circular orbit of radius *r*, the circumference is $2\pi r$, and so de Broglie's condition is:

$$2\pi r = n\lambda, \ n=1,2,3.....$$

Since the de Broglie expression relates the wavelength to the momentum and, hence, velocity, this implies:

$$2\pi r = n\lambda = nhp = nhmv = nhrmvr = nhrL$$

This expression can be rearranged to give Bohr's formula for the quantization of the angular momentum:

$$L = nh^2\pi = n\hbar$$

$$(\hbar = h^2\pi)$$

Equation 8.3.4 Quantization of the Angular Momentum

Classical angular momentum *L* for a circular motion is equal to the product of the radius of the circle and the momentum of the moving particle *p*.

$$L = rp = rmv \text{ (for a circular motion)}$$

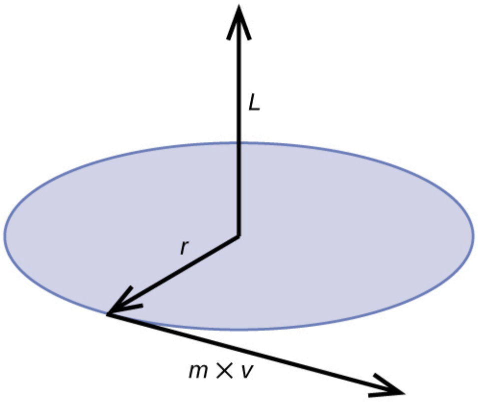


Figure 8.3.2. The diagram shows angular momentum for a circular motion.

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their “slits,” since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 8.3.3. shows an interference pattern. It is strikingly similar to the interference patterns for light shown in the example determining the frequency and wavelength of radiation in topic 8.1. The wave–particle duality of matter can be seen in Figure 8.3.3. by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron’s motion. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.

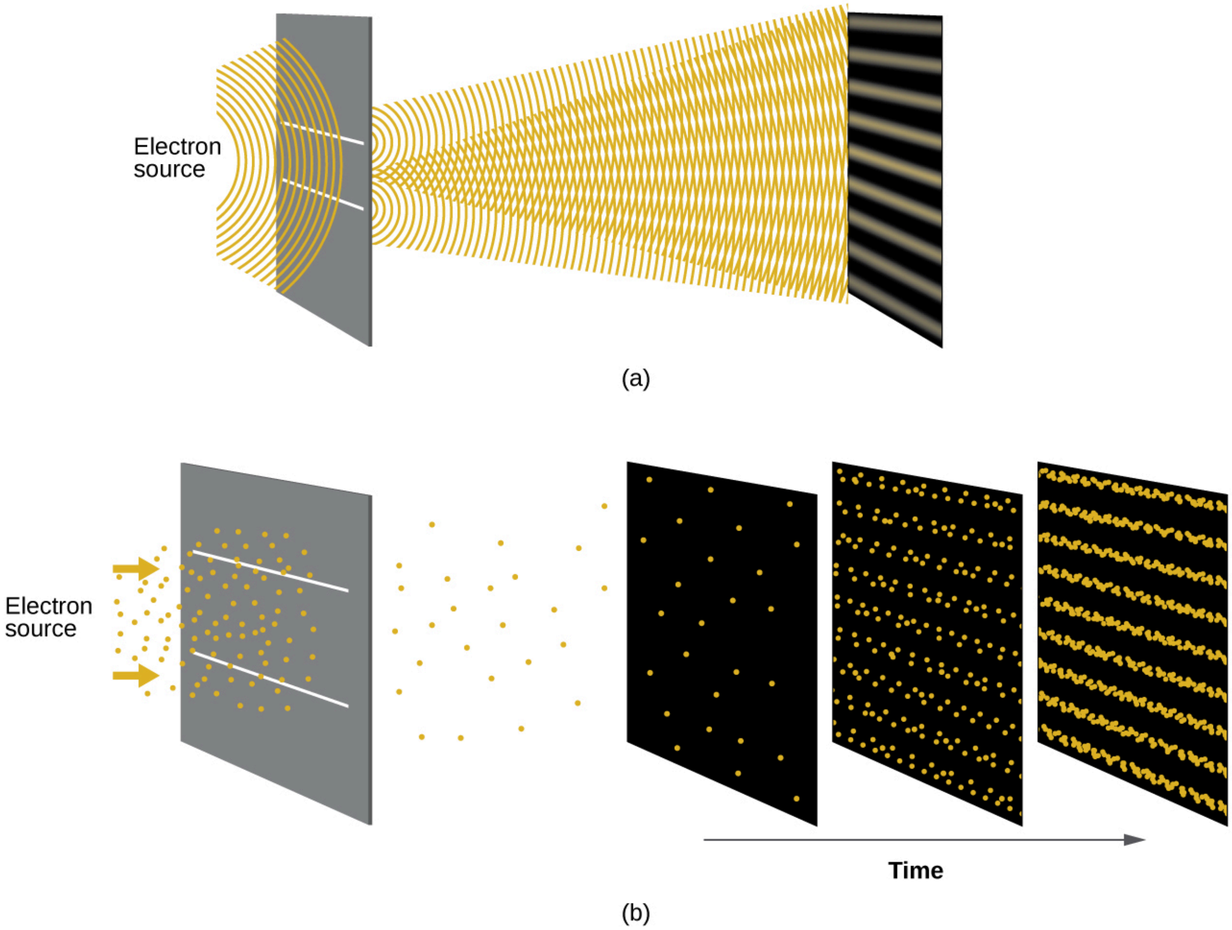


Figure 8.3.3. (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. The electrons pass through very closely spaced slits, forming an interference pattern, with increasing numbers of electrons being recorded from the left image to the right. With only a few electrons recorded, it is clear that the electrons arrive as

individual localized “particles,” but in a seemingly random pattern. As more electrons arrive, a wavelike interference pattern begins to emerge. Note that the probability of the final electron location is still governed by the wave-type distribution, even for a single electron, but it can be observed more easily if many electron collisions have been recorded.

View the Dr. Quantum – Double Slit Experiment cartoon for an easy-to-understand description of wave–particle duality and the associated experiments.

Example 8.3.1 – Calculating the Wavelength of a Particle

If an electron travels at a velocity of 1.000×10^{7} m s^{-1} and has a mass of 9.109×10^{-28} g, what is its wavelength?

Solution

We can use de Broglie’s equation to solve this problem, but we first must do a unit conversion of Planck’s constant. You learned earlier that 1 J = 1 kg m^2/s^2. Thus, we can write $h = 6.626 \times 10^{-34}$ J s as 6.626×10^{-34} kg m^2/s.

$$\lambda = hmv$$

$$= 6.626 \times 10^{-34}\ \mathrm{kgm^2/s}\ (9.109 \times 10^{-31}\ \mathrm{kg})(1.000 \times 10^{7}\ \mathrm{m/s})$$

$$= 7.274 \times 10^{-11}\ \mathrm{m}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

Check Your Learning 8.3.1 – Calculating the Wavelength of a Particle

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m s^{-1}, assuming that it can be modeled as a single particle.

Answer

1.9×10^{-34} m. We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle’s position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the **Heisenberg uncertainty principle**: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. For a particle of mass m moving with velocity v_x in the x direction (or equivalently with momentum p_x), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x, must be greater than or equal to $\hbar / 2$ (recall that $\hbar = h / (2\pi)$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta px = (\Delta x)(m\Delta v) \geq \hbar / 2$$

Equation 8.3.5 Heisenberg Uncertainty Principle

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position (Δx) has a value of, say, 1 pm (10^{-12} m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$\Delta p = m\Delta v = h(2\Delta x) = (1.055 \times 10^{-34}\,kgm^2 / s)(2 \times 1 \times 10^{-12}\,m) = 5 \times 10^{-23}\,kgm / s$$

The value of $\hbar$ is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as $\Delta E\,\Delta t \geq \hbar / 2$. As will be discussed later, even the vector components of angular momentum cannot all be specified exactly simultaneously.

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics. Recall that the equations of motion obtained from classical mechanics are trajectories where, at any given instant in time, both the position and the momentum of a particle can be determined exactly. Heisenberg's uncertainty principle implies that such a view is untenable in the microscopic domain and that there are fundamental limitations governing the motion of quantum particles. This does not mean that microscopic particles do not move in trajectories, it is just that measurements of trajectories are limited in their precision. In the realm of quantum mechanics, measurements introduce changes into the system that is being observed.

Read this article that describes a recent macroscopic demonstration of the uncertainty principle applied to microscopic objects.

★ Questions

1. Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.
2. Calculate the wavelength of a neutron that is moving at 3.00×10^3 m/s (in Å or pm).
3. Calculate the wavelength (in meters) associated with a 42 g baseball with speed of 80 m/s.
4. Calculate the de Broglie wavelengths of the following:
    a) An 8g bullet with velocity $340ms^{-1}$.
    b) A 10^{-5}g particle with velocity $10^{-5}ms^{-1}$.
    c) A 10^{-8}g particle with velocity $10^{-8}ms^{-1}$.

d) An electron moving with velocity 4.8×10^{6} ms^{-1}.

Answers

1. 9.95×10^{-35}
2. 1.32 Å, or 132 pm
3. 1.97×10^{-34} m
4. (a) 2.44×10^{-33} (b) 6.626×10^{-21} (c) 6.626×10^{-15} (d) 1.52×10^{-10}

8.4 - QUANTUM MECHANICS

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, as Bohr had argued, Erwin Schrödinger extended de Broglie's work by incorporating the de Broglie relation into a wave equation, deriving what is today known as the *Schrödinger equation*. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra, and he did so without having to invoke Bohr's assumptions of stationary states and quantized orbits, angular momenta, and energies; quantization in Schrödinger's theory was a natural consequence of the underlying mathematics of the wave equation. Like de Broglie, Schrödinger initially viewed the electron in hydrogen as being a physical wave instead of a particle, but where de Broglie thought of the electron in terms of circular stationary waves, Schrödinger properly thought in terms of three-dimensional stationary waves, or **wavefunctions**, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi$$

Equation 8.4.1 Schrödinger Equation

$\hat{H}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom), ψ is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

You may also have heard of Schrödinger because of his famous thought experiment. This story explains the concepts of superposition and entanglement as related to a cat in a box with poison.

Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding of these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an *n* value, where *n* = 1, 2, 3, …. Generally speaking, the energy of an electron in an atom is greater for greater values of *n*. This number, ***n***, is referred to as the principal quantum number. The **principal quantum number** defines the location of the energy level. It is essentially the same concept as the *n* in the Bohr atom description. Another name for the principal quantum number is the shell number. The **shells** of an atom can be thought of concentric spheres radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure 8.4.1.). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

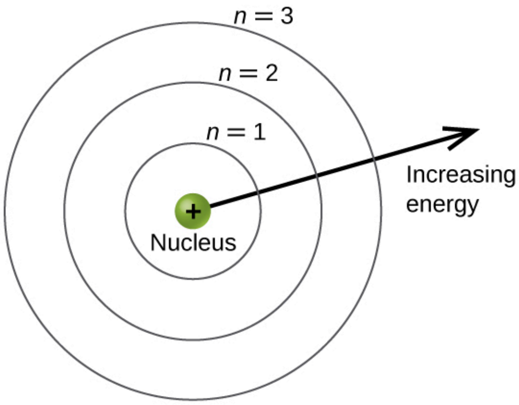


Figure 8.4.1. Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\Delta E = E_{final} - E_{initial}$$
$$= -2.18 \times 10^{-18} ((1 / n_f^2) - (1 / n_1^2))\ J$$

The values n_f and n_i are the final and initial energy states of the electron. The example calculating the energy and wavelength of electron transitions in a one–electron (Bohr) system in topic 8.2 of the chapter demonstrates calculations of such energy changes.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An

atomic orbital, which is distinct from an *orbit*, is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is ℓ (lowercase letter L), the **angular momentum quantum number**. It is an integer that defines the shape of the orbital, and takes on the values, $l = 0, 1, 2, \ldots, n - 1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. The principal quantum number defines the general size and energy of the orbital. The l value specifies the shape of the orbital. Orbitals with the same value of l form a **subshell**. In addition, the greater the angular momentum quantum number, the greater is the angular momentum of an electron at this orbital.

Orbitals with $l = 0$ are called ***s*** **orbitals** (or the *s* subshells). The value $l = 1$ corresponds to the *p* orbitals. For a given n, ***p*** **orbitals** constitute a *p* subshell (e.g., 3*p* if $n = 3$). The orbitals with $l = 2$ are called the ***d*** **orbitals**, followed by the *f-, g-, and h-*orbitals for $l = 3, 4, 5$, and there are higher values we will not consider.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a *radial node*. The number of radial nodes in an orbital is $n – l – 1$.

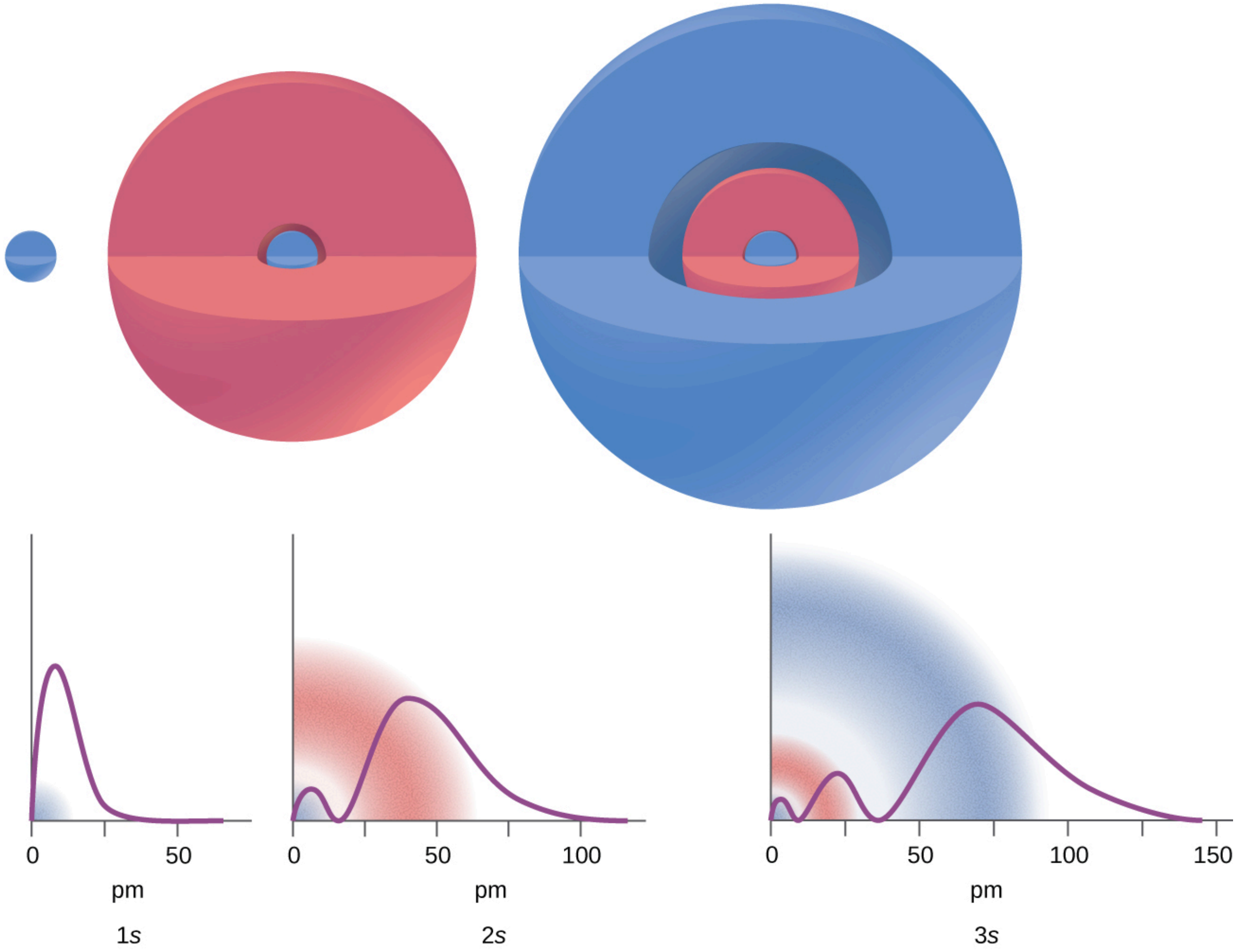


Figure 8.4.2. The graphs show the probability (*y* axis) of finding an electron for the 1*s*, 2*s*, 3*s* orbitals as a function of distance from the nucleus.

Consider the examples in Figure 8.4.2. The orbitals depicted are of the *s* type, thus *l* = 0 for all of them. It can be seen from the graphs of the probability densities that there are 1 – 0 – 1 = 0 places where the density is zero (nodes) for 1*s* (*n* = 1), 2 – 0 – 1 = 1 node for 2*s*, and 3 – 0 – 1 = 2 nodes for the 3*s* orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and ***f* orbitals** are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

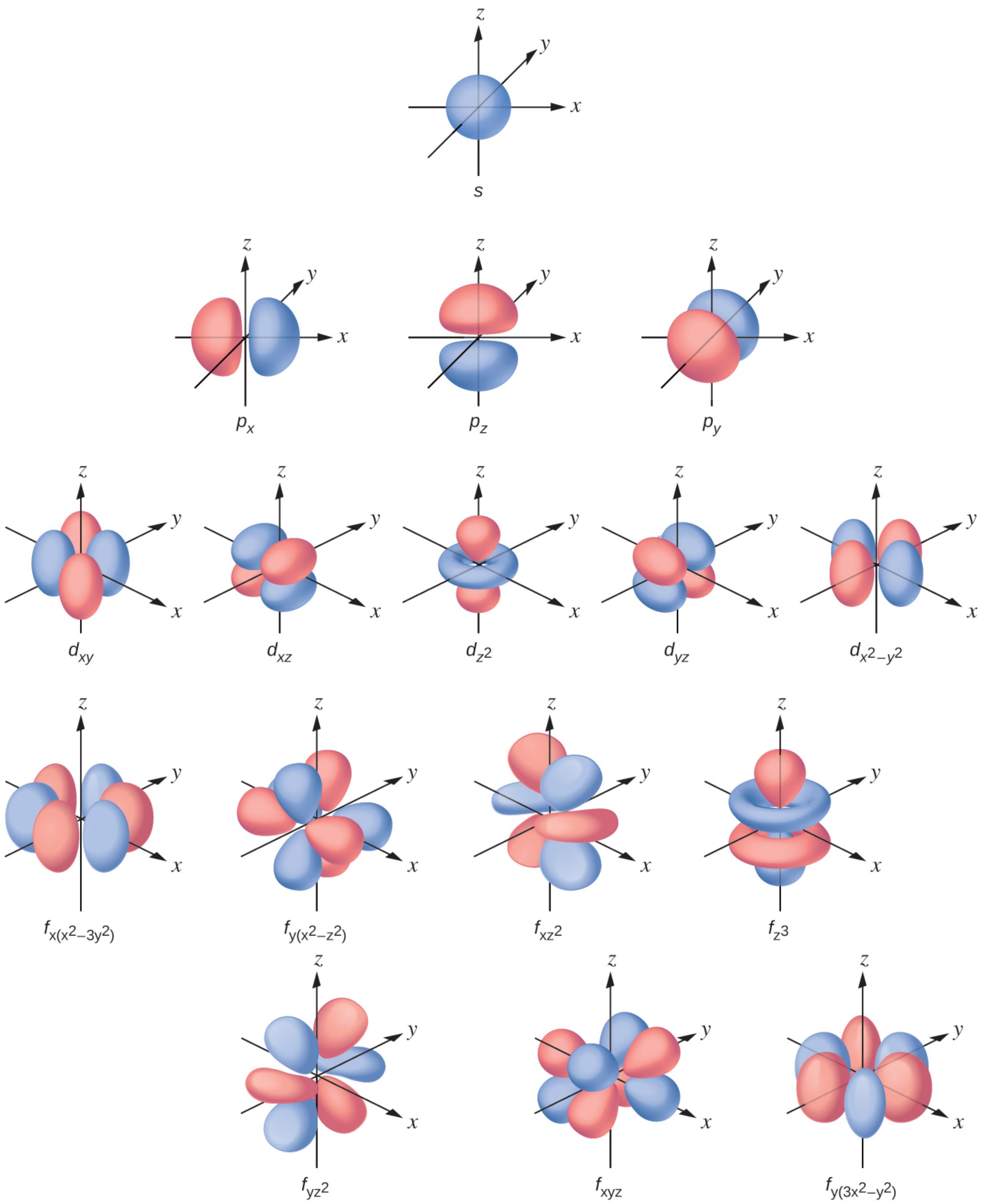


Figure 8.4.3. Shapes of *s*, *p*, *d*, and *f* orbitals.

If an electron has an angular momentum ($l \neq 0$), then this vector can point in different directions. In addition, the *z* component of the angular momentum can have more than one value. This means that if a magnetic field is applied in the *z* direction, orbitals with different values of the *z* component of the angular momentum will have different energies resulting from interacting with the field. The **magnetic quantum number**, called m_ℓ, specifies the *z* component of the angular momentum for a particular orbital. For example, for an *s* orbital, $l = 0$, and the only value of m_l is zero. For *p* orbitals, $l = 1$, and m_l can be equal to −1, 0, or +1. Generally speaking, m_l can be equal to $-l, -(l - 1), \ldots, -1, 0, +1, \ldots, (l - 1), l$. The total number of possible orbitals with the same value of *l* (a subshell) is $2l + 1$. Thus, there is one *s*-orbital for $l = 0$, there are three *p*-orbitals for $l = 1$, five *d*-orbitals for $l = 2$, seven *f*-orbitals for $l = 3$, and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure 8.4.3.

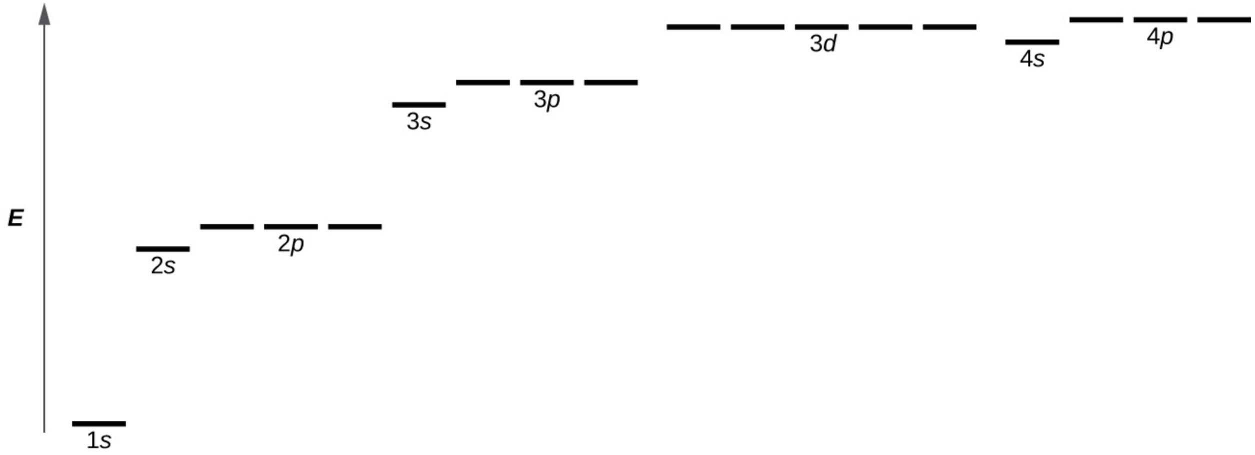


Figure 8.4.4. The chart shows the energies of electron orbitals in a multi-electron atom.

Figure 8.4.4. illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number $l = 0$ for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, *n*, are called **degenerate orbitals**. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on Figure 8.4.4. Orbitals within the same subshell (for example *ns, np, nd, nf*, such as 2*p*, 3*s*) are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or m_s.

The other three quantum numbers, *n*, *l*, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely different quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. Think of a planet for example, regardless of the position of direction of the planetary axis, it can only rotate in two directions: "clockwise" or "counterclockwise". One of the two quantized states is termed the α state, with the *z* component of the spin being in the positive direction of the *z* axis. This corresponds to the spin quantum number $\mathrm{m_s}$ = 12. The other is called the β state, with the *z* component of the spin being negative and $\mathrm{m_s}$ = -12. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $\mathrm{m_s}$ = -12 and $\mathrm{m_s}$ = 12 are different if an external magnetic field is applied.

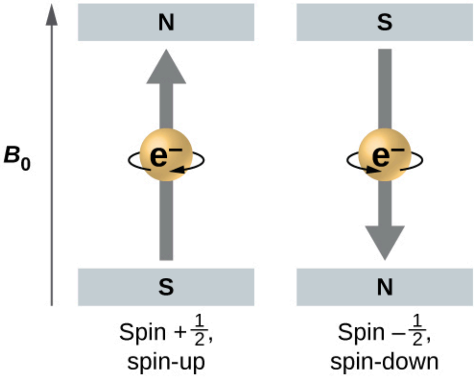


Figure 8.4.5. Electrons with spin values ±12 in an external magnetic field.

Figure 8.4.5. illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the 12 spin quantum number and down (in the negative *z* direction) for the spin quantum number of -12 (Note: the up and down directions are completely arbitrary, and are results of unanimous agreement to denote them as such). A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on Figure 8.4.5.) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $\mathrm{m_s}$ = 12 has a slightly lower energy in an external field in the positive *z* direction, and an electron with $\mathrm{m_s}$ = -12 has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

★ Questions

1. How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

2. What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

3. Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

4. Answer the following questions:

   a) Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.

   b) How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

5. Identify the subshell in which electrons with the following quantum numbers are found:

   a) $n = 2, l = 1$

   b) $n = 4, l = 2$

   c) $n = 6, l = 0$

6. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

7. Identify the subshell in which electrons with the following quantum numbers are found:

   a) $n = 3, l = 2$

   b) $n = 1, l = 0$

   c) $n = 4, l = 3$

8. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

Answers

1. Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, $n = 1, 2, 3, \ldots$, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same

spatial extent; the angular momentum quantum number *l*, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same *l* (and *n*) all have the same energy; and the orientation quantum number *m*, which is a measure of the *z* component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [*s* orbitals] can have zero angular momentum).

2. n = 1,2,3,4...
    - l = 0 to (n-1)
    - m_l = -1 to +1
    - ms = -½ to +½
3. n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_l determines the orientation of the orbitals of the same l value with respect to one another. ms determines the spin of an electron.
4.
    - (a)
        - shell: set of orbitals in the same energy level
        - subshell: set of orbitals in the same energy level and same shape (s, p, d, or f)
        - orbital: can hold up to 2 electrons
    - (b)
        - shell: set of orbitals in the same energy level
        - subshell: set of orbitals in the same energy level and same shape (s, p, d, or f)
        - orbital: can hold up to 2 electrons
5. (a) 2*p*; (b) 4*d*; (c) 6*s*
6. (a) 3 orbitals; (b) 5 orbitals; (c) 1 orbital
7. (a) 3*d;* (b) 1*s;* (c) 4*f*
8. (a) 5 orbitals ;(b) 1 orbital ;(c) 7 orbitals

8.5 - ELECTRON CONFIGURATION IN ATOMS

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers n, l, and m_l), but only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values (±12), no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons.

The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in the following table.

Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed Values	Physical Meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general value of energy for an electron in the orbital
angular momentum or azimuthal quantum number	l	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	Number and orientation of the orbitals in the subshell
spin quantum number	m_s	12 , -12	direction of the intrinsic quantum "spinning" of the electron

Example 8.5.1 – Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the n = 4 shell of an atom.

Solution

For n = 4, l can have values of 0, 1, 2, and 3. Thus, *s*, *p*, *d*, and *f* subshells are found in the n = 4 shell of an atom. For l = 0 (the *s* subshell), m_l can only be 0. Thus, there is only one 4*s* orbital. For l = 1 (*p*-type orbitals), m can have values of −1, 0, +1, so we find three 4*p* orbitals. For l = 2 (*d*-type orbitals), m_l can have values of −2, −1, 0, +1, +2, so we have five 4*d* orbitals. When l = 3 (*f*-type orbitals), m_l can have values of −3, −2, −1, 0, +1, +2, +3, and we can have seven 4*f* orbitals. Thus, we find a total of 16 orbitals in the n = 4 shell of an atom.

Check Your Learning 8.5.1 – Working with Shells and Subshells

Identify the subshell in which electrons with the following quantum numbers are found: (a) n = 3, l = 1; (b) n = 5, l = 3; (c) n = 2, l = 0.

Answer

(a) 3*p* (b) 5*f* (c) 2*s*

Example 8.5.2 – Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) n = 2, (b) n = 5, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When n = 2, there are four orbitals (a single 2*s* orbital, and three orbitals labeled 2*p*). These four orbitals can contain eight electrons.

(b) When n = 5, there are five subshells of orbitals that we need to sum:

1 orbital labeled 5s
3 orbitals labeled 5p
5 orbitals labeled 5d
7 orbitals labeled 5f
+9 orbitals labeled 5g
25 orbitals total

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell n will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$

Check Your Learning 8.5.2 – Maximum Number of Electrons

If a shell contains a maximum of 32 electrons, what is the principal quantum number, n?

Answer

n = 4

Example 8.5.3 – Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	**n**	**l**	**m_l degeneracy**	**Radial nodes (no.)**
4f				
	4	1		
	7		7	3
5d				

Solution

The table can be completed using the following rules:

The orbital designation is nl, where $l = 0, 1, 2, 3, 4, 5, \ldots$ is mapped to the letter sequence s, *p*, *d*, *f*, *g*, *h*, …,

The m_l degeneracy is the number of orbitals within an l subshell, and so is $2l + 1$ (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).

The number of radial nodes is equal to $n - l - 1$.

Orbital	**n**	**l**	**m_l degeneracy**	**Radial nodes (no.)**
4f	4	3	7	0
4p	4	1	3	2
7f	7	3	7	3
5d	5	2	5	2

Check Your Learning 8.5.3 – Working with Quantum Numbers

How many orbitals have $l = 2$ and $n = 3$?

Answer

The five degenerate 3*d* orbitals

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, *n*, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of *l* differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 8.5.1. depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

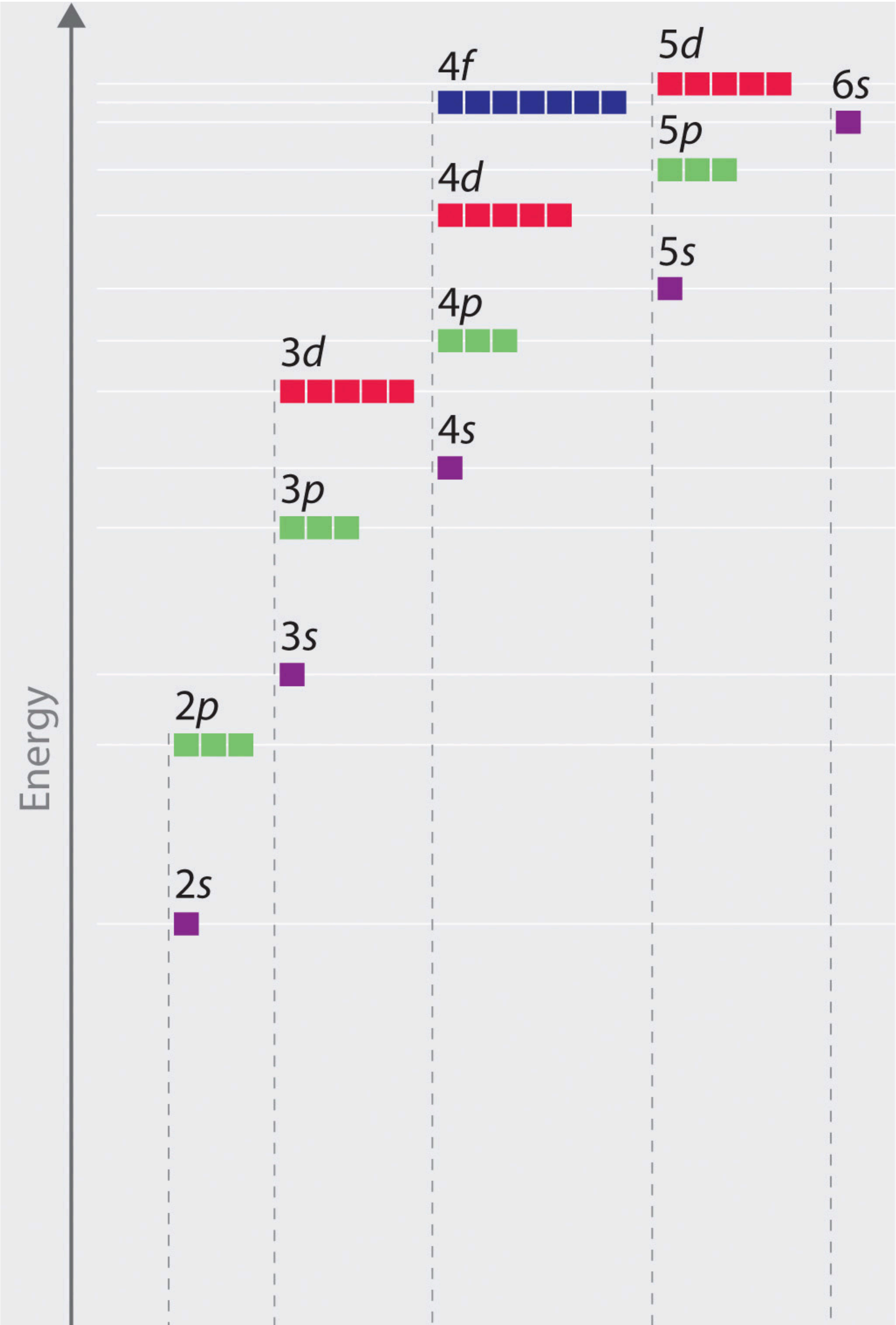

Energy
2s
2p
3s
3p
3d
4s
4p
4d
4f
5s
5p
5d
6s

Figure 8.5.1. Energy diagram showing the approximate relative energy levels of atomic orbitals in an atom with two or more electrons.

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have +*Z* charges). This phenomenon is called *shielding* and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 8.5.2.):

The number of the principal quantum shell, *n*,
The letter that designates the orbital type (the subshell, *l*), and
A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (*n*) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

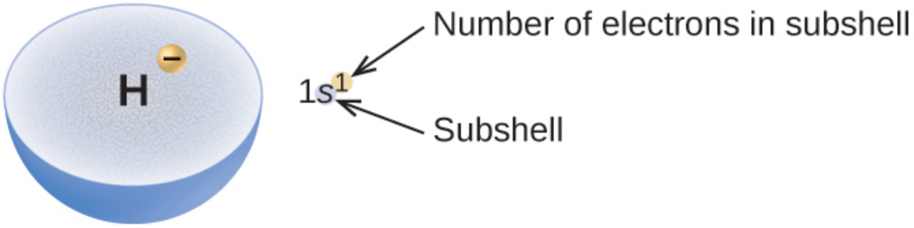


Figure 8.5.2. The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can "build" the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* ("to build up"). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 8.5.1.), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 8.5.3. illustrates the traditional way to remember the filling order for atomic orbitals. Since the arrangement of the periodic table is based on the electron configurations, Figure 8.5.4. provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

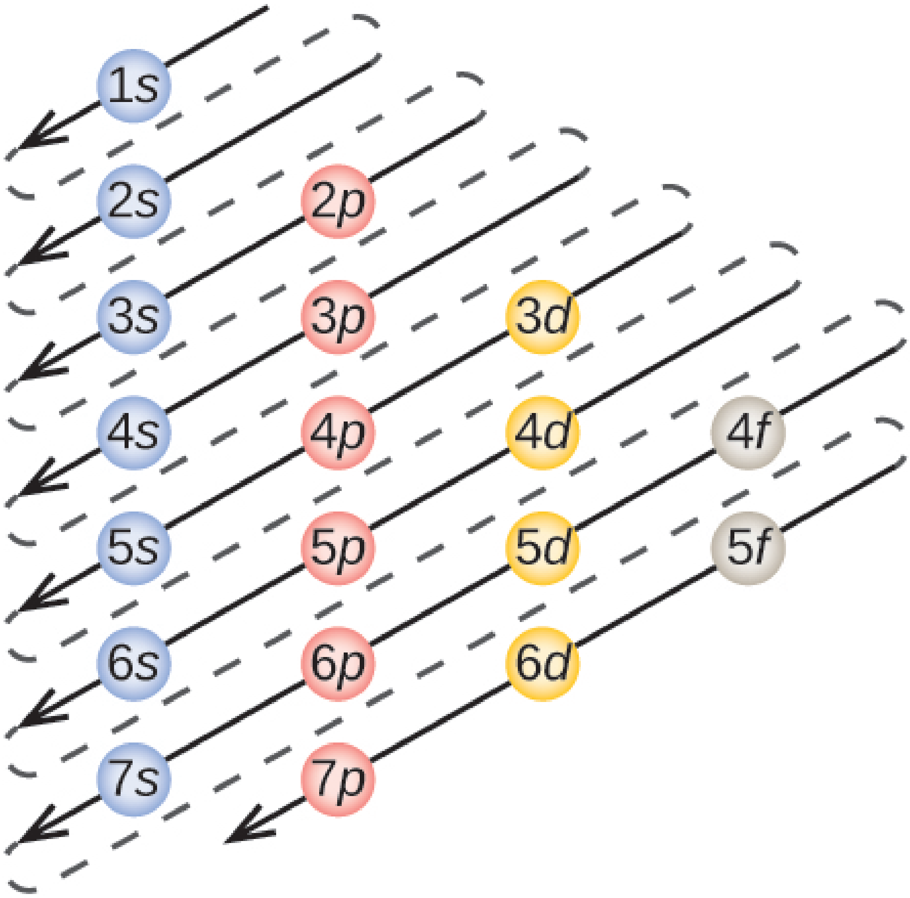


Figure 8.5.3. The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the *s* orbitals with each *n* shell on a separate row. Repeat for *p*, *d*, and *f*. Be sure to only include orbitals allowed by the quantum numbers (no 1*p* or 2*d*, and so forth). Finally, draw diagonal lines from top to bottom as shown.

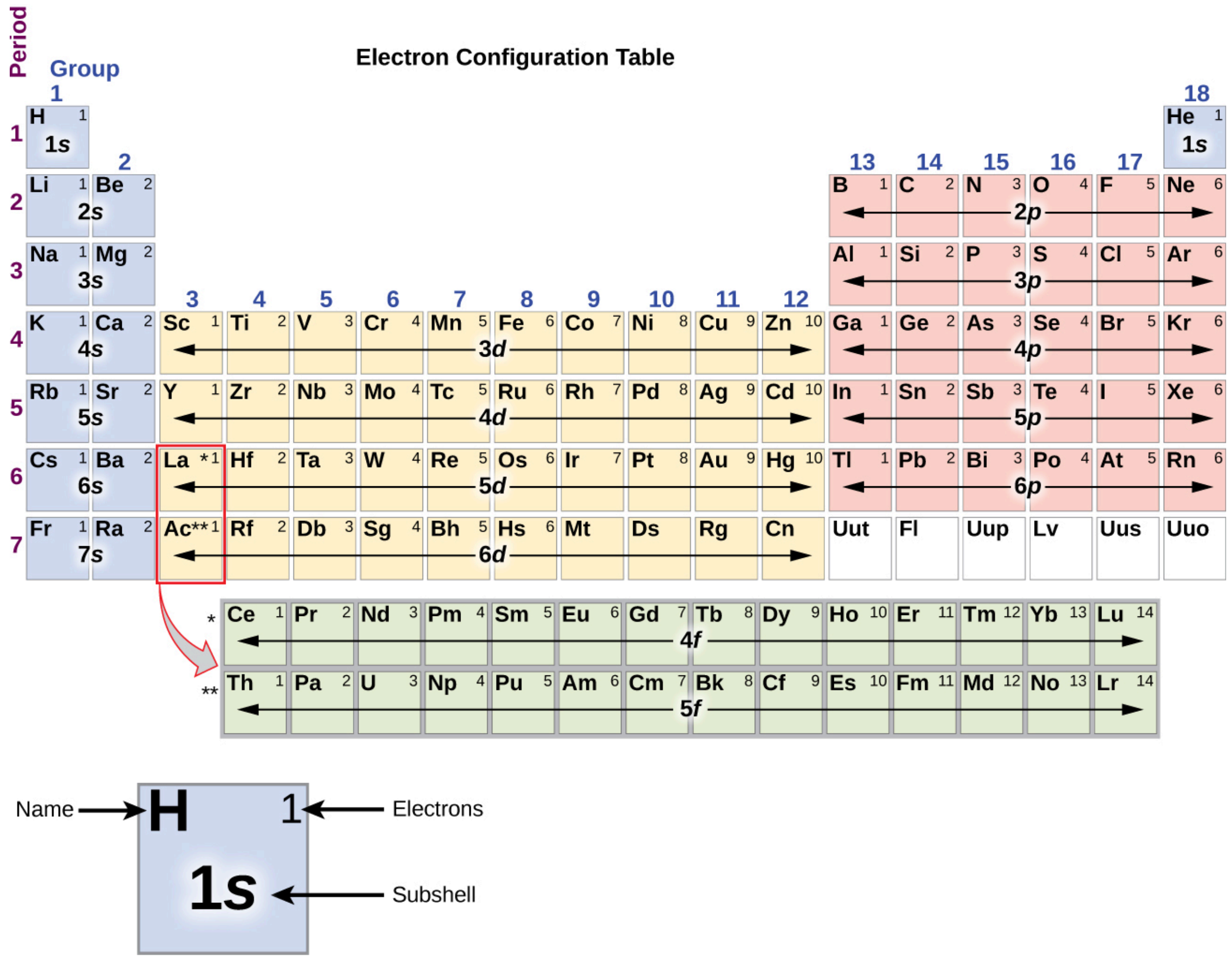
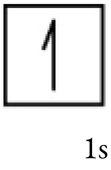


Figure 8.5.4. This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 8.5.3. or Figure 8.5.4., we would expect to find the electron in the 1*s* orbital. By convention, the m_s = +12 value is usually filled first. The electron configuration and the orbital diagram are:

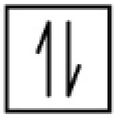
$$He^1s^1$$



Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, m_s = +12). The second electron also goes into the 1*s* orbital and fills that orbital.

The second electron has the same *n*, *l*, and m_l quantum numbers, but must have the opposite spin quantum number, m_s =-12. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

He^1 s^2

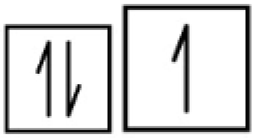


1s

The *n* = 1 shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure 8.5.3.or Figure 8.5.4.). Thus, the electron configuration and orbital diagram of lithium are:

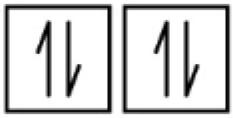
Li 1s^2 2s^1



1s 2s

An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

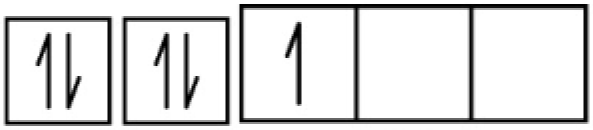
Be 1s^2 2s^2



1s 2s

An atom of boron (atomic number 5) contains five electrons. The *n* = 1 shell is filled with two electrons and three electrons will occupy the *n* = 2 shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (*ml* = −1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

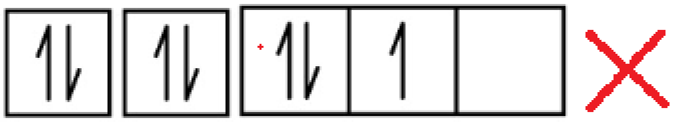
B 1s^2 2s^2 2p^1



1s 2s 2p

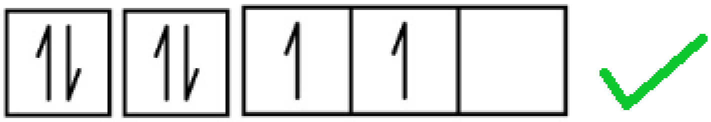
Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

C $1s^2 2s^2 2p^2$



1s 2s 2p

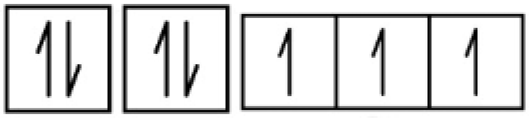
C $1s^2 2s^2 2p^2$



1s 2s 2p

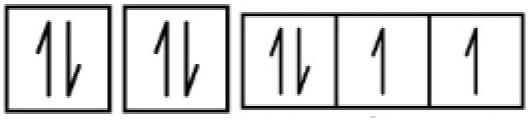
Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the n= 1 and the n = 2 shells are filled. The electron configurations and orbital diagrams of these four elements are:

N $1s^2 2s^2 2p^3$



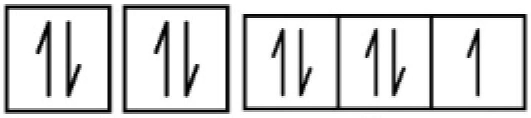
1s 2s 2p

O $1s^2 2s^2 2p^4$



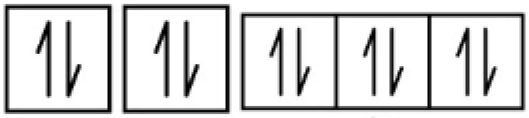
1s 2s 2p

F $1s^2 2s^2 2p^5$



1s 2s 2p

Ne $1s^2 2s^2 2p^6$

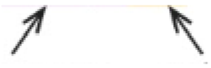


1s 2s 2p

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the $3s$ orbital, giving a $1s^22s^22p^63s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 8.5.5.). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^22s^22p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

Na $1s^2 2s^2 2p^6 3s^1$

Abbreviation [Ne]3 s^1



Core electrons Valence electrons

Figure 8.5.5. A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence s subshell outside a filled set of inner shells.

Li:[He] $2s^1$

Na:[Ne] $3s^1$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^23p^1$, is analogous to its family member boron, [He]$2s^22p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to n = 3.

Figure 8.5.6. shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

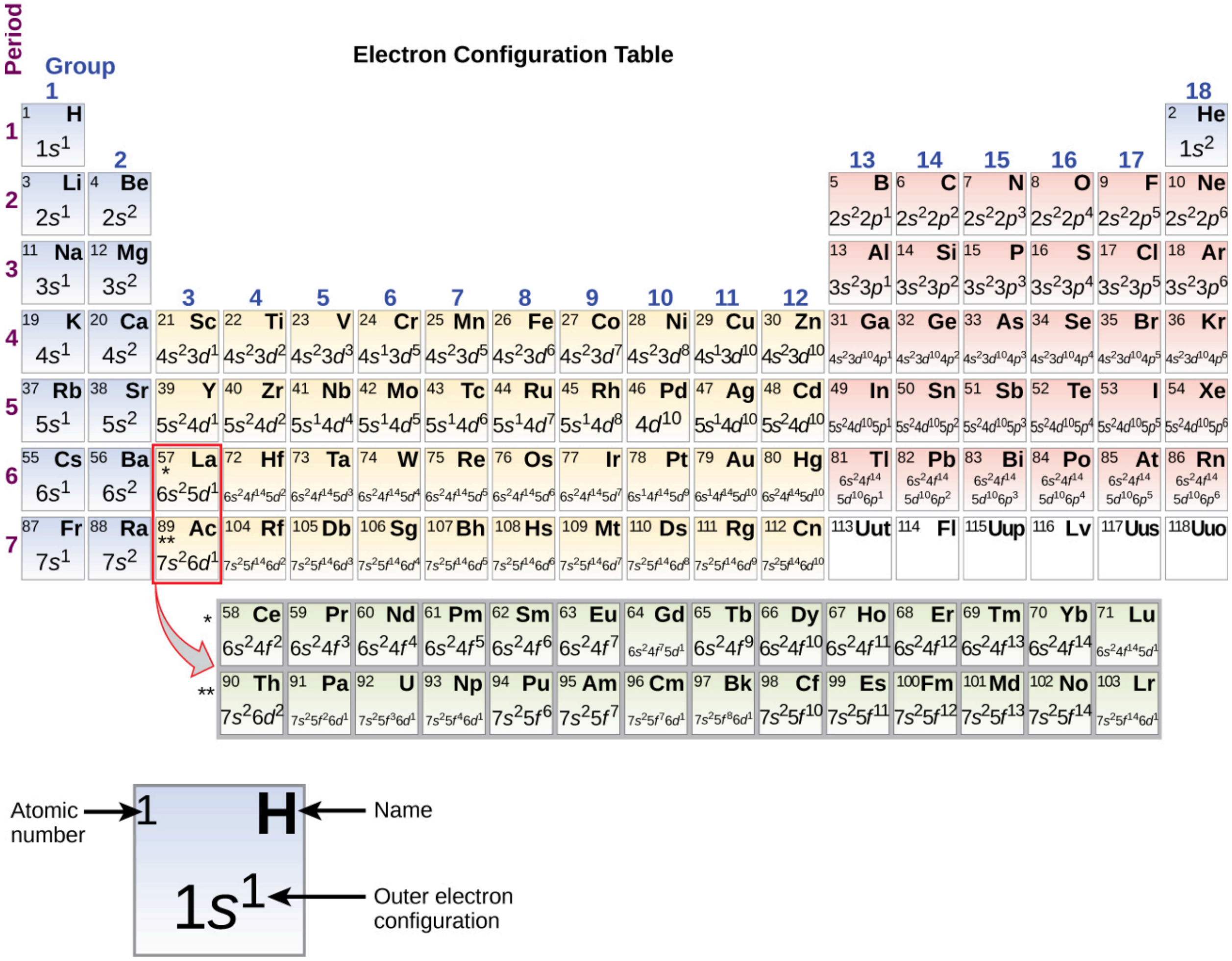


Figure 8.5.6. This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure 8.5.6.). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper

(Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the (n – 1) shell next to the n shell to bring that (n – 1) shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the (n – 2) shell to bring that shell from 18 electrons to a total of 32 electrons.

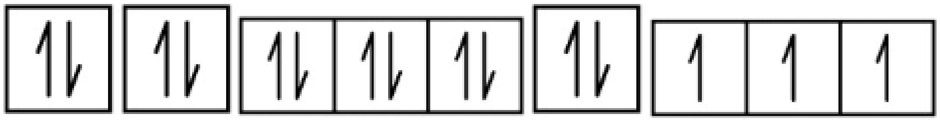
Example 8.5.4 – Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$



1s 2s 2p 3s 3p

The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The *ml* value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of +12 for the spin quantum number; thus, ms = +12.

Check Your Learning 8.5.4 – Quantum Numbers and Electron Configurations

Identify the atoms from the electron configurations given:

(a) $[\mathrm{Ar}]4s^2 3d^5$

(b) $[\mathrm{Kr}]5s^2 4d^{10} 5p^6$

Answer

(a) Mn (b) Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 8.5.3. or Figure 8.5.4. For instance, the electron configurations (shown in Figure 8.5.6.) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability.

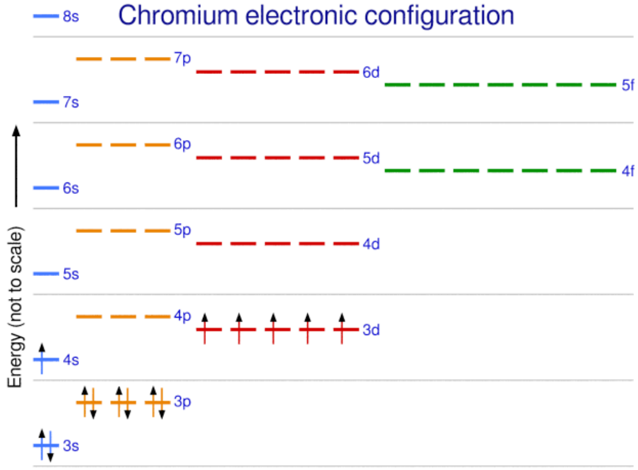


Figure 8.5.7 Chromium electron configuration demonstrating exceptions to subshell filling.

This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration [Kr]$5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually [Kr]$5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 8.5.6.), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 8.5.6, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 8.5.6. show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

Main group elements (sometimes called *representative elements*) are those in which the last electron added enters an *s* or a *p* orbital in the outermo**valence shell**st shell, shown in blue and red in Figure 8.5.6. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration $[\text{Ar}]4s^2 3d^{10} 4p^1$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.

Transition elements or *transition metals*. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and (*n* – 1) *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 8.5.6.) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 8.5.6.), and we will adopt this usage in this textbook.

Inner transition elements are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 8.5.6. The valence shells of the inner transition elements consist of the (*n* – 2)*f*, the (*n* – 1)*d*, and the *ns* subshells. There are two inner transition series:

The lanthanide series: lanthanide (La) through lutetium (Lu)

The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configuration of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For electrons in the shell with the highest value of *n* are removed first. Recall that the quantum number *n* denotes the size of the orbital (higher *n* value denotes a larger orbital). Thus these electrons are furthest from the nucleus, and as a result are the first to be removed. This explains why 4*s* electrons are removed before 3*d* electrons. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 8.5.5 – Predicting Electron Configurations of Ions

What is the electron configuration of:

(a) Na^+

(b) P^{3-}

(c) Al^{2+}

(d) Fe^{2+}

(e) Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

(a) Na: $1s^22s^22p^63s^1$. Sodium cation loses one electron, so Na^+: $1s^22s^22p^63s^1$ = Na^+: $1s^22s^22p^6$.

(b) P: $1s^22s^22p^63s^23p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s22s22p63s23p6$.

(c) Al: $1s^22s^22p^63s^23p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^22s^22p^63s^23p^1$ = Al^{2+}: $1s^22s^22p^63s^1$.

(d) Fe: $1s^22s^22p^63s^23p^64s^23d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^22s^22p^63s^23p^64s^23d^6$ = $1s^22s^22p^63s^23p^63d^6$.

(e). Sm: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$ = $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64f^5$.

Check Your Learning 8.5.5 – Predicting Electron Configurations of Ions

Which ion with a +2 charge has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^5$? Which ion with a +3 charge has this configuration?

Answer

Tc^{2+}, Ru^{3+}

★ Questions

1. Using complete subshell notation (1s22s22p6, and so forth), predict the electron configuration of each of the following atoms:

   a) N
   b) Si
   c) Fe
   d) Te
   e) Tb

2. What additional information do we need to answer the question "Which ion has the electron configuration $1s^22s^22p^63s^23p^6$"?

3. Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

   a) N
   b) Si
   c) Fe

d) Te

e) Mo

4. Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

5. Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a −2 charge has this configuration?

6. Which of the following has two unpaired electrons?

a) Mg

b) Si

c) S

d) Both Mg and S

e) Both Si and S.

7. Which atom would be expected to have a half-filled 4*s* subshell?

8. Thallium was used as a poison in the Agatha Christie mystery story "The Pale Horse." Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

9. Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

10. Give two possible sets of four quantum numbers for the electron in an H atom.

11. How many subshells are completely filled with electrons for Na? How many subshells are unfilled?

12. What is the maximum number of electrons in the entire $n = 2$ shell?

13. Write the complete electron configuration for each atom.

a) Si, 14 electrons

b) Sc, 21 electrons

14. Write the complete electron configuration for each atom.

a) Cd, 48 electrons

b) Mg, 12 electrons

15. Write the abbreviated electron configuration for each atom in Question 13.

16. Write the abbreviated electron configuration for each atom in Question 14.

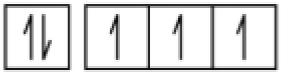
17. Draw electron configuration energy diagram for potassium.

Answers

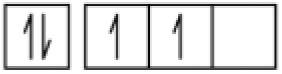
1. (a) $1s^2\ 2s^2\ 2p^3$; (b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$; (c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$; (d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^4$; (e) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6^{s2}\ 4f^9$

2. The charge on the ion

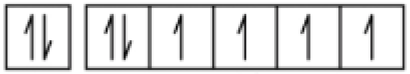
3.

(a) 

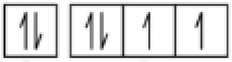
2s 2p

(b) 

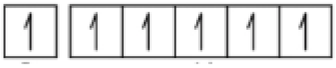
3s 3p

(c) 

4s 3d

(d) 

5s5p

(e) 

5s4d

4. Zr
5. Rb$^+$, Se^{2-}
6. Although both (b) and (c) are correct, (e) encompasses both and is the best answer.
7. K
8. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 4f^{14} 5d^{10}$
9. Co has 27 protons, 27 electrons, and 33 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$, I has 53 protons, 53 electrons, and 78 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$.
10. 1, 0, 0, ½ and 1, 0, 0, -½
11. Three subshells (1*s*, 2*s*, 2*p*) are completely filled, and one shell (3*s*) is partially filled.
12. 8 electrons
13.

a) $1s^2 2s^2 2p^6 3s^2 3p^2$

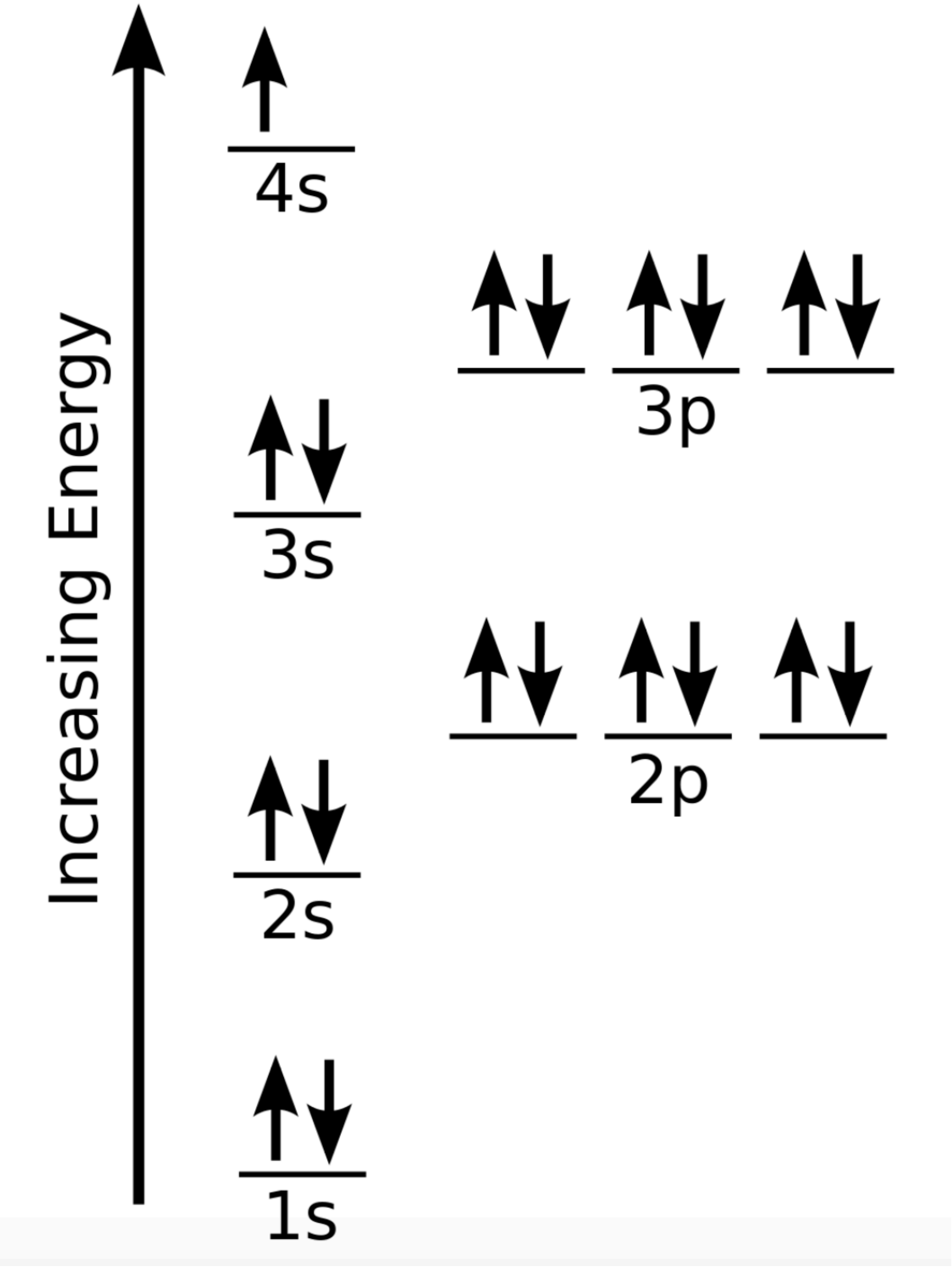
b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

14.

a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$

b) $1s^2 2s^2 2p^6 3s^2$

15. [Ne]$3s^2 3p^2$
16. [Ar]$4s^2 3d^1$
17.


Increasing Energy
4s
3p
3s
2p
2s
1s

8.6 - GENERAL ATOMIC PROPERTIES

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure 8.6.1. shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion. The barium cation is written Ba^{2+}, not Ba^{+2}.

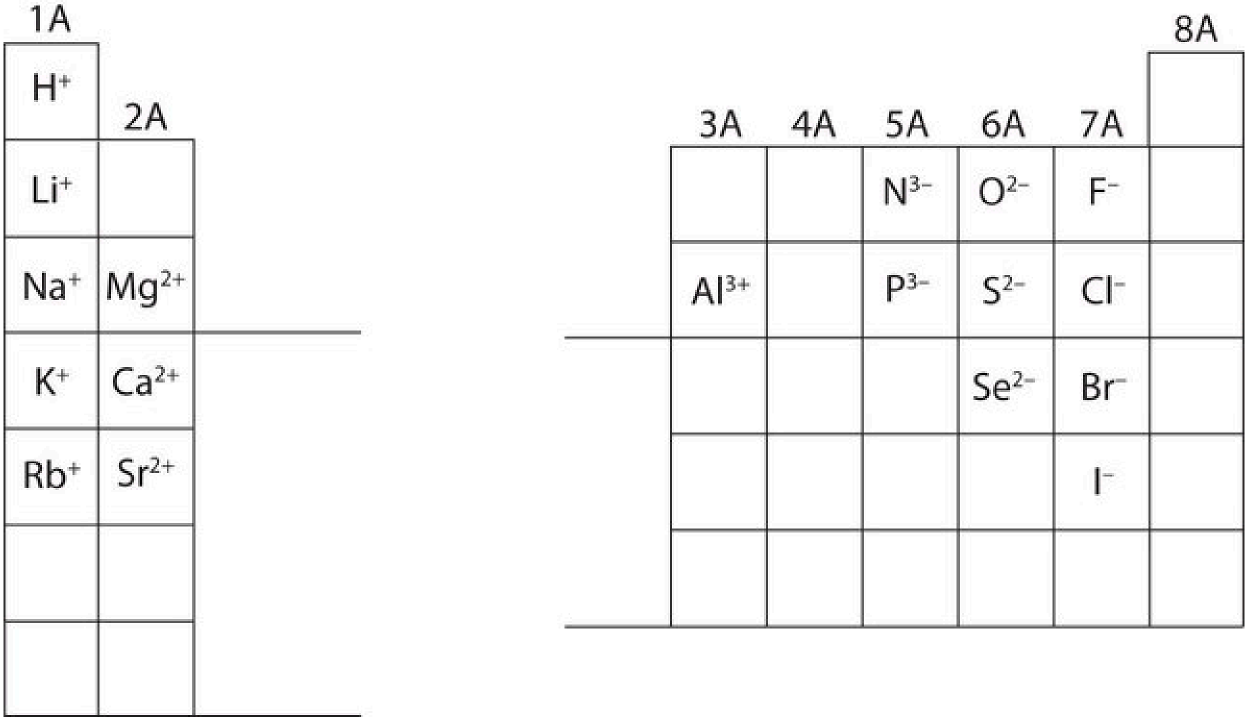


Figure 8.6.1. Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

Magnetic Properties

The **magnetic moment** of a system measures the strength and the direction of its magnetism. The term itself usually refers to the **magnetic dipole moment**. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism. Only paramagnetism and diamagnetism are discussed here.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can orient in either direction, they exhibit magnetic moments that can align with a magnet. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (that is best understood with molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet.

As shown in the video, since molecular oxygen, O_2, is paramagnetic, it is attracted to the magnet. In contrast, molecular nitrogen, N_2, has no unpaired electrons and it is diamagnetic (discussed below); it is therefore unaffected by the magnet.

Note: Paramagnetism is a form of magnetism whereby materials are *attracted* by an externally applied magnetic field.

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a *d*-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are not defined as paramagnetic: they are considered diamagnetic because all *d*-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as *ferromagnetism*, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly *repelled* by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 8.6.2.

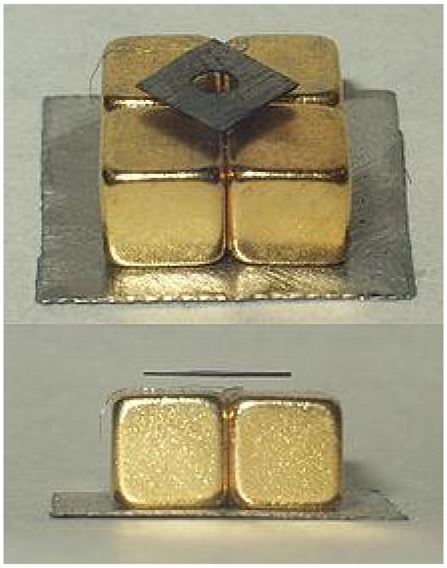


Figure 8.6.2. Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). Image used with permission from Wikipedia.

Note: diamagnetic materials are *repelled* by the applied magnetic field.

Diamagnetism, to a greater or lesser degree, is a property of all materials and always makes a weak contribution to the material's response to a magnetic field. For materials that show some other form of magnetism (such paramagnetism), the diamagnetic contribution becomes negligible.

How to Tell if a Substance is Diamagnetic or Paramagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

Find the electron configuration

Draw the valence orbitals

Look for unpaired electrons

Determine whether the substance is paramagnetic (one or more electrons unpaired) or diamagnetic (all electrons paired)

Example 8.6.1 – Chlorine Atoms

Are chlorine atoms paramagnetic or diamagnetic?

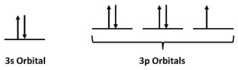
Solution

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Since there is an unpaired electron, Cl atoms are paramagnetic (but weakly since only one electron is unpaired).

Check Your Learning 8.6.1 – Chlorine Atoms

Indicate whether boron atoms are paramagnetic or diamagnetic.

Answer

The B atom has $2s^22p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Example 8.6.2 – Zinc Atoms

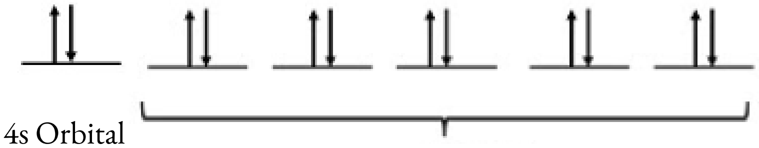
Are zinc atoms paramagnetic or diamagnetic?

Solution

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^23d^{10}$

Step 2: Draw the valence orbitals



4s Orbital

3d Orbitals

Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

Check Your Learning 8.6.2 – Zinc Atoms

Indicate whether F^- ions are paramagnetic or diamagnetic.

Answer

The F^- ion has $2s^22p^6$ as the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

★ Questions

1. Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.
2. Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?
3. How many unpaired electrons are found in oxygen atoms ?
4. How many unpaired electrons are found in bromine atoms?
5. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answers

1. An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.
2. Oxygen
3. The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.
4. The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.
5. The Fe^{2+} ion has $3d^6$ as the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

8.7 - PERIODIC TRENDS AND VARIATION OF PROPERTIES

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Explore visualizations of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius** (Figure 8.7.1.), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in the following table and Figure 8.7.1. The trends for the entire periodic table can be seen in Figure 8.7.1.

Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

Table 8.7.1 Covalent Radii of the Halogen Group Elements

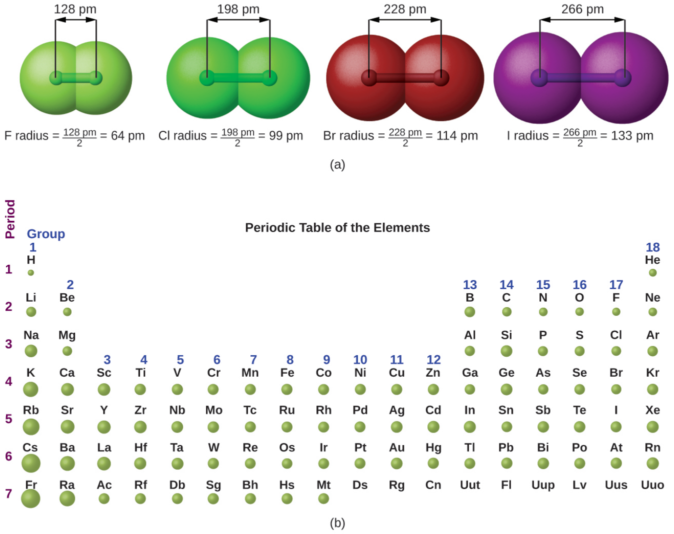


Figure 8.7.1. (a) The covalent radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

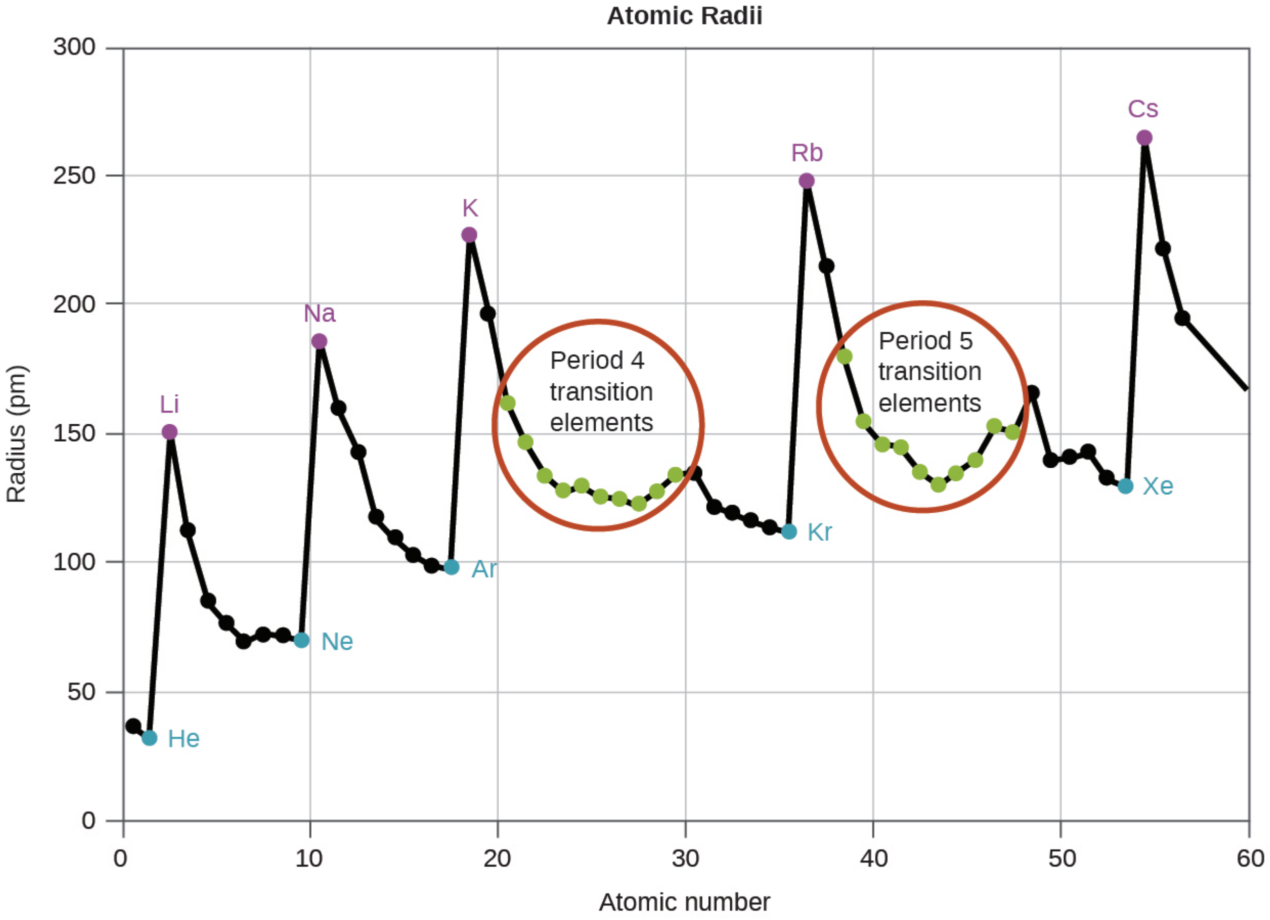


Figure 8.7.2. Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

As shown in Figure 8.7.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge, Z_{eff}**. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Zeff=Z\text{-shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the (*n* – 1)*d* electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 8.7.1 – Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

Check Your Learning 8.7.1 – Sorting Atomic Radii

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

Variation in Atomic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 8.7.3.). For example, the covalent radius of an aluminum atom ($1s^22s^22p^63s^23p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} cation ($1s^22s^22p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.

Figure 8.7.3. The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, *n*.

An anion (negatively charged ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 8.7.3.). For example, a sulfur atom ([Ne]$3s^23p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ([Ne]$3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N^{3-}, O^{2-}, F^{-}, Ne, Na^{+}, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^{-}, Ar, K^{+}, Ca^{2+}, and Sc^{3+} ([Ne]$3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE_1). The first ionization energy for an element, X, is the energy required to form a gas-phase cation with a +1 charge:

X(g)→X++e-IE1

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

X+(g)→X2++e-IE2

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are *endothermic* and IE values are always *positive*. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure 8.7.5. graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 8.7.5. Within a period, the IE_1 generally increases with increasing Z. Down a group, the IE_1 value generally decreases with increasing Z. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the s electrons are lower in energy than the p electrons.

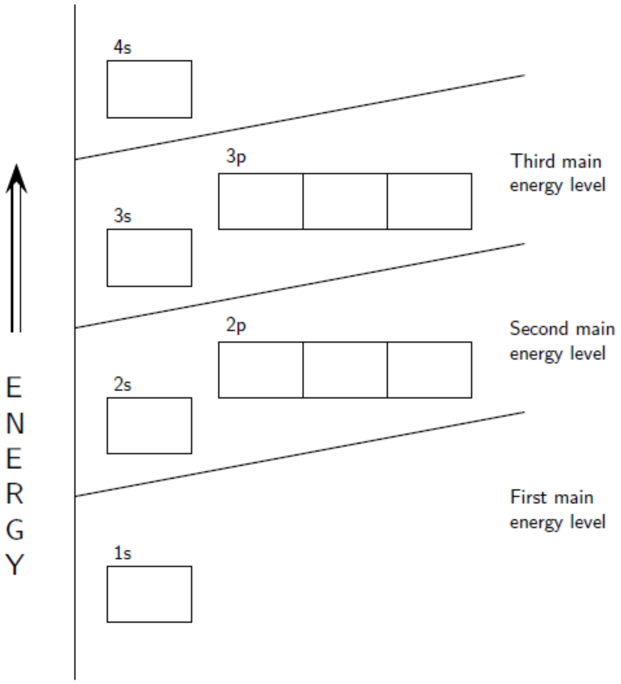


Figure 8.7.4. Energy level diagram

This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ([He]$2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ([He]$2s^2 2p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

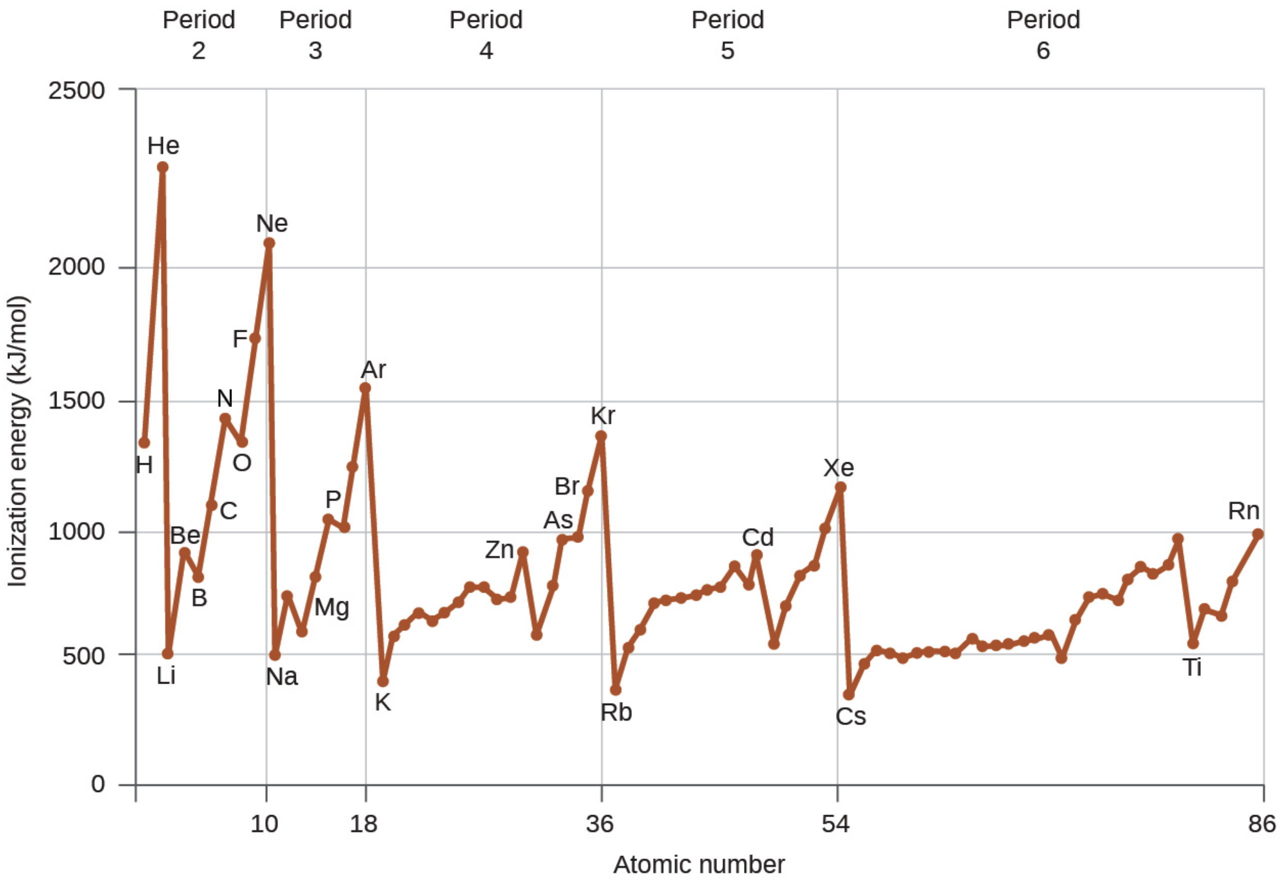
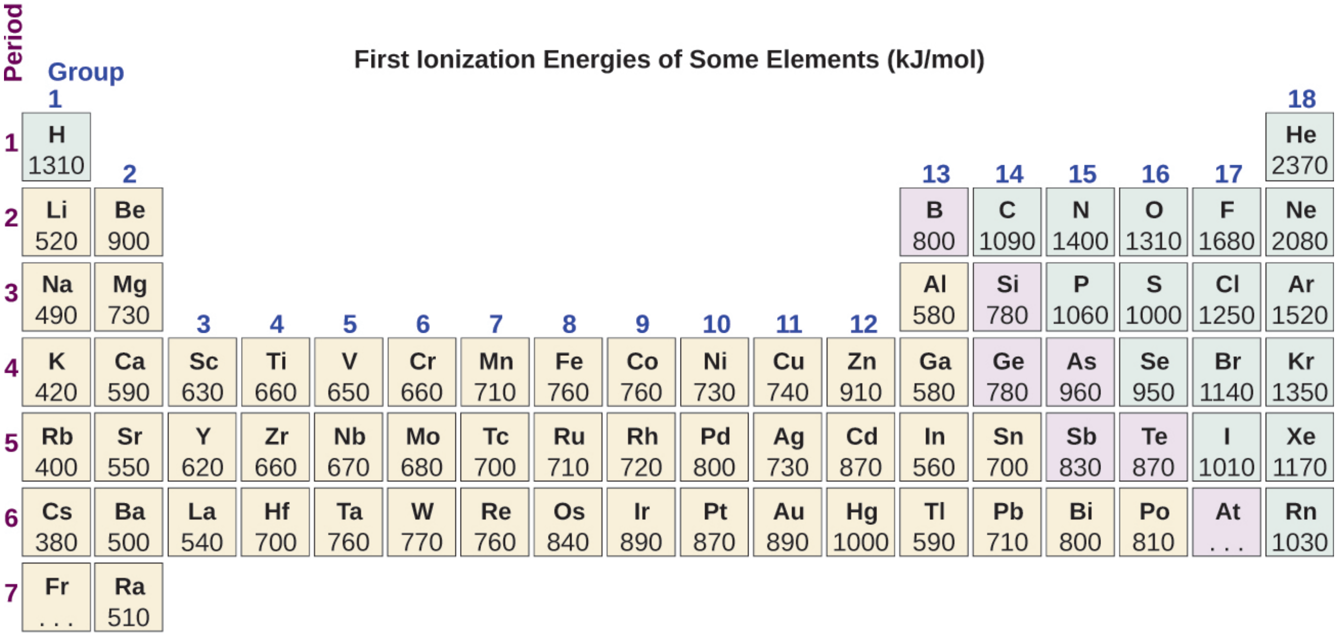


Figure 8.7.5. The first ionization energy of the elements in the first five periods are plotted against their atomic number.



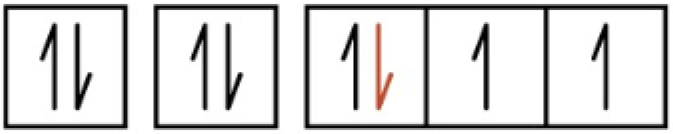
First Ionization Energies of Some Elements (kJ/mol)

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1310																	He 2370
2	Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At . . .	Rn 1030
7	Fr . . .	Ra 510																

Figure 8.7.6. This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 8.7.6.).

O $1s^2 2s^2 2p^4$



1s 2s 2p

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, *successive ionization energies for one element always increase*. As seen in the table below, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Successive Ionization Energies for Selected Elements (kJ/mol)

Element	**IE_1**	**IE_2**	**IE_3**	**IE_4**	**IE_5**	**IE_6**	**IE_7**
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Table 8.7.2 Successive Ionization Energies for Selected Elements (kJ/mol)

Example 8.7.2 – Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(\text{Tl}) < IE_1(\text{Al})$. Ionizing the third electron from Al ($\text{Al}^{2+}?\text{Al}^{3+}+\text{e}^-$) requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(\text{Al}) < IE_3(\text{Al})$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: $IE_1(\text{Tl}) < IE_1(\text{Al}) < IE_3(\text{Al}) < IE_2(\text{Na})$.

Check Your Learning 8.7.2 – Ranking Ionization Energies

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

Variation in Electron Affinities

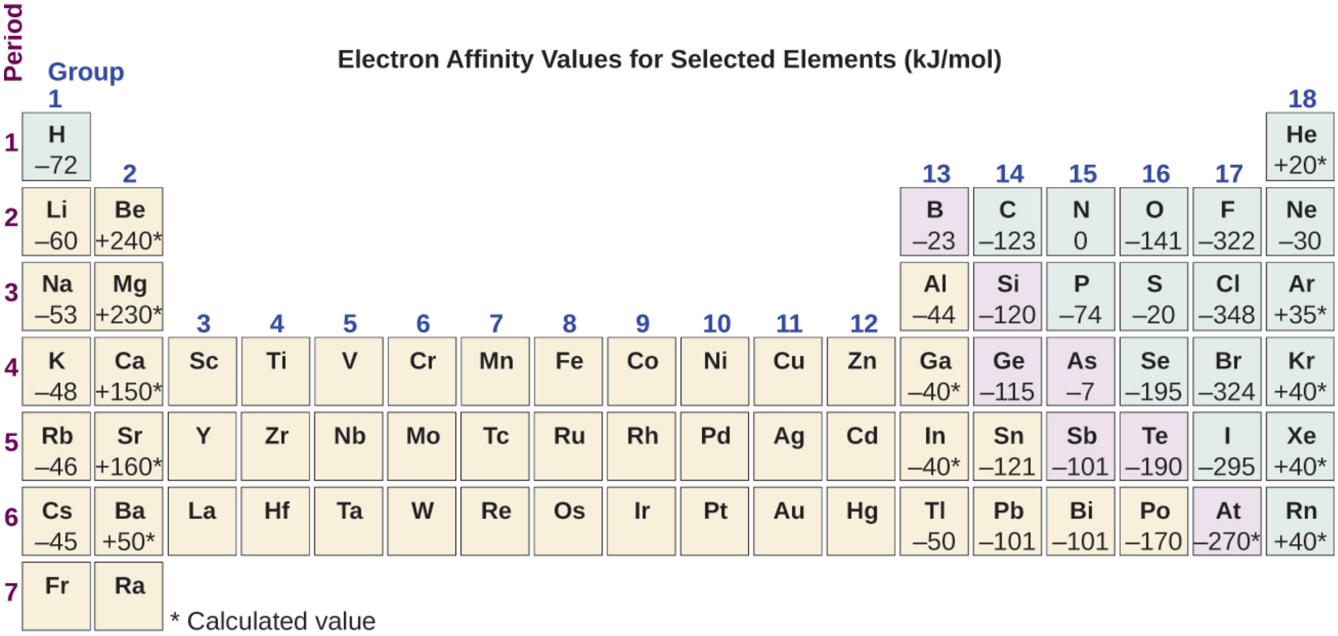
The **electron affinity (EA)** is the energy change for the process of *adding* an electron to a gaseous atom to form an anion (negative ion).

$$\text{X}\,(g) + \text{e}^- \rightarrow \text{X}^-\,(g)\ \text{EA}_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 8.7.7. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the largest negative value (and thus, releases the most energy) of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.



Electron Affinity Values for Selected Elements (kJ/mol)

Group

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H –72																	He +20*
2	Li –60	Be +240*											B –23	C –123	N 0	O –141	F –322	Ne –30
3	Na –53	Mg +230*											Al –44	Si –120	P –74	S –20	Cl –348	Ar +35*
4	K –48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga –40*	Ge –115	As –7	Se –195	Br –324	Kr +40*
5	Rb –46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In –40*	Sn –121	Sb –101	Te –190	I –295	Xe +40*
6	Cs –45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl –50	Pb –101	Bi –101	Po –170	At –270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure 8.7.7. This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Variation in Electronegativities

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity, defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound* (its effect on chemical bonding is discussed in greater detail in Section 9.3). Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found on the left side of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom's electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.

Electronegativity is a function of:

the atom's *ionization energy* (how strongly the atom holds on to its own electrons) and

the atom's *electron affinity* (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

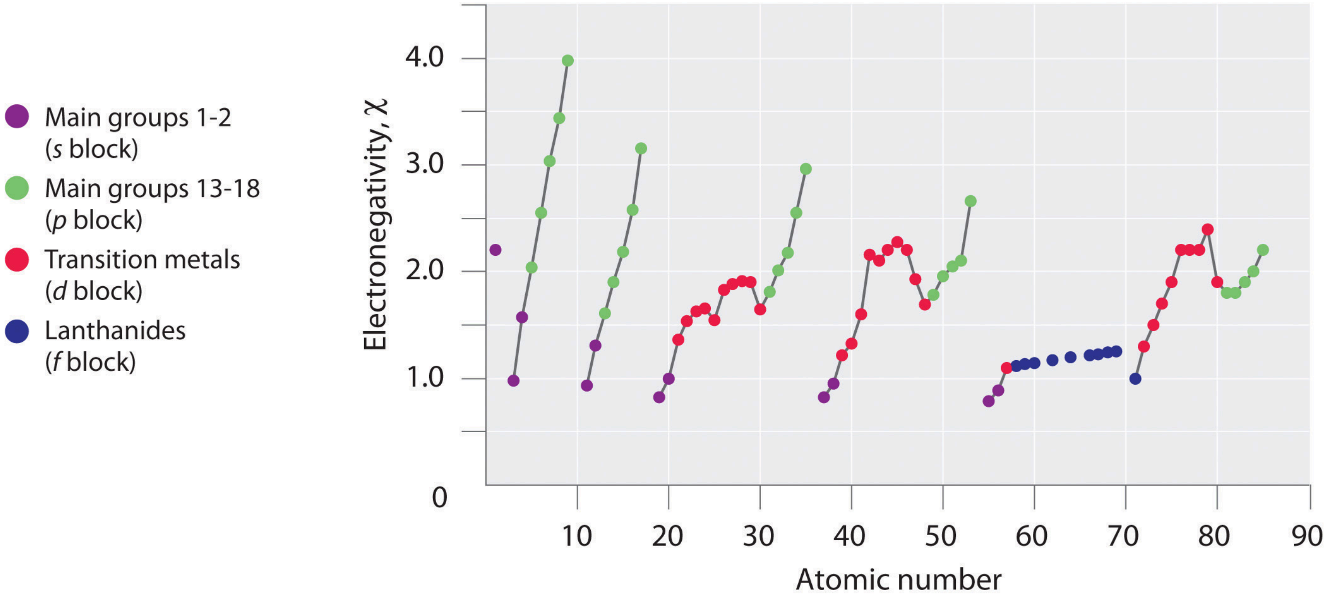


Figure 8.7.8. A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table.

Periodic variations in Pauling's electronegativity values are illustrated in Figures 8.8.7 and 8.8.8. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

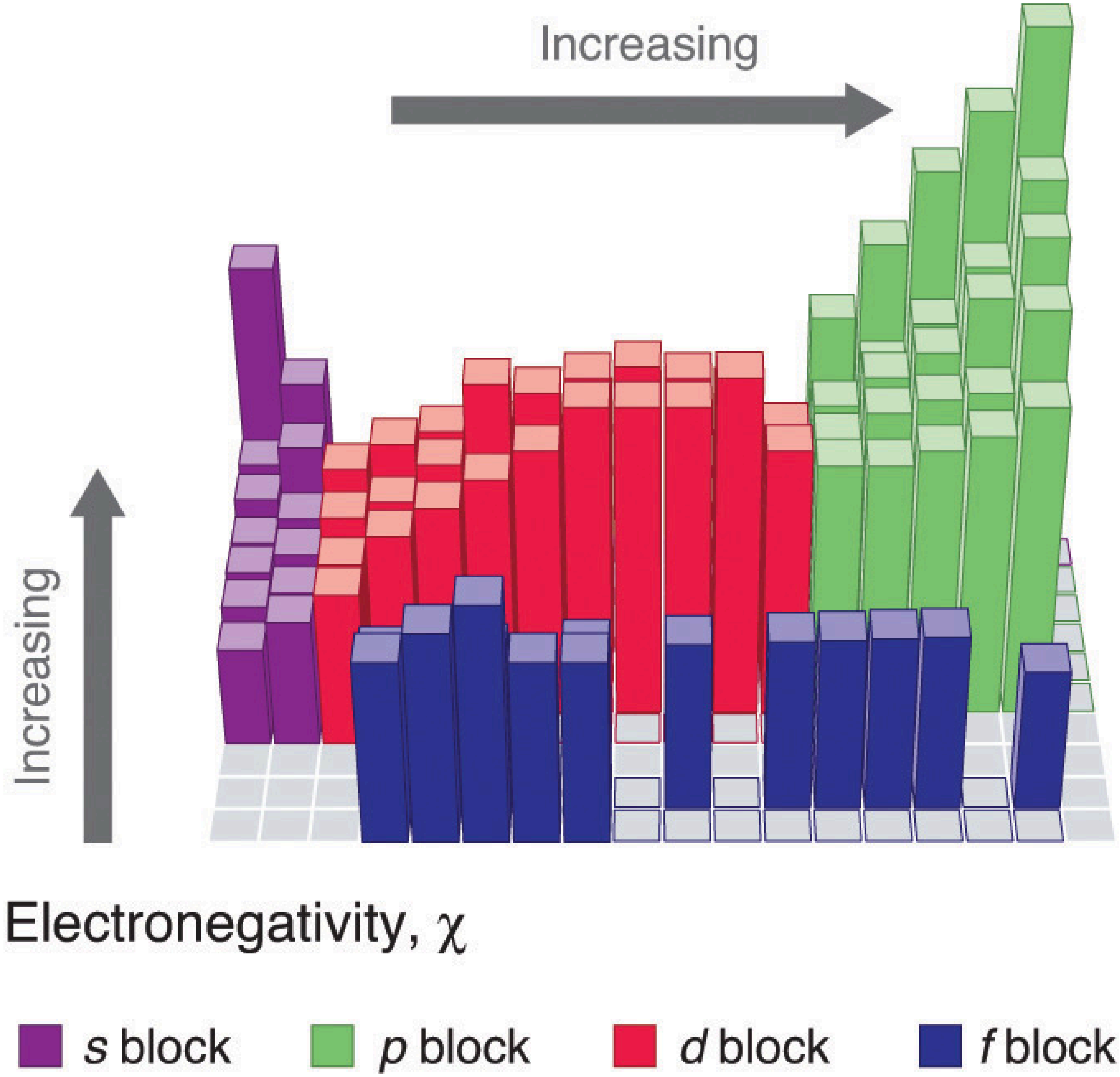
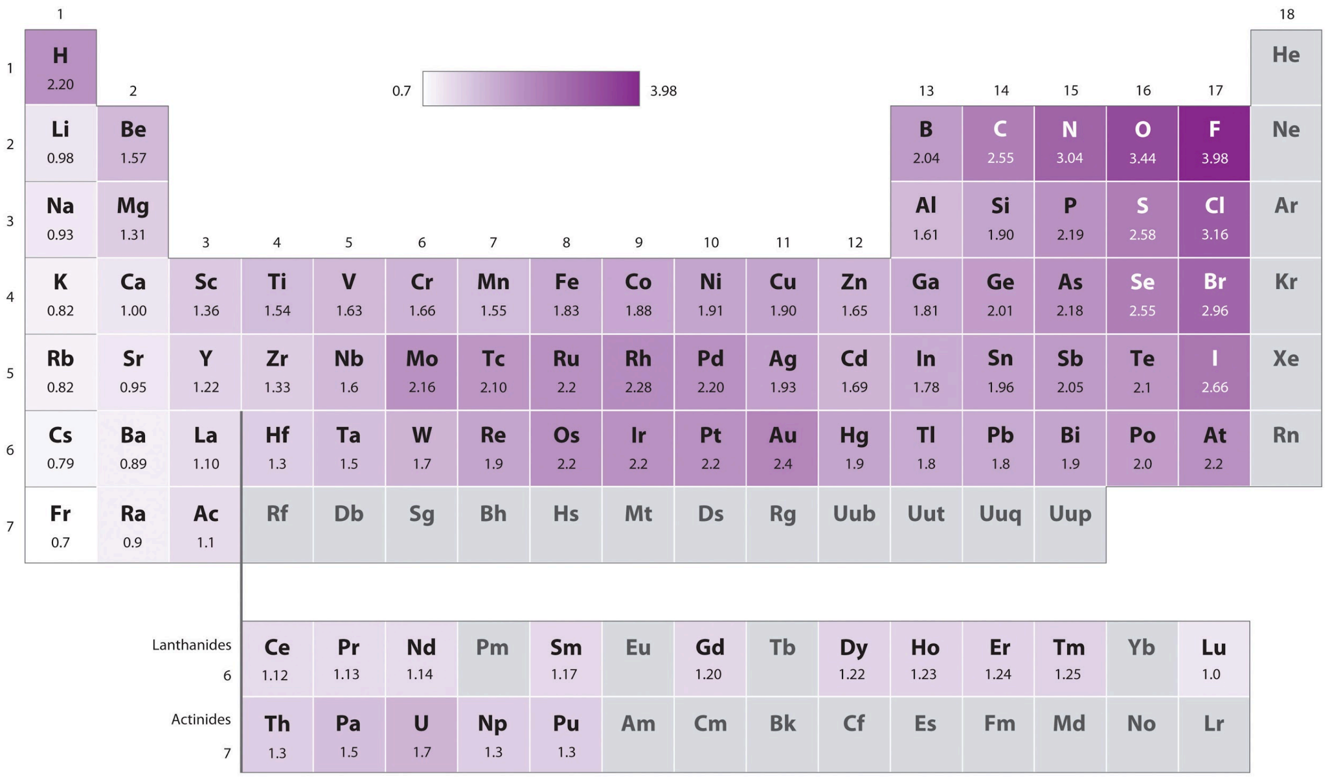


Figure 8.7.9. Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 2.10	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe
6	Cs 0.79	Ba 0.89	La 1.10	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			

Lanthanides 6	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb	Lu 1.0
Actinides 7	Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 8.7.10. Pauling Electronegativity Values on the periodic table.

Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.

★ Questions

1. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

2. Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

3. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

4. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

5. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

6. Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

7. Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?

8. Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, B^{r-}, K^{+}, Mg^{2+}.

9. Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$$E(g) \text{ ? } E^{+}(g) + e^{-}$$

10. Which main group atom would be expected to have the lowest second ionization energy?

11. On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answers

1. Cl
2. O
3. Rb < Li < N < F
4. 15 (5A)
5. Mg < Ca < Rb < Cs
6. $Si^{4+} < Al^{3+} < Ca^{2+} < K^{+}$
7. Se, As^{-}
8. $Mg^{2+} < K^{+} < Br^{-} < As^{3-}$
9. O, IE_1
10. Ra
11. Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

CHAPTER 9

9.1 - ATOMIC PROPERTIES OF CHEMICAL BONDS

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds – the topic of discussion in this chapter.

Types of Chemical Bonds

Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond will be discussed and the general properties found in typical substances in which each bond type occurs.

Ionic bonds result from *electrostatic forces that exist between ions of opposite charge*. These bonds typically involve a metal atom bonding with a nonmetal atom.

Covalent bonds *result from the sharing of electrons between two atoms*. These bonds typically involve one nonmetallic element bonding with another.

Metallic bonds are found in solid metals (copper, iron, aluminum), where the metal atoms form a lattice structure and bonding electrons are free to move throughout the 3-dimensional structure.

In this text, ionic bonds are covered in Section 9.2 whereas covalent bonding is explained in Section 9.3. However, metallic bonding will be discussed in further detail in your future chemistry courses (such as CHM2353: Descriptive Inorganic Chemistry) and so will not be covered in this book.

Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called **Lewis electron dot symbols** (often shortened to **Lewis symbols**) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Lewis symbols:

are a convenient representation of valence electrons

allow you to keep track of valence electrons during bond formation

consist of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]$3s^2 3p^4$, thus there are *six* valence electrons. Its Lewis symbol would therefore be:

Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis symbol is constructed as follows:

The number of dots in the Lewis symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis symbols for the elements in period 3 are given in Figure 9.1.1.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for phosphorus in Figure 9.1.1. The Lewis symbol explains why phosphorus, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Aluminum, which also has three unpaired valence electrons in its Lewis symbol, also tends to form compounds with three bonds, whereas silicon, with four unpaired valence electrons in its Lewis symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

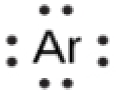
Atoms	Electron Configuration	Lewis Symbol
sodium	[Ne] $3s^1$	
magnesium	[Ne] $3s^2$	
aluminum	[Ne] $3s^2 3p^1$	
silicon	[Ne] $3s^2 3p^2$	
phosphorus	[Ne] $3s^2 3p^3$	
sulfur	[Ne] $3s^2 3p^4$	
chlorine	[Ne] $3s^2 3p^5$	
argon	[Ne] $3s^2 3p^6$	

Figure 9.1.1. Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

9.2 - IONIC BONDING

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 9.2.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.

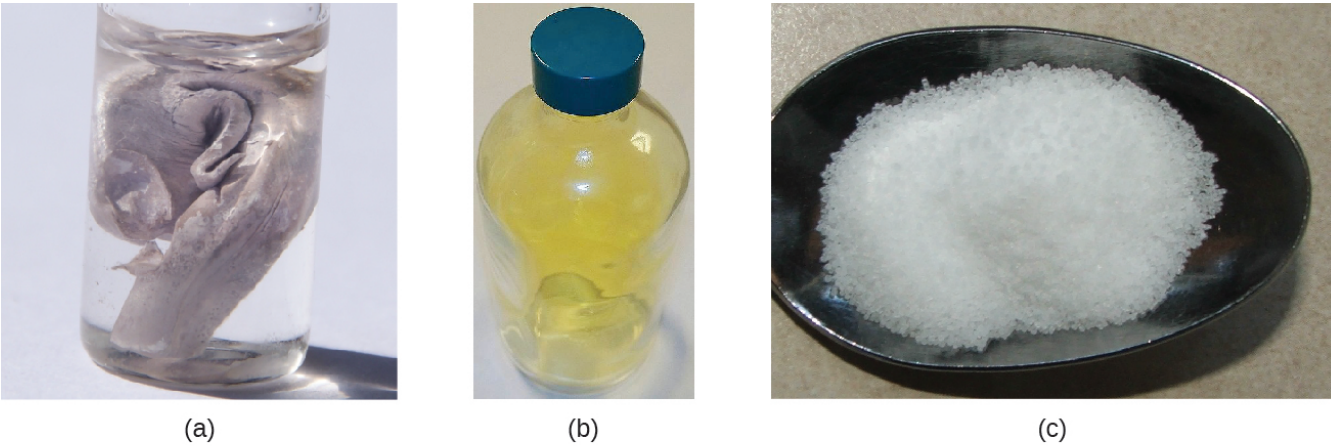
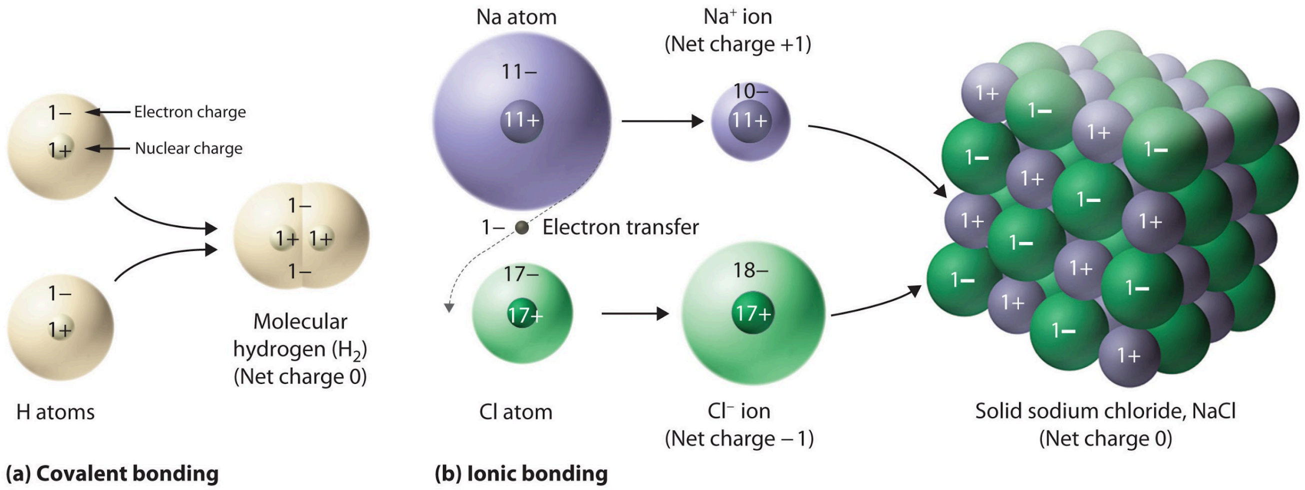


Figure 9.2.1. (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by “Jurii”/Wikimedia Commons)

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure 9.2.2). Therefore, since it is impossible to define a "molecule" of an ionic compound, we use an *empirical formula* (e.g. NaCl) instead of a *molecular formula* to represent the unit cell, and thus the simplest whole number ratio of elements present in the crystal lattice.

Figure 9.2.2. The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na^+ and Cl^- ions form a three-dimensional solid that is held together by attractive electrostatic interactions.



The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. In the next section, we'll examine this attractive force in detail.

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy ($\Delta H_{lattice}$)** of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX\,(s) \rightarrow M^{n+}\,(g) + X^{n-}\,(g) \qquad \Delta H_{lattice}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be endothermic (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy *released* when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{lattice}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous

Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{\text{lattice}}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = C(Z^+)(Z^-)R_0$$

Equation 9.2.1 Lattice Energy of an Ionic Crystal

in which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and R_0 is the interionic distance (the sum of the radii of the positive and negative ions). *Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease.* When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 9.2.1 – Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

Check Your Learning 9.2.1 – Lattice Energy Comparisons

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl? Refer to the figure below of ionic radii to assist you in answering this question.

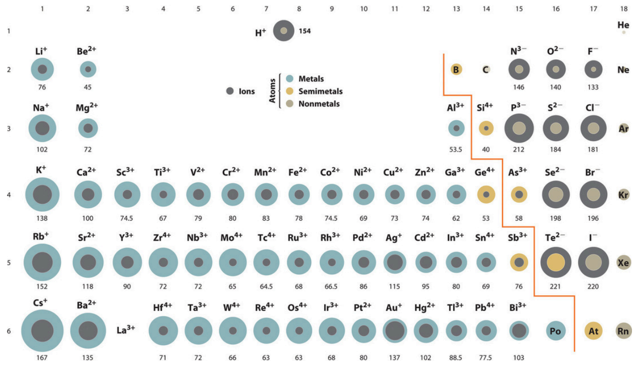


Figure 9.2.3. Periodic table with ionic radii of the most common ionic states of the elements, with the grey regions indicating the ionic radii and the colored regions the neutral radii.

Answer

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

★ Questions

1. Does a cation gain protons to form a positive charge or does it lose electrons?

2. Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

3. Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

a) P
b) Mg
c) Al
d) O
e) Cl
f) Cs

4. Write the electron configuration for each of the following ions:

a) As^{3-}
b) I^{-}
c) Be^{2+}
d) Cd^{2+}
e) O^{2-}
f) Ga^{3+}
g) Li^{+}
h) N^{3-}
i) Sn^{2+}
j) Co^{2+}
k) Fe^{2+}
l) As^{3+}

5. Why is it incorrect to speak of a molecule of solid NaCl?

6. For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

a) MgO
b) SrO
c) KF
d) CsF
e) MgF_2

★★ Questions

7. The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

8. Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and K^{+} have similar radii; S^{2-} and Cl^{-} have similar radii. Explain your choices.

a) K_2O or Na_2O
b) K_2S or BaS
c) KCl or BaS
d) BaS or $BaCl_2$

Answers

1. The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

2. P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

3. (a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}

4. (a) $[Ar]4s^2 3d^{10} 4p^6$; (b) $[Kr]4d^{10} 5s^2 5p^6$ (c) $1s^2$ (d) $[Kr]4d^{10}$; (e) $[He]2s^2 2p^6$; (f) $[Ar]3d^{10}$; (g) $1s^2$ (h) $[He]2s^2 2p^6$ (i) $[Kr]4d^{10} 5s^2$ (j) $[Ar]3d^7$ (k) $[Ar]3d^6$, (l) $[Ar]3d^{10} 4s^2$

5. NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

6. d)

7. 4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

8. (a) Na_2O; Na^{+} has a smaller radius than K^{+}; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

9.3 - COVALENT BONDING

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called covalent bonds.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction *between* molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, when ionic compounds are dissolved in water, it produces an aqueous solution that is a good conductor of electricity (due to the dissociation of the cations and anions). However, when covalent compounds are dissolved in water, they tend to ionize poorly or not at all, resulting in aqueous solutions of very weak conductivity. As pure substances, since they are electrically neutral, they are poor conductors of electricity in any state (pure liquid, solid, or gas).

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 9.3.1 illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the x-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the x-axis), their atomic orbitals begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

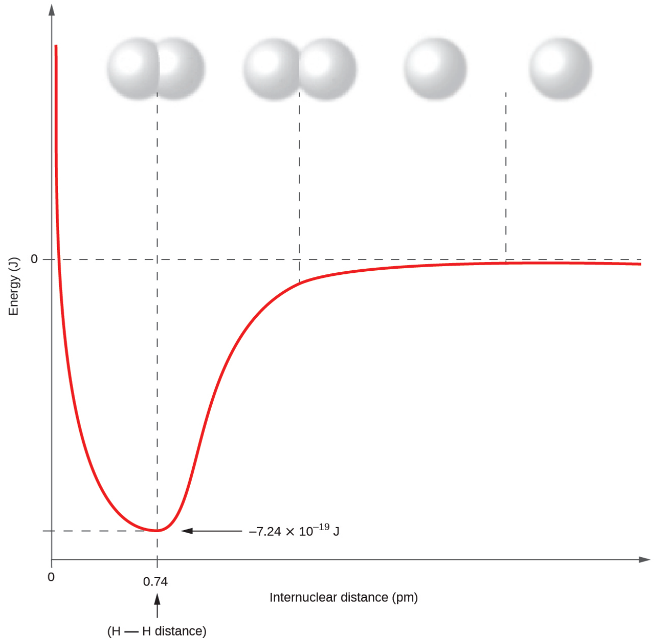


Figure 9.3.1. The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved. These graphs, where potential energy is plotted as a function of internuclear distance, are known as *Morse Curves*.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$H_2(g)\ ?\ 2H(g) \quad \Delta H = 436\text{ kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2H(g)\ ?\ H_2(g) \quad \Delta H = -436\text{ kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a **pure covalent bond** (or **nonpolar covalent bond**). Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$Cl + Cl \rightarrow Cl_2$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are of different elements, the bonding electrons may still be shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a **polar covalent bond**, characterized by a *partial* positive charge on one atom and a *partial* negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 9.3.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 9.3.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

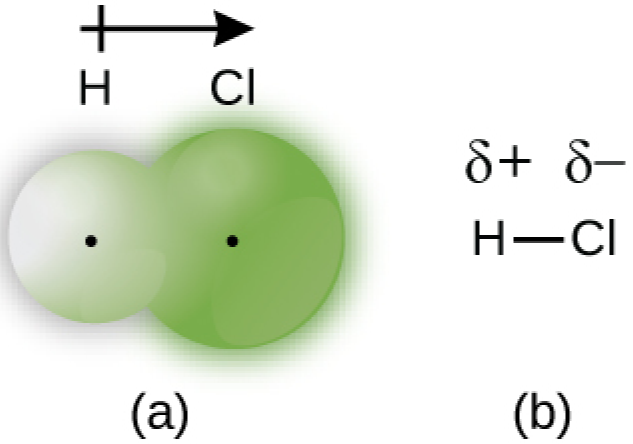


Figure 9.3.2. (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ^+ and δ^- indicate the polarity of the H–Cl bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ^+) or a partial negative charge (δ^-). This symbolism is shown for the H–Cl molecule in Figure 9.3.2.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called **electronegativity**. Electronegativity (EN) is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 9.3.4 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 9.3.3). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with other atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

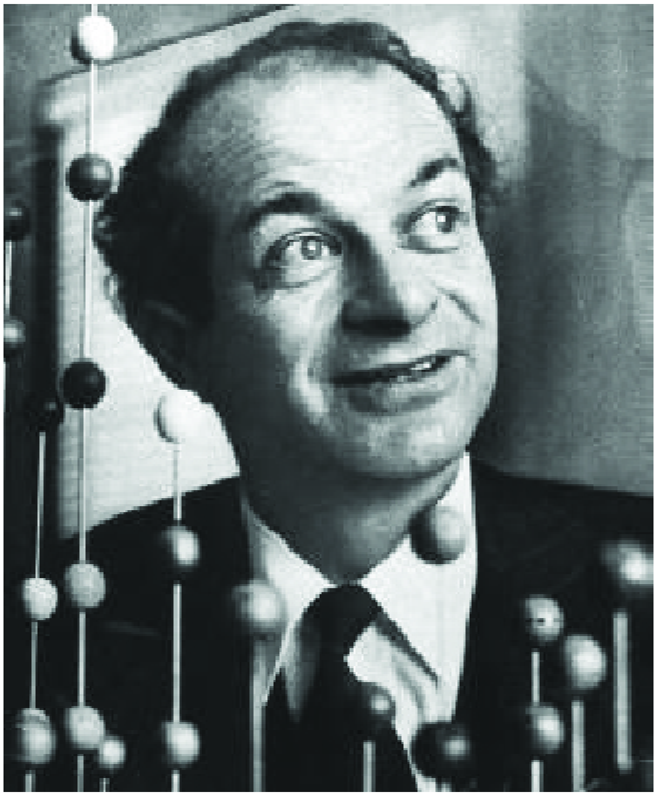


Figure 9.3.3. Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

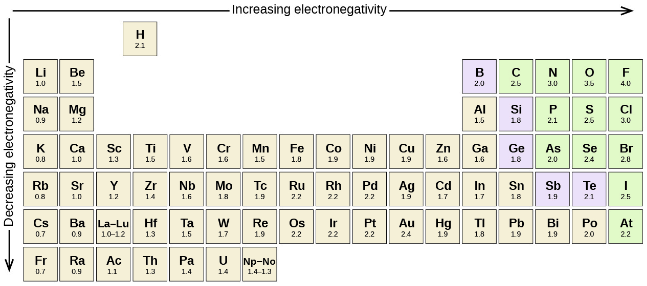


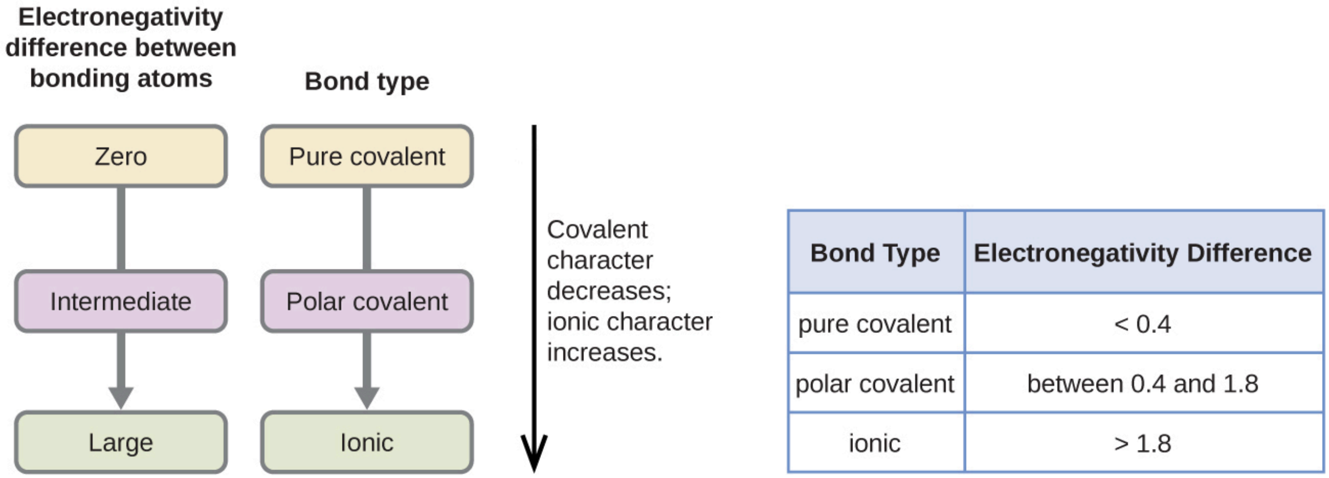
Figure 9.3.4. The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a *measurable physical quantity*, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol (this is discussed in detail in section 8.7). Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a *bond*. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale, with values ranging from 0 to 4. You may encounter other tables of electronegativity values which may slightly differ from those derived by Pauling, due to differences in how those values were determined. In general, however, the periodic trends described above still hold true, regardless of how the EN values are defined.

Electronegativity and Bond Type

The absolute value of the *difference* in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 9.3.5 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 9.3.5. As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 9.3.5. It's important to note that this table is just a general guide to determining the type of bond between atoms – many exceptions exist. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

Hence, keep in mind that at the end of the day, the best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Example 9.3.1 – Electronegativity and Bond Polarity

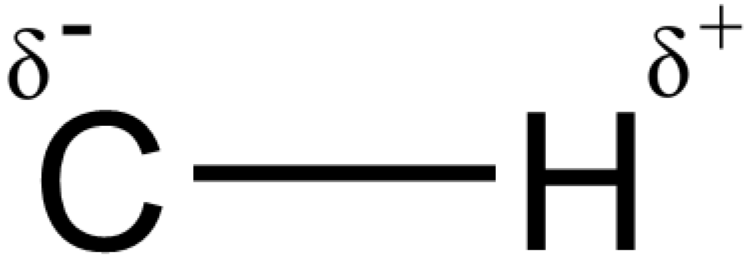
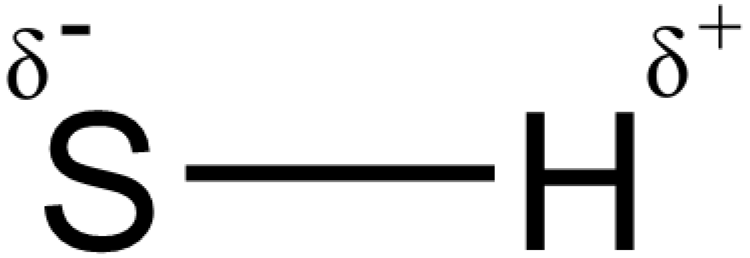
Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 9.3.4, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. The table below shows these bonds in order of increasing polarity.

Bond Polarity and Electronegativity Difference

Bond	**ΔEN**	**Polarity**
C–H	0.4	
S–H	0.4	
C–N	0.5	

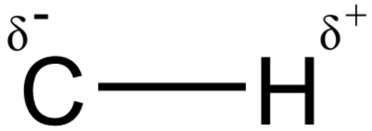
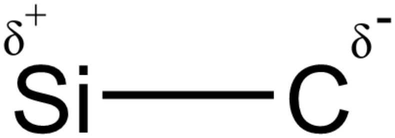
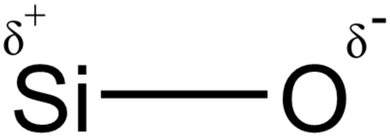
N–H	0.9	
C–O	1.0	
O–H	1.4	

Table 9.3.1 Bond Polarity and Electronegativity Difference

Check Your Learning 9.3.1 – Electronegativity and Bond Polarity

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 9.3.4, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	
Si–C	0.7	
Si–O	1.7	

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy (see previous discussion on the "Formation of Covalent Bonds"). The stronger a bond, the greater the energy required to break it.

The energy required to break a specific covalent bond in one mole of gaseous molecules is called the **bond energy** or the **bond dissociation energy (BE)**. The bond energy for a diatomic molecule, $D_{X–Y}$, is defined as the standard enthalpy change for the endothermic reaction:

$$XY\,(g) \rightarrow X\,(g) + Y\,(g) \quad DX - y = \Delta H^{\circ}$$

For example, the bond energy of the pure covalent H–H bond, $D_{H–H}$, is 436 kJ per mole of H–H bonds broken:

$$H_2\,(g) \rightarrow 2H\,(g) \quad DH\text{-}H = \Delta H^{\circ} \ =436kJ$$

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH_4, 1660 kJ, is equal to the standard enthalpy change of the reaction:

$$CH_4\,(g) \rightarrow C\,(g) + 4H\,(g) \quad \Delta H^{\circ} = 1660kJ$$

The average C–H bond energy, D_{C-H}, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the *average bond energy*, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds, with a comparison of bond lengths and bond strengths, appear in the table below. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C–O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

Table 9.3.2 Average Bond Lengths and Bond Energies for Some Common Bonds

★ Questions

1. What information can you use to predict whether a bond between two atoms is covalent or ionic?

2. Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

a) Cl_2CO
b) MnO
c) NCl_3
d) $CoBr_2$
e) K_2S
d) CO
f) CaF_2
g) HI
h) CaO
i) IBr
j) CO_2

3. From its position in the periodic table, determine which atom in each pair is more electronegative:

a) Br or Cl
b) N or O
c) S or O
d) P or S
e) Si or N
f) Ba or P
g) N or K

4. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

a) C, F, H, N, O
b) Br, Cl, F, H, I
c) F, H, O, P, S
d) Al, H, Na, O, P
e) Ba, H, N, O, As

5. Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

6. Identify the more polar bond in each of the following pairs of bonds:

a) HF or HCl
b) NO or CO
c) SH or OH
d) PCl or SCl
e) CH or NH
f) SO or PO

g) CN or NN

7. Which bond in each of the following pairs of bonds is the strongest?

a) C–C or C=C

b) C–N or C≡N

c) C≡O or C=O

d) H–F or H–Cl

e) C–H or O–H

f) C–N or C–O

8. Using the standard enthalpy of formation data in Appendix, show how the standard enthalpy of formation of HCl(*g*) can be used to determine the bond energy (in kJ).

9. Using the standard enthalpy of formation data in Appendix, determine which bond is stronger: the S–F bond in SF4(*g*) or in SF6(*g*)?

10. Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:

Answers

1. Hints that can be used in order to determine if a molecule is either ionic or covalent include the location of the elements and the electronegativity difference. The further apart molecules are, the higher the electronegativity difference will be indicating its bond character. As well, calculating the electronegativity difference will indicate if it is either ionic or covalent in behaviour. The larger the value will characterize as ionic versus smaller values will characterize as covalent.

2. Ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

3. (a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

4. (a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

5. N, O, F, and Cl

6. (a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

7. (a) C=C; (b) C≡N; (c) C≡O; (d) H–F; (e) O–H; (f) C–O

8.

$$HCl_{(g)} \rightarrow 12H_{2\,(g)} + 12Cl_{2\,(g)} \quad \Delta H_1^\circ = -\Delta H^\circ_{f[HCl(g)]}$$

$$12H_{2\,(g)} \rightarrow H_{(g)} \quad \Delta H_2^\circ = \Delta H^\circ_{f[H(g)]}$$

$$12Cl_{2\,(g)} \rightarrow Cl_{(g)} \quad \Delta H_3^\circ = -\Delta H^\circ_{1[Cll(g)]}$$

$$HCl_{(g)} \rightarrow H_{(g)} + Cl_{(g)} \quad \Delta H^\circ_{298} = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ$$

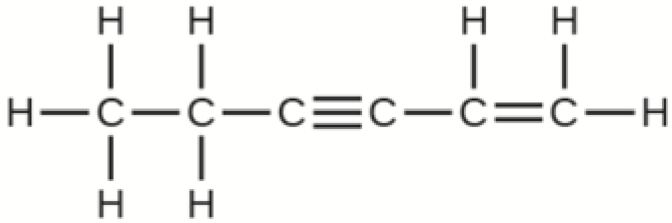
$$D_{\mathrm{HCl}} = \Delta H^{\circ}_{298} = \Delta H^{\circ}_{\mathrm{f[HCl(g)]}} + \Delta H^{\circ}_{\mathrm{f[Cl(g)]}}$$

$$= -(-92.307\ \mathrm{kJ}) + 217.97\ \mathrm{kJ} + 121.3\ \mathrm{kJ}$$

$$= 431.6\ \mathrm{kJ}$$

9. The S–F bond in SF_4 is stronger.

10. The C-C single bonds are longest.

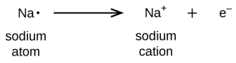


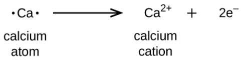
9.4 - DEPICTING MOLECULES AND IONS WITH LEWIS STRUCTURES

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting chemical bonds and structures, namely Lewis symbols for ionic compounds and Lewis structures for molecular compounds.

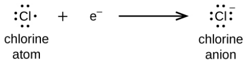
Lewis Symbols – Ionic Compounds

Recall that Lewis symbols can be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:





Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



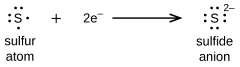


Figure 9.4.1 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

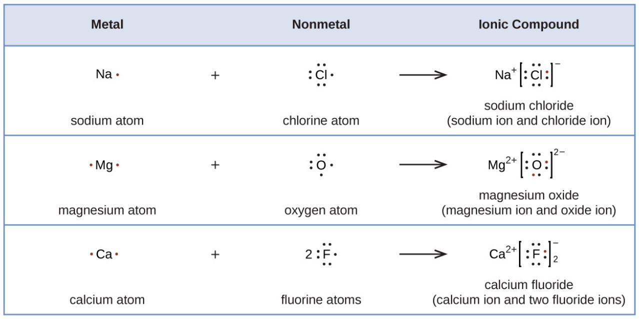


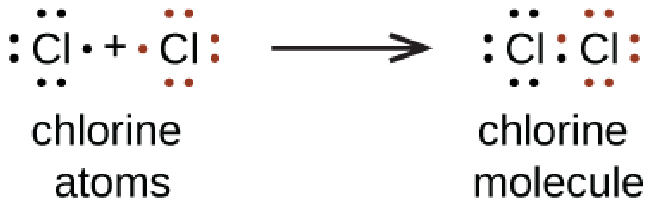
Figure 9.4.1. Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures – Molecular Compounds

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in **Lewis**

structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:

The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called **lone pairs**) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

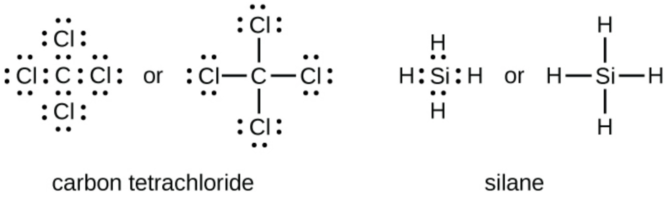


A single shared pair of electrons is called a **single bond**. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

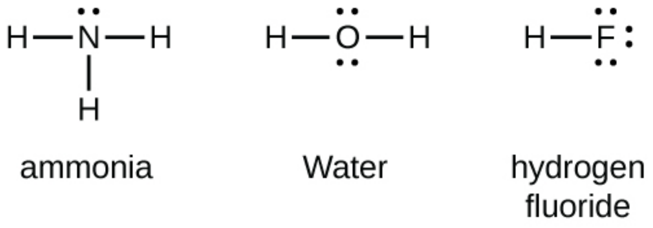
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the **octet rule**.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated below for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements, lanthanides, and actinides also do not follow the octet rule.



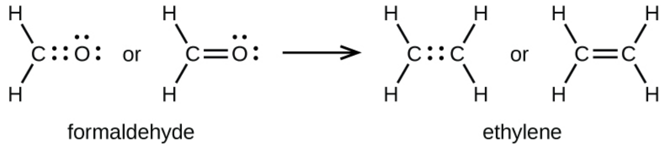
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:

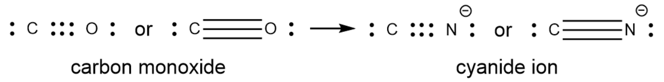
Double and Triple Bonds



As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A **double bond** forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

A **triple bond** forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):

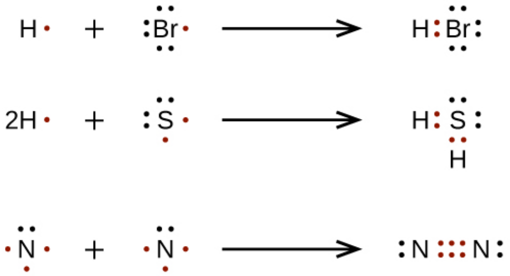




In the Lewis bonding model, we frequently describe the number of electron pairs that hold two atoms together as the **bond order**. For a single bond, such as the C–C bond in $H_3C–CH_3$, the bond order is one. For a double bond (such as $H_2C=CH_2$), the bond order is two. For a triple bond, such as $HC≡CH$, the bond order is three. Fractional bond orders are also possible, which we will see later on in our discussion of resonance structures.

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.

Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).

Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.

Place all remaining electrons on the central atom.

Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

For a molecule, we add the number of valence electrons on each atom in the molecule:

SiH_4
Si: 4 valence electrons/atom x 1 atom = 4
+ H: 1 valence electron/atom x 4 atoms = 4
= 8 valence electrons

For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

CHO_2^-
C: 4 valence electrons/atom x 1 atom = 4
H: 1 valence electrons/atom x 1 atom = 1
O: 6 valence electron/atom x 2 atoms = 12
+1 additional electron = 1
= 18 valence electrons

For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

NO^+
N: 5 valence electrons/atom x 1 atom = 5
O: 6 valence electron/atom x 1 atoms = 6
+-1 electron (positive charge) = -1
= 10 valence electrons

Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

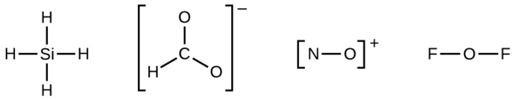
OF_2

O: 6 valence electrons/atom x 1 atom = 6

+F: 7 valence electron/atom x 2 atoms = 14

= 20 valence electrons

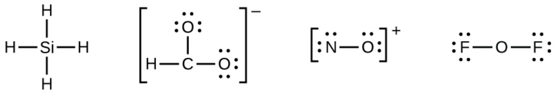
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

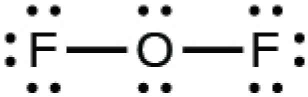
There are no remaining electrons on SiH_4, so it is unchanged:



4. Place all remaining electrons on the central atom.

For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.

For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

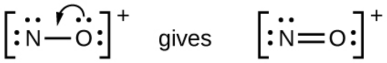


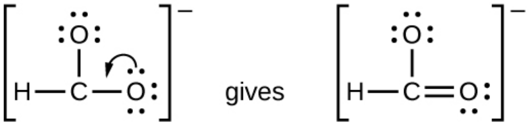
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

SiH_4: Si already has an octet, so nothing needs to be done.

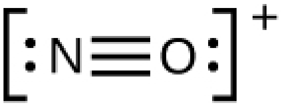
CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:

NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:





This still does not produce an octet, so we must move another pair, forming a triple bond:



In OF_2, each atom has an octet as drawn, so nothing changes.

Example 9.4.1 – Writing Lewis Structures – 1

NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

1. *Calculate the number of valence electrons.*

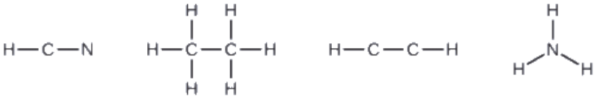
HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10

H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14

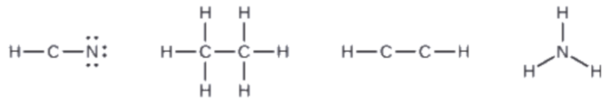
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10

NH_3: (5 × 1) + (3 × 1) = 8

2. *Draw a skeleton and connect the atoms with single bonds.* Remember that H is never a central atom:



3. *Where needed, distribute electrons to the terminal atoms:*



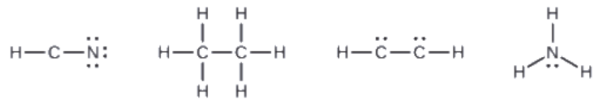
HCN: six electrons placed on N

H_3CCH_3: no electrons remain

HCCH: no terminal atoms capable of accepting electrons

NH_3: no terminal atoms capable of accepting electrons

4. *Where needed, place remaining electrons on the central atom:*



HCN: no electrons remain

H_3CCH_3: no electrons remain

HCCH: four electrons placed on carbon

NH_3: two electrons placed on nitrogen

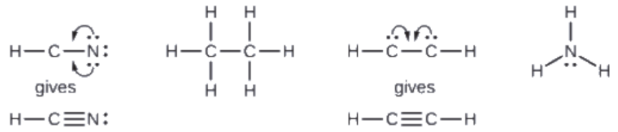
5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

HCN: form two more C–N bonds

H_3CCH_3: all atoms have the correct number of electrons

HCCH: form a triple bond between the two carbon atoms

NH_3: all atoms have the correct number of electrons



Check Your Learning 9.4.1 – Writing Lewis Structures – 1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer

Example 9.4.2 – Writing Lewis Structures – 2

Write the Lewis electron structure for each species.

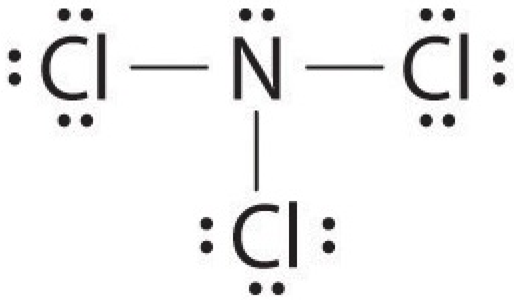
(a) NCl_3

(b) S_2^{2-}

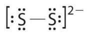
(c) NOCl

Solution

(a) Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for $(3 \times 2) + (3 \times 2 \times 3) = 24$ electrons. We then place the remaining 2 electrons on the central N:



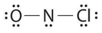
(b) In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



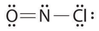
(c) Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:

O – N – Cl

Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:

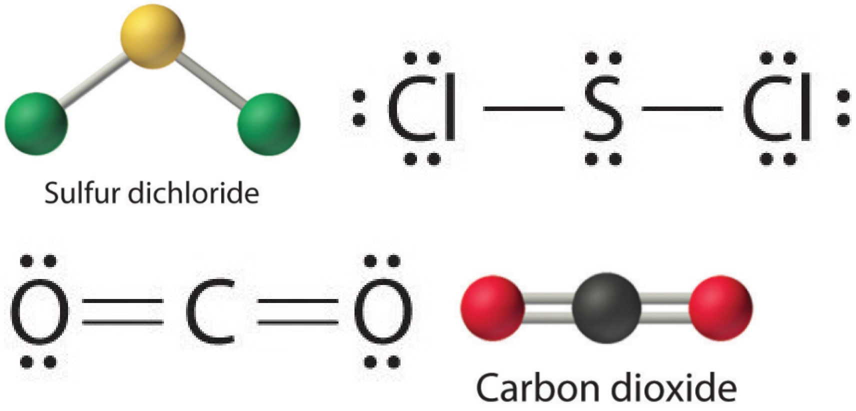


All atoms now have octet configurations.

Check Your Learning 9.4.2 – Writing Lewis Structures – 2

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer



Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.

Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.

Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

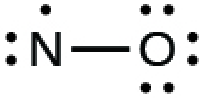
We call molecules that contain an odd number of electrons **free radicals**. Nitric oxide, NO, is an example of an odd-electron molecule; one way this species is produced is in internal combustion engines when oxygen and nitrogen react at high temperatures.

To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:

N–O

3.*Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

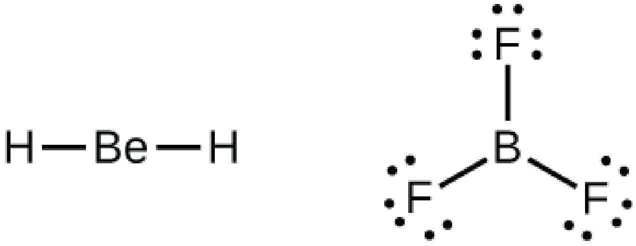


4.*Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.

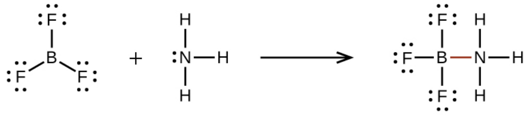
5.*Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons)

Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called **hypervalent molecules** (or referred to as having **expanded octets**). Figure 9.4.2 shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

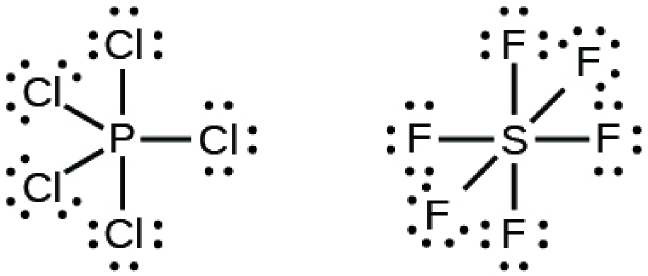
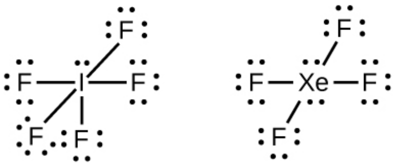


Figure 9.4.2. In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:

You may be wondering why the structures were drawn with non-90º angles in the above scheme. The angles shown reflect the relative geometry of the atoms and lone pairs in the overall molecule. This will become more clear after the section explaining VSEPR theory When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.



Example 9.4.3 – Writing Lewis Structures: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

1. *Calculate the number of valence electrons:*

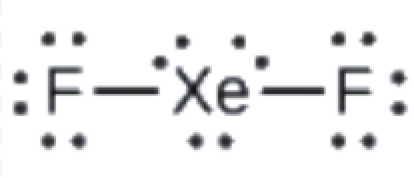
$$XeF_2: 8 + (2 \times 7) = 22$$

$$XeF_6: 8 + (6 \times 7) = 50$$

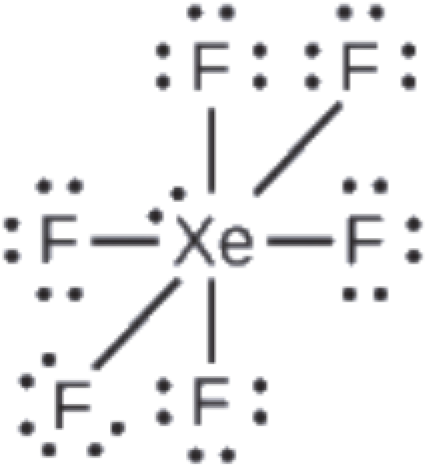
2. *Draw a skeleton joining the atoms by single bonds.* Xenon will be the central atom because fluorine cannot be a central atom:

3. *Distribute the remaining electrons.*

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



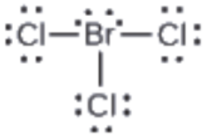
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:

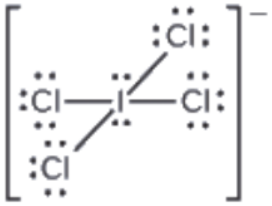


Check Your Learning 9.4.3 – Writing Lewis Structures: Octet Rule Violations

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Answer





Calculating Formal Charge

As we have seen in some cases, there is seemingly more than one valid structure for a molecule. We introduce the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

The **formal charge** of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

formal charge = # valence shell electrons (free atom) – # lone pair electrons – (1 / 2) # bonding electrons

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

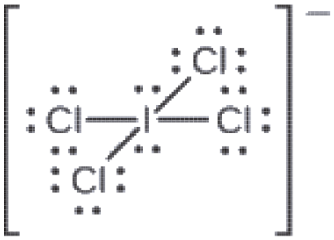
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 9.4.4 – Calculating Formal Charge from Lewis Structures – 1

Assign formal charges to each atom in the interhalogen ion ICl_4^-.

Solution

1. *We divide the bonding electron pairs equally for all I–Cl bonds:*



2. *We assign lone pairs of electrons to their atoms*. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

3. *Subtract this number from the number of valence electrons for the neutral atom:*

I: 7 – 8 = –1

Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Check Your Learning 9.4.4 – Calculating Formal Charge from Lewis Structures – 1

Calculate the formal charge for each atom in the carbon monoxide molecule:

:C≡O:

Answer

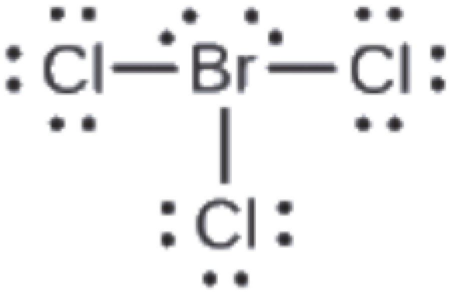
C −1, O +1

Example 9.4.5 – Calculating Formal Charge from Lewis Structures – 2

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*



2. *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons and the Br atom has seven electrons.

3. *Subtract this number from the number of valence electrons for the neutral atom.* This gives the formal charge:

Br: 7 – 7 = 0

Cl: 7 – 7 = 0

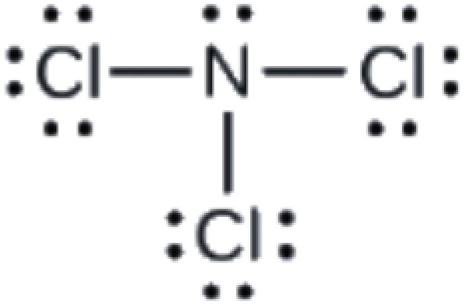
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Check Your Learning 9.4.5 – Calculating Formal Charge from Lewis Structures – 2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.

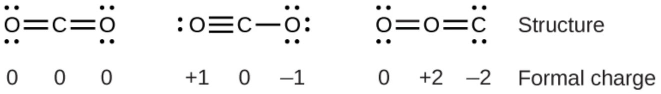
If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.

Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.

When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

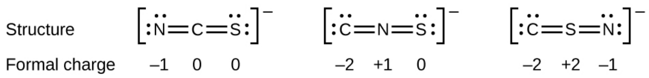
To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).



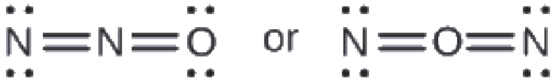
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^-, NCS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).



Example 9.4.6 – Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution

Determining formal charge yields the following:

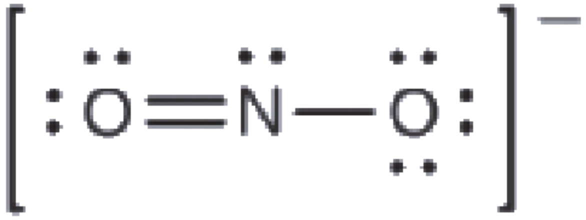
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:

The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

Check Your Learning 9.4.6

What is the most likely molecular structure for the nitrite (NO_2^-) ion?

Solution



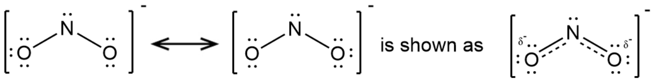
Resonance

You may have noticed that the nitrite anion in the example above can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

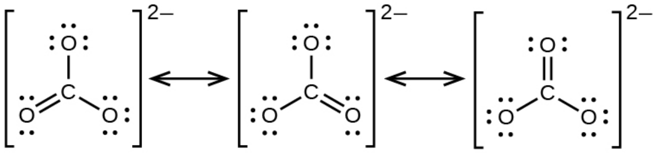
It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. In terms of bond orders, this corresponds to the *average* between a bond order of 1 and 2; hence, we say that each nitrogen-oxygen bond has a bond order of 1.5.

We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-}, provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same, each one the average of two single bonds and one double bond. This corresponds to a bond order of 4/3, or
$1.\bar{3}$

Drawing Resonance Structures – Additional Practice
This online interactive site includes many examples to practice drawing resonance structures.

★ Questions

1. Write the Lewis symbols for each of the following ions:
   - a) As^{3-}
   - b) I^{-}
   - c) Be^{2+}
   - d) O^{2-}
   - e) Ga^{3+}
   - f) Li^{+}

g) N^{3-}

2. Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

a) MgS
b) Al_2O_3
c) $GaCl_3$
d) K_2O
e) Li_3N
f) KF

3. Write Lewis structures for the following:

a) O_2
b) H_2CO
c) AsF_3
d) ClNO
e) $SiCl_4$
f) H_3O^+
g) NH^{4+}
h) BF^{4-}
i) HCCH
j) ClCN
k) C_2^{2+}

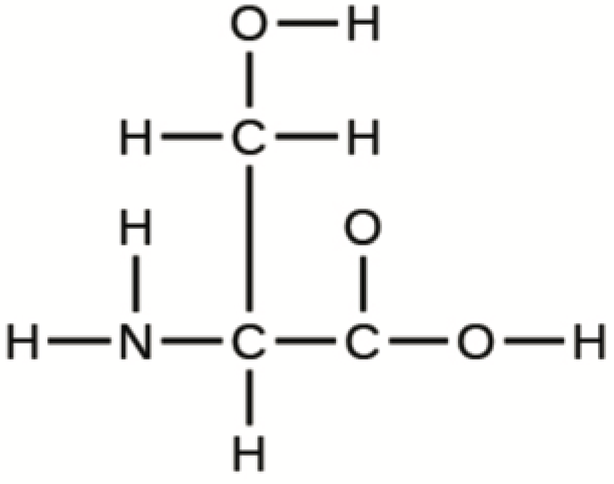
4. Write Lewis structures for the following:

a) SeF_6
b) XeF_4
c) $SeCl^{3+}$
d) Cl_2BBCl_2 (contains a B–B bond)

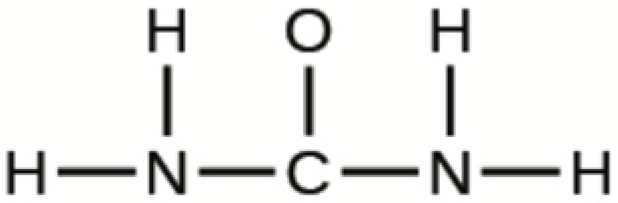
5. Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

6. The arrangement of atoms in several biologically important molecules is given below. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

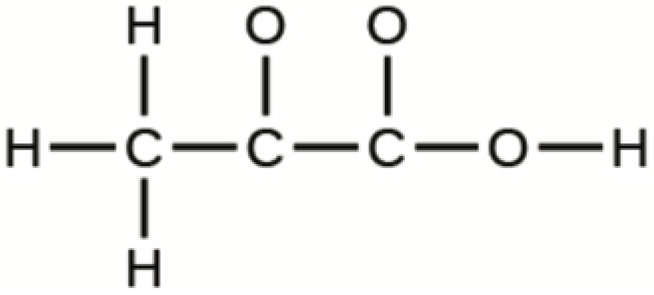
a) The amino acid serine:



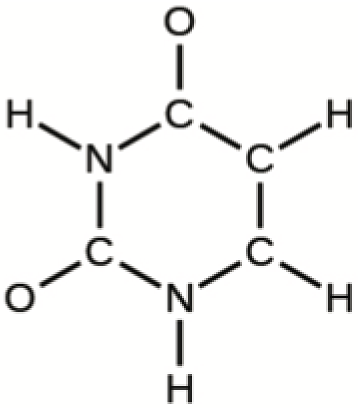
b) Urea:



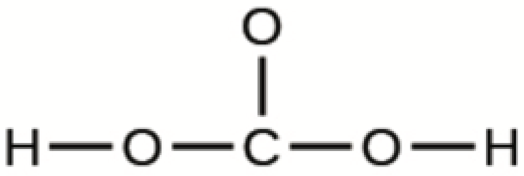
c) Pyruvic acid:



d) Uracil:



e) Carbonic acid:



7. How are single, double, and triple bonds similar? How do they differ?

★★ Questions

8. Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the C^{l-} ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

9. Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

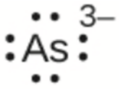
10. Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

11. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

Answers

1.

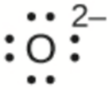
a) Eight electrons



b) Eight electrons

c) No electrons, Be^{2+}

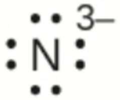
d) Eight electrons



e) No electrons, Ga^{3+}

f) No electrons, Li^{+}

g) Eight electrons



2.

a) 

b) 

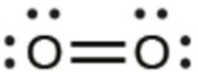
c) 

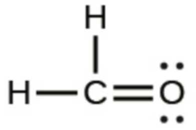
d) 

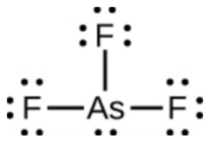
e) 

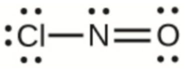
f) 

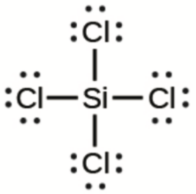
3. In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

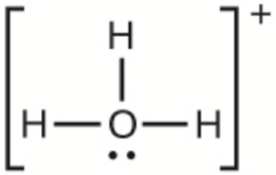
a) 

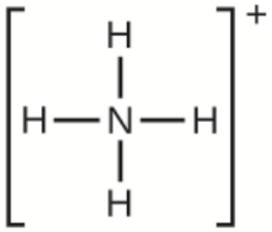
b) 

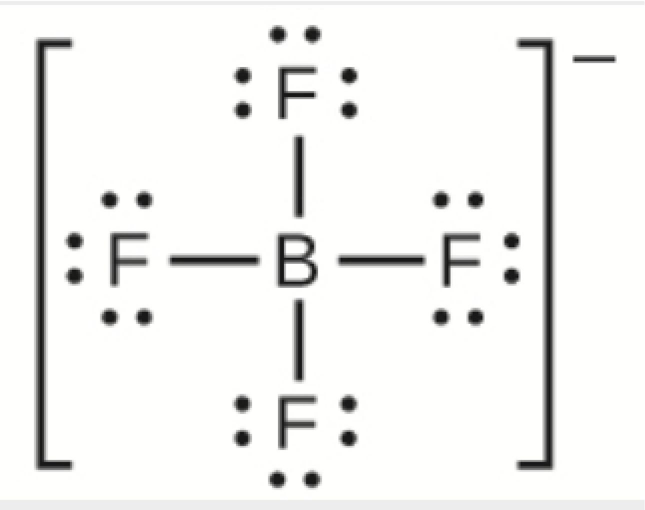
c) 

d) 

e) 

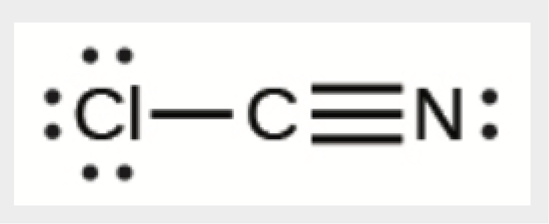
f) 

g) 



h)

i)



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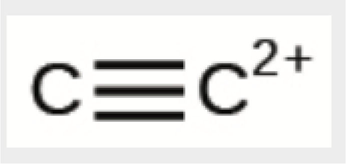
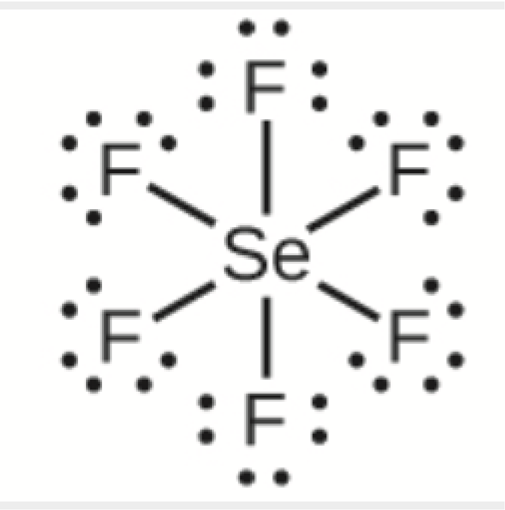
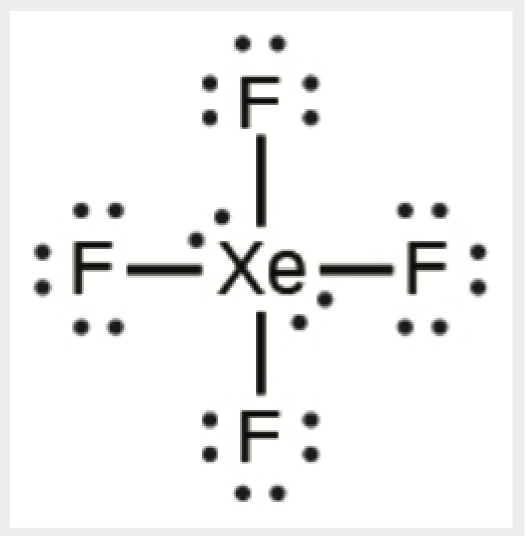


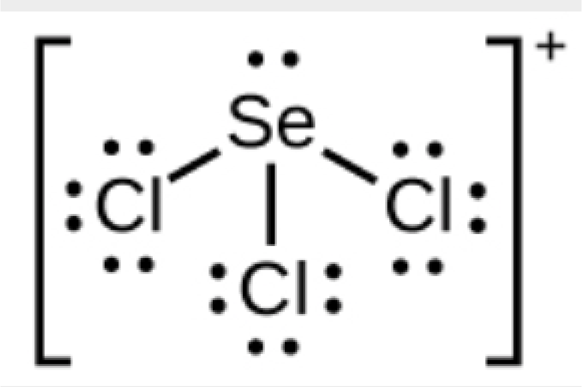
k)

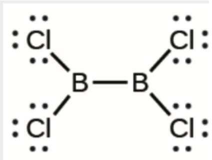
4.



a)

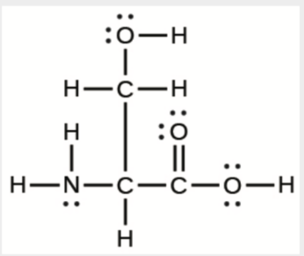
b) 

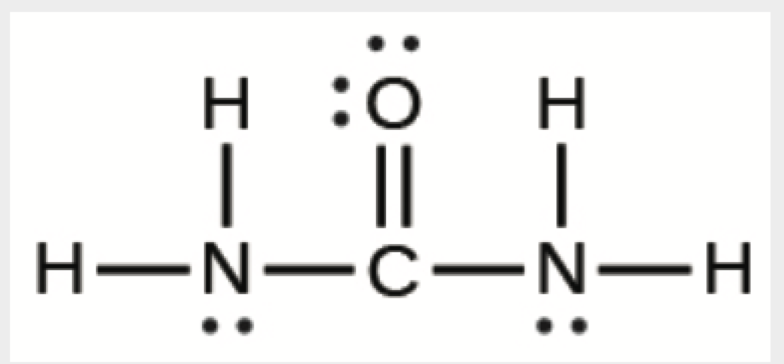
c) 

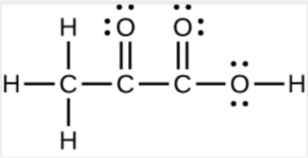
d) 

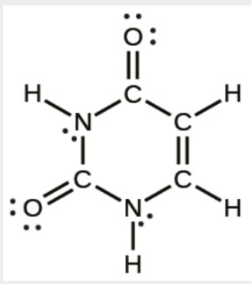
5. 

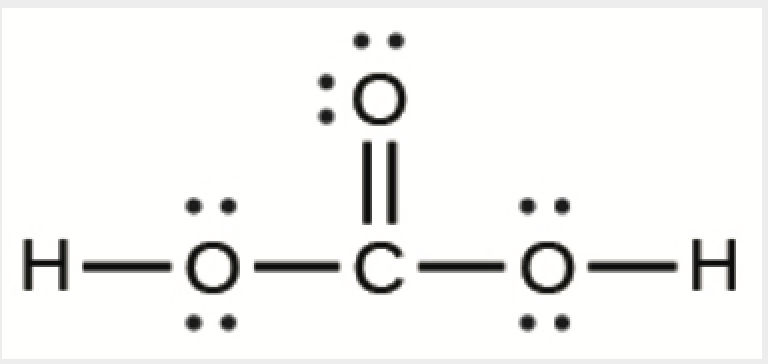
6.

a) 

b) 

c) 

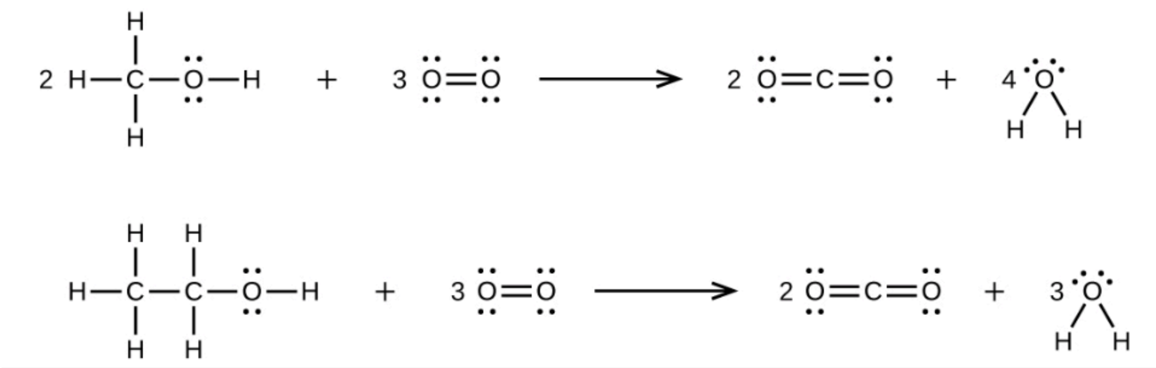
d) 

e) 

7. Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

8. Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

9.



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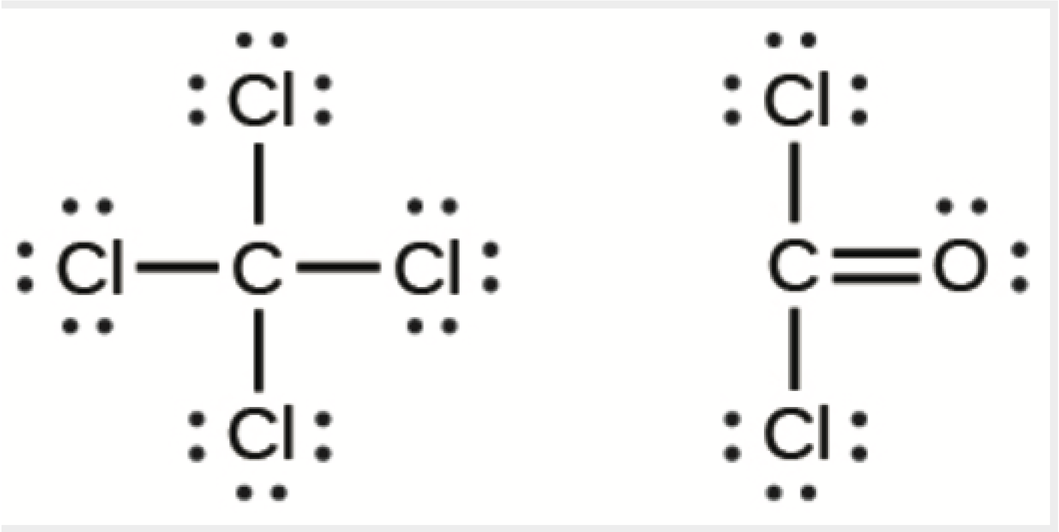
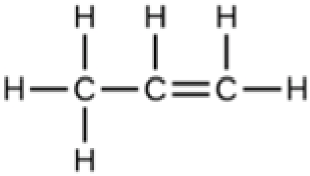


11.



9.5 - VESPR

Bond Angles & Distances

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 9.5.1). A **bond angle** is the angle between any two bonds that include a common atom, usually measured in degrees. A **bond length** (or **bond distance**) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond lengths are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

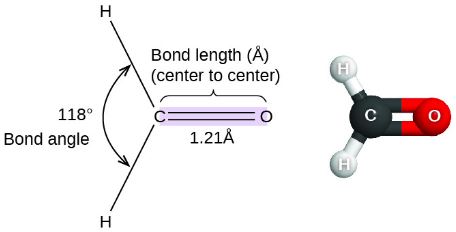


Figure 9.5.1. Bond lengths (distances) and angles are shown for the formaldehyde molecule, H_2CO.

VESPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 9.5.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 9.5.2).

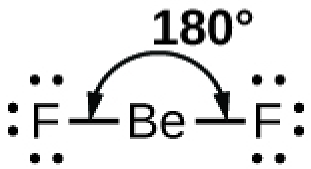


Figure 9.5.2. The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 9.5.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a **linear** geometry; three regions form a **trigonal planar** geometry; four regions form a **tetrahedral** geometry; five regions form a **trigonal bipyramidal** geometry; and six regions form an **octahedral** geometry.

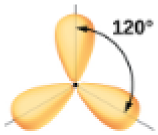
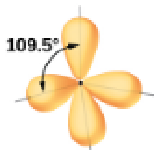
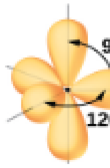
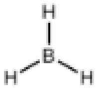
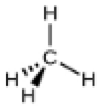
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron or unshared pairs)
Spatial arrangement				
Line-dash-wedge notation	H—Be—H			
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angle An attached atom may b plane of the triangle) or axia plane of the triangle)

Figure 9.5.3. The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-Pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 9.5.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the **electron-pair geometry**. The structure that includes only the placement of the atoms in the molecule is called the **molecular structure**. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 9.5.4). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 9.5.5).

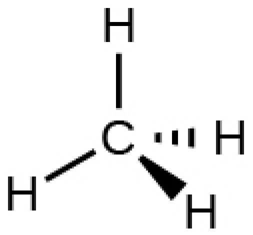


Figure 9.5.4. The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

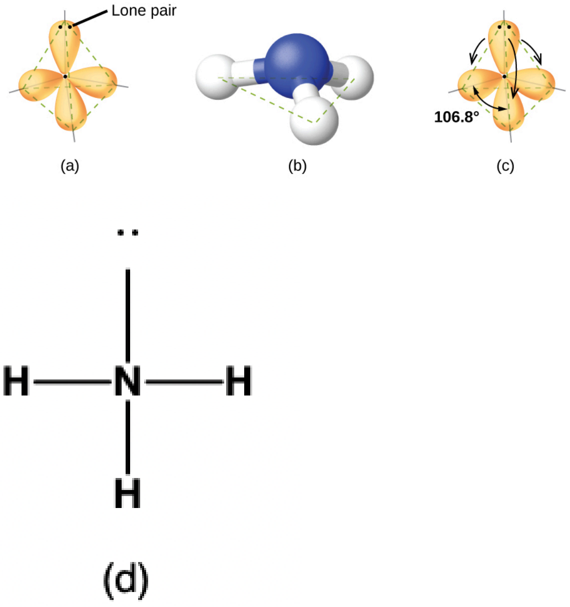


Figure 9.5.5. (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair

and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°. (d) Lewis structure of NH_3.

As seen in Figure 9.5.5, small distortions from the ideal angles in Figure 9.5.3 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

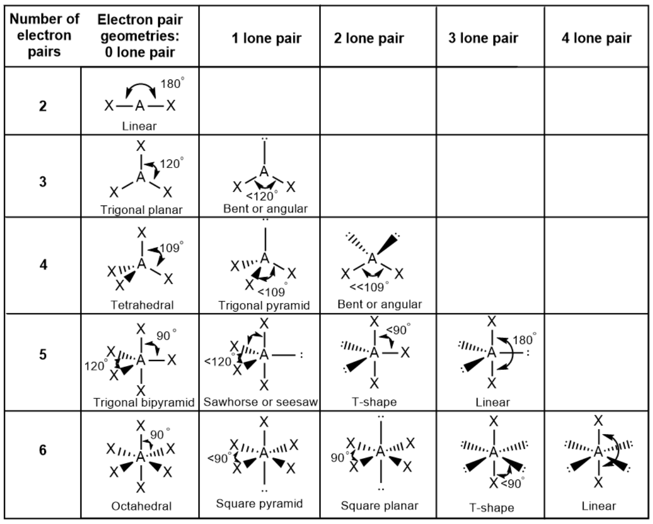
lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure 9.5.1). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

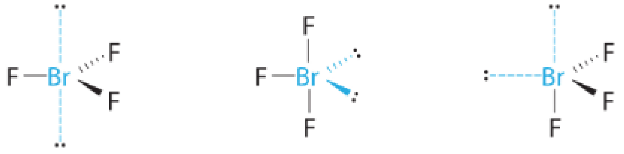
In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 9.5.5) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 9.5.3) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 9.5.5). Figure 9.5.6 illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.



Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pair	3 lone pair	4 lone pair
2	180° Linear				
3	120° Trigonal planar	<120° Bent or angular			
4	109° Tetrahedral	<109° Trigonal pyramid	<<109° Bent or angular		
5	90° 120° Trigonal bipyramid	<120° Sawhorse or seesaw	<90° T-shape	180° Linear	
6	90° Octahedral	<90° Square pyramid	90° Square planar	<90° T-shape	Linear

Figure 9.5.6. The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure 9.5.6) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 9.5.8: an **axial position** (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an **equatorial position** (three positions form an equator around the middle of the molecule). As shown in Figure 9.5.6, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles.



Lone pairs axial (a) | Lone pairs equatorial (b) | Lone pairs axial and equatorial (c)

Interactions

90° LP-LP001

90° LP-BP643

Figure 9.5.7 Demonstration of Axial and Equatorial lone pair interactions.

In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 9.5.8). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

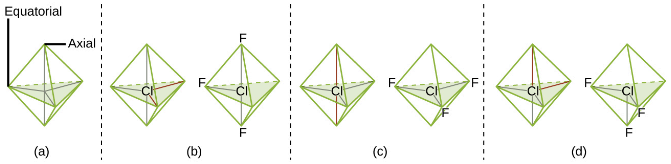


Figure 9.5.8. (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 9.5.6).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

Write the Lewis structure of the molecule or polyatomic ion.

Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.

Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 9.5.6, first column).

Use the number of lone pairs to determine the molecular structure (Figure 9.5.6). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

Example 9.5.1 – Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

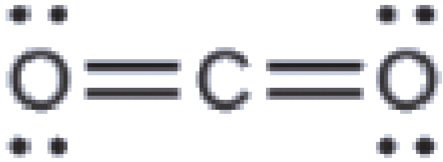
Predict the electron-pair geometry and molecular structure for each of the following:

(a) carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels

(b) boron trichloride, BCl_3, an important industrial chemical

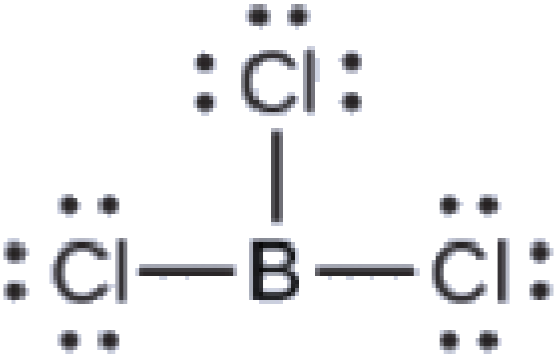
Solution

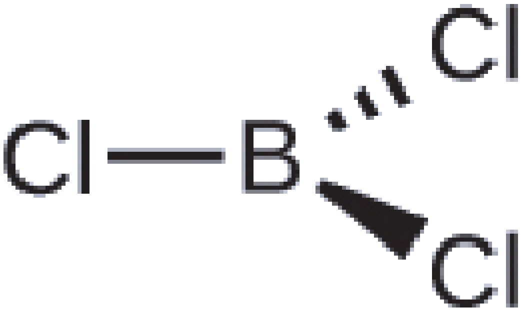
(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:





Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure .

The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Check Your Learning 9.5.1 – Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

Carbonate, CO_3^{2-}, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

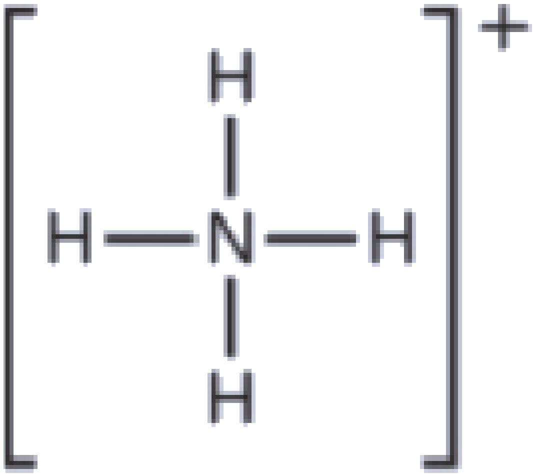
The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Example 9.5.2 – Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 9.5.6). Therefore, the electron pair geometry of NH_4^+ is tetrahedral, and the molecular structure is also tetrahedral: (Figure 9.5.9).

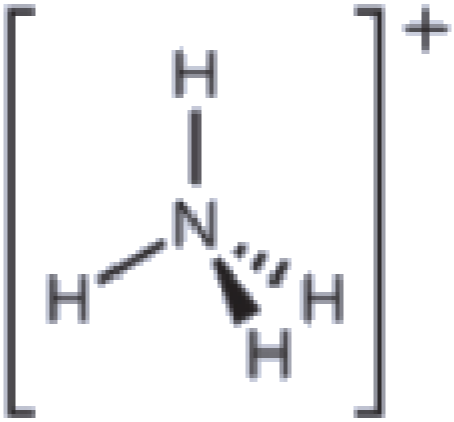


Figure 9.5.9. The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Check Your Learning 9.5.2 – Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

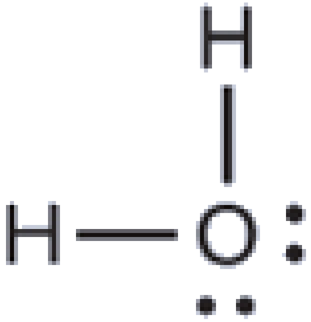
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 9.5.3 – Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (Figure 9.5.10), as indicated in Figure 9.5.6. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

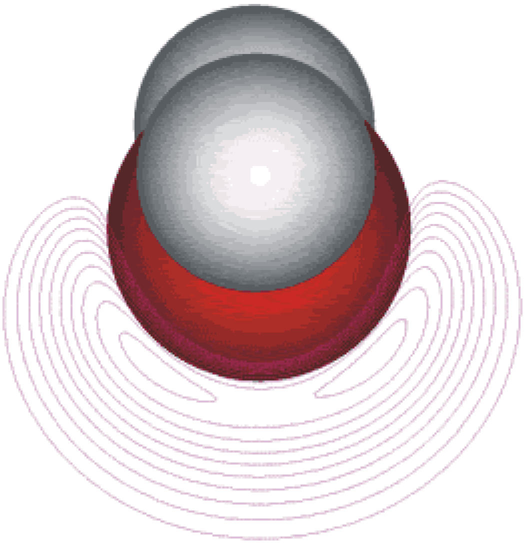


Figure 9.5.10. (a) H_2O has four regions of electron density around the central atom (Two atoms and 2 electron pairs), so it has a tetrahedral electron-pair geometry. Two of the electron regions are lone pairs, so the molecular structure is bent.

Check Your Learning 9.5.3 – Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

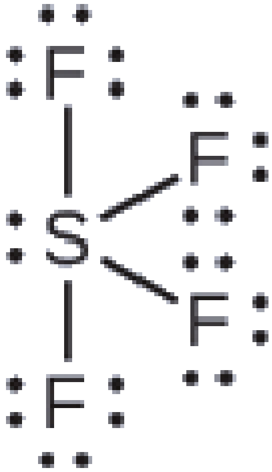
electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example 9.5.4 – Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure 9.5.11) is that of a seesaw (Figure 9.5.6).

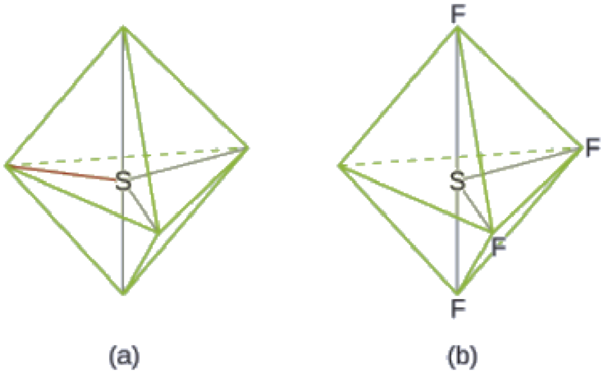


Figure 9.5.11. (a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Check Your Learning 9.5.4 – Predicting Electron-pair Geometry and Molecular Structure: SF_4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Answer

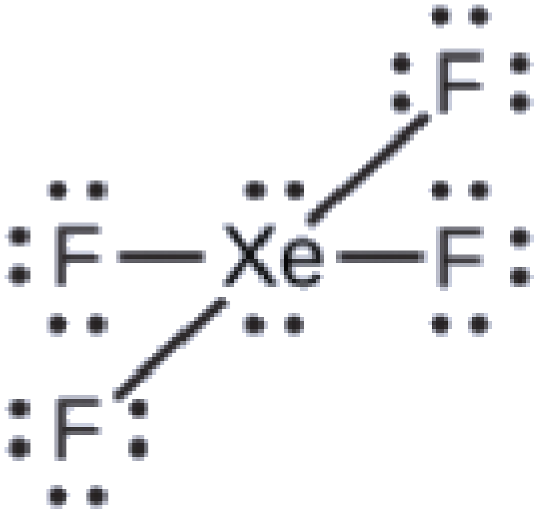
The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Example 9.5.5 – Predicting Electron-pair Geometry and Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (Figure 9.5.6), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 9.5.12). The five atoms are all in the same plane and have a square planar molecular structure.

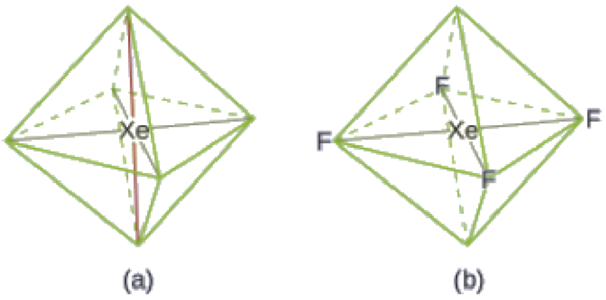


Figure 9.5.12. (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four

bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Check Your Learning 9.5.5 – Predicting Electron-pair Geometry and Molecular Structure: XeF_4

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Answer

electron pair geometry: trigonal bipyramidal; molecular structure: linear

Example 9.5.6 – Predicting Molecular Structure – VSEPR Summary

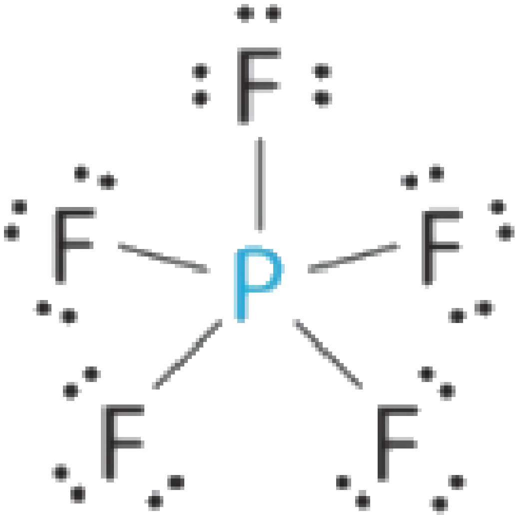
Using the VSEPR model, predict the molecular geometry of each molecule or ion.

(a) PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)

(b) H_3O^+ (hydronium ion)

Solution

(a) The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is

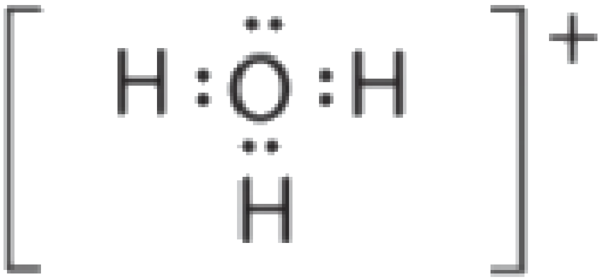


There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.

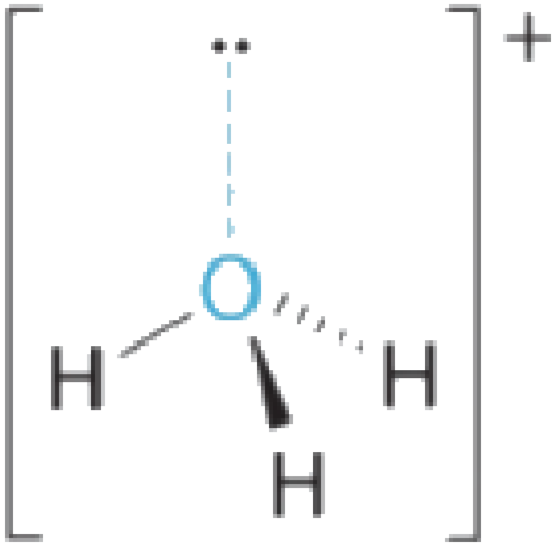
(b) The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

With three bonding pairs and one lone pair, we expect the interactions between lone (nonbonding) and bonding pairs of electrons to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of repulsions between the lone pair (nonbonding) and bonding pairs of electrons:



Check Your Learning 9.5.6 – Predicting Molecular Structure – VSEPR Summary

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

(a) XeO_3

(b) PF_6^-

(c) NO_2^+

Answer

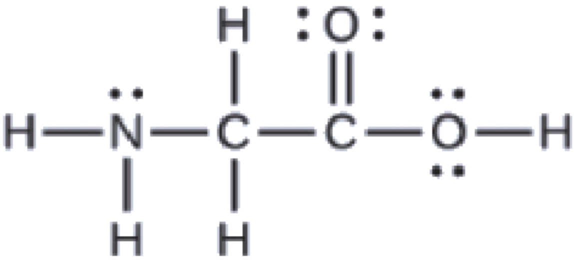
(a) trigonal pyramidal; (b) octahedral; (c) linear

Molecular Structure for Multicenter Molecules

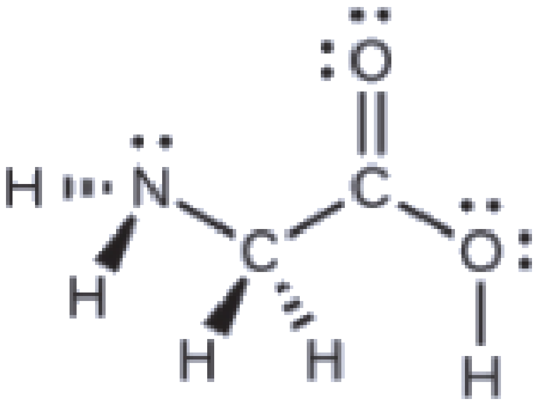
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

Example 9.5.7 – Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

nitrogen––four regions of electron density; tetrahedral

carbon (CH_2)––four regions of electron density; tetrahedral

carbon (CO_2)—three regions of electron density; trigonal planar

oxygen (OH)—four regions of electron density; tetrahedral

The local structures:

nitrogen––three bonds, one lone pair; trigonal pyramidal

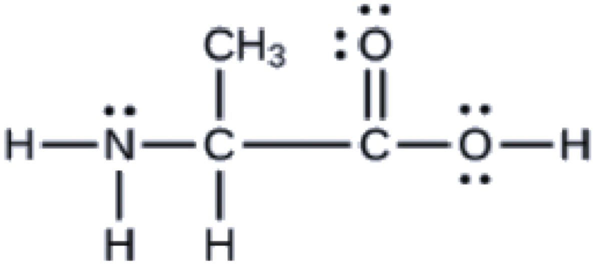
carbon (CH_2)—four bonds, no lone pairs; tetrahedral

carbon (CO_2)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar

oxygen (OH)—two bonds, two lone pairs; bent (109°)

Check Your Learning 9.5.7 – Predicting Structure in Multicenter Molecules

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer

electron-pair geometries: nitrogen––tetrahedral; carbon (CH)—tetrahedral; carbon

(CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—bent (109°)

VSEPR – Interactive Activity

This molecular shape simulator from PhET lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a **bond dipole moment**. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a **vector**, a quantity having both direction and magnitude (Figure 9.5.13). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

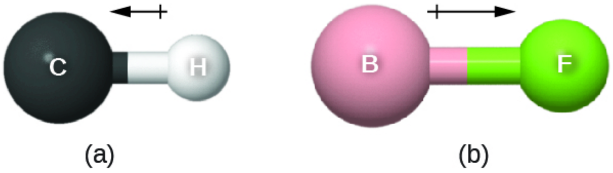


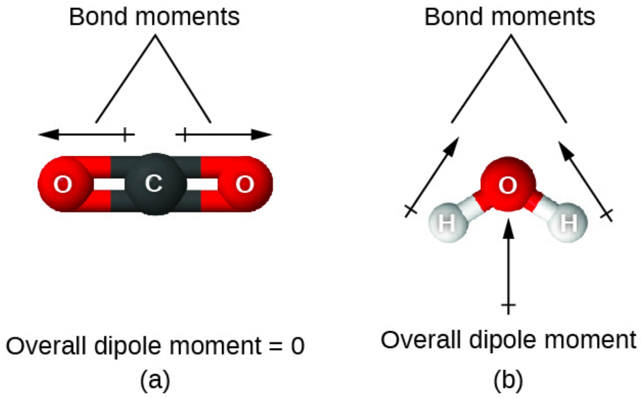
Figure 9.5.13. (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a **polar molecule** (or **dipole**); otherwise the molecule is said to be nonpolar. The **dipole moment** measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

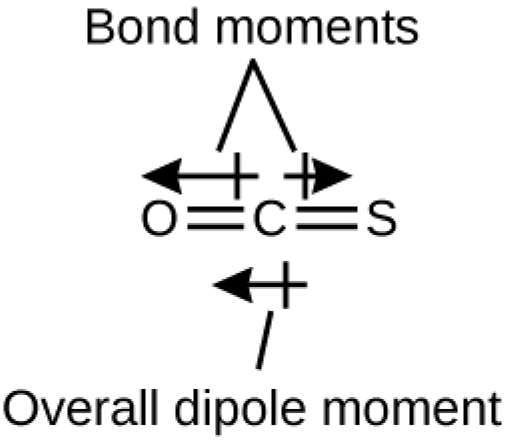
For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 9.5.14). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 9.5.14), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

Figure 9.5.14. The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

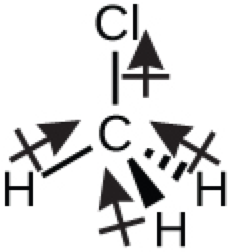


The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

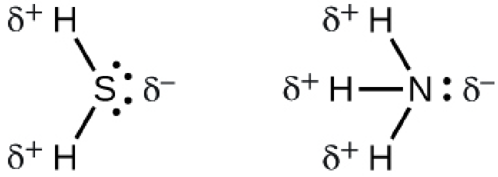


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is another example of a polar molecule. Although the polar C−Cl and C−H bonds are arranged in a tetrahedral geometry, the C−Cl bonds have a larger bond moment than the C−H bond, and the bond moments do not completely cancel each other. All of the dipoles have an upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3. A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:



To summarize, to be polar, a molecule must:

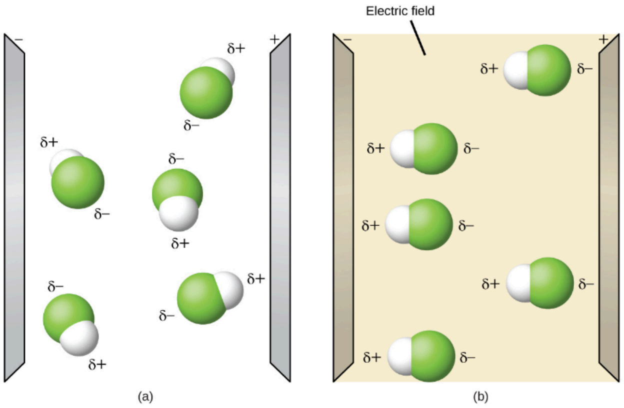
Contain at least one polar covalent bond.

Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 9.5.15). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

Figure 9.5.15. (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.



Molecular Polarity – Interactive Activity

This molecule polarity simulation from PhET provides many ways to explore dipole moments of bonds and molecules.

★ Questions

1. Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.
2. Explain the difference between electron-pair geometry and molecular structure.
3. Explain how a molecule that contains polar bonds can be nonpolar.
4. Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

   a) SF_6
   b) PCl_5

c) BeH_2
d) CH_3^+

5. What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

a) ClF_5
b) ClO_2^-
c) $TeCl_4^{2-}$
d) PCl_3
e) SeF_4
f) PH_2^-

6. Identify the electron pair geometry and the molecular structure of each of the following molecules:

a) ClNO (N is the central atom)
b) CS_2
c) Cl_2CO (C is the central atom)
d) Cl2SO (S is the central atom)
e) SO_2F_2 (S is the central atom)
f) XeO_2F_2 (Xe is the central atom)
g) $ClOF_2^+$ (Cl is the central atom)

7. Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

a) ClF_5
b) ClO_2^-
c) $TeCl_4^{2-}$
d) PCl_3
e) SeF_4
f) PH_2^-
g) XeF_2

8. Which of the following molecules have dipole moments?

a) CS_2
b) SeS_2
c) CCl_2F_2
d) PCl_3 (P is the central atom)
e) ClNO (N is the central atom)

9. The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

10. Is the Cl_2BCl2 molecule polar or nonpolar?

11. Describe the molecular structure around the indicated atom or atoms:

a) The sulfur atom in sulfuric acid, H_2SO_4 $[(HO)_2SO_2]$

b) The chlorine atom in chloric acid, HClO3 [$HOClO_2$]
c) The oxygen atom in hydrogen peroxide, HOOH
d) The nitrogen atom in nitric acid, HNO_3 [$HONO_2$]
e) The oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]
f) The central oxygen atom in the ozone molecule, O_3
g) Each of the carbon atoms in propyne, CH_3CCH
h) The carbon atom in Freon, CCl_2F_2
i) Each of the carbon atoms in allene, H_2CCCH_2

★★ Questions

12. A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

Answers

1. The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

2. Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

3. As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from one another), the molecule can be nonpolar.

4.

a) Both the electron geometry and the molecular structure are octahedral.
b) Both the electron geometry and the molecular structure are trigonal bipyramid.
c) Both the electron geometry and the molecular structure are linear.
d) Both the electron geometry and the molecular structure are trigonal planar.

5.

a) electron-pair geometry: octahedral, molecular structure: square pyramidal;
b) electron-pair geometry: tetrahedral, molecular structure: bent;
c) electron-pair geometry: octahedral, molecular structure: square planar;
d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal;
e) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw;
f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

6.

a) electron-pair geometry: trigonal planar, molecular structure: bent (120°);
b) electron-pair geometry: linear, molecular structure: linear;

c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar;

d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal;

e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral;

f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw;

g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

7. All of these molecules and ions contain polar bonds. Only ClF_5, ClO_2^-, PCl_3, SeF_4, and PH_2^- have dipole moments.

8. SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

9. P

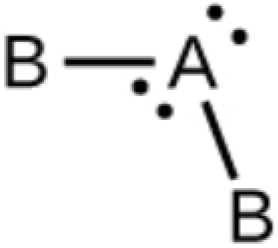
10. Nonpolar

11. (a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) CH_3CCH tetrahedral, CH_3CCH linear; (h) tetrahedral; (i) H_2CCCH_2 linear; H_2CCCH_2 trigonal planar

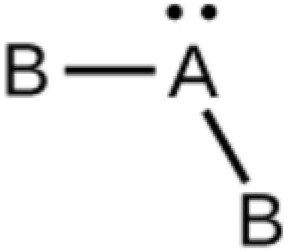
12.

a) CO_2, linear

b) H_2O, bent with an approximately 109° angle



c) SO_2, bent with an approximately 120° angle



END OF CHAPTER QUESTIONS

QUESTIONS

Chapter 1 – Stoichiometry

Topics included in the chapter:

- The mole
  - # of moles, atoms…
  - Finding mass and molar mass
- Determining chemical formulae
  - molecular/empirical formula
  - % composition
  - Balancing equations/making equations
- Reaction stoichiometry
  - Limiting reagents
  - Rest is similar to the 2 topics above
- Solution stoichiometry
  - Molarity and molality
  - % by mass, volume…
- Redox reactions
  - Oxidation states
  - Half reaction – basic and acidic conditions

Questions:

1. The percent composition of an unknown gas is 41.95% C, 22.35% O, 29.36% N, et 6.34% H. What is the empirical formula of the unknown gas?
2. Balance the following chemical equation, using half-reactions, in basic conditions:

$$MnO_4\,(aq) + C_6H_{12}O_4\,(aq) \rightarrow Mn^{2+}\,(aq) + HCO_3\,(aq)$$

3. An aqueous solution with a percent by mass of 20.0% for C_2H_5OH (C_2H_5OH is the only solute). The density of the solution is 0.945 g/mL. Calculate the molarity, molality and the mole fraction of C_2H_5OH in the solution.
4. Out of Na *(s)*, Na^+ *(aq)*, NaCl *(s)*, Cl_2 *(g)* and Cl^- *(aq)*, which of the following is an oxidant?
5. What is the oxidation state of C in HCN (note that carbon is the central atom, H is the least

electronegative of the three and N is the most electronegative of the three)?

6. 205.0 g of H_2O, 225.0 g of O_2 and 240.0 g of P_4 reaction together based on the following equation:

$$6\,H_2O + 5\,O_2 + P_4 \rightarrow 4\,H_3PO_4$$

   What is the mass (in grams) of H3PO4 produced? What is the mass (in grams) total of the excess reagents that did not react?

7. Walmart sells antifreeze, an aqueous solution that is 28.6% ethylene glycol ($C_2H_6O_2$) by mass. If the density of this solution is 1.03 g/cm^3, calculate its molality.
8. A salesman comes to your door and tells you that the tap water in your neighbourhood has recently been tested and high levels of lead (Pb) have been found. He can sell you a purification device for $7500 that can attach to your tap and remove the lead ions from the water. He wants to test your water to see if it is needed; all he needs from you is a small sample of tap water (100.0 mL).
   1. His test kit uses the following half reactions to test for the lead ions. Find the overall balanced redox reaction, under basic conditions (including phases).
      1. $Pb^{2+}(aq) \rightarrow Pb\,(s)$
      2. $CN^{-}(aq) \rightarrow CNO^{-}\,(aq)$
   2. Identify the oxidizing agent and the reducing agent in your reaction above.
9. Which compound has the highest oxidation state of nitrogen:
   1. NO^+
   2. N_2
   3. NO_3^-
   4. NO_2
   5. N_2O
   6. NH_3
10. Complete combustion of a 1.119 g sample of an unknown gaseous compound (consisting of C, H, and S) yields 2.020 g of CO_2, 0.689 g of H_2O, and some SO_2.
    1. Find the number of moles of each element in the sample.
    2. What is the empirical formula of the compound?

Chapter 2 – Gases

Concepts included in Chapter 2:

- Intermolecular forces
  - Identifying forces and explaining their relative strengths/behaviour in a molecule
- Gases and periodic table
  - Trends
- Measuring variable of gases
  - Intro to PV=nRT

  - Changing from bar to atm …
- Gas Laws *experiment 1*
  - Uses of different laws and applying them
  - PV=nRT and use n to calculate mass…
- Gas mixtures and Partial pressures
  - Finding molar mass from PV=nRT and mass
  - Determining molecular formulas
  - Partial pressures
- Kinetic-molecular theory of gases (ideal gas behaviour)
  - Behaviours explained
  - Root mean squared
  - Average kinetic energy
- Diffusion and effusion
  - Explaining these 2 concepts and applying them
- Real/non-ideal gas behaviours
  - explaining /applying concepts to questions and graphs

Questions:

1. If we react 88.8 g of C_2H_5OH *(l)* and 88.8 g of O_2 *(g)* in a combustion reaction producing CO_2 *(g)* and H_2O *(l)*. The combustion is held in a 10.0 L steel container and the temperature is fixed at 25.00 °C. What is the mass of CO_2 *(g)* produced? Ignoring the vapour pressures of C_2H_5OH *(l)* and H_2O *(l)*, what is the total pressure (in atm) before and after the reaction? (hint: these two values are not necessarily the same) Finally, what is the average speed of the CO_2 *(g)* molecules at the end of the reaction?
2. The percent composition of an unknown gas is 40.84% C, 20.40% O, 29.77% N and 9.00% H. What is the empirical formula? If the unknown gas has a density of 11.07 g/L a temperature of 777 K and a pressure of 1.00 atm, what is the molecular formula?
3. In a 33.3 L steel container, there is 88.8g CO_2 *(g)*, 77.7g of N_2 *(g)*, and some O_2 *(g)*. The temperature is 25 °C and the pressure is 5.555 atm. What is the molar mass of O_2 *(g)*.
   1. Mass by volume of a sample of only CO_2 *(g)* is 1.55 g/L. The pressure is 2.22 atm. What is the average speed of the CO_2 *(g)* molecules?
4. In a 10.0 L steel container, we have 19.9 g of N_2 *(g)*. The pressure is 2.50 atm. What is the average speed of the N_2 *(g)* molecules? Let's say we add 19.9 g of O_2 *(g)* in the container. The temperature is adjusted to 25 °C and the volume is fixed at 10.0 L. What is the total pressure?
5. A one litre balloon is filled with neon gas. A hole is made in the balloon and the gas effuses at a rate of 0.0280 mol/hr. If the same balloon is refilled with argon at the same pressure and temperature, its rate of

effusion would be _____________.

6. The ideal gas law works best at low temperatures and high pressures. Circle the correct answer.
    1. True
    2. False
7. When Dr. Fox goes scuba diving, she uses NITROX, a special blend of enriched air that allows for more repetitive dives by reducing the build-up of nitrogen in the blood (that way, she won't get "the bends"!). The local scuba shop prepares 7.20 L tanks of NITROX by mixing 25.0 g of O_2 with 42.0 g of N_2 at a temperature of 25.0^{o}C.
8. What is the mole fraction of each gas in the mixture?
9. What is the partial pressure of each gas, in bar?
10. The following reaction, occurring in a sealed vessel, has a percent yield of 94.9%: $2\ NaN_3\,(s) \rightarrow 2\ Na\,(l) + 3N_2\,(g)$
    1. What volume of N_2, measured at 735 mmHg and 26.0^{o}C, is produced when 75.0 g of sodium azide decomposes?

Chapter 3 – Thermochemistry

Topics included in Chapter 3:

- Introduction to thermochemistry
    - Conservation of energy
    - System, surroundings, universe
- Types of energy
    - exothermic/endothermic
    - Internal energy
    - -q = q
- First law of thermodynamics
    - Internal energy continued
    - Introduction of work and enthalpy
- Enthalpy
    - Enthalpy, $q = mc\Delta T$
    - Looking for different variables using variations of the enthalpy equation
- Calorimetry
    - Calculations in isolation (in a calorimeter)
- Hess' Law

Questions:

1. In a bomb calorimeter with a constant volume, we combusted 1.22 g of $C_6H_{10}O$ *(l)* (hint: the combustion is a reaction with a substance reacting with $O_{2(g)}$ to produce CO_2 *(g)* and H_2O *(l)*). The bomb calorimeter has a heat capacity of 3.50 kJ K^{-1} and is containing 2.725 kg of water. The specific heat capacity of water is 4.184 J K^{-1} g^{-1}. The temperature of the calorimeter and the water raises from 20.50 ∘C to 23.25 ∘C. With this given information, calculate Q, W, ΔH and ΔU if we did combustion with one mole of $C_6H_{10}O$ *(l)* under constant pressure of 1.00 bar at 25.00 ∘C.
2.
    1. We place 100.0 g of 100.00 ∘C metal in 222.2 g of water which is 10.00 ∘C. The water is in a cup that is at the same temperature as the water. The heat capacity of the cup is 500 J K^{-1}. The final temperature of the metal, water and the cup are 13.33 ∘C. What is the specific heat capacity of the metal?
    2. The combustion of one mole of methane (CH_4 *(g)*) releases 891 kJ of heat. We want to heat 6.66 kg of water from 20.00 ∘C to 30.00 ∘C. If the methane is at 25.0 ∘C and has a pressure of 1.00 atm, which volume of CH_4 *(g)* should we have?
3. We have 437 g of water in a container. The temperature of the water and of the container is 23.0 ∘C. We have a piece of iron weighing 122g at a temperature of 57.0 ∘C and we place it in the water of the container. The specific heat capacities a the water and iron are 4.184 J K^{-1} g^{-1} and 0.44 J/ (g ∘C) respectively. The heat capacity of the container is 217 J/ ∘C. What is the final temperature of the water, iron and container?
4. With the given information:

$$CH_3OH\ (l) + \tfrac{3}{2}O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l) \qquad \Delta H = -726.4\ kJ$$

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H = -393.5\ kJ$$

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (l) \qquad \Delta H = -285.8\ kJ$$

$$CH_3OH\ (l) \rightarrow CH_3OH\ (g) \qquad \Delta H = +37.4\ kJ$$

    1.
    2. Calculate the values for ΔU and ΔH for the formation of one mole of CH_3OH *(g):*
    3. $C\ (graphite) + 2\ H_2\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow CH_3OH\ (g)$
5. When the power was turned off to a 125 L water heater, the temperature of the water dropped from 75.0°C to 22.5°C. The amount of heat, in kilojoules, transferred to the surroundings was: ___________________.
6. This past summer, Dr. Fox went scuba diving in False Bay, South Africa, where the water temperature was a chilly 13.5°C. Despite wearing two 5 mm thick neoprene wetsuits, Dr. Fox still lost body heat at a rate of 38.0 J per second. How much body heat, in kJ, was lost over the course of a 45.0 min dive?
7. For the following reaction: $2\ C_2H_6\ (g) + 7\ O_2\ (g) \rightarrow 4\ CO_2\ (g) + 6\ H_2O\ (l)$ ΔH=-3119kJ
    1. How much heat, in kJ, is associated with the combustion of 10.0 g of ethane?

2. What is the quantity of work, in kJ, evolved in the combustion of 10.0 g of ethane at 25.00^{o}C? (Assume an exact stoichiometric quantity of oxygen is present).

Chapter 4 – Chemical Equilibrium (Mz)

Topics discussed include:

- Introduction to chemical equilibrium
    - Written answers to questions – about reversibility, rate constants…
- The equilibrium constant and reaction quotient
    - Intro to K (when it is bigger or smaller than 1 and what that means) and Q (what that represents)
    - Q and K together in questions – what way will the equilibrium shift
- Solving equilibrium problems
    - K and Kp questions
    - Finding concentration and partial pressures
- Le Chatelier's principle
    - Effects on equilibrium based on what is changed and is explained via the principle.

Questions:

1.
    1. For the reaction 2 A *(aq)* → 2 B *(aq)* + C *(aq),* the equilibrium constant is 2.22 at 25.0 ∘C. If the concentrations of B *(aq)* and C *(aq)* are 0.277 M and 0.444 M respectively, what is the concentration of A *(aq)* necessary to have free energy, G, of -5.00 kJ? Note that the temperature is always 25.0 ∘C.
    2. For the reaction 2 A *(g)* → 2 B *(g)* + C *(g),* we only start with A *(g)* and B *(g),* and the partial pressure of A is double that of B. There is no C *(g).* The total pressure originally is 6.00 atm. We reach equilibrium. The finale pressure is now 6.80 atm. What is the value of G° for this reaction. Note that the temperature is always 25.0 ∘C.
2. For the reaction A *(aq)* + B *(aq)* → 2 C *(aq),* the value of G° is +4.77 kJ (or kJ/mol) at 25.0 ∘C. The initial concentrations for A *(aq),* B *(aq)* and C *(aq)* are 0.322 M, 0.244 M and 0.455 M respectively. What is the concentration of C *(aq)* once we reach equilibrium at 25.0 ∘C?
3. The formation constant, K_f, of Ag(CN)2- is 3.0 x 10^{20}. We put 6.66 g of $AgNO_3$ in a 1.000 L of a 0.800 M solution with CN^-. assume the volume remains fixed at 1.000 L. What are the concentrations of Ag^+ *(aq),* CN^- *(aq)* and $Ag(CN)_2^-$ at equilibrium? The reaction involved: Ag^+ *(aq)* + 2 CN^- *(aq)* → $Ag(CN)_2^-$ *(aq)*
4. Consider the following reaction: A *(g)* + 2 B *(g)* ⇌ 2 C *(g),* To a 2.50 L flask, A and B are added at initial pressures of 0.500 bar each. The mixture was allowed to equilibrate at 1000 K and the flask was found to contain 0.0147 mol of C.

   1. How much heat, in kJ, is associated with the combustion of 8.50 g of ethane?
   2. What is the quantity of work, in kJ, evolved in the combustion of 8.50 g of ethane at 25.00°C? (Assume an exact stoichiometric quantity of oxygen is present).
5. Consider the following gaseous reaction:
   1. 
   2. An equimolar mixture of CH_4 and CO_2, with a total pressure of 20.0 bar, are placed in a 1.00 L flask and allowed to equilibrate at 1200 K. At equilibrium, the flask is found to contain 19.6 bar of hydrogen. What is the value of K of the reaction?
6. Given the information below, the value of the equilibrium constant for the reaction:
   1. $A(g) + 2B(g) \rightleftharpoons 2C(g)$ is:
   2. $2A(g) \rightleftharpoons 2X(g)$ $K_p = 35.5$
   3. $2C(g) \rightleftharpoons X(g) + B(g)$ $K_p = 7.2$

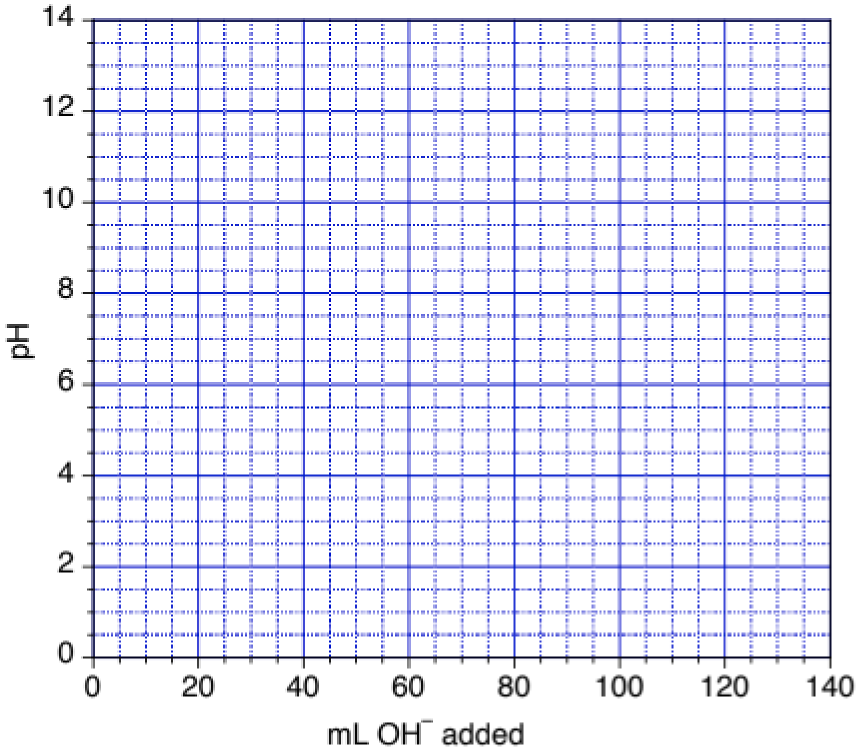
Chapter 5 – Acid/Base Equilibria

Topics discussed include:

- Acid-base definitions and conjugate acid-base pairs
  - Identifying conjugate and labelling an equation with acid-base pairing
- Autoionization of water and pH/pOH
  - Amphiprotic species
  - pH and pOH calculations
  - Ion concentration calculations
- Acid/Base strength
  - Strength of species identified based on behaviour/structure, and comparing its strength to other compounds
  - Ka/Kb calculations
  - Equilibrium concentration calculations
- Polyprotic acids
  - Calculating concentrations with the multiple Ka and Kb values
- Acid strength of hydrides and oxoacids
- Hydrolysis of salt solutions
  - Classifying salts as neutral, acidic or base
- Lewis acid and bases
  - Drawing lewis structures

Questions:

1. NH_3 *(aq)* is a weak base with a dissociation constant, K_b, of 1.8 x 10^{-5}. What is the pH of an aqueous solution 0.333 M in NH_4Cl?
2. At 25.0 ∘ C, we place 2.33 g of acid, HA, in enough water to produce 25.0 mL of solution. The original pH is 1.44. We titrate this solution with a 0.222 M solution of NaOH and we need 22.2 mL to reach the equivalence point.
    1. What is the molar mass of HA?
    2. What is the ionization constant, K_a, of HA?
    3. What would the pH be of a 2.000 M solution in NaA?
3.
    1. For the following reaction 2 A *(aq)* $\rightleftharpoons$ B *(aq)* + C *(aq)*, the equilibrium constant is 5.55 at 25.0 ∘ C. The initial concentrations for A *(aq)*, B *(aq)* and C *(aq)* are 0.444 M, 0.555 M and 0.666 M respectively. What is the concentration of A *(aq)* at equilibrium at 25.0 ∘ C?
    2. We have a 666 mL aqueous solution of NaOH. we add an excess of $AL(NO_3)_3$ to produce the precipitate $Al(OH)_3$ *(s)*. We produce 0.0888 g of $Al(OH)_3$ *(s)*. What was the original pH of the solution?
4. After a vacation of scuba-diving, Dr. Fox has to clean and rinse all her scuba gear before putting it back into storage. She wants to use "Diver's Buddy Scuba Shampoo", a commercially available aqueous solution of trimethylamine ($N(CH_3)_3$, K_b = 6.31 x 10^{-6}). Dr. Fox measures the pH of the solution and finds it to be 10.55. What is the concentration of trimethylamine in the shampoo, in mol/L?
5. You are performing a titration of 80.0mL of 0.0900 M HCN with 0.0900 M NaOH. Determine the pH of the solution:
    1. Initially
    2. At the half-equivalence point
    3. At the equivalence point
    4. Use these values to sketch a titration curve on the graph provided.



5.

Chapter 6 – Ionic Equilibria in Aqueous Systems (JT)

Topics discussed include:

- Common ion effect
  - Ksp questions and using Ksp to find concentrations
- Buffer solutions *experiment 3*
- Acid-base reactions and titrations *experiment 4*
- Equilibria of slightly soluble ionic compounds
  - Ksp and predicting precipitations

Questions:

1. The solubility constant for $Mg(PO_4)_2$ is 1.0 x 10-24. Calculate the solubility (in g/L) of $Mg(PO_4)_2$ in
   1. Pure water
   2. A 0.30 M solution of $Mg(NO_3)_2$
2. We prepare a buffer solution by reacting 12.1 g of NH_3 and 6.2 g of HCl in enough water to produce 1.000 L of solution. The ionization constant for the weak base (NH_3) is 1.8×10^{-5}.
   1. What is the pH of the solution?

   2. What would the pH of the solution be if we would add 1.00 g of NaOH (assume that the volume remains the same)?
   3. What would the pH of the solution if we would add 1.00 g of HCl (assume that the volume remains the same)?
3. What volume of a 0.277 M solution is needed to add to acetic acid, CH_3COOH, to neutralize 28.0 mL of a 0.348 M solution of $Ba(OH)_2$? $Ba(OH)_2$ is a strong base and acetic acid is a weak acid with a pKa of 4.74. What is the pH of the solution at the equivalence point?
4. The ionization constant for acetic acid, CH_3COOH, is 1.8 x 10-5. What is the pH of a solution if we add 0.847 g of sodium acetate, CH_3COONa, to pure water and the final volume is 100.0 mL.
5. You wish to prepare a buffer solution with pH = 9.45.
   1. How many grams of $(NH_4)2SO_4$ would you add to 425 mL of 0.258 M NH_3 to do this? You may assume that the solution's volume remains constant. K_b of $NH_3 = 1.8\times10^{-5}$
   2. You have access to additional 0.258 M NH_3 and more solid $(NH_4)2SO_4$. Which buffer component, and how much (in g or mL) would you add to 0.100 L of the buffer in part (a) to change its pH to 9.30? You may assume that the solution's volume remains constant.
6. A student mixes 31.0 mL of 2.74 M $Pb(NO_3)_2$ *(aq)* with 20.0 mL of 0.00163 M NaI *(aq)*.
   1. Identify the expected precipitate
   2. What are the values of $[Pb^{2+}]$, $[Na^+]$, $[NO_3^-]$ and $[I^-]$ after the solution has reached equilibrium at 25°C? You may assume volumes are additive.
7. From the list below, circle the basic salts and underline the neutral salts
   1. KCl
   2. $FeCl_3$
   3. NH_4Br
   4. $Ca(CN)_2$
   5. LiF
   6. $CuNO_3$

SOLUTIONS

Chapter 1 – Stoichiometry

1.

$$\begin{aligned}
C &= \frac{41.95\ g}{12.01\ g} = \frac{3.493}{1.393} = 2.5 \quad \therefore C : 2.5 \times 2 = 5 \\
O &= \frac{22.35\ g}{16.00\ g} = \frac{1.397}{1.397} = 1 \quad \therefore O : 1 \times 2 = 2 \\
N &= \frac{29.36\ g}{14.01\ g} = \frac{2.096}{1.397} = 1.5 \quad \therefore N : 1.5 \times 2 = 3 \\
H &= \frac{6.34\ g}{1.01\ g} = \frac{6.277}{1.397} = 4.5 \quad \therefore H : 4.5 \times 2 = 9
\end{aligned}$$

$\therefore$ the empirical formula of the unknown gas is $C_5O_2N_3H_9$

2. (1) Balancing: MnO_4^- *(aq)* → Mn^{2+} *(aq)*

MnO_4^- *(aq)* → Mn^{2+} *(aq)* + 4 H_2O

MnO_4^- *(aq)* + 8 H^+ → Mn^{2+} *(aq)* + 4 H_2O

3 OH^- + MnO_4^- *(aq)* + 8 H^+ → Mn^{2+} *(aq)* + 4 H_2O + 8 OH^-

8 H_2O + MnO_4^- *(aq)* → Mn^{2+} *(aq)* + 4 H_2O + 8 OH^-

4 H_2O + MnO_4^- *(aq)* → Mn^{2+} *(aq)* + 8 OH^-

4 H_2O + MnO_4^- *(aq)* + 5 e^- → Mn^{2+} *(aq)* + 8 OH^- (x 28)

(2) Balancing $C_6H_{12}O_4$ *(aq)* → 6 HCO_3^- *(aq)*

14 H_2O + $C_6H_{12}O_4$ *(aq)* → 6 HCO_3^- *(aq)*

14 H_2O + $C_6H_{12}O_4$ *(aq)* → 6 HCO_3^- *(aq)* + 34 H^+

34 OH^- + 14 H_2O + $C_6H_{12}O_4$ *(aq)* → 6 HCO_3^- *(aq)* + 34 H^+ + 34 OH^-

34 OH^- + 14 H_2O + $C_6H_{12}O_4$ *(aq)* → 6 HCO_3^- *(aq)* + 34 H_2O

34 OH^- + $C_6H_{12}O_4$ *(aq)* → 6 HCO_3^- *(aq)* + 20 H_2O

34 OH^- + $C_6H_{12}O_4$ *(aq)* → 6 HCO_3^- *(aq)* + 20 H_2O + 28 e^- (x 5)

(3) Combine half equations for the final answer: 12 H_2O + 28 MnO_4^- *(aq)* + 5 $C_6H_{12}O_4$ *(aq)* 28 Mn^{2+} *(aq)* + 54 OH^- + 30 HCO_3^- *(aq)*

3.

$$(1)\ Molarity = \frac{20\ g}{100\ g} \times \frac{1\ mol}{46.081\ g} \times \frac{0.945\ g}{1\ mL} \times \frac{1000\ mL}{1\ L} = 4.10\frac{mol}{L}$$

$$(2)\ Molality = 20\ g \times \frac{1\ mol}{46.081\ g} \times \frac{1}{0.08\ kg\ of\ solvent} = 5.43\frac{mol}{kg\ solvent}$$

(3) ? Mole C_2H_5OH = $20\ g \times \frac{1\ mol}{46.081\ g} = 0.434\ mol$

? Mole Water (solvent) = $80\ g \times \frac{1\ mol}{18.019\ g} = 4.44\ mol$

? Mole Fraction = $\frac{0.434\ mol}{0.434\ mol\ + 4.44\ mol} = 0.089$

4. Cl_2 *(g)*

5. +2

6. (1) calculate the number of moles of H_3PO_4 that would be produced to determine the limiting reagent:

$$a)\quad H_2O = \frac{205.0\ g\ H_2O}{(16.00 + (2 \bullet 1.008))\frac{g}{mol}} \times \frac{4\ mol\ of\ H_3PO_4}{6\ mol\ of\ H_2O} = 7.5858\ mol\ H_3PO_4$$

$$b)\quad O_2 = \frac{225.0\ g\ O_2}{(16.00\ \bullet 2)\frac{g}{mol}} \times \frac{4\ mol\ of\ H_3PO_4}{5\ mol\ of\ O} = 5.6250\ mol\ H_3PO_4$$

$$c)\quad P_4 = \frac{240.0\ g\ P_4}{(4\ \bullet 30.97)\frac{g}{mol}} \times \frac{4\ mol\ of\ H_3PO_4}{1\ mol\ P_4} = 7.7494\ mol\ H_3PO_4$$

O_2 is the limiting reagent

$$\therefore 5.6250\ mol\ H_3PO_4 \times [(3)(1.008) + 3.097 + (4)(16.00)]\frac{g}{mol} = 551.2\ g\ H_3PO_4$$

(2) The mass of the excess reagents that did not react:

Excess mass = (205.0 + 225.0 + 240.0) g – 551.2 g = 118.8 g

7. 28.6% by mass means there are 28.6 g $C_2H_6O_2$ in 100 g of solution. Therefore, the mass of water in the solution is the difference between these values:

	$C_2H_6O_2$	H_2O	SOLUTION
Mass (g)	28.6	71.4	100
Molar Mass (g/mol)	62.07		
Mol	0.461		

$$\therefore molarity = ?\frac{mol\ C_2H_6O_2}{kg\ H_2O} = \frac{0.461\ mol}{71.4\ g\ H_2O} \times \frac{100\ g}{kg} = 6.5\frac{mol}{kg}$$

8.

$2\ e^- + Pb^{2+}$ *(aq)* → Pb *(s)*

$2\ OH^-$ *(aq)* + CN^- *(aq)* → CNO^- *(aq)* +H_2O *(l)* + 2 e-

____

CN^- *(aq)* + $2\ OH^-$ *(aq)* + Pb^{2+} *(aq)* → CNO^- *(aq)* + H_2O *(l)* + Pb *(s)*

Reducing agent → CN^- *(aq)*Oxidizing Agent → Pb^{2+} *(aq)*

9. NO_3^-

10.

a)

$$?mol\ C = 2.020\ g\ CO_2 = \frac{mol\ CO_2}{44.01\ g\ CO_2} \times \frac{1\ mol\ C}{1\ mol\ CO_2} = 0.0460\ mol\ C$$
$$?mol\ H = 0.689\ g\ H_2O = \frac{mol\ H_2O}{18.02\ g\ H_2O} \times \frac{2\ mol\ H}{1\ mol\ H_2O} = 0.0765\ mol\ H$$
$$?g\ C = 0.0460\ mol\ C \times \frac{12.011\ g\ C}{mol\ C} = 0.552\ g\ C$$
$$?g\ H = 0.0765\ mol\ H \times \frac{1.008\ g\ H}{1\ mol\ H} = 0.0771\ g\ H$$
$$\therefore\ ?g\ S = 1.119\ g\ sample - 0.552\ g\ C - 0.0771\ g\ H = 0.0490\ g\ S$$
$$?mol\ S = 0.0490\ g\ S \times \frac{1\ mol\ S}{32.066\ g\ S} = 0.0153\ mol\ S$$

b)

$$C_{\frac{0.0460}{0.0153}}H_{\frac{0.0765}{0.0153}}S_{\frac{0.0153}{0.0153}} = C_3H_5S$$

Chapter 2 – Gases

1. (1) Balanced chemical equation: C_2H_5OH *(l)* + 3 O_2 *(g)* → 2 CO_2 *(g)* + 3 H_2O *(l)*

(2) Find the mass of CO_2 *(g)*:

$$C_2H_5OH : \frac{88.8\ g}{46.08\ g} \times \frac{2\ mol\ CO_2}{1\ mol\ C_2H_5OH} = 3.854\ mol\ CO_2$$
$$O_2 : \frac{88.8\ g}{32.00\ g} \times \frac{2\ mol\ CO_2}{3\ mol\ O_2} = 1.850\ mol\ CO_2$$

- O_2 is the limiting reagent ∴ mass of CO_2 = (1.850 mol)(44.01g/mol) = 81.4 g

(3)

$$P_{before} = P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{(2.775\ mol)\left(0.082056\frac{L\bullet atm}{mol\bullet K}\right)\left(298.15\ K\right)}{(10.0\ L)} = 6.70\ atm$$

$$P_{after} = P_{CO_2} = \frac{n_{CO_2}RT}{V} = \frac{(1.850\ mol)\left(0.082056\frac{L\bullet atm}{mol\bullet K}\right)\left(298.15\ K\right)}{(10.0\ L)} = 4.53\ atm$$

(4)

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{(3)\left(0.082056\frac{L\bullet atm}{mol\bullet K}\right)(298.15\ K)}{0.04401\frac{kg}{mol}}} = 411\frac{m}{s}$$

2. (1)

$$C = \frac{40.84\ g}{12.01\ g} = \frac{3.400}{1.275} = 2.666 \quad \therefore C : 2.666 \times 3 = 8$$
$$O = \frac{20.40\ g}{16.00\ g} = \frac{1.275}{1.275} = 1 \quad \therefore O : 1 \times 3 = 3$$
$$N = \frac{29.77\ g}{14.01\ g} = \frac{2.125}{1.275} = 1.666 \quad \therefore N : 1.666 \times 3 = 5$$
$$H = \frac{9.00\ g}{1.01\ g} = \frac{8.911}{1.275} = 7 \quad \therefore H : 7 \times 3 = 21$$

∴ the empirical formula of the unknown gas is $C_8O_3N_5H_{21}$

(2)

$$M = \frac{density \bullet R \bullet T}{P} = \frac{(11.07\frac{g}{L})\left(0.082056\frac{L\bullet atm}{mol\bullet K}\right)\left(777\ K\right)}{1.00\ atm} = 705.8\frac{g}{mol}$$
$$Molar\ mass\ ratio = \frac{705\frac{g}{mol}}{235.3\frac{g}{mol}\ of\ C_8O_3N_5H_{21}} = 3$$

∴ the molecular formula of the unknown gas is $C_{24}O_9N_{15}H_{63}$

3. (a)

$$n_T = \frac{P_T V}{RT} = \frac{(5.555\ atm)(33.3\ L)}{\left(0.082056\ \frac{L\bullet atm}{mol\bullet K}\right)\left(298.15\ K\right)} = 7.5611\ mol$$

$$n_{O_2} = n_T - n_{CO_2} - n_{N_2} = 7.5611\ mol - \frac{88.8\ g}{44.01\frac{g}{mol}} - \frac{77.7\ g}{28.02\frac{g}{mol}} = 2.770\ mol$$

? mass O_2 = (2.770 mol)(32.00 g/mol) = 88.7 g

(b)

$$M = \frac{(density)RT}{P} \rightarrow T = \frac{PM}{(density)(R)} = \frac{(2.22\ atm)\left(44.01\frac{g}{mol}\right)}{\left(1.555\ \frac{g}{L}\right)} = 765.7\ K$$

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{(3)\left(8.3145\frac{J}{K\bullet mol}\right)\left(765.7\ K\right)}{0.04401\frac{kg}{mol}}} = 659\frac{m}{s}$$

4. (1)

$$n_{N_2} = \frac{19.9\ g}{(2)\left(14.01\frac{g}{mol}\right)} = 0.71021\ mol$$

Find the initial temperature:

$$PV = nRT \ \rightarrow\ T = \frac{PV}{nR} = \frac{(2.50\ atm)(10.0\ L)}{(0.71021\ mol)\left(0.082056\frac{L\bullet atm}{mol\bullet K}\right)} = 428.99\ K$$

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{(3)\left(8.3145\frac{J}{K\bullet mol}\right)\left(428.9\ K\right)}{0.02802\frac{kg}{mol}}} = 618\frac{m}{s}$$

5. 0.020 mol/hr

6. False

7. (a)

$$?mol\ O_2 = 25.0\ g\ O_2 = \frac{mol\ O_2}{31.998\ g\ O_2} = 0.781\ mol\ O_2$$

$$?mol\ N_2 = 42.0\ g\ N_2 = \frac{mol\ N_2}{28.014\ g\ O_2} = 1.500\ mol\ N_2$$

$$Total\ mol = 0.781 + 1.500 = 2.281$$

$$?\chi\ N_2 = \frac{1.500\ mol}{2.281\ mol} = 0.658$$

$$?\chi\ O_2 = \frac{0.781\ mol}{2.281\ mol} = 0.342$$

(b)

$$Total\ P = \frac{(Total\ n)RT}{V} = \frac{(2.281\ mol)\left(0.083145\frac{L\bullet bar}{mol\bullet K}\right)\left(298\ K\right)}{7.20\ L} = 7.85\ bar$$
$$P\ of\ N_2 = \chi_{N_2} \times Total\ P = (0.658)(7.85\ bar) = 5.16\ bar$$
$$P\ of\ O_2 = \chi_{O_2} \times Total\ P = \left(0.342\right)\left(7.85\ bar\right)$$

8.

$$?theoretical\ mol\ N_2 = 70\ g\ NaN_3 \times \frac{mol\ NaN_3}{65.0\ g\ NaN_3} \times \frac{3\ mol\ N_2}{2\ mol\ NaN_3} = 1.730\ mol$$
$$?actual\ mol\ N_2 = 1.730\ mol \times 0.949 = 1.642\ mol\ N_2$$
$$P = 735\ mm\ Hg \times \frac{1\ atm}{760\ mm\ Hg} = 0.967\ atm$$
$$T = 26.0^{\circ}C + 273.15 = 299.15\ K$$

Chapter 3 – Thermochemistry

1. (1) calculate the value of q for the combustion of 1.22 g of $C_6H_{10}O_{(l)}$ at a constant volume (which means that q = ΔU)

$q_{reaction}$ = ΔU = – q_{water} – q_{cal}

$q_{reaction}$ = – $m_{H2O} \cdot c \cdot \Delta T_{H2O}$-($C_{cal} \cdot \Delta T_{cal}$)

$q_{reaction}$ = -(2725 g)(4.188 J/g·K)(2.75 K) – (3500 J/K)(2.75 K)

$q_{reaction}$ = – 40988 J

$q_{reaction}$ = – 40.988 kJ

For one mole; there is 98.14 g

$$\therefore\ \frac{98.14\ g}{1.22\ g} = \frac{x\ kJ}{-40.988\ kJ}$$

x = ΔU = – 3297 kJ

(2) now, we will find Q, W, ΔH and ΔU at constant pressure. But ΔU is always -3297 kJ

$$\Delta H = \Delta U + RT\,\Delta n_{gas} = -3297000\ J + \left(8.3145\frac{J}{mol\bullet K}\right)(298015\ K)\left(-2\ mol\right)$$
$$\Delta H = -3302\ kJ = q(constant\ pressure)$$
$$\Delta U = q + w\ \ \rightarrow\ \ w = \Delta U - q = -3297\ kJ - (-3302\ kJ) = +5\ kJ$$

2. (a)

$$-q_M = q_{water} + q_{cup}$$

$$-m_M c_M \Delta T_M = m_{water} c_{water} \Delta T_{water} + m_{cup} c_{cup} \Delta T_{cup}$$

$$-(100.0\ g)c_M\,(-86.67\ K) = (222.2\ g)\left(4.184\frac{J}{g \bullet K}\right)(3.33\ K) + \left(500\frac{J}{K}\right)\left(3.33\ K\right)$$

$$8670c_M = 4760.9$$

$$c_M = 0.549\frac{J}{g \bullet K}$$

(b)

$$\text{(b) } q = mc\,\Delta T = (6660\ g)\left(4.184\frac{J}{g \bullet K}\right)(10.00\ K) = 278654\ J = 278.654\ kJ$$

$$\therefore\ \frac{278.654\ kJ}{891\ kJ} = \frac{x\ mole}{1\ mole}$$

x = 0.3128 mol

3. The heat that leaves the iron enters the water and the container:

$q_{water} + q_{container} = -\ q_{Fe}$

$m_{water} c_{water} \Delta T_{water} + m_{container} c_{container} \Delta T_{container} = -m_{Fe} c_{Fe} \Delta T_{Fe}$ (note: ΔT_{water} = $\Delta T_{container}$ and all will have the same final temperature)

$$\left[(437\ g)\left(4.184\frac{J}{g \bullet {}^\circ C}\right) + \left(217\frac{J}{{}^\circ C}\right)\right](T_f - 23.0\,{}^\circ C) = -(122\ g)\left(0.444\frac{J}{g \bullet {}^\circ C}\right)\left(T_f - 57.0\,{}^\circ C\right)$$

$$T_f\left[\left(2045.4\frac{J}{{}^\circ C}\right) + \left(54.2\frac{J}{{}^\circ C}\right)\right] = 3087.6\ J + 47044.2\ J$$

$$T_f = \frac{50131.8\ J}{2099.6\ J/{}^\circ C} = 23.9\ {}^\circ C$$

4. (1) Use Hess' Law

$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta H = -\ 393.5\ kJ$

$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$ $\Delta H = 2(-\ 285.8\ kJ) = -\ 571.6\ kJ$

$CO_2\ (g) + 2\ H_2O\ (l) \rightarrow CH_3OH\ (l) + 32\ O_2\ (g)$ $\Delta H = -(-\ 726.4\ kJ) = +726.4\ kJ$

$CH_3OH\ (l) \rightarrow CH_3OH\ (g)$ $\Delta H = +\ 37.4\ kJ$

$C\ (graphite) + 2\ H_2\ (g) + 12\ O_2\ (g) \rightarrow CH_3OH\ (g)$ $\Delta H = -201.3\ kJ$

(2)

$$\Delta H = \Delta U + RT\Delta n_{gas} \quad \rightarrow \quad \Delta U = \Delta H - RT\Delta n_{gas}$$

$$\Delta U = -201.3\ kJ - \frac{\left(8.3145\frac{J}{K\bullet mol}\right)\left(298.15\ K\right)\left(-\frac{2}{3}mol\right)}{\frac{1000\ J}{1\ kJ}}$$

$$\Delta U = -201.3\ kJ - (-3.7kJ) = -197.6\ kJ$$

5.

$$?kJ = 45.0\ min \times \frac{60\ s}{1\ min} \times \frac{38.0\ J}{s} \times \frac{1\ kJ}{1000\ J} = 102.6\ kJ$$

Technically, the sign here should be negative since heat is leaving, but since this is already acknowledged in the question, it's not needed.

6. q = mcΔT = – 2.75 × 10^4 kJ

7. (a)

$$?mol\ C_2H_6 = 10.0\ g \times \frac{mol}{30.07\ g} = 0.3326\ mol$$

$$?mol\ kJ\ heat = 0.3326\ mol\ C_2H_6 \times \frac{-3119\ kJ}{2\ mol\ C_2H_6} == -518kJ$$

(b)

$$?mol\ O_2 = 0.3326\ mol \times \frac{7\ mol\ O_2}{2\ mol\ C_2H_6} = 1.164\ mol$$

$$?mol\ CO_2 = 0.3326\ mol \times \frac{4\ mol\ CO_2}{2\ mol\ C_2H_6} = 0.6652\ mol$$

$$T = 25.00^{\circ}C + 273.15 = 298.15\ K$$

$$W = -\Delta nRT = -[0.6552 - (1.164 + 0.3326)]mol \times 8.3145\frac{J}{mol \bullet K} \times 298.15\ K = +2.06\ kJ$$

Chapter 4 – Chemical Equilibrium

1.

(a) $\Delta G^{\circ} = -R \bullet T \bullet \ln(K) = -\left(8.3145 \frac{J}{mol \bullet K}\right)(298.15\ K) \bullet \ln(2.22) = -1977\ J$

$$\Delta G = \Delta G^{\circ} + (R \bullet T \bullet \ln(Q)) \quad \rightarrow \quad -5000\ J = -1977\ J + \left(8.3145 \frac{J}{mol \bullet K}\right)\left(298.15\ K\right) \bullet \ln(Q)$$

$$\ln(Q) == 1.2195 \quad \rightarrow \quad Q = e^{-1.2195} = 0.2954$$

$$Q = 0.2954 = \frac{[B][C]^2}{[A]^2} \quad \rightarrow \quad [A] = \sqrt{\frac{[B][C]^2}{0.2954}}$$

$$[A] = \sqrt{\frac{(0.277)(0.444)^2}{0.2954}} = 0.430\ M$$

(b)

	2 A *(g)*	2 B *(g)* +	C *(g)*
I	4.00 atm	2.00 atm	———
C	-2x	+ 2x	+x
E	4.00 – 2x	2.00 + 2x	x

$$P_T = 6.80\ atm = P_A + P_B + P_C = (4.00 - 2x) + (2.00 + 2x) + x = 6.00 + x$$

$$6.80 = 6.00 + x \quad \rightarrow \quad x = 0.80$$

$$\therefore x = 0.80\ atm\ which\ means\ P_A = 2.40\ atm,\ P_B = 3.60\ atm,\ and\ P_C = 0.80\ atm$$

$$K = \frac{(P_B)^2\left(P_C\right)}{(P_A)^2} = \frac{(3.60)^2\left(0.80\right)}{(2.40)^2} = 1.80$$

$$\Delta G^{\circ} = -R \bullet T \bullet \ln(K) = \left(8.3145 \frac{J}{mol \bullet K}\right)\left(298.15\ K\right) \bullet \ln(1.80) = -1.46\ kJ$$

2.

$$K = e^{\frac{-\Delta G^{\circ}}{RT}} = e^{-\frac{-4770\ J}{\left(8.3145 \frac{J}{mol \bullet K}\right)(298.15\ K)}} = 0.1460$$

	A *(aq)* +	B *(aq)* ⇌	2 C *(aq)*
I	0.322 M	0.244 M	0.455 M
C	-x	-x	+2x
E	0.322 – x	0.244 – x	0.455 + 2x

$$K = \frac{[C]^2}{[A][B]} = \frac{4x^2 + 1.82x + 0.2070}{x^2 - 0.566x + 0.0786} = 3.854x^2 + 1.903x + 0.1955$$

$3.854x^2 + 1.903x + 0.1955 = 0 \rightarrow x = -0.146$ and -0.348

(note that x is found using the quadratic formula and x = -0.348 is impossible)
[C] = 0.455 + 2x = 0455 + (2)(- 0.146) = 0.164 M

3. Note that the molar mass of $AgNO_3$ is 169.87 g/mol

$$n_{AgNO_3} = n_{Ag} = \frac{6.66\ g}{169.87 \frac{g}{mol}} = 0.03903\ mol$$

	Ag^+ *(aq)* +	2 CN^- *(aq)* ⇌	$Ag(CN)_2^-$ *(aq)*
I	0.03903	0.800	—
C	-0.03903	-20.03903	+0.03903
E	—	0.72194	0.03903

Note: a small amount of $Ag(CN)_2^-$ will react to regenerate Ag^+ … the concentrations of CN^- and $Ag(CN)_2^-$ are not affected.

$$3.0\times10^{20}=\frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]}\quad\rightarrow\quad 3.0\times10^{20}=\frac{0.03903}{[Ag^+](0.72194)^2}$$

$$[Ag^+]=\frac{0.03903}{(3.0\times10^{20})(0.72194)^2}$$

$$[CN^-]=0.722\ M$$

$$[Ag(CN)_2^-]=0.0390\ M$$

4. (a)

$$Total\ P at\ EQM=\frac{nRT}{V}=\frac{(0.0147\ mol)\left(0.083145\frac{L\bullet bar}{mol\bullet K}\right)(1000\ K)}{2.50\ L}=0.489\ bar$$

	A *(g)*	2 B *(g)*	2 C *(g)*
I	0.500	0.500	0
C	-0.245	-0.245	+0.489
E	0.255	0.011	0.489

$$K_P=\frac{(C)^2}{(A)(B)^2}=\frac{(0.489)^2}{(0.255)(0.011)}=7.75\times10^3$$

(b)

$$K_C=\frac{K_P}{(RT)^n}=\frac{7750}{(0.083145\times1000)^{2-3}}=6.44\times10^5$$

5. P_{total} = 20.0 bar = P_{CH4} + P_{CO2}. Since n_{CH4} = n_{CO2} (equimolar), that means each gas has an initial partial pressure of 10.0 bar.

	CH_4 *(g)*	CO_2 *(g)*	2 CO *(g)*	2 H_2 *(g)*
I	10.0	10.0	0	0
C	-x	-x	+2x	+2x
E	0.246	0.2	19.6	19.6

$$K_P = \frac{(CO)^2(H_2)^2}{(CH_4)(CO_2)} = \frac{(19.6)^2(19.6)^2}{(0.2)(0.2)} = 3.7 \times 10^6$$

6. 0.83

Divide Equation 1’s equilibrium constant by 2 and multiple Equation 2’s equilibrium constant by -1 (as you have to flip it); Add modified equilibrium constants to get 0.83.

Chapter 5 -Acid/Base Equilibria

1. NH_4^+ *(aq)* ⇌ NH_3 *(aq)* + H^+ *(aq)*

E: 0.333 – x 0.333 x x

$$K_a of\ NH_4^+ = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{x^2}{0.333} \rightarrow x = [H^+] = 1.36 \times 10^{-5}$$

pH = -log(1.36 x 10^{-5}) = 4.87

2. (a)

$$C_AV_A = C_BV_B \rightarrow C_A = \frac{C_BV_B}{V_A} = \frac{(0.222\ M)(22.2\ mL)}{(25.0\ mL)} = 0.1971\ M$$
$$\frac{x}{0.1971\ mol} = \frac{25.0\ mL}{1000.0\ mL} \rightarrow x = 0.004928\ mol$$
$$MM = \frac{2.33\ g}{0.004928\ mol} = 473\frac{g}{mol}$$

(b) HA *(aq)* ⇌ H^+ *(aq)* + A^- *(aq)*

E: 0.1971 – x x x

$$x = [H^+] = 10^{-PH} = 10^{-1.44} = 0.0363\ M$$
$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.0363)^2}{(0.1971 - 0.0363)} = 8.2 \times 10^{-3}$$

(c) A^- *(aq)* + H_2O *(l)* ⇌ HA *(aq)* + OH^- *(aq)*

E: 2.000 – x 2.000 x x

$$K_b = \frac{[HA][OH^-]}{[A^-]} \rightarrow 1.22 \times 10^{-12} = \frac{x^2}{2.000} \rightarrow x = [OH^-] = 1.56 \times 10^{-6}$$
$$pOH = -\log\left(1.56 \times 10^{-6}\right) = 5.81$$

pH = 8.19

3. (a)

	2 A *(aq)* ⇌	B *(aq)* +	C *(aq)*
I	0.444	0.555	0.666
C	-2x	+x	+x
E	0.444 – 2x	0.555 + x	0.666 + x

$$K = \frac{[B][C]}{[A]^2} \rightarrow 5.55 = \frac{(0.555 + x)(0.666 + x)}{(0.444 - 2x)^2} = \frac{x^2 + 1.221x + 0.36963}{4x^2 - 1.776x + 0.19714} = 21.2x^2 - 11.0778x + 0.7245$$

$21.2x^2 - 11.0778x + 0.7245 = 0$ → x = 0.4459 and 0.0765 (Note: use quadratic formula to find values for x and x = 0.4459 is impossible so we use 0.0765)

[A] = 0.44 – 2(0.0765) = 0.291 M

(b)

$$n_{Al(OH)_3} = \frac{0.0888\ g}{78.00 \frac{g}{mol}} = 0.001138\ mol$$
$$n_{OH^-} = 3 \times n_{AL(OH)_3} = 0.003415\ mol$$
$$[OH^-] = \frac{0.003415\ mol}{0.666\ L} = 0.005128 \frac{mol}{L}$$

$$\therefore \text{ pOH} = 2.29 \text{ and pH} = 11.71$$

4.

pOH = 14 – pH – 3.45

$[OH^-] = 10^{-3.45} = 3.55 \times 10^{-4}$ M

Let B represent the base, $N(CH_3)_3$,

	B	H_2O	OH^-	HB^+
I	[B]	–	0	0
C	-x	–	+x	+x
E	[B] – x	–	x	X

$$K_b = \frac{[OH^-][HB^+]}{[B]} \quad \rightarrow \quad 6.31 \times 10^{-6} = \frac{x^2}{[B]-x} = \frac{x^2}{[B]} = \frac{(3.55 \times 10^{-4})^2}{[B]}$$

[B] = 0.0200 M

Check: $\frac{3.55 \times 10^{-4}}{0.0200} \times 100\% = 1.8\% \quad \rightarrow \quad \text{Passes}$

5. (a) Initial pH

	HA	H_2O	H_3O^+	A^-
I	0.090	–	0	0
C	-x	–	+x	+x
E	0.090 – x	–	x	X

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \rightarrow \quad 6.2 \times 10^{-10} = \frac{x^2}{0.090 - x} = \frac{x^2}{0.090}$$
$$x = 7.47 \times 10^{-6}\ M = [H_3O^+]$$

Check: $\frac{7.47 \times 10^{-6}}{0.090} \times 100\% = 0.008\% \quad \rightarrow \quad \text{Passes}$

(b) At half equivalence point: pH = pK_a = -log(6.2 x 10^{-10}) = 9.21 (after 40 mL added)

(c) At the equivalence point

mol HA = mol OH- added = 0.0072 mol (this corresponds to adding 80.0 mL of base)

new [A-] = 0.0072 mol/(0.080 L + 0.080 L) = 0.0450 M

OCl^- is a conjugate base of a weak acid, so it hydrolyzes:

	A^-	H_2O	HA	OH^-
I	0.045	–	0	0
C	-x	–	+x	+x
E	0.045 – x	–	x	x

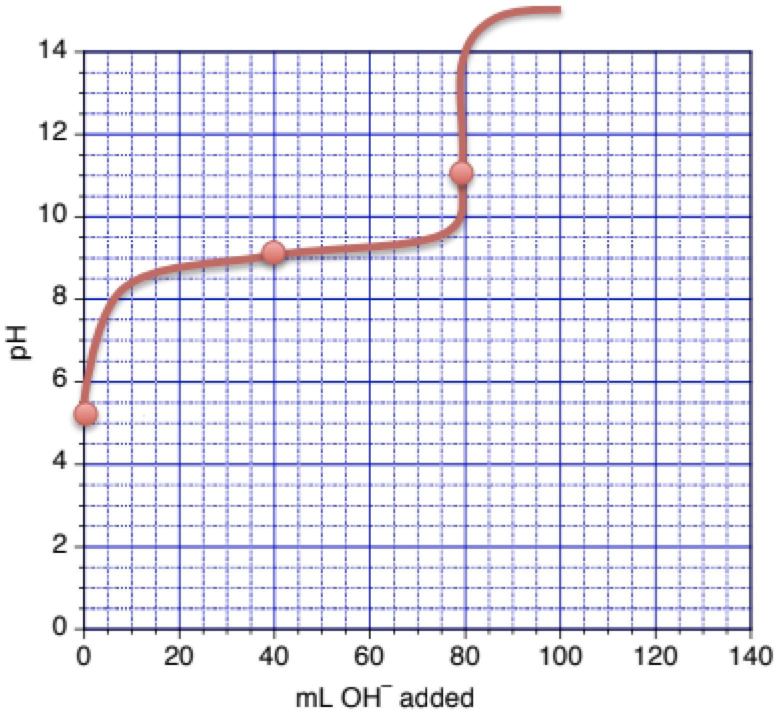
$$K_b = \frac{K_w}{K_a} = \frac{[HA][OH^-]}{[A^-]}$$
$$\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5} = \frac{x^2}{0.045 - x} = \frac{x^2}{0.045}$$
$$x = 8.5 \times 10^{-4}\ M = [OH^-]$$

$x = 8.5 \times 10^{-4}$ M = [OH-]

pOH = -log(8.5 x 10^{-4}) = 3.07

pH = 14 – 3.07 = 10.93

(d)



Chapter 6 – Ionic Equilibria in Aqueous Systems

1. (a) The molar mass of $Mg(PO_4)_2$ is 262.86 g/mol

	$Mg(PO_4)_2$ *(s)* ⇌	$3\ Mg^{+}$ *(aq)* +	$2\ PO_4^{3-}$ *(aq)*
I	—	—	—
C	—	+ 3x	+ 2x
E	—	3x	2x

$$K_{sp} = \left[Mg^{2+}\right]^3 \left[PO_4^{3-}\right]^2 \quad \rightarrow \quad 1.0 \times 10^{-24} = (3x)^3(2x)^2 = 108x^5 \quad \rightarrow \quad x = 6.213 \times 10^{-6} \frac{mol}{L}$$

$$solubility = \left(6.213 \times 10^{-6} \frac{mol}{L}\right)\left(262.86 \frac{g}{mol}\right) = 1.6 \times 10^{-3} \frac{g}{L}$$

(b)

	$Mg(PO_4)_2$ *(s)* ⇌	$3\ Mg^{+}$ *(aq)* +	$2\ PO_4^{3-}$ *(aq)*
I	—	0.30	—
C	—	+ 3x	+ 2x
E	—	0.30 + 3x 0.30	2x

$$K_{sp} = \left[Mg^{2+}\right]^3 \left[PO_4^{3-}\right]^2 \quad \rightarrow \quad 1.0 \times 10^{-24} = (0.30)^3(2x)^2 = 108x^5 \quad \rightarrow \quad x = 3.0429 \times 10^{-12} \frac{mol}{L}$$

$$solubility = \left(3.0429 \times 10^{-12} \frac{mol}{L}\right)\left(262.86 \frac{g}{mol}\right) = 8.0 \times 10^{-10} \frac{g}{L}$$

2. (a)

	NH_3 *(aq)* +	H^+ *(aq)* ⇌	NH_4^+ *(aq)*
I	0.7103	0.1701	—
C	– 0.1701	– 0.1701	+ 0.1701
E	0.5402	—	0.1701

$$pH = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right) = 9.255 + \log\left(\frac{0.5402}{0.1701}\right) = 9.76$$

(b) 1.00 g of NaOH (0.0250 mol) consumes 0.0250 mol of NH_4^+ *(aq)* and produces 0.0250 mol of NH_3 *(aq)*

$$pH = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right) = 9.255 + \log\left(\frac{0.5402 + 0.0250}{0.1701 - 0.0250}\right) = 9.85$$

(c) 1.00 g of HCl (0.0274 mol) consumes 0.0274 mol of NH_3 *(aq)*and produces 0.0274 mol of NH_4^+ *(aq)*

$$pH = pK_a + \log\left(\frac{[NH_3]}{[NH_4^+]}\right) = 9.255 + \log\left(\frac{0.5402 - 0.0274}{0.1701 + 0.0274}\right) = 9.68$$

3. The $Ba(OH)_2$ has 2 groups of OH^-, so $C_AV_A = 2\ C_BV_B$

$$V_A = \frac{2C_BV_B}{C_A} = \frac{2(0.348\ M)(280\ mL)}{0.277\ M} = 70.4\ mL$$

- At the equivalence point, the volume is (70.4 mL + 28.0 mL) = 98.4 mL
- All of the acetic acid is converted to CH_3COO^-; a weak base:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{10^{-4.74}} = 5.5 \times 10^{-10}$$

$$C_1 = \frac{C_2 V_2}{V_1} \quad \rightarrow \quad [CH_3COO^-] = \frac{(0.277\ M)(70.4\ mL)}{98.4\ mL} = 0.198\ M$$

CH_3COO^- *(aq)* + H_2O *(l)* ⇌ CH_3COOH *(aq)* + OH^- *(aq)*

0.198 – x ≈ 0.198 x x

$$5.5 \times 10^{-10} = \frac{x^2}{0.198} \quad \rightarrow \quad x = [OH^-] = 1.04 \times 10^{-5}$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{1.04 \times 10^{-5}} = 5.6 \times 10^{-10}$$

pH = 9.02

4.

K_a 1.8×10^{-5}

$$?moles\ CH_3COONa = \frac{0.847\ g}{82.03 \frac{g}{mol}} = 0.01033\ \ mol$$

$$[CH_3COO^-] = \frac{0.01033\ mol}{0.100\ L} = 0.1033\ M$$

CH_3COO^- *(aq)* + H_2O *(l)* ⇌ CH_3COOH *(aq)* + OH^- *(aq)*

0.1033 – x ≈ 0.1033 x x

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \rightarrow \quad 5.6 \times 10^{-10} = \frac{x^2}{0.1033} \quad \rightarrow \quad x = 7.6 \times 10^{-6}$$

∴ $[OH^-] = 7.6 \times 10^{-6}$ → pOH= -log(7.610-6) = 5.12

pH = 14 – pOH → pH=8.88

5. (a)

$$K_a = \frac{Kw}{Kb} = \frac{1.0\ \times\ 10^{-14}}{1.8\ \times\ 10^{-5}}$$

---

pH = pK_a - $\log(\frac{[NH3]}{[NH4+]})$ → 9.45 = $-\log(5.5 \times 10^{-10})$ - $\log(\frac{[NH3]}{[NH4+]})$

$\log(\frac{[NH3]}{[NH4+]})$ = 9.45 - 9.26 = 0.19 → $(\frac{[NH3]}{[NH4+]})$ = $10^{0.`9}$ = 1.1

∴ $[NH_4+]$ = 1.55 x $[NH_3]$ = 1.55 x 0.258 M = 0.17 M

? g $(NH_4)_2SO_4$ = 0.425 L x 0.19 M NH_4+ x $\frac{1\ mol\ (NH4)2SO4}{2\ mol\ NH4+}$ x $\frac{132.1\ g}{mol}$ = 4.8 g

(b)

$$\text{pH} = \text{pK}_a - \log\left(\frac{[NH3]}{[NH4+]}\right)$$

$$9.30 = 9.26 - \log\left(\frac{[NH3]}{[NH4+]}\right)$$

$$\log\left(\frac{[NH3]}{[NH4+]}\right) = 9.30 - 9.26 = 0.04 \rightarrow \left(\frac{[NH3]}{[NH4+]}\right) = 10^{0.04} = 1.1$$

To lower pH to 9.30, we need to add acid. But how much?

$[NH_3] = 0.258\ \text{M}$ and $[NH_4{+}] = 0.17\ \text{M} + x$

$$\therefore \frac{[NH3]}{[NH4+]} = \frac{0.258}{0.17 + x} = 1.1 \rightarrow x = 0.062\ \text{M}$$

$$?\ \text{g}\ (NH_4)_2SO_4 = 0.100\ \text{L} \times 0.062\ \text{M}\ NH_4{+} \times \frac{1\ mol\ (NH4)2SO4}{2\ mol\ NH4+} \times \frac{132.1\ g}{mol} = 0.41\ \text{g}$$

Amount: 0.41 g

6. (a) PbI_2

(b)

$$?\ \text{mol}\ Pb^{2+} = 2.74\ \text{M}\ Pb(NO_3)_2 \times \frac{1\ mol\ Pb2+}{1\ mol\ Pb(NO3)2} \times 0.0310\ L = 8.494 \times 10^{-2}\ \text{mol}$$

$$?\ \text{mol}\ NO^-_3 = 2.74\ \text{M}\ Pb(NO_3)_2 \times \frac{2\ mol\ NO3-}{1\ mol\ Pb(NO3)2} \times 0.0310\ L = 0.1699\ \text{mol}$$

$$?\ \text{mol}\ Na^+ = 0.00163\ \text{M}\ NaI \times \frac{1\ mol\ Na+}{1\ mol\ NaI} \times 0.0200\ L = 3.26 \times 10^{-5}\ \text{mol}$$

$$?\ \text{mol}\ I^- = 0.00163\ \text{M}\ NaI \times \frac{1\ mol\ I-}{1\ mol\ NaI} \times 0.0200\ L = 3.26 \times 10^{-5}\ \text{mol}$$

	Pb^{2+}	I-	PbI_2 (s)
B	8.494×10^{-2} mol		0
A		3.26×10^{-5} mol	
M	$-0.5 \times 3.26 \times 10^{-5}$ mol	-3.26×10^{-5} mol	$+0.5 \times 3.26 \times 10^{-5}$ mol
A	8.494×10^{-2} mol	0	1.63×10^{-5} mol

1.63×10^{-5} mol of PbI_2 precipitates and total volume is 20.0 mL + 30.0 mL = 51.0 mL

? $[Pb^{2+}]$ = 8.494 x 10^{-2} mol/0.0510 L = 1.665 M

? $[NO^{-}{}_3]$ = 0.1699 mol/0.0510 L = 3.33 M

? $[Na^{+}]$ = 3.26 x 10^{-5} mol/0.0510 L = 6.39 x 10^{-4} M

? [I-] = 0 mol/0.0510 L = 0 M

7. Circled → $Ca(CN)_2$ and LiF

Underlined → KCl and $CuNO_3$

APPENDICES

APPENDIX A | THE PERIODIC TABLE OF ELEMENTS

REFERENCE

1. Periodic Table of Elements – IUPAC: International Union of Pure and Applied Chemistry. https://iupac.org/what-we-do/periodic-table-of-elements/ (accessed Aug 9, 2020).

APPENDIX B | PROPERTIES OF THE ELEMENTS

Element	Symbol	Atomic Number (Z)	Atomic Mass^{1,2}	State (standard conditions)	Common Oxidation States	Mass no. of Stal
Actinium	Ac	89	[227]	solid	+3	
Aluminum	Al	13	26.98	solid	+3	27
Americium	Am	95	[243]	solid	+3, +4, +5, +6	
Antimony	Sb	51	121.8	solid	+3, +5	121, 123
Argon	Ar	18	39.95	gas	0	36, 38, 40
Arsenic	As	33	74.92	solid	+3, +5, -3	75
Astatine	At	85	[210]	solid		
Barium	Ba	56	137.3	solid	+2	130, 132, 134, 13
Berkelium	Bk	97	[247]	solid	+3, +4	
Beryllium	Be	4	9.012	solid	+2	9
Bismuth	Bi	83	209.0	solid	+3, +5	209
Bohrium	Bh	107	[264]	solid*	+7*	
Boron	B	5	10.81	solid	+3	10, 11
Bromine	Br	35	79.90	liquid	+1, +5, -1	79, 81
Cadmium	Cd	48	112.4	solid	+2	106, 108, 110, 11 116
Calcium	Ca	20	40.08	solid	+2	40, 42, 43, 44, 46
Californium	Cf	98	[251]	solid	+3	
Carbon	C	6	12.01	solid	+2, +4, -4	12, 13

Cerium	Ce	58	140.1	solid	+3, +4	136, 138, 140, 14
Cesium	Cs	55	132.9	solid	+1	133
Chlorine	Cl	17	35.45	gas	+1, +5, +7, -1	35, 37
Chromium	Cr	24	52.00	solid	+2, +3, +6	50, 52, 53, 54
Cobalt	Co	27	58.93	solid	+2, +3	59
Copernicium	Cn	112	[285]	liquid/gas*	+2, +4*	
Copper	Cu	29	63.55	solid	+1, +2	63, 65
Curium	Cm	96	[247]	solid	+3	
Darmstadtium	Ds	110	[271]	solid*	+2, +4, +6*	
Dubnium	Db	105	[262]	solid*	+5*	
Dysprosium	Dy	66	162.5	solid	+3	156, 158, 160, 16
Einsteinium	Es	99	[252]	solid	+3	
Erbium	Er	68	167.3	solid	+3	162, 164, 166, 16
Europium	Eu	63	152.0	solid	+2, +3	151, 153
Fermium	Fm	100	[257]	solid	+3	
Flerovium	Fl	114	[289]	liquid/gas*	+2, +4*	
Fluorine	F	9	19.00	gas	-1	19
Francium	Fr	87	[223]	solid/liquid*	+1	
Gadolinium	Gd	64	157.3	solid	+3	152, 154, 155, 15

Gallium	Ga	31	69.72	solid	+3	69, 71
Germanium	Ge	32	72.63	solid	+2, +4	70, 72, 73, 74, 7
Gold	Au	79	197.0	solid	+1, +3	197
Hafnium	Hf	72	178.5	solid	+4	174, 176, 177, 1
Hassium	Hs	108	[265]	solid*	+8*	
Helium	He	2	4.003	gas	0	3, 4
Holmium	Ho	67	164.9	solid	+3	165
Hydrogen	H	1	1.008	gas	+1	1, 2
Indium	In	49	114.8	solid	+3	113, 115
Iodine	I	53	126.9	solid	+1, +5, +7, -1	127
Iridium	Ir	77	192.2	solid	+3, +4	191, 193
Iron	Fe	26	55.85	solid	+2, +3	54, 56, 57, 58
Krypton	Kr	36	83.80	gas	0	78, 80, 82, 83, 8
Lanthanum	La	57	138.9	solid	+3	138, 139
Lawrencium	Lr	103	[260]	solid	+3	
Lead	Pb	82	207.2	solid	+2, +4	204, 206, 207, 2
Lithium	Li	3	6.94	solid	+1	6, 7
Livermorium	Lv	116	[293]	solid*	+2, +4*	
Lutetium	Lu	71	175.0	solid	+3	175, 176

Magnesium	Mg	12	24.31	solid	+2	24, 25, 26
Manganese	Mn	25	54.94	solid	+2, +3, +4, +7	55
Meitnerium	Mt	109	[268]	solid*	+1, +3, +6*	
Mendelevium	Md	101	[258]	solid	+2, +3	
Mercury	Hg	80	200.6	liquid	+1, +2	196, 198, 199, 20
Molybdenum	Mo	42	95.95	solid	+6	92, 94, 95, 96, 97
Moscovium	Mc	115	[290]	solid*	+1, +3*	
Neodymium	Nd	60	144.2	solid	+3	142, 143, 144, 14
Neon	Ne	10	20.18	gas	0	20, 21, 22
Neptunium	Np	93	[237]	solid	+3, +4, +5, +6	
Nickel	Ni	28	58.69	solid	+2, +3	58, 60, 61, 62, 64
Nihonium	Nh	113	[286]	solid*	+1, +3*	
Niobium	Nb	41	92.91	solid	+3, +5	93
Nitrogen	N	7	14.01	gas	+1, +2, +3, +4, +5, -1, -3	14, 15
Nobelium	No	102	[259]	solid	+2, +3	
Oganesson	Og	118	[294]	solid*	0, +2, +4*	
Osmium	Os	76	190.2	solid	+3, +4	184, 186, 187, 18
Oxygen	O	8	16.00	gas	-2	16, 17, 18
Palladium	Pd	46	106.4	solid	+2, +3	102, 104, 105, 10

Phosphorus	P	15	30.97	solid	+3, +5, -3	31
Platinum	Pt	78	195.1	solid	+2, +4	190, 192, 194, 19
Plutonium	Pu	94	[244]	solid	+3, +4, +5, +6	
Polonium	Po	84	[209]	solid	+2, +4	
Potassium	K	19	39.10	solid	+1	39, 40, 41
Praseodymium	Pr	59	140.9	solid	+3	141
Promethium	Pm	61	[145]	solid	+3	
Protactinium	Pa	91	231.0	solid	+4, +5	231
Radium	Ra	88	[226]	solid	+2	
Radon	Rn	86	[222]	gas	0	
Rhenium	Re	75	186.2	solid	+4, +6, +7	185, 187
Rhodium	Rh	45	102.9	solid	+3	103
Roentgenium	Rg	111	[282]	solid*	+3, +5, -1*	
Rubidium	Rb	37	85.47	solid	+1	85, 87
Ruthenium	Ru	44	101.1	solid	+3	100, 101, 102, 10
Rutherfordium	Rf	104	[267]	solid*	+4	
Samarium	Sm	62	150.4	solid	+2, +3	144, 147, 148, 14
Scandium	Sc	21	44.96	solid	+3	45
Seaborgium	Sg	106	[269]	solid*	+6*	

Selenium	Se	34	78.97	solid	+4, +6, -2	74, 76, 77, 78, 80
Silicon	Si	14	28.09	solid	+2, +4, -4	28, 29
Silver	Ag	47	107.9	solid	+1	107, 109
Sodium	Na	11	22.99	solid	+1	23
Strontium	Sr	38	87.62	solid	+2	84, 86, 87, 88
Sulfur	S	16	32.06	solid	+4, +6, -2	32, 33, 34, 36
Tantalum	Ta	73	180.9	solid	+5	180, 181
Technetium	Tc	43	[97]	solid	+4, +6, +7	
Tellurium	Te	52	127.6	solid	+4, +6, -2	120, 122, 123, 12 130
Tennessine	Ts	117	[294]	solid*	+1, +3, +5*	
Terbium	Tb	65	158.9	solid	+3	159
Thallium	Tl	81	204.4	solid	+1, +3	203, 205
Thorium	Th	90	232.0	solid	+4	232
Thulium	Tm	69	168.9	solid	+3	169
Tin	Sn	50	118.7	solid	+2, +4	112, 114, 115, 11 120, 122, 124
Titanium	Ti	22	47.87	solid	+2, +3, +4	46, 47, 48, 49, 50
Tungsten	W	74	183.8	solid	+6	180, 182, 183, 18
Uranium	U	92	238.0	solid	+3, +4, +5, +6	234, 235, 238
Vanadium	V	23	50.94	solid	+2, +3, +4, +5	50, 51

Xenon	Xe	54	131.3	gas	0	124, 126, 128, 12 134, 136
Ytterbium	Yb	70	173.0	solid	+2, +3	168, 170, 171, 17
Yttrium	Y	39	88.91	solid	+3	89
Zinc	Zn	30	65.38	solid	+2	64, 66, 67, 68, 70
Zirconium	Zr	40	91.22	solid	+4	90, 91, 92, 94, 96

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[1] Atomic masses are given to four significant figures where possible.

[2] Atomic masses given in brackets denote the mass of the longest-lived isotope.

[3] Includes radioactive isotopes of very long lifetimes, whose terrestrial abundance is effectively stable.

*Predicted.

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APPENDIX C | ESSENTIAL MATHEMATICAL CONCEPTS

Scientific/Exponential Notation

Scientific (or exponential) notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$1000 = 1 \times 10^{3}$

$100 = 1 \times 10^{2}$

$10 = 1 \times 10^{1}$

$1 = 1 \times 10^{0}$

$0.1 = 1 \times 10^{-1}$

$0.001 = 1 \times 10^{-3}$

$2386 = 2.386 \times 1000 = 2.386 \times 10^{3}$

$0.123 = 1.23 \times 0.1 = 1.23 \times 10^{-1}$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for very large and very small numbers. For example, $1\,230\,000\,000 = 1.23 \times 10^{9}$, and $0.00000000036 = 3.6 \times 10^{-10}$.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Adding Exponentials

Example C.1

Add 5.00×10^{-5} and 3.00×10^{-3}.

Solution

3.00×10-3=300×10-5(5.00×10-5)+(300×10-5)=305×10-5=3.05×10-3

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Subtracting Exponentials

Example C.2

Subtract 4.0×10^{-7} from 5.0×10^{-6}.

Solution

4.0×10-7=0.40×10-6

(5.0×10-6)-(0.40×10-6)=4.6×10-6

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Multiplying Exponentials

Example C.3

Multiply 4.2×10^{-8} by 2.0×10^{3}.

Solution

(4.2×10-8)×(2.0×103)=(4.2×2.0)×10-8++3=8.4×10-5

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Dividing Exponentials

Example C.4

Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

3.6×10-56.0×10-4=3.66.0×10(-5)-(-4)=0.60×10-1=6.0×10-2

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Squaring Exponentials

Example C.5

Square the number 4.0×10^{-6}.

Solution

4.0×10-62=4×4×102×-6=16×10-12=1.6×10-11

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Cubing Exponentials

Example C.6

Cube the number 2×10^{4}.

Solution

$$2\times1043=2\times2\times2\times103\times4=8\times1012$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Finding the Square Root of Exponentials

Example C.7

Find the square root of 1.6×10^{-7}.

Solution

$$1.6\times10\text{-}7=16\times10\text{-}816\times10\text{-}8=16\times10\text{-}8=16\times10\text{-}82=4.0\times10\text{-}4$$

Significant Figures

A beekeeper reports that he has 525 341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more reasonable if the beekeeper had reported the number 525 000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no useful meaning in this situation. When reporting quantities, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

Addition and Subtraction with Significant Figures

Example C.8

Add 4.383 g and 0.0023 g.

Solution

4.383 g
0.0023 g
image
4.385 g

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Multiplication and Division with Significant Figures

Example C.9

Multiply 0.6238 by 6.6.

Solution

$$0.6238 \times 6.6 = 4.1$$

When we take the *log* of a number, we express that number in scientific notation (
a×10b

) and compute the *log* for both terms *a* and 10^b separately (based on the rule for the logarithm of a product of two numbers). The value obtained from *log* (*a*) will be expressed to the same number of significant figures, and this is then added to the value for *log* (10^b).

Logarithmic Operations with Significant Figures

Example C.10

Take the base-10 logarithm of 22.38.

Solution

$\log22.38=\log2.238\times101=\log2^{-}.238^{-}+\log101=0.3498^{-}60\ldots+1.00000\ldots=1.3499^{-}$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

NOTE: The material discussed briefly here about significant figures is covered in much greater detail in “Significant Figures and Uncertainty” of the introductory chapter – see that section for more detailed explanations, examples and practice exercises concerning the use of significant figures.

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	-1
0.01	10^{-3}	-3

Table C.1 Logarithms and Exponential Numbers

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

0.03918=10-1.4069=1101.4069

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (*ln*) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

The logarithm of a product of two numbers is the sum of logarithms of the two numbers.

$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y$$

The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.

logxy=logx-logy,

and
lnxy=lnx-lny

The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

The Solution of Quadratic Equations

One form of mathematical functions you're probably very familiar with are linear functions (or first-order polynomials) – those that are described by the well-known equation $y = mx + b$, where m defines the slope of the line and b is the value dictating the y-intercept of the line on the graph. In other words, computing multiple x,y pairs from a single function, graphing them and connecting all points together gives a straight line on the Cartesian plane. Any other data point you produce from the function will always lie on the plotted line.

Another form of common mathematical functions are second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

x=-b±b2-4ac2a

This is commonly known as the quadratic formula. The derivation to solve for x can be done in various ways, one of which is shown below:

ax2+bx+c=04a2x2+4abx+4ac=04a2x2+4abx=-4ac4a2x2+4abx+b2=b2-4ac2ax+b2=b2-4ac2ax+b=±b2-4ac2ax=-b±b2-4acx=-b±b2-4ac2a

Solving Quadratic Equations

Example C.11

Solve the quadratic equation $3x^2 + 13x - 10 = 0$

Solution

Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

x=-13±132-4×3×(-10)2×3

x=-13±169+1206=-13±2896=-13±176

The two roots are therefore

x=-13+176=23

and

x=-13-176=-5

Two-Dimensional ($x - y$) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (*x*), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (*y*).

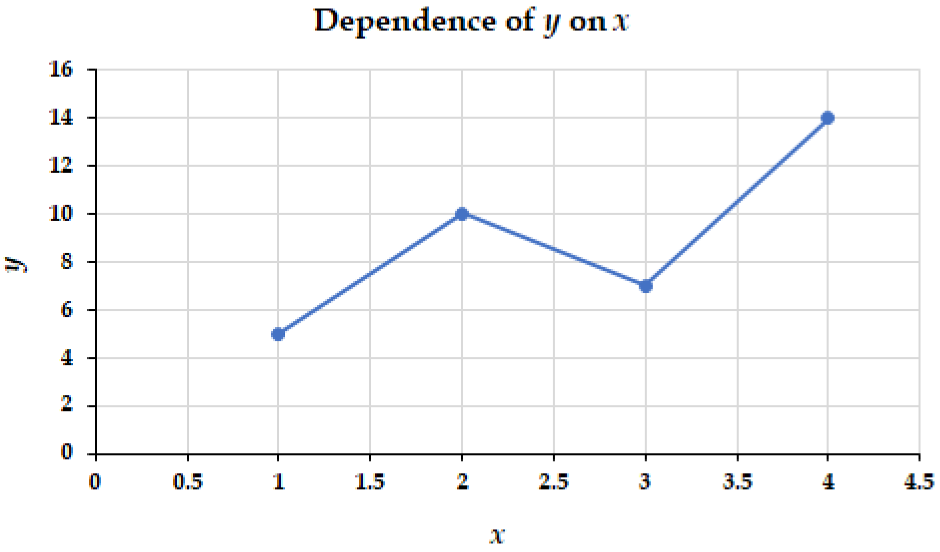
When the value of *y* is changing as a function of *x* (that is, different values of *x* correspond to different values of *y*), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (*x*,*y*) data pairs.

Graphing the Dependence of *y* on *x*

Example C.12

x	*y*
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of *y* on *x*.



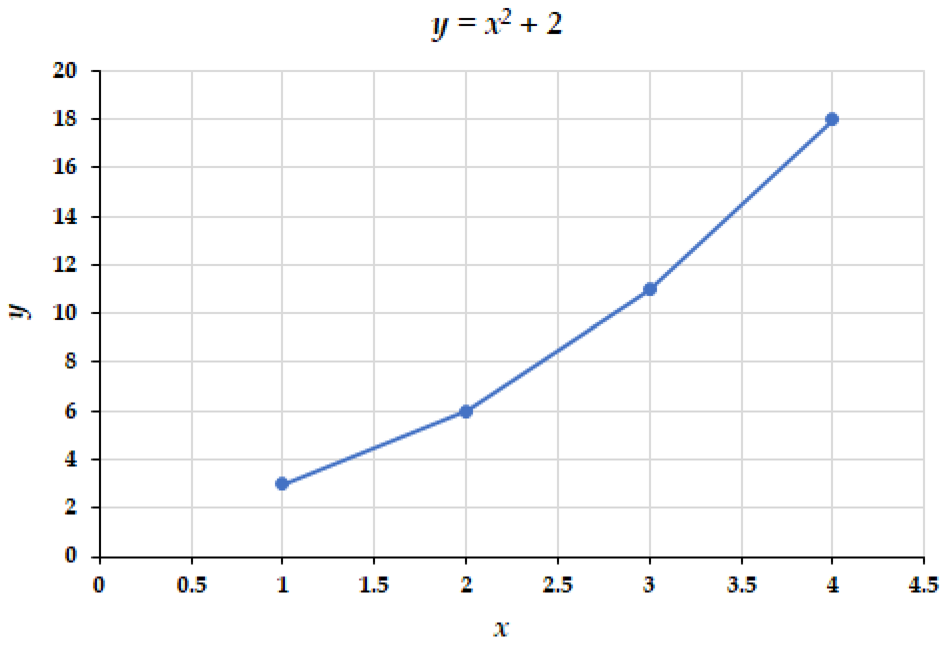
If the function that describes the dependence of *y* on *x* is known, it may be used to compute *x*,*y* data pairs that may subsequently be plotted.

Plotting Data Pairs

Example C.13

If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



APPENDIX D | UNITS AND CONVERSION FACTORS

Factor	Name	Abbreviation	Factor	Name	Abbreviation
10^{1}	deca	da	10^{-1}	deci	d
10^{2}	hecto	h	10^{-2}	centi	c
10^{3}	kilo	k	10^{-3}	milli	m
10^{6}	mega	M	10^{-6}	micro	μ
10^{9}	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a
10^{21}	zetta	Z	10^{-21}	zepto	z
10^{24}	yotta	Y	10^{-24}	yocto	y

Table D.1 SI prefixes

SI unit: metre (m)		
1 metre (m)	≈	39.37 inches (in.)
1 centimetre (cm)	=	0.01 m
1 millimetre (mm)	=	0.001 m
1 kilometre (km)	=	1000 m
1 angstrom (Å)	=	10^{-8} cm
	=	10^{-10} m
1 inch (in.)	=	2.54 cm (exact, definition)

Table D.2 Units of Length

SI unit: cubic metre (m^3)		
1 litre (L)	=	0.001 m^3
	=	1000 cm^3
1 millilitre (mL)	=	0.001 L
	=	1 cm^3
1 microlitre (μL)	=	10^{-6} L
	=	10^{-3} cm^3

Table D.3 Units of Volume

SI unit: kilogram (kg)		
1 gram (g)	=	0.001 kg
1 milligram (mg)	=	0.001 g
1 kilogram (kg)	=	1000 g
	≈	2.205 lb
1 ton (metric)	=	1000 kg
1 pound (lb)	≈	0.4535924 kg
	=	16 ounces
1 atomic mass unit (amu)	≈	1.66054×10^{-27} kg

Table D.4 Units of Mass

SI unit: joule (J)		
1 joule (J)	=	$1\ \text{kg} \cdot \text{m}^2/\text{s}^2$
	≈	9.4778×10^{-4} BTU[1]
1 thermochemical calorie (cal)	≈	4.184 J
	≈	4.184×10^{7} erg
1 erg	=	10^{-7} J
1 electron-volt (eV)	≈	1.60218×10^{-19} J
	≈	23.061 kcal mol^{-1}
1 nutritional calorie (Cal)	=	1000 cal
	≈	4184 J

Table D.5 Units of Energy

SI unit: kelvin (K)		
0 kelvin (K)	=	-273.15°C
	=	-459.67°F
K	=	°C + 273.15
°C	=	59 (°F – 32)
°F	=	95 (°C) + 32

Table D.6 Units of Temperature

SI unit: pascal (Pa)		
1 pascal (Pa)	=	N m^{-2}
	=	kg m^{-1} s^{-2}
1 Torr	=	1 mm Hg
1 atmosphere (atm)	=	760 mm Hg
	=	760 Torr
	=	101 325 N m^{-2}
	=	101 325 Pa
	=	1.01325 bar
1 bar	=	10^5 Pa
	=	10^5 kg m^{-1} s^{-2}

Table D.7 Units of Pressure

Dimensional Analysis

Dimensional analysis is a form of proportional reasoning. It uses conversion factors to convert a quantity from one unit to another.

Quantity with desired unit = **Quantity with given unit** × **Conversion factor**

In general, this method starts with the given value that will then be multiplied or divided by a known ratio or proportion. When setting up the ratios, the unit in the denominator must match that of the numerator of the given value. Continuing with the unit of the numerator in the next ratio, it has to match the denominator of the following ratio or of the units necessary for the answer.

For example, say you were trying to convert 3.41 grams of He to a number of atoms of He. You would identify 3.41 grams as the given quantity with grams as the given unit. The first step is always to place the given quantity in front of your equation. Then find a ratio that will help you convert the units of grams to atoms. As you probably have already guessed, you need to use a couple of ratios to help you in this problem. The ratio that 4.002 g of He = 1 mole (molar mass) will help you in this problem. Avogadro's number, 6.022 x 10^{23} atoms = 1 mole, will also help you in this problem. Then you set up your ratios so that your units will cancel successfully (the same unit must be in the numerator of the equation and also in the denominator of the equation). Lastly, multiply through to get your final answer. As always, your final answer should contain the correct number of sig figs and the correct units.

3.41g×1mole4.002g×6.022×1023atoms1mole=5.13×1023atoms

Flipping the Conversion Factor

Note that a conversion factor can be flipped. For example, days are converted to hours by multiplying the days by the conversion factor of 24. The conversion can be reversed by dividing the hours by 24 to get days. The reciprocal 1/24 could be considered the reverse conversion factor for an hours-to-days conversion. The term "conversion factor" is the multiplier, not divisor, which yields the result.

Consider the following relationship

1kg1000g=1000g1kg

Both fractions are equal to 1 when the units are ignored. As the quotients are both equal to 1, it does not change the equation, just the relative numerical values with various units.

Solving Dimensional Analysis Problems

When doing dimensional analysis problems, follow this list of steps:

Identify the given amount with the given units (see previous concept for additional information).

Identify conversion factors that will help you get from your original units to your desired unit.

Set up your equation so that your undesired units cancel out to give you your desired units. A unit will cancel out if it appears in both the numerator and the denominator during the equation.

Multiply through to get your final answer. Don't forget the units and sig figs!

Example Problems

How many hours are in 3 days?

Solution:

1. Identify the given: 3 days

2. Identify conversion factors that will help you get from your original units to your desired unit: 24hours1day

3. Set up your equation so that your undesired units cancel out to give you your desired units: 3 days ×

24hours1day

4. Multiply through to get your final answer: 72 hours

Converting between moles and grams

Find the amount of moles in 22.34 g of water.

Solution

22.34gH2O×1molH2O18gH2O=1.24molesH2O

APPENDIX E | FORMULAS & FUNDAMENTAL PHYSICAL CONSTANTS

Key Formulas

General

$$n = \frac{m}{\mathcal{M}}$$

$$c = \frac{n}{V}$$

$$\%\ yield = \frac{actual\ yield}{theoretical\ yield} \times 100\%$$

$$\chi_A = \frac{n_A}{n_T}$$

Gases

$$PV = nRT$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_T = \sum_{i=1}^{n} P_i = P_1 + P_2 + P_3 + \cdots + P_n$$

$$P_A = \chi_A P_T$$

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT}$$

$$E_K = \frac{1}{2}m\overline{u^2}$$

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

$$\frac{Rate\ A}{Rate\ B} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

Thermochemistry

$$\Delta U = q + W \qquad W_{system} = -P\Delta V = -\Delta nRT \qquad \Delta H = \Delta U + P\Delta V$$

$$q_P = \Delta U + P\Delta V \qquad q = mc\Delta T \qquad q = n\Delta H$$

$$\Delta H_{rxn}{}^{\circ} = \sum n\Delta H_f{}^{\circ}{}_{products} - \sum n\Delta H_f{}^{\circ}{}_{reactants}$$

Chemical Equilibrium

$$K_P = K_C(RT)^{\Delta n} \qquad \ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Acid/Base Equilibria

$$\mathrm{pOH} = -\log\,[\mathrm{OH^-}] \qquad \mathrm{pH} = -\log\,[\mathrm{H_3O^+}] \qquad \mathrm{pH} + \mathrm{pOH} = 14$$

$$K_a \times K_b = K_W \qquad \mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right) \qquad \mathrm{pH} = \frac{\mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}}{2}$$

Chemical Kinetics

$$[A]_t = [A]_0 - kt$$

$$\ln[A]_t = \ln[A]_0 - kt$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Atomic Structure

$$E = h\nu$$

$$c = \nu\lambda$$

$$\Delta E = -R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Fundamental Physical Constants

Name and Symbol	Value
atomic mass unit (amu)	$1.6605390 \times 10^{-27}$ kg
Avogadro's number (N_A)	6.0221408×10^{23} mol^{-1}
Boltzmann's constant (k_B)	1.380648×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75882002 \times 10^{11}$ C kg^{-1}
electron charge (e)	$1.60217662 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093836 \times 10^{-31}$ kg
Faraday's constant (F)	9.6485333×10^{4} C mol^{-1}
gas constant (R)	8.314460 J mol^{-1} K^{-1}
	8.20573×10^{-2} L atm mol^{-1} K^{-1}
	8.314460 m^{3} Pa mol^{-1} K^{-1}
	8.314460 L kPa mol^{-1} K^{-1}
	8.314460×10^{-2} bar L mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 273.15 K	22.41396 L mol^{-1}
molar volume of an ideal gas, 1 bar, 273.15 K	22.71095 L mol^{-1}
neutron rest mass (m_n)	$1.6749275 \times 10^{-27}$ kg
Planck's constant (h)	$6.6260700 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726219 \times 10^{-27}$ kg
Rydberg constant (R_H)	$1.0973731568 \times 10^{7}$ m^{-1}

	$2.1798723 \times 10^{-18}$ J
speed of light (in vacuum) (*c*)	2.99792458×10^{8} m s^{-1}

Table E.1 Fundamental Physical Constants and their Values

REFERENCE

1. “CODATA Recommended Values of the Fundamental Physical Constants: 2018” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

APPENDIX F | WATER PROPERTIES

Temperature[1]	Density[2]
0	999.84
4	999.9749 (density maximum)
10	999.7027
15	999.1026
20	998.2067
22	997.7730
25*	997.0470
30	995.6488
40	992.2152
60	983.20
80	971.79
99.974	958.37

Table F.1 Water Density (kg/m^3) at Different Temperatures (°C)

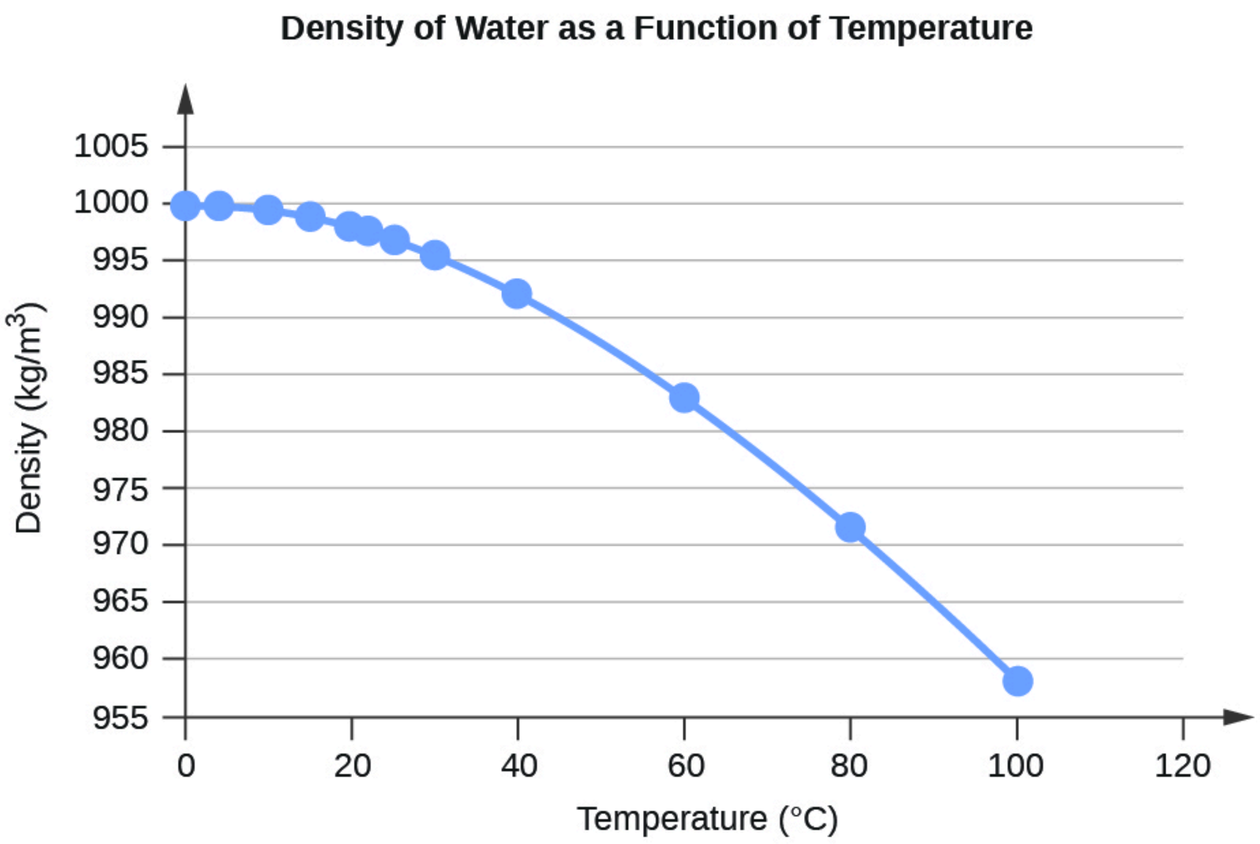


Figure F.1 Density of Water as a Function of Temperature

Temperature	Vapour Pressure (Torr)	Vapour Pressure (Pa)
-10	1.95	259.9
-5	3.08	401.7
-2	3.88	517.7
0.01	4.59	611.6
2	5.30	706.0
4	6.10	813.6
6	7.02	935.4
8	8.05	1073.0
10	9.21	1228.2
12	10.52	1402.8
14	11.99	1599.0
15	12.79	1705.6
16	13.64	1818.8
18	15.49	2064.7
19	16.48	2197.8
20	17.55	2339.3
21	18.66	2487.7
22	19.84	2645.3

23	21.08	2810.4
24	22.40	2985.8
25	23.78	3169.9
26	25.23	3363.9
27	26.75	3567.0
28	28.38	3783.1
29	30.06	4007.8
30	31.86	4247.0
35	42.20	5626.7
40	55.39	7384.9
45	71.93	9589.8
50	92.65	12352
55	118.1	15752
60	149.6	19946
65	187.7	25022
70	234.0	31201
75	289.2	38563
80	355.6	47414
85	433.6	57815

90	526.4	70182
95	634.0	84529
99	733.2	97759
100	760.7	1.0142×10^5
101.0	787.49	1.0499×10^5

Table F.2 Water Vapour Pressure at Different Temperatures (°C)

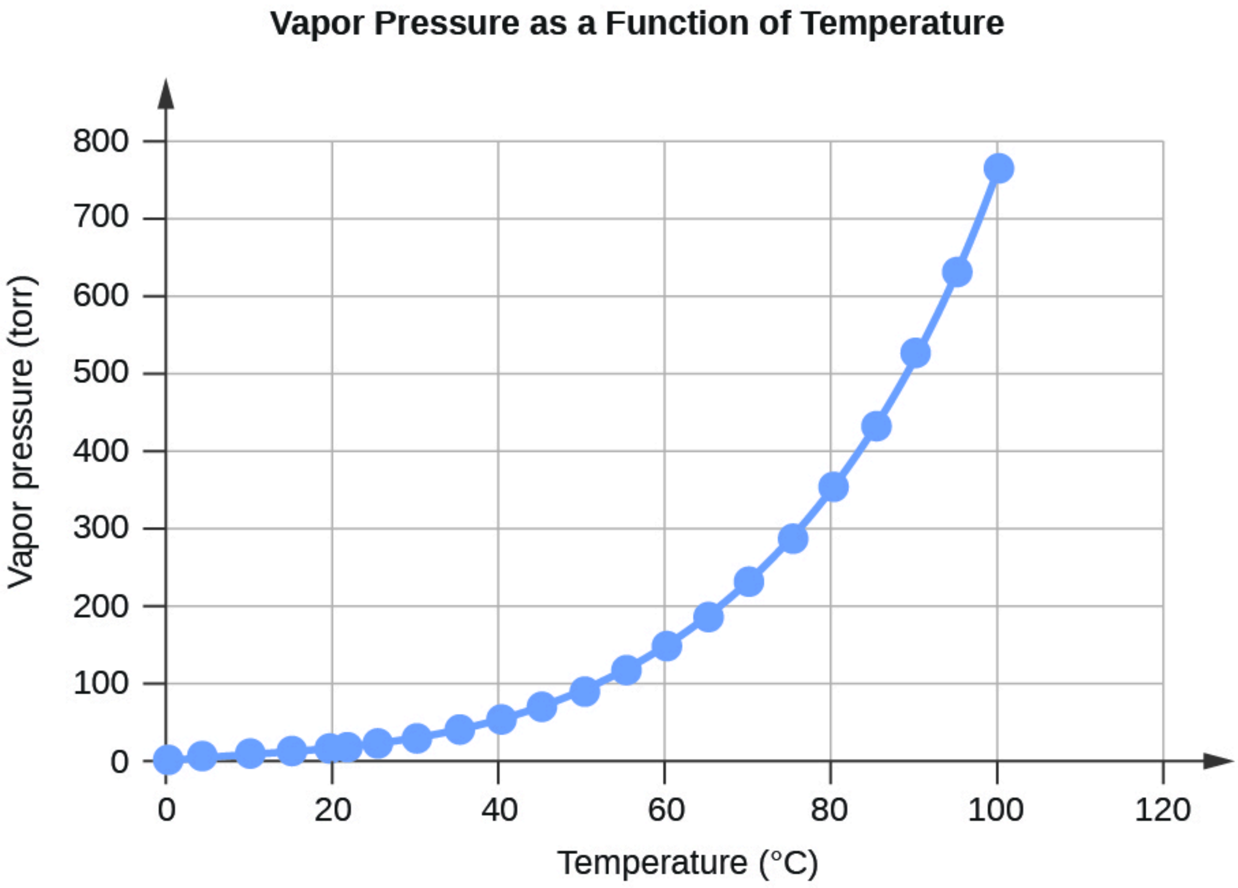


Figure F.2 Vapour Pressure as a Function of Temperature

Water K_W and pK_W at Different Temperatures (°C)

Temperature	K_W 10^{-14}	pK_W ^{3}
0	0.113	14.947
5	0.184	14.734
10	0.292	14.534
15	0.453	14.344
20	0.684	14.165
25	1.012	13.995
30	1.469	13.833
35	2.089	13.680
40	2.917	13.535
45	4.018	13.396
50	5.433	13.265
55	7.244	13.140
60	9.550	13.020
75	20.14	12.696
100	55.98	12.252

Table F.3 Water K_W and pK_W at Different Temperatures (°C)

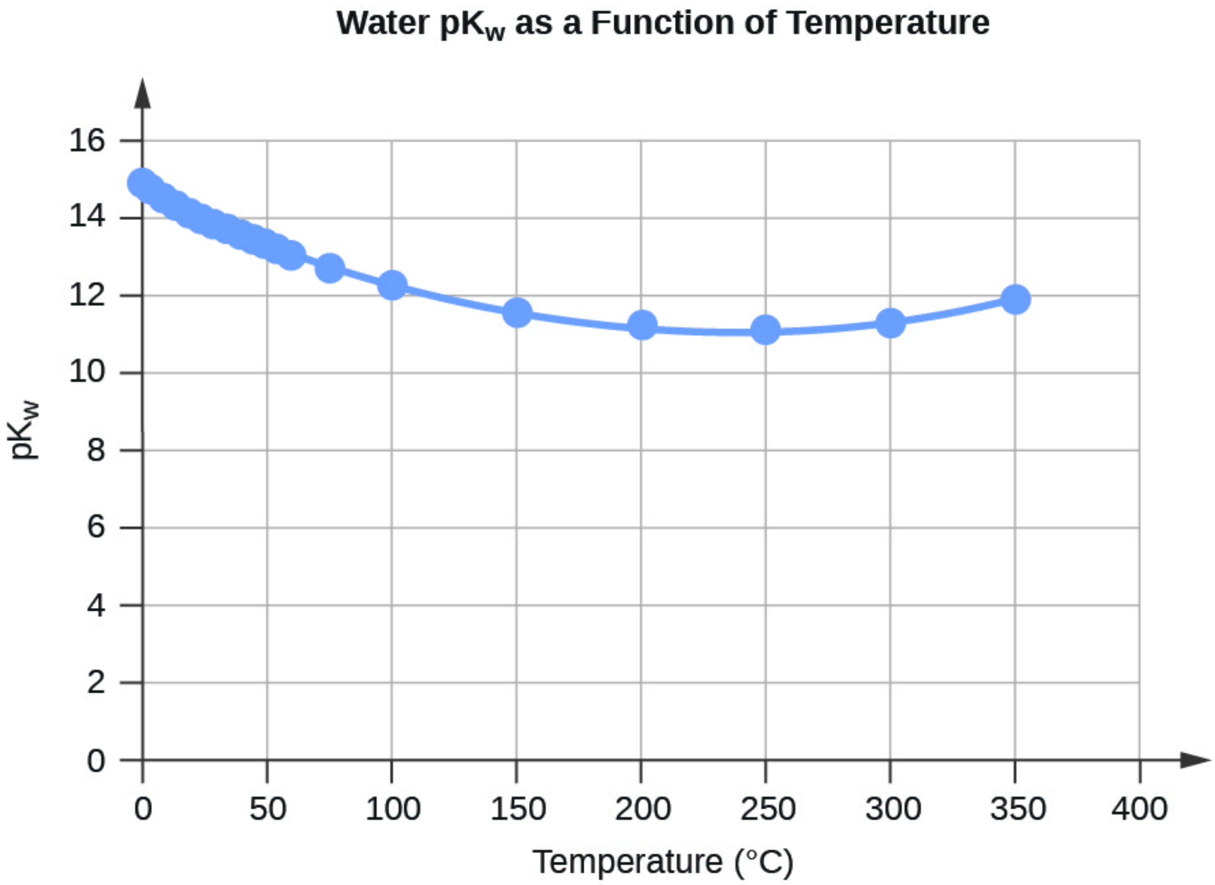


Figure F.3 Water pK_W as a Function of Temperature

Specific Heat Capacity for Water
c (H_2O (l)) = 4.184 J K^{-1} g^{-1}
c (H_2O (s)) = 2.13 J K^{-1} g^{-1}
c (H_2O (g)) = 2.01 J K^{-1} g^{-1}

Table F.4 Specific Heat Capacity of Water

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

	Temperature (K)	ΔH (kJ/mol)
melting (ΔH_{fus})	273.15	6.01
boiling (ΔH_{vap})	373.15	40.65 (43.98 at 298 K)

Table F.5 Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

$K_f = 1.86°\text{C kg mol}^{-1}$ (cryoscopic constant)

$K_b = 0.513°\text{C kg mol}^{-1}$ (ebullioscopic constant)

Table F.6 Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

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[1] Data for t < 0 °C are for supercooled water

[2] For all calculations in the course, unless otherwise noted, assume that the density of water is 1000 kg/m^3 = 1.00 g/mL at 25°C

[3] $pK_W = -\log_{10}(K_W)$

REFERENCES

1. “Ionization Constant of Normal and Heavy Water” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

2. “Standard Density of Water” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

3. “Vapor Pressure, Enthalpy of Vaporization, and Surface Tension of Water” in CRC Handbook of Chemistry and Physics, 101st Edition (Internet Version 2020), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

4. “Vapor Pressure of Water from 0 to 370°C” in CRC Handbook of Chemistry and Physics, 89th Edition (Internet Version 2008), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

APPENDIX G | STANDARD ENTHALPIES OF FORMATION FOR SELECTED SUBSTANCES

All enthalpies of formation listed below for selected substances are defined at the standard state of 298.15 K and 1 bar (100 kPa).

Standard Thermodynamic Properties for Selected Substances	
Substance	**$\Delta H_f°$ (kJ mol^{-1})**
Aluminum	
Al *(s)*	0.0
Al *(g)*	330.0
Al^{3+} *(aq)*	-531.0
Al_2O_3 *(s)*	-1675.7
AlF_3 *(s)*	-1510.4
$AlCl_3$ *(s)*	-704.2
$AlCl_3{\cdot}6H_2O$ (*s*)	-2691.57
Al_2S_3 (*s*)	-724.0
$Al_2(SO_4)_3$ (*s*)	-3445.06
Antimony	
Sb *(s)*	0.0
Sb *(g)*	262.3
Sb_4O_6 (*s*)	-1440.55
$SbCl_3$ (*g*)	-313.8
$SbCl_5$ *(g)*	-394.34
Sb_2S_3 *(s)*	-174.89

$SbCl_3$ *(s)*	-382.2
SbOCl *(s)*	-374.0
Arsenic	
As *(s)*	0.0
As (*g*)	302.5
As_4 (*g*)	143.9
As_4O_6 (*s*)	-1313.94
As_2O_5 (*s*)	-924.9
$AsCl_3$ (*g*)	-261.5
As_2S_3 (*s*)	-169.0
AsH_3 (*g*)	66.44
H_3AsO_4 (*s*)	-906.3
Barium	
Ba (*s*)	0.0
Ba (*g*)	180.0
Ba^{2+} (*aq*)	-537.6
BaO (*s*)	-548.0
$BaCl_2$ (*s*)	-855.0
$BaSO_4$ (*s*)	-1473.2

Beryllium	
Be (*s*)	0.0
Be (*g*)	324.0
BeO (*s*)	-609.4
Bismuth	
Bi (*s*)	0.0
Bi (*g*)	207.1
Bi_2O_3 (*s*)	-573.9
$BiCl_3$ (*s*)	-379.1
Bi_2S_3 (*s*)	-143.1
Boron	
B (*s*)	0.0
B (*g*)	565.0
B_2O_3 (*s*)	-1273.5
B_2H_6 (*g*)	36.4
H_3BO_3 (*s*)	-1094.3
BF_3 (*g*)	-1136.0
BCl_3 (*g*)	-403.8
$B_3N_3H_6$ (*l*)	-541.0

HBO_2 (*s*)	-794.3
Bromine	
Br_2 (*l*)	0.0
Br_2 (*g*)	30.9
Br (*g*)	111.9
Br^- (*aq*)	-121.6
BrF_3 (*g*)	-255.6
HBr (*g*)	-36.3
Cadmium	
Cd (*s*)	0.0
Cd (*g*)	111.8
Cd^{2+} (*aq*)	-75.9
CdO (*s*)	-258.4
$CdCl_2$ (*s*)	-391.5
$CdSO_4$ (*s*)	-933.3
CdS (*s*)	-161.9
Calcium	
Ca (*s*)	0.0
Ca (*g*)	177.8

Ca^{2+} (*aq*)	-542.8
CaO (*s*)	-634.9
$Ca(OH)_2$ (*s*)	-985.2
$CaSO_4$ (*s*)	-1434.5
$CaSO_4{\cdot}2H_2O$(*s*)	-2022.63
$CaCO_3$ (*s*) (calcite)	-1207.6
$CaSO_3{\cdot}H_2O$ (*s*)	-1752.68
Carbon	
C (*s*) (graphite)	0.0
C (*s*) (diamond)	1.9
C (*g*)	716.7
CO (*g*)	-110.5
CO_2 (*g*)	-393.5
$CO_3{}^{2-}$ (*aq*)	-677.1
CH_4 (*g*)	-74.6
CH_3OH (*l*)	-239.2
CH_3OH (*g*)	-201.0
CCl_4 (*l*)	-128.2
CCl_4 (*g*)	-95.7

$CHCl_3$ (*l*)	-134.1
$CHCl_3$ (*g*)	-102.7
CS_2 (*l*)	89.0
CS_2 (*g*)	116.7
C_2H_2 (*g*)	227.4
C_2H_4 (*g*)	52.4
C_2H_6 (*g*)	-84.0
CH_3CO_2H (*l*)	-484.3
CH_3CO_2H (*g*)	-432.2
C_2H_5OH (*l*)	-277.6
C_2H_5OH (*g*)	-234.8
HCO_3^- (*aq*)	-692.0
C_3H_8 (*g*)	-103.8
C_6H_6 (*g*)	82.9
C_6H_6 (*l*)	49.1
CH_2Cl_2 (*l*)	-124.2
CH_2Cl_2 (*g*)	-95.4
CH_3Cl (*g*)	-81.9
C_2H_5Cl (*l*)	-136.8

C_2H_5Cl (*g*)	-112.1
C_2N_2 (*g*)	306.7
HCN (*l*)	108.9
HCN (*g*)	135.1
Cesium	
Cs^+ (*aq*)	-258.3
Chlorine	
Cl_2 (*g*)	0.0
Cl (*g*)	121.3
Cl^- (*aq*)	-167.2
ClF (*g*)	-50.3
ClF_3 (*g*)	-163.2
Cl_2O (*g*)	80.3
Cl_2O_7 (*l*)	238.1
Cl_2O_7 (*g*)	272.0
HCl (*g*)	-92.3
$HClO_4$ (*l*)	-40.6
Chromium	
Cr (*s*)	0.0

Cr (*g*)	396.6
CrO_4^{2-} (*aq*)	-881.2
$Cr_2O_7^{2-}$ (*aq*)	-1490.3
Cr_2O_3 (*s*)	-1139.7
CrO_3 (*g*)	-292.9
$(NH_4)_2Cr_2O_7$ (*s*)	-1806.7
Cobalt	
Co (*s*)	0.0
Co^{2+} (*aq*)	-58.2
Co^{3+} (*aq*)	92.0
CoO (*s*)	-237.9
Co_3O_4 (*s*)	-891.0
$Co(NO_3)_2$ (*s*)	-420.5
Copper	
Cu (*s*)	0.0
Cu (*g*)	337.4
Cu^+ (*aq*)	71.7
Cu^{2+} (*aq*)	64.8
CuO (*s*)	-157.3

Cu_2O (*s*)	-168.6
CuS (*s*)	-53.1
Cu_2S (*s*)	-79.5
$CuSO_4$ (*s*)	-771.4
$Cu(NO_3)_2$ (*s*)	-302.9
Fluorine	
F_2 (*g*)	0.0
F (*g*)	79.4
F^- (*aq*)	-332.6
F_2O (*g*)	24.5
HF (*g*)	-273.3
Hydrogen	
H_2 (*g*)	0.0
H (*g*)	218.0
H^+ (*aq*)	0
OH^- (*aq*)	-230.0
H_3O^+ (*aq*)	-285.8
H_2O (*l*)	-285.8
H_2O (*g*)	-241.8

H_2O_2 (*l*)	-187.8
H_2O_2 (*g*)	-136.3
HF (*g*)	-273.3
HCl (*g*)	-92.3
HBr (*g*)	-36.3
HI (*g*)	26.5
H_2S (*g*)	-20.6
H_2Se (*g*)	29.7
Iodine	
I_2 (*s*)	0.0
I_2 (*g*)	62.4
I (*g*)	106.8
I^- (*aq*)	-55.2
IF (*g*)	-95.7
Icl (*g*)	17.8
IBr (*g*)	40.8
IF_7 (*g*)	-943.91
HI (*g*)	26.5
Iron	

Fe (*s*)	0.0
Fe (*g*)	416.3
Fe^{2+} (*aq*)	-89.1
Fe^{3+} (*aq*)	-48.5
Fe_2O_3 (*s*)	-824.2
Fe_3O_4 (*s*)	-1118.4
$Fe(CO)_5$ (*l*)	-774.0
$Fe(CO)_5$ (*g*)	-733.87
$FeCl_2$ (*s*)	-341.8
$FeCl_3$ (*s*)	-399.5
FeO (*s*)	-272.0
$Fe(OH)_2$ (*s*)	-569.0
$Fe(OH)_3$ (*s*)	-823.0
FeS (*s*)	-100.0
Fe_3C (*s*)	25.1
Lead	
Pb (*s*)	0.0
Pb (*g*)	195.2
Pb^{2+} (*aq*)	-1.7

PbO (*s*) (yellow)	-217.3
PbO (*s*) (red)	-219.0
$Pb(OH)_2$ (*s*)	-515.9
PbS (*s*)	-100.4
$Pb(NO_3)_2$ (*s*)	-451.9
PbO_2 (*s*)	-277.4
$PbCl_2$ (*s*)	-359.4
Lithium	
Li (*s*)	0.0
Li (*g*)	159.3
Li^+ (*aq*)	-278.5
LiH (*s*)	-90.5
Li(OH) (*s*)	-487.5
LiF (*s*)	-616.0
Li_2CO_3 (*s*)	-1215.9
Magnesium	
Mg^{2+} *(aq)*	-466.9
Manganese	
Mn (*s*)	0.0

Mn (*g*)	280.7
Mn^{2+} (*aq*)	-220.8
MnO (*s*)	-385.2
MnO_2 (*s*)	-520.0
Mn_2O_3 (*s*)	-959.0
Mn_3O_4 (*s*)	-1387.8
MnO_4^{-} (*aq*)	-541.4
MnO_4^{2-} (*aq*)	-653.0
Mercury	
Hg (*l*)	0.0
Hg (*g*)	61.4
Hg^{2+} (*aq*)	171.1
Hg_2^{2+} (*aq*)	172.4
HgO (*s*) (red)	-90.8
HgO (*s*) (yellow)	-90.5
$HgCl_2$ (*s*)	-224.3
Hg_2Cl_2 (*s*)	-265.4
HgS (*s*) (red)	-58.2
HgS (*s*) (black)	-53.6

$HgSO_4$ (*s*)	-707.5
Nickel	
Ni^{2+} (*aq*)	-54.0
Nitrogen	
N_2 (*g*)	0.0
N (*g*)	472.7
NO (*g*)	91.3
NO_2 (*g*)	33.2
N_2O (*g*)	81.6
N_2O_3 (*g*)	86.6
NO_3^- (*aq*)	-207.4
N_2O_4 (*g*)	11.1
N_2O_5 (*g*)	13.3
NH_3 (*g*)	-45.9
NH_4^+ (*aq*)	-132.5
N_2H_4 (*l*)	50.6
N_2H_4 (*g*)	95.4
NH_4NO_3 (*s*)	-365.6
NH_4Cl (*s*)	-314.4

NH_4Br (*s*)	-270.8
NH_4I (*s*)	-201.4
NH_4NO_2 (*s*)	-256.5
HNO_3 (*l*)	-174.1
HNO_3 (*g*)	-133.9
Oxygen	
O_2 (*g*)	0.0
O (*g*)	249.2
O_3 (*g*)	142.7
Phosphorus	
P_4 (*s*)	0.0
P_4 (*g*)	58.9
P (*g*)	316.5
PH_3 (*g*)	5.4
PCl_3 (*g*)	-287.0
PCl_5 (*g*)	-374.9
P_4O_6 (*s*)	-1640.1
P_4O_{10} (*s*)	-2984.0
PO_4^{3-} (*aq*)	-1277.4

HPO_3 (*s*)	-948.5
HPO_4^{2-} (*aq*)	-1292.1
$H_2PO_4^{2-}$ (*aq*)	-1296.3
H_3PO_2 (*s*)	-604.6
H_3PO_3 (*s*)	-964.4
H_3PO_4 (*s*)	-1284.4
H_3PO_4 (*l*)	-1271.7
$H_4P_2O_7$ (*s*)	-2241.0
$POCl_3$ (*l*)	-597.1
$POCl_3$ (*g*)	-558.5
Potassium	
K (*s*)	0.0
K (*g*)	89.0
K^+ (*aq*)	-252.4
KF (*s*)	-567.3
KCl (*s*)	-436.5
Rubidium	
Rb^+ (*aq*)	-251.2
Silicon	

Si (*s*)	0.0
Si (*g*)	450.0
SiO_2 (*s*)	-910.7
SiH_4 (*g*)	34.3
H_2SiO_3 (*s*)	-1188.7
H_4SiO_4 (*s*)	-1481.1
SiF_4 (*g*)	-1615.0
$SiCl_4$ (*l*)	-687.0
$SiCl_4$ (*g*)	-657.0
SiC (*s, beta cubic*)	-65.3
SiC (*s, alpha hexagonal*)	-62.8
Silver	
Ag (*s*)	0.0
Ag (*g*)	284.9
Ag^+ (*aq*)	105.6
Ag_2O (*s*)	-31.1
AgCl (*s*)	-127.0
Ag_2S (*s*)	-32.6
Sodium	

Na (*s*)	0.0
Na (*g*)	107.5
Na^+ (*aq*)	-240.1
Na_2O (*s*)	-414.2
NaCl (*s*)	-411.2
Strontium	
Sr^{2+} (*aq*)	-545.8
Sulfur	
S_8 (*s*) (rhombic)	0.0
S (*g*)	277.2
S^{2-} (*aq*)	33.1
SO_2 (*g*)	-296.8
SO_3 (*g*)	-395.7
SO_4^{2-} (*aq*)	-909.3
$S_2O_3^{2-}$ (*aq*)	-652.3
H_2S (*g*)	-20.6
HS^- (*aq*)	-17.6
H_2SO_4 (*l*)	-814.0
HSO_4^{2-} (*aq*)	-887.3

$H_2S_2O_7$ (*s*)	-1273.6
SF_4 (*g*)	-763.2
SF_6 (*g*)	-1220.5
SCl_2 (*l*)	-50.0
SCl_2 (*g*)	-19.7
S_2Cl_2 (*l*)	-59.4
S_2Cl_2 (*g*)	-19.50
$SOCl_2$ (*g*)	-212.5
$SOCl_2$ (*l*)	-245.6
SO_2Cl_2 (*l*)	-394.1
SO_2Cl_2 (g)	-364.0
Tin	
Sn (*s*)	0.0
Sn (*g*)	301.2
SnO (*s*)	-280.7
SnO_2 (*s*)	-577.6
$SnCl_4$ (*l*)	-511.3
$SnCl_4$ (*g*)	-471.5
Titanium	

Ti (*s*)	0.0
Ti (*g*)	473.0
TiO_2 (*s*)	-944.0
$TiCl_4$ (*l*)	-804.2
$TiCl_4$ (*g*)	-763.2
Tungsten	
W (*s*)	0.0
W (*g*)	849.4
WO_3 (*s*)	-842.9
Zinc	
Zn (*s*)	0.0
Zn (*g*)	130.4
Zn^{2+} (*aq*)	-153.9
ZnO (*s*)	-350.5
$ZnCl_2$ (*s*)	-415.1
ZnS (*s*)	-206.0
$ZnSO_4$ (*s*)	-982.8
$ZnCO_3$ (*s*)	-812.8
Complexes	

$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	-898.7
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	-896.2
$NH_4[Co(NH_3)_2(NO_2)_4]$	-837.6
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	-2733.0
$[Co(NH_3)_4Cl_2]Cl$, *cis*	-874.9
$[Co(NH_3)_4Cl_2]Cl$, *trans*	-877.4
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	-689.5
$[Co(en)_2Cl_2]Cl$, *cis*	-681.2
$[Co(en)_2Cl_2]Cl$, *trans*	-677.4
$[Co(en)_3](ClO_4)_3$	-762.7
$[Co(en)_3]Br_2$	-595.8
$[Co(en)_3]I_2$	-475.3
$[Co(en)_3]I_3$	-519.2
$[Co(NH_3)_6](ClO_4)_3$	-1034.7
$[Co(NH_3)_5NO_2](NO_3)_2$	-1088.7
$[Co(NH_3)_6](NO_3)_3$	-1282.0
$[Co(NH_3)_5Cl]Cl_2$	-1017.1
$[Pt(NH_3)_4]Cl_2$	-725.5
$[Ni(NH_3)_6]Cl_2$	-994.1

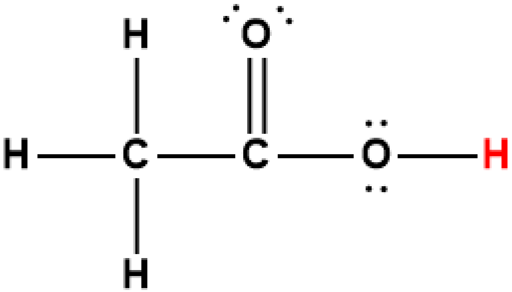
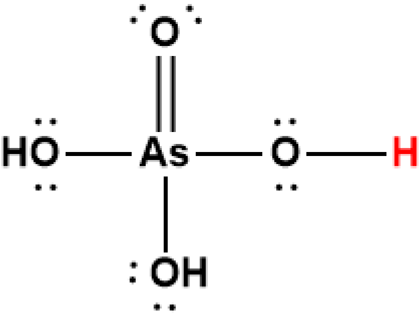
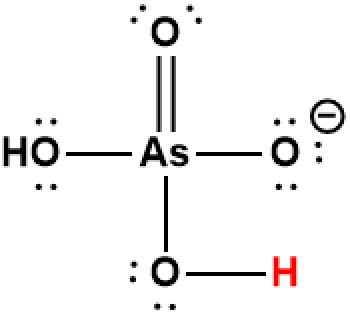
$[Ni(NH_3)_6]Br_2$	-923.8
[Ni(NH3)6]I2	-808.3

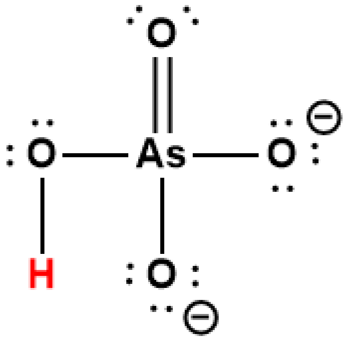
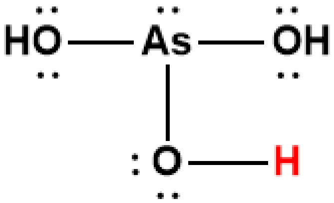
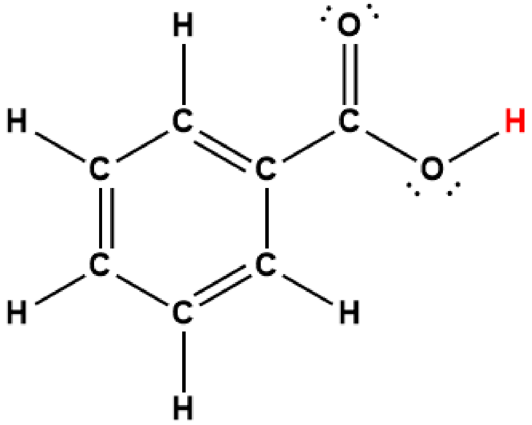
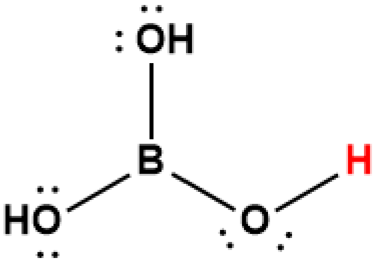
REFERENCE

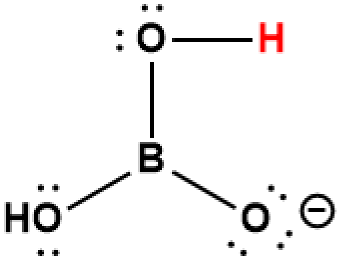
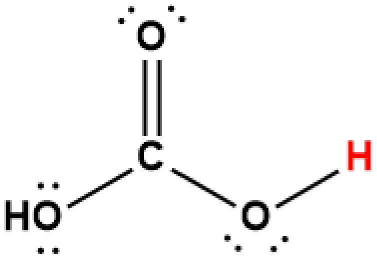
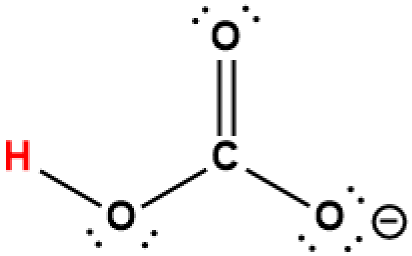
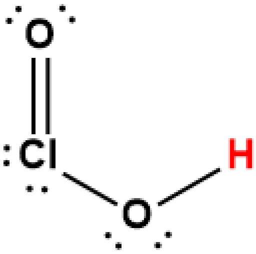
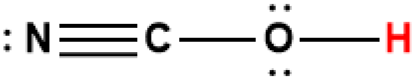
1. “Standard Thermodynamic Properties of Chemical Substances” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

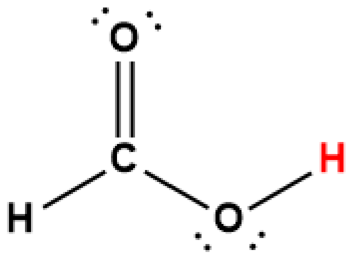
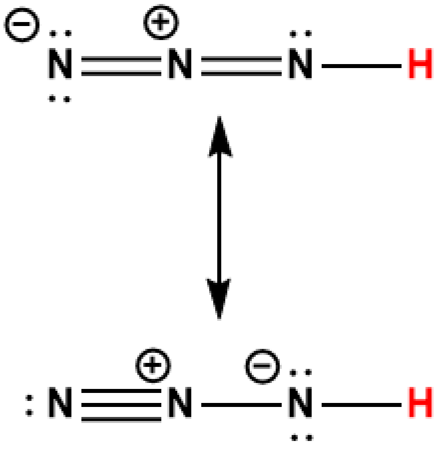
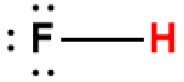
APPENDIX H | IONIZATION CONSTANTS OF WEAK ACIDS

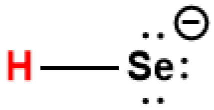
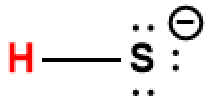
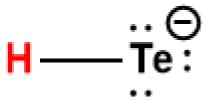
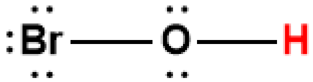
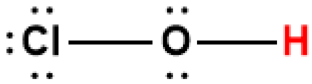
Ionization Constants of Weak Acids

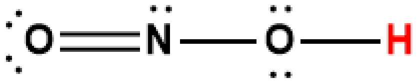
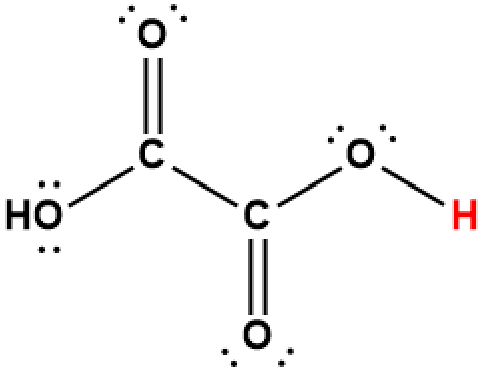
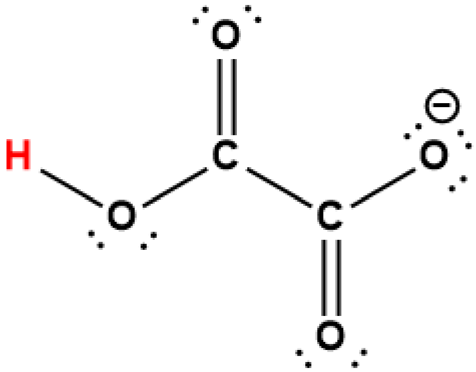
Acid	**Formula**	**K_a at 25°C**	**Lewis Structure**[1]
acetic	CH_3COOH	1.75×10^{-5}	
arsenic	H_3AsO_4	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	

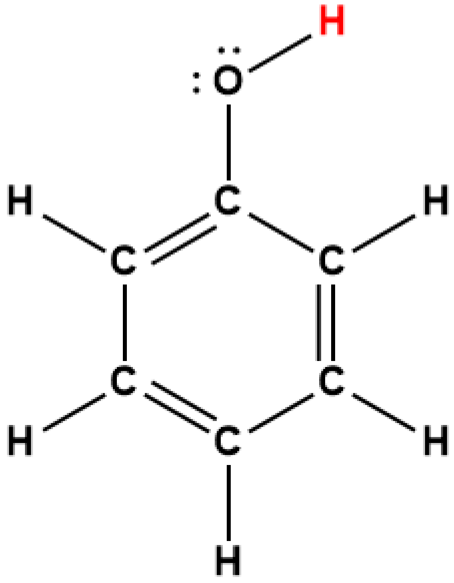
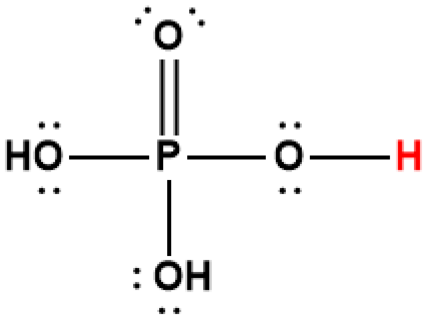
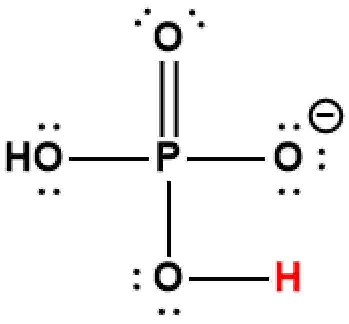
	$HAsO_4^{2-}$	5.1×10^{-12}	
arsenous	H_3AsO_3	5.1×10^{-10}	
benzoic	C_6H_5COOH	6.25×10^{-5}	
boric	H_3BO_3	5.4×10^{-10}	

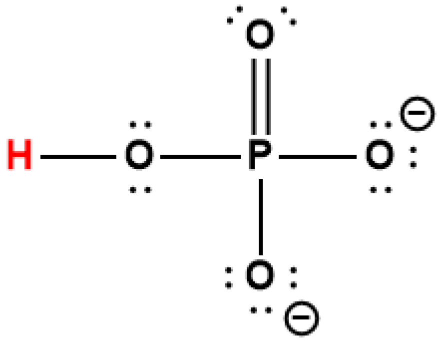
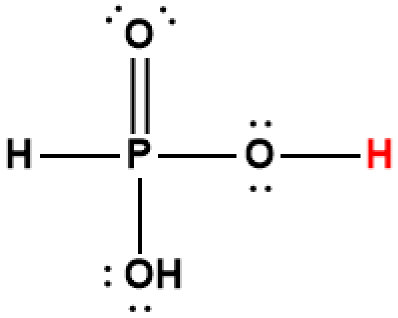
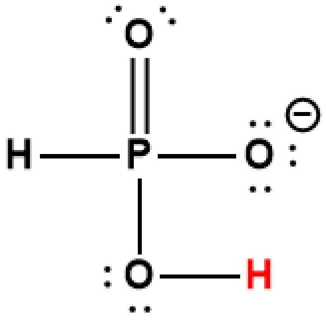
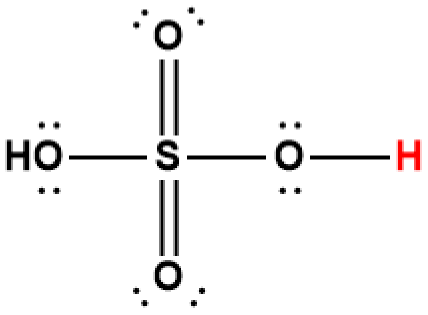
	$H_2BO_3^-$	1×10^{-14}*	
carbonic	H_2CO_3	4.5×10^{-7}	
	HCO_3^-	4.7×10^{-11}	
chlorous	$HClO_2$	1.1×10^{-2}	
cyanic	HOCN	3.5×10^{-4}	

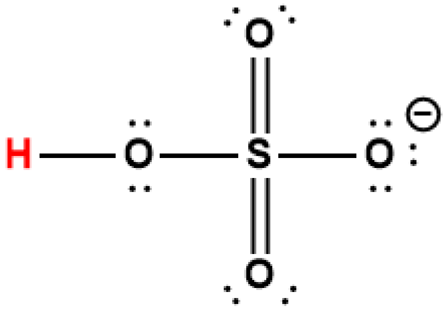
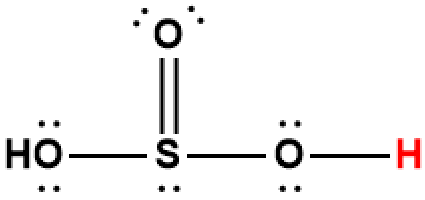
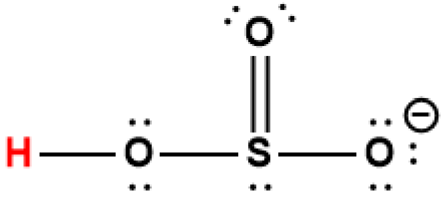
formic	HCOOH	1.8×10^{-4}	
hydrazoic	HN_3	2×10^{-5}	
hydrocyanic	HCN	6.2×10^{-10}	
hydrofluoric	HF	6.3×10^{-4}	
hydrogen peroxide	H_2O_2	2.4×10^{-12}	

hydrogen selenide	H_2Se	1.3×10^{-4}	
	HSe^-	1.0×10^{-11}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1×10^{-19}	
hydrogen telluride	H_2Te	2×10^{-3}	
	HTe^-	1×10^{-11}	
hypobromous	HOBr	2.8×10^{-9}	
hypochlorous	HOCl	4.0×10^{-8}	

nitrous	HNO_2	5.6×10^{-4}	
oxalic	$H_2C_2O_4$	5.6×10^{-2}	
	$HC_2O_4^-$	1.5×10^{-4}	

phenol	C_5H_5OH	1.0×10^{-10}	
phosphoric	H_3PO_4	6.9×10^{-3}	
	$H_2PO_4^{-}$	6.2×10^{-8}	

	HPO_4^{2-}	4.8×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfuric	H_2SO_4	*strong acid*	

	HSO_4^-	1.0×10^{-2}	
sulfurous	H_2SO_3	1.4×10^{-2}	
	HSO_3^-	6×10^{-8}	

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[1] Hydrogen atom indicated in red represents the donated proton in an acid-base reaction.

* Represents the lower limit value.

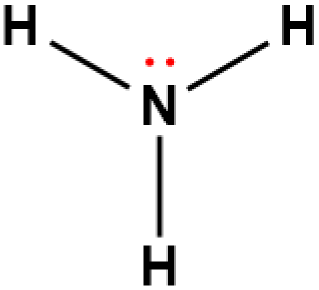
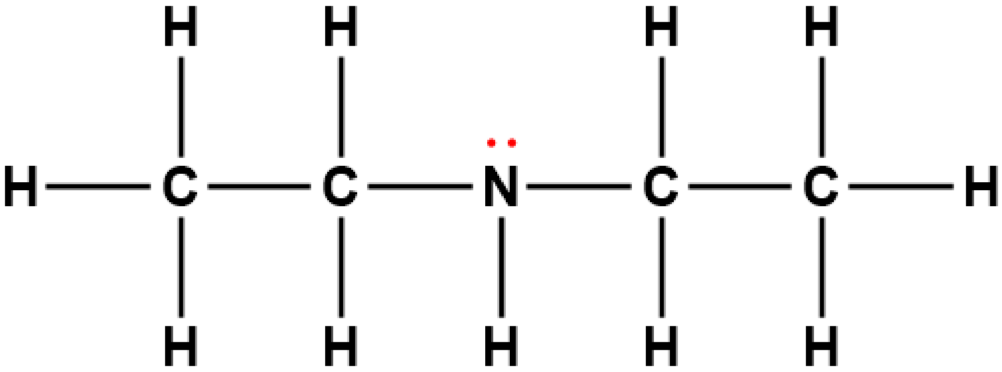
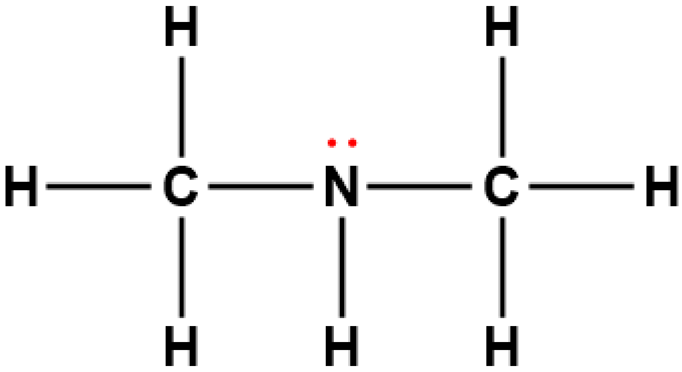
REFERENCES

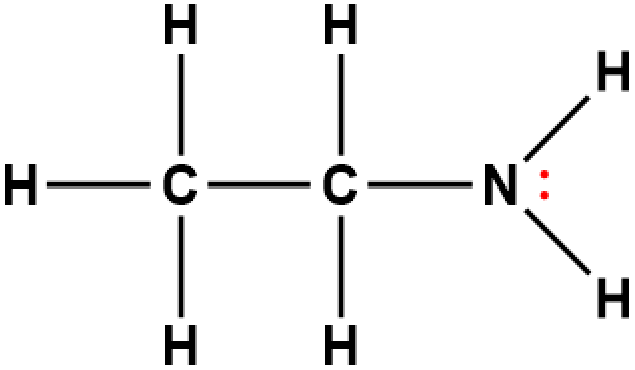
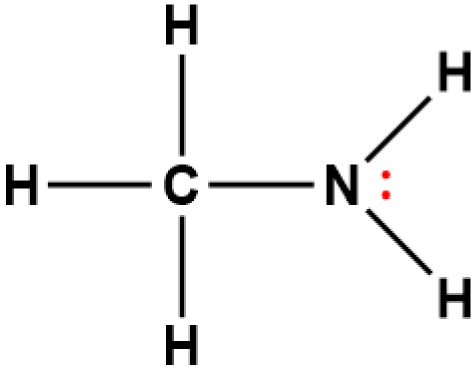
1. “Dissociation Constants of Inorganic Acids and Bases” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

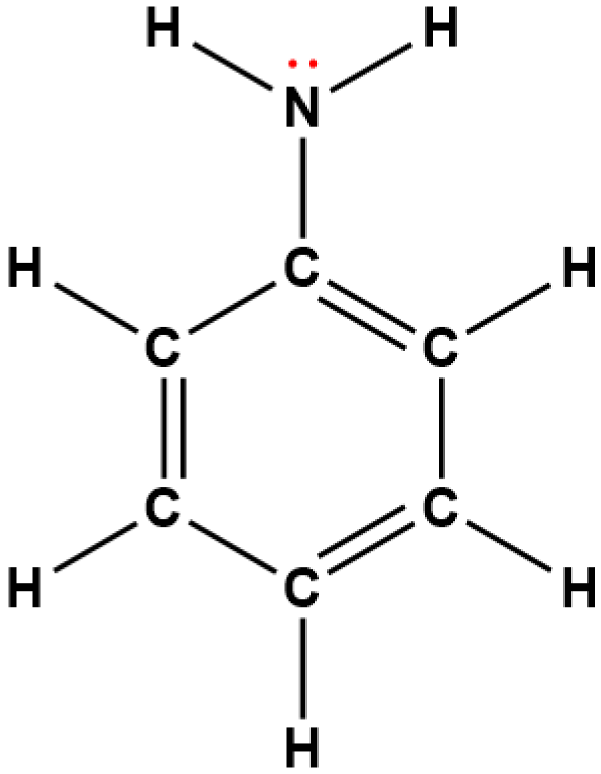
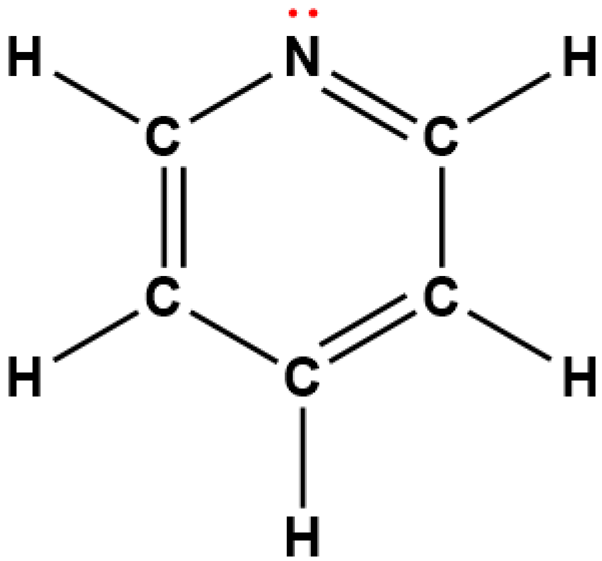
2. “Dissociation Constants of Organic Acids and Bases” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

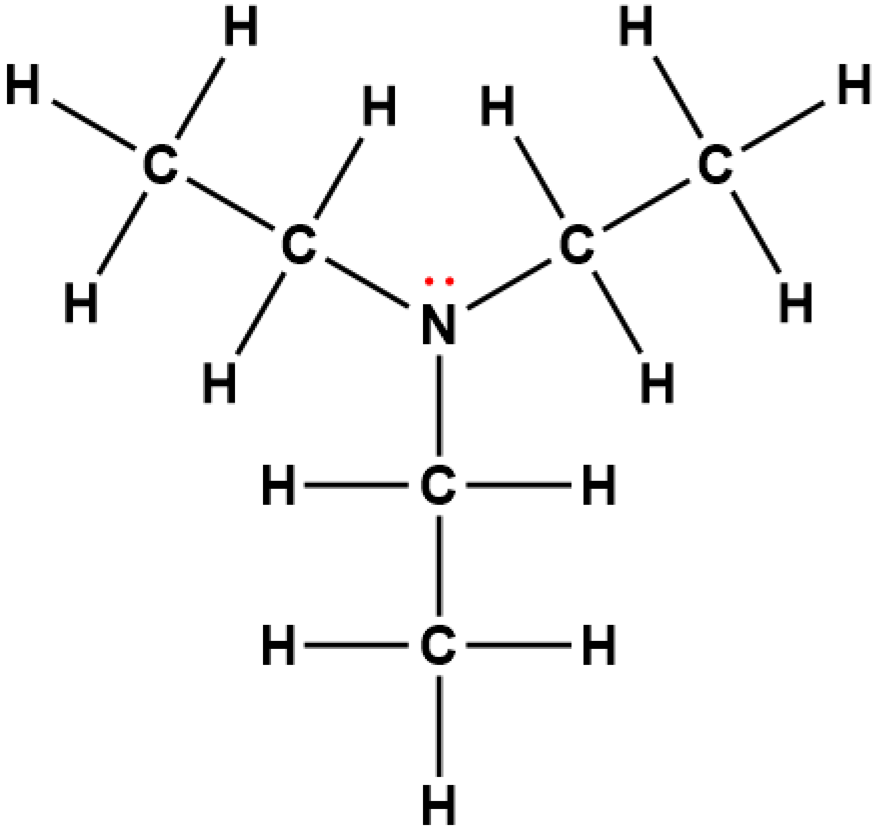
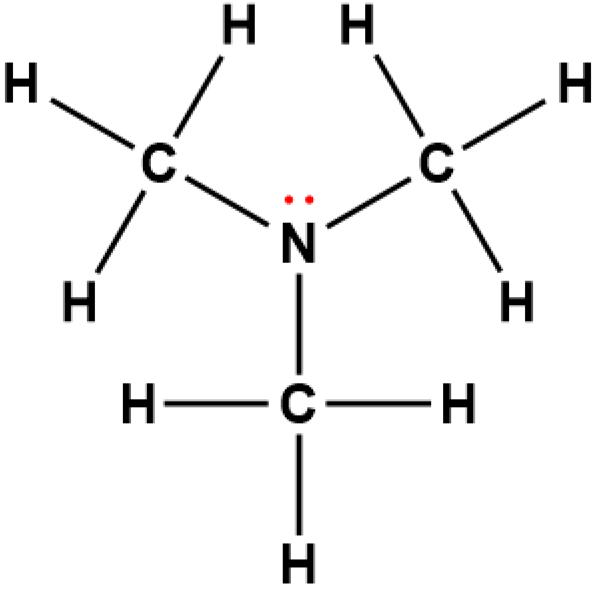
APPENDIX I | IONIZATION CONSTANTS OF WEAK BASES

Ionization Constants of Weak Bases

Base	Formula	K_b at 25°C	Lewis Structure[1]
ammonia	NH_3	1.8×10^{-5}	
diethylamine	$(C_2H_5)_2NH$	6.9×10^{-4}	
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	

ethylamine	$C_2H_5NH_2$	4.5×10^{-4}	
methylamine	CH_3NH_2	4.6×10^{-4}	

phenylamine (aniline)	$C_6H_5NH_2$	7.4×10^{-10}	
pyridine	C_5H_5N	1.7×10^{-9}	

triethylamine	$(C_2H_5)_3N$	5.6×10^{-4}	
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	

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[1] Electrons indicated in red participate in accepting a proton from an acid in an acid-base reaction.

REFERENCES

1. “Dissociation Constants of Inorganic Acids and Bases” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

2. “Dissociation Constants of Organic Acids and Bases” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

APPENDIX J | FORMATION CONSTANTS FOR COMPLEX IONS

Formation Constants for Complex Ions

Equilibrium	K_f
$Al^{3+} + 6F^{-} \rightleftharpoons [AlF_6]^{3-}$	7×10^{19}
$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3×10^{7}
$Cd^{2+} + 4CN^{-} \rightleftharpoons [Cd(CN)_4]^{2-}$	3×10^{18}
$Co^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^{5}
$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	2.3×10^{33}
$Cu^{+} + 2CN \rightleftharpoons [Cu(CN)_2]^{-}$	1.0×10^{16}
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.7×10^{13}
$Fe^{2+} + 6CN^{-} \rightleftharpoons [Fe(CN)_6]^{4-}$	1.5×10^{35}
$Fe^{3+} + 6CN^{-} \rightleftharpoons [Fe(CN)_6]^{3-}$	2×10^{43}
$Fe^{3+} + 6SCN^{-} \rightleftharpoons [Fe(SCN)_6]^{3-}$	3.2×10^{3}
$Hg^{2+} + 4Cl^{-} \rightleftharpoons [HgCl_4]^{2-}$	1.1×10^{16}
$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	2.0×10^{8}
$Ag^{+} + 2Cl^{-} \rightleftharpoons [AgCl_2]^{-}$	1.8×10^{5}
$Ag^{+} + 2CN^{-} \rightleftharpoons [Ag(CN)_2]^{-}$	1×10^{21}
$Ag^{+} + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^{+}$	1.7×10^{7}
$Zn^{2+} + 4CN^{-} \rightleftharpoons [Zn(CN)_4]^{2-}$	2.1×10^{19}
$Zn^{2+} + 4OH^{-} \rightleftharpoons [Zn(OH)_4]^{2-}$	2×10^{15}

$Fe^{3+} + SCN^{-} \rightleftharpoons [Fe(SCN)]^{2+}$	8.9×10^{2}
$Ag^{+} + 4SCN^{-} \rightleftharpoons [Ag(SCN)_4)]^{3-}$	1.2×10^{10}
$Pb^{2+} + 4I^{-} \rightleftharpoons [PbI_4]^{2-}$	3.0×10^{4}
$Pt^{2+} + 4Cl^{-} \rightleftharpoons [PtCl_4]^{2-}$	1×10^{16}
$Cu^{2+} + 4CN \rightleftharpoons [Cu(CN)_4]^{2-}$	1.0×10^{25}
$Co^{2+} + 4SCN^{-} \rightleftharpoons [Co(SCN)_4]^{2-}$	1×10^{3}

APPENDIX K | SOLUBILITY RULES FOR COMMON IONIC COMPOUNDS IN WATER

Solubility Rules for Common Ionic Compounds in Water

Soluble compounds contain group 1 metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium ion (NH_4^+) the halide ions (Cl^-, Br^-, and I^-) the acetate ($C_2H_3O_2^-$), bicarbonate (HCO_3^-), nitrate (NO_3^-), and chlorate (ClO_3^-) ions the sulfate (SO_4^{2-}) ion	**Exceptions** to these solubility rules include halides of Ag^+, Hg_2^{2+}, and Pb^{2+} sulfates of Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+}, and Sr^{2+}
Insoluble compounds contain carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), phosphate (PO_4^{3-}), and sulfide (S^{2-}) ions hydroxide ion (OH^-)	**Exceptions** to these insolubility rules include compounds of these ions with group 1 metal cations and ammonium ion hydroxides of group 1 metal cations and Ba^{2+}

APPENDIX L | SOLUBILITY PRODUCTS OF COMMON SALTS

Solubility Products	
Substance	**K_{sp} at 25°C**
Aluminum	
$Al(OH)_3$	2×10^{-32}
Barium	
$BaCO_3$	2.58×10^{-9}
$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}
$BaSO_4$	1.08×10^{-10}
$BaCrO_4$	1.17×10^{-10}
BaF_2	1.84×10^{-7}
$Ba(OH)_2 \cdot 8H_2O$	2.55×10^{-4}
$Ba_3(PO_4)_2$	6×10^{-39}
$Ba_3(AsO_4)_2$	1.1×10^{-13}
Bismuth	
$BiO(OH)$	4×10^{-10}
$BiOCl$	1.8×10^{-31}
Bi_2S_3	1×10^{-97}
Cadmium	
$Cd(OH)_2$	7.2×10^{-15}

CdS	1.0×10^{-28}
$CdCO_3$	1.0×10^{-12}
Calcium	
$Ca(OH)_2$	5.02×10^{-6}
$CaCO_3$	3.36×10^{-9}
$CaSO_4{\cdot}2H_2O$	3.14×10^{-5}
$CaC_2O_4{\cdot}H_2O$	2.32×10^{-9}
$Ca_3(PO_4)_2$	2.07×10^{-33}
$CaHPO_4$	7×10^{-7}
CaF_2	3.45×10^{-11}
Chromium	
$Cr(OH)_3$	6.7×10^{-31}
Cobalt	
$Co(OH)_2$	5.92×10^{-15}
CoS (α)	5×10^{-22}
CoS (β)	3×10^{-26}
$CoCO_3$	1.4×10^{-13}
$Co(OH)_3$	2.5×10^{-43}
Copper	

CuCl	1.72×10^{-7}
CuBr	6.27×10^{-9}
CuI	1.27×10^{-12}
CuSCN	1.77×10^{-13}
Cu_2S	2.5×10^{-48}
$Cu(OH)_2$	2.2×10^{-20}
CuS	8.5×10^{-45}
$CuCO_3$	2.5×10^{-10}
Iron	
$Fe(OH)_2$	4.87×10^{-17}
$FeCO_3$	3.13×10^{-11}
FeS	3.7×10^{-19}
$Fe(OH)_3$	2.79×10^{-39}
Lead	
$Pb(OH)_2$	1.43×10^{-20}
PbF_2	3.3×10^{-8}
$PbCl_2$	1.70×10^{-5}
$PbBr_2$	6.60×10^{-6}
PbI_2	9.8×10^{-9}

$PbCO_3$	7.40×10^{-14}
PbS	7×10^{-29}
$PbCrO_4$	2×10^{-16}
$PbSO_4$	1.3×10^{-8}
$Pb_3(PO_4)_2$	1×10^{-54}
Magnesium	
$Mg(OH)_2$	5.61×10^{-12}
$MgCO_3{\cdot}3H_2O$	2.38×10^{-6}
$MgNH_4PO_4$	3×10^{-13}
MgF_2	5.16×10^{-11}
MgC_2O_4	7×10^{-7}
Manganese	
$Mn(OH)_2$	2×10^{-13}
$MnCO_3$	2.24×10^{-11}
MnS	2.3×10^{-13}
Mercury	
$Hg_2O{\cdot}H_2O$	3.6×10^{-26}
Hg_2Cl_2	1.43×10^{-18}
Hg_2Br_2	6.40×10^{-23}

Hg_2I_2	5.2×10^{-29}
Hg_2CO_3	3.6×10^{-17}
Hg_2SO_4	6.5×10^{-7}
Hg_2S	1.0×10^{-47}
Hg_2CrO_4	2×10^{-9}
HgS	1.6×10^{-54}
Nickel	
$Ni(OH)_2$	5.48×10^{-16}
$NiCO_3$	1.42×10^{-7}
NiS (α)	4×10^{-20}
NiS (β)	1.3×10^{-25}
Potassium	
$KClO_4$	1.05×10^{-2}
K_2PtCl_6	7.48×10^{-6}
$KHC_4H_4O_6$	3×10^{-4}
Silver	
12 Ag_2O ($Ag^+ + OH^-$)	2×10^{-8}
$AgCl$	1.77×10^{-10}
$AgBr$	5.35×10^{-13}

AgI	8.52×10^{-17}
AgCN	5.97×10^{-17}
AgSCN	1.03×10^{-12}
Ag_2S	1.6×10^{-49}
Ag_2CO_3	8.46×10^{-12}
Ag_2CrO_4	1.12×10^{-12}
$Ag_4Fe(CN)_6$	1.55×10^{-41}
Ag_2SO_4	1.20×10^{-5}
Ag_3PO_4	8.89×10^{-17}
Strontium	
$Sr(OH)_2{\cdot}8H_2O$	3.2×10^{-4}
$SrCO_3$	5.60×10^{-10}
$SrCrO_4$	3.6×10^{-5}
$SrSO_4$	3.44×10^{-7}
$SrC_2O_4{\cdot}H_2O$	4×10^{-7}
Thallium	
TlCl	1.86×10^{-4}
TlSCN	1.57×10^{-4}
Tl_2S	6×10^{-22}

$Tl(OH)_3$	1.68×10^{-44}
Tin	
$Sn(OH)_2$	5.45×10^{-27}
SnS	1×10^{-26}
$Sn(OH)_4$	1.0×10^{-57}
Zinc	
$ZnCO_3$	1.46×10^{-10}

REFERENCE

1. “Solubility Product Constants of Inorganic Salts” in CRC Handbook of Chemistry and Physics, 100th Edition (Internet Version 2019), John R. Rumble, ed., CRC Press/Taylor & Francis, Boca Raton, FL.

APPENDIX M | GLOSSARY

Absolute rate theory (see **transition state theory**) **(7.6)**

Absolute zero (2.3)

Minimum possible temperature, labeled 0 K (zero kelvins); temperature at which the volume of a gas would be zero according to Charles's law

Accuracy (III)

How closely a measurement aligns with a correct value

Acid ionization (5.1)

Reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

Acid ionization constant (K_a) (5.3)

Equilibrium constant for an acid ionization reaction

Acid-base indicator (6.3)

Weak acid or base whose conjugate partner imparts a different solution color; color change indicates the equivalence point of a titration; used in visual assessments of solution pH

Acidic (5.2)

A solution in which $[H_3O^+] > [OH^-]$

Actinide (V)

Inner transition metal in the bottom of the bottom two rows of the periodic table

Activated complex (7.5)

Unstable combination of reactant species formed during a chemical reaction; corresponds to the highest energy transitional point in the elementary step

Activation energy (E_a) (7.5)

Minimum amount of kinetic energy molecules must possess in order for an effective collision to occur and for a reaction to take place

Actual yield (1.3)

The actual amount of product formed in a chemical reaction

Alkali metal (V)

Element in group 1; e.g. Li, Na, K

Alkaline earth metal (V)

Element in group 2; e.g. Mg, Ca, Sr

Alpha particle (α particle) (IV)

Type of radioactive emission producing a positively charged particle consisting of two protons and two neutrons (equivalent to a helium nucleus)

Amontons's law (see **Gay-Lussac's law**) **(2.4)**

Amphipathic (1.4)

Describes molecules possessing both hydrophobic (nonpolar; *water-fearing*) and hydrophilic (polar; *water-loving*) parts

Amphiphilic (see **amphipathic**) **(1.4)**

Amphiprotic (5.2)

Species that can act as a proton donor or a proton acceptor in a Bronsted-Lowry acid-base reaction

Amphoteric (5.2)

Species that can act as either an acid or a base

Amplitude (8.1)

Magnitude of the wave's displacement, corresponding to one-half the height between peaks and troughs; related to the intensity of a wave

Analyte (6.3)

Chemical species of interest of unknown concentration

Angular momentum quantum number (ℓ) (8.4)

Quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

Anion (V)

Species with an overall negative charge; e.g. chloride ion (Cl^-), phosphate ion (PO_4^{3-}), acetate ion (CH_3COO^-)

Aqueous solution (1.4)

Solution for which water is the solvent

Arrhenius acid (5.1)

Compound that increases the hydrogen ion concentration in aqueous solution

Arrhenius base (5.1)

Compound that increases the hydroxide ion concentration in aqueous solution

Arrhenius equation (7.5)

Mathematical relationship between a reaction's rate constant, activation energy, and temperature

Atmospheric pressure (2.3)

Pressure that the air exerts on the surface of the Earth

Atom (I)

Smallest particle of an element that maintains the identity of that element and can enter into a chemical combination

Atomic mass (V)

Average mass of atoms of an element (calculated as the weighted average of the masses of the isotopes that compose an element), expressed in *amu*

Atomic mass unit (*amu*) (V)

Unit of mass equal to

112

of the mass of a ^{12}C atom

Atomic number (*Z*) (V)

Number of protons in the nucleus of an atom

Atomic orbital (8.4)

Mathematical function that describes the behavior of an electron in an atom (also called the wavefunction); defines a specific set of principal, angular momentum, and magnetic quantum numbers for an electron

Aufbau principle (8.5)

Procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time; electrons fill the lowest energy orbitals first

Autoionization (5.2)

Reaction between identical species yielding ionic products; for water, this reaction involves water molecules acting as both acids (proton donors) and bases (proton acceptors) with each other to yield hydronium and hydroxide ions

Average rate of reaction (7.2)

Rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

Avogadro's law (2.4)

Volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Avogadro's number (N_A) (1.1)

The experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} mol^{-1}

Axial position (9.5)

Location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

Balanced equation (1.2)

Chemical equation with equal numbers of atoms for each element in the reactant and product

Bar (bar) (2.3)

Unit of pressure; 1 bar = 100,000 Pa

Barometer (2.3)

Device used to measure atmospheric pressure

Base ionization (5.1)

Reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Base ionization constant (K_b) (5.3)

Equilibrium constant for a base ionization reaction

Basic (5.2)

A solution in which $[H_3O^+] < [OH^-]$

Bimolecular reaction (7.7)

Elementary reaction involving two reactant species

Binary acid (VII)

Compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H+ ions when dissolved in water); e.g. HCl, HBr, H_2S

Binary compound (VI)

Compound containing two different elements

Blackbody (8.1)

Idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

Bohr's model (8.2)

Structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius

Bomb calorimeter (3.5)

Device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

Bond angle (9.5)

Angle between any two covalent bonds that share a common atom

Bond dipole moment (9.5)

Separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

Bond dissociation energy (*BE*) (9.3)

Energy required to break a covalent bond in a gaseous substance

Bond distance (see **bond length**) **(9.5)**

Bond energy (see **bond dissociation energy (*BE*)**) **(9.3)**

Bond length (9.5)

Distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

Bond order (9.4)

Number of pairs of electrons between two atoms; it can be found by the number of bonds in a Lewis structure or by the difference between the number of bonding and antibonding electrons divided by two

Boyle's law (2.4)

Volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Brønsted-Lowry acid (5.1)

Any species that can donate a proton to another molecule

Brønsted-Lowry base (5.1)

Any species that can accept a proton from another molecule

Buffer (6.2)

Mixture of appreciable amounts of a weak acid-base pair; the buffer resists dramatic changes in pH when small amounts of acid or base are added

Buffer capacity (6.2)

Amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit); in other words, the amount of acid or base a buffer can counteract

Buret (6.3)

Precisely calibrated volumetric delivery tube used for the precise delivery of variable liquid volumes, such as in a titration analysis

Calorie (cal) (3.1)

Unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

Calorimeter (3.5)

Device used to measure the amount of heat absorbed or released in a chemical or physical process

Calorimetry (3.5)

Process of measuring enthalpy changes for chemical reactions

Catalyst (7.1)

Substance that lowers the activation energy of a specific reaction by providing an alternate reaction pathway, thereby increasing the rate of a reaction without itself being consumed by the reaction

Cation (V)

Species with an overall positive charge; e.g. Ca^{2+}, NH_4^+, H_3O^+

Celsius (°C) (II)

Unit of temperature; water freezes at 0°C and boils at 100°C on this scale

Charles's law (2.4)

Volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

Chemical change (I)

Change producing a different kind of matter from the original kind of matter; it is the process of demonstrating a chemical property

Chemical equation (1.2)

Concise way, using symbols or formulas, of representing a chemical reaction

Chemical property (I)

Behavior that is related to the change of one kind of matter into another kind of matter; it is a characteristic that describes how matter changes form in the presence of other matter

Chemical symbol (V)

One-, two-, or three-letter abbreviation used to represent an element or its atoms; e.g. C (for carbon), Cu (for copper), Xe (for xenon)

Chemical thermodynamics (3.2)

Area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

Chemistry (I)

Study of the composition, properties, and interactions of matter with other matter and with energy

Closed system (3.1)

System that can exchange energy but not matter with its surroundings

Coefficient (1.2)

The number placed in front of symbols or formulas in a chemical equation indicating their relative amount and placed when there's more than one molecule of a substance

Collision theory (7.5)

Model that emphasizes the energy and orientation of molecular collisions in chemical reactions to explain and predict reaction kinetics

Colour-change interval (6.3)

Range in pH over which the color change of an indicator is observed

Combustion analysis (1.2)

Gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

Combustion reaction (1.5)

Redox chemical reaction in which a reactant combines with oxygen to produce oxides of all other elements as products; produces significant amounts of energy in the form of heat and, sometimes, light

Common ion effect (6.1)

Effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

Complete ionic equation (1.4)

The chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

Compound (I)

Pure substance that can be decomposed into two or more elements

Compressibility factor (*Z*) (2.8)

Ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation; measure of the extent of deviation from ideal gas behaviour

Concentrated (1.4)

The qualitative term for a solution containing solute at a relatively high concentration

Concentration (*C*) (1.4)

A quantitative measure of the amount of solute dissolved in a given amount of solvent

Conjugate acid (5.1)

Substance formed when a base gains a proton

Conjugate base (5.1)

Substance formed when an acid loses a proton

Continuous spectrum (8.1)

Electromagnetic radiation given off in an unbroken series of wavelengths, containing all colours of light (e.g., white light from the sun)

Coordinate covalent bond (5.6)

Covalent bond in which both electrons originated from the same atom

Core electron (8.5)

Electron in an atom that occupies the orbitals of the inner shells

Covalent bond (VI)

Chemical bond formed by two atoms sharing electrons (attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms)

Covalent radius (8.7)

One-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

Cubic centimetre (cm^3 or cc) (II)

Volume of a cube with an edge length of exactly 1 cm

Cubic metre (m^3) (II)

SI unit of volume; volume of a cube with an edge length of exactly 1 m

***d* orbital (8.4)**

Region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $\ell = 2$.

Dalton (Da) (V)

Alternative unit equivalent to the atomic mass unit

Dalton's atomic theory (IV)

Set of postulates that established the fundamental properties of atoms

Dalton's law of partial pressures (2.5)

Total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases

Dative bond (see **coordinate covalent bond**) **(5.6)**

Degenerate orbitals (8.4)

Orbitals that have the same energy

Density (ρ) (II)

A physical property defined as the ratio of mass to volume for a substance or object

Diamagnetism (8.6)

Magnetic state of substances characterized by paired electrons; diamagnetic substances are (weakly) repelled by an applied magnetic field

Differential rate law (see **rate law**) **(7.3)**

Diffusion (2.7)

Movement of an atom or molecule from a region of relatively high concentration to one of relatively low concentration (discussed in Chapter 2 with regard to gaseous species, but applicable to species in any phase)

Dilute (1.4)

A qualitative term for a solution containing solute at a relatively low concentration; also refers to the act of adding solvent, which decreases the concentration of the solute in the solution

Dilution (1.4)

Process of adding solvent to a solution in order to lower the concentration of solutes

Dimensional analysis (II)

Versatile mathematical approach that can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities

Dipole (see **polar molecule**) **(9.5)**

Dipole moment (9.5)

Property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

Dipole-dipole attraction (2.1)

Intermolecular force caused by molecules with a permanent dipole

Diprotic acid (5.4)

Acid containing two ionizable hydrogen atoms per molecule

Diprotic base (5.4)

Base capable of accepting two protons

Dispersion force (2.1)

Intermolecular force between two rapidly fluctuating, temporary dipoles, caused by the instantaneous positions of electrons in molecules; significant only when particles are very close together

Dissociation constant (K_d) (5.6)

Equilibrium constant for the decomposition of a complex ion into its components

Dissolved (1.4)

Describes the process by which solute components are dispersed in a solvent

Double bond (9.4)

Covalent bond in which two pairs of electrons are shared between two atoms

Effective nuclear charge (Z_{eff}) (8.7)

Charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding; net nuclear charge felt by valence electrons

Effusion (2.7)

Transfer of gaseous atoms or molecules from a container to a vacuum through very small openings

Electromagnetic radiation (8.1)

Energy transmitted by waves that have an electric-field component and a magnetic-field component

Electromagnetic spectrum (8.1)

Full span of the possible wavelengths, frequencies, and energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays

Electron (e^-) (IV)

Negatively charged, subatomic particle of relatively low mass located outside the nucleus

Electron affinity (EA) (8.7)

Energy change associated with addition of an electron to a gaseous atom or ion

Electron configuration (8.5)

Listing that identifies the electron occupancy of an atom's shells and subshells

Electron-pair geometry (9.5)

Arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

Electronegativity (EN) (9.3)

Relative tendency of an atom to attract electrons in a bond to itself

Element (I)

Substance that is composed of a single type of atom; a substance that cannot be broken down into simpler chemical substances by ordinary chemical means; e.g. hydrogen, zinc, argon

Elementary reaction (7.7)

Reaction that takes place in a single step, precisely as depicted in its chemical equation

Empirical formula (1.2)

Formula showing the composition of a compound given as the simplest whole-number ratio of atoms

Empirical formula mass (1.2)

Sum of average atomic masses for all atoms represented in an empirical formula

Endothermic process (3.2)

Chemical reaction or physical change that absorbs heat

Endpoint (6.3)

Measured volume of titrant solution that yields the change in sample solution appearance (e.g. colour change) or other property expected for stoichiometric equivalence

Energy (E) (3.1)

Capacity to supply heat or do work

Enthalpy (*H*) (3.4)

Sum of a system's internal energy and the mathematical product of its pressure and volume

Enthalpy change (Δ*H*) (3.4)

Heat released or absorbed by a system under constant pressure during a chemical or physical process

Entropy (*S*) (4.4)

Level of randomness (or disorder) of a system, or a measure of the energy dispersal of the molecules in the system

Equatorial position (9.5)

One of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

Equilibrium (4.1)

State of a reversible reaction in which the forward and reverse processes occur at equal rates

Equilibrium constant (*K*) (4.2)

Value of the reaction quotient for a system at equilibrium; relates to the ratio of products and reactants at equilibrium; may be expressed using concentrations (K_c) or partial pressures (K_p)

Equivalence point (6.3)

Volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

Exact number (III)

Number derived by counting or by definition; technically has an infinite number of significant figures

Excess reactant (1.3)

Reactant present in an amount greater than required by the reaction stoichiometry

Excited electronic state (8.2)

State having an energy greater than the ground-state energy

Excited state (see **excited electronic state**) **(8.2)**

Exothermic process (3.2)

Chemical reaction or physical change that releases heat

Expanded octet (9.4)

Describes a hypervalent molecule, which contains at least one main group element that has more than eight electrons in its valence shell

Expansion work (3.3)

Work done as a system expands or contracts against external pressure

Extensive property (I)

Property of a substance that depends on the amount of the substance

***f* orbital (8.4)**

Multilobed region of space with high electron density, describes orbitals with $\ell = 3$

Fahrenheit (°F) (2.3)

Unit of temperature; water freezes at 32 °F and boils at 212 °F on this scale

First law of thermodynamics (3.3)

Internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Formal charge (9.4)

Charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

Formation constant (K_f) (5.6)

Equilibrium constant for the formation of a complex ion from its components

Free radical (9.4)

Molecule that contains an odd number of electrons

Frequency (ν) (8.1)

Number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

Fundamental unit of charge (V)

Also called the elementary charge; equals the magnitude of the charge of an electron (e^-) with $e = 1.602 \times 10^{-19}$ C

Gas (I)

State in which matter has neither definite volume nor shape

Gay-Lussac's law (2.4)

Pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Graham's law of effusion (2.7)

Rates of diffusion and effusion of gases are inversely proportional to the square roots of their molecular masses

Ground electronic state (8.2)

State in which the electrons in an atom, ion, or molecule have the lowest energy possible

Ground state (see **ground electronic state**) **(8.2)**

Group (V)

Vertical column of the periodic table

Half-life of a reaction ($t_{1/2}$) (7.3)

Amount of time required for the concentration of a reactant to drop to one half of its initial concentration

Half-reaction (1.5)

The individual oxidation or reduction reaction of a redox reaction

Half-reaction method (1.5)

Method of balancing redox reactions by writing and balancing the individual half-reactions

Halogen (V)

Element in group 17; e.g. fluorine (F), chlorine (Cl), bromine (Br)

Heat (*q*) (3.2)

Transfer of thermal energy between two bodies

Heat capacity (*C*) (3.5)

Extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

Heisenberg uncertainty principle (8.3)

Rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

Henderson-Hasselbalch equation (6.2)

Logarithmic version of the acid ionization constant expression, conveniently formatted for calculating the pH of buffer solutions

Hertz (Hz) (8.1)

Unit of frequency, which is the number of cycles per second, s^{-1}

Hess's law (3.6)

If a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

Heterogeneous catalyst (7.8)

Catalyst present in a different phase from one or more of the reactants (e.g. furnishing a surface at which a reaction can occur)

Heterogeneous equilibrium (4.2)

Equilibrium in which reactants and products occupy two or more different phases

Heterogeneous mixture (I)

Combination of substances with a composition that varies from point to point

Homogeneous catalyst (7.8)

Catalyst present in the same phase as the reactants

Homogeneous equilibrium (4.2)

Equilibrium in which all reactants and products occupy the same phase

Homogeneous mixture (I)

Combination of substances with a composition that is uniform throughout

Hund's rule (8.5)

Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

Hydrate (VII)

Compound containing one or more water molecules bound within its crystals; e.g. $CuSO_4{\cdot}5H_2O$, $CaSO_4{\cdot}2H_2O$

Hydrocarbon (3.6)

Compound composed only of hydrogen and carbon; the major component of fossil fuels

Hydrogen bonding (2.1)

Intermolecular force that occurs when exceptionally strong dipoles attract; these interactions exist when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

Hydronium ion (H_3O^+) (5.1)

Actual chemical species that represents a hydrogen ion combining with a water molecule in aqueous solution

Hydrophilic (1.4)

The tendency to weakly interact with and not mix well with water molecules

Hydrophobic (1.4)

The tendency to strongly interact with and mix well with water molecules

Hypervalent molecule (see **expanded octet**) **(9.4)**

Ideal gas (2.4)

Hypothetical gas whose physical properties are perfectly described by the gas laws; it conforms exactly to the tenets of the kinetic molecular theory

Ideal gas constant (*R*) (2.4)

Constant derived from the ideal gas equation R = 0.08206 L atm mol^{-1} K^{-1} or 8.314 L kPa mol^{-1} K^{-1}

Ideal gas law (2.4)

Relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

Induced dipole (2.1)

Temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

Inert gas (see **noble gas**) **(V)**

Initial rate of reaction (7.2)

Instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

Instantaneous dipole (2.1)

Temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

Instantaneous rate of reaction (7.2)

Rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

Integrated rate law (7.3)

Equation that relates the concentration of a reactant to elapsed time of reaction

Intensive property (I)

Property of a substance that is independent of the amount of the substance

Interference pattern (8.1)

Pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

Intermediate (7.7)

Species produced in one elementary step of a reaction mechanism and consumed in a subsequent step; does not appear in the overall balanced equation

Intermolecular force (2.1)

Non-covalent attractive force between atoms, molecules, and/or ions

Internal energy (*U*) (3.2)

Total of all possible kinds of energy present in a substance or substances

Ion (V)

Species with an overall electric charge

Ion product (*Q*) (6.4)

Product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression; analogous to the reaction quotient (Q) discussed for gaseous equilibria

Ion-product constant for water (K_W) (5.2)

Equilibrium constant for the autoionization of water; represents the product of the hydrogen ion and hydroxide ion concentrations; $K_W = 1.0 \times 10^{-14}$ at 25°C

Ionic bond (VI)

Electrostatic forces of attraction between the oppositely charged ions of an ionic compound

Ionic compound (VI)

Compound composed of cations and anions combined in ratios, yielding an electrically neutral substance; e.g. Na_2SO_4, MgO, $NaHCO_3$

Ionization energy (IE) (8.7)

Energy required to remove an electron from a gaseous atom or ion

Isoelectronic (8.7)

Group of ions or atoms that have identical electron configurations

Isolated system (3.1)

System that exchanges neither energy nor matter with the surroundings

Isomers (1.2)

Compounds with the same chemical formula but different structures

Isotopes (IV)

Atoms of the same element that contain the same number of protons but different numbers of neutrons; e.g. examples of isotopes for carbon are ^{12}C (stable and most abundant), ^{13}C (also stable), and ^{14}C (radioisotope)

Joule (J) (3.1)

SI unit of energy; 1 J = 1 kg m^2 s^{-2} and 4.184 J = 1 cal

Kelvin (K) (II)

SI unit of temperature; 273.15 K = 0 ºC

Kilogram (kg) (II)

Standard SI unit of mass; 1 kg = approximately 2.2 pounds

Kinetic energy (E_k) (3.1)

Energy of a moving body, in joules, equal to 1/2 mv^2 (where m = mass and v = velocity)

Kinetic molecular theory (2.6)

Theory based on simple principles and assumptions that effectively explains ideal gas behavior by helping us understand gases at the molecular level and their physical properties

Lanthanide (V)

Inner transition metal in the top of the bottom two rows of the periodic table

Lattice energy ($\Delta H_{lattice}$) (9.2)

Energy required to separate one mole of an ionic solid into its component gaseous ions

Law of conservation of matter (I)

When matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

Law of constant composition (see **law of definite proportions**) **(IV)**

Law of definite proportions (IV)

All samples of a pure compound contain the same elements in the same proportions by mass

Law of multiple proportions (IV)

When two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

Le Châtelier's principle (4.4)

An equilibrium subjected to stress will shift in a way to counter the stress and re-establish equilibrium

Length (II)

Measure of one dimension of an object

Leveling effect of water (5.3)

Observation that acid-base strength of solutes in a given solvent is limited to that of the solvent's characteristic acid and base species (in water, hydronium and hydroxide ions, respectively)

Lewis acid (5.6)

Any species that can accept a pair of electrons and form a coordinate covalent bond

Lewis acid-base adduct (5.6)

Compound or ion that contains a coordinate covalent bond between a Lewis acid and a Lewis base

Lewis acid-base chemistry (5.6)

Reactions involving the formation of coordinate covalent bonds

Lewis base (5.6)

Any species that can donate a pair of electrons and form a coordinate covalent bond

Lewis electron dot symbol (see **Lewis symbol**) **(9.1)**

Lewis structure (9.4)

Diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol (9.1)

Symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

Ligand (5.6)

Molecule or ion acting as a Lewis base in complex ion formation; bonds to the central atom of the complex

Limiting reactant (1.3)

Reactant present in an amount lower than required by the reaction stoichiometry; it runs out first for a given chemical reaction and thus limits the amount of product generated

Line spectrum (8.2)

Electromagnetic radiation emitted at discrete wavelengths (i.e. contains only certain colours of light) by a specific atom (or atoms) in an excited state

Linear (9.5)

Shape in which two outside groups are placed on opposite sides of a central atom

Lipophilic (1.4)

The tendency to strongly interact with and mix well with lipids (fats/oils) and non-polar solvents

Liquid (I)

State of matter that has a definite volume but indefinite shape

Litre (L) (II)

Also called a cubic decimetre; unit of volume; 1 L = 1,000 cm^3

London dispersion force (see **dispersion force**) **(2.1)**

Lone pair (9.4)

Two (a pair of) valence electrons that are not used to form a covalent bond

Magnetic dipole moment (see **magnetic moment**) **(8.6)**

Magnetic moment (8.6)

Measure of the magnetic strength and direction of a system; a vector quantity

Magnetic quantum number (m_ℓ) (8.4)

Quantum number signifying the orientation of an atomic orbital around the nucleus

Main-group element (V)

Element in groups 1, 2, and 13–18

Manometer (2.3)

Device used to measure the pressure of a gas trapped in a container

Mass (m) (I)

Fundamental property indicating amount of matter

Mass number (A) (V)

Sum of the numbers of neutrons and protons in the nucleus of an atom

Mass percentage (*m/m %*) (1.4)

The ratio of solute-to-solution mass expressed as a percentage

Mass-volume percent (*m/v %*) (1.4)

The ratio of solute mass to solution volume expressed as a percentage

Matter (I)

Anything that occupies space and has mass

Mean free path (2.7)

Average distance a molecule travels between collisions

Metal (V)

Element that is shiny, ductile, malleable, good conductor of heat and electricity; e.g. iron (Fe), copper (Cu), zinc (Zn)

Metalloid (V)

Element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals; e.g. boron (B), silicon (Si), arsenic (As)

Method of initial rates (7.3)

Common experimental approach to determining rate laws that involves measuring the instantaneous reaction rate upon mixing the reactants

Metre (m) (II)

Standard metric and SI unit of length

Midpoint (6.3)

Point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present; occurs halfway to the equivalence point

Millilitre (mL) (II)

1/1,000 of a liter; equal to 1 cm^3

Mixture (I)

Physical combination of more than one substance; can then be separated into its components by physical means

Molality (*b*) (1.4)

A concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

Molar mass (M_m) (1.1)

Mass in grams of 1 mole of a substance

Molar solubility (6.4)

Solubility of a compound expressed in units of moles per liter (mol/L)

Molarity (*M*) (1.4)

Unit of concentration, defined as the number of moles of solute dissolved in 1 litre of solution

Mole (*n*) (1.1)

Amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C; equals 6.022 × 10^{23} things

Mole fraction (*X*) (2.5)

Ratio of the molar amount of a mixture component to the total number of moles of all mixture components

Molecular formula (1.2)

Formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

Molecular structure (9.4 & 9.5)

Arrangement of atoms in a molecule or ion; in VSEPR theory, it refers to a structure that includes only the placement of the atoms in the molecule

Molecularity (7.7)

Number of reactant species involved in an elementary reaction

Molecule (I)

Bonded collection of two or more atoms of the same or different elements; e.g. water (H_2O), glucose ($C_6H_{12}O_6$), ozone (O_3)

Monatomic ion (VI)

Ion composed of a single atom; e.g. K^+; O^{2-}, Fe^{3+}

Monoprotic acid (5.4)

Acid containing one ionizable hydrogen atom per molecule

Net ionic equation (1.4)

The chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

Neutral (5.2)

Describes a solution in which $[H_3O^+] = [OH^-]$

Neutralization reaction (5.5)

Reaction of an acid and a base to produce water and a salt

Neutron (IV)

Uncharged, subatomic particle located in the nucleus

Noble gas (V)

Element in group 18; e.g. helium (He), neon (Ne), krypton (Kr)

Node (8.1)

Any point of a standing wave with zero amplitude

Nomenclature (VI)

System of rules for naming objects of interest; in chemistry, a very specific system for naming compounds, in which unique substances get unique names

Nonmetal (V)

Element that appears dull, poor conductor of heat and electricity; e.g. carbon (C), phosphorus (P), sulphur (S)

Nonpolar covalent bond (see **pure covalent bond**) **(9.3)**

Nucleus (IV)

Massive, positively charged center of an atom made up of protons and neutrons

Octahedral (9.5)

Shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

Octet rule (9.4)

Guideline which states that main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

Open system (3.1)

System that exchanges both matter and energy with its surroundings

Orbital diagram (8.5)

Pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

Overall reaction order (7.3)

Sum of the reaction orders for each substance represented in the rate law

Oxidant (see **oxidizing agent**) **(1.5)**

Oxidation (1.5)

Loss of one or more electrons by an atom; an increase in oxidation number

Oxidation number (1.5)

The charge each atom of an element would have in a compound if the compound were ionic

Oxidation state (see **oxidation number**) **(1.5)**

Oxidation-reduction reaction (1.5)

A chemical reaction that involves the transfer of electrons, hence it involves a change in oxidation number for one or more reactant elements

Oxidizing agent (1.5)

A substance that brings about the oxidation of another substance, and in the process becomes reduced

Oxoacid (VII)

Compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H+ ions when dissolved in water); e.g. HNO_3, H_2SO_4, H_3PO_4

Oxoanion (VII)

Polyatomic anion composed of a central atom bonded to oxygen atoms; e.g. sulfite (SO_3^{2-}), nitrate (NO_3^-), perchlorate (ClO_4^-)

p **orbital (8.4)**

Dumbbell-shaped region of space with high electron density, describes orbitals with $\ell = 1$

Paramagnetism (8.6)

Magnetic state of substances characterized by one or more unpaired electrons; paramagnetic substances are attracted by an externally applied magnetic field

Partial pressure (2.5)

Pressure exerted by an individual gas in a mixture

Parts per billion (ppb) (1.4)

The ratio of solute-to-solution mass multiplied by 10^9

Parts per million (ppm) (1.4)

The ratio of solute-to-solution mass multiplied by 10^6

Pascal (Pa) (2.3)

SI unit of pressure; $1 \text{ Pa} = 1 \text{ N/m}^2$

Path function (3.3)

Function that depends on the path taken to reach that specific value

Pauli exclusion principle (8.5)

Specifies that no two electrons in an atom can have the same value for all four quantum numbers

Percent composition (1.1)

Percentage by mass of the various elements in a compound

Percent ionization (5.3)

Ratio of the concentration of ionized acid to initial acid concentration expressed as a percentage

Percent yield (1.3)

A measure of the efficiency of a reaction expressed as a percentage of the theoretical yield; actual yield divided by theoretical yield times 100% to give a percentage between 0% and 100%

Period (V)

Horizontal row of the periodic table

Periodic table (V)

Table of the elements that places elements with similar chemical properties close together

pH (5.2)

Logarithmic measure of the concentration of hydronium ions in a solution (calculated as the negative logarithm of the hydronium ion concentration)

Photon (8.1)

Smallest possible discrete packet of electromagnetic radiation, a particle of light

Physical change (I)

Change in the state or properties of matter that changes one or more of its physical properties without changing its chemical composition

Physical property (I)

Characteristic of matter that is not associated with any change in its chemical composition

Plasma (I)

Gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pOH (5.2)

Logarithmic measure of the concentration of hydroxide ions in a solution (calculated as the negative logarithm of the hydroxide ion concentration)

Polar covalent bond (9.3)

Covalent bond between different atoms of different electronegativities, which cause an imbalance of electron distribution; a covalent bond with a partially positive end and a partially negative end

Polar molecule (9.5)

Molecule with an overall dipole moment

Polarizability (2.1)

Measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

Polyatomic ion (VI)

Ion composed of more than one atom; e.g. hydroxide ion (OH^-), carbonate ion (CO_3^{2-}), dichromate ion ($Cr_2O_7^{2-}$)

Potential energy (E_{pot}) (3.1)

Energy of a particle or system of particles derived from relative position, composition, or condition

Pre-exponential factor (A) (7.5)

Proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

Precipitate (6.1)

Insoluble product that forms from reaction of soluble reactants

Precipitation reaction (1.4)

A reaction that produces one or more insoluble products; when reactants are ionic compounds, sometimes called double-displacement or metathesis

Precision (III)

How closely a measurement matches the same measurement when repeated

Pressure (P) (2.3)

Force exerted per unit area

Principal quantum number (n) (8.4)

Quantum number specifying the shell an electron occupies in an atom

Product (1.2)

A substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

Proton (IV)

Positively charged, subatomic particle located in the nucleus

Proust's law (see **law of definite proportions**) **(IV)**

Pure covalent bond (9.3)

Covalent bond between atoms of identical electronegativities

Pure substance (I)

Homogeneous substance that has a constant composition; types of pure substances include elements and compounds

Quantization (8.1)

Limitation of some property to specific discrete values, not continuous

Quantum mechanics (8.4)

Field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

Quantum number (8.2)

Number having only specific allowed values and used to characterize the arrangement of electrons in an atom

Rare gas (see **noble gas**) **(V)**

Rate constant (*k*) (7.3)

Proportionality constant in a rate law specific to each reaction at a particular temperature

Rate equation (see **rate law**) **(7.3)**

Rate law (7.3)

Mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

Rate of diffusion (2.7)

Amount of gas diffusing through a given area over a given time

Rate of reaction (7.1)

Measure of the speed at which a chemical reaction takes place

Rate-determining step (7.7)

Slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

Rate-limiting step (see **rate-determining step**) **(7.7)**

Reactant (1.2)

Substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

Reaction coordinate diagram (7.8)

Used in chemical kinetics to illustrate the progression and various properties of a reaction

Reaction mechanism (7.7)

Stepwise sequence of elementary reactions by which a chemical change takes place

Reaction order (7.3)

Value of an exponent in a rate law (for example, zero order for 0, first order for 1, second order for 2, and so on)

Reaction profile (see **reaction coordinate diagram**) **(7.8)**

Reaction quotient (*Q*) (4.2)

Mathematical function describing the relative amounts of reactants and products in a reaction mixture; may be expressed in terms of concentrations (Q_c) or pressures (Q_p)

Redox reaction (see **oxidation-reduction reaction**) **(1.5)**

Reducing agent (1.5)

A substance that brings about the reduction of another substance, and in the process becomes oxidized

Reductant (see **reducing agent**) **(1.5)**

Reduction (1.5)

The gain of one or more electrons by an atom; a decrease in oxidation number

Replacement reaction (see **single-displacement reaction**) **(1.5)**

Representative element (see **main-group element**) **(V)**

Resonance (9.4)

Situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

Resonance forms (9.4)

Two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

Resonance hybrid (9.4)

Average of the resonance forms shown by the individual Lewis structures

Reversible reaction (4.1)

Chemical reaction that can proceed in both the forward and reverse directions under given conditions

Root mean square velocity (u_{rms}) (2.6)

Measure of average velocity for a group of particles calculated as the square root of the average squared velocity

Rounding (III)

Procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

***s* orbital (8.4)**

Spherical region of space with high electron density, describes orbitals with $\ell = 0$

Saturated (6.1)

Of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

Second (s) (II)

SI unit of time

Selective precipitation (6.4)

Process in which ions are separated using differences in their solubility with a given precipitating reagent

Semimetal (see **metalloid**) **(V)**

Shell (8.4)

Atomic orbitals with the same principal quantum number, *n*

Shielding (8.7)

Refers to the blocking of valence shell electron attraction by the nucleus due to the presence of inner-shell electrons

SI units (International System of Units) (II)

Standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

Significant digits (see **significant figures**) **(III)**

Significant figures (III)

The limit of the number of places a measurement can be properly expressed with

Single bond (9.4)

Bond in which a single pair of electrons is shared between two atoms

Single-displacement reaction (1.5)

Redox reaction involving the oxidation of an elemental substance by an ionic species; one element is substituted for another element in a compound

Solid (I)

State of matter that is rigid, has a definite shape, and has a fairly constant volume

Solubility (6.1)

Extent to which a solute may be dissolved in water, or any solvent

Solubility product constant (K_{sp}) (6.1)

Equilibrium constant for the dissolution of an ionic compound

Solute (1.4)

Solution component present in a concentration less than that of the solvent; minor component of a solution

Solution (see **homogeneous mixture**) **(I)**

Solvent (1.4)

Solution component present in a concentration that is higher relative to other components; the major component of a solution

Specific heat capacity (*c*) (3.5)

Intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

Spectator ion (1.4)

An ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Spin quantum number (m_s) (8.4)

Number specifying the electron spin direction, either +12 or −12

Stability constant (see **formation constant (K_f)**) **(5.6)**

Standard atmosphere (atm) (2.3)

Unit of pressure; 1 atm = 101,325 Pa = 760 mmHg

Standard conditions of temperature and pressure (STP) (2.1)

273.15 K (0 °C) and 1 bar (100 kPa)

Standard enthalpy of combustion ($\Delta H_c°$) (3.6)

Heat released when one mole of a compound undergoes complete combustion under standard conditions

Standard enthalpy of formation ($\Delta H_f°$) (3.6)

Enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

Standard molar volume (2.4)

Volume of 1 mole of gas at STP, approximately 22.7 L for gases behaving ideally

Standard state (3.4)

Set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Standing wave (8.1)

Localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

State function (3.3)

Property depending only on the state of a system, and not the path taken to reach that state

Stationary wave (see **standing wave**) **(8.1)**

Stepwise ionization (5.4)

Process in which a polyprotic acid is ionized by losing protons sequentially

Stoichiometric factor (1.3)

The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

Stoichiometry (1.3)

Relationships between the amounts of reactants and products of a chemical reaction

Strong acid (5.3)

Acid that reacts completely (100% ionization) when dissolved in water to yield hydronium ions

Strong base (5.3)

Base that reacts completely (100% ionization) when dissolved in water to yield hydroxide ions

Structural formula (1.2)

Shows the atoms in a molecule and how they are connected

Subshell (8.4)

Atomic orbitals with the same values of n and ℓ

Supersaturated (6.1)

Of concentration that exceeds solubility (more than the normal maximum amount of solute in it); a nonequilibrium state

Surroundings (3.1)

All matter other than the system being studied

System (3.1)

Portion of matter undergoing a chemical or physical change being studied

Temperature (*T*) (3.2)

Intensive property of matter that is a quantitative measure of "hotness" and "coldness;" measure of the average amount of kinetic energy a system contains

Termolecular reaction (7.7)

Elementary reaction involving three reactant species

Tetrahedral (9.5)

Shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

Theoretical yield (1.3)

Amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Thermal energy (3.2)

Kinetic energy associated with the random motion of atoms and molecules

Thermochemistry (3.1)

Study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

Titrant (6.3)

Solution containing a known concentration of substance that will react with the analyte in a titration analysis

Titration curve (6.3)

Plot of some sample property (such as pH) versus volume of added titrant

Torr (2.3)

Unit of pressure; another name for a millimetre of mercury; 1 Torr = 1760 atm

Transition element (V)

Element in groups 3–12; e.g. iron (Fe), tungsten (W), silver (Ag)

Transition metal (see **transition element**) **(V)**

Transition state (*‡*) (see **activated complex**) **(7.5)**

Transition state theory (7.6)

Theory which says that between the state where molecules are reactants and the state where molecules are products, there is the transition state where reactants are combined in a species called the activated complex

Trigonal bipyramidal (9.5)

Shape in which five outside groups are placed around a central atom such that three form a flat triangle with

120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

Trigonal planar (9.5)

Shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

Triple bond (9.4)

Bond in which three pairs of electrons are shared between two atoms

Triprotic acid (5.4)

Acid that contains three ionizable hydrogen atoms per molecule

Uncertainty (III)

Estimate of amount by which measurement differs from true value

Unified atomic mass unit (*u*) (V)

Alternative unit equivalent to the atomic mass unit

Unimolecular reaction (7.7)

Elementary reaction involving a single reactant species

Unit (II)

Elementary reaction involving a single reactant species

Valence electrons (8.5)

Electrons in the outermost or valence shell (highest value of n) plus any electrons in the last unfilled subshell of a ground-state atom; the electrons most likely involved in chemical reactions

Valence shell (8.5)

Outermost and highest-numbered shell of electrons in a ground-state atom

Valence shell electron-pair repulsion theory (VSEPR) (9.5)

Theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

Van der Waals equation (2.8)

Modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior, correcting for intermolecular forces and the volume of gas molecules

Van der Waals force (2.1)

Attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Van't Hoff Equation (4.4)

Linear relation between ln K and the standard enthalpies and entropies, describing the temperature dependence of the equilibrium constant

Vapour (2.2)

Material in the gas phase due to evaporation

Vapour pressure of water (2.5)

Pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

Vector (9.5)

Quantity having magnitude and direction

Volume (*V*) (II)

Amount of space occupied by an object

Volume percentage (*v/v %*) (1.4)

The ratio of solute-to-solution volume expressed as a percentage

Wave (8.1)

Oscillation of a property over time or space; can transport energy from one point to another

Wave-particle duality (8.1)

Observation that elementary particles can exhibit both wave-like and particle-like properties

Wavefunction (ψ) (8.4)

Mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

Wavelength (λ) (8.1)

Distance between two consecutive peaks or troughs (or other corresponding points) in a wave

Weak acid (5.3)

Acid that reacts only to a slight extent (less than 100% ionization) when dissolved in water to yield hydronium ions

Weak base (5.3)

Base that reacts only to a slight extent (less than 100% ionization) when dissolved in water to yield hydroxide ions

Weight (I)

Force that gravity exerts on an object

Work (*w*) (3.1)

Energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

APPENDIX N | ATTRIBUTIONS

1 – Stoichiometry

1.1 – The Mole

This chapter contains material and exercises taken from Section 3.1 "Formula Mass and the Mole Concept" and its exercises, respectively, of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-7,
Examples 1.1.1, 1.1.2, 1.1.3, 1.1.4, 1.1.5 and 1.1.6,
"Check your learning" 1.1.1, 1.1.2, 1.1.3, 1.1.4, 1.1.5 and 1.1.6, and
Table 1.1.1.

This chapter also contains material taken from Section 1.5 "Density and Percent Composition: Their Use in Problem Solving" of the Chemistry Libretexts textmap for General Chemistry: Principles and Modern Applications (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, including:

Paragraph 10, and
Example 1.1.7.

This chapter contains content taken from 3.2 – Determining Empirical and Molecular Formulas, including paragraphs 8 and 9.

This chapter contains material taken from Section 3.1 "Formula Mass and the Mole Concept" of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license including the end of section 1.1 questions and its answers.

This chapter contains original material by Jessica Thomas including the material in the brackets of example 1.1.1 and the answers for the end of section 1.1 questions 1 and 7.

This chapter contains original material by Leanne Trepanier and Nathan Biniam including the answers to the end of section 1.1 questions 5 and 8.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, examples and tables.

This chapter contains figures 1.1.1, 1.1.2, 1.1.3 and 1.1.4 taken from 3.1 – Formula Mass and the Mole Concept.

1.2 – Determining Chemical Formulae

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 2.3 "Atomic Structure and Symbolism,"
The "In case you're interested … Mass Spectrometry" box
Section 2.4 "Chemical Formulas" and its exercises,
Paragraphs 2-6 and 11,
Section 3.2 "Determining Empirical and Molecular Formulas" and its exercises,
Paragraphs 12-16 and 18-23,
Examples 1.2.1, 1.2.2 and 1.2.4,
"Check your learning" 1.2.1 and 1.2.2,
Section 4.1 "Writing and Balancing Chemical Equations" and its exercises,
Paragraphs 24-33,
The "Balancing Chemical equations – additional practice" box,
Section 4.5 "Quantitative Chemical Analysis,"
Paragraph 17,
Examples 1.2.3 and 1.2.5,
"Check your learning" 1.2.3 and 1.2.7,
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This chapter also contains an exercise taken from Section 1.3 "Introduction to Combustion Analysis" of the open textbook resource Physical Methods in Chemistry and Nano Science (by Raja and Barron) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY 4.0 license.

This chapter also contains an example and exercises taken from the exercises of Section 3 "Stoichiometry" of the Chemistry Libretexts textmap for Chemistry: The Central Science (by Brown, LeMay, Busten, Murphy, and Woodward) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 4.0 license.

This chapter contains example 1.2.4 taken from 3.2 – Determining Empirical and Molecular Formulas.

This chapter contains end of section 1.2 questions 1 and 2 and its answers taken from Section 2.4 "Chemical Formulas" of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains end of section 1.2 questions 3-6 and its answers taken from Section 3.2 "Determining Empirical and Molecular Formulas" of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains end of section 1.2 questions 7 and 8, and its answers taken from Exercises 3. E "Stoichiometry (Exercises)" of the Chemistry Libretexts textmap for Chemistry: The Central Science (by

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This chapter includes original material written by Mahdi Zeghal including paragraph 1 and 7-9, brackets in the second sentence of paragraph 3, brackets in the first sentence of paragraph 4, brackets in the second sentence of paragraph 6, brackets in the fourth sentence of paragraph 11, brackets of the first sentence in paragraph 17, the "combustion analysis problems – underlying assumption" box, the third paragraph under the solution of "Check your learning" 1.2.4 and the first sentence in the "Balancing Chemical equations – additional practice" box.

This chapter contains original material by Geneviève O'Keefe including the fourth sentence in paragraph 6 and paragraph 10.

This chapter contains original material by Leanne Trepanier and Nathan Biniam including the answers to the end of section 1.2 questions 5 and 11.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and examples.

This chapter contains figure 1.2.9 taken from "Atomic Structure and Symbolism."

This chapter contains figures 1.2.1, 1.2.2, 1.2.3 and 1.2.4 taken from "Chemical Formulas."

This chapter contains figures 1.2.5, 1.2.6 and 1.2.7 taken from "Determining Empirical and Molecular Formulas."

This chapter contains figures 1.2.11 and 1.2.12 taken from "Writing and Balancing Chemical Equations."

This chapter contains figure 1.2.8 taken from "Quantitative Chemical Analysis."

1.3 – Reaction Stoichiometry

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 4.3 "Reaction Stoichiometry" and its exercises,
Paragraphs 1-8,
Examples 1.3.1, 1.3.2, 1.3.3, 1.3.4,
"Check your learning" 1.3.4,
End of chapter 1.3 questions 1-8, and
Section 4.4 "Reaction Yields" and its exercises,
Paragraphs 9-15,

Examples 1.3.5, and 1.3.6,

"Check your learning" 1.3.5 (a), and

End of chapter 1.3 questions 9-12,

both used under a CC BY 4.0 license.

This chapter contains original content created by Jessica Thomas including example 1.3.5 question and answer for b, and the question and answer for example 1.3.6.

This chapter contains original answers for questions 1, 2, 5, 6, 8, 9, 10 and 12 created by Nathan Biniam and Leanne Trepanier.

This chapter contains original content by Geneviève O'Keefe including the numbering of certain figures and the answer to question 5 at the end of this section.

This chapter contains original content by Derek Fraser-Halberg including the numbering of figures and equations.

This chapter contains figures 1.3.1 and 1.3.2 taken from Section 4.3 "Reaction Stoichiometry."

This chapter contains figures 1.3.3 and 1.3.4 taken from Section 4.4 "Reaction Yields."

1.4 – Solution Stoichiometry

This chapter contains material and exercises taken from Section 3.3 "Molarity" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-5 and 19-22,

Examples 1.4.1, 1.4.2, 1.4.3, 1.4.4, 1.4.5, 1.4.11, 1.4.12, 1.4.13, and

"Check your learning" 1.4.1, 1.4.2, 1.4.3, 1.4.4, 1.4.5, 1.4.11, 1.4.12, and 1.4.13.

This chapter also contains material taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project:

"Fundamental Characteristics of Water," a section of Aquatic Chemistry (by Chieh) of the Chemistry Libretexts supplemental modules on environmental chemistry, used under a CC BY-NC-SA 3.0 license,

Paragraphs 17 and 18,

Section 7.6 "Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations," a section of the Chemistry Libretexts textmap for *Introductory Chemistry* (by Tro), used under a CC BY-NC-SA 3.0 license,

Paragraphs 24-29,

Examples 1.4.14 and 1.4.16,

"Check your learning" 1.4.15 and 1.4.16, and

Section 16.11 "Molality," a section of *Introductory Chemistry (CK-12)*, used under a CC BY-NC 4.0 license,

Paragraphs 14-16, and

Example 1.4.10.

This chapter contains original content by Dr. Brandi West including the second sentence of paragraph 24.

This chapter contains original content by Jessica Thomas including sentence 2 in paragraph 9, the sentence in example 1.4.6 above the subtitle "Check your learning", the question and answer for (a) in "Check your learning" 1.4.9, the last sentence in paragraph 20, the 3 first numbered points under "Molecular, complete ionic, and net equations" and the end of chapter questions from 8 to 16.

This chapter contains original answers for questions 7 to 18 created by Nathan Biniam and Leanne Trepanier.

This chapter contains the equation for point 1 under "Molecular, complete ionic, and net equations" (Acid-Base Reactions).

This chapter contains the equation for point 2 under "Molecular, complete ionic, and net equations" (5.6 – Oxidation-Reduction (Redox) Reactions).

This chapter contains an exercise and its answer for the end of chapter question 21 taken from Section 4.2 "Classifying Chemical Reactions" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures and equations.

This chapter contains figures and material from (3.4 – Other Units for Solution Concentrations) including figures 1.4.3, 1.4.4, 1.4.5 and 1.4.7 and paragraphs 6 and 8 to 13, first sentence in paragraph 1, examples 1.4.6, 1.4.7, 1.4.8, and 1.4.9, and "Check your learning" 1.4.6, 1.4.7, 1.4.8, and 1.4.9 (b).

This chapter contains figures 1.4.1, 1.4.2, and 1.4.6 taken from "Molarity."

This chapter contains figures 1.4.8 taken from "Writing Chemical Equations for Reactions in Solution-Molecular, Complete Ionic, and Net Ionic Equations."

1.5 – Redox Reactions

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 4.2 "Classifying Chemical Reactions" and its exercises,
Paragraphs 1-3 and 5-9,
Examples 1.5.1 and 1.5.2,
"Check your learning" 1.5.1 and 1.5.2, and
Section 17.1 "Review of Redox Chemistry" and its exercises,
Examples 1.5.3 and 1.5.5, and
"Check your learning" 1.5.4 and 1.5.5,
both used under a CC BY 4.0 license.

This chapter contains original content by Mahdi Zeghal including:

Sentences within steps of example 1.5.5, “Tips and Tricks – oxidation and reduction acronyms”,

In paragraph 5: The “(e.g)” for points 1, 2, and 4, and the last part of the sentence, under bullet point 4, after the last comma in both points 4.2 and 4.3,

Paragraph 6,

Sentence 1 and 5 in paragraph 10, as well as steps 1 and 9, and

“Note” in example 1.5.3 and the sentence in example 1.5.3 about step 7 of the example’s solution.

This chapter contains original content by Geneviève O’Keefe including the second and last sentence in paragraph 1.

This chapter contains original content by Geneviève O’Keefe and Derek Fraser-Halberg including the numbering of figures and equations.

This chapter contains original answers for questions 1, 3, 5, 10 and 11 created by Nathan Biniam and Leanne Trepanier.

This chapter contains figure 1.5.2 taken from “Classifying Chemical Reactions.”

Chapter 1 Key Terms

The definitions for the following key terms were adapted from the Chapter 2 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Empirical formula	**Isomers**	**Molecular formula**	**Structural formula**

The definitions for the following key terms were adapted from the Chapter 3 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Aqueous solution
Avogadro’s number (N_A)
Concentrated
Concentration (*C*)
Dilute
Dilution
Empirical formula mass
Mass percentage (*m/m %*)
Mass-volume percent (*m/v %*)
Molar mass (M_m)
Molarity (*M*)
Mole (*n*)
Parts per billion (ppb)
Parts per million (ppm)
Percent composition
Solute
Solvent
Volume percentage (*v/v %*)

The definitions for the following key terms were adapted from the Chapter 4 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Actual yield
Balanced equation
Coefficient
Combustion analysis
Combustion reaction
Complete ionic equation
Excess reactant
Limiting reactant
Net ionic equation
Oxidation number
Oxidation-reduction reaction
Oxidizing agent
Percent yield
Precipitation reaction
Product
Reactant
Reducing agent
Single-displacement reaction
Spectator ion
Stoichiometric factor
Stoichiometry
Theoretical yield

The definitions for the following key terms were adapted from the Chapter 11 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Amphipathic
Molality (*b*)

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Chemical equation
Coefficient
Combustion reaction
Concentration
Dilute
Half-reaction
Half-reaction method
Limiting reactant
Mole (*n*)
Oxidation
Oxidation-reduction reaction
Percent yield
Reduction
Single-displacement reaction
Solute
Solvent

The definitions for the following key terms were adapted from another open textbook resource of the Open Education Resource (OER) LibreTexts Project:

Hydrophilic and **hydrophobic** – from "Fundamental Characteristics of Water," a section of Aquatic Chemistry (by Chieh) of the Chemistry Libretexts supplemental modules on environmental chemistry, used under a CC BY-NC-SA 3.0 license.

2 – Gases

2.1 – Intermolecular Forces

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 10.1 "Intermolecular Forces" and its exercises,
Paragraphs 1-22,
Example 2.1.1,
"Check your learning" 2.1.1 – 2.13,
Figures 2.1.1 – 2.1.13, and
Questions and Answers 2, 5, 6 and 7.

This chapter also contains material taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project:

Section 3.7 "Intermolecular forces," a unit section of the course CHEM1130 Principles of Chemistry I (from the Northern Alberta Institute of Technology), used under a CC BY-NC-SA 3.0 license,
Paragraph 23,
Questions 1, 3, and 4, and

Answers 1, 2, 3, 4, 5, 6, and 7.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Sentence 3 in paragraph 3,

Sentence 4 in paragraph 16, and

Answer for "Check your learning" 2.1.3.

This chapter contains original content by Jessica Thomas including:

Summary at the end of chapter.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures and equations.

This chapter contains original answers for questions 5 created by Nathan Biniam and Leanne Trepanier.

2.2 – Gases and the Periodic Table

This chapter contains material taken from Section 10.1 "Characteristics of Gases" of the Chemistry Libretexts textmap for *Chemistry: The Central Science* (by Brown, LeMay, Busten, Murphy, and Woodward) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 4.0 license, including:

Paragraphs 1-3,

Examples,

"Check your learning", and

Figure 2.2.1.

This chapter contains original content by Jessica Thomas and Dr. Kathy-Sarah Focsaneanu including:

Questions and answers 1 and 2.

2.3 – Measuring Variables of Gases

This chapter contains material and/or examples taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project:

Section 2.2 "Expressing Units," a section of *Beginning Chemistry* (by Ball), used under a CC BY-NC-SA 4.0 license,

Paragraphs 18-19,

Figure 2.3.5, and

Section 2.4 "Temperature," a unit section of the course CHM101: Chemistry and Global Awareness (by Gordon from Furman University), used under a CC BY-NC-SA 4.0 license,

Paragraphs 20-26,

Example 2.3.6,

Figure 2.3.6, and

Section 5.2 "Gas Pressure and Its Measurement," a section of the Chemistry Libretexts textmap for

Chemistry – The Molecular Nature of Matter and Change (by Silberberg), used under a CC BY-NC-SA 3.0 license,

Paragraphs 8-16

Examples 2.3.4, 2.3.5,

Figures 2.3.2, 2.3.3, 2.3.4,

"Check your learning" 2.3.3, 2.3.4, 2.3.5, and

Sections 9.3 "Pressure" and 9.4 "Measurement of Pressure," sections of *ChemPRIME* (by Moore et al.), both used under a CC BY-NC-SA 4.0 license,

Paragraphs 1-7,

Examples 2.3.1, 2.3.3,

Figure 2.3.1,

"Check your learning" 2.3.2, and

Questions 8 and 9.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Changes made on paragraphs 9, 12, 15, 18, and 23, and

End of the chapter questions 1, 2, 3, 5, 6, and 11.

This chapter contains original content by Derek Fraser-Halberg including:

End of the chapter answers.

This chapter contains original content by Mahdi Zeghal including:

Subheading for figure 2.3.1.

This chapter contains original content by Leanne Trepanier and Derek Fraser-Halberg including the numbering of figures and equations.

2.4 – Gas Laws

This chapter contains material and exercises taken from Section 9.2 "Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-25,

Examples 2.4.1 – 2.4.6,

Figures 2.4.1 – 2.4.10,

"Check your Learning" 2.4.1 – 2.4.6,

Questions 1-14, and

Answers 11 and 14.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Changes to titles, equations and figures.

This chapter contains original content by Leanne Trepanier and Geneviève O'Keefe including the numbering of equations, figures and answers 1, 3, 4, 5, 7, 9, and 10.

This chapter contains original content by Mahdi Zeghal including change to the CHEM1311 Laboratory section.

This chapter contains original answers for questions 2, 6, 8, 12 and 13 created by Nathan Biniam.

2.5 – Gas Mixtures and Partial Pressures

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 9.3 "Stoichiometry of Gaseous Substances, Mixtures, and Reactions" and its exercises,
Paragraphs:
Under Equation 2.5.1 (Whole paragraph),
Paragraph 4 Sentence 2,
Paragraph 5 (Whole paragraph),
Paragraph 6 (Whole paragraph),
Paragraph 7 (Whole paragraph),
Examples,
Figure 2.5.1, and
"Check your learning".

2.6 – Kinetic-Molecular Theory of Gases (Ideal Gas Behaviours)

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 9.5 "The Kinetic-Molecular Theory" and its exercises,
Paragraphs 1-12,
Example 2.6.1,
Figures 2.6.1, 2.6.2, 2.6.3, 2.6.4, 2.6.5, and
"Check your Learning" 2.6.1.

This chapter contains original content by Leane Trapier and Derek Fraser-Halberg including numbering of equations and equation subheadings.

This chapter contains original content by Jessica Thomas including:
Sentence 1 from paragraph 9 (added "where M is the average mass of the particles"),
Paragraph 10 (added "(to extend your learning, check out the derivation for KE_{avg} here):"),
Sentence 1 of the answer to "Check your learning" 2.6.1, and
Questions 1-8.

This chapter contains original content by Geneviève O'Keefe including:

Inserting "decrease both" to Charles's Law – sentence 3, and

Answers 2, 5 and 7.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Added "Gay-Lussac's law" to " The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I – Amontons' ",

Added a paragraph under equation 2.6.2, and

Added "expressed in kilograms" to paragraph 9.

This chapter contains original content by Nathan Biniam including:

End of chapter answers 1, 3, 4, 6, and 8.

2.7 – Diffusion and Effusion

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 9.4 "Effusion and Diffusion of Gases" and its exercises,

Paragraphs 1-10,

Examples 2.7.1, 2.7.2, 2.7.3,

Figures 2.7.1, 2.7.2, 2.7.3, and

"Check your Learning" 2.7.1, 2.7.2, 2.73.

This chapter contains original content by Genevieve O'Keefe including:

First two sentences in paragraph 1,

Paragraph 6 sentence 1,

Example 2.7.3,

Paragraph 1 Sentence 3,

Solution – Sentence 4,

Above "Check your Learning" 2.7.3, Paragraph was added,

Wrote "In Case You're Interested… Use of Diffusion for Nuclear Energy Applications: Uranium Enrichment" Section, and

Answers for questions 1, 3, 5, 7, and 9.

This chapter contains original content by Jessica Thomas including:

Questions 1 to 9.

This chapter contains original content by Mahdi Zeghal including:

Added to sentence 1 in the section "The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II,

Example 2.7.3 "Elements and Molar Masses", and

Answer for question 6.

This chapter contains original content by Leanne Trepanier including:

Answers for questions 2, 3, 4, 8, and

Edit to questions 1 and 8.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Paragraph 7,

Example 2.7.1,

Added a couple words to the first paragraph, and

Whole solution (else than the equation).

This chapter contains original content by Leane Trapier and Derek Fraser-Halberg including numbering of equations and equation subheadings.

2.8 – Real/Non-Ideal Gas Behaviours

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, including:

Section 9.6 "Non-Ideal Gas Behavior" and its exercises,

Paragraphs 1-9,

Example 2.8.1,

Table 2.8.1,

Figures 2.8.1, 2.8.2, 2.8.3, 2.8.4, and

"Check your Learning" 2.8.1.

This chapter contains original content by Jessica Thomas including:

Questions 1-7.

This chapter contains original content by Leanne Trepanier including:

Answer for question 4 sentence 2 and 3.

This chapter contains original content by Geneviève O'Keefe including:

Answer for questions 1, 3, 5, and 7.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Sentence 3 in paragraph under Figure 2.8.3,

Figure 2.8.2 sentence 2, and

Small edits on paragraph under figure 2.8.2.

This chapter contains original content by Nathan Biniam including:

Answers for questions 2, 4, 6

This chapter contains original content by Leane Trapier, Jessica Thomas and Derek Fraser-Halberg including numbering of equations and equation subheadings.

Chapter 2 Key Terms

The definition for the following key term was adapted from the Chapter 1 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Fahrenheit (°F)

The definitions for the following key terms were adapted from the Chapter 9 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Absolute zero
Avogadro's law
Bar (bar)
Barometer
Boyle's law
Charles's law
Compressibility factor (Z)
Dalton's law of partial pressures
Diffusion
Effusion
Gay-Lussac's law
Graham's law of effusion
Ideal gas
Ideal gas constant (R)
Ideal gas law
Kinetic molecular theory
Manometer
Mean free path
Mole fraction (X)
Partial pressure
Pascal (Pa)
Pressure (P)
Rate of diffusion
Root mean square velocity (u_{rms})
Standard atmosphere (atm)
Standard molar volume
Torr
Van der Waals equation
Vapour pressure of water

The definitions for the following key terms were adapted from the Chapter 10 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Dispersion force
Hydrogen bonding
Induced dipole
Instantaneous dipole
Intermolecular force
Polarizability
Van der Waals force

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Absolute zero

Compressibility factor (Z)

Dipole-dipole attraction

Dispersion force

Ideal gas

Kinetic molecular theory

Torr

Van der Waals equation

Vapour

The definition for the following key term was adapted from another open textbook resource of the Open Education Resource (OER) LibreTexts Project:

Atmospheric pressure – from *ChemPRIME* (by Moore et al.), used under a CC BY-NC-SA 4.0 license.

3 – Thermochemistry

3.1 – Introduction to Thermochemistry

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 5.1 "Energy Basics",
Paragraphs 1-8,
Figure 3.1.1, and
Section 5.2 "The First Law of Thermodynamics",
Paragraphs 14-15, and
Figures 3.1.3.
This chapter contains original content by Leanne Trepanier including answers for questions 1, 2, and 4.
This chapter contains original content by Mahdi Zeghal including:
Figure 3.1.1 subheading,
Wrote titles,
Wrote the section "Measuring Nutritional Calories", and
Added a couple words to the last sentence in paragraph 11.
This chapter contains original content by Dr. Brandi West including:
Sentence 1 in paragraph 1 in the section "Energy in the Universe",
Added a couple of words to questions 1-4, and

Wrote an answer for question 3 and 4.

This chapter contains original content by Geneviève O'Keefe including:

Added a couple words to the last sentence in paragraph 11,

Wrote the title and the first sentence of the section "Energy in the Universe",

"Measuring Nutritional Calories" paragraph 3 last sentence,

Sentences 3-5 in paragraph 7, and

Paragraph 10.

This chapter contains original content by Derek Fraser-Halberg including questions 1-4.

3.2 – Types of Energy

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Sections 5.1 "Energy Basics" and 5.3 "Enthalpy,"

Paragraphs 1, 2, 3 (last sentence), 4-7,

"Check your Learning" 3.2.1,

Example 3.2.2,

Figures 3.2.1, 3.2.2, 3.2.3, 3.2.4,

"Internal Energy," a section of Thermodynamics (contributed by Alborzfar) of the Chemistry Libretexts supplemental modules on physical and theoretical chemistry,

Paragraphs 3 Sentence 1-2,

"Work and Heat," a section of *General Chemistry Supplement* (by Eames), used under a CC BY 4.0 license,

Paragraphs 12 Sentences 1-4 and Sentence 13,

Section 1.2 "Heat as a Mechanism to Transfer Energy," a unit section of the course General Chemistry 2B Honors,

Paragraphs 8-10,

Section 5.4 "Enthalpy of Reaction," a section of the Chemistry Libretexts textmap for *Chemistry: The Central Science*,

Paragraphs 12 Sentences 5-8,

Section 7.2 "Work and Heat," a unit section of the hybrid course CHEM 051 – Fundamentals Of Chemistry I,

Paragraph 11, and

Example 3.2.1.

This chapter contains original content by Leanne Trepanier including the numbering of equations and the answer for question 5.

This chapter contains original content by Geneviève O'Keefe including adding a couple words to questions 1 and 5.

This chapter contains original content by Derek Fraser-Halberg including adding a couple words to questions 1.

This chapter contains original content by Nathan Biniam including the numbering of equations and answers for questions 1 – 4.

3.3 – First Law of Thermodynamics

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, including:

Section 5.3 "Enthalpy",

Paragraphs 1 (Sentences 1-3), 3 (Sentences 2-8), 4, 5, 7, and

Figures 3.3.1 and 3.3.3.

This chapter contains original content by Leanne Trepanier including:

The numbering of equations,

Questions 1, 2, 4 and 5, and

Answers 1-4.

This chapter contains original content by Dr. Brandi West including:

Paragraphs 1 last Sentence,

Paragraph 2,

Paragraph 3 first Sentence,

Change of titles,

Paragraph 6,

Options for questions 2 and 5,

Question 3 and 6, and

Answers for question 5.

3.4 – Enthalpy

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Sections 5.2 "Calorimetry" and 5.3 "Enthalpy," and its exercises,

Paragraphs 1-6, 7 (from Section 5.3) 8-11,

Figure 3.4.1,

Examples 3.4.1, 3.4.2,

"Check your Learning" 3.4.1, 3.4.2,

Questions 1-8, and

Answers 6 and 8.

This chapter contains original content by Leanne Trepanier, Mahdi Zeghal, Nathan Biniam and Derek Fraser-Halberg including the numbering equations, answers and subheadings.

This chapter contains original content by Dr. Brandi West including:

Question 3 and answer.

3.5 – Calorimetry

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Sections 5.1 "Energy Basics,"
Paragraphs 3-7, 9 -11, 13-15,
Examples 3.5.1, 3.5.2,
Figure 3.5.1,
"Check your Learning" 3.5.2,
5.2 "Calorimetry,"
Paragraphs 1 (Sentences 1-4), 17-20, 21 (Sentences 4, 5), 24-27, 29,
Examples 3.5.2 – 3.5.7,
Figures 3.5.6, 3.5.8,
"Check your Learning" 3.5.3 – 3.5.8,
Venkateswaran, R. General Chemistry,
CHM1311 Laboratory | Experiment 2: Enthalpy of Various Reactions, and
Exercises,
Questions 1-13.

This chapter contains original content by Leanne Trepanier and Nathan Biniam including the numbering of equations.

This chapter contains original content by Geneviève O'Keefe including:
Paragraph 1 sentences 5-8,
Paragraph 8 and 12,
Paragraph 15 sentences 2 and 5,
Paragraph 16 sentence 1,
Subtitles,
Paragraph 20 sentences 1-3,
Paragraph 21-22,
Added a sentence in example 3.5.4 and 3.5.5 solution,
Added a paragraph to "Check your learning" 3.5.6 solution,
Added a paragraph to example 3.5.6 solution,
Did the section "In Case You're Interested…. Thermochemistry of Hand warmers"
Did the section "Bomb Calorimetry – Video",
Example 3.5.7 Part (b), and
Answers for questions 5, 7, 9 and 10.

This chapter contains original content by Dr. Brandi West including:
Solution for example 3.5.7.

This chapter contains original content by Mahdi Zeghal including:

Table of Specific Heats of Common Substances at 25°C and 1 bar.

3.6 – Hess' Law

This chapter contains material taken from Sections 5.1 "Energy Basics" and 5.3 "Enthalpy" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Section 5.3 "Enthalpy" and its exercises,

Paragraphs 2-15,

Examples 3.6.1 – 3.6.7,

Figures 3.6.1 – 3.6.5,

"Check your learning" 3.6.1 – 3.6.7, and

Section 5.4 "Enthalpy of Reaction" and "Enthalpy Changes in Reactions" of the Chemistry Libretexts textmap for *Chemistry: The Central Science*,

Paragraph 1.

This chapter contains original content by Dr. Brandi West including:

Added sentence 3 -6 in paragraph 1,

Added sentence 3 under figure 3.6.1, and

Added "Kilo – watts hours" to question 20 Part (f).

This chapter contains original content by Leanne Trepanier including:

Numbering of equations.

This chapter contains original content by Leane Trapier, Nathan Biniam and Dr. Kathy-Sarah Focsaneanu including end of the chapter questions.

This chapter contains original content by Nathan Biniam including the end of the chapter answer (Geneviève O'Keefe did the answer for question 18) and table 3.6.2.

Chapter 3 Key Terms

The definitions for the following key terms were adapted from the Chapter 5 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Bomb calorimeter
Calorie (cal)
Calorimeter
Chemical thermodynamics
Endothermic process
Energy (E)
Enthalpy (H)
Enthalpy change (ΔH)
Exothermic process
Expansion work
First law of thermodynamics
Heat (q)
Heat capacity (C)
Hess's law
Hydrocarbon
Internal energy (U)
Joule (J)
Kinetic energy (E_k)
Potential energy (E_{pot})
Specific heat capacity (c)
Standard enthalpy of combustion ($\Delta H_c°$)
Standard enthalpy of formation ($\Delta H_f°$)
Standard state
State function
Surroundings
System
Temperature (T)
Thermal energy
Thermochemistry
Work (w)

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Calorimetry
Temperature (T)

The definitions for the following key terms were adapted from other open textbook resources of the Open Education Resource (OER) LibreTexts Project:

Closed system, isolated system, and **open system** – from Section 5.2 "The First Law of Thermodynamics" of the Chemistry Libretexts textmap for *Chemistry: The Central Science* (by Brown, LeMay, Busten, Murphy, and Woodward), used under a CC BY-NC-SA 4.0 license, and

Path function – from "State vs. Path Functions," a section of Fundamentals of Thermodynamics (contributed by Billings, Morris, Starr, and Oberoi) of the Chemistry Libretexts supplemental modules on physical and theoretical chemistry, used under a CC BY-NC-SA 3.0 license.

4 – Chemical Equilibrium

4.1 – Introduction to Chemical Equilibrium

This chapter contains material and exercises taken from Section 13.1 "Chemical Equilibria" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter also contains material taken from the following open textbook resources:

Section 13.1 "Chemical Equilibria," a section of *Chemistry* (by Rice University), used under a CC BY 4.0 license, and

Section 15.2 "The Equilibrium Constant Expression," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, including:

Paragraphs 13-15, and Sentence 2 in Paragraph 17,

Equations 4.1.1 and 4.1.2,

Example 4.1.1, and

"Check your learning" 4.1.1.

This chapter includes material taken from 13.1 – Chemical Equilibria, including paragraphs 1-9 and 11, and the "Equilibrium and soft drinks" box.

This chapter includes original content by Dr. Kathy-Sarah Focsaneanu including the first sentence for the answer to question 4 of the end of section 4.1 questions.

This chapter includes original material by Mahdi Zeghal including the sentence after the dash in paragraph 1, paragraphs 10 and 16, the first and last sentence of paragraph 11, the "note" under equation 4.1.2, table 4.1.1, the last 2 sentences of paragraph 17, and the "when should I use a one sided arrow?" box.

This chapter includes original material by Leanne Trepanier and Nathan Biniam including the answer to the end of section 4.1 questions 2 and 4.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, tables and equations.

This chapter includes figures 4.1.1, 4.1.2, 4.1.3, and 4.1.4 taken from 13.1 – Chemical Equilibria.

This chapter includes figure 4.1.5 taken from "The Equilibrium Constant Expression."

4.2 – The Equilibrium Constant & Reaction Quotient

This chapter contains material and exercises taken from Section 13.2 "Equilibrium Constants" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraph 3.

This chapter also contains material taken from Sections 15.2 "The Equilibrium Constant Expression," 15.3 "Relationships Involving Equilibrium Constants," and 15.5 "The Reaction Quotient, Q – Predicting The Direction of Net Change" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, including:

Section 15.2:
Paragraphs 2 and 5-9,
Equations 4.2.1, 4.2.2 and 4.2.3,
Example 4.2.1,
"Check your learning" 4.2.1 and 4.2.2,
Section 15.3:
Paragraphs 10-18,
"Summary" above example 4.2.2,
Equations 4.2.4 and 4.2.5,
Examples 4.2.2, 4.2.3 and 4.2.5,
"Check your learning" 4.2.3 and 4.2.5, and
Section 15.5:
Paragraphs 19-20 and 22-23, and
Equation 4.2.8.

This chapter contains material taken from 13.2 – Equilibrium Constants including:
The bullet points under paragraph 3 and the section of written below equation 4.2.6,
Equations 4.2.6 and 4.2.7,
Examples 4.2.4, 4.2.6, 4.2.7 and 4.2.8, and
"Check your learning" 4.2.4, 4.2.6, 4.2.7 and 4.2.8.

This chapter includes end of section 4.2 questions and its answers taken from Section 13.2 "Equilibrium Constants" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter includes original material by Dr. Kathy-Sarah Focsaneanu including:
The section of writing after the "and" in Sentence 3 of Paragraph 2,
The second sentence of the third bullet point under Paragraph 3,
"Further discussion about activities can be found here.",
The second sentence under the solution for (a) and (d) of example 4.2.1,
The last sentence of Paragraph 15,
The second sentence in Paragraph 16,
The description for K_P and R under equation 4.2.6,
The second sentence in the flagged box under equation 4.2.7, and
The last sentence of Paragraph 21.

This chapter includes original material by Mahdi Zeghal including:

Paragraphs 1, 4, 21 along with its bullet points,

The third bullet point and the last part of the sentence after the comma of bullet point 4 under paragraph 3,

"Note" under paragraph 4,

The last sentence of paragraph 7,

The brackets in paragraph 13,

Under "summary", the brackets in bullet point 1 and 2, as well as all of the third bullet point,

The first sentence of the flagged box under equation 4.2.7,

"Note" under the flagged box, and

The "CHM 1311 Pointers" box.

This chapter includes original material by Leanne Trepanier and Nathan Biniam including answers for end of section 4.2 questions 2, 3, 5, 10, 11, 12, 15 and 17.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures and equations.

This chapter contains figure 4.2.1 taken from "The Reaction Quotient, Q – Predicting The Direction of Net Change".

4.3 – Solving Equilibrium Problems

This chapter contains material taken from Section 13.4 "Equilibrium Calculations" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter also contains material and exercises taken from Section 15.7 "Equilibrium Calculations – Some Illustrative Examples" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license.

Examples 4.3.3 and 4.3.6, and

"Check your learning" 4.3.3 and 4.3.7.

This chapter contains material taken from 13.4 – Equilibrium Calculations including:

Paragraphs 1-9, 10 and the bullet points underneath, 11-12, 15-16 and 18-23,

Examples 4.3.1, 4.3.2, 4.3.4, 4.3.5, 4.3.7 and 4.3.8, and

"Check your learning" 4.3.1, 4.3.2, 4.3.4, 4.3.5, 4.3.6, 4.3.8 and 4.3.9.

This chapter contains paragraph 14 taken from The Equilibrium Constant.

This chapter contains end of section 4.3 questions 1-17 taken from 15.3 – Solving Equilibrium Problems.

This chapter contains original material by Dr. Kathy-Sarah Focsaneanu including the blurb above "calculation of an equilibrium constant".

This chapter contains original material by Mahdi Zeghal including:

Paragraph 13 and 17,

"Note" below the solution of example 4.3.5,

The beginning of the third sentence, before the semi colons, of paragraph 22,

"Note" below paragraph 23,

Flagged box under the "Check your learning" 4.3.8, and

The second sentence, the portion after the dash in the fifth sentence, seventh to ninth sentence and the portion after the dash in the tenth sentence in the solution for example 4.3.8.

This chapter includes original material by Leanne Trepanier and Nathan Biniam including the answers to the end of section 4.3 questions 1-17.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains figure 4.3.2 taken from "Equilibrium Calculations – Some Illustrative Examples".

4.4 – Le Châtelier's Principle

This chapter contains material and exercises taken from the following sections of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, including:

Section 12.7 "Catalysis,"

Paragraph 24, and

Section 13.3 "Shifting Equilibria: Le Châtelier's Principle" and its exercises,

all used under a CC BY 4.0 license.

This chapter also contains material and/or examples taken from the following open textbook resources:

Section 13.3 "Shifting Equilibria: Le Châtelier's Principle," a section of *Chemistry* (by Rice University), used under a CC BY 4.0 license,

Paragraphs 1-16 and 25-32,

"Effect of Change in Pressure on Equilibrium – Video Demonstration",

Table 4.4.1,

Section 14.E "Principles of Chemical Equilibria (Exercises)," exercises of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license,

Section 19.2 "The Concept of Entropy," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license,

Section 19.7 "ΔG° and K as Functions of Temperature," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license,

Paragraphs 20-23,

Equation 4.4.1,

Example 4.4.1,

"Check your learning" 4.4.1, and

Section 95 "Shifting Equilibria: Le Chatelier's Principle," a section of *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license,

The "In case you're interested… equilibria in the garden" box.

This chapter contains end of section 4.4 questions 1-16 and its answers taken from Section 13.3 "Shifting Equilibria: Le Châtelier's Principle" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains original material written by Dr. Kathy-Sarah Focsaneanu including the brackets in the second sentence of paragraph 18.

This chapter includes original material written by Mahdi Zeghal including:

Paragraphs 17-19 and 33,

The bullet points under equation 4.4.1,

First and last sentence of paragraph 23,

"Note" below paragraph 23,

"Note" in paragraph 24,

First 2 sentences in paragraph 25,

Flagged box below paragraph 25, and

Last sentence in the "In case you're interested… equilibria in the garden" box.

This chapter contains original material by Leanne Trepanier and Nathan Biniam including the answers to the end of section 4.4 questions 4, 8, 9, 11, 12, 14, 15, and 16.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, tables, equations and examples.

This chapter contains figures 4.4.1 and 4.4.3 taken from "Shifting Equilibria: Le Châtelier's Principle,".

This chapter contains figure 4.4.2 taken from "ΔG° and K as Functions of Temperature,".

This chapter contains figure 4.4.4 taken from "Shifting Equilibria: Le Chatelier's Principle,".

Chapter 4 Key Terms

The definitions for the following key terms were adapted from the Chapter 13 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Equilibrium
Equilibrium constant (K)
Heterogeneous equilibrium
Homogeneous equilibrium
Le Châtelier's principle
Reaction quotient (Q)
Reversible reaction

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Entropy (S)
Equilibrium constant (K)

The definition for the following key term was adapted from another open textbook resource of the Open Education Resource (OER) LibreTexts Project:

van't Hoff Equation – from Section 19.7 "ΔG° and K as Functions of Temperature," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), used under a CC BY-NC-SA 3.0 license.

5 – Acid/Base Equilibria

5.1 – Acid-Base Definitions & Conjugate Acid-Base Pairs

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 14.1 "Brønsted-Lowry Acids and Bases" and its exercises
Paragraphs 12, 16-18,
Questions 1-7, and
Section 16.1 "Arrhenius Theory: A Brief Review"
Paragraphs 1-11, and
Figure 5.1.1.

This chapter contains original content by Mahdi Zeghal including:
Added sentence 3 in paragraph 18, and
End of the chapter answers 2, 3, 4 and 7.

This chapter contains original content by Leanne Trepanier including:
Answers for questions 1 and 6.

This chapter contains original content by Derek Fraser-Halberg including the labeling of figures and equations, writing the answer for question 5, and helping write question 7.

This chapter contains content by Dr. Kathy-Sarah Focsaneanu including:

Paragraph 6 sentences 1-3,

Figure 5.1.1 subheading,

Paragraph 4 sentences 1-3,

Added “dissociates (break apart)” to paragraph 7 sentence 1,

Added an equation under paragraph 8,

Added “when dissolved in water” to the end of paragraph 9,

Added sentence 1 to paragraph 10,

Added a couple words to sentences 2 and 4 in paragraph 10,

Wrote paragraph 11,

Added a lot to paragraph 12,

Added to the first and last sentence of paragraph 13,

Wrote paragraph 14 with Brandi,

Wrote sentence 1, 2, 3, 5 in paragraph 15,

Added a couple of words to sentence 1 and 4 in paragraph 18,

Added to sentence 1 in paragraph 19, and

Wrote paragraphs 22 and 23.

This chapter contains original content by Geneviève O’Keefe including:

Added a couple words to sentence 4 in paragraph 15.

This chapter contains original content by Dr. Brandi West including:

Wrote paragraph 9,

Added to the first and last sentence of paragraph 13,

Wrote the last sentence in paragraph 14,

Added a couple sentences (1, 2, 3, 5) to paragraph 15,

Wrote paragraphs 16 and 17,

Wrote sentence 1-4 in paragraph 18, and

Wrote paragraph 21.

5.2 – Autoionization of Water & pH/pOH

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Sections 14.1 “Brønsted-Lowry Acids and Bases” and 14.2 “pH and pOH,” and its exercises,

Paragraphs 1-21,

Figures 5.2.1 – 5.2.5,

Examples 5.2.1 – 5.2.5,

“Check your Learning” 5.2.1 – 5.2.5,

Questions 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, and

Answers 4, 6, 8, 10, 12, 14.

This chapter includes original material by Leanne Trepanier, Mahdi Zeghal and Derek Fraser-Halberg including:

The numbering of equations,

Subheadings, and

Leanne Trepanier and Derek Fraser-Halberg wrote end of the chapter questions 1, 2, 3, and 5, as well as answers for questions 1-3.

This chapter contains original content by Mahdi Zeghal including:

Wrote paragraph 8,

Added a couple words to sentence 1 in paragraph 10,

Wrote the paragraph above figure 5.2.3, and

Wrote sentence 2 in paragraph 20.

This chapter contains original content by Geneviève O'Keefe including:

Added a couple words to the solution for example 5.2.2,

Wrote the equations between paragraph 2 and 3, and

Added a couple words to paragraph 21.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Added a couple of words to the first and last sentence in paragraph 1,

Added the options to example 5.2.3,

Added "such as those in Table 5.2.1 below" to paragraph 14, and

Added "solutions (pH > 7)." to the last sentence in paragraph 15.

This chapter contains original content by Dr. Brandi West including:

Wrote paragraph 1,

Wrote answer for "Check your learning" 5.2.1, and

Wrote paragraph 15 with Dr. Kathy-Sarah Focsaneanu.

5.3 – Acid/Base Strength

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 14.3 "Relative Strengths of Acids and Bases" and its exercises,

Paragraphs 1-50,

Figures 5.3.1 – 5.3.9,

"Check your Learning" 5.3.1 – 5.3.9,

Examples 5.3.1 – 5.3.9,

Questions 1-24, and

Answers 1, 2, 6, 9, 11, 12, 14, 15, 17, 19, 21, 23, 24, 25, 27, 28, 30, 31, 32 and 34.

This chapter contains original content by Derek Fraser-Halberg including the numbering of equations and labelling of figures.

This chapter contains original content by Geneviève O'Keefe including:

Paragraph 5, and

Answer for question 16.

This chapter contains original content by Mahdi Zeghal including:

Paragraph 2 sentences 3 and 4,

Paragraph 3 sentence 2,

Subheading for figure 5.3.2,

Paragraph 9,

Most of paragraph 13 including the title “Try it For Yourself – Percent Ionization and $[H_3O^+]_{eq}$ against Initial Acid Concentration”,

Example 5.3.6 solution sentence 3,

Table 5.3.1, and

Added a couple words to sentence 2 for the solution for “Check your learning” 5.3.2.

5.4 – Polyprotic Acids

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 14.5 “Polyprotic Acids” and its exercises,

Paragraphs 1-21,

Example 5.4.1,

Questions 1-5,

“Check your learning” 5.4.1 – 5.4.2, and

An example/exercise taken from “Solutions of Polyprotic Acid/Base Systems, Problem D” of the topic Acid-Base Chemistry,

Example 5.4.2.

This chapter contains original content by Leanne Trepanier including:

The numbering of equations, and

Answers for questions 3 and 5.

This chapter contains original content by Mahdi Zeghal including:

Wrote paragraph 4 and 10, and

Created a table above example 5.4.1.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Added a couple words to paragraph 2,

Added two sentences under paragraph 5,

Made changes to the first and last sentence in paragraph 10,

Made slight changes to the table’s names,

Added a couple words to the second sentence in the answer for “Check your learning” 5.4.1 answer, and

Added an equation to the third ionization.

This chapter contains original content by Geneviève O’Keefe including answers for the first question.

This chapter contains original content by Derek Fraser-Halberg including the numbering of equations and subheading.

This chapter contains original content by Nathan Biniam including the answer for “Check your learning” 5.4.2 and answers for questions 2 and 4.

5.5 – Hydrolysis of Salt Solutions

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 14.4 “Hydrolysis of Salts” and its exercises,

Examples 5.5.1 – 5.5.3,

“Check your learning” 5.5.1 – 5.5.2,

Figure 5.5.2,

Section 12.5 “Strong and Weak Acids and Bases and their Salts,” a section of *Beginning Chemistry*,

Paragraph 2, and

Section 14.4 “Hydrolysis of Salt Solutions,”

Paragraphs

1, 3, 4, 5, 6, 7, and

the first two paragraphs under the title “The Ionization of Hydrated Metal Ions”,

Figure 5.5.3, 5.5.1,

Example 5.5.5, and

“Check your Learning” 5.5.5.

This chapter contains original content by Leanne Trepanier and Derek Fraser-Halberg including the numbering of equations.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Wrote sentence 5 in paragraph 3,

Wrote last sentence in paragraph 15,

Example 5.5.3 sentences 7 and 8,

“Check your learning” 5.5.3,

Wrote first sentence in the section “The Ionization of Hydrated Ions”, and

Added a couple of words to the first sentence in the second paragraph in the section “The Ionization of Hydrated Ions.”

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

Wrote sentence 6 and 7 in paragraph 3.

This chapter contains original content by Geneviève O’Keefe and Nathan Biniam including answers for the questions.

This chapter contains material and exercises taken from the following sections of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD:

Section 15.2 “Lewis Acids and Bases” and its exercises,

Paragraphs 1-21,

Questions 1-16,

Section 15.2 "Lewis Acids and Bases,"

"Check your learning" 5.6.2,

Example 5.6.2, and

Section 16.9 "Lewis Acids and Bases," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications*,

Example 5.6.1, and

"Check your learning" 5.6.1.

This chapter contains original content by Leanne Trepanier including:

The numbering of equations,

Options for question 11, and

Answers for questions 2, 4 and 15 part B.

This chapter contains original content by Derek Fraser-Halberg including:

The numbering of equations,

Options for questions 12 and 13,

Added a couple words to answer 9, and

Wrote the answer for questions 14 and a bit of 15.

This chapter contains original content by Dr. Kathy-Sarah Focsaneanu including:

First paragraph,

Paragraph 6 sentence 1,

Answer for "Check your Learning" 5.6.1, paragraph 1 sentence 1,

Paragraph 6 sentence 2, and

Example 5.6.2 solution sentence 4, 7, 8 and 9.

This chapter contains original content by Geneviève O'Keefe including:

Wrote "Check your learning" 5.6.1 solution,

Added a couple words to paragraph 3 last sentence, and

Answers for question 1, 3, 5, 6, 7, 8, 9 and 13.

Chapter 5 Key Terms

The definitions for the following key terms were adapted from the Chapter 4 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Strong acid	**Strong base**	**Weak acid**	**Weak base**

The definitions for the following key terms were adapted from the Chapter 14 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Acid ionization
Acid ionization constant (K_a)
Acidic
Amphiprotic
Amphoteric
Autoionization
Base ionization
Base ionization constant (K_b)
Basic
Conjugate acid
Conjugate base
Diprotic acid
Diprotic base
Ion-product constant for water (K_W)
Leveling effect of water
Monoprotic acid
Percent ionization
Stepwise ionization
Triprotic acid
pH
pOH

The definitions for the following key terms were adapted from the Chapter 15 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Coordinate covalent bond
Dissociation constant (K_d)
Formation constant (K_f)
Lewis acid
Lewis acid-base adduct
Lewis acid-base chemistry
Lewis base
Ligand

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Amphiprotic
Arrhenius acid
Arrhenius base
Autoionization
Brønsted-Lowry acid
Brønsted-Lowry base
Hydronium ion (H_3O^+)
Ion-product constant for water (K_W)
Neutralization reaction
pH
pOH

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6 – Buffers and Titrations (Ionic Equilibria in Aqueous Systems)

6.1 – Common-Ion Effect

This chapter contains material and exercises taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project, including:

Section 17.1 "Common-Ion Effect in Acid-Base Equilibria," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), used under a CC BY-NC-SA 3.0 license,

Paragraphs 1-2 and 7-9,

Examples 6.1.1 and 6.1.2, and

Section 17.E "Exercises," exercises of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), used under a CC BY-NC-SA 3.0 license, including

end of section questions 1 – 6 and its answers.

This chapter contains material taken from Dr. Kathy Sarah-Focsaneanu including:

The third and fourth sentence of paragraph 2,

The descriptive sentences in the solution of example 6.1.1,

Paragraphs 3-6,

The last sentence of paragraph 7,

Examples 6.1.3 and 6.1.4,

The captions for figures 6.1.1 and 6.1.2,

The blurb above figure 6.1.1,

The first sentence of paragraph 9, and

"Check your learning" 6.1.4.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of examples.

This chapter contains figures 6.1.1 and 6.1.2 taken from "Common-Ion Effect in Acid-Base Equilibria."

6.2 – Buffer Solutions

This chapter contains material taken from Section 14.6 "Buffers" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Points 1 and 2 under "Selection of suitable buffer mixtures,"

Paragraphs 6, 11 and 12,

The "Henderson-Hasselbalch Equation" and "Medicine: Buffer system in Blood" sections, and

"Lawrence Joseph Henderson and Karl Albert Hasselbalch" box.

This chapter also contains material taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project:

Section 17.2 "Buffered Solutions," a section of the Chemistry Libretexts textmap for *Chemistry: The Central Science* (by Brown, LeMay, Busten, Murphy, and Woodward), used under a CC BY-NC-SA 4.0 license,

Paragraphs 13, and

"Introduction to Buffers," a section of Buffers (contributed by Pietri and Land) of the Chemistry Libretexts supplemental modules on physical and theoretical chemistry, used under a CC BY-NC-SA 3.0 license.

This chapter contains material taken from Buffers including:

Paragraphs 1 and 7-9,

Example 6.2.1, and

"Check your learning" 6.2.1.

This chapter contains original material by Dr. Kathy-Sarah Focsaneanu including:

The blurbs under "How Buffers work" and above "Acidic Buffers: aqueous mixtures of HA + A^-",

Paragraphs 2 and 10,

The last sentence of paragraph 5,

(c) in example 6.2.1,

The first sentence in solution (b) in example 6.2.1, and

The first 2 blurbs under "Medicine: the Buffer System in Blood".

This chapter contains original material by Jessica Thomas including paragraphs 3-5, and "Buffering Action Curves".

This chapter contains original material by Geneviève O'Keefe including "note" in example 6.2.1 for solution (a) under point 4.

This chapter contains figures 6.2.1, 6.2.2 and 6.2.3 taken from "Buffers".

This chapter contains figure 6.2.4 taken from "Buffered Solutions".

6.3 – Acid-Base Reactions & Titrations

This chapter contains material taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project:

Section 14.10 "Titration Curves," a section of *ChemPRIME* (by Moore et al.), used under a CC BY-NC-SA 4.0 license,

The "When is a titration finished" box,

Section 17.3 "Acid-Base Titrations," a section of the Chemistry Libretexts textmap for *Chemistry: The Central Science* (by Brown, LeMay, Busten, Murphy, and Woodward), used under a CC BY-NC-SA 4.0 license,

Paragraphs 1, 18-20, 22-31 and 33-46,

Examples 6.3.1 and 6.3.2,

"Check your learning" 6.3.1, 6.3.2 and 6.3.3,

Sections 17.3 "Acid-Base Indicators" and 17.4 "Neutralization Reactions and Titration Curves," sections of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), both used under a CC BY-NC-SA 3.0 license,

Paragraphs 2, 4-17, and

"pH and Food Color," a section of Foods (contributed by Vitz et al.) of the Chemistry Libretexts ancillary materials, used under a CC BY-NC-SA 3.0 license,

Table 6.3.1.

This chapter contains original material written by Dr. Kathy-Sarah Focsaneanu including:

Paragraphs 3 and 21,

Sentences 3-6 in paragraph 12,

The second and third sentence in paragraph 14,

The second sentence in paragraph 18,

The second and third sentence in paragraph 19,

Sentences starting after the ash in sentence 2 to 3 in paragraph 23,

First and last sentence of 24,

The sentence above " Calculating the pH during the Titration",

The "equilibrium arrows" box,

All the BAMA boxes,

The second sentence in paragraph 32,

Paragraph 2 in the solution for example 6.3.2,

"Check your learning" (a) 6.3.2,

The first sentence of paragraph 37, and

The brackets in the first sentence of paragraph 38.

This contains original material written by Jessica Thomas including the first sentence in the "equilibrium arrows" box, and the first sentence in paragraph 32.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of examples, figures and tables.

This chapter contains figure 6.3.1 taken from "pH and Food Color."

This chapter contains figures 6.3.2, 6.3.3 and 6.3.4 taken from "Acid-Base Indicators."

This chapter contains figures 6.3.5, 6.3.6, 6.3.7 and 6.3.8 taken from "Acid-Base Titrations."

6.4 – Equilibria of Slightly Soluble Ionic Compounds

This chapter contains material and exercises taken from Section 15.1 "Precipitation and Dissolution" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

End of chapter 6.4 questions 1-11 and its answers.

This chapter also contains material taken from Section 18.1 "Solubility Product Constant, Ksp" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, including:

Paragraphs 10-12.

"Solubility Rules," a section of Solubility (contributed by Mursa and Busch) of the Chemistry Libretexts supplemental modules on physical and theoretical chemistry, used under a CC BY-NC-SA 3.0 license, including:

Paragraphs 1-3, and

Points made under "Solubility rules".

This chapter contains material taken from 15.1 Precipitation and Dissolution – Chemistry including:

Paragraphs 4-9, 13-16, and 19-26,

Examples 6.4.1, 6.4.2, 6.4.3, 6.4.4, 6.4.5, 6.4.6, 6.4.8 6.4.9, 6.4.10 and 6.4.11,

"Check your learning" 6.4.1, 6.4.2, 6.4.3, 6.4.4, 6.4.5, 6.4.6, 6.4.10, 6.4.11, 6.4.12 and 6.4.13,

Table 6.4.1,

Equation 6.4.1, and

The "Using Barium Sulfate for medical imaging" and "The Role of Precipitation in Wastewater Treatment" boxes.

This chapter contains example 6.4.7 taken from 18.3: Common-Ion Effect in Solubility Equilibria.

This chapter contains "Check your learning" 6.7.8 taken from 17.4: Solubility Equilibria.

This chapter contains original material by Dr. Kathy-Sarah Focsaneanu including:

The first sentence in paragraph 4,

The portion of the sentence after the italicized words in paragraph 5,

Paragraph 17,

Everything under the subtitle "Effect of pH on solubility" including "Check your learning" 6.4.9, and

The first paragraph under the solution of example 6.4.11.

This chapter contains original answers for the end of section 6.4 questions 2, 3 and 6 created by Nathan Biniam and Leanne Trepanier.

This chapter contains original answers for the end of section 6.4 question 10 created by Geneviève O'Keefe.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of examples, figures, tables and equations.

This chapter contains figures 6.4.1, 6.4.3, 6.4.4, and 6.4.5 taken from 15.1 Precipitation and Dissolution – Chemistry.

This chapter contains figure 6.4.2 taken from "Solubility Product Constant, Ksp."

Chapter 6 Key Terms

The definitions for the following key terms were adapted from the Chapter 4 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Analyte
Buret
Endpoint
Equivalence point
Precipitate
Titrant

The definitions for the following key terms were adapted from the Chapter 11 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Saturated
Solubility
Supersaturated

The definitions for the following key terms were adapted from the Chapter 14 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Acid-base indicator
Buffer
Buffer capacity
Colour-change interval
Henderson-Hasselbalch equation
Titration curve

The definitions for the following key terms were adapted from the Chapter 15 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Common ion effect
Molar solubility
Selective precipitation
Solubility product constant (K_{sp})

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Acid-base indicator	**Buffer**	**Buret**
Analyte	**Buffer capacity**	**Supersaturated**

The definitions for the following key terms were adapted from other open textbook resources of the Open Education Resource (OER) LibreTexts Project:

Ion product (*Q*) – from Section 18.1 "Solubility Product Constant, Ksp" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), used under a CC BY-NC-SA 3.0 license, and

Midpoint – from Section 17.3 "Acid-Base Titrations," a section of the Chemistry Libretexts textmap for *Chemistry: The Central Science* (by Brown, LeMay, Busten, Murphy, and Woodward), used under a CC BY-NC-SA 4.0 license.

End of Chapter 6 Questions

This chapter contains translated questions 1-4 and solutions from Dr. Alain St-Amant's past exams, which permission was granted.

7 – Chemical Kinetics

7.1 – Introduction to Reaction Rates

This chapter contains material and exercises taken from Sections 12.1 "Chemical Reaction Rates" and 12.2 "Factors Affecting Reaction Rates," and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

"Chemical Reaction Rates,"
Paragraphs 1, 2 and 6-9,
Equation 7.1.2, and
"Factors Affecting Reaction Rates,"

Paragraphs 10-14,

The "Reaction of Cesium with Water" and "Factors affecting reaction rates – interactive activity" boxes, and

Equation 7.1.1.

This chapter also contains material taken from Section 14.1 "The Rate of a Chemical Reaction" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license.

This chapter contains material taken from 14.2 – Reaction Rates including paragraphs 3-5 and equations 7.1.1.

This chapter contains material taken from 12.2 – Factors Affecting Reaction Rates including paragraph 15.

This chapter contains original material by Mahdi Zeghal including paragraph 1, the first sentence in paragraph 9 and the first sentence of paragraph 12.

This chapter contains end of chapter 7.1 questions 1 and 2, and the answer to question 1 taken from Section 12.2. "Factors Affecting Reaction Rates" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains end of chapter 7.1 questions 3 and 4, and its answers taken from Section 12.1 "Chemical Reaction Rates" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains original answers for the end of chapter 7.1 question 2 created by Nathan Biniam and Leanne Trepanier.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter contains figures 7.1.2 and 7.1.3 taken from "Factors Affecting Reaction Rates,"

This chapter contains figure 7.1.1 taken from 14.2 – Reaction Rates.

7.2 – Measuring & Expressing Reaction Rates

This chapter contains material taken from Section 12.1 "Chemical Reaction Rates" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 14, 16, 19 and 20, and

"Reaction Rates in analysis – Test strips for urinalysis" box.

This chapter also contains material taken from Section 14.2 "Measuring Reaction Rates" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, including:

Paragraphs 1-13, 24 and 25, and

Equation 7.2.1.

This chapter contains original material by Mahdi Zeghal including the last sentence of paragraph 3, paragraph 11, the last sentence of paragraph 13, paragraph 16, 19, 21 and 22.

This chapter contains original material by Geneviève O'Keefe including paragraph 18.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter includes figures 7.2.2 and 7.2.5 taken from "Chemical Reaction Rates".

7.3 – Rate Laws

This chapter contains material and exercises taken from Sections 12.3 "Rate Laws" and 12.4 "Integrated Rate Laws," and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

"Rate Laws",

Paragraphs 1, 2 and 4-8,

Table 7.3.1, and

"Integrated Rate Laws,"

Paragraphs 17-21 and 27, and

Equation 7.3.3.

This chapter also contains material and taken from the following open textbook resources:

Sections 12.3 "Rate Laws" and 12.4 "Integrated Rate Laws", sections of *Chemistry* (by Rice University), used under a CC BY 4.0 license,

Sections 14.3 "Concentration and Rates (Differential Rate Laws)" and 14.4 "The Change of Concentration with Time (Integrated Rate Laws)," sections of the Chemistry Libretexts textmap for *Chemistry: The Central Science* (by Brown, LeMay, Busten, Murphy, and Woodward) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 4.0 license,

This chapter contains content from "Concentration and Rates (Differential Rate Laws)" including:

Paragraphs 10-16,

Example 7.3.2,

Equations 7.3.1, and 7.3.2,

"Check your learning" 7.3.3,

Table 7.3.2

This chapter contains content from "The Change of Concentration with Time (Integrated Rate Laws)," including:

Paragraphs 22-26,

Sections 14.5 "First-Order Reactions" and 14.6 "Second-Order Reactions," sections of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, This chapter contains material from “First-Order Reactions” including:

Paragraphs 28-30 and 32-36,

Example 7.3.5,

“Check your learning” 7.3.6,

This chapter contains material from “Second-Order Reactions,” including:

Paragraphs 37-50,

Equation 7.3.4,

Example 7.3.10,

“Check your learning” 7.3.11,

Table 7.3.3, and

Section 24 “Kinetics,” exercises accompanying the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license.

This chapter includes material taken from 12.3 – Rate Laws including:

Paragraph 2,

Examples 7.3.1, 7.3.3 and 7.3.6,

“Check your learning” 7.3.1, 7.3.4 and 7.3.6.

This chapter includes material taken from 12.4 – Integrated Rate Laws including:

Examples 7.3.7, 7.3.8, 7.3.9 and 7.3.11,

“Check your learning” 7.3.8, 7.3.9, 7.3.10 and 7.3.12, and

Paragraph 51.

This chapter includes material taken from 14.3 – Effect of Concentration on Reaction Rates including:

Example 7.3.4, and

“Check your learning” 7.3.5.

This chapter contains original material by Mahdi Zeghal including the fourth sentence in paragraph 1 to the last one, the first sentence in paragraph 19, the second to last sentence in paragraph 23, and paragraph 31.

This chapter contains original content by Geneviève O’Keefe and Derek Fraser-Halberg including the numbering of figures, tables and equations.

This chapter contains figure 7.3.2, 7.3.3 and 7.3.4 taken from “The Change of Concentration with Time (Integrated Rate Laws).”

This chapter contains figure 7.3.5 taken from “First-Order Reactions.”

This chapter contains figure 7.3.8 taken from “Second-Order Reactions.”

7.4 – Reaction Kinetics: Summary

This chapter contains material taken from Section 14.7 “Reaction Kinetics: A Summary” of the Chemistry

Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, including:

Paragraphs 1-4,

Figure 7.4.1,

Example 7.4.1, and

"Check your learning" 7.4.1.

7.5 – Collision Theory

This chapter contains material and exercises taken from Section 12.5 "Collision Theory" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-6, and

End of chapter 7.5 questions and its answer 1-8.

This chapter contains material taken from 12.5 – Collision Theory including:

Paragraphs 7-15,

Example 7.5.1, and

"Check your learning" 7.5.2.

This chapter contains original answers for the end of chapter 7.5 questions 3 and 5 created by Nathan Biniam and Leanne Trepanier.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains figure 7.5.1 taken from "Collision Theory".

This chapter contains figures 7.5.2, 7.5.3, 7.5.4, and 7.5.5.

7.6 – Transition State Theory

This chapter contains material taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project:

Section 9.7 "Theories of Reaction Rates," a section of the Chemistry Libretexts textmap for *Physical Chemistry for the Biosciences* (by Chang), used under a CC BY-NC-SA 3.0 license,

Paragraphs 1-4 and 6-9,

"Gibbs (Free) Energy," a section of Energies and Potentials (contributed by Doan, Le, and Lower) of the Chemistry Libretexts supplemental modules on physical and theoretical chemistry, used under a CC BY-NC-SA 3.0 license,

The first sentence of paragraph 5, and

"SN2," a section of Substitution Reactions (contributed by Curtis, Mooney, and Banks) of the Chemistry Libretexts supplemental modules on organic chemistry, used under a CC BY-NC-SA 3.0 license.

This chapter contains original material by Jessica Thomas including the last sentence of paragraph 5.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains figure 7.6.1 taken from "Theories of Reaction Rates."

7.7 – Reaction Mechanisms

This chapter contains material taken from Section 12.6 "Reaction Mechanisms" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains exercises taken from Section 14.10 "Reaction Mechanisms" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license.

This chapter contains material taken from 12.6 – Reaction Mechanisms including:

Paragraphs 1-28,

Example 7.7.2,

"Check your learning" 7.7.2.

This chapter contains original material by Jessica Thomas including the last sentence of paragraph 25.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains end of chapter 7.7 questions 1-3 and its answers taken from 14.10 – Reaction Mechanisms.

This chapter contains figures 7.7.1 and 7.7.2 taken from 12.6 – Reaction Mechanisms.

7.8 – Catalysis

This chapter contains material taken from Section 12.7 "Catalysis" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains material taken from 12.7 – Catalysis including:

Paragraphs 1, 3-11,

Example 7.8.1,

"Check your learning" 7.8.1, and

The "Mario J. Molina", "Glucose-6-Phosphate Dehydrogenase Deficiency", "Automobile Catalytic Converters", and "Enzyme Structure and function" boxes.

This chapter contains original content by Mahdi Zeghal including paragraph 2 and all the bullet points directly below it and above paragraph 3.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains figures 7.8.1, 7.8.2, 7.8.3, 7.8.4, 7.8.5, 7.8.6, and 7.8.7 taken from 12.7 – Catalysis.

Chapter 7 Key Terms

The definitions for the following key terms were adapted from the Chapter 12 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Activated complex
Activation energy (E_a)
Arrhenius equation
Average rate of reaction
Bimolecular reaction
Catalyst
Collision theory
Elementary reaction
Heterogeneous catalyst
Homogeneous catalyst
Initial rate of reaction
Instantaneous rate of reaction
Integrated rate law
Intermediate
Method of initial rates
Molecularity
Overall reaction order
Pre-exponential factor (A)
Rate constant (k)
Rate law
Rate of reaction
Rate-determining step
Reaction coordinate diagram
Reaction mechanism
Reaction order
Termolecular reaction
Unimolecular reaction

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Activated complex
Activation energy (E_a)
Catalyst
Half-life of a reaction ($t_{1/2}$)
Heterogeneous catalyst
Intermediate
Method of initial rates
Rate constant (k)

The definition for the following key term was adapted from another open textbook resource of the Open Education Resource (OER) LibreTexts Project:

Transition state theory – from Section 9.7 "Theories of Reaction Rates," a section of the Chemistry Libretexts textmap for *Physical Chemistry for the Biosciences* (by Chang), used under a CC BY-NC-SA 3.0 license.

End of chapter 7 Questions

This chapter contains translated questions 1-4 and solutions from Dr. Alain St-Amant's past exams, which permission was granted.

8 – Atomic Structure (Quantum Theory and Electron Configurations)

8.1 – The Nature of Light

This chapter contains material taken from Section 6.1 "Electromagnetic Energy" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-9 and 11-19,

"Wireless Communication" and "Dorothy Hodgkin" box,

Examples 8.1.1, 8.1.2 and 8.1.3,

"Check your learning" 8.1.1, 8.1.2 and 8.1.3, and

Equation 8.1.1.

This chapter contains exercises taken from the following open textbook resources:

Section 8.1 "Electromagnetic Radiation," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license,

End of chapter 8.1 questions 8 and 9, and

Section 55 "Light," a section of *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license,

End of chapter 8.1 questions 1-7.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter contains original content created by Jessica Thomas including paragraph 10.

This chapter contains figures 8.1.1, 8.1.2, 8.1.3, 8.1.4, 8.1.5, 8.1.6, 8.1.7, 8.1.8, 8.1.9 and 8.1.10 taken from "Electromagnetic Energy."

8.2 – Atomic Spectra

This chapter contains material and exercises taken from Sections 6.1 "Electromagnetic Energy" and 6.2 "The Bohr Model," and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

"Electromagnetic Energy,"

Paragraph 1-6,

Equation 8.2.1, and

"The Bohr Model,"

Paragraphs 7-18,

Equations 8.2.2 and 8.2.3,

Examples 8.2.1 and 8.2.2, and

"Check your learning" 8.2.1 and 8.2.2.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter contains original answers for the end of chapter 8.2 questions 2 and 8-10 created by Nathan Biniam and Leanne Trepanier.

This chapter contains the end of chapter 8.2 questions and its answers taken from the Chapter 6 exercises.

This chapter contains figures 8.2.3 and 8.2.4 taken from "The Bohr Model."

This chapter contains figure 8.2.1 and 8.2.2 taken from "Electromagnetic Energy."

8.3 – Wave-Particle Duality of Matter & Energy

This chapter contains material taken from Section 6.3 "Development of Quantum Theory" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 4-12,

Equation 8.3.3 and 8.3.5,

"Dr. Quantum" link,

Example 8.3.1, and

"Check your learning" 8.3.1.

This chapter also contains material/exercises taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project, including:

"Exercises (Problems)," exercises of an exam of the course CHEM 107B: Physical Chemistry for Life Scientists I (from the University of California Davis), used under a CC BY-NC-SA 3.0 license,

End of chapter 8.3 questions 3 and 4, and its answers,

Section 7.3 "The Wave-Particle Duality of Matter and Energy," a section of the Chemistry Libretexts textmap for *Chemistry – The Molecular Nature of Matter and Change* (by Silberberg), used under a CC BY-NC-SA 3.0 license,

Paragraphs 1-3,

Equations 8.3.1 and 8.3.2,

End of chapter 8.3 questions 1 and 2, and its exercises, and

Section 8.5 "Two Ideas Leading to a New Quantum Mechanics," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), used under a CC BY-NC-SA 3.0 license.

This chapter contains original content created by Jessica Thomas including the third sentence to the last sentence of paragraph 11 and the third sentence to the last sentence of the caption of figure 8.3.3.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter includes figures 8.3.1 and 8.3.3 taken from "Development of Quantum Theory".

This chapter includes figures 8.3.2 taken from 6.3 – Development of Quantum Theory.

8.4 – Quantum Mechanics

This chapter contains material and exercises taken from Section 6.3 "Development of Quantum Theory" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-21, and

Equation 8.4.1.

This chapter contains original content by Dr. Kathy Sarah-Focsaneanu including the content in the brackets of the first sentence in paragraph 11.

This chapter contains original content created by Jessica Thomas including the last sentence of paragraph 11 and the first three sentences of paragraphs 16.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter contains the end of chapter 8.4 questions 1, 3, 5 and 7 and its answers taken from Chapter 6 exercises.

This chapter contains original answers for the end of chapter 8.4 questions 2, 4, 6 and 8 created by Nathan Biniam and Leanne Trepanier.

This chapter contains figures 8.4.1, 8.4.2, 8.4.3, 8.4.4 and 8.4.5 taken from "Development of Quantum Theory."

8.5 – Electron Configuration in Atoms and Characteristics

This chapter contains material and exercises taken from Sections 6.3 "Development of Quantum Theory" and 6.4 "Electronic Structure of Atoms (Electron Configurations)," and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:
"Development of Quantum Theory",
Paragraphs 1 and 2,
Table "Quantum Numbers, Their Properties and Significance",
Examples 8.5.1, 8.5.2 and 8.5.3,
"Check your learning" 8.5.1, 8.5.2 and 8.5.3, and
"Electronic Structure of Atoms (Electron Configurations),"
Paragraph 3-29,
Examples 8.5.4 and 8.5.5, and
"Check your learning" 8.5.4 and 8.5.5.

This chapter also contains exercises taken from Section 52 "Organization of Electrons in Atoms," a section of *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license.

This chapter contains original content by Dr. Kathy Sarah-Focsaneanu including figure 8.5.1, taken from her course content.

This chapter contains original content created by Jessica Thomas including the last four sentences of the caption of figure 8.5.3.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter contains end of chapter 8.5 questions from 1-9 and its answers taken from Section 6.4 "Electronic Structure of Atoms (Electron Configurations)" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains end of chapter 8.5 questions from 10-17 and its answers taken from Section 52 "Organization of Electrons in Atoms" of *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license.

This chapter contains figures 8.5.1, 8.5.2, 8.5.3, 8.5.4 and 8.5.5 taken from Section 6.4 "Electronic Structure of Atoms (Electron Configurations)" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter contains figure 8.5.7 taken from the Chromium page of WebElements, https://www.webelements.com, accessed August 2020.

8.6 – General Atomic Properties

This chapter contains exercises taken from the Chapter 8 Exercises of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter also contains material and/or exercises taken from the following open textbook resources of the Open Education Resource (OER) LibreTexts Project, including:

Section 4.1 "Ions – Losing and Gaining Electrons," a unit section of the course CHE 1305 – Introductory Chemistry (from Lubbock Christian University), used under a CC BY-NC-SA 3.0 license,

Paragraph 1, and

Section 9.6 "Magnetic Properties," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), used under a CC BY-NC-SA 3.0 license,

Paragraphs 2-8,

"Note" under paragraphs 4 and 6,

Examples 8.6.1 and 8.6.2,

"Check your learning" 8.6.1 and 8.6.2.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains end of chapter 8.6 questions 1 and 2, and its answers taken from https://cnx.org/contents/havxkyvS@12.1:M3s_Xl4y@12/Molecular-Orbital-Theory

This chapter contains end of chapter 8.6 questions 3-5, and its answers taken from "Magnetic Properties."

This chapter contains figure 8.6.1 taken from "Ions – Losing and Gaining Electrons."

This chapter contains figures 8.6.2 taken from "Magnetic Properties."

8.7 – Periodic Trends & Variation of Properties

This chapter contains material and exercises taken from Section 6.5 "Periodic Variations in Element Properties" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-22,

Examples 8.7.1 and 8.7.2,

"Check your learning" 8.7.1 and 8.7.2, and

Tables 8.7.1 and 8.7.2.

This chapter also contains material and exercises taken from Section 8.4 "Bond Polarity and Electronegativity" of the Chemistry Libretexts textmap for *Chemistry: The Central Science* (by Brown, LeMay, Busten, Murphy, and Woodward) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 4.0 license, including:

Paragraphs 23-30,

This chapter contains original material by Jessica Thomas including the caption made for figure 8.7.10.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures and tables.

This chapter contains figures 8.7.1, 8.7.2, 8.7.3, 8.7.5, 8.7.6 and 8.7.7 taken from "Periodic Variations in Element Properties."

This chapter contains figures 8.7.8, 8.7.9 and 8.7.10 taken from "Bond Polarity and Electronegativity."

This chapter contains figure 8.7.4 taken from Section 3.4 "Energy quantisation and electron configuration" of the open textbook resource *Siyavula textbooks: Grade 10 Physical Science* (on OpenStax) by the Free High School Science Texts Project, used under a CC BY 3.0 license.

Chapter 8 Key Terms

The definition for the key term "**amplitude**" was adapted from Section 6.1 "Electromagnetic Energy" of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

The definitions for the following key terms were adapted from the Chapter 6 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Angular momentum quantum number (ℓ)
Atomic orbital
Aufbau principle
Blackbody
Bohr's model
Continuous spectrum
Core electron
Covalent radius
***d* orbital**
Degenerate orbitals
Effective nuclear charge (Z_{eff})
Electromagnetic radiation
Electromagnetic spectrum
Electron affinity (EA)
Electron configuration
Excited electronic state
***f* orbital**
Frequency (ν)
Ground electronic state
Heisenberg uncertainty principle
Hertz (Hz)
Hund's rule
Interference pattern
Ionization energy (IE)
Isoelectronic
Line spectrum
Magnetic quantum number (m_ℓ)
Node
Orbital diagram
***p* orbital**
Pauli exclusion principle
Photon
Principal quantum number (n)
Quantization
Quantum mechanics
Quantum number
***s* orbital**
Shell
Spin quantum number (m_s)
Standing wave
Subshell
Valence electrons
Valence shell
Wave
Wave-particle duality
Wavefunction (ψ)
Wavelength (λ)

The definitions for the following key terms were adapted from the Glossary of the open textbook resource *Introductory Chemistry – 1st Canadian Edition* (by Key and Ball), used under a CC BY-NC-SA 4.0 license:

Atomic orbital
Aufbau principle
Continuous spectrum
Effective nuclear charge (Z_{eff})
Electromagnetic spectrum
Line spectrum
Valence electrons
Valence shell

The definitions for the following key terms were adapted from other open textbook resources of the Open Education Resource (OER)

LibreTexts Project:

Diamagnetism, magnetic moment, and **paramagnetism** – from Section 9.6 "Magnetic Properties," a section of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.), used under a CC BY-NC-SA 3.0 license, and

Shielding – from Section 6.17 "Electron Shielding," a section of *Introductory Chemistry (CK-12)*, used under a CC BY-NC 4.0 license.

End of Chapter 8 Questions

This chapter contains translated questions 1-2 and solutions from Dr. Alain St-Amant's past exams, which permission was granted.

9 – Molecular Bonding

9.1 – Atomic Properties of Chemical Bonds

This chapter contains material and exercises taken from Section 7.3 "Lewis Symbols and Structures" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

This chapter also contains material taken from Section 10.1 "Lewis Theory: An Overview" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

9.2 – Ionic Bonding

This chapter contains material and exercises taken from Sections 7.1 "Ionic Bonding" and 7.5 "Strengths of Ionic and Covalent Bonds," and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

This chapter contains material from "Ionic Bonding" including paragraphs 1 through 4 and the first sentence in paragraph 5,

This chapter contains material from "Strengths of Ionic and Covalent Bonds,"including paragraphs 6 to 8, example 9.2.1 and "Check your learning" 9.2.1.

This chapter contains original content by Dr. Kathy Sarah-Focsaneanu including the last sentence in both paragraph 4 and 5.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and equations.

This chapter contains end of chapter 9.2 questions and answers for 1-9 taken from Chapter 7 exercises.

This chapter contains figures 9.2.1 and 9.2.1 taken from "Ionic Bonding."

9.3 – Covalent Bonding

This chapter contains material and exercises taken from Sections 7.2 "Covalent Bonding" and 7.5 "Strengths of Ionic and Covalent Bonds," and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

"Covalent Bonding" including paragraphs 1 to 16, examples 9.3.1, "Check your learning" 9.3.1 and table 9.3.1, and

"Strengths of Ionic and Covalent Bonds," including paragraphs 17-22 and table 9.3.2.

This chapter contains original content by Dr. Kathy Sarah-Focsaneanu including the last sentence in the caption of figure 9.3.1 and the last sentence in paragraph 13.

This chapter contains original content by Mahdi Zeghal including the second sentence in paragraph 15.

This chapter contains original answers for questions 1 and 7 created by Nathan Biniam and Leanne Trepanier.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures, and tables.

This chapter includes figures 9.3.1, 9.3.2, 9.3.3 and 9.3.4 taken from "Covalent Bonding."

9.4 – Depicting Molecules and Ions with Lewis Structures

This chapter contains material and exercises taken from Sections 7.3 "Lewis Symbols and Structures" and 7.4 "Formal Charges and Resonance," and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

"Lewis Symbols and Structures,"

Paragraphs 1-12, 14-25 and all points made under these paragraphs,

Examples 9.4.1, and 9.4.3,

"Check your learning" 9.4.1, 9.4.3,

"Formal Charges and Resonance,"

Paragraphs 25-35, 37-40 and all points made under these paragraphs,

Examples 9.4.4, and 9.4.5 and 9.4.6,

"Check your learning" 9.4.4, and 9.4.5 and 9.4.6, and

Chapter 7 Exercises,

The end of chapter 9.4 question 1-8 and its answers.

This chapter also contains material taken from Section 10.2 "Covalent Bonding: An Introduction" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license.

This chapter contains material from 8.5 – Drawing Lewis Structures seen in example 9.4.2 and "Check your learning" 9.4.2.

This chapter contains original content by Dr. Kathy Sarah-Focsaneanu including the part in brackets in the second sentence of paragraph 23.

This chapter contains original content by Mahdi Zeghal including the 13th paragraph and the last sentence both in paragraph 36 and 40.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains figure 9.4.1 taken from "Lewis Symbols and Structures."

9.5 – VSEPR

This chapter contains material and exercises taken from Section 7.6 "Molecular Structure and Polarity" and its exercises, respectively, of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license, including:

Paragraphs 1-28, and the numbered points under paragraph 15,
Examples 9.5.1, 9.5.2, 9.5.3, 9.5.4, 9.5.5, and 9.5.7,
"Check your learning" 9.5.1, 9.5.2, 9.5.3, 9.5.4, 9.5.5, and 9.5.7, and
"VSEPR" and "Molecular polarity" interactive activity.

This chapter also contains material taken from Section 10.7 "Shapes of Molecules" of the Chemistry Libretexts textmap for *General Chemistry: Principles and Modern Applications* (by Petrucci et al.) as part of the Open Education Resource (OER) LibreTexts Project, used under a CC BY-NC-SA 3.0 license, including:

Example 9.5.6, and
"Check your learning" 9.5.6.

This chapter contains original content by Geneviève O'Keefe and Derek Fraser-Halberg including the numbering of figures.

This chapter contains original content by Derek Fraser-Halberg including the part of the caption in brackets of (a) in figure 9.5.10.

This chapter contains end of 9.5 chapter questions from 1-12 and its answers taken from Chapter 7 exercises.

This chapter contains figure 9.5.7 taken from 10.2 – VSEPR Theory – The Five Basic Shapes.

This chapter contains figures 9.5.1, 9.5.2, 9.5.3, 9.5.4, 9.5.5, 9.5.6, 9.5.8, 9.5.9, 9.5.10, 9.5.11, 9.5.12, 9.5.13, 9.5.14, and 9.5.15 taken from "Molecular Structure and Polarity."

Chapter 9 Key Terms

The definitions for the following key terms were adapted from the Chapter 7 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Axial position
Bond angle
Bond dipole moment
Bond dissociation energy (*BE*)
Bond length
Dipole moment
Double bond
Electron-pair geometry
Electronegativity (EN)
Equatorial position
Expanded octet
Formal charge
Free radical
Lattice energy ($\Delta H_{lattice}$)
Lewis structure
Lewis symbol
Linear
Lone pair
Molecular structure
Octahedral
Octet rule
Polar covalent bond
Polar molecule
Pure covalent bond
Resonance
Resonance forms
Resonance hybrid
Single bond
Tetrahedral
Trigonal bipyramidal
Trigonal planar
Triple bond
Valence shell electron-pair repulsion theory (VSEPR)
Vector

The definitions for the following key terms were adapted from the Chapter 8 Key Terms of the open textbook resource *Chemistry 2e* (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license:

Bond order
Polar covalent bond

End of Chapter 9 Questions

This chapter contains translated questions 1-3 and solutions from Dr. Alain St-Amant past exams, which permission was granted.

Appendices

For appendices not included here, their data/content was retrieved from non-OER sources (e.g. journal, online database) and these were referenced at the end in a "References" section.

Appendix C | Essential Mathematics

This appendix contains material taken from Appendix B "Essential Mathematics" of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license. Modifications/additions to the material were made by Mahdi Zeghal, as indicated below.

This appendix contains original content by Mahdi Zeghal, including replacing the phrase "exponential arithmetic" with "scientific notation" or "exponential notation," the paragraph and example on logarithmic operations with significant figures within the subsection "Significant Figures," the note referring to the section "Significant Figures and Uncertainty" in the introductory chapter which goes into greater detail on significant figures, the first paragraph, first sentence of the second paragraph, and third paragraph and algebraic derivation of the quadratic formula in the subsection "The Solution of Quadratic Equations," and the two graphs in the subsection "Two-Dimensional ($x - y$) Graphing."

Appendix D | Units & Conversion Factors

This appendix contains material taken from Appendix C "Units and Conversion Factors" of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license. This includes Tables D.2 to D.5 and Table D.7.

This appendix also contains material taken from Chapter 3 "Decimal multiples and sub-multiples of SI units" of the brochure The International System of Units (SI) by the *Bureau international des poids et mesures* (BIPM), used under a CC BY 4.0 license. This includes Table D.1.

This appendix also contains original content by Mahdi Zeghal, including the inclusion of the SI unit for each variable at the top of Tables D.2 to D.7, the definition of a pound in ounces, the definition of an atomic mass unit (amu), the definitions of a joule, the table "Units of Temperature," and the definition of an atmosphere (atm) in $N\ m^{-2}$.

This appendix also contains material taken from “Dimensional Analysis” of the open-education resource and course Boundless Chemistry (on Lumen Learning), used under a CC BY 4.0 license. This includes all material under the heading “Dimensional Analysis” (except the second sentence of the first paragraph and the equation visual diagram), which has been rearranged and organized differently in certain paragraphs (in particular, paragraphs two, four, and five.

This appendix also contains material taken from Dr. Kathy-Sarah Focsaneanu’s course notes, include the second sentence and the equation visual diagram under the heading “Dimensional Analysis.”

Appendix E | Formulas & Fundamental Physical Constants

This appendix contains material taken from Dr. Kathy-Sarah Focsaneanu’s course data sheet, including all material under the heading “Key Formulas.”

Appendix F | Water Properties

This appendix contains material taken from Appendix E “Water Properties” of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license. This includes all figures.

This appendix also contains material taken from Dr. Kathy-Sarah Focsaneanu’s course data sheet, including Table F.4.

Appendix G | Standard Enthalpies of Formation for Selected Substances

This appendix contains material taken from Appendix G “Standard Thermodynamic Properties for Selected Substances” of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license. This includes the data for all substances not found from the appendix’s reference.

Appendix J | Formation Constants for Complex Ions

This appendix contains material taken from Appendix G “Formation Constants for Complex Ions” of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

Appendix K | Solubility Rules for Common Ionic Compounds in Water

This appendix contains material taken from Section 4.2 "Classifying Chemical Reactions" of the open textbook resource *Chemistry* (on BC Open Textbooks) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license.

Appendix L | Solubility Products of Common Salts

This appendix contains material taken from Appendix J "Solubility Products" of the open textbook resource Chemistry 2e (on OpenStax) by Flowers, Theopold, Langley, and Robinson, PhD, used under a CC BY 4.0 license. This includes the data for all substances not found from the appendix's reference.

APPENDIX O | SUGGESTED EDITS

As with all publications, there is a chance that small oversights (ex. typo, formatting error, broken link, etc.) may exist in the textbook. If you run into such an issue, please complete the following form to alert the authors of the issue so they can fix it in real time. The link to this form can be found below: https://forms.gle/tw5vjeADk3oaiw459. Thank you kindly for your time.