INTERACTIVE CHEMISTRY

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Wisconsin Chemistry (Moore, Zhou, and Garand)

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This text was compiled on 03/09/2025

TABLE OF CONTENTS

1: Unit One

2: Unit Two

3: Unit Three

4: Unit Four

5: Unit Five

6: Appendix

7: Review Section

Index

Glossary

Detailed Licensing

Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing****.*

Introduction

This online learning system been created specifically to support you in Chemistry 109 at the University of Wisconsin-Madison. It is more than a textbook and includes more than chemistry. We hope that it helps you learn chemistry and learn how to succeed in this and other challenging courses. For a 15-minute overview of what one aspect of chemistry is all about, take a look at this video.

Before proceeding further, make sure you have a course notebook in which you can write about what you are learning. Your notebook can be pencil-and-paper, a tablet, a laptop, or some other device, but it needs to be with you whenever you are studying and learning chemistry and it needs to be easy for you to write and draw in. Writing will help you to learn and to record important information so you can review what your have learned. Writing about what you are learning should become a useful habit in your career.

? Activity 1: How Do You Study?

Think about how you have studied in courses you have taken in the past. For example, you have almost certainly taken high school chemistry. How did you study in that course? In your course notebook, write a few sentences describing your study habits. What did you do each day? Each week? Before each exam? What seemed to work well? What did you not do, but think you should have? (Don't go further until you have written something.)

We asked you to think about how you study because an important goal of this course is that you learn better ways to learn. One of those better ways is to make certain you are engaged and active as you learn. Another is to prepare your own set of notes about the topic you are studying. The activity you just did should be the first entry in your learning notes for this course; we will ask you to refer to it after you have more experience in Chem 109. Many scientists carry with them at all times a notebook in which they write about what they learn from seminar presentations, conversations, and journal articles. Scientists also jot down questions that occur to them—sometimes these become research topics. We strongly encourage you to do the same thing.

Let's begin by building on what you just wrote in your course notebook. We often hear from students that "Chemistry 109 was the course where I learned how to learn." That's great. It means that we helped students learn how to learn more effectively. In today's rapidly changing job market, it's crucial to be able to learn something new every day. Another important goal is that you learn lots of chemistry, because most biological/medical/engineering disciplines are based on solid understanding of chemical principles. We assume that you want to learn chemistry and want to be able to use what you learn in your future endeavors. So how do you do it?

Learning Requires Your Effort

The secret to successful learning is that learning does not just happen: *Learning is something you do to yourself*. Nobody can learn for you or force you to learn. Learning is not just attending class, reading books, viewing videos, or even studying. Learning requires specific activities and repetition of those activities over an extended period.

Neuroscience has revealed a lot about the best ways you can learn. Learning is a biochemical process that enhances signals among neuron cells in your brain. (This four-minute video summarizes how this works: https://www.youtube.com/watch?v=U8Eieult80U.) To learn a new idea you first need to make sense of it (understand it), which means connecting it with things already in your memory. For example, when studying acids and bases try to connect what you are learning with household products you are familiar with such as vinegar and ammonia. The more connections you can make the better you will remember. You can strengthen the connections through recall—the more often you bring a new idea back to mind the easier you can retrieve it later.

When you try to understand something your brain is working hard to establish the right connections among neurons to link the new idea to what you already know. Sometimes this happens quickly—an "Aha!" moment, but it may take several tries with the same new idea before the right connections happen. Either way, understanding requires highly focused attention and active brain work on your part. It cannot be done if you are multitasking or distracted. You have to be actively concentrating on the new idea. (Multitasking while learning will hurt your grades: see this study.)

Remembering also requires your active participation. Memories are not imprinted in your brain—neurons are not permanently linked—so memories must be reconstructed. The more often they are reconstructed the easier the next reconstruction becomes. In neuroscience lingo, a pattern of synaptic activity can produce a long-lasting increase in signal transmission among the neurons involved. Thus, using an idea helps you remember that idea and makes the idea easier to use later. Mental practice is important.

Knowledge Involves More Than Information

Information is available everywhere; you can Google almost anything. But “just the facts” is not enough. Knowledge involves understanding something well enough that you can recognize connections among facts, evaluate information to decide which facts are useful (and which are fake), and think creatively. Knowledge involves those connections among neurons that will fire when you are trying to solve a problem.

Unfortunately, neuroscience has found no method for transferring knowledge from a teacher’s brain to a student’s. A teacher can lead you to information, provide useful insights, and inspire you to do the necessary work, but it is your job to convert that information into knowledge. The information will mostly be symbolic—words, numbers, diagrams, videos—so you will need to know what those symbols mean. New knowledge depends on previous knowledge to which you can make connections. And, once you have made those connections, you need to practice using them as often as possible so you can remember. You may understand everything that you hear in a lecture, but if you don’t practice applying your understanding to new but related situations, you won’t be able to use your understanding (or even remember it) when it really counts: on an exam, in a different course, or in real life situations.

? Activity 2: Section Summary

- Summarize in two sentences (in your course notebook) what you have learned from this section. What is the important take-away?
- Refer to what you wrote earlier about study habits. Based on what you have learned here, write in your course notebook changes you will make in how you will study for this course.

How Will This Course Help Me Learn?

This course has many features designed to help you learn chemistry. It is organized into units, each of which ends with an exam. Within each unit there is a weekly schedule. Within each week there are whole-class meetings where lecture and group work will be done, a discussion section for group work, and a laboratory session. Each of these meetings has a pre-class activity that will make sure you have the background needed for the class session. There are post-exam activities that will ask you to reflect on your study habits and what you have learned. There will be activities during each class period, and there is homework each week. Laboratory work enables you to learn techniques and apply what you have learned in class. All course information is available in a course management system called Canvas. An online system called Piazza allows you to post questions anytime and get responses quickly. Your course instructor will have office hours during which difficult material can be discussed and explained: make use of them!

How Should I Use These Pre-class Materials?

This pre-class learning system is different from a typical textbook. It is online. It is interactive. Sometimes it asks you to discover things for yourself, instead of reading about them. To use it effectively you must participate in all interactive components. For example, so far there have been two “Activities” in blue-shaded boxes. Did you do what these activities asked you to do? There will also be “Exercises” in purple-shaded boxes and opportunities for “Applying Core Ideas” in green shaded boxes. Much of what you need to learn is in these boxes. The boxes will ask you to do something, to answer a question, or to think about ideas. These processes are essential to your learning. *Do not skip them!*

In this course you will encounter many facts and concepts. These are like stones that might be assembled to build a home or even a cathedral. Part of what we hope you will learn is how to select appropriate facts and concepts and build them into larger structures that help you address important unsolved problems. Learning how to select appropriate building stones, fit them together, and add mortar to hold them in place is an important goal—one that we will do our best to help you achieve. We want you to depart this course with beautiful mental structures that will serve you well in the future. Your active participation and intellectual involvement in the pre-class materials and all other aspects of this course is a cornerstone for building toward that goal.

What Does This Mean for Me?

There is no way round the fact that learning is work—very rewarding work, but work nonetheless. You need to make sure that you align your efforts with what is known about brains, information, and knowledge. Here’s how to do that most effectively.

- Assign yourself at least one regular time each day when you will concentrate on learning chemistry without interruptions or distractions.

- Schedule those times so that you can prepare for each class meeting: during classes we will assume that you know what you were assigned to learn and without that prior knowledge you will have a hard time learning more.
- Arrange your schedule so that you get a good night's sleep every night–this really helps!
- Make sure you get plenty of exercise–don't just sit and study.
- Participate actively in group work in whole-class and discussion sections: if you don't understand something, ask; if someone else has a question, practice what you have learned by explaining the idea to them.
- Write in your course notebook about the important concepts during each whole-class and discussion section; fill in gaps in your notes by consulting this online learning system, Piazza, other resources, or your lecturer during office hours.
- If you are not sure you understand a chemistry problem or concept, post a question on Piazza and participate in the online discussion; go to Piazza often to see what others are asking.
- Begin studying for the first exam the first day of the semester: learning requires repeated practice over an extended period, so cramming for an exam doesn't yield long-lasting results.
- At least once a week spend 5-10 minutes thinking about which topics you have mastered and which you need to work on more; exams in this course allow you to select among several questions and you need to be able to recognize which ones you will be able to answer best.
- Constantly test yourself to make sure you can apply what you have learned; believing you know something is not the same as actually knowing it.
- Form or join a study group that meets regularly to work on homework, discuss difficult concepts, and helps each other prepare for exams.

? Activity 3: Study Schedule

- Write a two- or three-sentence summary of this section.
- Set up a weekly study schedule and write it in your course notebook; you will probably need to change this schedule later, but get it written now.

What Will I Learn in Chemistry 109?

When you complete Chemistry 109 you will be able to

1. Describe fundamental chemical concepts and principles. These include structure and properties of atoms, models for bonding and molecular geometry, intermolecular forces, organic molecules and functional groups, biomolecules and polymers, kinetics and reaction mechanisms, equilibria and thermodynamics, acid-base chemistry, and electrochemistry.
2. Invoke models of atoms, molecules, and their interactions to qualitatively explain observed macroscopic phenomena, including the organization of the periodic table, chemical and physical characteristics of organic compounds, the rates of chemical reactions, equilibrium concentrations, and electrical currents generated by electrochemical cells.
3. Apply quantitative chemical models to predict thermodynamics, equilibrium concentrations, rates of reaction, and voltages of electrochemical cells.
4. Design, conduct, and analyze experiments pertaining to chemical concepts included in the course while developing fundamental skills in safe laboratory practices, accurate chemical measurements, and sample isolation and analysis techniques.
5. Demonstrate abilities as reflective, self-directed learners who can assess their work, identify their misconceptions, and critically evaluate information from a variety of sources.
6. Articulate the rationale behind experimental observations and the answers to conceptual problems using clear, concise, and scientifically appropriate language.
7. Solve a wide variety of integrative chemistry problems that connect several concepts and their applications to real world situations.

? Activity 4: Goals

Think about how your personal goals mesh with these course goals. If you are aiming for a certain major or a particular career, how will the outcomes listed above help you achieve your career goals? Write a few sentences about this in your course notebook

CHAPTER OVERVIEW

1: Unit One

1.1: Day 1- Chemistry, Matter, Energy, Models

1

Day 1: Chemistry, Matter, Energy, Models

Welcome to Chemistry 109!

If you have not yet worked through the Introduction, please do so before beginning this section.

Today's work begins with a review of important fundamentals of chemistry. We expect that you are familiar with these ideas and are ready to use them to help you learn more chemistry. Then we introduce fundamental ideas about energy and matter. These ideas will recur throughout this course and we expect they will serve you well during your entire career

D1.1 Substances and Chemical Reactions

A fundamental aspect of chemistry is that substances change into other substances. *A process in which one or more substances changes into one or more different substances* is called a **chemical reaction**. This course aims to enhance your understanding of substances and chemical reactions. For a specific substance, what properties can you expect? Given one or two substances, is a reaction likely? When a reaction occurs, what new substances are formed? How is energy related to chemical reactions? Can we make new substances that have properties we want (such as alleviating disease)? Ability to answer such questions is valuable in a broad range of fields, from physics to pharmacy.

Activity 1: Chemical Reactions

Here are videos of some chemical reactions. Watch each reaction carefully and write down your observations.

Reaction of copper with air and of copper oxide with hydrogen:

https://mediaspace.wisc.edu/id/1_ly43nvus

Reaction of lead nitrate aqueous solution with potassium iodide solution:

https://mediaspace.wisc.edu/id/1_init9r1n

Reactions of Li, Na, and K with air and of Li, Na, K, Rb, and Cs with water:

https://mediaspace.wisc.edu/id/1_k9nbvl8a

For each chemical reaction, write a few sentences in your class notebook describing the reaction: How do you know that a reaction occurred? What are similarities and differences among the reactions you observed? How do temperature and other variables affect the reactions?

Saying that one substance changes into another is not very precise without a definition of what a substance is. In chemistry, a **substance** is *matter that, when purified, has specific, characteristic properties and composition*. For example, all samples of pure copper have an orange, lustrous surface; all conduct electricity equally well; all react with dry air to produce a black substance; and all consist solely of copper. The American Chemical Society currently lists more than 160 million chemical substances in a data base. New substances are being synthesized every day.

Because there are so many chemical substances, it is useful to develop categories and classifications to help guide our thinking. The most important is that chemical substances are composed of only a few chemical elements (118 of which have been discovered so far). A **chemical element** is *a substance that cannot be changed by chemical reaction into two or more different substances.* Elements combine to form **chemical compounds**, *substances that can be decomposed by chemical reactions into two or more new substances.* If you know something about the chemical elements and how they combine to form chemical compounds, you can predict properties of a wide range of substances and often predict which substances are likely to react to form what products.

Another useful classification is to divide the elements into metals and nonmetals. Metals conduct electricity as both solids and liquids, have lustrous surfaces when pure, can be pounded into different shapes and drawn into wires, and conduct heat well. Nonmetals have very small electrical conductivity and have a broad range of other properties. Six elements, the metalloids, have properties intermediate between metals and nonmetals.

Chemical reactions and the classifications of substances discussed so far are based on what are called macroscopic observations. **Macroscopic** refers to *things large enough to be seen and manipulated in a laboratory* (or anywhere else). Enhancing your understanding of the macroscopic world is a goal of this course.

D1.2 Atoms, Molecules, and Ions

A different fundamental aspect of chemistry is that we can better understand elements, compounds, and reactions if we build models based on tiny particles that are constantly in motion: atoms and molecules.

An **atom** is *the tiniest particle of an element that has the chemical properties of that element*. Atoms are extremely small, with sizes on the order of 100 pm to 350 pm (1 pm = 10^{-12} m). The smallest thing discernible with the most powerful optical microscope is more than 1000 times bigger than an atom. A **molecule** is *two or more atoms connected by chemical bonds*. **Atomic scale** or **sub-microscopic** scale refers to *things about the same size as atoms and molecules*. Chemists build atomic-scale models to interpret and predict macroscopic phenomena. For example, many substances consist of molecules; the properties of these molecular substances can be predicted if we know which atoms make up their molecules and how those atoms are arranged.

Atoms contain three kinds of particles: **protons**, **neutrons**, and **electrons**. Atoms are identified by the *number of protons in the nucleus*, the **atomic number**. Protons are positively charged. Neutrons have no electric charge. Electrons have negative charge with the same magnitude as a proton's positive charge. Protons and neutrons have much greater mass than electrons and are found in the **nucleus**, *a very small volume in the center of an atom that contains most of the atom's mass*. Electrons, which constitute less than 1/1000 the mass of an atom occupy 99.9999999999999% of the space the atom occupies. When a chemical reaction occurs, atoms remain unchanged, except that a few electrons in the outer part of one atom may transfer to the outer part of another atom. Before and after any chemical reaction the same number of atoms of each type is present; this is known as the law of conservation of matter. When copper metal reacted with oxygen from air to form copper oxide in the first video in Activity 1, the copper oxide included all the copper atoms that originally were in the copper that reacted. When hydrogen reacted with the copper oxide those copper atoms remained on the surface as copper metal.

Ions can form from atoms or molecules. An **ion** is *an atom or molecule that has gained or lost one or more electrons and therefore has a negative or positive electric charge*. For example, when copper reacts with oxygen, the product consists of copper(II) ions and oxide ions. In a copper(II) ion a Cu atom has lost two electrons to form an ion with two units of excess positive charge, Cu^{2+}; in an oxide ion an O atom has gained two electrons to form an ion with two units of excess negative charge, O^{2-}. When a molecule gains or loses electrons, polyatomic ions form: the molecule NO_2 forms both a positive ion, NO_2^+ and a negative ion, NO_2^-, by loss and gain of one electron.

D1.3 Chemical Symbols, Formulas, and Equations

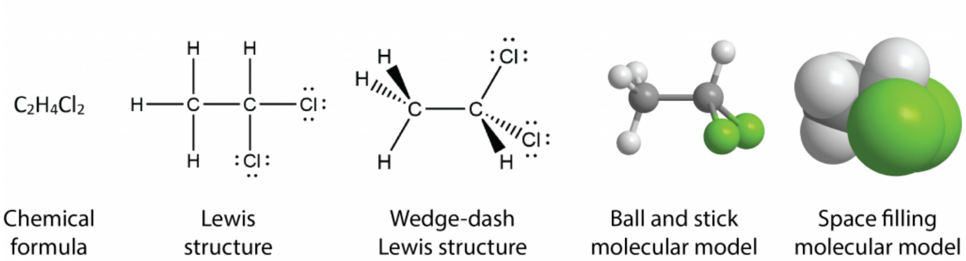
It is convenient to deal with macroscopic properties and atomic-scale models by defining symbols to represent elements, compounds, atoms, molecules, and structures. For example, the symbol Li can represent the element lithium or it can represent a lithium atom. When Li is used to represent the element, it should bring to mind various properties: Li is a metal that can be cut with a knife; Li reacts fairly quickly with air; Li reacts vigorously with water. When Li is used to represent a lithium atom, we can use numbers to indicate how many Li atoms are present. For example, 2 Li represents two lithium atoms. In Li_2O, the formula for one substance that forms when lithium reacts with oxygen, the subscript "2" indicates that there are two Li atoms for every one O atom. Li_2O also represents the macroscopic substance lithium oxide, which has specific properties including high melting point (1438 °C) and high solubility in water.

Symbols can also represent chemical reactions. When lithium reacts with water the chemical equation is

$$2\,Li(s) + 2\,H_2O(l) \rightarrow H_2(g) + 2\,LiOH(aq)$$

The letters in parentheses (s, *l*, g, and aq) indicate that lithium, water, hydrogen, and lithium hydroxide are solid, liquid, gas, and an aqueous solution. The chemical symbols and formulas indicate that lithium and water are reactants and hydrogen and lithium hydroxide solution are products. The coefficients indicate how much of each reactant reacts away and how much of each product forms. The quantities can be expressed on the atomic scale as two lithium atoms reacting with two water molecules to give one hydrogen molecule and two lithium ions and two hydroxide ions in solution. (Lithium hydroxide consists of lithium ions, each with one unit of positive charge, and hydroxide ions, each with one unit of negative charge.) The quantities can be scaled up by a factor of $6.02214076 \times 10^{23}$ (Avogadro's number) and the equation says that two moles of solid lithium reacts with 2 moles of liquid water to give one mole of gaseous hydrogen and two moles of lithium hydroxide dissolved in water.

For molecules, symbolism can indicate which atoms are bonded to which other atoms, what types of bonds are present, and how the atoms are arranged in three-dimensional space. These structures illustrate some of the possibilities:



The chemical formula tells only the number of each kind of atom in the molecule. The Lewis structure indicates which atoms are bonded to which. The wedge-dash structure indicates that the molecule is three-dimensional, which is shown more clearly in the ball-and-stick model. (To see and manipulate a three-dimensional ball-and-stick model, click here.) Finally, in the space-filling model the sizes of all atoms and the molecule as a whole are shown; it is clear that a chlorine atom is bigger than a carbon atom, which is bigger than a hydrogen atom. The last two models are more pictorial than symbolic, but they are still representations of something we cannot see. None of these representations is the molecule itself; all provide useful information about its properties.

Chemists use representations such as these all the time and move effortlessly from one to the other as they think about molecules. Some imagination and much experience using these symbolic representations will enable you to make predictions about properties of substances and chemical reactions.

D1.4 The Periodic Table

As you saw in the videos in Activity 1, the elements Li, Na, K, Rb, and Cs have similar properties and react with air and water in similar ways. In addition, all these elements react with fluorine, chlorine, bromine, and iodine to form similar compounds: LiF, NaF, KF, RbF, CsF, LiCl, NaCl etc. (These compounds are referred to collectively as “salts” because their properties are similar to those of table salt, NaCl.) The reaction of Na(s) with Cl_2(g) to form NaCl(s) is shown in this video.

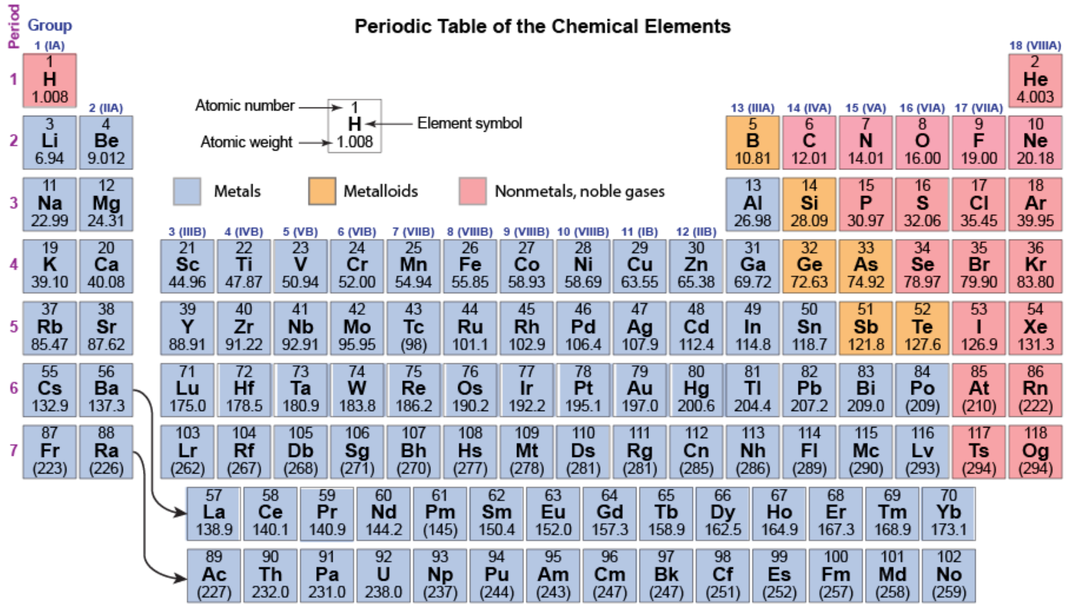
https://mediaspace.wisc.edu/id/1_zygntgnp

The elements Li, Na, K, Rb, and Cs are called **alkali metals**. *The elements F, Cl, Br, and I* are called **halogens.** (“Halogen” comes from Greek *hals*, *halo*—”salt”.) All halogens consist of diatomic molecules, such as Cl_2. Another group of elements, Be, Mg, Ca, Sr, and Ba also have similar physical properties, react with air and water (but more slowly than alkali metals), and react with halogens to form compounds with formulas like BeF_2, $BeCl_2$, $MgCl_2$, etc. *Be, Mg, Ca, Sr, and Ba* are known as **alkaline earth metals** or alkaline earths. Just before the turn of the 20th century, chemists discovered another group of similar elements: He, Ne, Ar, Kr, and Xe. All are gases that undergo almost no chemical reactions, so *He, Ne, Ar, Kr, and Xe* are called **noble gases**. (One meaning of “noble” is “unreactive”.)

Here is a list of the first twenty elements in order of increasing atomic number:

H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca

The noble gases, alkali metals, alkaline earth metals, and halogens are color coded. Notice that the colors repeat periodically—every eight elements. About 150 years ago, Russian chemist Dmitri Mendeleev recognized this periodicity and created a table with horizontal rows of elements in atomic-weight order and groups of similar elements in vertical columns. Since Mendeleev’s time many more elements have been discovered: there are 118 in the modern periodic table below. But the idea of rows (periods) across which properties of elements vary and columns (groups) of elements with similar properties remains.



Periodic Table of the Chemical Elements

Period \ Group	1 (IA)	2 (IIA)	3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8 (VIIIB)	9 (VIIIB)	10 (VIIIB)	11 (IB)	12 (IIB)	13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)	18 (VIIIA)
1	1 **H** 1.008																	2 **He** 4.003
2	3 **Li** 6.94	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
3	11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.63	33 **As** 74.92	34 **Se** 78.97	35 **Br** 79.90	36 **Kr** 83.80
5	37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
6	55 **Cs** 132.9	56 **Ba** 137.3	71 **Lu** 175.0	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	103 **Lr** (262)	104 **Rf** (267)	105 **Db** (268)	106 **Sg** (271)	107 **Bh** (270)	108 **Hs** (277)	109 **Mt** (278)	110 **Ds** (281)	111 **Rg** (281)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (289)	115 **Mc** (290)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)
			57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.1		
			89 **Ac** (227)	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)		

Atomic number → 1
H ← Element symbol
Atomic weight → 1.008

🟦 Metals 🟧 Metalloids 🟥 Nonmetals, noble gases

Each group (column) is identified by two numbers. The alkali-metal group is group 1 or IA; the alkaline-earth group is group 2 or IIA; the halogen group is group 17 or VIIA; and the noble-gas group is group 18 or VIIIA. The first number is designated by the International Union of Pure and Applied Chemistry; the second is more commonly used in the United States.

Down the left side of the table, the periods (rows) are numbered from 1 to 7. The first period contains only two elements; the second and third periods contain eight elements each; the fourth and fifth periods each contain 18 elements; and the sixth and seventh periods contain 32 elements. (Some elements in these latter two periods have been moved to the bottom of the table so it can fit on a printed page and be big enough to read. The curved arrows show where these elements should fit.)

The table is color coded to indicate whether an element is a metal, a metalloid, or a nonmetal. **Metals** *conduct electricity, have lustrous surfaces when pure, combine with other metals to form alloys, and are malleable and ductile*. The electrical conductivity of metals increases as temperature decreases. **Non-metals** *are electrical insulators, usually are brittle as solids but may be liquids or gases at room temperature, and combine with other nonmetals by forming covalent bonds*. Metalloids are intermediate between metals and nonmetals, **Metalloids** *have lower electrical conductivity than metals but their conductivity increases as temperature increases.*

Most elements are metals (the large blue-gray area); only 20 elements are nonmetals and six are metalloids. Notice that some groups, such as groups 14 (IVA) and 15 (VA) contain nonmetals, metalloids, and metals. This means that properties (electrical conductivity, for example) of some elements in these groups are significantly different from properties of other elements in the group; that is, in some groups elements are not as similar to each other as in the alkali-metal group. In all groups, however, the formulas of compounds are similar. For example, in group 14 (IVA), all elements form oxides with formulas XO_2: CO_2, SiO_2, GeO_2, SnO_2, and PbO_2. (Fl, flerovium, has been formed in quantities of only a few atoms in a particle accelerator, so the formula of its oxide has not been determined experimentally.)

Similarity of chemical formulas for elements in the same periodic group involves **valence**, the *combining power of an atom*. For example, sodium has a valence of 1 and so does chlorine; therefore, sodium and chlorine form the compound NaCl in which sodium atoms and chlorine atoms combine in a 1:1 ratio. Oxygen has a valence of 2; therefore the formula for sodium oxide is Na_2O—it takes two valence 1 sodium atoms to satisfy oxygen's valence of 2. From this you should be able to predict that the valence of C (or Si, Ge, Sn, or Pb) is 4 because the formula of carbon dioxide is CO_2.

D1.5 Matter, Energy, Models

In this course you will be asked to examine data and draw conclusions, to explain phenomena by applying basic principles, and to build models from which you can predict physical and chemical properties. Two important and interconnected ideas are fundamental:

- The spatial arrangement of atomic-level particles (structure) can predict macroscopic properties and chemical reactivity;
- Energies of atomic-level particles can be used to explain atomic-level structures and macroscopic energy changes.

Atomic-scale particles adopt structures with minimum energy, unless energy is transferred to them from an external source. Therefore it is useful to be able to calculate quantitatively or predict qualitatively whether one situation has higher or lower energy than another. Chemistry often involves electrically-charged atomic-scale particles, such as protons, electrons, or ions. The potential energy of two point electric charges (charges that occupy a single geometric point) can be calculated using an equation derived from Coulomb's law:

$$E_{\text{p}} = k_e \frac{Q_1 Q_2}{r}$$

In this equation k_{e} is a proportionality constant equal to 8.99×10^9 J m C^{-2},Q_1 and Q_2 are electric charge values, and r is the distance between the charges. Thus, the magnitude of the potential energy of two charged particles is proportional to the size of each charge and is inversely proportional to the distance between the charges. The energy is positive if the charges of the two particles have the same sign (both positive or both negative). The energy is negative if the charges are opposite—opposite charges attract and lower potential energy is the result. The direct proportionality to electric charge and inverse proportionality to distance enable qualitative predictions: Larger opposite charges closer together result in lower energy and hence greater stability.

Activity 2: Potential Energy and Distance between Ions

Activity 3: Evaluating and Modifying a Model

At the atomic level, particles are most stable when energy is minimum. This happens for a sodium ion and a chloride ion when the ions are 276 pm apart (lowest point in the blue curve in Activity 3). Curves like this can be used to describe attractive forces between atoms, molecules, or ions. Particles attract each other so their potential energy decreases as they get closer, but eventually there are repulsive forces that prevent them from being in the same place at the same time. The balance of these forces results in a curve with a minimum at some distance of separation. The depth of the minimum indicates how strongly the particles attract.

D 1.6 Structure, Energy, and States of Matter

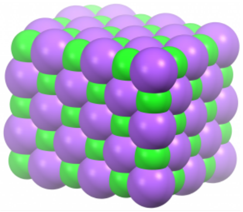
The idea that atomic-scale particles attract one another and adopt a low-energy arrangement unless energy is supplied from an external source can be applied to changes from solid to liquid to gas.

The **kinetic-molecular theory** states that *atomic-level particles are in constant, random motion*. How fast the particles move depends on temperature. As temperature increases the average speed of the particles increases; hence their kinetic energies also increase. The average of the energies of the particles is proportional to the absolute temperature (in units of kelvins). Near 0 K the particles have very little kinetic energy and adopt a structure with minimum potential energy.

Activity 4: Atomic-level View of Solids, Liquids, and Gases

Temperature and motion of particles affect whether a substance is a solid, liquid, or gas. View this simulation of the behavior of noble gas atoms in solids, liquids, and gases. Choose "States", then choose "Neon" (upper right corner). Click on each of the boxes: "Solid", "Liquid", and "Gas" (or use "Heat" (below the container of molecules) to raise the temperature).

Based on the simulation, write in your notebook a description of the differences in position and movement of the molecules in solids, liquids, and gases.



A tiny portion of solid sodium chloride. Each green sphere represents a sodium ion. Each purple sphere represents a chloride ion.

Let's apply these ideas to sodium chloride, which is a solid at low temperature. Sodium ions and chloride ions are packed closely together in a regular pattern, as seen in the diagram at the right. This arrangement minimizes the potential energy by bringing oppositely charged particles closer together. A little above 0 K the ions are in motion: each vibrates a bit around its specific location, but no ion has sufficient kinetic energy to overcome the Coulomb's-law attractions that hold it in place. Thus, no ion exchanges place with any other ion. This atomic-scale structure is consistent with macroscopic properties: a solid is rigid because the regular pattern of its structure does not change.

As temperature increases the average kinetic energy of the ions increases: the ions move more, vibrating farther from their average positions. On the macroscopic scale, the solid expands because each vibrating ion pushes against neighboring ions. Pushing neighboring ions away enlarges the space occupied by each ion and the crystal's volume increases. Eventually, the vibrations are large enough that ions can move relative to each other and the regular arrangement becomes much more random: the solid melts. Ions are still close together but they can move past one another, so the liquid has no specific shape. The liquid is fluid and can be poured. For sodium chloride, because the potential energy is lowered a lot by Coulomb's-Law attractions among the ions, the temperature required for melting is high: 1074 K (801 °C).

Further increase in temperature makes the motion of the atoms faster and at 1738 K (1465 °C) the liquid sodium chloride boils, forming a gas. The sodium ions and chloride ions move much further apart, which means they bump into each other much less often. The gas is fluid but expands to fill whatever volume is available and has much lower density than the liquid or solid.

D1.7 What's Ahead?

Throughout this course you will build on the fundamental ideas of chemistry developed in this section. You will begin by studying the properties of atoms and how those properties vary depending on position in the periodic table. This will lead to how atoms lose or gain electrons to form ions and how atoms share electrons to form molecules, both of which are related to valence. Based on the properties of atomic-scale atoms and ions, you will be able to understand properties of metals and ionic compounds. The number and variety of molecules is very large so a lot of your study will involve how atoms bond to each other to form molecules and how molecular structures affect properties and reactivity of molecular substances. Then we will consider how fast chemical reactions go and to what extent products of those reactions can be formed from a given set of reactants. These ideas will then be applied to two important classes of reactions: acid-base reactions and oxidation-reduction reactions.

Bon voyage!

Activity 5: Wrap-up

In your notebook, write a summary of the important ideas in this day's work. Write your summary so that you can refer back to it, should you need to refresh your memory, and so that you can use it to review for exams.

Day 1 Pre-Class Podia Problem: Describe Chemistry

In most pre-class assignments we will include a Podia question that may require numerical, text, and/or image-based responses. Each pre-class Podia question is based on the pre-class material and working through the pre-class material will help you formulate your response. Consider the problem and write down/draw out your solution in your class notebook.

Two days before the next whole-class session, the pre-class Podia question will become visible in Podia (within the "Whole Class" section), where you can submit your solution. [For example, the Podia question in a Wednesday pre-class assignment will open by Monday evening.]

When you come to the next whole-class session, the class leader will choose one or more student-submitted solutions and explain why they are (or are not) effective scientific statements. These questions are designed to hone your skills so that you can solve mastery problems you will encounter on exams.

Click on the relevant open Podia question and submit your answer there. Your submission to instructor-opened questions will be anonymous to your classmates, and you can only view your own submission. (If you make a separate post, you will not be anonymous.)

You may find Podia sign-in instructions here.

Your first pre-class Podia question is designed to help you learn how Podia works. **Write a short sentence about chemistry. Accompany your sentence with an image (sketched by you) that you think is a good example of chemistry. See whether your class leader selects your submission as a good one to show (anonymously) to the class.**

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

1.2: Day 2- Atomic Spectra and Atomic Orbitals

s2

Day 2: Atomic Spectra and Atomic Orbitals

If you have not yet worked through the Introduction and Day 1, please do so before beginning this section.

D2.1 Electromagnetic Radiation

The periodic table (Section D1.4) summarizes much information about chemical elements. That information can be better understood by assuming that both physical and chemical properties of the different elements depend on differences in the underlying structures of their atoms. An important way to learn about the structures of atoms is to study how energy, in the form of electromagnetic radiation, interacts with matter.

Activity 1: Preparation—Atomic Spectra and Atomic Structure

In your course notebook, make a heading for Atomic Spectra and Atomic Structure. After the heading write down what you remember about atomic spectra from courses you have already taken. Also write what you recall about the relation of spectra to atomic structure—how electrons are arranged in atoms. If there is anything you remember being puzzled about, write that down as well. We will ask you to refer back to what you have written when you complete this section.

Electromagnetic radiation consists of *oscillating, perpendicular electric and magnetic fields that travel through space and can transfer energy*. The oscillating fields (waves) are characterized by wavelength (λ, measured in meters, m) and frequency ($\boldsymbol{\nu}$, measured in hertz, Hz or s^{-1}). In a vacuum, electromagnetic radiation travels at the speed of light (c):

$$\lambda\nu = c = 2.998 \ \times \ 10^8 \ \frac{m}{s}$$

Electromagnetic radiation occurs in *small, indivisible quantities of energy* called **photons**. The energy of a photon, E_{photon}, can be determined from either its frequency or its wavelength:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

In this equation h represents Planck's constant; $h = 6.626 \times 10^{-34}$ J s.

Your calculation in Exercise 1 showed that the energy of a single photon is quite small. Most interactions of electromagnetic radiation and matter involve lots of photons and lots of atoms. The total energy transferred is proportional to the number of photons, N. If all photons have the same frequency,

$$E_{\text{electromagnetic radiation}} = N \times E_{\text{photon}} = Nh\nu = N\frac{hc}{\lambda}$$

Notice that electromagnetic radiation has been described as involving wave motion and also as a number of particles (photons). Originally, scientists thought that electromagnetic radiation could be described entirely by a wave model, but that model was unable to predict all experimental observations. Consequently, both wave and particle models need to be combined for full understanding of electromagnetic radiation.

Figure 1 shows the enormous range of all types of electromagnetic radiation: Frequencies of 10^5 Hz to 10^{20} Hz, that is, wavelengths of 10^3 m (km) to 10^{-12} m (pm) have been observed. What we can see, visible light, is only a tiny portion (380-740 nm) of that range.

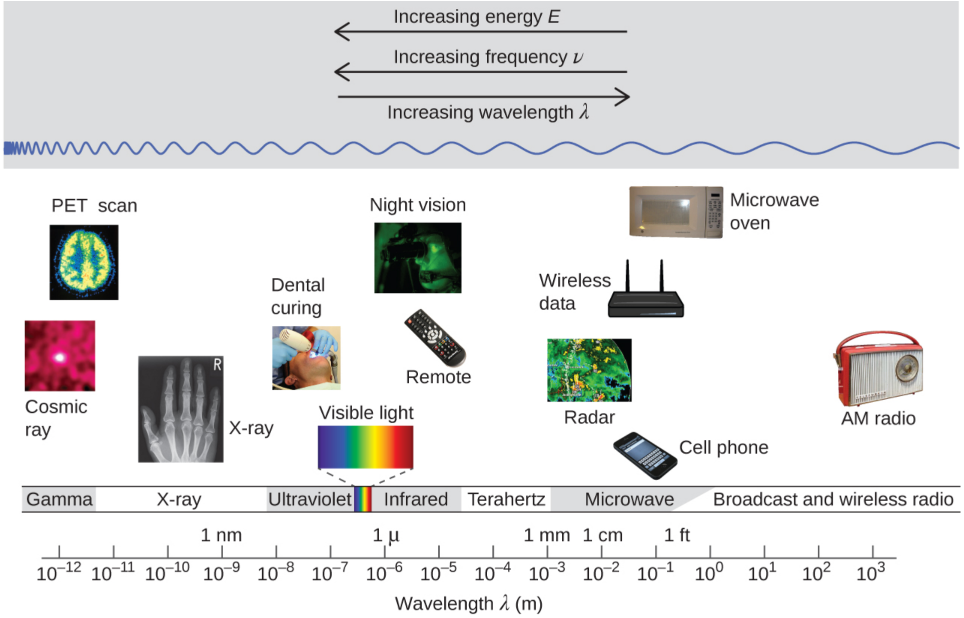


Figure 1. *Portions of the electromagnetic spectrum are shown. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credits: "Cosmic ray": NASA; "PET scan": NIH; "X-ray": Dr. Jochen Lengerke; "Dental curing": Department of the Navy; "Night vision": Department of the Army; "Remote": Emilian Robert Vicol; "Cell phone": Brett Jordan; "Microwave oven": Billy Mabray; "Ultrasound": Jane Whitney; "AM radio": Dave Clausen)*

Different parts of the electromagnetic spectrum typically use different units: Low-energy photons, such as microwaves and radio waves, are specified in frequencies (MHz or GHz); mid-energy photons, such as infrared and visible light, are specified in wavelengths (µm, nm, pm, or Å); high-energy photons, such as x-rays and gamma-rays, are specified in energies (keV or MeV).

Our eyes detect visible-range photons, allowing us to see the world around us. But scientific instruments allow us to "see" lots more by detecting photons over a much wider range of energies. For example, studies of atomic spectra, experiments involving interaction of gaseous matter with visible, ultraviolet, and infrared light, led to better understanding of the structure of atoms.

D2.2 Atomic Spectra

Heating a gaseous element at low pressure or passing an electric current through the gas imparts additional energy into the atoms. These higher energy atoms can then release the additional energy by emitting photons. For instance, the colors of "neon" signs are produced by passing electric current through low-pressure gases. Interestingly, the photons emitted by the higher-energy atoms have only a few specific energies, thereby producing a **line spectrum** consisting of *very sharp peaks (lines) at a few specific frequencies*. Line spectra were intriguing because there was no reason to expect that some frequencies would be preferred over others.

Each element displays its own characteristic set of lines. For example, when electricity passes through a tube containing H_2 gas at low pressure, the H_2 molecules are broken apart into separate H atoms and the H atoms emit a purple color. Passing the purple light through a prism produces the uppermost line spectrum shown in Figure 2: the purple color consists of four discrete visible wavelengths: 656.4 nm, 486.2 nm, 434.1 nm, and 410.2 nm.

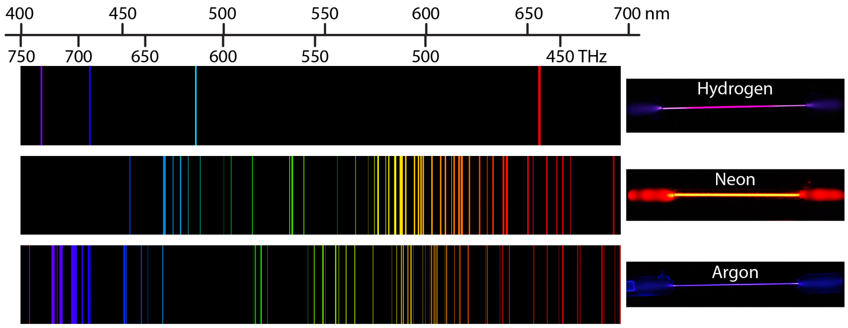


***Figure 2**. The line spectra of excited hydrogen, neon, and argon atoms; the photon wavelength and frequency scales are shown on top. The colors of the discharge lamps are shown on the right. (Images from Prof. Jircitano and smart elements) [JWM note: change figure to show frequencies as well as wavelengths. Also, we need a better attribution for the figure.]*

The H-atom emission spectrum also contains lines in the ultraviolet and infrared ranges. In 1888, Johannes Rydberg developed an equation that predicts wavelengths for all hydrogen emission lines:

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Here, n_1 and n_2 are positive integers with $n_2 < n_1$, and the Rydberg constant $R_\infty = 1.09737316 \times 10^7\ \text{m}^{-1}$.

Because the wavelengths of hydrogen emission lines were measured to very high accuracy, the Rydberg constant could be determined very precisely. That a simple formula involving integers could account for such precise measurements seemed astounding at the time.

Exercise 2: Hydrogen-Atom Emission

Use the Rydberg equation to calculate the wavelength of the photon emitted by a hydrogen atom when $n_2 = 3$ and $n_1 = 7$.

D2.3 Atomic Energy Levels

Why should a hydrogen atom emit only four specific colors of visible light? To understand this better, we need to know more about the energy of the atom and how energy depends on atomic structure. Any atom consists of a tiny nucleus surrounded by one or more electrons. The simplest atom, a hydrogen atom, has one proton as the nucleus and one electron outside the nucleus. According to Coulomb’s law, the electron and proton attract.

Activity 2: Line Spectra and Energies

Think about the implications of line spectra. If a hydrogen atom emits only four specific wavelengths in the visible region, what does this imply regarding the energies of the emitted photons? Why should only these four wavelengths be emitted, but none of the other possible wavelengths? Write your explanation in your notebook.

The model currently used to describe the distribution of electrons in an atom has these attributes:

- The energies of electrons in an atom are restricted to **energy levels**, which are *specific allowed energies*.
- Each line in the spectrum of an element results when an electron’s energy changes from one energy level to another; *a change from one electronic energy level to another* is called an **electronic transition**.
- Electrons are distributed in *regions centered on the nucleus*, called **shells**; each shell has a different average distance from the nucleus.
- As described by Coulomb’s law, an electron’s energy increases with increasing average distance from the nucleus; that is, with increasing size of an electron shell.
- Both energy levels and shells are described by **quantum numbers**, *numbers restricted to specific allowed values*; the electron energies are said to be **quantized**, *restricted to discrete energy levels*.

An atom is most stable when it has the lowest possible energy. The *lowest energy electronic state of an atom* is called its **electronic ground state** (or simply **ground state**). Any higher energy state of an atom is called an **electronic excited state** (or simply an **excited state**).

Figure 3 shows the first few energy levels of a hydrogen atom. The atom is in its ground state when its electron is in the $n = 1$ (lowest energy) level. When a photon is absorbed by a ground state hydrogen atom, as shown on the left side of Figure 3, the energy of the photon moves the electron to a higher n (higher energy) level, and the atom is now in an excited state.

An atom in an excited state can release the extra energy as a single photon if the electron returns to its ground state (say, from $n = 5$ to $n = 1$), or the energy can be released as two or more lower energy photons if the electron falls to an intermediate state then to the ground state (say, from $n = 5$ to $n = 2$, emitting one photon, then from $n = 2$ to $n = 1$, emitting a second photon).

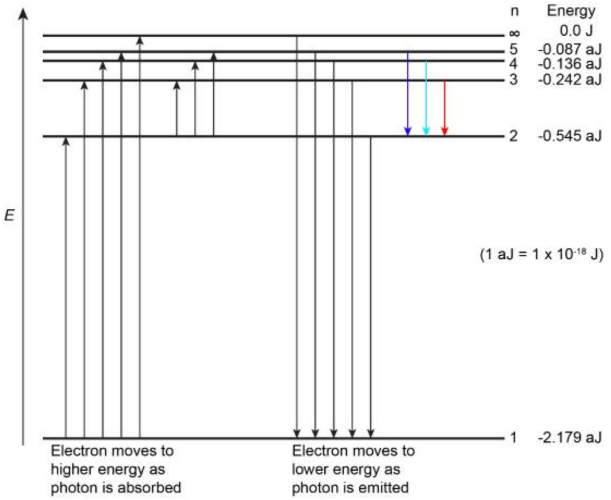


Figure 3. *The horizontal lines show the relative energy levels in the modern model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these levels. The n = 1-5 levels are shown explicitly; the energy levels are closer together as n→∞. As n→∞, potential energy approaches zero. (Colored arrows show the colors of visible emissions.)*

D2.4 The Quantum Mechanical Model of the Hydrogen Atom

If we could calculate the energy for each energy level, we could predict the emission spectrum for hydrogen. In 1926, Erwin Schrödinger applied **quantum mechanics ,***a model that uses both wave and particle analogies to describe atomic-scale matter,* to the hydrogen atom. Instead of viewing the electron as a particle, Schrödinger applied mathematics appropriate for three-dimensional stationary *waves* constrained by electrostatic potential (Coulomb's-law attraction between electron and nucleus). For each wave he derived *a mathematical function to describe the wave,* a **wave function**. The wave function is typically designated by the Greek letter ψ.

Schrödinger showed that these wave functions could be used to calculate allowed energies of a hydrogen atom. The calculated energies are given by this equation:

$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, \ldots$$

where the proportionality constant $k = 2.179 \times 10^{-18}$ J, and n is a quantum number restricted to positive integer values.

In an electronic transition, an electron moves from one energy level to a different energy level. The energy of the corresponding photon is the energy difference between the two energy levels, an initial level with energy E_i and a final level with energy E_f.

$$\Delta E = E_f - E_i = -k\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

A *positive* ΔE means that the atom's energy increased, corresponding to *absorption* of a photon: the photon's energy has been added to the atom's initial energy. Similarly, a *negative* ΔE means that the atom has lost energy through *emission* of a photon.

Conservation of energy requires that the energy of the photon, $E_\mathrm{photon} = hc/\lambda$, equals the absolute value of the energy difference, $|\Delta E|$, for emission or absorption. The sign of ΔE indicates whether the photon was absorbed (+) or emitted (−).

The equation Schrödinger obtained is equivalent to the equation Rydberg used to calculate hydrogen emission lines:

$$E_{\text{photon}} = \frac{hc}{\lambda} = |\Delta E| = \left| -k \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right|$$

$$\frac{1}{\lambda} = \frac{k}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_\infty \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

and thus, $R_\infty = k/(hc)$. Substituting values for k, h, and c into this equation gives $R_\infty = 1.097\times 10^7\ \text{m}^{-1}$, which is the same as the experimental Rydberg constant to four significant figures. That a wave model could reproduce these highly accurate energy levels was strong evidence that quantum mechanics is an appropriate atomic-level model.

D2.5 Wave-Particle Duality

The combined wave and particle model is referred to as **wave-particle duality**. Its impact in describing atomic-scale particles (protons and electrons) is dramatic: wave-particle duality implies that we should not just think of an electron as located at a specific position around a nucleus or moving in a specific direction and with a specific speed: the wave-like electron seems to be all around the nucleus at once! In other words, the wave nature of an electron is just as important in describing its properties as its particle nature.

An important consequence of wave-particle duality is the **Heisenberg uncertainty principle**: *it is impossible to determine the exact position and the exact momentum of an atomic-level particle simultaneously.* This means that, if we know exactly where an electron is at one instant, we have no idea where it will be an instant later; or, if we know an electron's exact speed and direction, we have no information about where it is. As a result of the uncertainty principle, the best we can do is determine *the probability of finding an electron at a specific position*; that probability is proportional to the square of the wave function, ψ^2.

The **electron-density distribution** (or just **electron density**) is *the three-dimensional distribution of electron probability*, which can be derived from the square of a wave function. *Wave functions and their electron-density distributions* are called **orbitals**. It is these orbitals that help us understand atomic properties, chemical bonds, and forces between molecules.

A graphic way of showing electron-density distribution (depicting an orbital) is by the density of shading or stippling. That is, we draw lots of dots or darker shading where the probability is high and we draw fewer dots where the probability is low. For example, consider the wave shown below in red along with its square shown in blue. Wherever there is a maximum in the square of the wave function (blue curve), there are many dots. Where the wave function (and therefore also its square) approaches zero, there are few dots.

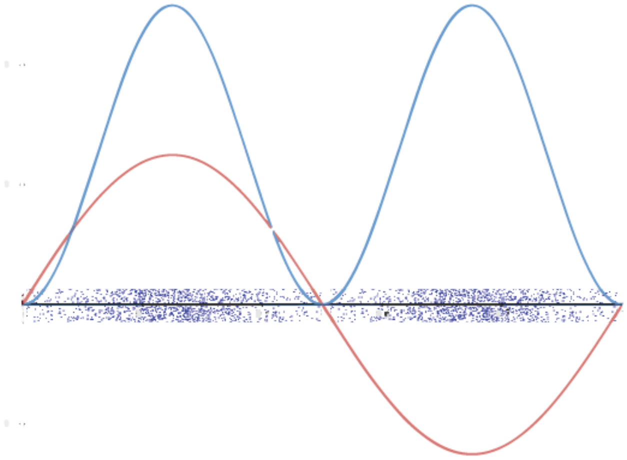


***Figure 4**. The function sin(x) is plotted from 0 to 1 (red line). The square of the function, sin^2(x), is plotted in blue. The density of dots shown in the band along the horizontal axis is proportional to sin^2(x).*

Such a way to visualize electron density is quite useful for a 3-D view of the electron density surrounding a nucleus. For example, you can see the electron-density distribution of a hydrogen atom in its ground state in this video, where the hydrogen atom is rotated around its nucleus.

Activity 3: Electron Density Distribution for H Atom

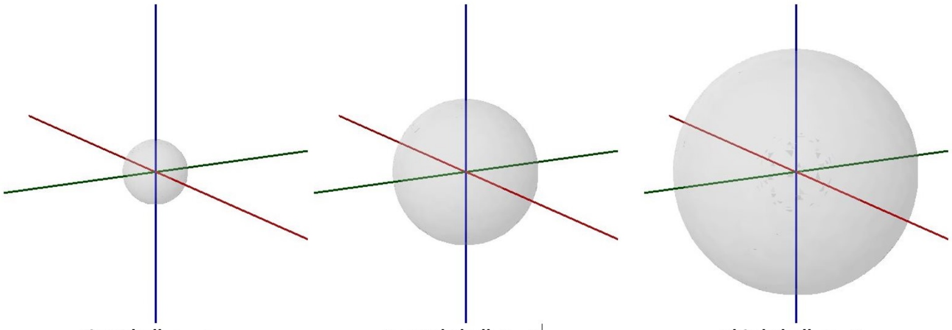
In your class notebook write a description of (1) the shape of the electron density distribution for a ground-state H atom and (2) how electron density changes with distance from the nucleus. (The nucleus is located at the intersection of the three axes: *x*, *y*, and *z* axes).

In the electron-density diagram below, click on the white cross that corresponds to the lowest electron density.

Based on the density of dots in the diagram, make a graph with electron density on the vertical axis and distance from the nucleus on the horizontal axis. How is a graph of wave function versus distance from the nucleus related to the graph you made?

Similar to dot-density diagrams, but visually simpler while conveying a little less information, are 3-D boundary-surface plots, which show a surface that has the same shape as the electron density distribution and encloses some fraction, such as 90%, of the electron density. That is, if we could repeatedly locate the electron exactly, nine times out of ten the electron would be located inside the boundary surface. The figure below shows how a boundary surface is related to the dot-density plot you have already viewed. Move the slider at the bottom to change from dot-density to boundary-surface diagram.

Visualizing electron-density distributions confirms an idea mentioned earlier: there are *shells* of electron density, concentric spheres each farther from the nucleus. The orbitals that belong to a given shell have the same quantum number, *n* and their electron density is approximately the same average distance from the nucleus. The principal quantum number *n* dictates the overall *size* of the orbital.



First Shell, $n = 1$ **Second Shell, $n = 2$** **Third Shell, $n = 3$**

Figure 5. *The boundary-surface diagrams of the first three shells for a hydrogen atom, showing their relative sizes.*

As *n* gets larger, the radius, *r*, of the electron shell gets larger, and E_n becomes less negative—closer to zero. Therefore, the limits $n \longrightarrow \infty$ and $r \longrightarrow \infty$ imply that $E_n = 0$ corresponds to **ionization** of the atom, *complete separation of the electron from the nucleus*. Thus, for a hydrogen atom in the ground state, the ionization energy is:

$$\Delta E = E_{n\to\infty} - E_1 = 0 - \frac{-k}{1^2} = k = 2.179 \times 10^{-18}\ \mathrm{J}$$

Another interesting aspect is that while we know E_n, which is the *total* energy of the electron, we cannot measure the electron's kinetic energy (or its velocity) and potential energy separately. We know from Coulomb's law that the potential energy changes as a function of *r*. Since the electron density is distributed over a range of *r*, there's a range of potential energy, and hence a range of kinetic energy—when the electron's potential energy is higher, its kinetic energy would be lower. This uncertainty is again related to the wave nature of the electron. However, knowing the total energy, E_n, is quite sufficient for us!

Activity 4: Wrap-up—Atomic Spectra and Atomic Structure

Review what you wrote about atomic spectra and atomic structure at the beginning of this section. Update the information based on what you have learned. Write a summary that will be a good study aid when you review for an exam.

D2.6 Atomic Orbitals and Quantum Numbers

Quantum Numbers: n, ℓ, m_ℓ

The atomic wave functions can be defined using three quantum numbers: n, ℓ, and m_ℓ. Each wave function corresponds to an *atomic orbital*. Each atomic orbital defines a region in the atom within which electron probability density is large.

The energy of a hydrogen atom orbital depends on the **principal quantum number**, ***n***:

$$E_n = -\frac{2.179\ \times\ 10^{-18}\ \mathrm{J}}{n^2}, n = 1, 2, 3, \ldots$$

As discussed above, the size of the orbital (the average distance of the electron from the nucleus) increases as n increases. The farther the electron is from the nucleus, the higher (less negative) the energy is.

The second quantum number, ℓ, is the **orbital quantum number** (sometimes called *azimuth* or *angular-momentum* quantum number). It determines the *shape* of the electron-density distribution. ℓ is an integer with values ranging from 0 to $n - 1$; that is, $\ell = 0, 1, 2, \ldots, n - 1$. Thus, an orbital with $n = 1$ can have only one value of ℓ, $\ell = 0$, whereas $n = 2$ permits $\ell = 0$ and $\ell = 1$, and so on.

Values of ℓ are designated using letters:

$\ell = 0$	***s*** orbitals
$\ell = 1$	***p*** orbitals
$\ell = 2$	***d*** orbitals
$\ell = 3$	***f*** orbitals
$\ell = 4$	***g*** orbitals
$\ell = 5$	***h*** orbitals

Activity 5: Shapes of Hydrogen-Atom Orbitals

View the shapes of *s*, *p*, and *d* orbitals shown in these videos:
1s orbital *2p* orbital *3d* orbital

In your class notebook write a description of the shape of the electron density distribution for each orbital. Also, make a rough drawing of the corresponding boundary-surface diagram for each dot-density diagram.

The **magnetic quantum number**, $\boldsymbol{m_\ell}$, specifies the *spatial orientation* of a particular orbital. Values of m_ℓ can be any integer from $-\ell$ to ℓ. For example, for an *s* orbital, $\ell = 0$, and the only value of m_ℓ is 0; thus there is only a single *s* orbital. For *p* orbitals, $\ell = 1$, and m_ℓ can be equal to –1, 0, or +1; thus there are three different *p* orbitals, which are commonly shown as p_x, p_y, and p_z, oriented along the *x*, *y*, and *z* axes.

The total number of possible orbitals with the same value of ℓ is $2\ell + 1$. There are five *d* orbitals, seven *f* orbitals, and so forth. The sizes and shapes of *s*, *p*, and *d* orbitals in the first three shells are shown in Figure 6. Each of these orbitals corresponds to a different set of n, ℓ, and m_ℓ values.

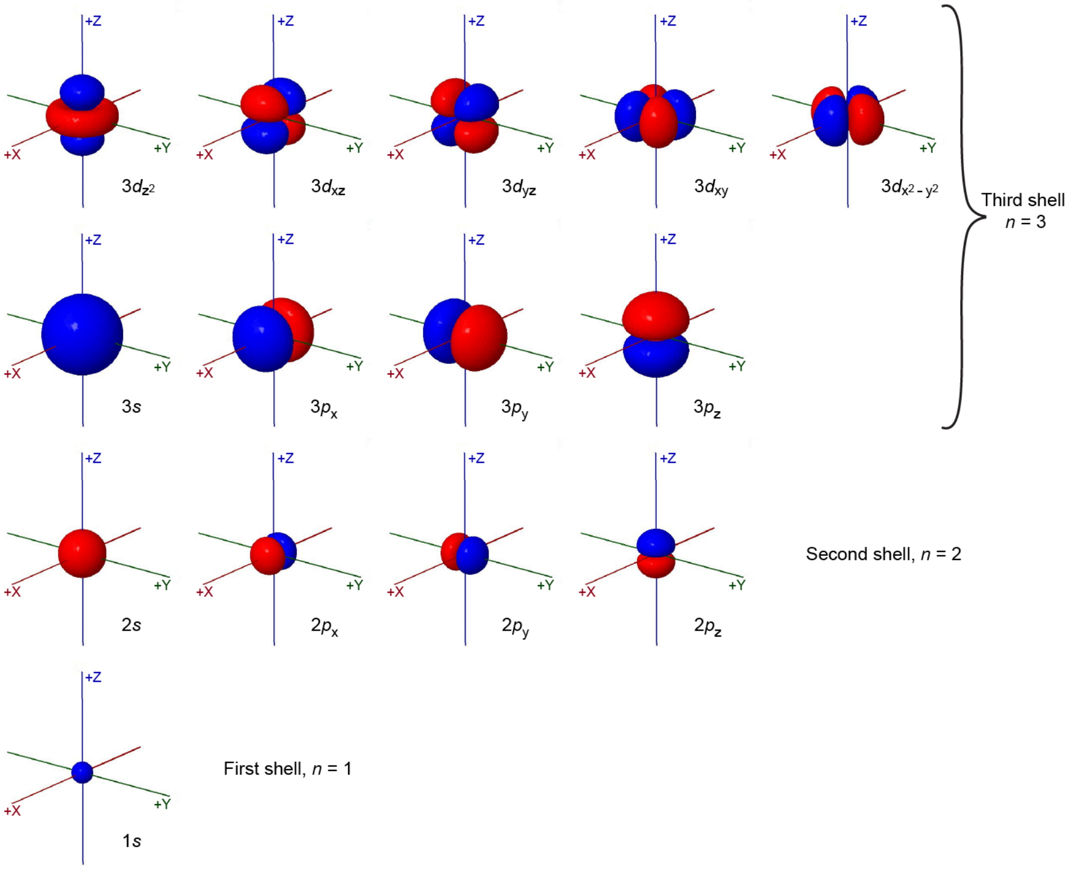


Figure 6. *Sizes and shapes of electron-density distribution for the orbitals in the first three shells of the hydrogen atom. Summing electron density over all orbitals in a shell results in the spherical electron density distributions shown in Figure 5.*

Exercise 5: Electron-Density Distance from Nucleus

All orbitals with the same value of n and ℓ form a **subshell**. For example, the 2p_x, 2p_y, *and* 2p_z orbitals constitute the 2*p* subshell because each of these orbitals has *n* = 2 and ℓ = 1. The number of orbitals in a subshell equals the number of different values for the m_ℓ quantum number. Each shell contains *n* subshells: for example, when *n* = 3, there is a 3*s*, a 3*p*, and a 3*d* subshell, corresponding to the three possible ℓ values of 0, 1 and 2.

Orbital Phases and Nodes

Figure 6 shows some atomic orbitals as either all blue or all red (for example, 1*s* and 2*s*), while other orbitals contain both colors (for example, the 2*p* orbitals). The blue and red colors show *the mathematical sign of the wave function*, a property called the **phase** of the wave function. Most wave functions are positive in some regions and negative in others. Phase is important when wave functions on two atoms interact to form a chemical bond.

The relationship between wave function and electron density is depicted more explicitly in Figure 7. In the middle row, boundary-surface diagrams from Figure 6 show the sizes and shapes of electron-density distributions for the 1*s*, 2*s*, and one of the 2*p* orbitals. In the top row are the corresponding wave functions (ψ); the bottom row shows electron density, ψ^2.

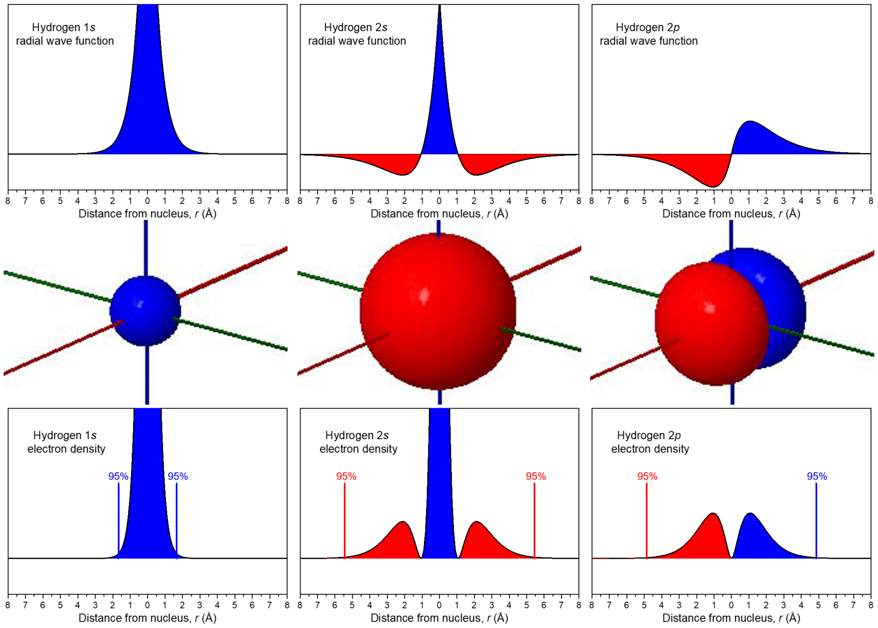


***Figure 7**. The boundary-surface diagrams from Figure 6 for 1s, 2s, and 2p orbitals are reproduced in the middle. The corresponding wave function is shown on top and electron density shown on the bottom. Each wave function is colored similar to the boundary-surface diagram to highlight its phases.*

The wave functions and electron-density functions are color coded to show the regions where $\psi > 0$ as blue and the areas where $\psi < 0$ as red. *A surface where the wave function changes sign* is called a **node**. At a node, $\psi = 0$ and therefore the probability of finding the electron in that surface is also 0.

For the 1*s* orbital, there are no nodes; its wave function only has positive values. For the 2*s* orbital, there is one node at r = 1.05 Å; the wave function goes from positive values near the nucleus to negative values farther out. (You cannot see this node in the boundary-surface diagram, because the node is a sphere that is within the volume enclosed by the boundary surface.) *A node that occurs at a specific value of r* is a **radial node**, and therefore radial nodes have a spherical shape. The 3*s* orbital, for example, has two radial nodes enclosed within the boundary-surface diagram.

Each 2*p* orbital has one node. Look at the boundary-surface diagram to verify that this node is planar instead of spherical. *Non-spherical nodes* are **angular nodes**. For example, the $2p_x$ orbital has one angular node: the *yz* plane; ψ is equal to 0 at all points in the *yz* plane, rather than at any specific r value. You can see the presence of angular nodes clearly in boundary-surface diagrams.

An orbital has $n - 1$ nodes, of these, $n - 1 - \ell$ are radial nodes, and the number of angular nodes corresponds to the value of ℓ. A generalization that is true for all kinds of waves is that the greater the total number of nodes, the higher the energy. The phase of the wave function differs on either side of a node, because the wave function changes from one mathematical sign to the other as it crosses a node. Visually, we represent these different phases, and the presence of nodes, with different colors in the boundary-surface diagram.

Activity 6: Radial and Angular Nodes

Fourth Quantum Number, m_s

The fourth quantum number, called the **spin quantum number**, $\boldsymbol{m_s}$, differs from the other three quantum numbers in that it describes the electron rather than the orbital. An electron has a very small magnetic field. Moving a macroscopic charge in a circular path produces a magnetic field, so initially the electron's magnetic field was attributed to its spinning like a top; hence the name "spin quantum number". The electron's magnetic field can have two quantized states: either "up" or "down". This gives two possible m_s values, $m_s = +½$ or $m_s = -½$. When an electron occupies an orbital, we typically depict these two possible m_s values as an ↑ or ↓ arrow.

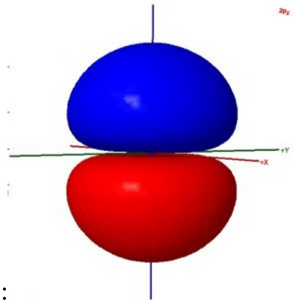
Exercise 6: Quantum Numbers

Activity 7: Summary of Quantum Numbers

> In your class notebook make a table summarizing the names, symbols, allowed values, and important properties of the four quantum numbers. (You can use this table for studying later.) If you are studying with someone else, make your tables independently and then compare.
>
> When you are satisfied with your table, compare it with ours.

Day 2 Pre-Class Podia Problem: Atomic Orbitals

This Podia problem is based on today's pre-class material; working through that material will help you solve the problem.



Consider these two sentences:

- The surface shown in this illustration of an atomic orbital is chosen so that the entirety of the electron's wave function is enclosed.
- The colors in the diagram represent regions of opposite electron spin.

Decide whether each sentence is correct. Rewrite all incorrect text so that it is correct. Be brief but include all important ideas and use scientifically appropriate language.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

1.3: Day 3- Orbital Energy and Electron Configuration

c3

Day 3: Orbital Energy and Electron Configuration

D3.1 Atoms with More than a Single Electron

Activity 1: Reflection

In your course notebook, make a heading for electron configurations and write down what you remember about electron configurations for atoms from your previous experience. Also note any aspects of electron configurations that puzzle you. We will ask you to refer back to what you have written when you complete this section.

The ideas already developed about quantum numbers, orbitals, and sizes and shapes of electron-density distributions apply to all atoms. However, when there are two or more electrons in an atom there are repulsive forces between the electrons as well as attractive forces between electrons and the nucleus. These repulsions affect electron energies.

For example, the energy levels in a He^+ ion (which, like H, has a single electron) are significantly lower than in a H atom because of the stronger Coulomb's law attraction between the one electron and the 2+ charge of the He nucleus. However, in a He atom, which has two electrons, electron-electron repulsions between the electrons raise energy levels significantly compared to He^+, and a He atom is not as stable as we might have expected.

For atoms with many electrons, the effect of electron-electron repulsions differs for different subshells. Therefore orbital energy depends on both n and ℓ quantum numbers. For the same value of n (the same shell), as ℓ increases the energy also increases. Thus *s*-subshell electrons have lower energy than *p*-subshell electrons, which are lower than *d*-subshell electrons, and so forth. Orbitals within the same subshell (for example $2p_x$, $2p_y$, and $2p_z$) all have the same energy; *orbitals that have the same energy* are said to be **degenerate**.

The Austrian physicist Wolfgang Pauli formulated what is now called the **Pauli exclusion principle**:

- Each electron in an atom must have a *different* set of values for the four quantum numbers.
  - If two electrons share the same orbital (have the same n, ℓ, and m_ℓ), then their spin quantum numbers m_s must have different values; we say the two electrons have opposite spin.
- Because m_s can only have two values, +½ or -½, no more than two electrons can occupy the same orbital.

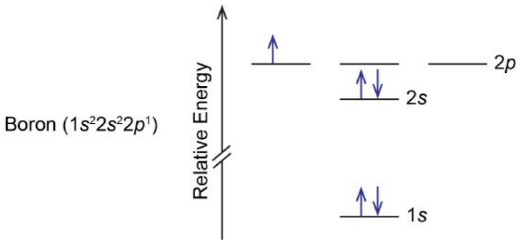
By applying the Pauli exclusion principle, the arrangement of electrons in any multi-electron atom can be determined by recognizing that the ground state of an atom has all its electrons in orbitals with the lowest energies possible.

Activity 2: Arrangement of Electrons in Li

D3.2 Orbital Energy Level Diagrams

An **orbital energy level diagram** (or just **orbital diagram)***shows the relative energies of orbitals and how electrons are distributed among orbitals within a subshell*. In an orbital energy level diagram, individual orbitals are usually represented by horizontal lines whose vertical position conveys the relative energies of the orbitals. The electrons are represented as arrows with the direction of the arrow communicating the sign of m_s (the ↑ arrow represents $m_s = +½$ and the ↓ arrow represents $m_s = -½$).

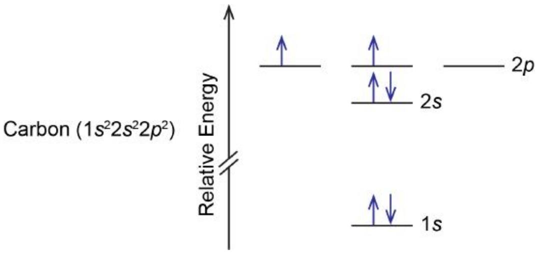
For example, a boron atom has this orbital energy level diagram:



As illustrated by the boron example, an orbital diagram includes all orbitals in all subshells within a partially occupied shell, even if some orbitals are unoccupied. Note that the three 2*p* orbitals are degenerate, so the electron can occupy any one of them.

A carbon atom has six electrons, so there are two electrons in the 2*p* subshell. These two electrons could (1) pair in a single 2*p* orbital or (2) occupy separate orbitals but with opposite spin or (3) occupy separate orbitals but with parallel spin. All three possibilities are valid based on quantum numbers and the Pauli principle, but only one is lowest in energy. Electrons having parallel spins cannot occupy the same space (the same orbital), so repulsions between them must be smaller than if they had opposite spins. Thus option 3 is lowest in energy and therefore represents the ground state of a carbon atom; options 1 and 2 represent excited states.

According to **Hund's rule**, *the lowest energy configuration has the maximum number of unpaired electrons with parallel spin* within a set of degenerate orbitals. Thus, the orbital diagram for the ground state of carbon is



D3.3 Electron Configurations

The *specific arrangement of electrons in atomic orbitals* is called the **electron configuration** of the atom. It determines many physical and chemical properties of that atom. The periodic table, which is arranged in accordance with the properties of the elements, can therefore be used to predict the ground state electron configurations of atoms.

An electron configuration is written symbolically to provide three pieces of information: the principal quantum number (shell number), *n*; a letter that designates the subshell (*s*, *p*, *d*, etc.); a superscript showing the number of electrons in that particular subshell. For example, the notation $2p^4$ indicates 4 electrons in a *p* subshell (ℓ = 1) with a principal quantum number (*n*) of 2.

For any element, the ground state electron configuration can be built up by starting with hydrogen and following the atomic-number order through the periodic table. To go from one element to the next, add one proton (and one or more neutrons) to the nucleus and one electron to the lowest energy subshell that has an incompletely filled orbital. Repeat until you reach the desired element. This *process of filling electrons into orbitals* is called the **aufbau principle**, from the German word *Aufbauen* ("to build up"). Watch the video in Figure 1 to see how to use the aufbau principle to determine the electron configurations of oxygen and chromium.

https://mediaspace.wisc.edu/id/0_sr9om3nc?playerId=25717641

Figure 1. *View this video to see how to use the periodic table to predict electron configurations.*

Writing the complete electron configuration all the time can be cumbersome, so chemists often abbreviate by using the **noble-gas notation**. For example, the ground-state electron configuration of vanadium (V) is $1s^22s^22p^63s^23p^64s^23d^3$. The noble gas that immediately precedes V is argon (Ar); it has a ground-state electron configuration of $1s^22s^22p^63s^23p^6$, which can be represented as [Ar]. Thus the ground-state electron configuration of V can be shortened to $[\text{Ar}]4s^23d^3$, and it communicates the same information as the complete electron configuration. A list of ground state electron configurations for all elements in the appendix uses noble-gas notation.

The aufbau principle is based on the concept that for ground-state electron configurations, an electron occupies a lower energy atomic orbital rather than occupying a higher energy orbital. Hence, the fact that we observe the 4*s* orbital fill before the 3*d* orbitals indicates that the 4*s* orbital is lower in energy. Similarly, a 6*s* orbital is lower in energy compared to a 4*f* orbital.

The energy difference between *s*, *p*, *d*, and *f* subshells causes orbitals with different *n* values to have similar energies. In many cases these energies are so similar that there are exceptions to the periodic-table prediction of electron configuration. These exceptions occur for *d*-block and *f*-block elements, but not for *s*-block and *p*-block elements.

D3.4 Valence Electrons

Valence, the combining power of an atom, was defined near the end of Section D1.4. Ground state electron configurations of atoms provide insights into valence: for example, why does sodium oxide have formula Na_2O but magnesium oxide is MgO?. When two atoms approach and form a chemical bond, the electron density farthest from the nucleus of each atom, in the higher-energy orbitals, interacts with electron density in the other atom. Electrons in lower-energy orbitals, whose electron density is nearer the nucleus, are less important.

Electrons can be separated into two groups: **valence electrons** *occupy the outermost orbitals* of an atom; **core electrons** *occupy inner orbitals, with electron density closer to the nucleus*. When an electron configuration is written using the noble-gas notation, all electrons represented by the noble-gas symbol in brackets are core electrons. Electrons beyond the noble-gas configuration are valence electrons if they are in the outermost shell of the atom (have the highest n value) or if they are in incompletely filled subshells. For example, consider vanadium, V: $[Ar]4s^2 3d^3$. There are five valence electrons: two 4s electrons and three 3d electrons. There are 18 core electrons in the 1s, 2s, 2p, 3s, and 3p subshells. The fact that V has five valence electrons results in V forming compounds in which the valence of vanadium ranges from 2 to 5. For example, fluorides of vanadium have formulas VF_2, VF_3, VF_4, and VF_5.

An American chemist, G. N. Lewis**,** suggested a simple way to keep track of the number of valence electrons: draw dots around the symbol of an element to represent the valence electrons. The element symbol then represents the nucleus and core electrons of an atom. *A diagram in which dots represent valence electrons* is called a **Lewis diagram**. Lewis diagrams are most useful for the main-group (representative) elements. Here are Lewis diagrams for atoms of elements in the third row of the periodic table:

When drawing a Lewis diagram dots are added one at a time to each of the four sides of the element symbol. If there are more than four dots to add, dots are paired. Lewis originated the idea that when an atom bonds to another atom the valence electrons rearrange to form an **octet**, a stable configuration of valence electrons (s^2p^6) that corresponds to each noble gas at the right side of a row in the periodic table. Thus electron configurations and Lewis diagrams for atoms can predict how an atom forms chemical bonds, an idea that we will explore later.

Exercise 4: Lewis Diagrams

In your notebook write a Lewis diagram for each element:
B Ge Br K Sr Se Xe Sc

D3.5 Effective Nuclear Charge

Periodic trends in atomic properties can be predicted by applying these ideas about electron-nucleus attraction and electron-electron repulsion:

- Electron-density distributions are in shells that increase in size as the principal quantum number, n, increases. Electrons in larger shells are, on average, farther from the nucleus and less strongly attracted.
- Electrons repel other electrons, raising electrostatic potential energy. This partly counteracts the lowering of energy due to attraction of an electron by the nucleus. Electrons are said **screen** or **shield** other electrons from nuclear charge.

The electron density for a core electron (an electron in an inner shell) is, on average, closer to the nucleus than the electron density for a valence electron. Thus, core electrons can significantly counteract the effect of nuclear attraction. Consider a lithium atom (Li, $1s^2 2s^1$), which has three protons in the nucleus. Because the 2s orbital is larger than the 1s orbital, the 1s electron density is mostly located between the nucleus and the 2s electron density. (Move the slider in the middle of Figure 2 to see how much of the 1s electron density lies between the nucleus and 2s electron density.) Thus, the two 1s electrons repel the 2s electron away from the nucleus, counteracting part of the 3+ charge of the nucleus.

Figure 2. *Electron-density distribution of Li 1s electrons and a Li 2s electron. Use the slider in the center of the diagram to alternate between the two distributions. (The nucleus is at the intersection of the axes.)*

To account for such electron-electron repulsions, we use an **effective nuclear charge**, $\boldsymbol{Z_{eff}}$, *the positive nuclear charge (given by the atomic number) reduced by the repulsion of a specific electron by all the other electrons*. In the case of the Li 2s electron, quantum mechanics calculates that the repulsions from the two 1s electrons reduces the nuclear charge by 1.72; that is, Z_{eff} for the 2s

electron is 3 − 1.72 = 1.28. If *all* the electron density of the 1*s* electrons were between the nucleus and the 2*s* electron, Z_{eff} would be reduced to 1.

Activity 3: Effective Nuclear Charge

D3.6 Periodic Variation in Atomic Radius

Given that electron density is distributed throughout space but concentrated near the nucleus, it is hard to define the size of an atom. Typically, chemists think of atoms as spheres with radii on the order of tens to hundreds of picometers. One way to determine atomic radii is to measure the distance between atomic nuclei in homonuclear diatomic molecules. (Homonuclear means two atoms of the same element bonded to each other.) The radius of one atom is half the internuclear distance. A second way is to measure the distance between the nuclei of two atoms in a solid metal, where each atom touches several nearest neighbors. Once a set of atomic radii has been determined, these values can be used to estimate the lengths of bonds that have not yet been measured.

Figure 3. *Atomic radius as a function of atomic number. Click on each "+" for a description of an important trend.*

Activity 4: Periodic Variation of Atomic Radii

Day 3 Pre-Class Podia Problem: Quantum Numbers and the Periodic Table

This Podia problem is based on today's pre-class material; working through that material will help you solve the problem.

In a hypothetical parallel universe, the quantum numbers are defined differently: n, ℓ, and m_s obey the same rules as in our universe, but m_ℓ cannot have negative values. Thus, a *p* subshell contains only two *p* orbitals, a *d* subshell contains three *d* orbitals, and so forth. The energies of the subshells are the same as in our universe. In your notebook, answer each question below and explain each answer clearly, concisely, and with scientifically appropriate language.

1. Draw a periodic table for the hypothetical universe.
2. Determine the atomic number of the fourth noble gas element.
3. Write the electron configuration of a stable ion formed by element number 6.
4. Write the electron configuration of a stable ion formed by element number 18.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

1.4: Day 4- Periodic Trends; Forces between Atoms

4

Day 4: Periodic Trends; Forces between Atoms

In addition to atomic radius, several other properties vary depending on position in the periodic table. Like atomic radius, these properties depend on effective nuclear charge and size of atomic shell.

D4.1 Periodic Variation in Ionization Energies

The quantum mechanics model for the hydrogen atom (Section D2.4) discussed ionization of the hydrogen atom: excitation of the electron from the $n = 1$ level to the limit of $n \rightarrow \infty$:

$$\Delta E = E_{n\rightarrow\infty} - E_1 = 0 - \frac{-k}{1^2} = k = 2.179\ \times\ 10^{-18}\ \mathrm{J}$$

Ionization energy (**IE**), *the minimum energy required to remove an electron from the atomic orbital it occupies (exciting it to n =* ∞*)*, also applies to multi-electron atoms. As shown in this table of ionization energies, there are successive ionization energies, one for each electron.

The first ionization energy (IE_1) is the minimum energy required to remove the least tightly bound electron, i.e. the electron in the highest energy orbital. It corresponds to the process:

$$\mathrm{X}(g) \rightarrow \mathrm{X}^+(g) + \mathrm{e}^-\ \Delta\mathrm{E} = \mathrm{IE}_1$$

The second ionization energy (IE_2) is the minimum energy required for removing an electron from the 1+ cation, corresponding to:

$$\mathrm{X}^+(g) \rightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^-\ \Delta\mathrm{E} = \mathrm{IE}_2$$

And so forth.

Electrons in atoms have lower potential energy than when separated from the atom, so energy is always *required* to remove the electrons from atoms or ions. Ionization is an endothermic process and IE values are always positive.

Ionization energies can be determined experimentally from atomic spectra or by shining light on a gas-phase sample and successively increasing the photon energy until ejection of an electron is observed. Such experiments also give us direct information about the atomic orbital the electron was occupying.

Activity 1: Periodic Variation of First Ionization Energy

In the preceding activity, you developed a general rule that across a period, IE_1 increases with increasing atomic number, Z; down a group, IE_1 decreases with increasing Z. Look at Figure 1 below and make certain you see how the data in the figure support both trends. There are a few systematic deviations from these trends, which also can be seen in Figure 1.

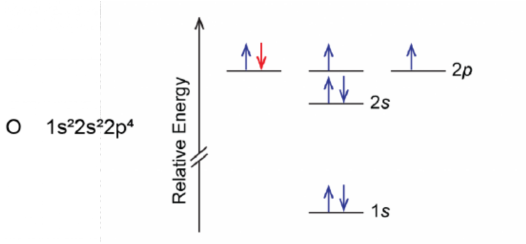
Activity 2: Deviations from IE Trends

Examine data presented in Figure 1. Identify all deviations from the trend that ionization energy increases across a period and decreases down a group. Click on each deviation involving an element in Period 1, Period 2, or Period 3.

Figure 1. *The first ionization energies of elements in the first five periods are plotted against atomic numbers.*

Activity 3: Explaining Deviations from IE Trends

Another deviation occurs when a subshell becomes more than half filled. For example, oxygen's IE_1 is slightly lower than that for nitrogen. The orbital diagram of oxygen shows that the last electron added (red) is forced to pair with another electron, because the 2*p* subshell is more than half full.



Loss of the electron (colored red in the orbital diagram) yields a greater reduction of electron–electron repulsion because there are no longer two electrons in the same orbital. This makes it easier to lose one electron from O and the ionization energy is smaller than expected. The same explanation applies to the dip for sulfur after phosphorus in Figure 1.

Looking at the successive IEs in the appendix, we see that for any element, $IE_1 < IE_2 < IE_3$, and so forth, and this is due to the greater Z_{eff} in successively more positive ions. However, sometimes the increase in successive IE is larger than expected. For example, consider the data in Table 1:

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	419	3069	4438	5876	7975	9620	11385
Ca	590	1145	4941	6465	8142	10496	12350
Sc	633	1244	2388	7130	8877	10720	13314
Ga	579	1982	2962	6194	8299	10874	13585
Ge	760	1537	3301	4409	9012	11183	13981
As	947	1949	2731	4834	6040	12302	14183

Table 1. Successive Ionization Energies (IEs) for Some Period-4 Elements (kJ/mol)

Activity 4: Successive Ionization Energies

These observed ionization energies are consistent with the idea of valence electrons—electrons in outer shell(s) that are less bound and more energetically accessible, allowing them to participate in chemical transformations.

D4.2 Periodic Variation in Electron Affinities

Electron affinity (EA) is defined as *the change in energy when an electron is added to an atom to form an anion*. The first EA corresponds to adding one electron to an atom:

$$X(g) + e^{-} \rightarrow X^{-}(g) \quad \Delta E = EA_1$$

Many elements have *negative* EA_1, which means that the energy of the 1− anion is *lower* than the energy of the atom plus the free electron; that is, the anion is more stable.

For other elements, EA_1 is *positive*, meaning that the anion is *less* stable compared to the parent atom plus a free electron. For these elements, an input of energy is required to form the anion, and, in the gas phase, the anion dissociates to yield the neutral atom and a free electron because the latter are lower in energy.

Activity 5: Electron Affinity Trends

D4.3 Electron Configurations of Monoatomic Ions

When atoms lose electrons or gain electrons, Ions form. It is useful to know what kinds of ions form and what their properties are. A **monoatomic ion** is a *single atom that has gained or lost one or more electrons. A positively charged ion*, a **cation**, forms when an atom loses one or more electrons. *A negatively charged ion*, an **anion**, forms when an atom gains one or more electrons.

Nonmetallic elements on the far right side of the periodic table (except the noble gases) have higher ionization energies and more negative electron affinities. It is energetically more favorable for them to gain electrons and form anions and less energetically favorable for them to form cations. For example, elements in groups VIIA, VIA, and some in VA can gain 1, 2, or 3 electrons, respectively, to achieve the electron configuration of a noble gas (a full octet, s^2p^6 in the outermost shell).

Metallic elements on the left side of the periodic table have lower ionization energies and less negative (or positive) electron affinities. It is energetically more favorable for them to form cations. For examples, elements in groups IA, IIA, and IIIA can lose 1, 2, or 3 electrons, respectively, to achieve a full octet (plus additional filled *d* and *f* subshells).

To find the ground state electron configuration of a monoatomic ion, start with the electron configuration of the corresponding atom and remove (or add) an appropriate number of electrons from (or to) the valence orbital(s) of the atom. Here are some examples:

$$\text{K}([\text{Ar}]4s^1) \longrightarrow \text{K}^+([\text{Ar}]) + \text{e}^-$$

$$\text{Ga}([\text{Ar}]3d^{10}4s^24p^1) \longrightarrow \text{Ga}^{3+}([\text{Ar}]3d^{10}) + 3\text{e}^-$$

$$\text{O}(1s^22s^22p^4) + 2\text{e}^- \longrightarrow \text{O}^{2-}(1s^22s^22p^6 \text{ or } [\text{Ne}])$$

When transition elements and inner transition elements form cations, electron(s) in the *outer-most shell* (largest *n*) are removed before any *d* or *f* electrons. For example, when Fe loses two electrons to form Fe^{2+}, the two 4s electrons are lost:

$$\text{Fe}([\text{Ar}]3d^64s^2) \longrightarrow \text{Fe}^{2+}([\text{Ar}]3d^6) + 2\text{e}^-$$

This happens because electrons in the 3*d* subshell are very effective at screening the 4*s* electrons from the nucleus but much less effective at screening each other. Quantum mechanics calculates that the effective nuclear charge experienced by a 4*s* electron in Fe is 2.1, while the effective nuclear charge experienced by a 3*d* electron is 4.3. After 4*s* electrons have been removed, some 3d electrons can also ionize. Here are more examples:

$$\text{V}([\text{Ar}]3d^34s^2) \longrightarrow \text{V}^{5+}([\text{Ar}]) + 5\text{e}^-$$

$$\text{Re}([\text{Xe}]4f^{14}5d^56s^2) \longrightarrow \text{Re}^{2+}([\text{Xe}]4f^{14}5d^5) + 2\text{e}^-$$

Exercise 3: Electron Configurations for Monoatomic Ions

In your notebook write the correct electron configuration for each ion listed here:

Sr^{2+} Te^{2-} Al^{3+} Fe^{3+} Nd^{4+}

Ions and atoms that have the *same* electron configuration are **isoelectronic**. For example, the isoelectronic Na^+, Ne, and F^- all have ground state electron configuration of $1s^22s^22p^6$ (or [Ne]). For main-group elements, the most commonly formed ions are isoelectronic with a noble gas; that is, these ions have complete octets.

D4.4 Unpaired Electrons and Magnetism

One way chemists have discovered information about electron configurations of ions involves magnetism. You are probably familiar with refrigerator magnets, iron magnets, or neodymium (rare earth) magnets. These exhibit **ferromagnetism**, *a strong attraction to a magnetic field that is easily observable and sometimes can be made permanent*. All substances exhibit **diamagnetism**, *a very weak repulsion from a magnetic field* that can only be observed in extremely large magnetic fields. Because diamagnetism is so weak, it is usually too small to notice.

In addition to diamagnetism, some substances also exhibit **paramagnetism**, *an attraction to a magnetic field that is not as strong as ferromagnetism but much stronger than diamagnetic repulsion*. Paramagnetism arises due to the presence of unpaired electrons. Each electron has a tiny magnetic field; that is, each electron is a tiny magnet. When a macroscopic magnet comes near a paramagnetic substance, most of the unpaired electron magnets align with the magnetic field, causing the substance to be attracted to the magnet (Figure 2).

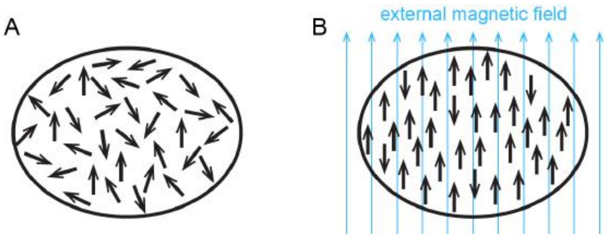


Figure 2. ***Paramagnetism***. ***A.*** *In the absence of a magnetic field, unpaired-electron magnetic moments (arrows) are oriented randomly in all directions.* ***B.*** *In a magnetic field, magnetic moments orient in the same direction as the field, except for a few that orient in the opposite direction. The substance is attracted to a magnet, but not as strongly as a ferromagnetic substance. When the magnetic field is removed, the electron magnetic moments revert to the random arrangement in part a.*

Figure 3 shows how ferromagnetism differs from paramagnetism.

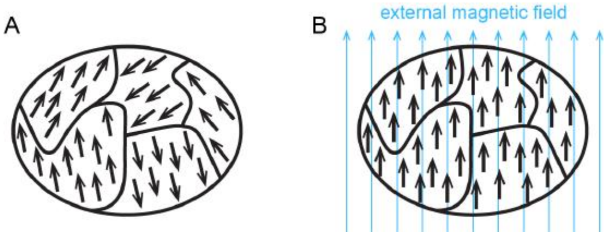


Figure 3. Ferromagnetism. *In a ferromagnetic substance, all atoms within a region (called a magnetic domain) have their electron magnetic moments aligned the same way.* ***A.*** *In the absence of a magnetic field, the domains are randomly oriented.* ***B.*** *In a magnetic field, all domains (and all electron magnetic moments) align with the field. Because all moments align with the field, the substance is strongly attracted to a magnet. When the magnetic field is removed, the domains may remain aligned (resulting in a permanent magnet) or they may revert to the random orientation of domains.*

When electrons are paired in an orbital, their opposite magnetic moments create opposite magnetic fields that cancel each other: substances with all electrons paired are neither paramagnetic nor ferromagnetic. They exhibit only diamagnetism and are said to be diamagnetic. For example, argon has a ground state electron configuration of $1s^22s^22p^63s^23p^6$, where each subshell is full and each orbital therein contains a pair of electrons with opposite spins. Hence, a sample of argon is diamagnetic.

Paramagnetic and diamagnetic materials do not act as permanent magnets. A magnetic field is required to align the magnetic moments and make them magnetic. The magnitude of paramagnetism can be measured by weighing a sample with a highly sensitive balance and then weighing it again with a strong magnet just below the sample. A sample that is attracted to the magnet appears heavier because the magnet attracts it downward. The increase in apparent weight is proportional to the number of unpaired electrons.

Activity 6: Ionization of Transition Metals

D4.5 Ionic Radii

Ionic radius is *the radius of a sphere representing a cation or an anion*; it can be determined from structures of ionic crystals.

Cations have fewer electrons than the uncharged atoms from which they are derived. Hence, there is less electron-electron repulsion (that is, larger Z_{eff}), which makes a cation's radius smaller than the corresponding uncharged atom's radius. For example, the atomic radius of Al ($[\text{Ne}]3s^23p^1$) is 143 pm, which is more than twice as large as the 68 pm ionic radius of Al^{3+} ([Ne]). Often, as in the case of Al, formation of a cation involves removal of all electrons from the outermost shell of an atom, which means the remaining electrons are in a smaller shell—another reason why cations are smaller than the atoms from which they form.

For the same element, cations with larger positive charges are smaller than cations with smaller charges. For example, V^{2+} has an ionic radius of 93 pm, while that of V^{3+} is 78 pm. (An uncharged V atom has an atomic radius of 135 pm.)

Anions have more electrons and therefore greater electron-electron repulsion (that is, smaller Z_{eff}) than the neutral atoms from which they are derived. Thus, an anion's radius is larger than the parent atom's radius. For example, the ionic radius of S^{2-} ($[\text{Ne}]3s^23p^6$) is 170 pm, larger than the 104 pm atomic radius of S ($[\text{Ne}]3s^23p^4$).

Periodic trends in radii of a set of anions (or cations) with the *same* charge are similar to the atomic-radius trends. For instance, proceeding down a group, radii of 1+ cations generally increase as atomic number increases, corresponding to the increase in the principal quantum number, *n*.

For isoelectronic species (ions or atoms with the same electron configuration, Section D4.3), the greater the nuclear charge (number of protons), the smaller the atomic/ionic radius. This implies that isoelectronic anions are larger than the neutral atom which is larger than the cations.

In Days 2 and 3 and above, we have discussed atomic structure and electron density as well as periodic trends in effective nuclear charge, size of atoms, ionization energies, and electron affinities. All of these are central to understanding properties and chemical reactivity of the elements. Next, we apply those ideas to the noble gases and to metals.

Applying Core Ideas: Two Similar Atoms, Two Very Different Substances

Section D1.5 introduced the idea that atoms, molecules, and oppositely charged ions attract and that their potential energy can be described by a curve that starts at zero when the particles are far apart, falls to a minimum, and increases when the particles are very close together. The depth of the minimum in such a curve can be related to physical properties such as boiling points, because atomic-level particles gain energy as temperature increases.

Consider the boiling points of the first five noble gases in the table below.

Noble Gas	Atomic Number	Atomic Radius (pm)	Boiling Point (K)
He	2	31	4.22
Ne	10	68	27.1
Ar	18	91	87.4
Kr	36	108	119.9
Xe	54	126	165

Based on the boiling point data, for which noble gas is the attraction between particles greatest? Which noble gas has the deepest minimum in its curve of potential energy vs distance between atoms? In your notebook, answer these questions. Then use one set of axes and sketch the potential-energy curve for each of the five noble gases in the table, describe the curves in words and explain why you drew the curves as you did.

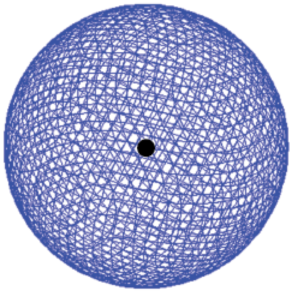
Based on the experimental data and the curves you drew, correlate the size of the attraction between atoms with the number of electrons and the size of each atom. Write several sentences in your notebook describing the correlation.

Now consider iron, which has atomic number 26 and atomic radius 126 pm (the same radius as Xe, but fewer electrons). Based on this information, sketch the potential energy curve for iron atoms on the graph you made for the noble gases. Describe the curve in words and explain why you drew the curve as you did.

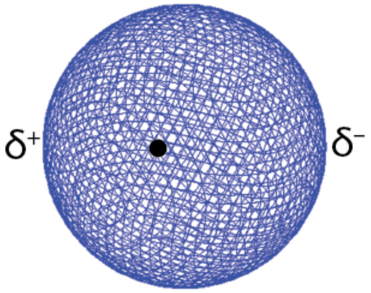
Does what you predicted for iron make sense?

D4.6 Forces Between Atoms

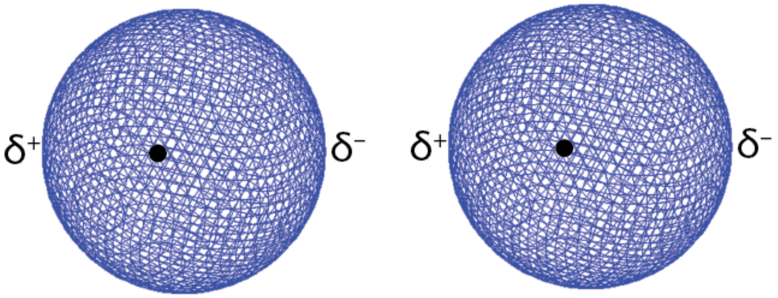
Based only on experimental data for noble gases, one might predict that iron would be a gas at room temperature, but iron is a solid. Attractive forces between iron atoms must be a lot stronger than attractive forces between noble-gas atoms. To make sense of the difference between xenon and iron, we need a better model for forces between atoms.



(a) On average a xenon atom's electron density is symmetric around its nucleus.



(b) The xenon atom's electron density can briefly shift to the right. This forms a dipole with excess negative charge on the right side and excess positive charge on the left.



(c) If a second Xe atom is nearby, the second atom's electron density is affected by the unsymmetric electron density of the first atom. The second atom is induced to becom a dipole. The two dipoles attract because excess negative charge in the left dipole is close to excess positive charge in the right dipole.

Figure 4. *Simplified explanation of attraction between two Xe atoms.*

Let’s begin by thinking about attractions between xenon atoms. On average the electron density distribution of the 54 electrons surrounding a xenon nucleus is spherically symmetric. That is, no matter which direction you go from the nucleus, the electron density is the same at the same distance from the nucleus. However, there can be very brief deviations or fluctuations from this average. In 1928 German-American physicist Fritz London used quantum mechanics to show how such fluctuations could lead to attractive forces between atoms and other atomic-scale particles.

Here is a simplified explanation using a Xe atom as an example. Consider a fluctuation in which there is slightly more electron density on one side of the nucleus than on the other. Such a brief deviation creates a **dipole**, *a distribution of electric charge where one side is more positive and the other side is more negative*. The dipole only occurs for an instant and is therefore called an instantaneous dipole. This is shown in Figure 4, parts a and b, where δ^+ and δ^- indicate tiny fractions of the charge of an electron.

If a second Xe atom is close to the first one when the instantaneous dipole forms, for example, on the right of the first one as in Figure 4, part c, the excess negative charge on the right of the first Xe atom repels the electrons on the second Xe atom. This forms a second dipole, again for only an instant. The second dipole is said to be induced by the first one. The positively charged end of the second dipole is attracted to the negatively charged end of the first dipole. For the instant that the dipoles exist, there is a weak attraction between the two atoms.

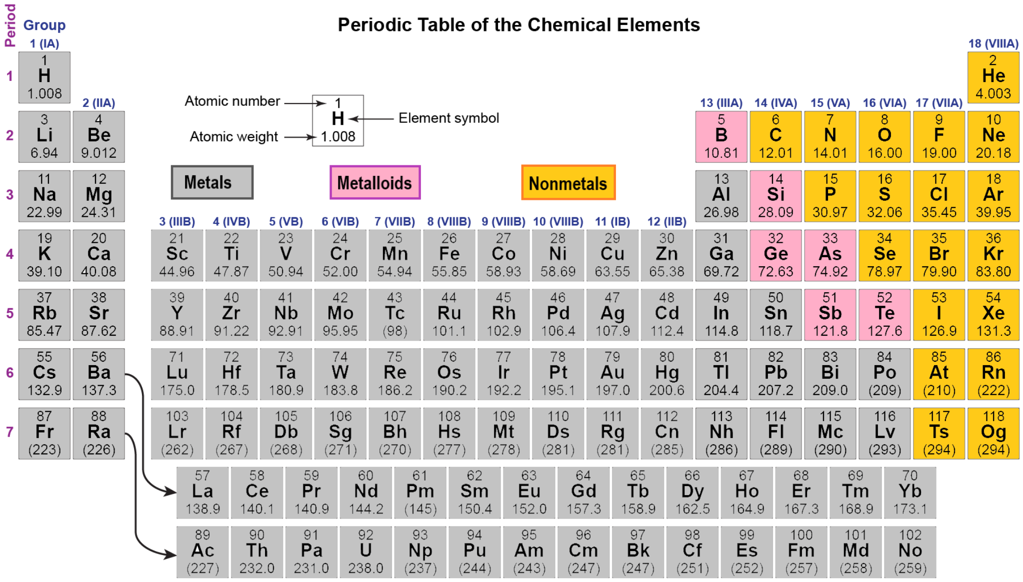
These *weak attractive forces due to instantaneous fluctuations in electron density* are called **London dispersion forces**; we will often refer to them as **LDFs.** LDFs are present between all atomic-scale particles: atoms, molecules, and ions. The size of the attractive force depends on the number of electrons in a particle and how easily the electron density distribution can be distorted from its average shape.

Activity 7: LDFs and Noble Gas Boiling Points

D4.7 Metals

Based on iron’s boiling point of 3135 K (2862 °C), the forces between iron atoms must be much greater than just LDFs. What you have already learned about atomic structure, effective nuclear charge, and valence electrons can be used to make sense of the much larger forces that attract iron atoms, as well as atoms of other metals.

Metals, which include most of the elements in the periodic table (Figure 5), *have characteristic macroscopic properties: they conduct heat and electricity well when they are solids or liquids; they have lustrous (metallic-looking) solid surfaces; and they deform, rather than shatter, when hammered (they are malleable)*. Many metals are hard, quite strong, and useful as construction materials. What gives rise to these characteristics?



Period	Group 1 (IA)	2 (IIA)	3 (IIIB)	4 (IVB)	5 (VB)	6 (VIB)	7 (VIIB)	8 (VIIIB)	9 (VIIIB)	10 (VIIIB)	11 (IB)	12 (IIB)	13 (IIIA)	14 (IVA)	15 (VA)	16 (VIA)	17 (VIIA)	18 (VIIIA)
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (267)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (278)	110 Ds (281)	111 Rg (281)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (290)	116 Lv (293)	117 Ts (294)	118 Og (294)
			57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1		
			89 Ac (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)		

Figure 5. *In this periodic table metals are colored gray, metalloids (intermediate between metals and nonmetals) are colored pink, and nonmetals are colored gold.*

Metallic substances are made of atoms whose valence electron(s) can be removed with relatively low quantities of energy; that is, elements with relatively low ionization energies. Valence electrons of metals experience lower effective nuclear charge than valence electrons of nonmetals; hence, metals tend to form positive ions and nonmetals tend to form negative ions.

In a metallic solid, atoms are packed closely (Figure 6). One model describes solid metals at the atomic scale as atoms surrounded by mobile valence electrons—a so-called "sea" of electrons. Each "atom" consists of the nucleus and core electrons; that is, a positively charged ion that has lost all its valence electrons. The loosely-bound valence electrons are shared (delocalized) among many different atoms. *Electrostatic attractions between the sea of shared valence electrons and the metal ions* is known as **metallic bonding**. The strength of metallic bonding increases as the number of valence electrons shared in the electron sea increases.

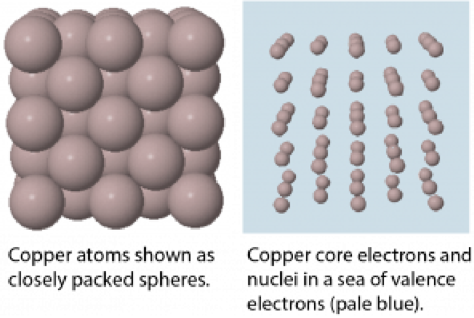


Figure 6. Models of solid copper. *In solid copper Cu atoms are packed closely in a 3-D cubic pattern (left). Metallic bonding involves a sea of valence electrons surrounding the nucleus and core electrons of each copper atom (right).*

Because the valence electrons are delocalized over many metal atoms, if one atom moves relative to others, the attraction between valence electrons and atomic cores remains; that is metallic bonding is not specific to a particular direction. This characteristic accounts for many of the observed physical properties of metals.

Activity 8: Metallic Bonding

Day 4 Pre-Class Podia Problem: Chemical Combinations

This Podia problem is based on today's pre-class material; working through that material will help you solve the problem.

When nonmetals combine with other nonmetals, compounds form with subscripts that are small whole numbers, such as CO and CO_2. When metals combine with nonmetals, formulas of compounds are analogous, such as $FeCl_2$ and $FeCl_3$. When metals combine with other metals, however, they form alloys, substances that have metallic properties but can consist of many different compositions. For example, sodium and potassium can form alloys in which the ratio of sodium atoms to potassium atoms varies from all sodium to all potassium. Thus, if you wrote a formula for sodium-potassium alloy as Na_xK, x could have any value from zero to infinity.

Think about why metals should be different in this way. Then write an explanation for the different behavior.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

1.5: Day 5- Ionic Compounds; Covalent Bonding

5

Day 5: Ionic Compounds; Covalent Bonding

Applying Core Ideas: Two Substances, Some Similarities, Some Big Differences

calcium fluoride

iron

Compare iron, which melts at 1811 K (1538 °C), and calcium fluoride, which melts at 1691 K (1418 °C). Are the forces between atomic-level particles similar in iron and calcium fluoride? Write in your notebook an explanation of your answer to this question.

Consider some other properties of iron and calcium fluoride.

Iron has typical metallic properties: pure solid iron has metallic luster, is malleable, and conducts electricity.

Calcium fluoride has significantly different properties: as a solid it is brittle, does not look metallic, and does not conduct electricity; when molten, calcium fluoride does conduct electricity though.

It appears that these two substances have similar attractions between atomic-level particles, but quite different properties. We need a better atomic-scale model to make sense of these differences.

D5.1 Ionic Compounds

In metals, which have low effective nuclear charges (and low ionization energies), it is relatively easy to form positive ions within a sea of electrons so that attractions among the ions and the electrons hold the atoms together. What happens when an atom with a low ionization energy interacts with an atom with a large negative electron affinity? In such a case, transfer of one or more electrons from the atom with the low ionization energy to the one with the high electron affinity can be energetically favorable. For example, consider transfer of an electron from a Li atom to a F atom to form a cation and anion close together: an *ion pair*, $Li^+F^–$.

Activity 1: Analyzing Formation of an Ion Pair

From the activity above, you've worked out that the formation of the ion pair is associated with a negative ΔE: the joined ion pair is *lower in total energy* (*more stable*) than the two atoms from which it formed.

The gain and loss of electron(s) in forming an ion-pair typically results in a full octet for the cation and anion. For example:

$$\mathrm{Na}([\mathrm{Ne}]3s^1) + \mathrm{Cl}([\mathrm{Ne}]3s^2 3p^5) \longrightarrow \mathrm{Na}^+([\mathrm{Ne}]) + \mathrm{Cl}^-([\mathrm{Ar}])$$

$$\mathrm{Mg}([\mathrm{Ne}]3s^2) + \mathrm{O}(1s^2 2s^2 2p^4) \longrightarrow \mathrm{Mg}^{2+}([\mathrm{Ne}]) + \mathrm{O}^{2-}([\mathrm{Ne}])$$

$$\mathrm{Ca}([\mathrm{Ar}]4s^2) + 2\mathrm{F}(1s^2 2s^2 2p^5) \longrightarrow \mathrm{Ca}^{2+}([\mathrm{Ar}]) + 2\mathrm{F}^-([\mathrm{Ne}])$$

When a large number of ions form, anions and cations form a structure, called an ionic crystal lattice, where there are equal numbers of anions and cations (so there is zero total electric charge); in the lattice each anion has several cations as its nearest neighbors, and each cation has several anions as its nearest neighbors (see example in Figure 1). This arrangement maximizes anion-cation attractions (smaller *r* results in lower Coulomb's law energy) and minimizes anion-anion and cation-cation repulsions (greater *r* between anions and between cations). *A compound made up of anions and cations* is called an **ionic compound** and *the overall attraction making an ionic crystal lattice stable* is called **ionic bonding**.

Figure 1. *Ionic crystal lattice. Cations (smaller spheres) and anions (larger spheres) are arranged so that there is a net attraction that makes the collection of ions stable. Move the slider to change the diameters of the ions and show lines indicating the lattice. (This is a small section of the lattice, which extends millions of times farther in all three dimensions.)*

For example, when sodium cations (Na^+) and bromide anions (Br^-) come together, the crystal lattice of the compound sodium bromide, Figure 1, contains one Na^+ (green) for each Br^- (violet). The chemical formula representing the part of the lattice shown in Figure 1 is $Na_{75}Br_{75}$ because there are 75 Na^+ and 75 Br^- ions. The actual crystal is much larger so the subscripts in the formula of a real crystal would be huge. A **formula unit** is *a group of chemical symbols that indicates the smallest whole number ratio of ions of each kind that make up the substance*, and is typically used as the formula for ionic compounds. Thus, the formula unit (and the formula) for sodium bromide is NaBr.

All chemical substances are overall electrically neutral. Thus, in an ionic compound, the positive charge from all the cations must equal to the negative charge from all the anions. In other words, the subscripts in a formula unit of an ionic compound must result in equal quantities of positive and negative charges. If we know the charges of the ions, then we can write the formula.

Activity 2: Predicting Chemical Formulas

Some ions consist of a group of atoms with an overall charge. Examples are sulfate dianion, SO_4^{2-}, dihydrogen phosphate anion, $H_2PO_4^-$, and ammonium cation, NH_4^+. It is quite useful to be able to recognize such polyatomic ions and their charges. If you need to refresh your knowledge of polyatomic ions, use the reference table as you do the next two exercises.

D5.2 Lattice Energy

Refer back to Activity 1. The third step involved bringing one Li^+ ion close to one F^- ion, which lowered the energy. When a large number of oppositely charged ions are brought close together to form a crystal lattice (Figure 1), the energy is lowered even more, because more ions are close together in a structure where attractive forces predominate over repulsive forces.

The **lattice energy** of an ionic compound is defined as *the decrease in energy when the ionic crystal lattice forms from the separated ions*. Lattice energy can be calculated using a modified form of Coulomb's law; some calculated lattice energies are in Table 1. (Note that because lattice energy is defined as a *decrease* in energy, a large positive lattice energy corresponds to a large negative ΔE, that is, a very stable (low energy) ionic solid.)

Substance	Lattice Energy (kJ/mol)
NaI	682
CaI_2	1971
MgI_2	2293
NaOH	887
Na_2O	2481
$NaNO_3$	755
$Ca_3(PO_4)_2$	10,602
$CaCO_3$	2804

Table 1. Representative calculated lattice energies. Data from *CRC Handbook of Chemistry and Physics* (2004).

Lattice energies have a wide range of values depending on which ions make up a compound. Consider, for example, why the lattice energy increases as you go from NaI, to CaI_2, to MgI_2 (first three rows in Table 1).

According to Coulomb's law,

$$E_{\mathrm{p}} = k_e \frac{Q_1 Q_2}{r}$$

the lattice energy is directly proportional to the sizes of the charges on the ions and inversely proportional to the distance between them (the sum of their ionic radii). Thus, we can compare NaI, CaI_2, and MgI_2 with respect to magnitudes of charges and sizes of ions.

Magnitudes of Charges: NaI consists of 1+ ions and 1− ions; CaI_2 and MgI_2 consist of 2+ ions and 1− ions.

Because the magnitude of Q_1Q_2 is larger, the lattice energies of CaI_2 and MgI_2 should be larger than for NaI.

Sizes of ions: All three compounds contain I^- anions, so we only need to compare cation radii.

The radii of Ca^{2+} and Na^+ are similar. This can be estimated from the periodic table: Na^+ and Ca^{2+} are both smaller than K^+, Na^+ because it is above K^+ in the periodic table, and Ca^{2+} because it is isoelectronic with K+ but has more protons in the nucleus. It is reasonable to assume that the radii are not very different, and the ionic-radius table confirms this: Na^+ 116 pm; Ca^{2+} 114 pm. Thus, r is not a major factor affecting lattice energy for NaI and CaI_2.

The radius of Mg^{2+} is significantly smaller than for Ca^{2+} (and Na^+) because Mg is directly above Ca in the periodic table and the ions have the same charge. Thus, MgI_2 should have a larger lattice energy than CaI_2, which is consistent with the values in the table.

Activity 3: Comparing Lattice Energies

When looking at Table 1, you may have noticed that lattice energies for compounds containing 2+ and 2− ions are nearly quadruple those for similar compounds containing 1+ and 1− ions of similar size (compare $NaNO_3$ and $CaCO_3$). This observation is consistent with the general rule that lattice energies are highest for substances with small, highly charged ions.

D5.3 Properties of Ionic Compounds

The physical and chemical properties of an ionic compound are determined by the *ions* that that constitute the compound. The compound's properties are quite different from the properties of the elements that reacted to form the compound. For example, both sodium and chlorine react with water, but sodium chloride (NaCl) dissolves in water without reacting. In other words, sodium *ions* and chloride *ions* do not react with water, but sodium *atoms* and Cl_2*molecules* do.

https://mediaspace.wisc.edu/id/0_zns...&st=137&ed=154

Figure 2. *Sodium reacts vigorously with water, producing a gas and making the water basic (as indicated by the pink color of phenolphthalein in the water). Adding sodium ions to water, in the form of table salt, NaCl, is much less exciting!*

Ionic compounds have many physical properties in common:

- they usually have melting points and boiling points well above room temperature.
- they are crystalline solids with distinct crystal shapes
- they are brittle, will shatter if struck by a hammer, and can easily be cleaved (cleave means to break along smooth planes, as shown in this video).
- they are electrical insulators when solid but conduct electricity when molten (liquid). (See this video.)
- when an ionic compound dissolves in water, the solution conducts electricity much more effectively than pure water.

Because all ionic compounds have similar properties, it is useful to be able to identify an ionic compound from its chemical formula. In general, ionic compounds contain cations of metals from the left side of the periodic table and anions of nonmetals from the right side of the periodic table. If a compound's chemical formula contains a polyatomic ion, then the compound is an ionic compound.

The properties of ionic compounds can be interpreted in terms of ions. In the solid phase, ions are essentially fixed in their positions in a crystal lattice. Lattice shapes depend on the number and type of ions in the formula, but each lattice has a distinctive shape that results in the lowest energy (maximum lattice energy). Because distances between ions are small, lattice energies are large. It requires a lot of energy to overcome attractions among the ions, making the crystal hard. The lattice shape is related to the shape of the macroscopic crystal. When a crystal cleaves, the cleavage planes are parallel to planes in the crystal lattice. (To see why, watch this video.)

When an ionic solid melts, the anions and cations are free to move randomly among each other. Although the average minimum distance between ions is still small (just a little larger than in the crystalline solid), some anions may be next to other anions and some cations near other cations. Hence, the electrostatic attractions are not as strong and the electrostatic repulsions are greater than in the solid phase; that is, part of the lattice energy needs to be overcome before an ionic compound melts.

When an ionic compound boils to form a gas, the ions continue to move randomly but also are so far apart that their electrostatic attractions are negligible. All of the lattice energy must be overcome for an ionic compound to boil.

Electric current is the movement of electric charge from one place to another. Electric charge is carried by any moving charged particle. In a liquid ionic compound, where ions can move independently, electric charge is conducted by ions. When a solid ionic compound dissolves in water, the ions separate and can move independently throughout the solution. Movement of ions conducts electricity through the solution, just as it does in the molten liquid.

Activity 4: Explaining Properties of Ionic Compounds

Activity 5: Reflection

In your course notebook, write down as many properties of metals and of ionic compounds as you can remember. Then check to make certain your list is complete. Then write your explanation for each property in terms of ions, crystal lattices, attractive forces, and energy. Make sure your list provides a good summary you can use to review later for an exam.

Applying Core Ideas: Comparing Hydrogen Atoms and Helium Atoms

The boiling point of helium is 4.22 K (−268.93 °C), a consequence of very weak London dispersion forces (LDFs) between He atoms. Even when two He atoms are only a short distance apart, there is very little attraction.

When two H atoms get close there is a much stronger attraction: the two atoms become a H_2 molecule by forming a covalent chemical bond. For the H_2 molecules to have enough energy to break that bond, separating the two H atoms, the temperature needs to be similar to the temperature of the Sun (5778 K)!

Why do He atoms behave so differently from H atoms? We need to refine our models of structure and energy still further. This is done in the next sections.

D5.4 Covalent Bonding: Molecular Orbitals

Activity 6: Covalent Chemical Bonds

In your notebook, write a few sentences describing your understanding of covalent chemical bonds. What constitutes a covalent bond? How does it form? What holds the atoms together in a molecule? As you work through this section, make additional notes to review later.

If you wrote that a covalent bond involves sharing electrons between atoms, that's a good start. But how does sharing electrons hold atoms together?

Just as a balance of Coulomb's-law attractions and repulsions affects the electron(s) and nucleus in an atom, coulombic interactions affect electrons and nuclei in a molecule. The major difference is that in a molecule, each electron interacts with two or more nuclei; this additional interaction provides the stabilization that allows the molecule to exist. If a collection of separate atoms were more stable than a molecule, the molecule would simply fall apart into individual atoms.

Just as electron(s) occupy stable atomic orbitals around a single nucleus in an atom, electrons occupy stable orbitals around multiple nuclei in a molecule. *An orbital that extends over two or more atomic nuclei* is called a **molecular orbital (MO)**; in the MO model, a molecular orbital forms when atomic orbitals (AOs) overlap (or interpenetrate).

To understand this better, think about the formation of a H_2 molecule from two ground-state hydrogen atoms (labeled as H_A and H_B in Figure 3) . When H_A is sufficiently far away from H_B—for example, more than 400 pm apart (top of Figure 3)—its electron (e_A) occupies the lowest-energy atomic orbital, the 1*s* orbital. The same is true for H_B.

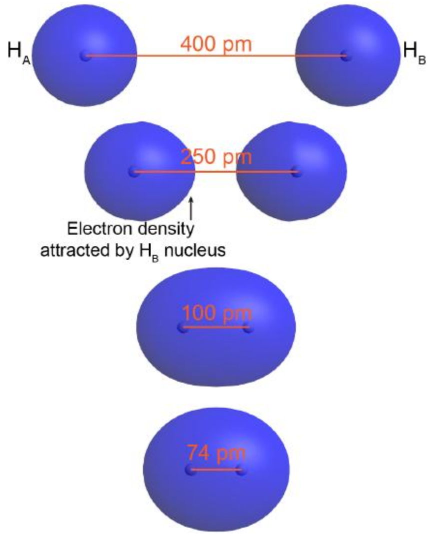


***Figure 3**. Evolution of electron density as two H atoms (H_A and H_B) approach each other. The electron densities are shown as boundary-surface plots.*

When H_A and H_B are closer, e_A begins to experience significant Coulomb's-law attraction towards H_B's nucleus. For example, at 250 pm apart (Figure 3, second from top) the orbital occupied by e_A is no longer spherical around H_A's nucleus but rather is distorted—there is more electron density on the side toward H_B. Although H_A's nucleus attracts e_A more strongly than H_B's nucleus does (because H_B's nucleus is screened by e_B), there is a net increase in the positive charge interacting with e_A. This lowers e_A's potential energy. The same argument applies to e_B.

When the two atoms are even closer—for example, 100 pm apart—e_A and e_B become *delocalized* over both nuclei: both electrons occupy a *molecular orbital*, which surrounds both nuclei. Notice that in this H_2 molecular orbital, there is significant electron density *in between* the two nuclei, attracting both nuclei. This *lowers* the overall energy relative to the energy of the two separate hydrogen atoms.

As the two atoms get closer still, there is a minimum in the overall energy for the molecule. For H_2 the minimum is at 74 pm (bottom of Figure 3). At internuclear distances smaller than 0.74 Å, the energy rises again due to increasing nucleus-nucleus repulsion. In a ground-state H_2 molecule *the distance between nuclei of two bonded atoms*, the **bond length**, is 74 pm.

Figure 4 allows you to explore how the electron density changes as two H atoms interact to form H_2 (or how an H_2 molecule dissociates into two separate H atoms). The blue dot on the potential energy curve shows the corresponding internuclear distance (bond length) and potential energy of the molecule. The ground-state H_2 molecule is more stable than the two separated ground-state H atoms. (The energy of the separated atoms is set to be 0 kJ/mol in Figure 4.) The magnitude of the energy reduction, 436 kJ/mol, is called the **bond energy**, *the energy required to break the bond, completely separating the atoms*.

***Figure 4**. A graph of energy versus distance between two hydrogen atoms shows minimum energy at a separation of 74 pm (the bond length). At the minimum, the energy is 436 kJ/mol less than the energy of the separated atoms; this is the bond energy.*

What we have just described is one of two ways that the two H 1*s* atomic orbitals can overlap/combine to form an H_2 molecular orbital. It occurs when the two 1*s* atomic orbitals are *in-phase*. **In-phase** means that *wave functions describing electrons A and B both have maxima in the same direction at the same time.*

The second possibility is that the two overlapping 1*s* atomic orbitals are **out-of-phase**, which means that *one atomic wave function is positive and the other atomic wave function is negative. This is* shown in Figure 5, where the two phases (positive and negative) are shown in green and yellow.

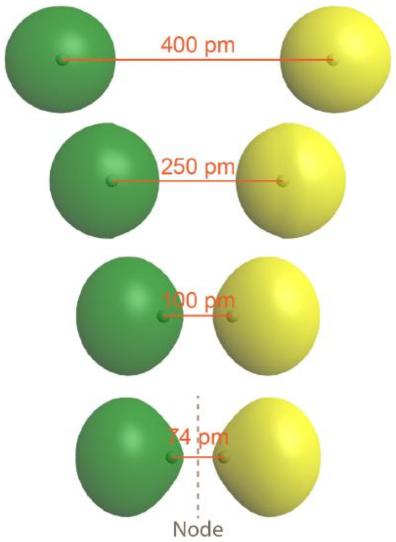


***Figure** 5. The out-of-phase combination of two H 1s atomic orbitals to form an H_2 molecular orbital. The electron densities are shown as boundary-surface plots.*

The result is a molecular orbital with a *node* halfway between the two H atoms. (The node, where electron density is zero, is a plane perpendicular to a line connecting the two nuclei, the internuclear axis). Note that the bottom depiction in Figure 5 is *a single molecular orbital* with one node, just as the bottom depiction in Figure 3 is a *single* molecular orbital but without a node.

As is true of atomic orbitals, a molecular orbital with more nodes has higher energy, which makes sense because the presence of the node reduces electron density between the nuclei (compared to the electron densities of the individual atoms). This reduction in electron density results in less electron-nucleus attraction than if the atomic orbitals had not interacted at all.

D5.5 Molecular Orbital (MO) Diagram

When two H atoms come together to form H_2, both in-phase overlap and out-of-phase overlap of 1*s* atomic orbitals are possible and both occur. Hence, *two* 1*s* atomic orbitals (AOs) overlap to form *two* molecular orbitals (MOs). This is true in general: the number of MOs formed equals the total number of AOs from which they are derived.

A **MO diagram** *shows the relative energies of MOs and AOs* and indicates which MOs form from overlap of which AOs. For example, Figure 6 shows the MO diagram of the H_2 molecule. *A MO lower in energy than the AOs from which it is derived* is called a **bonding MO**. An electron occupying this bonding MO increases the stability of the bond (strengthens the bond). The H_2 bonding MO is labeled “σ_{1s}“; the subscript “1*s*” designates that it is derived from the 1*s* AOs.

A MO higher in energy than the AOs from which it is derived is called an **antibonding MO**—an electron occupying this MO decreases the stability of the bond (weakens the bond). The H_2 antibonding MO is labeled as “σ^*_{1s}.”; the “*” denotes that it is an antibonding MO.

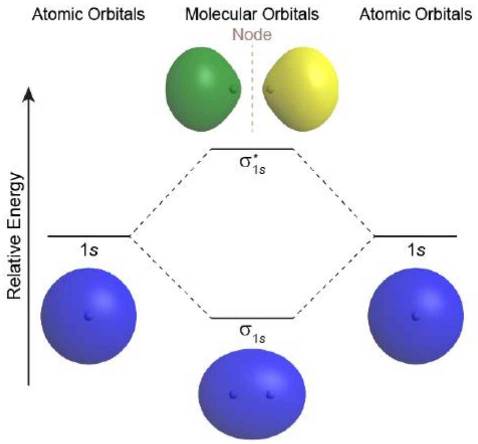
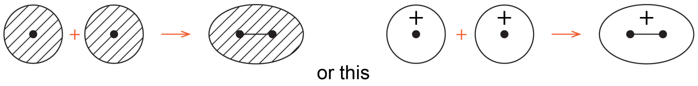


Figure 6. *Molecular-orbital energy-level diagram for a H_2 molecule. Electron densities of the atomic and molecular orbitals are shown as boundary-surface plots. The vertical axis is relative energy. Horizontally, atomic orbitals of the two separated H atoms are on either side and the molecular orbitals of the H_2 molecule is in the middle. This is typical for molecular-orbital diagrams.*

The Greek letter in the MO labels denotes the symmetry of the MO with respect to the internuclear axis (the line connecting the two nuclei). Greek letters σ, π, δ are analogous to the Roman letters *s*, *p*, *d* that designate shapes of atomic orbitals. *A MO that is cylindrically symmetric* is called a **sigma MO** and designated σ. (Cylindrically symmetric means that if you stood the molecule on end and spun it around the internuclear axis it would look the same all the time—just as a cylinder would look if you stood it on end and spun it).

Chemists often use simple 2D drawings to show both the shape and phase of AOs and MOs. So the sphere of a 1s AO is drawn as a circle and its phase is indicated by two different colors or shading/no shading or plus/minus sign. For example, formation of the σ_{1s} MO from two 1*s* AOs can be drawn as:



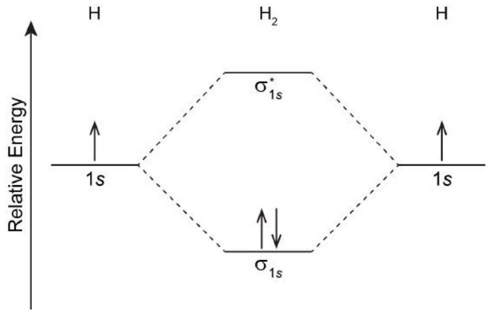
where the black dots represent H nuclei, the circles with hatching (or + sign) represent boundary-surface plots of H 1*s* AOs, each with positive phase, and the oval with hatching (or + sign) represents the H_2 σ_{1s} MO, also with positive phase.

D5.6 Electron Configurations and Bond Order

Just as an atom has an electron configuration, so does a molecule. The molecular ground-state electron configuration can be obtained by filling MOs, facilitated by MO diagrams such as the one shown in Figure 6, following rules similar to those for atomic electron configurations:

- Sum all the electrons from all the atoms that make up the molecule.
- Each MO can hold *at most* two electrons. (Two electrons occupying the same orbital must have opposite spin.)
- In the MO diagram the MOs are arranged in order of increasing energy.
- Add electrons to the lowest-energy MO first and then to successively higher-energy MOs (Aufbau principle)
- If two or more MOs have the same energy (are degenerate), apply Hund’s rule: assign one electron to each degenerate MO before pairing any electrons

For the H_2 molecule: there is one electron from each H atom, so there are two electrons in H_2. There is only one lowest-energy MO, σ_{1s}, therefore the two electrons, with opposite spin, will fill it. The ground state electron configuration of H_2 is $(\sigma_{1s})^2$.



$$\sigma_{1s} \tag{1.5.1}$$

Activity 7: Molecular Orbitals and Electromagnetic Radiation

The two electrons in the σ_{1s} MO, which are shared between the two H atoms, form a covalent bond. The configuration $(\sigma_{1s})^2$ indicates a *single, sigma* covalent bond. In general, a **covalent bond** involves *overlap of two or more AOs that leads to increased electron densities close to atomic nuclei so that the electrons' energies are lowered*. Electrons are shared between pairs of atomic nuclei, or more widely among several nuclei within a molecule.

In some cases more than two electrons can be shared between two nuclei. This gives rise to the idea of **bond order**, which is *the number of shared electron pairs between two atoms*. Using a MO diagram, bond order can be defined as:

$$\text{Bond Order} = \frac{1}{2}\left(n_{\text{bonding e}^-} - n_{\text{antibonding e}^-}\right) = \frac{1}{2}(n_{\text{b}} - n_{\text{a}})$$

where $n_{\text{bonding e}^-}$ is the number of electrons in bonding MOs and $n_{\text{antibonding e}^-}$ is the number of electrons in antibonding MOs. There is a factor 1/2 because two shared electrons make one bond. In general a greater number of shared electrons means a stronger bond, so the larger the bond order is, the stronger the bond is.

Activity 8: Molecular Orbitals for He

Day 5 Pre-Class Podia Problem: Melting Points of Salts

This Podia problem is based on today's pre-class material; working through that material will help you solve the problem.

The formulas and melting points of four salts are listed below. All four compounds have the same crystal lattice as NaCl. Write a clear, concise explanation of the differences in melting points using scientifically appropriate language and including any relevant data.

NaF 996 °C NaCl 801 °C KCl 770 °C CaO 2572 °C

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

1.6: Day 6- Molecular Orbitals; Lewis Structures

6

Day 6: Molecular Orbitals; Lewis Structures

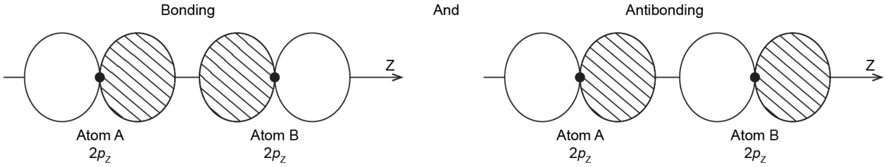
D6.1 Second-Row Diatomic Molecules

Let’s consider some slightly more complex examples of molecular orbitals. F_2, O_2, and N_2 are diatomic molecules formed by elements from the second row of the periodic table. These molecules contain many more electrons than H_2, and their molecular orbitals are derived from *p* atomic orbitals as well as *s* atomic orbitals.

Additional Practice

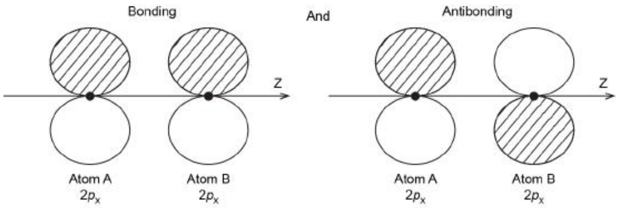
Now think about what happens when two atoms containing 2*p* atomic orbitals approach each other. Assume that the internuclear axis is the *z* axis. This means that the $2p_z$ atomic orbitals are aligned along the internuclear axis while the $2p_x$ and $2p_y$ atomic orbitals are oriented perpendicular to the internuclear axis.

When the two atoms approach, the bonding and antibonding overlap of the two $2p_z$ atomic orbitals occurs along the internuclear axis (*z* axis):



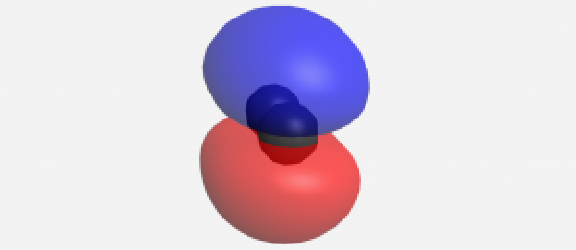
MOs derived from these two combinations are labeled σ_{2px} and σ^*_{2px}. *If you don’t understand why these MOs are have the label σ, review* Section D5.5.

It is also possible to make bonding and antibonding combinations from the two $2p_x$ AOs and from the two $2p_y$ AOs. Here is a diagram for the two ways the $2p_x$ AOs can overlap. Notice that the orbitals overlap side-by-side, not end-on, because the $2p_x$ AOs are aligned perpendicular to the internuclear axis (*z* axis).



Additional Practice

When two 2*p* AOs overlap side-by-side, the bonding MO formed is not symmetric with respect to rotation around the internuclear axis. Thus, the bond formed is not a σ bond. If you look down the internuclear (bond) axis, the “side view” of the MO looks similar to a 2*p* atomic orbital; this MO is called a π orbital.



When you look along the internuclear axis, a π MO looks like a p AO. π is the Greek letter corresponding to p, which is the reason for designating the MO as π. A π MO has one node (a horizontal plane in this case) that contains the internuclear axis.

Think about all atomic orbitals that are occupied in a fluorine atom, F: 1*s*, 2*s*, $2p_z$, $2p_x$, and $2p_y$. For each pair of AOs (such as 2*s* on atom A with 2*s* on atom B), overlap produces one bonding and one antibonding MO. There is σ and σ^* for 1*s* – 1*s*, 2*s* – 2*s*, and

$2p_z – 2p_z$ overlaps. There is π and π^* for $2p_x – 2p_x$, and $2p_y – 2p_y$ overlaps. These ideas result in the MO energy-level diagram shown here:

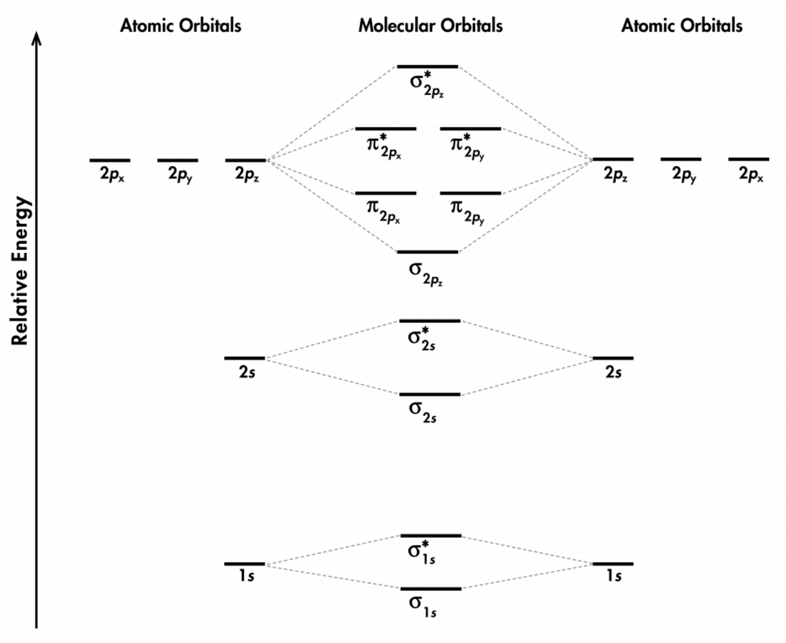


Figure 1. *Molecular orbital energy level diagram for a F_2 molecule.*

From the ten AOs (five from each F atom), ten MOs are formed in F_2. Note that whether a MO is bonding or antibonding is dependent on whether it is lower or higher in energy than the AOs from which it is derived. Hence, even though σ^*_{1s} is lower in energy than σ_{1s}, it is still an antibonding MO.

We also see in Figure 1 that the two π bonding MOs, π_{2px} and π_{2py}, are degenerate (have the same energy). This is because the side-by-side overlap of two $2p_x$ AOs is identical to the side-by-side overlap of two $2p_y$ AOs. They differ only in that π_{2px} and π_{2py} are perpendicular to each other, because the $2p_x$ AO is perpendicular to the $2p_y$ AO. Similar reasoning leads to the conclusion that the π^*_{2px} and π^*_{2py} MOs are also degenerate. Recognizing degenerate MOs is important when applying Hund’s rule to determine molecular electron configurations.

Figure 2 shows the formation of the two perpendicular π bonds as two N atoms approach each other. (The two molecular depictions in the figure represent the same N_2 molecule: one shows the $2p_x – 2p_x$ orbital overlap and the other shows the $2p_y – 2p_y$ orbital overlap.)

Figure 2*. A graph of energy versus distance between two nitrogen atoms. Boundary surface plots are shown for the two degenerate π bonding MOs formed from the in-phase overlap of the $2p_x$ AOs and the in-phase overlap of the $2p_y$ AOs. To watch the bond form, place the slider all the way to the right and then move it step-by-step toward the left.*

Additional Practice

Based on the electron configuration for the F_2 molecule, the π and π^* MOs are all filled; there is no net π bond in the molecule. This is reflected in the bond order calculation: F_2 has a bond order of 1, corresponding to a single σ bond.

D6.2 Bond Length and Bond Enthalpy

Formation of a stable covalent molecule involves sharing electrons between two or more nuclei (the electrons occupy molecular orbitals that increase electron density between nuclei). The **bond length** between any two adjacent nuclei in such a covalent molecule is the *distance between the two nuclei at the minimum energy in a graph of energy versus nuclear separation*. For example, the bond length in a H_2 molecule is 74 pm, as shown in Figure 3.

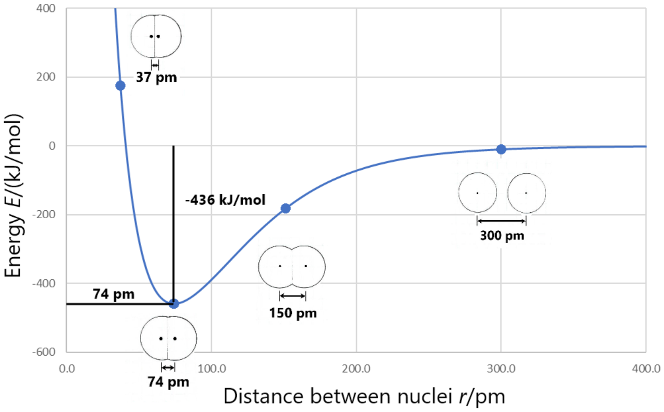


***Figure 3**. The bond length in a H_2 molecule is 74 pm. This is the distance between the two H-atom nuclei at the minimum in the curve of energy versus distance. Bond enthalpy is the energy required to separate two bonded atoms, which is the vertical distance from the minimum in the curve to zero on the graph, 436 kJ/mol.*

Bond enthalpy (also called **bond energy)** is the *enthalpy change when a chemical bond is broken*; that is, when two bonded atoms are completely separated. For example, Figure 3 shows that the bonded hydrogen atoms have energy of −436 kJ/mol relative to the separated hydrogen atoms. This means that the energy of the molecule must be increased by 436 kJ/mol to separate the atoms (break the bond). So the bond enthalpy for H_2 is 436 kJ/mol.

Lengths of single bonds can be roughly estimated by using the covalent radii of the bonded atoms. For example, adding the covalent radius of C (77 pm) to that of O (74 pm), estimates the length of a C—O bond to be 151 pm. This is quite close to the average C—O bond length of 143 pm. (Both of these values are estimates because covalent radii and bond lengths are averaged over many molecules and therefore are not exact for any specific molecule.)

In general, the bigger the atoms are, the longer the bond between them is. For example, consider the following trend in the average C-X bond lengths, where X is a halogen:

C-F	141 pm
C-Cl	176 pm
C-Br	191 pm
C-I	210 pm

Bond lengths are also dependent on bond order. For example, the C—C single bond has an average length of 154 pm, while a C=C double bond is 134 pm long, and a C≡C triple bond has an average length of 121 pm.

Comparisons of the average bond length and bond enthalpy values show a general trend: a covalent bond with a shorter bond length generally has a larger bond enthalpy.

D6.3 Bonding in Molecules with More Than Two Atoms

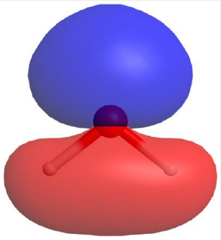
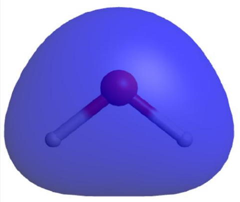
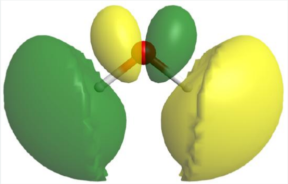
Molecules with three or more atoms have molecular orbitals that span the entire molecule. The MOs are derived from the overlap of AOs from all the atoms in the molecule. Both the MO wave functions and the structure of the energy-level diagram are much more complicated than for diatomic molecules, but mathematical techniques exist for calculating and displaying the electron densities that form chemical bonds. In this course we will not delve deeply into these more complicated cases except to make several general points:

- The number of MOs for a molecule equals the number of AOs on the atoms that make up the molecule.
- The energies of the MOs increase as the number of nodes in the MO increases.
- MOs can extend over the entire molecular structure; they are not necessarily confined to pairs of atoms.

While MOs provide accurate physical information about the molecule, such as energies of the valence electrons involved in a reaction, their visualization does not always provide easy chemical understanding. It is possible to “re-combine” the MOs in such a way that the electron densities are displayed as being localized between pairs of atoms or on individual atoms; this allows us to correlate MO derived electron densities with the more familiar Lewis structures, which represent electrons in chemical bonds as lines between pairs of atoms and electrons on a single atom as dots. We will discuss Lewis structures in more depth on Day 7.

Exercise 6: MOs for Polyatomic Molecules

Some of the molecular orbitals for a water molecule are shown here. Based only on what you know about the appearance of bonding and antibonding orbitals, rank these MOs from lowest-energy to highest-energy. *(Click on each image for a rotatable 3D view of the MO.)*

Activity 1: Reflection

Stop to think about molecular orbitals and bonding. Make a list of the main things you learned as you studied this topic both in today's work and the previous day's work. Your list should provide a summary you can use to review later for an exam.

D6.4 Lewis Structures for Covalent Molecules

Molecular orbitals for molecules with three or more atoms are complicated and hard to draw. Thus, although MOs would convey a more descriptive and accurate picture of electron distribution within a molecule, chemists often rely on simpler diagrams to depict the covalent bonding. It will aid your understanding of chemistry if you can connect these simpler diagrams mentally with the more complete picture given by MOs.

The most commonly used hand-drawn depiction is the **Lewis structure:***a diagram that represents atomic nuclei and core electrons by chemical symbols and valence electrons as dots or lines.* A Lewis structure is built by combining Lewis diagrams (Section D3.4) of the constituent atoms.

Activity 2: Lewis Diagrams

Consider each element listed below. In your course notebook write the electron configuration for an atom of each element, determine the number of valence electrons, and write a Lewis diagram (Section D3.4). How are the Lewis diagrams related to the position of each element in the periodic table?

N C S As O Br F Si H

In Lewis structures, a single covalent bond is drawn as *a pair of electron dots shared between two adjacent atoms*, a **bond pair**. Valence electrons that are not in a bond are shown as *pairs of dots associated with individual atoms*, **lone pairs**. For example:

In the Cl_2 molecule, each Cl atom has three lone pairs and the two Cl atoms share one bond pair. Hence, each Cl atom in Cl_2 has formed an *octet* (is surrounded by eight valence electrons).

For simplicity and clarity, a bond pair is typically represented by a line instead of a pair of dots:

Activity 3: Lewis Structure and Electron Sharing

The Octet Rule

The **octet rule** states that *atoms of main-group elements tend to gain, lose, or share enough electrons to form an octet* (eight valence electrons). Such noble-gas electron configurations with completely filled valence shells are more stable, and therefore should correspond to how the electrons are arranged in a molecule.

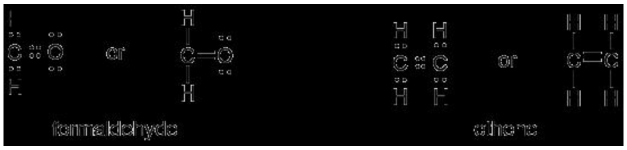
The Lewis diagram for an atom can be used to predict the number of bonds the atom will form. For example, a carbon atom has four valence electrons and therefore requires four more electrons to reach an octet:

It is important to keep in mind that it is impossible to *exceed* an octet for atoms in the second period. This is particularly relevant because you will encounter numerous molecules containing the elements C, N and O.

Finally, because a hydrogen atom needs only two electrons to fill its valence shell, H is an important exception to the octet rule and forms only one bond.

Double and Triple Bonds

Two atoms may need to share more than one pair of electrons to achieve the requisite octet. In other words, the bond order is greater than 1. A **double bond** consists of *two pairs of electrons being shared between two atoms*. For example:



A **triple bond** forms when *three pairs of electron are shared between two atoms*. For example:

Activity 4: Double and Triple Bonds

Write answers to these questions in your course notebook:

Write a Lewis structure for N_2 and a Lewis structure for O_2. Describe the type of bond in each case.

Do the N atoms in N_2 and the O atoms in O_2 follow the rule for number of bonds in Exercise 7?

Use the molecular-orbital energy level diagram in Figure 1 to calculate the bond order for N_2 and for O_2. How do the bond orders relate to the Lewis structures?

D6.5 General Guidance for Drawing Lewis Structures

Often you can draw a Lewis structure based on the number of bonds formed by each kind of atom. in more complicated cases, here is a step-by-step procedure for drawing Lewis structures of molecules and polyatomic ions:

1. Determine the total number of valence electrons by summing the number of valence electrons on all atoms.
    - For a polyatomic cation, subtract one electron for each positive charge.
    - For a polyatomic anion, add one electron for each negative charge.
2. Choose one or more central atoms; a central atom bonds to several other atoms and is usually the atom that forms the greatest number of bonds.
    - Usually the central atom is written first in a chemical formula, such as P in PCl_3.
    - If there are two or more central atoms, connect them using single bond lines.
3. Draw a skeleton structure of the molecule by arranging the other atoms (which are called terminal atoms) around the central atom or atoms.
    - Connect terminal atoms to the central atom(s) by single bond lines.
4. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
5. If there are still valence electrons available, place them on the central atom(s).

6. If the number of electrons around a central atom is less than an octet, rearrange the electrons to make multiple bonds with the central atom(s) until each atom has an octet.

Let’s apply these rules to a simple molecule, ammonia, NH_3.

Here is a more complicated case: ethene (ethylene), C_2H_4.

Exercise 8: Lewis Structures and Valence Electrons

If you were to build a Lewis structure for nitrate ion (NO_3^-), how many electrons would you need to allocate in your structure? (In other words, how many non-core electrons have to be in your structure?)

Exercise 9: Identifying Incorrect Lewis Structures

For each Lewis structure, determine whether the structure is correct. If the structure is incorrect, identify the error made in the representation.

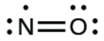
D6.6 Exceptions to the Octet Rule

Some stable covalent molecules contain one or more atoms that do not have an octet. Such molecules fall into three categories.

Odd-electron Molecules

A molecule that contains an odd number of electrons must have at least one electron unpaired and therefore must have an atom with fewer than eight electrons in its valence shell (typically it’s seven electrons). A *molecule with at least one unpaired electron* is called a **free radical**. Nitric oxide, NO, which is produced in internal combustion engines when oxygen and nitrogen react at high temperatures, is an example.

To draw the Lewis structure for an odd-electron molecule, follow the same steps as outlined previously, but recognize that an odd-electron molecule must have less than an octet on some atom. For example, the Lewis structure for NO is:

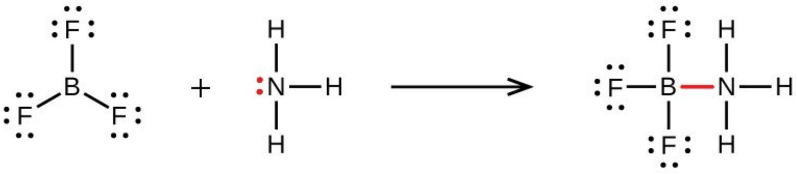


Forming a triple bond would cause either oxygen or nitrogen to exceed an octet, which is a very unlikely electron arrangement.

Molecules with an Incomplete Octet on a Central Atom

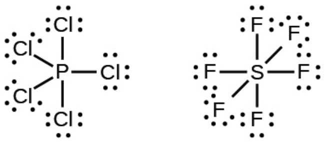
Some molecules contain a central atom that does not have a filled valence shell. Usually, these central atoms are from groups 2 (IIA) and 13 (IIIA). For example, the Lewis structure of beryllium chloride, $BeCl_2$, shows beryllium with only four electrons, and that of boron trifluoride, BF_3, shows boron with only six electrons.

It is possible to draw a structure for each of these molecules where there are double bonds to the central atom and therefore an octet. For example, BF_3 with one B=F double bond would satisfy the octet rule. However, experimental evidence tells us that the bond lengths in BF_3 are closer to B–F single bonds. The observed reactivity of BF_3 is also consistent with less than an octet on boron: BF_3 reacts readily with NH_3, with the lone pair on nitrogen (red) forming a bond (red) that completes the octet on the boron atom:



Molecules with More Than an Octet on a Central Atom

Some Lewis structures show more than four pairs of electrons around the central atom. This usually happens when the central atom is in the third or a higher period ($n \geq 3$). *Molecules with more than an octet around a central atom* are called **hypervalent molecules**. For example, in the Lewis structure for PCl_5, the central phosphorus atom is surrounded by five pairs of electrons. In SF_6, sulfur has six pairs of electrons.

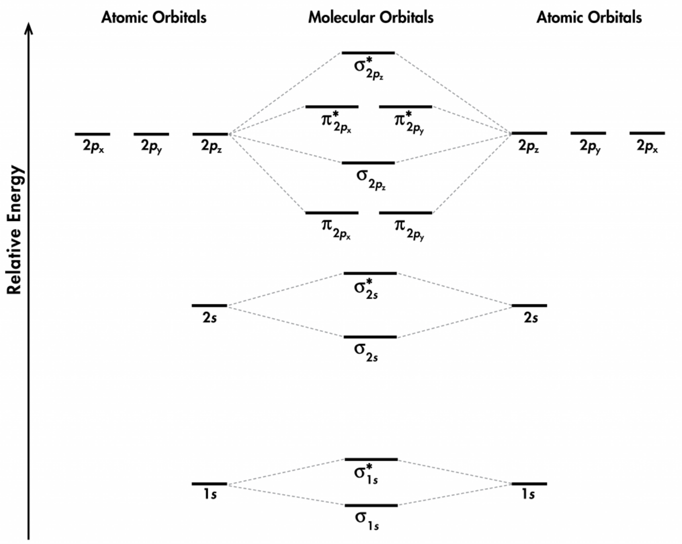


Day 6 Pre-class Podia Problem: Molecular Orbital Energy Levels

This Podia problem is based on today's pre-class material; working through that material will help you solve the problem.

The molecule C_2 is quite unstable and can only be isolated and studied experimentally in the gas phase. Molecular spectroscopy of C_2 reveals that a C_2 molecule in the ground state has no unpaired electrons.

1. Use the MO energy-level diagram in Figure 1 to predict the ground state electron configuration of C_2. Does your result agree with the experimental observation?
2. Consider the MO diagram below. Is this a better diagram than Figure 1 for C_2? Use scientifically appropriate language to explain which diagram is better.



Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

1.7: Day 7- Covalent Molecular Substances; Hydrocarbons

7

Day 7: Covalent Molecular Substances; Hydrocarbons

Applying Core Ideas: Comparing Hydrogen Molecules and Helium Atoms

The boiling point of helium is 4.22 K (−268.93 °C). The boiling point of hydrogen is 20.28 K (−252.87 °C). However, the attractive force between two hydrogen atoms 100 pm apart is almost 5000 times stronger than the attractive force between two helium atoms 100 pm apart.

Think about helium and hydrogen at the atomic scale. Then write in your notebook an explanation for the fact that both helium and hydrogen have very low boiling points but hydrogen's is higher.

D7.1 Covalent Molecular Substances

A substance made of molecules is called a **covalent molecular substance**. An important point in the activity you just completed is this: unlike ionic compounds, metals, or noble gases, where boiling involves freeing *ions* or *atoms* from each other, boiling a covalent molecular substance involves freeing *molecules* from each other. No covalent bonds are broken during the boiling process and the same molecules are present in the gas phase as were present in the liquid phase. The same reasoning applies to melting: covalent bonds between atoms within molecules are not broken, but forces between the molecules must be partially overcome.

Because there are many different kinds of nonmetal atoms that can form covalent bonds, and because molecules can consist of anywhere from two to many thousands of atoms, the range of properties of covalent molecular substances is much broader than for ionic compounds or metals. Many covalent molecular substances are liquids or gases: they melt (and some boil) below room temperature or not too far above. Covalent molecular substances do not conduct electricity well as solids or liquids, the solids may be weak and brittle or soft and waxy, and many are insoluble in water. We will begin to explore this broad range of molecules and properties in Unit 2. For now, we consider a single class of covalent molecular substances: hydrocarbons.

D7.2 Hydrocarbons

Many properties of substances that consist of covalently bonded molecules are exemplified by **hydrocarbons**, *compounds that contain only the elements carbon and hydrogen*. Carbon is unique among the elements in that carbon atoms can form long chains of carbon-carbon bonds. This happens because carbon atoms form strong single bonds to other carbon atoms and because carbon' has four valence electrons, resulting in four bonds per carbon atom. When all other bonds in a chain of carbon atoms are to hydrogen atoms, the molecule is a hydrocarbon. In addition to long chains, hydrocarbon molecules can have chains with branches; chains folded back on themselves to form rings; and chains, branched chains, or rings that include double or triple bonds. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory.

The most important reaction of hydrocarbons is combustion. The simplest example is combustion of methane:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta_r H = -802.3 \text{ kJ/mol}$$

Combustion of hydrocarbons is highly exothermic so hydrocarbons are excellent fuels. For example, methane (CH_4) is the principal component of natural gas, LP gas is mainly propane (C_3H_8) and butane (C_4H_{10}) . Other hydrocarbon fuels are acetylene, diesel fuel, jet fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons.

D7.3 Alkanes

The simplest hydrocarbons, **alkanes**, *contain only single bonds between carbon atoms*. Each of the carbon atoms in an alkane is bonded to four other atoms, each of which is either carbon or hydrogen. The bond enthalpies for C–C and C–H bonds are 346 and 436 kJ/mol, respectively. These strong bonds are difficult to break so alkanes are relatively unreactive.

Alkanes that do not contain rings of carbon atoms are called **acyclic alkanes**; they have the general molecular formula C_nH_{2n+2}. A molecular formula, such C_6H_{14} for the alkane named hexane, specifies how many atoms of each type are in the molecule; in C_6H_{14} there are 6 C atoms and 14 H atoms in each molecule. These alkanes are also called **saturated hydrocarbons** because *each C atom is bonded to the maximum possible number of H atoms*. The alkane molecule is said to be "saturated" with hydrogen.

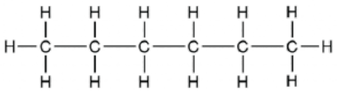
Figure 1. *Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane. Move the slider to see the various representations.*

Unbranched acyclic alkanes are often called “straight-chain” alkanes because the carbon atoms can be drawn in a single, straight row in the Lewis structure. However, the Lewis structure represents only some aspects of the molecule, not all. As the ball-and-stick and space-filling models of pentane in Figure 1 show, the C atoms do not lie in a completely straight line. Why there is a zigzag row of atoms is a topic for Unit 2.

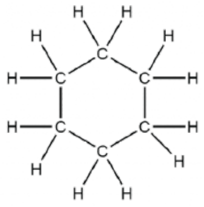
The structures of alkanes may also be represented by *condensed structural formulas*, such as CH_3CH_3 for ethane and $CH_3CH_2CH_2CH_2CH_3$ for pentane. Condensed structural formulas indicate how many H atoms are bonded to each C atom; they are related to Lewis structures, but all the bond symbols have been removed.

Branched alkanes contain more than one carbon chain. For example, 3-methylpentane has a branch at the third carbon atom along the chain. (The C atoms are numbered with subscripts to show that the branch occurs at the third C atom. The number of the C atom with the branch appears in the name. “*Meth*yl” refers to the group H_3C—, which is a *meth*ane molecule lacking one H nucleus.)

A **cycloalkane** *has at least one ring of carbon atoms*. Comparing a linear alkane with a cycloalkane shows that an additional C—C bond must be formed, which removes two hydrogen atoms. Consequently, the general formula for a cycloalkane containing one ring is C_nH_{2n}.



hexane (C_6H_{14})



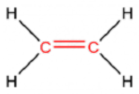
cyclohexane (C_6H_{12})

We refer to this *reduction in number of hydrogen atoms* as **degree of unsaturation**, One degree of unsaturation corresponds to having two hydrogen atoms fewer; a cycloalkane containing one ring has one degree of unsaturation. As in the case of the zigzag “straight-chain” alkane, the planar Lewis structure does not represent all aspects of the cyclohexane structure. The ring in cyclohexane is puckered and does not lie flat in a plane, as shown in this 3D model. The H atoms also are not in the plane of the screen.

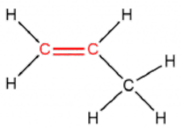
D7.4 Alkenes

Unsaturated hydrocarbons that contain one or more double bonds are called **alkenes**. The general molecular formula for alkenes with one double bond is C_nH_{2n}. The formula has two hydrogen atoms fewer than the corresponding alkane with same number of carbon atoms, and hence 1 degree of unsaturation. It is possible to have a ring of carbon atoms that contains a double bond. Cyclic alkenes have one degree of unsaturation from each cyclic structure and one from each C=C double bond.

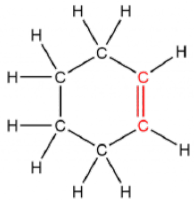
The carbon atoms involved in the double bond are *sp*^{2} hybridized, and therefore the local geometry there is trigonal planar. The presence of these double bond(s) is signified by the suffix *-ene* in the name. Ethene, C_2H_4, commonly called ethylene, is the simplest alkene. Some other examples include:



ethene (C_2H_4)



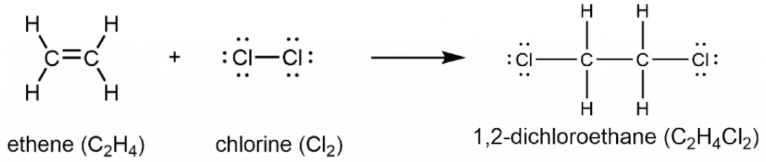
propene (C_3H_6)



cyclohexene (C_6H_{10})

The presence of the π bond makes alkenes much more reactive than alkanes because a carbon-carbon π bond is usually weaker and more easily disrupted than a σ bond. The double bond is therefore a **functional group**, *a specific structure that has similar chemical behavior in every molecule where it occurs*. For example, all alkenes can undergo a characteristic reaction, called an

addition reaction, *in which the π bond is broken and replaced by two additional σ bonds*. Hydrogen and halogen molecules can undergo addition reactions with alkenes, for example:



In this reaction, the π bond in the C=C double bond and the Cl-Cl σ bond are broken, and two C-Cl σ bonds are formed. The σ bond in the C=C double bond remains intact throughout the reaction. The reaction can occur relatively easily because the π bond is not as strong as the σ bond—that is, because the C=C double bond (bond enthalpy = 598 kJ/mol) is not twice as strong as the C-C single bond (bond enthalpy = 346 kJ/mol).

Activity 1: Analyzing an Addition Reaction

Think about the reaction of chlorine with ethane, CH_3CH_3. Can this be an addition reaction? Explain why or why not. What bonds need to be broken and formed if chlorine reacts with ethane and how does the reaction differ from the reaction of chlorine with ethene shown above? Do you expect the reaction of chlorine with ethane to be faster or slower than the reaction with ethene? Why?

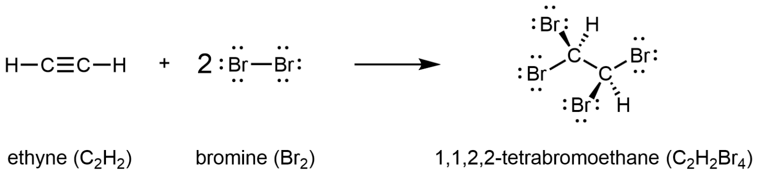
D7.5 Alkynes

An **alkyne** is *a hydrocarbon with one or more carbon-carbon triple bonds*. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The general molecular formula of an alkyne with one triple bond is C_nH_{2n-2}. The alkyne has four hydrogen atoms fewer than the corresponding alkane with same number of carbons, and hence 2 degrees of unsaturation.

The suffix *-yne* is used to indicate the presence of a triple bond. The simplest alkyne is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne is:

ethyne (acetylene)

Chemically, alkynes have reactivity similar to alkenes. Since the C≡C functional group has two π bonds, alkynes can react with twice as much reagent in an addition reaction. For example, acetylene can react with bromine in the following reaction:



D7.6 Petroleum Chemistry

Petroleum (from Latin, petra: “rock”, oleum: “oil”) *consists primarily of naturally occurring hydrocarbons*, predominantly alkanes and cycloalkanes. The alkane chains can be quite long, and properties such as melting point and boiling point usually vary smoothly and predictably as a function of the number electrons in various alkane molecules (Table 1).

Alkane	Molecular Formula	Number of Electrons	Melting Point (°C)	Boiling Point (°C)	Phase at Room Temperature
methane	CH_4	10	–182.5	–161.5	gas
ethane	C_2H_6	18	–183.3	–88.6	gas
propane	C_3H_8	26	–187.7	–42.1	gas
butane	C_4H_{10}	34	–138.3	–0.5	gas
pentane	C_5H_{12}	42	–129.7	36.1	liquid

Alkane	Molecular Formula	Number of Electrons	Melting Point (°C)	Boiling Point (°C)	Phase at Room Temperature
hexane	C_6H_{14}	50	–95.3	68.7	liquid
heptane	C_7H_{16}	58	–90.6	98.4	liquid
octane	C_8H_{18}	66	–56.8	125.7	liquid
nonane	C_9H_{20}	74	–53.6	150.8	liquid
decane	$C_{10}H_{22}$	82	–29.7	174.0	liquid
tetradecane	$C_{14}H_{30}$	114	5.9	253.5	solid
octadecane	$C_{18}H_{38}$	146	28.2	316.1	solid

Table 1. Melting and boiling points of alkanes.

Petroleum is the main source of hydrocarbon fuels, such as LP gas, gasoline, and fuel oil. These are separated by **fractional distillation**, *a process in which petroleum is boiled and the different hydrocarbons condense to liquids at different temperatures* (Figure 2). Fractional distillation takes advantage of the boiling-point differences of the various component substances (Table 1). The different boiling points arise from the differences in the London dispersion forces between molecules.

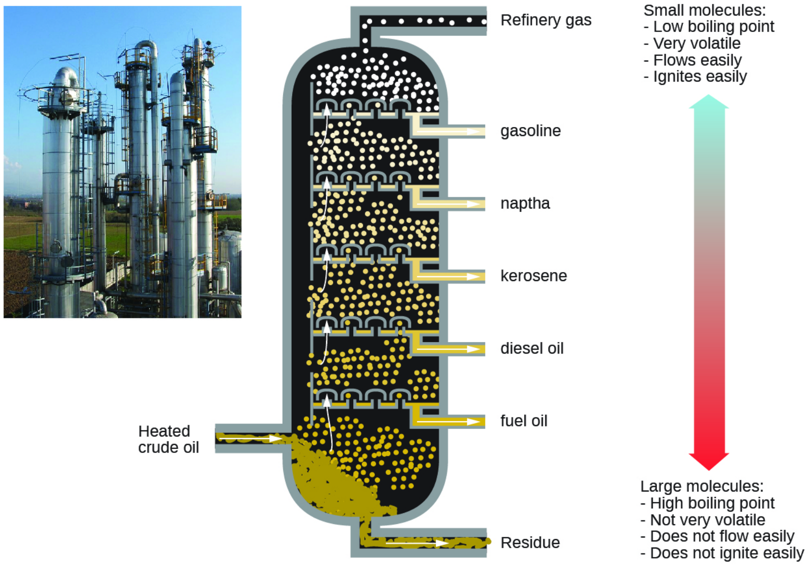


Figure 2. *In a column for the fractional distillation of crude oil, oil heated to about 425 °C in a furnace vaporizes when it enters the base of the tower. The vapors rise up the tower, cooling at each successive level. At first, mixtures of compounds with higher boiling points condense and are drawn off. As the vapors gradually cool, mixtures with lower, boiling points condense to liquids. All compounds in a mixture with about the same boiling point are called a petroleum fraction. (credit left: modification of work by Luigi Chiesa)*

Gasoline is *a liquid mixture of linear and branched alkanes, each containing five to twelve carbon atoms.* Gasoline contains various additives to improve its performance as a fuel. Kerosene, diesel fuel, motor oil, and fuel oil are primarily mixtures of alkanes made of larger molecules with more electrons than gasoline molecules. Provided there is plenty of oxygen available, combustion converts almost all the carbon in the alkane fuel to carbon dioxide and water. Thus combustion of alkanes invariably adds water vapor and CO_2 to the atmosphere—a human contribution to global warming.

Because there is greater demand for gasoline than for other components of petroleum, catalytic cracking is used in petroleum refining to break up larger molecules into smaller molecules, some of which are within the gasoline range of 5–12 carbon atoms. **Catalytic cracking** *involves temperatures of 480–550 °C and a catalyst—conditions that can break (crack) carbon-carbon bonds and rearrange molecular structures*. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller molecules, some of which have carbon-carbon double bonds. One possible reaction involving $C_{15}H_{32}$ might be:

$$C_{15}H_{32} \rightarrow 2\ C_2H_4\ \text{(ethene)} + C_3H_6\ \text{(propene)} + C_8H_{18}\ \text{(octane)}$$

The alkene products, ethene and propene, are important for producing other organic chemicals. The octane product is a component of gasoline. Note that catalytic cracking involves temperatures higher than fractional distillation as well as a catalyst in order to break carbon-carbon bonds (as opposed to overcoming LDFs between hydrocarbon molecules).

D7.7 Attractions Between Atomic-scale Particles

Consider the different ways atomic-scale particles attract other atomic-scale particles and how strengths of those attractions affect macroscopic properties. Noble-gas atoms have only weak London dispersion forces (LDFs) between them, leading to very low boiling points.

Metals consist of positive ions surrounded by valence electrons that are not associated with any specific positive ion (that is, with any specific metal-atom core). Attractions between metal atoms involve positive ions and electrons and therefore are much larger than attractions between noble-gas atoms. Metallic bonding becomes stronger as the number of valence electrons in the metal atom increases. Metal atoms are attracted strongly enough that most metals are solids at room temperature.

When an atom with low attraction for electrons (a metal atom with low ionization energy) approaches an atom with greater attractions for electrons (a nonmetal with large negative electron affinity), electron density can transfer from the metal atom to the nonmetal atom to form ions. Coulomb’s law attractions between ions are large and depend on the charges of the ions and the distance between the ions. This results in formation of ionic crystal lattices that require significant increase in temperature for melting or boiling.

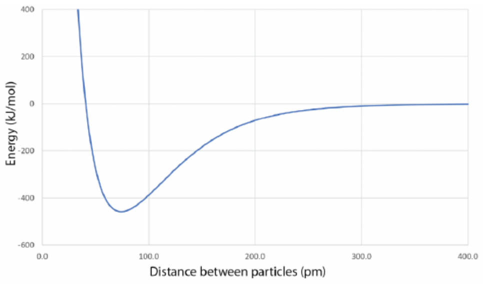
When two nonmetal atoms approach, the typical result is a covalent chemical bond, although there are cases such as He_2 where there are enough electrons to fill antibonding as well as bonding molecular orbitals and give a bond order of zero. The characteristics of covalent bonds depend on properties of the bonded atoms, such as size and number of electrons. Covalent bonds connect atoms to form molecules. The strengths of bonds in molecules are typically as large as or larger than the strengths of metallic bonds and ionic bonds. Thus, when a molecular substance melts or boils, atoms remain bonded and the atomic-scale particles in the liquid or gas phase are molecules.

For example, when NaCl melts, Na^+ ions and Cl^- ions break from the crystal lattice and move freely around each other. Breaking the ionic bonds requires significant energy, and hence NaCl has a high melting point of 801 °C. In contrast, when methane (CH_4) melts, individual methane (CH_4) molecules stay intact, but they can move freely around other methane molecules. The attractions between methane molecules must be partially overcome, but those attractions are not as strong as covalent bonds or ionic bonds. Hence, the melting point of methane is much lower than for NaCl. Methane melts at −182 °C.

Day 7 Pre-Class Podia Problem: Forces between Atomic-Scale Particles

This Podia problem is based on today’s pre-class material; working through that material will help you solve the problem.

Forces between atoms, ions, and molecules typically result in a graph of energy versus distance between particles that looks like this:



For each pair of substances listed below make a graph of energy versus distance between atomic-scale particles. Use a single set of coordinate axes for each pair. Then draw a curve like the one above for each substance in the pair. Your curves should be to scale relative to each other, but there is no need to put values on the tick marks along the axes. The relative depths of the minima and the relative positions of the minima along the horizontal axis are important.

1. NaCl and CaS
2. CH_4 and C_6H_{14}
3. Cr and Cs
4. Ne and CH_4

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CHAPTER OVERVIEW

2: Unit Two

2.1: Day 9- Bond Properties; Valence Bond Theory

8

Day 9: Bond Properties; Valence Bond Theory

D9.1 Bonds, Molecules, and Structures

In a molecule, atoms are connected by covalent bonds that result from overlap of atomic orbitals. Molecules can consist of a small or large number of atoms and may involve all the same kind or a dozen different kinds of atoms. The atoms can be connected by bonds in a variety of different ways, so there is a broad range of different molecular structures. Thus, there are many things a chemist needs to know about a molecule:

- What kinds of atoms and how many of each are in the molecule?
- Which atoms are bonded to which other atoms?
- What are the bond lengths between atoms?
- How strong are the bonds?
- What are the angles between the bonds?
- How are the atoms arranged in three-dimensional space?
- What kinds of attractions are there between molecules?
- How strong are the attractions between molecules?
- Are there noncovalent attractive forces within a large molecule, holding one part of the molecule to another?

At this point we have introduced the first four of these, using molecular formulas, Lewis structures, atomic radii/bond lengths, and bond enthalpies. For example, in a water molecule, the molecular formula H_2O indicates that there are two H atoms and one O atom. A Lewis structure, H–O–H shows that both H atoms are bonded to the O atom. The O–H bond length (94 pm) and bond enthalpy (467 kJ/mol) verify that the bonds are strong—separating the atoms is difficult.

But there is more to a water molecule than that. A ball-and-stick or space-filling model shows that the angle between the two O–H bonds is 104.5°—somewhat more than a right angle. Angles larger or smaller than 104.5° result in higher energy (lower stability). As a result of the shape and type of atoms in the water molecule, there are stronger forces between water molecules than between methane (CH_4) molecules, although both contain the same number of electrons.

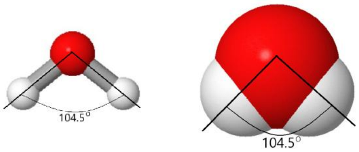


Figure 1. *Ball and stick and space-filling models of a water molecule showing the bond angle of 104.5°.*

As the number of atoms in a molecule increases the last four factors in the list above become more and more important. You will learn about them throughout this Unit, beginning with additional properties of chemical bonds in the next sections.

D9.2 Bond Polarity

If the two atoms that form a covalent bond are identical, as in H_2 or Cl_2, then the electrons in the bond must be shared equally between the two atoms. In a **pure covalent bond**, *shared electrons have an equal probability of being near each nucleus.*

On the other hand, if the two atoms are different, they may have different attractions for the shared electrons. When the *bonding electrons are attracted by one atom more than the other atom* the bond is called a **polar covalent bond**. For example, in HCl, the Cl atom attracts the bonding pair of electrons more than the H atom does, and electron density of the H–Cl bond is shifted toward the chlorine atom. Quantum mechanics calculations show that the chlorine atom, which has 17 protons, has electron density equivalent to 17.28 electrons and therefore a partial negative charge, $\delta^- = -0.28$. The hydrogen atom has a partial positive charge, $\delta^+ = +0.28$.

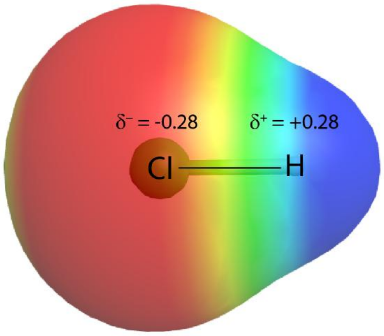


Figure 2*. The bond electron density in HCl is shifted toward the chlorine nucleus, making the molecule polar. Red color represents parts of the molecule surface that are more attractive to a positive charge near the molecule (more negative); blue areas are less attractive to an external positive charge (more positive).*

This *unequal distribution of electron density on two bonded atoms* produces a **bond dipole moment**, the magnitude of which is represented by μ (Greek letter mu). The dipole moment is equal to:

$$\mu = Qr$$

where Q is the magnitude of the partial charges (for HCl this is 0.28 times the charge of an electron) and r is the distance between the charges (the bond length). Bond dipole moments are measured in units of debyes (D); 1 D = 3.336×10^{-30} coulomb meter.

The bond dipole moment has both direction and magnitude and can be represented as a vector (Figure 3). A dipole vector is drawn as an arrow, with the arrowhead pointing to the partially negative end, and a small + sign on the partially positive end. The length of the arrow is proportional to the magnitude of the dipole moment.

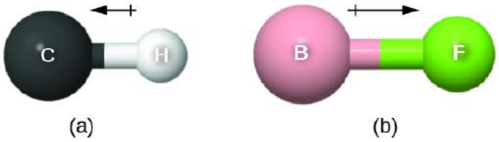


Figure 3. *(a) Bond dipole moment of a C-H bond. (b) Bond dipole moment of a B-F bond.*

D9.3 Electronegativity

The polarity of a covalent bond is determined by the difference between the electronegativities of the bonded atoms. **Electronegativity (EN)** is *the tendency of an atom in a molecule to attract bonding electron density.* Thus, in a bond, the more electronegative atom is the one with the δ^- charge.

The greater the difference in electronegativity between two bonded atoms is, the larger the shift of electron density in the bond toward the more electronegative atom is. Greater electronegativity difference, greater Δ(EN), gives larger partial charges on the atoms. Electronegativity values for most elements are shown in the periodic table in Activity 1; they also are tabulated in the appendix.

Activity 1: Periodic Trends in Electronegativity

Electronegativity, Electron Affinity, and Ionization Energy

These three properties are all associated with an atom gaining/losing electrons. Electron affinity and ionization energy are experimentally measurable physical quantities.

Electron affinity (EA) is the energy change when an isolated gas-phase atom acquires an electron; it is usually expressed in kJ/mol.

$$X(g) + e^- \rightarrow X^-(g) \quad \Delta E = EA_1$$

Ionization energy (IE) is the energy that must be transferred to an isolated gas-phase atom to remove an electron; it is also typically expressed in kJ/mol.

$$X(g) \rightarrow X^+(g) + e^- \quad \Delta E = IE_1$$

Electronegativity describes how strongly an atom attracts electron density in a bond. It is calculated, not measured, has an arbitrary relative scale, and has no units.

Activity 2: Electronegativity, Electron Affinity, and Ionization Energy

Electronegativity and Bond Type

The difference in electronegativity, Δ(EN), of two bonded atoms provides a rough estimate of polarity of the bond, and thus of the bond type. When Δ(EN) is very small (or zero), the bond is covalent and nonpolar. When Δ(EN) is large, the bond is polar covalent or ionic. (In a joined pair of ions, such as $Na^+Cl^−$, there is nearly complete transfer of valence electrons from one atom to another to produce a positive ion and a negative ion. The Na+ and $Cl^−$ ions form a dipole with δ^+ approximately equal to +1 and $\delta^−$ approximately −1.)

Δ(EN) spans a continuous scale and serves as a general guide; there is no definitive cutoff that defines a bond type. For example, HF has Δ(EN) = 1.8 and is considered a polar covalent molecule. On the other hand, NaI has a Δ(EN) of 1.7 but forms an ionic compound. When considering the covalent or ionic character of a bond, you should also take into account the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are usually described as covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic $NO_3^−$ anion, which has covalent bonds between N and O.

D9.4 Formal Charge

It is useful to consider how valence electrons are distributed in a molecule. **Formal charge,** the *charge an atom would have if the electron density in the bonds were equally shared between the atoms*, is one way to do this. For each atom in a Lewis structure, half of the electrons in bonds are assigned to the atom, and all lone-pair electrons (which are not shared with other atoms) are assigned to the atom.

An atom's formal charge is calculated as the difference between its number of valence electrons (in the unbonded, free atom) and its assigned number of electrons in the molecule:

$$\text{formal charge} = \text{number of valence } e^{-} - [\text{number of lone-pair } e^{-} + \tfrac{1}{2}(\text{number of bond-pair } e^{-})]$$

- If the assigned number of electrons equals the number of valence electrons, the atom has zero formal charge.
- If the assigned number of electrons exceeds the number of valence electrons, the atom has a negative formal charge.
- If the assigned number of electrons is less than the number of valence electrons, the atom has a positive formal charge.

Because formal charge counts all valence electrons in a molecule, the sum of the formal charges of all the atoms in a molecule or ion must equal the actual charge of the molecule or ion.

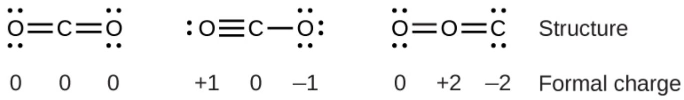
The formal charge for any given atom is not the same as its actual partial charge, such as those calculated in Section D9.2 above. This is because formal-charge calculations assume all covalent bonds are nonpolar, which is seldom the case except for homonuclear molecules.

Using Formal Charge to Predict the Most Likely Lewis Structure

While formal charges do not portray the true electron density distribution within a molecule, they nonetheless account for electron arrangement in a Lewis structure in units of a whole electron. Therefore, if following the steps for drawing Lewis structures lead to more than one possible arrangement of electrons and/or atoms for a given molecule, formal charges can help to decide which arrangement is likely to be the most stable, and hence the most likely Lewis structure for the given molecule.

- For an uncharged molecule, a Lewis structure in which all atoms have a formal charge of zero is preferable.
- The fewer atoms with nonzero formal charges, the better.
- The smaller the magnitude of the formal charges, the better.
- A Lewis structure with formal charges of the same sign (both + or both −) on adjacent atoms is less likely.
- Lewis structures with negative formal charges on more electronegative atoms are preferable.

For example, consider these three possible Lewis structures of carbon dioxide, CO_2:

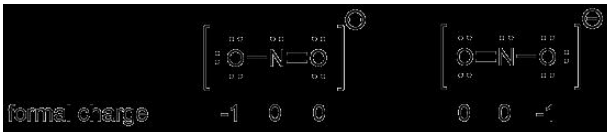


All structures have octets on each atom, but the structure on the left is preferable because all atoms have zero formal charge. The structure on the right is least likely because of the larger formal charges.

D9.5 Resonance Structures

In a single Lewis structure, a pair of electrons can only be depicted as shared between two atoms or localized to a single atom. However, as mentioned in Section D6.3, the molecular orbitals of a polyatomic molecule often span the entire molecule. For example, such *delocalized* electron distributions in π bonds can have a direct effect on molecular properties and chemical reactivity. Therefore, it is important to be able to use Lewis structures to indicate electron delocalization.

For example, two Lewis structures can be drawn for the nitrite anion, NO_2^-, both of which satisfy the guidelines for the best Lewis structure for NO_2^-:



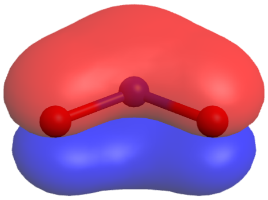
Note that in these two Lewis structures, each of the three atoms is in the same position. The difference is in the location of electrons. In other words, these two Lewis structures convey the idea that the π bond may be between left O and central N or between central N and right O.

If the NO_2^- molecule were correctly described by either one of the Lewis structures, we would expect one N-O bond to be longer than the other. However, experiments show that both bonds in NO_2^- are the same length. Moreover, the bonds are longer than a N=O double bond and shorter than a N-O single bond. Hence, neither Lewis structure is a correct depiction of the actual molecule, and the best representation of NO_2^- is an average of these two Lewis structures.

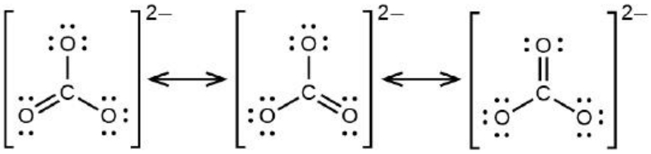
When the actual distribution of electrons is a *weighted average of a set of Lewis structures, those Lewis structures* are called **resonance structures**. T*he actual electronic structure of the molecule (the average of the resonance forms)* is called a **resonance hybrid**. A *double-headed arrow* between Lewis structures indicates that resonance structures are being depicted:

A molecule does *not* fluctuate between resonance structures; rather, the actual electronic structure is *always* the weighted average of the resonance structures. In other words, a single Lewis structure is insufficient to correctly represent the molecule (a shortcoming of a simple diagram), and a set of resonance structures (a resonance hybrid) is a better representation of electron density distribution in the molecule.

In the specific case of NO_2^-, the two resonance structures above are needed to correctly depict two π-bond electrons that are delocalized over the entire molecule (click on the image below for a rotatable 3D view of the π molecular orbital occupied by these two electrons):



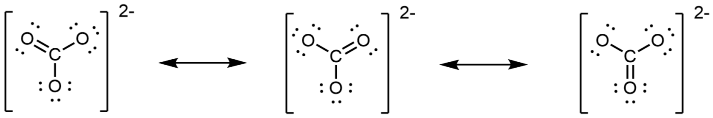
The carbonate anion, CO_3^{2-}, provides another example of insufficiency of a single Lewis structure and the need for a set of resonance structures:



Experiments show that all three C–O bonds are exactly the same. In other words, the two electrons in the π bond are delocalized over the entire molecule, as opposed to being only between one oxygen atom and the carbon atom.

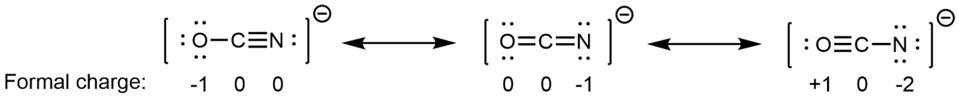
To summarize, in a single Lewis structure, bonding (σ or π) is always between two atoms. Hence, two or more Lewis structures are needed to properly describe a molecule with delocalized electrons (spread over three or more atoms). When drawing a set of resonance structures:

- Each resonance structure should have the same number of electrons.
    - Total formal charge is a useful tool for checking the number of electrons.
- Between resonance structures, atom locations are fixed: only the electrons move.
    - The skeleton structure of the molecule remains the same in all resonance structures.
    - However, you can draw a set of resonance structures in any perspective. For example, you could also draw the CO_3^{2-} resonance structures as



- Double-headed arrows between Lewis structures communicate that what is drawn is a set of resonance structures.

In NO_2^-, the two major resonance structures contribute equally to the resonance hybrid. Similarly, the three major resonance structures of CO_3^{2-} contribute equally to the resonance hybrid. However, it is possible for some structures in a resonance hybrid to be more important than others. For example, consider these three resonance structures of cyanate ion (OCN^-):

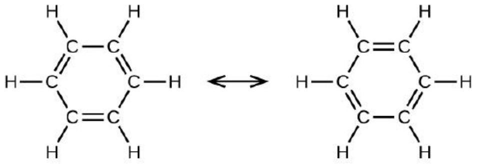


The atoms in each resonance structure have a full octet, but they differ in their formal charges. This implies that certain electron arrangements may be a bit more stable than others, and hence they do not contribute equally to the resonance hybrid.

From the formal-charge rules, we can estimate that the resonance structure on the right would contribute the least; that arrangement of electrons is the least stable of the three. The resonance structure on the left would contribute more than the middle structure because it has the -1 formal charge on the more electronegative O atom. (For OCN^-, high level quantum mechanics calculations show that the left structure contributes 61% to the resonance hybrid, the middle structure contributes 30%, and the right resonance structure contributes only 4%.)

D9.6 Aromatic Molecules

Benzene, C_6H_6, is representative of a large number of **aromatic compounds**. These compounds contain ring structures and exhibit bonding that must be described using resonance structures. The resonance structures for benzene are:



All six C-C bonds are equivalent and exhibit bond lengths that are intermediate between those of a C–C single bond and a C=C double bond.

The chemical reactivity of aromatic compounds differs from the reactivity of alkenes. For example, aromatic compounds do not undergo addition reactions. Instead, with the aid of a catalyst, they can undergo substitution reactions where one of the hydrogen atoms is replaced by a substituent: another atom or group of atoms. A substitution reaction leaves the delocalized double bonds intact.

D9.7 Valence Bond Theory

Lewis structures are easy-to-draw, planar representations of bonding in molecules. They help us to figure out and think about which atoms are bonded to which and whether bonds are single or multiple. However, by default, they do not represent the 3D geometry of a molecule, nor the molecular orbitals (MOs) that determine electron-density distributions.

You have probably used VSEPR to predict the 3D shapes of molecules. VSEPR involves counting electron regions (pairs) around a central atom, assuming that electron regions repel and stay as far apart as possible, and bonding terminal atoms to electron regions. VSEPR is often good at predicting the arrangement of bonds around an atom, and it is OK to use it to predict idealized linear, trigonal planar, and tetrahedral arrangements of bonds that you will encounter in this course, but VSEPR has significant limitations:

- VSEPR has little or no basis in modern quantum theory; you have just spent significant time studying quantum theory and we want you to be able to use that experience.
- It is often difficult to apply VSEPR to molecules described by two or more resonance structures (that is, molecules with delocalized electrons). Thus VSEPR makes it more difficult to understand many molecular structures—for example, structures of protein molecules.
- VSEPR assumes that lone pairs occupy more space than bond pairs, but there is no evidence, experimental or theoretical, to support that assumption; in fact, there is some evidence to the contrary.
- VSEPR assumes that all lone pairs are equivalent, but there is experimental evidence that they are not. For example, the two lone pairs in a water molecule do not have the same ionization energy and do not have equivalent probability distributions *(Journal of Chemical Education* **1987**, Vol. *64*, pp 124-128.).
- VSEPR often cannot explain relative bond angles. For example, why is the H-P-H angle in PH_3 93.5° while the H-N-H angle in NH_3 is 107.5°? (If the decrease in bond angle from the tetrahedral angle of 109.5° to 107.5° for NH_3 is due to a “fatter” lone pair, why does the angle decrease so much more for the larger P atom? A “fatter” lone pair should be less likely to repel the other bonds because they are farther apart.)

For these reasons, VSEPR is a model that has limited applicability. In this course we will use a better model—valence bond theory—which is consistent with modern quantum theory, makes more accurate and more comprehensive predictions than VSEPR, and is a better basis for understanding more advanced bonding topics. If you want to, it is OK to use VSEPR to predict idealized shapes, but applying the ideas presented in this section and sections D10.1 through D10.6 will allow you to describe structures with delocalized electrons better and predict bond angles more accurately.

Valence bond theory is *a model that focuses on the formation of individual chemical bonds, such as the formation of a σ bond between two atoms within a polyatomic molecule*. Like molecular orbital theory, valence bond theory deals with how atomic orbitals (AOs) change and combine when a molecule forms, but instead of forming MOs that span the whole molecule, valence bond theory combines valence orbitals of each atom individually so that the combination gives stronger bonding in specific directions. Hence, valence bond theory allows us to derive idealized 3D geometries for molecules based only on their Lewis structures, without having to perform any computation.

Valence bond theory uses the extent of orbital overlap to infer the strengths of chemical bonds: greater overlap leads to bonds that are stronger and hence a molecule that is more stable. For a given atom in a molecule, overlap with orbitals on other atoms can be greater when some or all of the atom’s AOs form hybrid orbitals. **Hybrid orbitals** are *combinations of valence atomic orbitals that emphasize concentration of electron density in specific directions*. A hybrid orbital’s greater electron density in a specific direction provides greater overlap with an orbital from another atom when forming a σ bond.

For an example of how orbital hybridization works, consider combining a single 2*s* AO with a single 2*p* AO, both on the same atom (Figure 4). The 2*s* AO is spherically symmetric, so it has the same phase (mathematical sign) on either side of the nucleus, but the 2*p* AO changes sign at the nucleus. Thus, on one side of the nucleus, the 2*s* and 2*p* AOs are in phase, while on the other side they are out of phase.

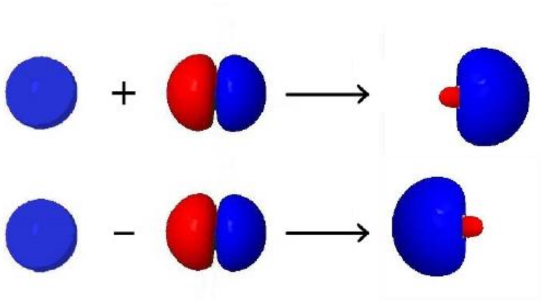


Figure 4. *Formation of sp hybrid orbitals. When the 2s AO and the 2p AO on the same atom are added (top), the sp hybrid orbital that is formed points toward the right—the region where both AOs have positive phase. When the 2p AO is subtracted from the 2s AO (bottom), the sp hybrid orbital formed points toward the left—the side where the two wave functions have opposite phase.*

If we add the two AOs, the new hybrid orbital will be larger on the side where the AOs are in phase and smaller on the other side where the AOs are out of phase. If we subtract them, the resultant hybrid orbital will be larger on the side where the AOs are out of phase and smaller where they are in phase. Hence, from one 2*s* AO and one 2*p* AO, we can derive two *sp* hybrid orbitals.

Activity 3: Orbital Hybridization

Day 9 Pre-class Podia Problem: Covalent Bonds

1. Consider these chemical bonds:

C–H C=C C–C C–Br C–F

Choose a pair of bonds from the list, predict which is longer, and write an explanation of your prediction.

Choose a pair of bonds from the list, predict which is stronger, and write an explanation of your prediction.

Choose a pair of bonds from the list, predict which is more polar, and write an explanation of your prediction.

2. NO is a molecule with an odd number of electrons. Write a Lewis structure for NO. Are there resonance structures? Is one resonance structure more dominant than another? If so, identify the more dominant structure and explain why it is more dominant.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

2.2: Day 10- Hybrid Orbitals; Molecular Geometry

9

Day 10: Hybrid Orbitals; Molecular Geometry

Valence bond theory and hybrid orbitals were introduced in Section D9.7. The ideas summarized here will be developed further in today's work:

- Hybrid orbitals are derived by combining two or more atomic orbitals from the valence shell of a single atom.
  - AOs are the most stable arrangement of electrons in isolated atoms.
  - Hybrid orbitals are important in molecules because they result in stronger σ bonding.
- Most σ bonds are formed from overlaps of hybrid orbitals. Most π bonds are formed from overlap of unhybridized AOs.
- The number of hybrid orbitals equals the number of valence AOs that were combined to produce the hybrid orbitals.
- The type of hybrid orbitals for each bonded atom in a molecule correlates with the local 3D geometry of that atom.
  - The type of hybrid orbitals for each atom can be determined from the Lewis structure (or resonance structures) of a molecule.
  - From the local 3D geometry of each atom, we can obtain the overall 3D geometry of the molecule.

D10.1 Types of Hybrid Orbitals

sp Hybrid Orbitals

Combining the valence s AO with one of the valence p AOs yields two degenerate ***sp* hybrid orbitals**, as shown in Figure 1 for the case of 2*s* and 2*p* AOs. The two *sp* hybrid orbitals are *oriented at 180° to each other*—a **linear geometry**. After the hybridization, there are two unhybridized 2*p* AOs left on the atom.

Because these hybrid orbitals are formed from one *s* AO and one *p* AO, they have a 1:1 ratio of "*s*" and "*p*" characteristics, hence the name "*sp*". One of the ways in which the hybrid orbitals exhibit their mixed "*s*" and "*p*" characteristics is in their energy. Specifically, the *sp* hybrid orbitals' relative energies are about half-way between the 2*s* and 2*p* AOs, as illustrated in Figure 1.

Figure 1. *Hybridization of the 2s and one of the 2p AOs forms two sp hybrid orbitals, oriented 180° with respect to each other; the two other 2p AOs remain unhybridized. (Move the slider to see the before/after of hybridization).*

The hybridized orbitals are not energetically favorable for an isolated atom. For example, a beryllium atom is lower in energy with its two valence electrons in the 2*s* AO than if the electrons were in the two *sp* hybrid orbitals. However, in a covalent molecule, the one large lobe of each *sp* hybrid orbital gives greater overlap with another orbital from another atom, yielding σ bonds that lower the molecule's energy.

sp^2 Hybridization

Combining one valence s AO and two valence p AOs produces three degenerate ***sp*^{2} hybrid orbitals**, as shown in Figure 2 for the case of 2*s* and 2*p* AOs. The three *sp*^{2} hybrid orbitals are *oriented at 120° with respect to each other and are in the same plane—a* ***trigonal planar*** *(or* ***triangular planar****) geometry.* Each hybrid orbital is pointed toward a different corner of an equilateral triangle. After hybridization, there is one unhybridized 2*p* AO left on the atom.

The *sp*^{2} hybrid orbitals have twice as much "*p*" character as "*s*" character; this is indicated by the superscript "2" in *sp*^{2}. Energetically, *sp*^{2} hybrid orbitals lie closer to the *p* AO than the *s* AO, as illustrated in Figure 2 (the *sp*^{2} hybrid orbitals are higher in energy than the *sp* hybrid orbitals).

Figure 2. *Hybridization of the 2s and two of the 2p AOs forms three sp*^{2} *hybrid orbitals, oriented 120° with respect to each other in the same plane; one of the 2p AOs remain unhybridized (move the slider around to see the before/after of hybridization).*

sp^3 Hybridization

Combining one valence s AO and all three valence p AOs produces four degenerate ***sp*^{3} hybridized orbitals**, as shown in Figure 4 for the case of 2*s* and 2*p* AOs. The four *sp*^{3} hybridized orbitals are *oriented at 109.5° with respect to each other, each pointing toward a different corner of a tetrahedron*—a **tetrahedral geometry**.

A *tetrahedron* is a three-dimensional object that has four equilateral triangular faces and four apexes (corners). All four corners are equivalent. See Figure 3.

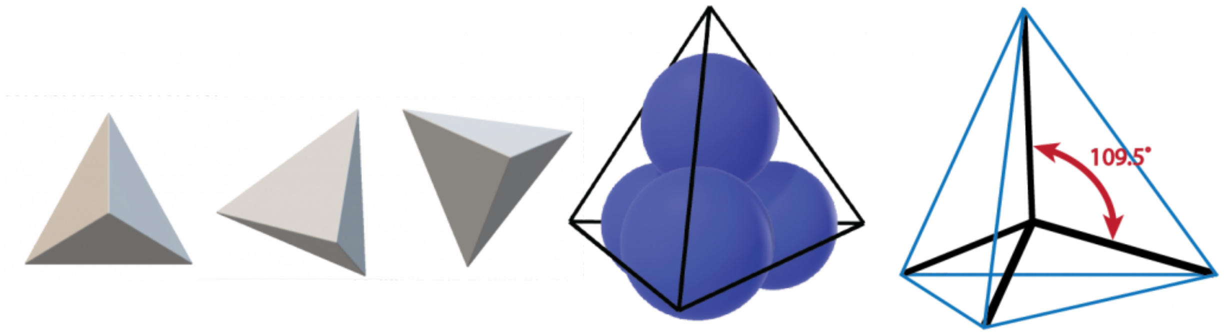


Figure 3. *A tetrahedron has four equilateral triangular sides and four apexes (corners). Three views of a tetrahedron are shown at left. Four* sp^3 *hybridized orbitals point from the tetrahedron's center toward the four corners. These hybrid orbitals form four bonds that point toward each corner of a tetrahedron. The angle between any two bonds is 109.5 degrees.*

An sp^3 hybrid orbital has 75% "*p*" character and 25% "*s*" character, a 3:1 ratio, hence the superscript "3" in its name. The sp^3 hybrid orbitals are higher in energy than the sp^2 hybrid orbitals, as illustrated in Figure 4.

Figure 4*. Hybridization of the 2s and all three 2p AOs forms four* sp^3 *hybrid orbitals, oriented 109.5° with respect to each other (move the slider around to see the before/after of hybridization).*

Formation of a σ bond

When a σ bond forms between two atoms, a hybrid orbital with one unpaired electron from one atom overlaps with a hybrid orbital with one unpaired electron from the other atom. The resulting σ bond is an orbital that contains a pair of electrons (just as a line in a Lewis structure represents two electrons in a σ bond). For example, Figure 5 shows the formation of a C-C σ bond from two sp^3 hybridized carbon atoms.

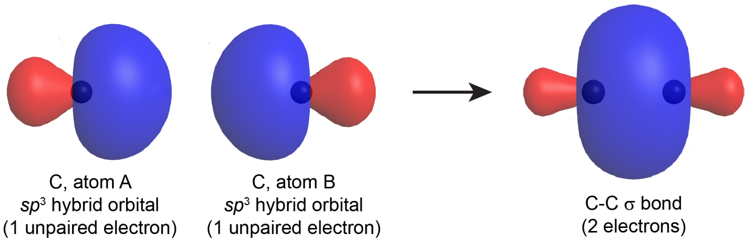


Figure 5*. An* sp^3 *hybrid orbital from carbon*$_A$ *overlaps with an* sp^3 *hybrid orbital from carbon*$_B$*, resulting in the formation of a C-C σ bond (in, for example,* $H_3C\text{-}CH_3$*).*

The σ bond thus formed by two hybrid orbitals (valence bond theory) is similar to a σ bond formed in a diatomic molecule as described by MO theory (Section D5.5). In polyatomic molecules with more than three atoms, the MOs are not localized between two atoms like this, but in valence bond theory, the bonds are described individually, between each pair of bonded atoms. Notice that in either MO or valence bond theory, the σ bond has a cylindrical symmetry with respect to the bonding axis.

If a hybridized orbital on an atom in a molecule has two electrons but is not pointing at another atom, the filled hybrid orbital is not involved in bonding. This corresponds to a lone pair on an atom in a Lewis structure.

D10.2 Predicting the Geometry of Bonds Around an Atom

Once you have drawn the best Lewis structure (or a set of resonance structures) for a molecule, you can use the structure(s) to assign hybridization to each atom, predict the geometric arrangement of bonds around each atom, and then predict the 3D structure for the molecule. This and the next few sections explain how this works.

For each atom in a molecule, determine the number of AOs that are hybridized, n_{hyb}, and use this value to predict hybridization.

- Count the number of σ bonds (n_σ) the atom forms.
    - A double (or triple) bond contains 1 σ bond and 1 (or 2) π bond(s).
- Are there any lone pairs on the atom?

- If yes: $n_{hyb} = n_\sigma + 1$
  - If no: $n_{hyb} = n_\sigma$
- Is an atom's n_{hyb} different in one resonance structure from another?
  - If yes, use the smaller n_{hyb} to determine hybridization.
- Use the value of n_{hyb} to determine the number of AOs combined and hence the type of hybridization:
  - For $n_{hyb} = 2$, the atom is *sp* hybridized (two AOs are combined);
  - for $n_{hyb} = 3$, the atom is sp^2 hybridized (three AOs are combined);
  - for $n_{hyb} = 4$, the atom is sp^3 hybridized (four AOs are combined);
  - An H atom in a molecule has $n_{hyb} = 1$. It is not hybridized; its electron is in the 1*s* AO when forming a σ bond.

These rules derive from the idea that hybridized orbitals form stronger σ bonds. Therefore, the more σ bonds to an atom, the more atomic orbitals are combined to form hybrid orbitals.

Activity 1: Molecular geometry of BeCl2

Activity 2: Molecular geometry of BF3

D10.3 Three-dimensional Bond Geometry

The two examples so far were a linear (one-dimensional) molecule, $BeCl_2$, and a planar (two-dimensional) molecule, BF_3. What happens when a molecule is three dimensional?

Activity 3: Molecular geometry of CH4

Activity 4: Molecular geometry of NH3

Wedge-dash Notation

The Lewis structures in the activities above are drawn using **wedge and dash notation.***Straight lines represent bonds in the plane of the page/screen, solid wedges represent bonds coming toward you out of the plane, and dashed wedges represent bonds going away from you behind the plane*.

Examine this 3D model of NH_3 and rotate it until it looks like the Lewis structure drawn in the answer in Activity 4. The NH_3 molecule has trigonal pyramidal geometry because the lone pair on nitrogen occupies one of the corners of a tetrahedron, leaving the three N-H bonds occupying the other three corners; this gives a three-cornered pyramid.

Redraw the Lewis structure you drew for ammonia in Activity 4 using wedge-dash notation. Then, rotate the 3D model until it matches your drawing. If you can find an orientation that matches, your wedge-dash Lewis structure is probably correct; if you cannot find a match, your Lewis structure is probably incorrect.

For simplicity, a wedge-dash Lewis structure draws as many as possible of a molecule's bonds in a plane. However, as is the case with CH_4 and NH_3, most molecules do not have all bonds in the same plane.

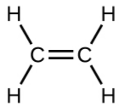
D10.4 Molecules with More Than One Central Atom

Larger molecules have more than one "central" atom with several other atoms bonded to it. The arrangement of bonds for each central atom can be predicted as described in the preceding sections. The way these local structures are oriented with respect to each other influences the overall molecular shape.

Activity 5: Molecules with Several Central Atoms

Double and Triple Bonds

The Lewis structure of ethene, C_2H_4, shows that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms:



Each carbon atom has n_{hyb} = 3 and therefore is sp^2 hybridized. Around each C atom there are three bonds in a plane. Two of the sp^2 orbitals form two C–H σ bonds and the third sp^2 orbital forms a C-C σ bond.

The double bond between the two C atoms contains a π bond as well as a σ bond. The π bond results from overlap of the unhybridized 2*p* AO on each carbon atom. The unhybridized 2*p* AO is perpendicular to the plane of the sp^2 hybrid orbitals (Figure 6). Thus when the 2*p* AOs overlap in a side-by-side fashion to form a π bond, the electron densities in the π bond are above and below the plane of the molecule (the plane containing the σ bonds).

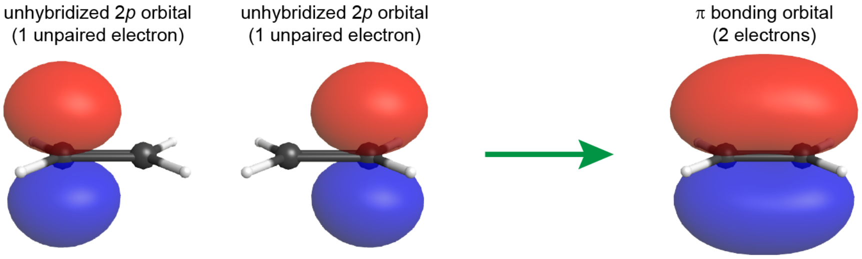


***Figure 6**. The ball-and-stick model of C_2H_4 is planar and roughly perpendicular to the plane of the page. The σ bonds are formed by overlap of sp^2 hybrid orbitals on each C atom with two H 1s orbitals and an sp^2 orbital on the other C atom. The unhybridized 2p AOs on the two C atoms (left) overlap side by side to form the π bond in C_2H_4 (right). Click on the image for a rotatable view of the π bond.*

If the plane containing the sp^2 hybrid orbitals of one carbon atom were rotated 90° relative to the other carbon, the two 2*p* AOs would also be rotated 90° to each other (Figure 7). The 2*p* AOs would no longer be able to overlap and the π bond cannot form.

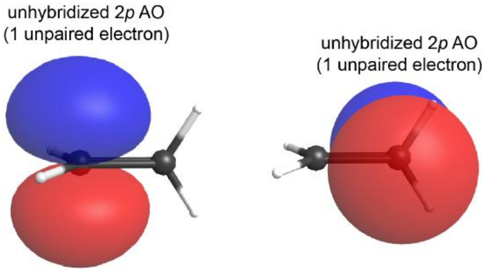


***Figure 7**. If one of the carbon in C_2H_4 is rotated relative to the other one, by 90°, the two 2p AOs are now perpendicular to each other, and the π bond can no longer be formed.*

This is a significant difference between σ and π bonds: one atom rotating around the internuclear axis with respect to the other atom does not change the extent to which the σ bonding orbitals overlap because the σ bond is cylindrically symmetric about the bond axis (see Figure 5); in contrast, rotation by 90° about the internuclear axis breaks the π bond entirely because the *p* orbitals can no longer overlap.

In acetylene, H−C≡C−H, each carbon atom has n_{hyb} = 2 and therefore is *sp* hybridized with two unhybridized 2*p* orbitals. One *sp* hybrid orbital from each C atom overlaps to form a C-C σ bond, the other *sp* hybrid orbital forms a C-H σ bond with a hydrogen atom. The unhybridized *2p* AOs overlap to form two *perpendicular* C-C π bonds (Figure 8). The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

***Figure 8.** In the C_2H_2 molecule, there are two C–H σ bonds and a C≡C triple bond. the triple bond involves one σ bond and two π bonds. The two π bonds are perpendicular to each other. Slide back and forth to see all the bonds; the molecule is fixed in the same perspective throughout.*

Because π bonds are formed from unhybridized *p* AOs, an atom that is involved in π bonding cannot be sp^3 hybridized.

Activity 6: Predicting Structure of a Molecule with Several Central Atoms

D10.5 Hybridization and Bond Angles

Think back to the example molecules CH_4 and NH_3 in Section D9.4. Both involve sp^3 hybridized orbitals on the central atom. In the case of CH_4, a 1*s* orbital on each of the four H atoms overlaps with each of the four sp^3 hybrid orbitals to form four bonds. All angles between pairs of C–H bonds are 109.5°. In NH_3 the situation is different in that there are only three H atoms. Three of the four sp^3 hybrid orbitals form three bonds to H atoms, but the fourth sp^3 hybrid orbital contains the lone pair. The lone pair is different from the H atoms, and this is important.

In earlier sections we described each of a set of four sp^3 hybridized orbitals as having ¼ *s* character and ¾ *p* character. This is what happens in CH_4. Each of the four C–H bonds involves a hybrid orbital that is ¼ *s* and ¾ *p*. Summing over the four bonds gives 4 × ¼ = 1 *s* orbital and 4 × ¾ = 3 *p* orbitals—exactly the number and type of AOs from which the hybrid orbitals were formed.

In NH_3, however, three of the four sp^3 hybrids form bonds to H atoms and the fourth involves a lone pair. In this and similar situations, the partial *s* and *p* characters must still sum to 1 and 3 but each hybrid orbital does not have to be the same as all the others. That is, a hybrid orbital forming an N–H bond could have more *p* character (and less *s* character) compared to the hybrid orbital involving the lone pair. The only requirement is that the total *s* character and the total *p* character, summed over all four hybrid orbitals, must be one s and three *p*.

A different ratio of *s* character and *p* character gives a different bond angle. For example, in sp^2 hybridized orbitals (with one-third *s* character and two-thirds *p* character) the angle between bonds is 120°, whereas, for sp^3 the angle is 109.5°. More *p* character results in a smaller bond angle. (This makes sense, because for the maximum *p* character, that is, for two unhybridized *p* orbitals, the bond angle would be 90° because the p orbitals are at 90°.)

How can you tell how much *s* character and how much *p* character is in a specific hybrid orbital? A MO-theory calculation can provide this information, but, for our purposes, a qualitative rule that indicates where there will be more p character is sufficient. **Bent’s rule** says that *a hybrid orbital on a central atom has greater p character the greater the electronegativity of the other atom forming a bond.* A lone pair is assigned zero electronegativity because there is no atom attracting electrons in the bond away from the central atom.

Applying Bent’s rule to NH_3, the three bonded H atoms have higher electronegativity than the lone pair (no atom) so we expect more *p* character in the hybrid orbitals that form the bond pairs. Thus, the angle between any two N–H bonds should be less than the tetrahedral angle. The experimentally measured angle is 106.7°, a bit less than the expected 109.5°.

Activity 7: Molecular geometry of H2O

In the H_2O molecule, two of the O’s sp^2 hybrid orbitals are involved in forming the O-H σ bonds. One of O lone pairs is in the other sp^2 hybrid orbital; the other O lone pair is in the unhybridized 2*p* AO. The overall molecular geometry is bent. If O had perfect sp^2 hybridization, the H-O-H angle would be 120°, but because the three hybrid orbitals are not equivalent, the angle deviates from ideal. To obtain an accurate bond angle requires an experiment or a high-level MO calculation.

D10.6 Hybridization in Resonance Hybrids

The assignment of hybridization and molecular geometry for molecules that have two or more major resonance structures is similar to the process discussed above, but remember that a set of resonance structures describes a single molecule. Hence the hybridization (and molecular geometry) assigned to one resonance structure must be the same as all other resonance structures in the set. Hence, when assigning hybridization, you should consider all the major resonance structures.

Consider Figure 9:

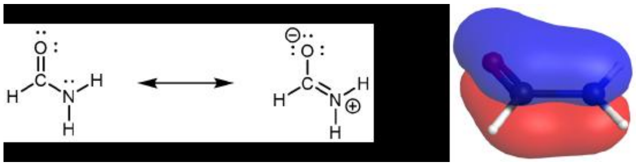


Figure 9*. The two major contributing resonance structures of formamide are shown on the left. The delocalized π MO of formamide is shown on the right. Click on the image to see a rotatable 3D structure.*

The delocalized π MO extends over the oxygen, carbon, and nitrogen atoms. One of the three AOs contributing to this π MO is an unhybridized 2*p* AO on the N atom. This is also described by the set of resonance structures, where there is double-bond character between O and C and between C and N. Therefore the nitrogen atom must have sp^2 hybridization (it forms three σ bonds) and a trigonal planar local geometry. This is more obvious when looking at the right resonance structure. When looking at the left resonance structure, you might be tempted to assign sp^3 hybridization to N given its similarity to ammonia (NH_3). However, this is a resonance structure; the set of resonance structures describes a molecule that cannot be described correctly by a single Lewis structure. Hence, the lone pair on N in the left resonance structure is in an unhybridized 2*p* AO.

All atoms must remain in the same positions from one resonance structure to another in a set of resonance structures. There cannot be a N atom that is trigonal pyramidal in one resonance structure and trigonal planar in another resonance structure, because the atoms attached to the N would have to change positions. Experimental evidence and high-level MO calculations show that formamide is a planar molecule.

Day 10 Pre-class Podia Problem: Three-dimensional Models and Lewis Structures

Here are three links to 3-D models of molecules. For each molecule rotate the model to observe the structure. Then draw *three* 3-D Lewis structures of each molecule, using wedge and dash notation. Each wedge-dash structure should be viewed from a *different* perspective. If there are any lone pairs and/or formal charges, be sure to include them.

Glycine is an amino acid, a component of protein molecules.

Acrolein is used to kill algae and weeds in irrigation ditches and other natural waters.

Methyl formate is used mainly in the manufacture of other chemicals.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

2.3: Day 11- Molecular Structure- Isomers

10

Day 11: Molecular Structure: Isomers

D11.1 Line Structures

Think about the importance of structures of covalent molecular substances. Hydrocarbons (Section D7.2) or closely related molecules are good examples because there are many different hydrocarbon molecules and many hydrocarbons have lots of atoms. Knowing which atoms are bonded to which and the different ways they are bonded enables predictions about the properties of the corresponding compounds.

For example, molecules of hydrocarbons in motor oil for automobiles contain from 16 to 20 carbon atoms and more than twice as many associated hydrogen atoms. Drawing Lewis structures for such large molecules takes time and can be overly complicated, so a simpler kind of drawing, called a line structure, is often used. In a **line structure** (also called a **skeletal structure**) for a hydrocarbon, *only the C–C bonds are shown; element symbols and C–H bonds are omitted*. Carbon atoms are represented by the end of a line or a juncture between two lines. Figure 1 shows an example line structure. Decide where each C atom and each H atom is in the line structure; then count the number of C and H atoms to verify that the line structure represents the same molecule as the Lewis structure.

Figure 1. *The molecule 3-ethyl-2-methylhexane can be represented as a full Lewis structure or a line structure. Move the slider to see either representation. Note that in the full Lewis structure, the methyl and ethyl groups are stretched out a bit to accommodate drawing all the bonds in those areas.*

Line structures are much easier to draw, and the general molecular structure of the carbon chain or chains is clearer. However, it is also much easier to make mistakes when drawing and reading line structures: an extra line is a whole extra CH_n group and it is also easier to miss some of the implied C-H bonds.

In line structures, atoms other than carbon and hydrogen are represented by their elemental symbols, and any H atoms bonded to them are shown explicitly (for example, see molecule C in the exercise above). In line structures, lone pairs on atoms are often omitted as well. Because C-H bonds and lone pairs are not shown, it is necessary to *include the formal charge on any atom that has a nonzero formal charge* when drawing a line structure. Otherwise, there would be a miscount of bonds or electrons.

D11.2 Isomeric Structures

When more than one molecular structure corresponds to the same molecular formula the two or more structures are called **isomeric structures**, or **isomers**. For example, there are two structures corresponding to the formula CHN. They are H–C≡N: (hydrogen cyanide) and H–N≡C: (hydrogen isocyanide). At room temperature and especially at lower temperatures, both structures exist as separate compounds. That is, the substance represented by one structure can be purified and separated from the other and each substance has different properties.

When molecular formulas are different, the formulas must describe substances with different properties because the formula tells how many atoms of each kind are in a molecule and chemical bonds would have to be broken to change the number or atoms or type of atoms. Breaking covalent bonds requires energy, and at room temperature very few molecules have enough energy for bond breaking to occur. Isomers occur when two different molecular structures with the same number of atoms of each type do not have sufficient energy to change from one structure to the other. For example, H–N≡C: does not change into H–C≡N: because the change requires breaking a N–H bond. At room temperature the H–N≡C: molecules do not have enough energy to overcome the bond enthalpy of the N–H bond, so they do not change; thus, H–N≡C: can be purified and separated from H–C≡N:.

Typically isomers are defined by whether they can interchange at room temperature. At room temperature molecules do not have sufficient energy to break most covalent bonds. Thus, if interchanging two structures requires breaking a covalent bond, the two structures are isomers. If the temperature is raised, the molecules have greater average energy and it becomes more likely that one structure can change into another. If the temperature is lowered, it becomes harder to interchange structures; that is, the average energy of the molecules is lower and structures that could interchange at room temperature no longer have sufficient energy.

D11.3 Conformations

At room temperature, molecules are in constant motion both with respect to other molecules and as a result of internal motions such as rotation of one part of a molecule relative to another part of the same molecule. Below is an animation of a butane molecule at room temperature. Notice that there is rotation around the central C–C single bond (which is kept stationary in the animation to show the rotation better) and also around the other C–C bonds. Such rotations in a molecule lead to different **conformations** or **conformers**, *structures that differ only because of rotations around single bonds*.

A link to an interactive elements can be found here.

***Figure 2**. Rotation around the C-C bonds in butane leads to various conformations of the molecule. The C-C bond in the center of the molecule is kept in the same position in this animation so that rotations around it are more obvious, but rotation occurs around all three C-C bonds. To see the rotations more clearly. stop the animation and drag the slider at the bottom. You can change the perspective from which you view the molecule by holding the mouse button down and moving the mouse. (Animation by Michael Aristov.)*

A link to an interactive elements can be found here.

***Figure 2a**. Rotation around the C-C bonds in butane leads to various conformations of the molecule. Here four conformations are projected onto a plane and drawn as wedge-dash structures. You can change the perspective from which you view the molecule by holding the mouse button down and moving the mouse. (Animation by Michael Aristov.)*

Activity 1: Depicting Conformers

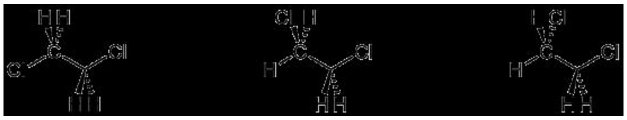
Rotations around C–C bonds require little energy because the molecular orbital of a σ covalent bond has cylindrical symmetry along the internuclear axis (Section D5.5, Section D10.1). Cylindrical symmetry means that regardless of how two σ-bonded atoms are rotated with respect to each other around the internuclear axis, the σ bond remains unbroken between them. For example, consider the rotation around the C-C bond in 1,2-dichloroethane:

https://wisc.pb.unizin.org/app/uploa...dout02.mp4?_=1

***Figure 3**. Rotation around the C-C bond in 1,2-dichloroethane. Energy (indicated by the readout and the green dot on the graph) varies with angle of rotation. Expanding the animation to full screen makes the graph easier to see. You can pause the video and adjust to various angles of rotation to find the corresponding energy. (Animation by Michael Aristov.)*

Notice in Figure 3 that complete rotation around the C–C bond requires an energy change of 40 kJ/mol. The bond enthalpy of a C–C bond is 346 kJ/mol, so the energy required for rotation is a bit more than one-tenth the energy required to break the bond. Because the energy required for rotation around single bonds is small, such rotations occur readily at room temperature for most molecules. Hence, at room temperature, one conformer cannot be isolated from another and chemists consider that *conformers represent the same chemical compound*, with the same name and the same physical properties. No bond breaking is needed to go from one conformer to another.

If you could see all molecular structures in a room-temperature sample of 1,2-dichloroethane at a specific instant, you would find all three of these structures:



Each structure corresponds to one of the minima in the energy curve in Figure 3. If, instead, you followed one molecule over time, you would see it go from one structure to the next as the C-C bond rotates (as seen in Figure 3). Because experiments are typically done at room temperature, we consider all three structures as conformers of the same molecule. You can draw any of them as a representation of 1,2-dichloroethane.

From this animation of a nonane molecule you can see that different conformers of the same molecule can adopt, at a first glance, dramatically different molecular shapes. If you change your viewpoint by moving the molecule with your mouse, you can see that the molecule also looks quite different from different perspectives.

A link to an interactive elements can be found here.

Given two or more Lewis structures, it is important that you can recognize whether they are conformers or isomers. Lewis structures or line structures that look quite different may be different conformers or the same conformer drawn from different perspectives; in either case, the structures represent the same substance.

A good way to tell whether two structures represent the same substance is to work out the correct name of each structure. If the names are the same, the structures represent conformers, not different substances. You will not be explicitly tested on naming compounds (nomenclature) in this course, but we strongly recommend that you study the section about alkanes in the appendix IUPAC nomenclature. IUPAC names are a systematic way of naming chemical compounds that can also help you when thinking about molecular structure. Going forward, if you encounter a name for a chemical compound that's unfamiliar to you, the IUPAC nomenclature appendix can help.

Activity 2 Identifying Conformers

Chemically, different conformers can affect the reactivity of a molecule. And on a larger scale, huge protein molecules adopt only a few of many possible conformations; the shapes of protein molecules are essential to their biological functions.

D11.4 Constitutional Isomers

Compounds with the same molecular formula but different atomic connectivity are called **constitutional isomers** (or **structural isomers**). For example, there are two alkanes with the formula C_4H_{10}:

Figure 4. *Click on the link to see a 3D rotatable model of n-butane and 2-methylpropane.*

The *n*– in *n*-butane stands for *normal*, meaning an unbranched carbon chain. Typically the "*n*-" is omitted and the compound is just named "butane"; it is assumed that you know that no prefix refers to the unbranched chain.

The traditional name of 2-methylpropane is isobutane. Many times, the "2-" is omitted and the compound is just called "methylpropane" because that's the only location for the methyl group to bond to (if the methyl is bonded to either end, the molecule is *n*-butane); hence there's no ambiguity by omitting the "2-".

Activity 3 Analyzing Constitutional Isomers

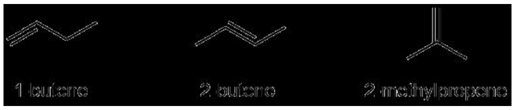
In your course notebook write an answer to each question and an explanation of your answer:

- Describe the shape of the *n*-butane molecule and how it differs from the shape of the 2-methylpropane molecule.
- Analyze the bonding in each molecule. Are all C atoms bonded to the same number of H atoms? If not, is the number of similarly bonded C atoms the same in each of the two structures ?
- To convert from *n*-butane to 2-methylpropane, would one or more chemical bonds need to be broken so that atoms could be re-arranged?
- Would you expect the physical properties (such as melting point and boiling point) to be different for the two substances?

To change from one constitutional isomer to another requires breaking and re-forming chemical bonds, which requires significant input of energy. At room temperature, very few molecules have that much energy. Therefore, constitutional isomers can be synthesized and separated from one another: *they are different substances*.

In addition to examining the connectivity in Lewis structures, another way to tell whether a Lewis structure represents the same molecule as another Lewis structure is to work out the IUPAC names for both structures. IUPAC names are designed so that the same structure always has the same name; if two structures are different, naming them correctly will result in different names.

Alkenes and alkynes can also exhibit constitutional isomerism. For example, the four carbon atoms in the chain of butene give rise to three different constitutional isomers:

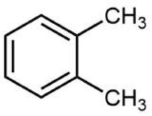


It's not just the π bond location that differs, be sure that you can deduce all the C-H and C-C bonds that need to be broken and re-formed going from one isomer to the another by looking at just the line structures. See the 3D models of 1-butene, 2-butene, and 2-methylpropene to verify.

And similarly, butyne can have two different constitutional isomers:

Exercise 4: Isomers of Substituted Benzenes

The structure of ortho-xylene is shown here:



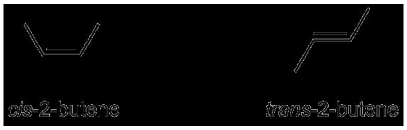
Click on each structure below that is a constitutional isomer of *ortho*-xylene.

D11.5 Stereoisomers: Geometric Isomers

Stereoisomers are *molecules that have the same molecular formula and the same atomic connectivity, but differ in the orientation of the atoms in 3D space*. Hence, molecules that are stereoisomers of each other stem from the same structural isomer. There are several different types of stereoisomers. First we will discuss the geometric isomers.

The two carbon atoms in a C=C double bond cannot freely rotate with respect to each other because such rotation requires breaking the π bond (see Section D10.4). Once the π bond is broken there would be free rotation around the remaining σ bond, but at room temperature most molecules do not have sufficient energy to break a π bond. Thus, there is no free rotation around a C=C double bond. This gives rise to **geometric isomers**, *stereoisomers that differ in the orientation of the groups connected to a C=C bond.*

For example, there are two geometric isomers of 2-butene, *cis*-2-butene and *trans*-2-butene:

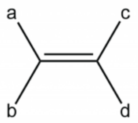


The isomer with *both methyl groups on the same side of the double bond* is called a ***cis*** **isomer** (above, the methyl groups are shown as both being above the double bond). The one with the *methyl groups on opposite sides* is called a ***trans*** **isomer**. Geometric isomers have different physical properties, such as boiling point, that make separating them possible. Hence *they are different substances*, and in nomenclature, they are distinguished by the “cis” and “trans” prefix. Figure 5 shows an animation of a cis-2-butene molecule showing conformations that are accessible at room temperature.

A link to an interactive elements can be found here.

Figure 5. *At room temperature a molecule of cis-2-butene can adopt many conformations, but none of them involve full rotation around the C=C bond to form trans-2-butene. (Animation by Michael Aristov.)*

Cis-trans isomerism is only possible when there are two different groups at each end of a double bond. For example, in an alkene molecule like this



there can be geometric isomers if a and b are different groups *and* c and d are different groups. If both groups on either end of the double bond were the same (a the same as b, or c the same as d), rotating around the double bond would not produce a different molecular structure.

D11.6 Stereoisomers: Enantiomers

Another type of stereoisomer is a pair of *molecules that are mirror images that cannot be superimposed on each other*. Such stereoisomers are called **enantiomers** (or **optical isomers**), and are described as being **chiral** (from the Greek word cheir, χειρ, meaning “hand”; your left and right hands exhibit chirality—they are non-superimposable mirror images of each other).

Most physical, chemical, and physiological properties of two enantiomeric substances are identical. Differences between enantiomers only become evident when the substances interact with other chiral molecules or environments. (An infamous example of a physiological difference is the drug thalidomide, where one isomer causes birth defects but the other does not.)

Most chiral molecules have at least *one atom that is bonded to four different* groups, a **chiral center**. Chiral centers are often marked with an asterisk (*) in molecular structures. A carbon atom that is a chiral center is referred to as an *asymmetric carbon atom* or a *chiral carbon atom*. For example, the carbon atom in bromochloroiodomethane is a chiral center and there are two enantiomeric isomers: the two mirror-image molecules of CHBrClI are not superimposable on each other (Figures 6 and 7).

A link to an interactive elements can be found here.

Figure 6. *Bromochloroiodomethane is a chiral molecule. Use the mouse to orient the molecules. At the beginning of the animation, the two enantiomers are shown as mirror images. then one molecule is rotated and moved on top of the other to show that these two mirror-image molecules are not superimposable. (Animation by Michael Aristov.)*
Figure 7. *Bromochloroiodomethane is a chiral molecule. The two enantiomers are shown as mirror images in one view. When you move the slider, the right molecule has been rotated so that the C-H and C-I bonds are aligned; rotation shows that these two mirror image molecules are not superimposable.*

Activity 4 Analyzing Enantiomers

Study Figure 6 and Figure 7 carefully. Make certain that you understand what superimpose means and why these two mirror-image molecules cannot be superimposed.

- Based on your observations, devise a method for distinguishing one structure from the other; that is, describe how you can tell that one molecule is different from the other. Write your method in your notebook.
- To convert from (*R*)-bromochloroiodomethane to (S)-bromochloroiodomethane, would one or more chemical bonds need to be broken so that atoms could be re-arranged? If so, describe which bonds could be broken and which could be formed to interchange the structures.

The difference between the two enantiomers may not appear to be significant, but you would have to at least partially break and re-form two σ bonds in order to go from one enantiomer to the other. Hence, enantiomeric structures represent different substances that can be separated from one another. Separation is often difficult and requires a chiral environment: a different chiral substance that interacts differently with the left-hand molecule compared to the right-hand molecule. A macroscopic analogy is this: if all the gloves you own were mixed up, you could separate left-hand gloves from right-hand gloves by how they interact with your right hand; all gloves that fit are right-handed.

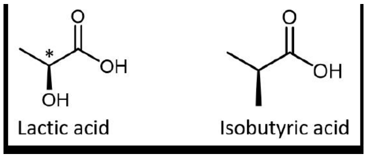
All molecules have a mirror image, but only chiral molecules have nonsuperimposable mirror images. Contrast CHBrClI with $CHCl_2I$ (dichloroiodomethane), which is shown in Figure 8. $CHCl_2I$ and its mirror image are superimposable. Thus $CHCl_2I$ is not a chiral molecule (it is said to be *achiral*). Two groups (the Cl atoms) bonded to the carbon atom in $CHCl_2I$ are the same, so there is no chiral center.

A link to an interactive elements can be found here.

Figure 8. *Dichlorofluoromethane is not chiral. The molecule and its mirror image are superimposable.*

Generally, the easiest way to spot a chiral center is to look for four different groups bonded to an atom. The “groups” are considered in their entirety, not just the atom that is directly bonded to the chiral center. For example, a methyl group is a different group from an ethyl group, which is different from a propyl group and so forth. Hence, alkanes can be chiral, for example:

Just because you see dashed and solid wedges in a structure, do not automatically assume that you are looking at a chiral center. For example, lactic acid has an asymmetric (chiral) carbon atom (denoted by *) and is a chiral molecule, while isobutyric acid is not a chiral molecule.



Make sure that you can recognize from the wedge-dash Lewis structure that the chiral carbon atom in lactic acid has four different groups around it but the corresponding carbon atom in isobutyric acid does not. Use these three links to access 3D rotatable models of the two enantiomers of lactic acid and the single structure of isobutyric acid. Lactic acid link 1. Lactic acid link 2. Isobutyric acid.

D11.7 Intermolecular Forces

Whether a covalent molecular substance is a solid, liquid, or gas at room temperature (or any other temperature) depends on the strengths of the attractive forces between the molecules that make up the substance. *Any attractive forces between molecules* are referred to as **intermolecular forces** (IMFs). Strengths of intermolecular forces vary widely, but IMFs are usually weaker than covalent bonds. One form of IMF, London dispersion forces, has already been discussed in Unit 1, where we indicated that boiling points reflect the energy needed to overcome intermolecular forces as molecules go from being in close proximity to each other in the liquid phase to being far apart in the gas phase. Thus, boiling points are good indicators of the relative strengths of IMFs of different molecular substances.

The boiling points of linear alkanes (C_nH_{2n+2}), with n = 1-20 are shown in Figure 9. The boiling points gradually increase with increasing length of the molecule. You should be able to explain this trend in boiling points based on LDFs.

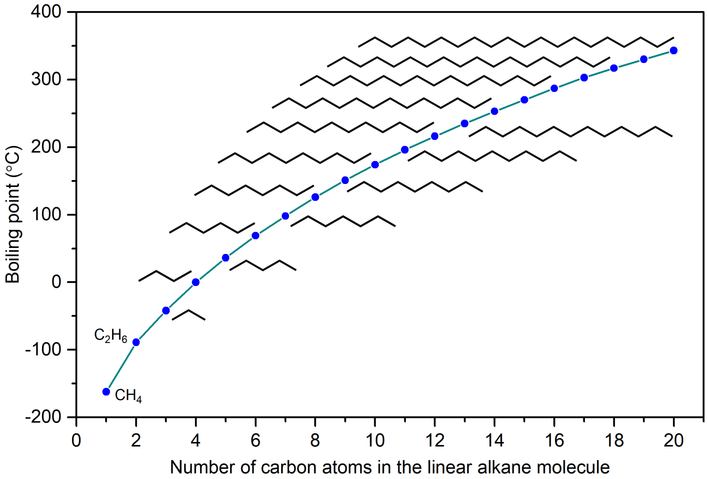


Figure 9. *Boiling points of linear alkanes as a function of number of carbon atoms in the molecule. The line structures of the n≥3 molecules are shown, where space permits.*

LDFs increase with number of electrons and also with ease of distortion of electron probability distribution in an atom or molecule. Because longer linear alkanes have more electrons, the LDFs increase and boiling points also increase.

Another factor that affects the strength of LDFs is molecular geometry. For example, the boiling points for *n*-pentane, isopentane (2-methylbutane), and neopentane (2,2-dimethylpropane) are 36 °C, 27 °C, and 9.5 °C, respectively, indicating that LDFs are greatest for *n*-pentane and least for neopentane.

Figure 10. *The strength of the LDFs increases with larger contact surface area between molecules, as demonstrated by the boiling points of these C_5H_{12} isomers. Use the slider to see total electron density views of the molecules and simple line drawings of the molecules. Click on the links to see rotatable models: 2,2-dimethylpropane; 2-methylbutane;n-pentane. Compare all three molecules in separate tabs in your browser to see that they are isomers and become less compact from left to right.*

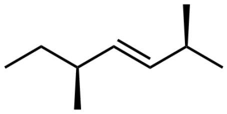
These three molecules are constitutional isomers and therefore have same number of electrons. In *n*-pentane, the open linear shape provides a *greater* surface area between molecules when they come in contact, resulting in *stronger* LDFs between the molecules. Neopentane has the most compact shape of the three, yielding the *smallest* surface area for intermolecular contact and, hence, the *weakest* LDFs.

Watch this video to learn more about Kellar Autumn's research that determined that LDFs are responsible for a gecko's ability to cling and climb.

Another physical property that is influenced by IMFs is the **viscosity** of a liquid, which is *a measure of the liquid's resistance to flow*. The stronger the IMFs, the more difficult it is for molecules to move past each other and the greater is the viscosity of the liquid. Alkane molecules can get quite large and Figure 9 shows that the strength of London dispersion forces is quite significant in larger alkanes (the boiling point of pentadecane $C_{15}H_{32}$ is 270°C). Hence, alkanes consisting of larger molecules also have higher viscosity. Some examples of uses for these long-chain alkanes are lubricating oil and paraffin wax. Alkanes with a chain length of 35 or more carbon atoms are found in asphalt (or bitumen), which is a sticky and highly viscous substance.

Day 11 Pre-class Podia Problem: Conformers and Isomers

Here is a structure of 2,5-dimethylhept-3-ene.



- There is one chiral carbon center in this molecule. Draw the structure and identify the chiral carbon with an asterisk (*).
- Draw a different conformation of the structure above.
- Draw the enantiomer of this molecule.
- Draw the geometric isomer of this molecule.
- Draw a constitutional isomer of this molecule that would be likely to have a higher boiling point.
    - Explain why you think this constitutional isomer would have a higher boiling point.
    - Draw a different conformation of this constitutional isomer.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

2.4: Day 12- Intermolecular Forces; Functional Groups

11

Day 12: Intermolecular Forces; Functional Groups

Applying Core Ideas: Comparing Propane and Dimethyl Ether

D12.1 Intermolecular Forces: Dipole-Dipole Attractions

The additional IMF alluded to in the Applying Core Ideas box is called **dipole-dipole attraction**, *attractive electrostatic forces between polar molecules*. The attractive force arises when the positive end of one molecular dipole interacts with the negative end of another molecular dipole **(**Figure 1).

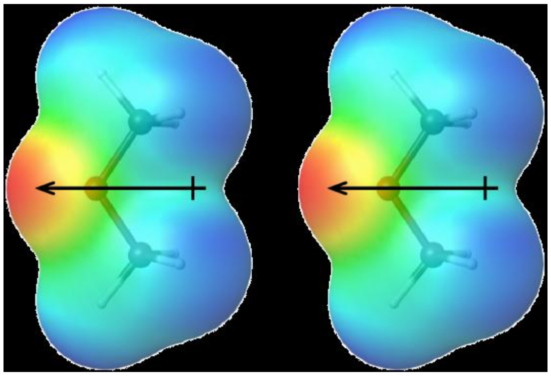


Figure 1. *One arrangement of two molecules that gives an attractive force between the partial negative end of one molecule and the partial positive end of another. Shown here is the dimethyl ether molecule. The molecular dipole moment is drawn as a dipole arrow on each molecule. On the colored space-filling molecular shape, red indicates greatest concentration of electron density and blue indicates least.*

The more polar a molecule is (that is, the larger its molecular dipole moment is), the stronger the dipole-dipole attractions are between molecules of that substance. Molecular polarity depends both on the sizes of the bond dipoles (that is, on electronegativity differences between pairs of bonded atoms) and the shape of the molecule. Physical properties of a substance are influenced by all IMFs between molecules of the substance, so it is important to consider both LDFs and dipole-dipole attractions when predicting properties such as boiling points.

How do we know whether a molecule has a dipole moment? In Section D9.2 we described polar covalent bonds—bonds in which there is an unequal distribution of electron density on two bonded atoms and hence a bond dipole moment. The sum of all bond dipole moments in a molecule gives a molecular dipole moment. *Molecules that have a molecular dipole moment* are called **polar molecules**; *molecules that have a zero (or near zero) molecular dipole moment* are called **nonpolar molecules**.

To predict whether a molecule is polar, first determine whether there are polar bonds by comparing electronegativities of each pair of bonded atoms. If electronegativity differences are small or zero, there are no polar bonds and the molecule must be nonpolar. If there are polar bonds, the molecule might be polar, but it is also possible that the bond dipoles might cancel. For example, both carbon dioxide (CO_2) and sulfur dioxide (SO_2) have polar bonds, but only SO_2 is polar. In CO_2, the central carbon has two σ bonds, it is *sp* hybridized, and therefore the molecule is linear. The bond dipoles are large ($\Delta EN = 3.5 - 2.6 = 0.9$) and equal in magnitude , but they are pointing in exact opposite directions. This results in a molecular dipole moment of zero. In SO_2, where the central S atom has two σ bonds and one lone pair, the S atom is sp^2 hybridized and the molecule is bent. Thus, the bond dipoles are also large ($\Delta EN = 3.5 - 2.6 = 0.9$), but they are at an angle and the resultant molecular dipole is not zero.

Bond dipoles behave as vectors, so if you are familiar with vector addition you can predict when bond dipoles cancel and when they do not. Another way to predict is this: molecules with all terminal atoms the same and no lone pairs on the central atom are nonpolar because of cancellation of bond dipoles. (In the case of a molecule with an odd number of electrons, a single electron on the central atom counts as a lone pair.) For multi-centered molecules, predicting molecular dipoles is trickier. Generally, if atoms have similar electronegativities, then bond dipoles are weak and the molecular dipole moment is small. For example, because C and

H have similar electronegativity, C-H bonds have small bond polarity, and hydrocarbon molecules are nonpolar. The dipole moment of propane, for example, is less than 0.1 D—essentially negligible.

D12.2 Functional Groups

There are more than twenty million known organic compounds, so it would be impossible to memorize chemical properties for each one. Fortunately, we can make use of functional groups to deduce the likely chemical and physical properties of a molecule. A **functional group** is *an atom or group of atoms that has similar chemical properties whenever it is present in a molecule*. Even if other parts of a molecule are quite different, a specific functional group usually reacts the same way.

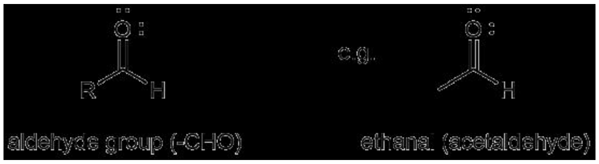
Because C–C and C–H bonds are strong, alkanes are unreactive at room temperature; they are used primarily as fuels (Section D7.2). The alkane parts of molecules usually don't participate in reactions and are not defined as functional groups. An **alkyl group** is *a portion of an alkane molecule bonded to something else*. Examples of alkyl groups are -CH_3 (methyl), -CH_3CH_2 (ethyl), and -$CH(CH_3)_2$ (2-propyl). (See alkane nomenclature for more examples.) We often use **R** (for the **R**est of the molecule) to designate any alkyl group (or sometimes another type of group) in a molecule. When there are two or more different alkyl groups, we use R, R', R", etc. For example, R and R', are trans to each other in the alkene structure below:

When a molecule is drawn using R or R' for alkyl groups, greater focus is put on a specific functional group, in this case, the alkene C=C bond.

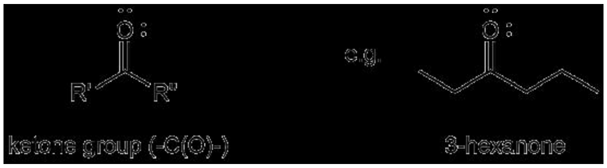
Sections D7.3 and D7.4 described the functional groups in alkenes and alkynes. The aromatic functional group was discussed in Section D9.6. The next few sections consider functional groups that contain heteroatoms: atoms other than carbon and hydrogen. Each of these functional groups has its own specific reactivity. Each functional group can also affect the types of intermolecular forces, giving rise to differing physical properties.

D12.3 Aldehydes and Ketones

An aldehyde or a ketone contains a **carbonyl group**, *a carbon atom double bonded to an oxygen atom*. The carbon atom in a carbonyl group is called the carbonyl carbon. In an **aldehyde** functional group, *the carbonyl carbon is also bonded to a hydrogen atom*. Hence, an aldehyde group can only bond to one R group (another carbon atom or a H atom), and the aldehyde group is always at the end of a chain of carbon atoms (click on the image below for a 3D model.)

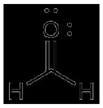


A **ketone** functional group *consists solely of the carbonyl group*. It bonds to two R groups, which may be the same or different, and is found partway along of a chain of carbon atoms. (click on the image below for a 3D model.)



The reactivity of both aldehydes and ketones are directly related to the reactivity of the carbonyl group.

Formaldehyde is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by mass.



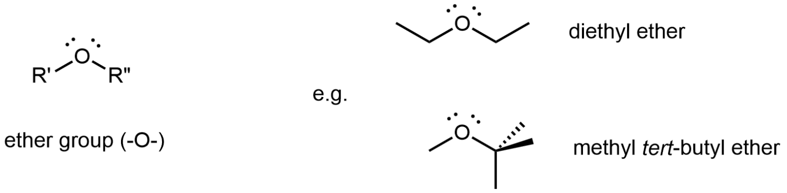
Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Dimethyl ketone, CH_3COCH_3, commonly called acetone, is the simplest ketone. It is a colorless liquid that can be made commercially by fermenting corn or molasses. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

Activity 1: Ketone Hybridization and Local Bond Geometry

D12.4 Ethers

An **ether** functional group *contains the group –O–*, which bonds to two different R groups and is found in the middle of a molecule.



Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are now used primarily as solvents for gums, fats, waxes, and resins. Methyl *tert*-butyl ether (abbreviated MTBE) is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

Activity 2: Ether Hybridization and Local Bond Geometry

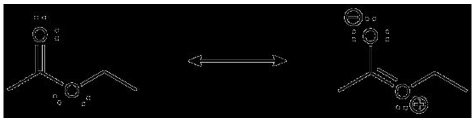
D12.5 Esters

An **ester** functional group *contains a carbonyl group with a second oxygen atom single bonded to the carbonyl carbon and also single bonded to another carbon atom*. A general ester structure has an R group bonded to the carbonyl carbon atom and another R group bonded to the second oxygen. It is a functional group that is found in the middle of a molecule. (Click on the image below for a 3D model.)

The ester functional group's carbon atom is sp^2 hybridized with a trigonal planar local geometry. Its carbonyl oxygen is *sp* hybridized, and one of its unhybridized 2*p* AOs forms the π bond with the carbon's unhybridized 2*p* AO. This oxygen also has two lone pairs: one occupies a *sp* hybrid orbital; the other occupies a 2*p* AO that is perpendicular to the π bond. The second oxygen (non-carbonyl oxygen) is sp^2 hybridized and has a bent local geometry. It also has two lone pairs, one in a sp^2 hybrid orbital, the other in the unhybridized 2*p* AO. See Figure 2 below.

Figure 2. *The ethyl acetate molecule, showing the orbitals of the carbonyl O lone pairs, carbonyl π bond, and non-carbonyl O lone pairs.*

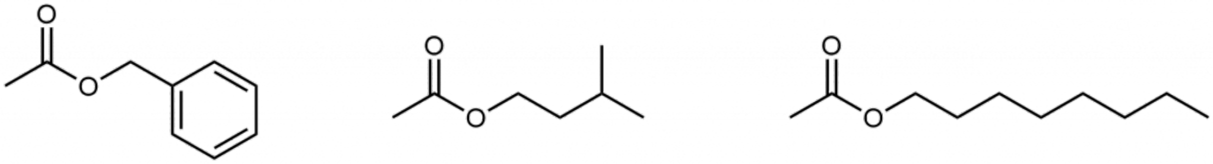
As shown in Figure 2, the 2*p* lone pair on the non-carbonyl O is aligned parallel to the *p* orbitals that form the π bond. This leads to some delocalization of the lone pair electron densities, which can be expressed by resonance structures:



While the resonance structure on the right makes only a minor contribution to the description of the ester molecule, that structure is important in understanding the ester's chemical and physical properties. For example, the -COO- ester group is planar, and the non-carbonyl C-O bond is not as freely rotatable as a typical single bond. Moreover, an ester's reactivity is quite different from that of a ketone or an ether, and hence an ester is a distinct functional group.

Activity 3: Ester Hybridization and Local Bond Geometry

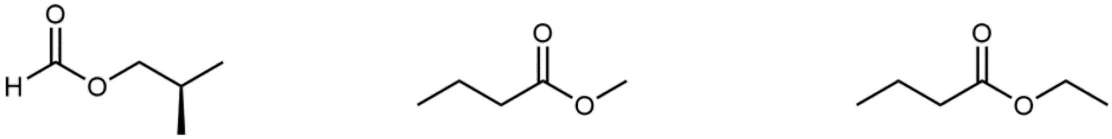
The odors of ripe bananas and many other fruits are due to the presence of esters.



benzyl acetate
(jasmine)

isopentyl acetate
(banana)

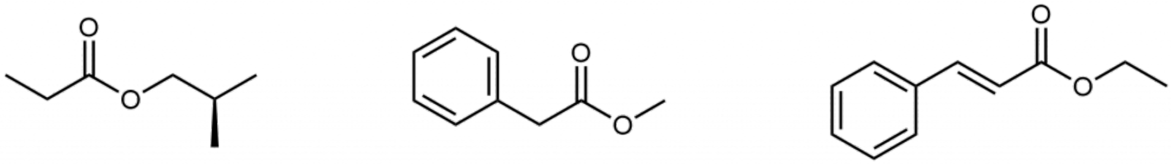
octyl acetate
(orange)



isobutyl formate
(raspberry)

methyl butyrate
(apple)

ethyl butyrate
(pineapple)



isobutyl propionate
(rum)

methyl phenylacetate
(honey)

ethyl cinnamate
(cinnamon)

Figure 3. *Structures of some esters that are responsible for the odors associated with various plants and their fruits. Many other esters and their odors are listed at this link.*

Day 12 Pre-class Podia Problem: Predicting Boiling Points

The observed boiling points for CCl_4 and $CHCl_3$ are:

$$CCl_4 : 77\ °C\ CHCl_3 : 61\ °C$$

Use your knowledge of intermolecular forces to write an explanation for why CCl_4 has a higher boiling point.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

2.5: Day 13- Alcohols, Carboxylic Acids, Amines, Amides; Hydrogen Bonding

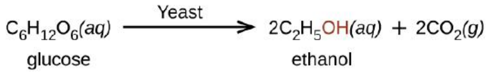
12

Day 13: Alcohols, Carboxylic Acids, Amines, Amides; Hydrogen Bonding

D13.1 Alcohols

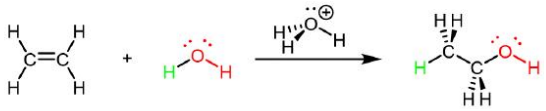
An **alcohol** functional group *contains a –OH (hydroxyl) group covalently bonded to a carbon atom*. (Note that the –OH group is covalently bonded—the OH is not a hydroxide ion.) The names of alcohols are derived from the names of the corresponding alkanes by removing the final "e" and adding "ol". For example, the structure of the simplest alcohol is derived from the structure of methane by replacing one H atom with an OH group (CH_3OH). It is named methanol .

Ethanol is produced by some species of yeast that catalyze fermentation of various sugars:



$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Yeast}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

Ethanol can also be synthesized using the addition reaction of ethene and water using an acid as a catalyst:



Exercise 1: Structures of Alcohols

Knowing how to systematically name compounds can be helpful, especially when trying to decipher whether the line structures shown are constitutional isomers or not. See the nomenclature appendix for additional descriptions on how to name alcohol compounds. (You will not be explicitly tested on nomenclature in this course.)

Alcohol molecules can be classified according to the number of alkyl groups attached to the carbon with the -OH group, as shown in Figure 1. If one alkyl group (or only hydrogen) is attached to that carbon, the alcohol is a *primary* (1º) alcohol. If two alkyl groups are attached, the alcohol is a *secondary* (2º) alcohol. If three alkyl groups are attached, the alcohol is a *tertiary* (3º) alcohol.

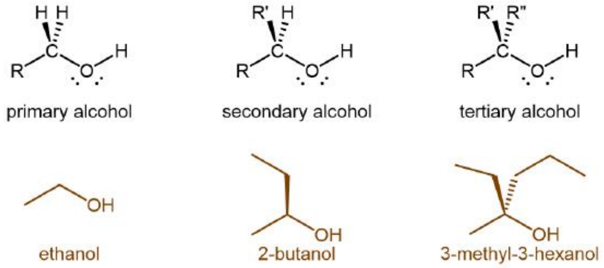
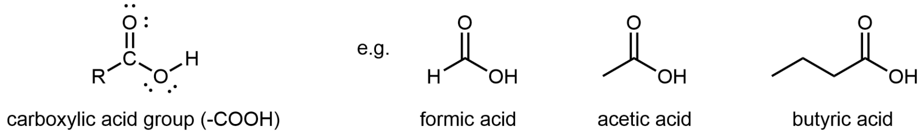


Figure 1*. Generic forms of 1º, 2º, and 3º alcohol; R, R', and R" designate alkyl groups that can be the same or different. In orange are example skeletal structures.. (Click each link for a rotatable 3D structure: ethanol, 2-butanol, and 3-methyl-3-hexanol)*

D13.2 Carboxylic Acids

A **carboxylic acid** functional group, -*COOH, has a carbonyl and a hydroxyl (-OH) group linked to the same carbon atom*. It differs from an ester in that the non-carbonyl oxygen is bonded to a hydrogen atom rather than an R group. Hence, carboxylic acid groups are found at one end of a molecule.



The simplest carboxylic acid is formic acid, known since 1670. Its name comes from the Latin word for ant, *formicus.* It is partially responsible for the pain and irritation of ants' and wasps' stings. Acetic acid is a main component (>4% by volume) of vinegar.

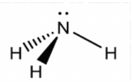
Cider vinegar is produced by allowing apple juice to ferment without oxygen present; yeast changes sugar to ethanol, which is then converted to acetic acid via biological oxidation. Butyric acid, a component of rancid butter and Limburger cheese, has a vile odor.

Carboxylic acid groups are acidic because their O-H bond can break relatively easily to yield -COO$^-$ and H$^+$, allowing them to donate a proton, H$^+$, to another molecule or ion. This acidity arises from the relative stability of the carboxylate anion, RCOO$^-$.

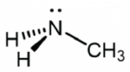
Activity 1: Resonance and Acidity of a Carboxylic Acid

D13.3 Amines

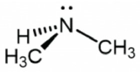
An **amine** functional group is *a derivative of ammonia that contains one or more carbon-nitrogen bonds*.



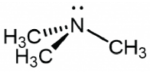
ammonia



methylamine



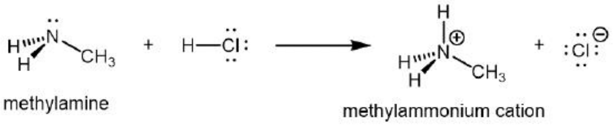
dimethylamine



trimethylamine

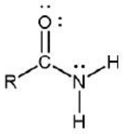
You can classify amine molecules by the number of C-N bonds. In the above example, methylamine is a *primary* (1º) amine, dimethylamine is a *secondary* (2º) amine, and trimethylamine is a *tertiary* (3º) amine. In this figure methyl groups are shown but any R group, such as ethyl, could replace any of the methyl groups.

Like ammonia, amines are basic due to the lone pair on the nitrogen atom, and can undergo acid-base reactions to form protonated amine cations analogous to the ammonium ion NH_4^+:

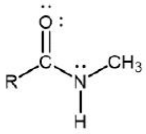


D13.4 Amides

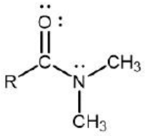
An **amide** functional group *contains a nitrogen atom connected to the carbon atom of a carbonyl group*. Like amines, amides can be classified by the number of carbon atoms bonded to the nitrogen:



Primary (1°) amide



Secondary (2°) amide



Tertiary (3°) amide

Activity 2: Amines, Amides, and Resonance Structures

Although the resonance structure with formal charges on O and N does not contribute as much to the resonance hybrid as the resonance structure without formal charges, it is crucial in understanding the chemical and physical properties of amide molecules. For example, the partial double bond character gives rise to a significant energy barrier for rotation of the C-N bond. And because the lone pair on the N atom is part of the π bonding network, the N atom in an amide is about 10^{10} times less basic than the N atom in an amine.

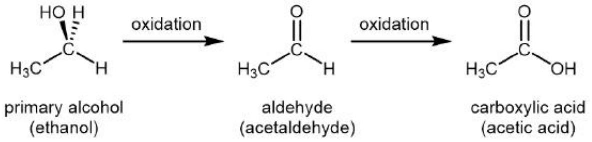
D13.5 Reactions of Alcohols, Amines, and Carboxylic Acids

Oxidation Reactions

All substances whose molecules contain hydrocarbon sections are combustible—the hydrocarbon parts can be oxidized completely to carbon dioxide and water. For many compounds controlled oxidation is more important than combustion because it can convert one type of functional group into another functional group, giving us chemical compounds useful in various applications. An example is oxidation of alcohols, which can be converted to aldehydes, ketones, or carboxylic acids.

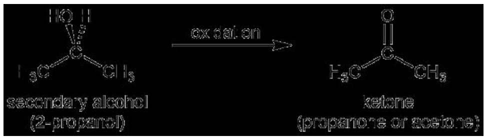
Oxidation of an organic compound can usually be recognized as either an addition of oxygen atom(s) to or removal of hydrogen atoms from the reactant molecule. The ease with which an alcohol can be oxidized and the extent of the oxidation depends on whether the alcohol is primary, secondary, or tertiary.

For a primary alcohol, controlled oxidation first produces an aldehyde. If there is an excess of oxidant, the aldehyde is further oxidized to a carboxylic acid:



Common oxidizing agents used in the laboratory for controlled oxidation are aqueous solution of potassium permanganate, $KMnO_4$(aq), or aqueous acidic potassium dichromate, $K_2Cr_2O_7$(*aq*).

For a secondary alcohol, the oxidation product is a ketone:

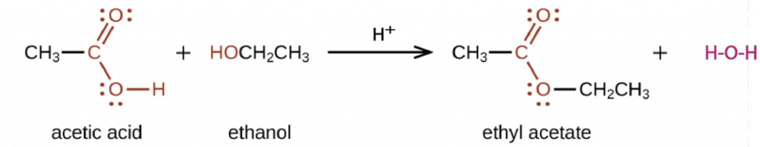


Ketones are difficult to oxidize further because, without breaking C–C bonds, there is no obvious way to add one more oxygen atom to the carbonyl carbon and there are no hydrogen atoms to remove from that carbon either.

Tertiary alcohols, with no hydrogen atoms attached to the carbon atom that is bonded to the –OH group, are difficult to oxidize. Tertiary alcohols do undergo combustion (to yield CO_2 and H_2O), but they usually do not undergo controlled oxidation.

Condensation Reactions

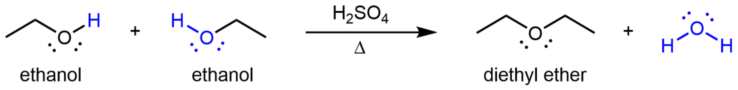
In a **condensation reaction**, *two molecules join to form a larger molecule and a small, stable molecule* such as H_2O or HCl. For example, ethyl acetate, $CH_3COOCH_2CH_3$, is formed when acetic acid reacts with ethanol in the presence of an acid catalyst:



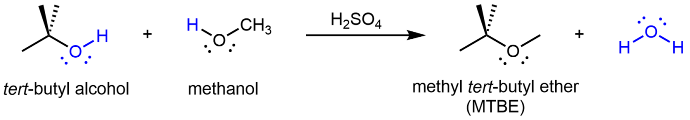
In general, condensation of a carboxylic acid and an alcohol produces an ester.

Condensation reactions are reversible: not all reactant molecules are converted to product molecules and, if product molecules are mixed, some reactant molecules form. *The reverse reaction of a condensation that produces water* is called a **hydrolysis reaction**. In hydrolysis, water breaks apart into H and OH with H attaching to one part the larger molecule and OH to another: hydrolysis comes from hydro, “water” and lysis, “breaking apart”.

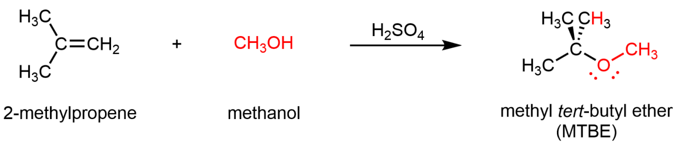
Ethers can be obtained from condensation reactions involving two alcohol molecules. If the two alcohol molecules are the same, a symmetric ether forms. For example, when ethanol is treated with a limited quantity of sulfuric acid and heated to 140 °C, diethyl ether and water are formed:



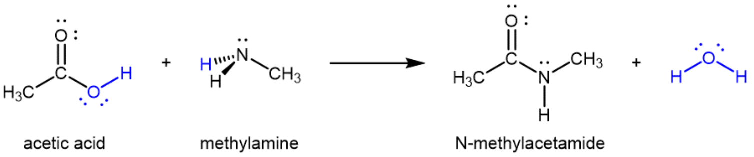
If the condensation reaction involves two different alcohols, an asymmetric ethers can form. For example:



Alternatively, addition reactions between alkenes and alcohols can form ethers. For example:



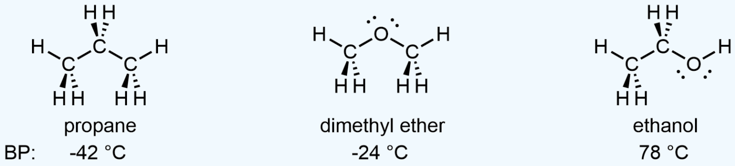
Amides can be produced from carboxylic acids and primary or secondary amines (or ammonia) via condensation reactions:



It is through this reaction that amino acids (molecules containing both an amine and a carboxylic acid functional group) link together in a polymer to form peptides and proteins.

Applying Core Ideas: Comparing Propane, Dimethyl Ether, and Ethanol

When we previously compared the boiling points of propane and dimethyl ether, we saw the effect of dipole-dipole attractions. Let's add ethanol to that comparison:



D13.6 Intermolecular Forces: Hydrogen Bonding

The additional IMF that exists between ethanol molecules, but does not exist between propane molecules or between dimethyl ether molecules, is called **hydrogen bonding**. It is *the interaction between an X–H covalent bond (X denotes a highly electronegative atom) and the lone pair on an electron rich atom, Z.* The hydrogen bonding interaction can be designated as X-H···Z (the "···" is the hydrogen bond itself).

Strong hydrogen bonding occurs between F-H, O-H, or N-H bond and an electron lone pair on another F, O, or N atom. F, O, and N, are among the most electronegative elements in the periodic table, a characteristic necessary for strong hydrogen bonding.

A hydrogen bond has about 5-10% the strength of a typical covalent bond. Part of this strength comes from dipole-dipole interactions, but more important is partial electron sharing that resembles the formation of a covalent bond. This is illustrated in Figure 2, which shows the hydrogen bond interaction between two water molecules. The left water molecule provides the O-H bond (we will denote this as O_L-H); the right water molecule provides the O atom with the lone pair (we will denote this as O_R).

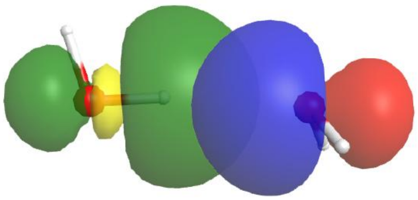


Figure 2*. The empty O_L-H σ* orbital (yellow/green) overlaps with the O_R lone pair (blue/red), forming a hydrogen bond.*

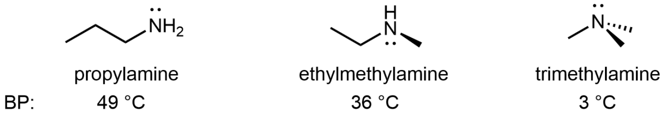
The empty O_L-H antibonding σ* orbital (yellow/green) overlaps with the orbital of the O_R atom's lone pair (blue/red). This overlap allows some electron density to be shared between the two water molecules, thus forming a hydrogen bond. If more electron density were to move from the O_R lone pair to the O_L-H σ* orbital, the antibonding orbital would be filled, the O_L-H bond would break, and a chemical reaction would have occurred—a new O_R-H bond would form, resulting in the right water molecule becoming H_3O^+:

$$H_2O + H_2O \longrightarrow OH^- + H_3O^+$$

Thus, forming a hydrogen bond resembles the formation of a covalent bond.

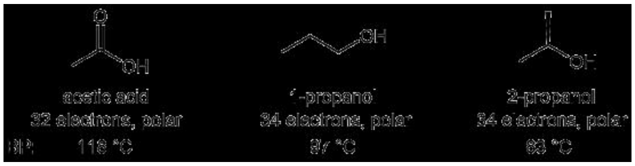
Activity 3: IMFs between Water Molecules and between Hydrogen Fluoride Molecules

For amines, 1º and 2º amines are capable of strong hydrogen bonding due to the presence of a N-H bond and the lone pair on the N atom, but 3º amines cannot form hydrogen bonds. For example, for the three amine isomers shown below, the boiling point of the 3º amine is significantly lower than the 1º and 2º isomers.



For amides, because the lone pair on N atom is part of the π bonding network, it is not available for hydrogen bonding. However, hydrogen bonds can still form in 1º and 2º amides between the N-H bond(s) and the lone pairs on the O atom.

Molecules containing the carboxylic acid functional group can also form hydrogen bonds. Pure acetic acid is called *glacial* acetic acid because its melting point of 16.6 °C is high enough that it can freeze in a cold laboratory. It is also quite thick and syrupy because the many hydrogen-bonding attractions between molecules result in high viscosity. The acidity of the carboxylic acid group enhances the O-H···O hydrogen-bond strength, such that hydrogen-bonding between carboxylic acid molecules is usually greater than between alcohol molecules. For example:



D13.7 Intermolecular Forces: Water Solubility

IMFs directly affect the water-solubility of a compound. Let's consider the alcohol functional group as an example.

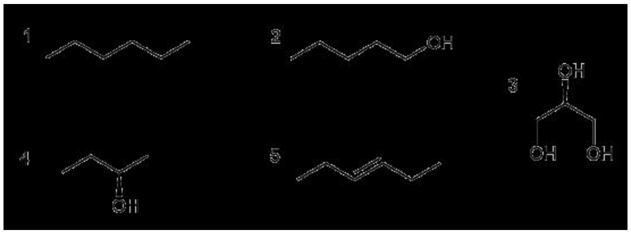
The -OH end of an alcohol molecule is **hydrophilic** ("water-loving"), *capable of strong intermolecular interactions with water molecules.* The dipole-dipole and hydrogen-bond interactions between alcohol and water molecules are similar in strength to those between alcohol and alcohol molecules or between water and water molecules. The hydrocarbon (alkyl) end of an alcohol molecule is essentially nonpolar and is **hydrophobic** ("water-fearing"), where the *intermolecular interactions between hydrophobic molecules and water molecules are weak* compared to IMFs between water-water molecules or hydrocarbon-hydrocarbon molecules.

Hence, although the size of the alkyl group has little influence on the reactivity of an alcohol molecule, it has a significant impact on the solubility of alcohols in water. Alcohols with small alkyl groups, e.g. methanol and ethanol, are completely **miscible** with water, which means *they have infinite mutual solubility* in water. Alcohols with larger alkyl groups, such as 1-octanol, are **immiscible** in water, which means that *when 1-octanol is added to water two layers form*. One layer is nearly pure water and the other layer nearly pure 1-octanol, because the solubility of each substance in the other is very low.

This is similarly true for the other polar and hydrogen-bonding functional groups. For example, acetic acid is miscible with water, while octanoic acid is immiscible with water.

Day 13 Pre-class Podia Problem: Functional Groups, Reactions, Solubility

Consider the structures shown below. List *all* substances that fall into each of the five categories below and explain why each substance fits each category you placed it in. Also explain why the other substances do not fit each category.



1. Contains a secondary alcohol functional group.
2. Is less soluble in water than 1-hexanol.

3. Has a higher boiling point than 1-hexanol.
4. Reacts with $K_2Cr_2O_7$(aq) to form a carboxylic acid.
5. Undergoes addition of water (with an acid catalyst) to form a secondary alcohol.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

2.6: Day 14- Macromolecules

13

Day 14: Macromolecules

Applying Core Ideas: Making Really Large Molecules

DNA is an example of a macromolecule—a huge molecule. A typical DNA molecule from the human genome is about 4 cm long and contains about 4 billion atoms. Suppose that you want to make a really, really big molecule like this. How might you go about it? What element or elements would likely be involved? What kind of chemical reaction might be used? Construct a model process, based on molecular structure and types of chemical reactions, that would enable synthesis of very large molecules. Write a description of the process in your notebook.

Polymers are *large molecules made by covalently linking many, many small molecules. The small molecules that link to form a polymer are* called **monomers**. Polymers can be natural (such as starch and proteins) or synthetic (such as nylon and polypropylene). Because they include a variety of structures and functional groups, polymers have a broad range of properties and uses that make polymer-based plastics integral parts of our everyday lives.

Polymers provide good examples of how we can apply models involving molecular structure, functional groups, and intermolecular attractions to explain and predict chemical and physical properties of materials.

D14.1 Addition Polymers

Addition polymers are *made by addition reactions*, wherein two molecules combine to form a single product molecule (see examples of addition reactions involving alkenes in Section D7.4). Typical monomers for addition polymerization have at least one double bond.

Figure 1 shows polyethylene, an addition polymer, forming from ethylene (ethene, $H_2C{=}CH_2$) monomers

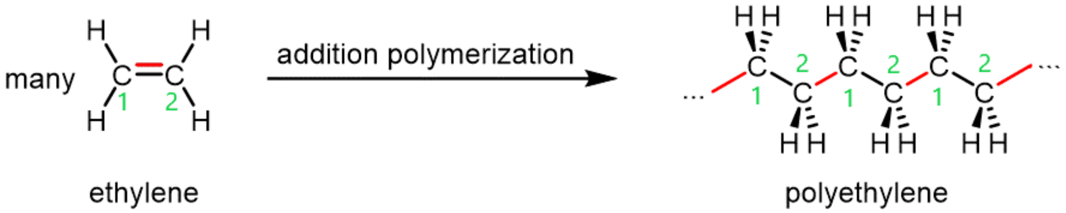
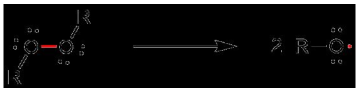


Figure 1. *The polymerization of ethylene to polyethylene is shown. The newly formed σ bonds between ethylene monomer units are highlighted in red (right); they are formed from the two electrons in the ethylene π bond (shown in red, left). Green carbon-atom numbers in the polymer correspond to the numbering in the ethylene structure.*

The reaction can be initiated by a molecule with an unpaired electron: a free radical. An example initiator is an organic peroxide, which can form two free radicals when the relatively weak O-O bond breaks:



Activity 1: Analyzing Peroxide Decomposition

When a radical encounters an ethylene monomer, the ethylene π bond breaks. One electron from the π bond goes to pair with the electron from the radical and form a σ bond. The other electron from the π bond remains a radical, and can go on to react with another ethylene monomer.

Figure 2. *Move the slider at the bottom to show steps in polymerization of ethylene. The curved arrows represent movement of π-bond electrons in the Lewis structure (that is, rearrangement of electron density). One π-bond electron pairs with another electron forming a new σ bond and the other becomes an unpaired electron in a new free radical.*

The process in Figure 2 repeats with many, many more monomers, sometimes as many as 100,000 units, yielding a long polymer chain of carbon atoms.

D14.2 Polymer Structure and Properties

In polyethylene, the addition reactions convert all ethylene double bonds to single bonds and join the monomers without losing any atoms. Hence, this polymer at a molecular level consists of a collection of long-chain alkane molecules, most of which contain tens of thousands of carbon atoms. Many of polyethylene's properties are what we would expect from this molecular composition.

If the intermolecular forces between the chains are smaller, so that it is easier for the molecules to move past one another, the polymer will be softer and easier to scratch. If the intermolecular forces between the chains are sufficiently strong to prevent motion of the molecules past one another, the polymer will be harder or more rigid. Because polyethylene is a mixture of long alkane molecules, each of slightly different chain length, it softens over a range of temperatures rather than having a single melting point. You may have noticed that some plastics, when wrapped around something in a microwave oven, soften and change shape but never become liquid.

This leads to an important idea in the field of materials science: materials can be "tuned" to give exactly the properties desired. By adjusting the strengths of the intermolecular forces one can obtain plastic materials with a range of properties.

For polyethylene, the extent of branching of a polymer strand can be varied. Depending on the production process, a polymer strand can be a very long linear chain or there can be branching in the chain:

Polymer properties can also be affected by cross linking. A **cross-link** is *a covalent σ bond between two separate polymer chains* that is not at the end of either chain.

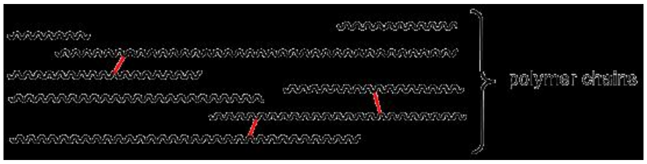


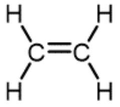
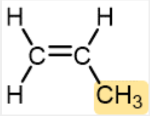
Figure 3. *Schematic representation of a polymer with a few cross-links (shown in red) between the chains.*

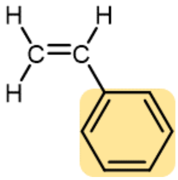
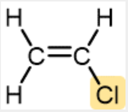
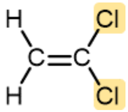
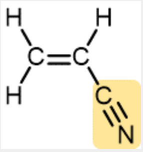
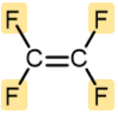
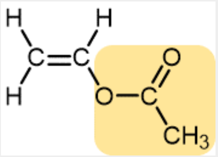
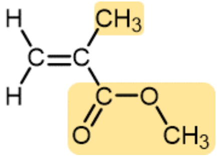
Cross links increase the molecular weight and limit the motions of the chains with respect to one another. With enough cross links, a sample of a polymer can become a three-dimensional network held by σ bonds—a single gigantic molecule. Another way to think about cross links: because they are covalent bonds, they are stronger than intermolecular forces between polymer chains and therefore amplify the effect of increasing intermolecular forces on polymer properties.

D14.3 Various Addition Polymers

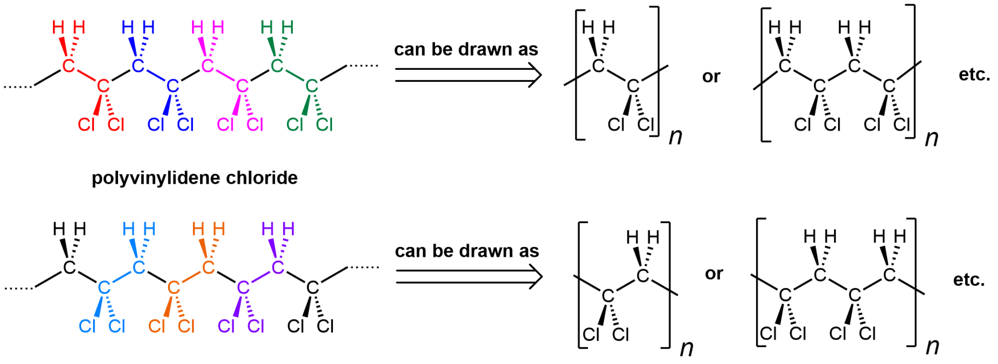
Table 1 below lists monomers for some well-known addition polymers and also some of their uses. You can probably find at least one example of each of them in your home. Each monomer is a variation of the ethylene (ethene) structure in which one or more H atoms has been replaced by another group (highlighted in the table). Such substitution(s) in the monomer allow the physical properties of the polymer, such as density, melting range, strength, and hydrophobicity, to be precisely controlled, and the polymer tailored for specialized uses. Note that in the equation below the polymer structure is specified by enclosing a single repeating unit in brackets and specifying the repeating nature by a subscript *n*.

Table 1. Monomers for Some Common Addition Polymers

Monomer	**Common Name**	**Polymer**	**Some Typical Uses**
	Ethylene	Polyethylene	Film for packaging and bags, toys, bottles, coatings
	Propylene	Polypropylene (Herculon)	Milk cartons, rope, outdoor carpeting

Monomer	Common Name	Polymer	Some Typical Uses
	Styrene	Polystyrene (Styrofoam, Styron)	Transparent containers, plastic glasses, refrigerators, styrofoam
	Vinyl chloride	Polyvinyl chloride (PVC)	Pipe and tubing, raincoats, curtains, phonograph records, luggage, floor tiles
	Vinylidene chloride	Polyvinylidene chloride (Saran)	Clinging food wrap
	Acrylonitrile	Polyacrylonitrile (Orlon, Acrilan)	Textiles, rugs
	Tetrafluoroethylene	Polytetrafluoroethylene (Teflon)	Nonstick pan coatings, bearings, gaskets
	Vinyl acetate	Polyvinyl acetate	Elmer’s glue, wood glue
	Methyl methacrylate	Polymethyl methacrylate (Plexiglass, Lucite)	Stiff, clear, plastic sheets, blocks, tubing, and other shapes

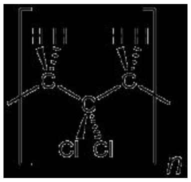
The notation where a repeating unit in a polymer chain is shown in brackets emphasizes that it is important to be able to recognize a repeating unit within a polymer chain. It is also important to be able to generate the full polymer structure from a repeating unit. Enclosed within the bracket can be one repeating unit (equivalent of a monomer), or two, or three, etc. Let’s use polyvinylidene chloride as an example:



Shown on the left is a polyvinylidene chloride polymer strand. The individual repeating units are color-coded. However, there are two ways to consider repeating units: starting at the CH_2 (top) or the CCl_2 (bottom). Either way is fine.

You can see that the repeating pattern in this polymer is alternating CH_2 and CCl_2. When you put a bracket around a repeating unit, you are communicating that what is outside of the bracket exactly repeats what is inside, starting immediately with the bonds that are divided by the bracket. Therefore, the leftmost carbon atom of the next repeating unit is directly bonded to the rightmost carbon of the unit shown.

In other words, something like the following is *incorrect* for depicting polyvinylidene chloride:



It is depicting a polymer where there are CH_2 unit bonded to CH_2 unit, which does not occur in polyvinylidene chloride. (this polymer is …-CH_2-CH_2-CCl_2-CH_2-CH_2-CCl_2-CH_2-CH_2-CCl_2-…)

D14.4 Conjugated Diene Polymers

Conjugated dienes (alkenes with two double bonds and a single bond in between) can be polymerized to form important substances, such as rubber. This occurs in nature as well as in the laboratory. The simplest conjugated diene is 1,3-butadiene; Figure 4 shows the 1,4-polymerization of this monomer. In the resulting polymer, a new σ bond (highlighted in red) is formed between carbon 1 of one monomer and carbon 4 of another monomer, and within each monomer, a π bond is moved to between carbon 2 and carbon 3.

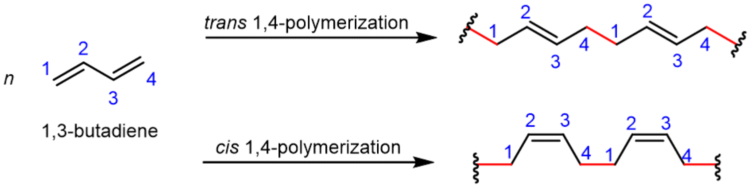


Figure 4. *1,4-polymerization of 1,3-butadiene. The carbons in a monomer unit are numbered for clarity. In the resulting polymer, a segment with two repeating units are shown, with the newly formed σ bond highlighted in red. The polymerization reaction can form trans or cis polymers.*

Let's consider the reaction in a bit more detail. During the polymerization reaction: one electron from the C_1=C_2 π bond in monomer B pairs with an electron from an adjacent monomer A to form a new σ bond involving C_1; similarly, one electron from the C_3=C_4 π bond in monomer B pairs with an electron from another adjacent monomer C to form a new σ bond involving C_4; the other electron from each π bond moves to the center of the molecule, and forms a new π bond between C_2 and C_3.

A link to an interactive elements can be found here.
Figure 5. 1,4-polymerization of 1,3-butadiene to form the cis polymer. *Upper: Run the animation to see the orbitals involved in the double bonds. The boxes represent a source of many monomer molecules (right) and the growing polymer chain (left). Lower: Move the slider to see the electron movements described in the text above. Each arrow represents movement of one electron and the electron movements are repeated for three monomers. Rotation around the sigma bond between* C_2 *and* C_3 *enables formation of either cis or trans polymer.*

Activity 2: 1,4-Addition Polymerization

Chemical reactions involving double bonds on adjacent polymer chains can lead to cross-linking, which enhances elasticity of the polymer. In 1839, Charles Goodyear discovered that when natural rubber was heated to 140–160 °C in the presence of sulfur, the rubber became tougher, more resistant to heat and cold, and more elastic. This process was later called **vulcanization** after Vulcan, the Roman god of fire and volcanos. Above 140 °C, S–S bonds in sulfur molecules, S_8, break, and linear chains of sulfur atoms form. These chains then react with some of the remaining double bonds in the polymer, forming cross links. The development of vulcanized rubber for automobile tires greatly aided the automobile industry.

Another important conjugated diene used in synthetic rubber is chloroprene (2-chloro-1,3-butadiene). Polymerized chloroprene was developed by DuPont and given the trade name *Neoprene*. Cross-linking in polychloroprene involves combination of two chlorine atoms from adjacent chains with a Zn^{2+} ion to form $ZnCl_2$. The C–Cl bonds in the uncross-linked polymer become C–C bonds—the cross-link. Cross-linking contributes to the overall elasticity of neoprene.

D14.5 Copolymers

Some of the most commercially important addition polymers are **copolymers**, made by *polymerizing a mixture of two or more monomers*. For example, styrene-butadiene rubber (SBR), which is a copolymer of 1,3-butadiene and styrene mixed in about a 3:1 ratio.

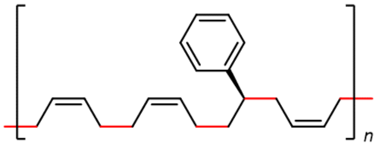


***Figure 5**. SBR consists of about a 3:1 ratio of 1,3-butadiene and styrene. Shown here is a single repeating unit of SBR, where the new C-C bonds formed during the polymerization process are highlighted in red.*

The properties of a copolymer are distinct from those of a mixture of the single polymers. For instance, the properties of SBR are different from a mixture containing polybutadiene and polystyrene, no matter what the ratio of the mixture is.

SBR was developed in the U.S. during World War II when important supplies of natural rubber were cut off. It is more resistant to abrasion and oxidation than natural rubber and can also be vulcanized. More than 40% of the synthetic rubber production is SBR, which is used in tire production. Several other types of rubber are copolymers, such as butyl rubber, which is copolymerized from 2-methylpropene ($H_2C{=}C(CH_3)_2$) and a small percentage of isoprene.

Day 14 Pre-class Podia Problem: Polymers and Intermolecular Forces

The strength or toughness of a polymeric material depends on strengths of intermolecular forces between polymer chains and several other factors. Assuming other factors are equal, compare the toughness/strength of polyethylene and polyacrylonitrile. Explain clearly which is stronger and why.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

2.7: Day 15- Condensation Polymers, Proteins

14

Day 15: Condensation Polymers, Proteins

D15.1 Condensation Polymers

A **condensation polymer** is *a polymer formed via a condensation reaction* (see Section D13.5). The very small molecule produced in each condensation can be H_2O, HCl, or some other simple molecule. Condensation polymerizations often, but not always, combines two different monomers in an alternating structure.

Condensation polymers usually grow by forming ester or amide linkages, where new C-O or C-N σ bonds form to link monomers. A typical monomer has a functional group at each end of the molecule. When one end of the monomer reacts and is added onto a polymer chain, the functional group at the other end remains and allows for further reaction to lengthen the polymer chain.

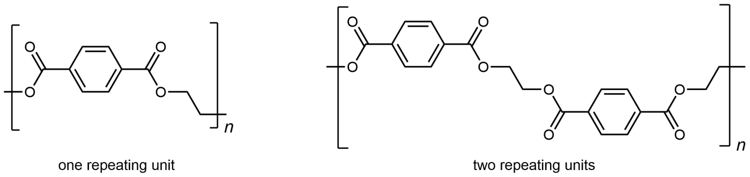
D15.2 Polyesters

A **polyester** is *a polymer where the individual units are held together by ester linkages*. For example, the common polyester *polyethylene terephthalate* (abbreviated as PET or PETE; has brand names such as Dacron or Mylar) consists of polymer chains formed from terephthalic acid (benzene-1,4-dicarboxylic acid) and ethylene glycol (ethane-1,2-diol) monomers.

The condensation reaction that results in the formation of the ester linkage in PET is shown in Figure 1. Repeated condensation reactions result in the step-wise growth of a polymer chain.

Figure 1. *The condensation reaction between terephthalic acid and ethylene glycol, forming an ester linkage, is shown. Click on the buttons for more information.*

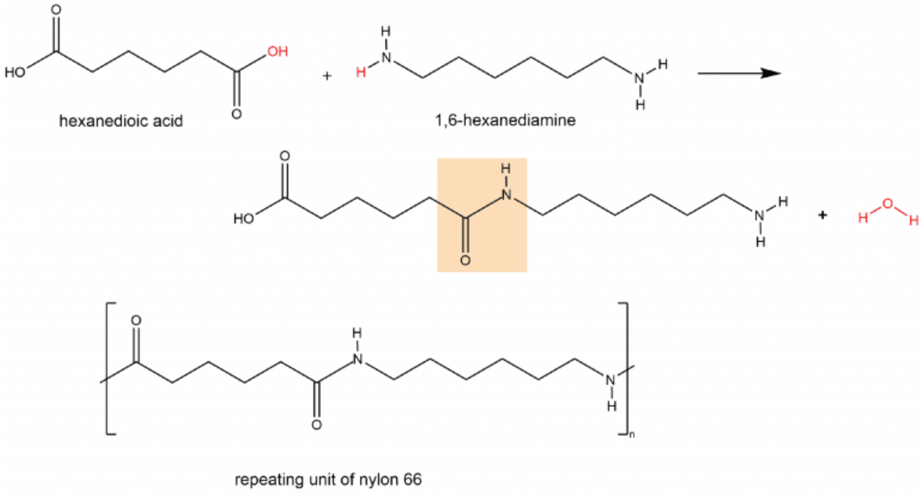
The repeating unit of PET is



The presence of ester groups, a polar functional group, on the polymer increases the intermolecular forces between polymer chains, and thereby increases the crystallinity and tensile strength of the polymer. PET makes for excellent fibers and are used in many fabrics. It is also used to make bottles for soda and other beverages. Polyester is biologically inert, so a knitted polyester tube can be used in surgery to repair or replace diseased sections of blood vessels.

D15.3 Polyamides

A **polyamide** is *a polymer in which the individual units are held together by amide linkages*. For example, nylon 66 is obtained from the monomers 1,6-hexanediamine and hexanedioic acid. The condensation reaction between these two monomers forms an amide linkage (highlighted):



On one end, the product molecule has a carboxylic acid group, which can undergo a condensation reaction with another 1,6-hexanediamine molecule. On the other end there is an amine group, which can react with another hexanedioic acid molecule. Such continuous condensation reactions lead to the formation of a nylon 66 polymer strand, the repeating unit of which is also shown above.

The "66" in nylon 66 stands for the six carbon atoms in each of the monomer molecules. Other nylons have different numbers of carbon atoms in the monomer molecules, such as nylon 510, which has 5 carbon atoms in the diamine (1,5-pentanediamine) and 10 carbon atoms in the diacid (decanedioic acid).

Nylon makes extremely strong threads and fibers because in addition to London dispersion forces and dipole-dipole attractions, there are hydrogen bonds between the polymer chains. Specifically, a hydrogen bond can form between a N-H in one strand and a carbonyl O lone pair in a neighboring strand.

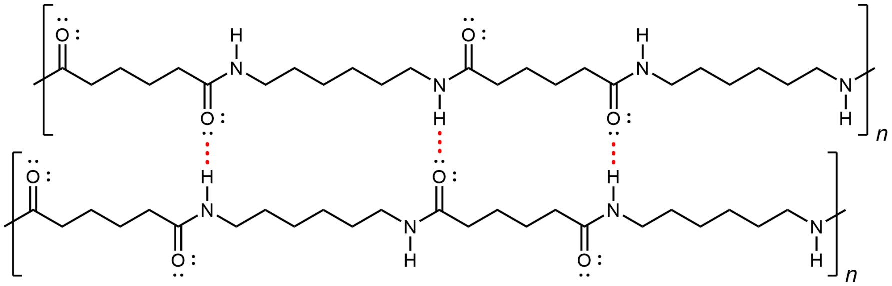
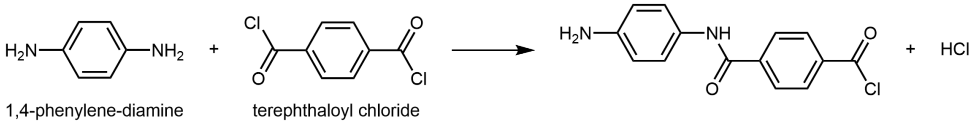


***Figure 2**. Two strands of nylon-6,6 polymer are shown; each strand is showing two repeating units. Hydrogen bonding, highlighted in red, can form between amide groups in different strands.*

If you pull on both ends of a nylon thread, after a slight stretch, it will resist breaking because of the strong IMFs that hold neighboring chains together.

Kevlar is a synthetic polymer made from 1,4-phenylenediamine and terephthaloyl chloride monomers. The byproduct of this condensation reaction is HCl.



The material has a high tensile-strength to weight ratio (it is about 5 times stronger than an equal weight of steel), making it useful for many applications from bicycle tires to sails to body armor.

Similar to nylon, part of Kevlar's strength is due to dipole-dipole interactions and hydrogen bonding (Figure 3) that increase intermolecular forces between polymer strands.

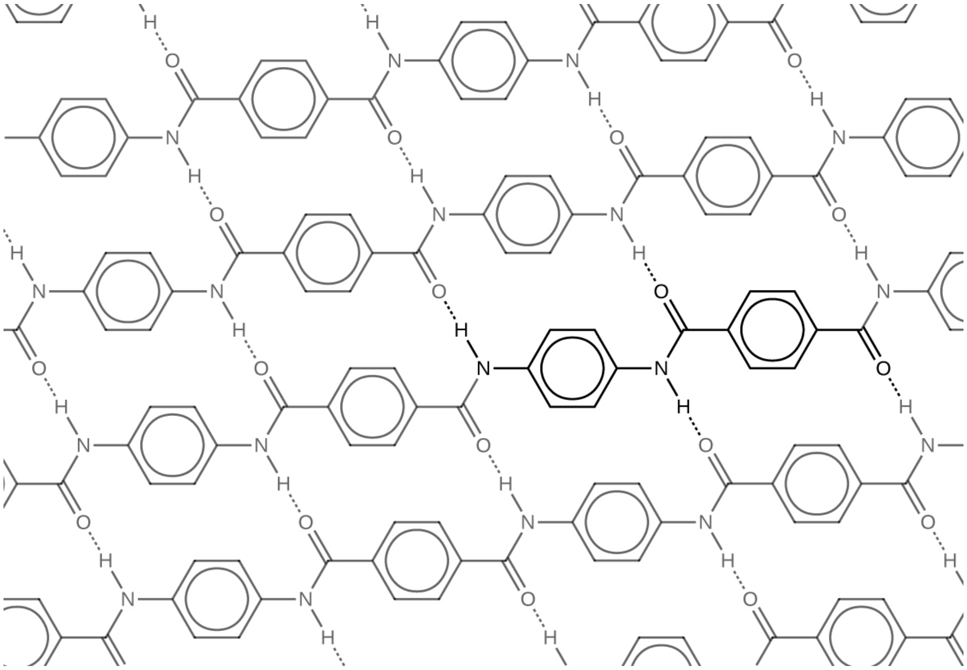


Figure 3. The diagram shows the polymer structure of Kevlar, with hydrogen bonds between polymer chains represented by dotted lines. One repeating unit of Kevlar is highlighted.

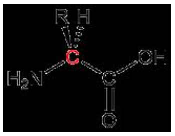
Notice that compared to nylon 66, the density of hydrogen bonds in Kevlar is higher, imparting stronger intermolecular forces.

Furthermore, Kevlar also has stronger London dispersion forces. Consider the repeating unit of Kevlar highlighted in Figure 3. It is a planar structure, with planar benzene rings connected by planar amide groups. Hence a single layer of Kevlar, as shown in Figure 3, is planar. When layers of Kevlar are placed on top of each other, they can be stacked very efficiently, allowing for maximal London dispersion forces.

In addition to its better-known uses, Kevlar is used in cryogenic applications because of its very low thermal conductivity. Kevlar maintains its high strength when cooled to liquid nitrogen temperatures (–196 °C). Many other plastics become brittle and break at that temperature.

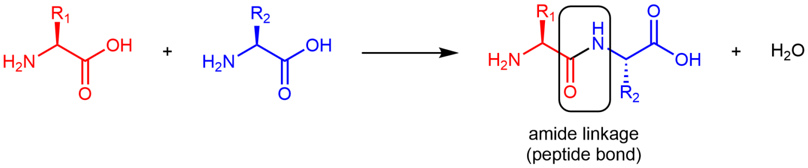
D15.4 Proteins

Proteins are *condensation polymers made from amino acids*. An **amino acid** consists of *a carbon atom (called the α carbon, shown in red below) bonded to a hydrogen atom, an amine group, a carboxylic acid group, and an R group, often called the side chain* .



Notice that the α carbon is chiral when the “R” group differs from the other three groups. About 500 naturally occurring amino acids are known, although only twenty are found in protein molecules in humans. Of these twenty amino acids, nineteen have a chiral α carbon.

Amino acids are linked together in proteins by amide linkages formed via condensation reactions. An amide linkage in a protein is often called a peptide bond.



Note that the reaction does not involve the α carbon atom, and the chirality at the α carbon is the same after the reaction as it was before. (In the equation above, R_2 is depicted with a dashed bond because the amino acid shown in blue has been flipped—rotated 180° around a horizontal axis—from the reactant to the product.)

Like all amide functional groups, the amide linkages in a protein strand are planar. The α carbon atoms, however, have tetrahedral local geometry. This *molecular chain of α carbons connected by amide groups*, is referred to as the **protein backbone**. It is the main chain of a strand of protein. The amino acid R groups are called **side chains** because *they are attached to, but branch off from, the main chain*.

15.5 Amino Acids

The twenty amino acids are often sorted into four groups—hydrophobic, polar but uncharged, basic, and acidic—depending on the nature of their side chains. The nine amino acids that have hydrophobic side chains are shown in Figure 4:

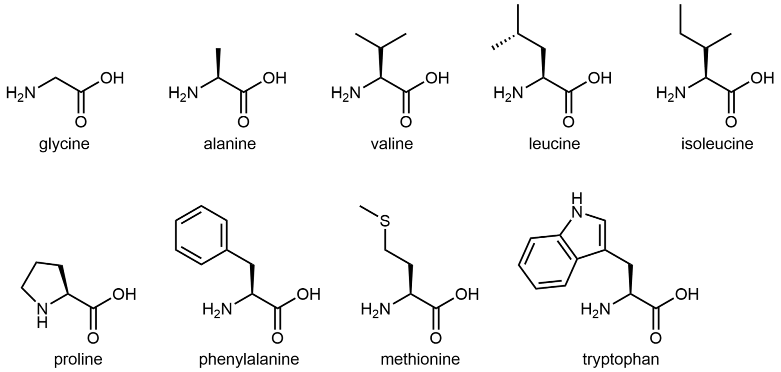


Figure 4. Amino acids with hydrophobic side chains. *The side chains of these amino acids are mainly composed of hydrocarbons.*

These hydrophobic side chains are composed mostly of carbon and hydrogen, have very small dipole moments, and tend not to mix with water. As we will see, this characteristic has important implications for a protein's structure.

The six amino acids shown in Figure 5 have side chains that are polar but neither acidic nor basic.

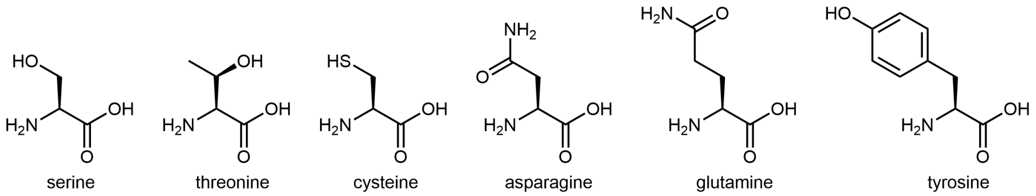


Figure 5. Amino acids with polar side chains that are neutral. *These side chains contain highly polar bonds whose dipoles do not cancel; most can also have strong hydrogen bonding attractions.*

The three amino acids in Figure 6 have side chains containing functional groups that are basic at neutral pH:

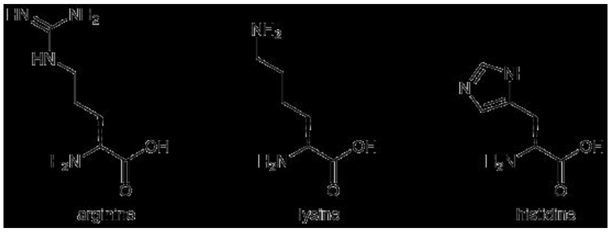


Figure 6. Amino acids with basic side chains. *A nitrogen atom in each of these side chains can accept a proton to form a positively charged ion.*

Activity 1: What Part of the Histidine Side Chain Is Most Basic?

And finally, Figure 7 shows two amino acids that have acidic side chains containing the carboxylic acid functional group:

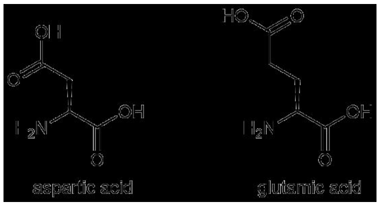


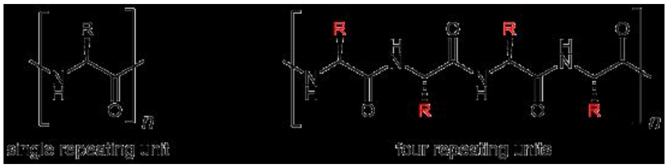
Figure 7. Amino acids with acidic side chains. *The carboxylic acid group in each of these side chains can donate a proton, forming a negative ion.*

D15.6 Protein Structure

Protein molecules are complicated: there are 20 different kinds of monomers that can be linked to form a huge number of different polymer chains. Thus protein structures are classified in several ways. Fundamental is the order in which the monomers are linked: the *primary structure*. Long protein backbones can adopt unique three-dimensional *secondary* and *tertiary* structures, both of which are dependent on the primary structure. When two or more protein strands of proteins are held together by intermolecular forces, they can also adopt specific *quaternary* structures.

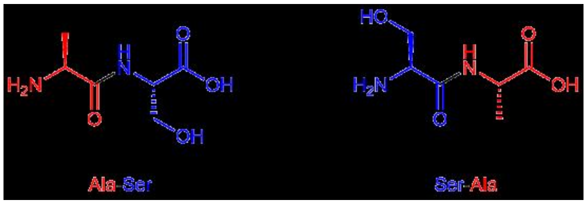
Primary Structure

A protein molecule is a polyamide (polypeptide), but because there are 20 different amino-acid monomers, a protein is a copolymer on steroids. Although the repeating unit is the amino-acid structure, there are 20 possibilities for each side chain (highlighted in red below):



Thus a large number of different protein-molecule structures are possible. Each possible copolymer structure has a unique sequence of side chains. *This specific sequence of amino acids* is called the protein’s **primary structure**.

By convention, protein sequences are written from the end with the free amine group (the N terminus) to the end with the free carboxyl group (the C terminus). For example, Ala-Ser (alanine-serine) differs from Ser-Ala (serine-alanine).



Exercise 2: Amino Acids in a Tripeptide

A table of amino acid structures can be found at this link.

Secondary Structure

A protein’s **secondary structure** is the *three dimensional shape of small segments of proteins*. In secondary structures amino acids that are not next to each other along the backbone are close enough to each other for hydrogen bonding. The type of secondary structure is defined by the pattern of *hydrogen bonds between amide groups that are not adjacent in the protein’s backbone*. Two common elements of secondary structure, which are present in over 60% of known proteins, are the α-helix and β-sheet.

The **α-helix** has *a helical structure where there are, on average, 3.6 amino acids per turn of the helix*. All the side chains project out from the helical axis.

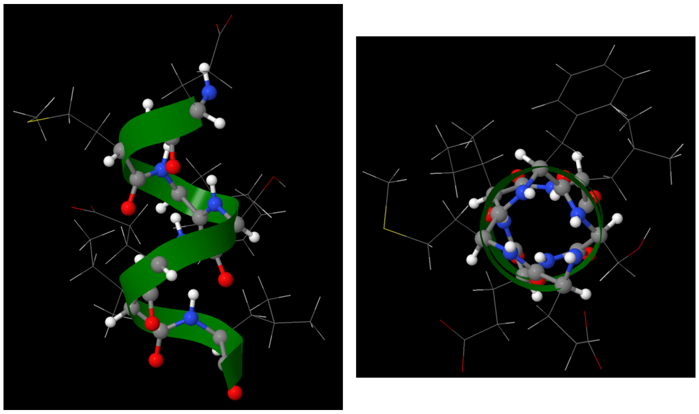


Figure 8. *A segment of a protein with α helix structure. This segment contains 7 amino acids. The protein backbone is shown with atoms-and-bonds; a green ribbon following the backbone highlights the general α helix structure. The side chains are shown in thin wire-frame. When looking down the helix (right), you can see that all the side chains project out from the helix. (PDB: 5L7B, 216-222)*

An α-helix has a regular pattern of hydrogen bonding between backbone amide groups, where the n^{th} amino acid is hydrogen-bonded to the $(n+4)^{th}$ amino acid. For example, as shown in Figure 9, the C=O of amino acid 1 forms a hydrogen bond with N-H of amino acid 5; the C=O of amino acid 2 forms a hydrogen bond with N-H of amino acid 6; etc. This regularly repeating hydrogen bonding is a prominent characteristic of an α-helix.

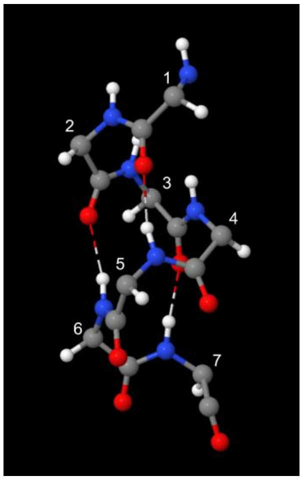


Figure 9. *The same segment of α helix as Figure 8, but with the side chains omitted and the α carbon of each amino acid numbered. Hydrogen bonds are shown as dotted lines.*

The **β-sheet** or **β-pleated sheet** consists of *stretches of the protein chain connected side-by-side by hydrogen bonds between backbone amide groups*.

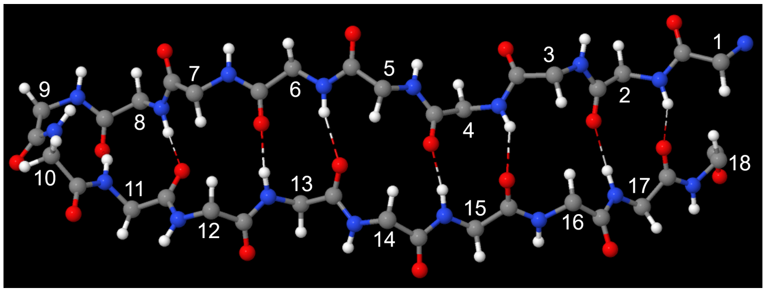


Figure 10. *A segment of a protein with β-sheet structure. This segment contains 18 amino acids (the α carbon of each amino acid is numbered). Only the protein backbone is shown; the side chains are omitted for clarity. (PDB: 5L7B, 188-205)*

Such backbone hydrogen bonding gives rise to a general pleated sheet appearance, hence the name. The side chains of the amino acids alternate above and below the β-sheet (Figure 11).

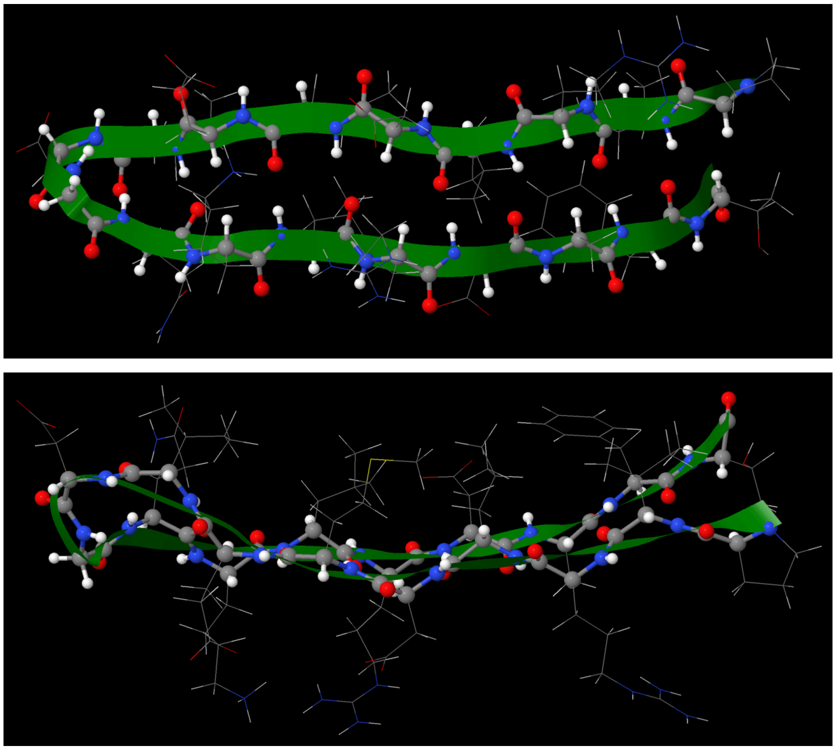


Figure 11*. The same segment of β-sheet as Figure 10. The protein backbone is shown with atoms-and-bonds; a green ribbon follows the backbone. The side chains are shown in thin wire-frame.*

The numerous backbone hydrogen bonds stabilize both the α helix and β sheet structures. These structures can combine to form various larger structures, called motifs, that are found in more than one protein structure.

Tertiary Structure

The **tertiary structure** of a protein is the *overall three-dimensional shape of the protein*. It is how α-helices, β-sheets, and motifs come together to form the overall structure. Tertiary structures are often defined by various intermolecular interactions involving the protein's side-chains as well as the environment the protein is in.

Two general kinds of proteins are found in cells, water soluble and water insoluble proteins. Water soluble proteins, which include enzymes and transport proteins, are found free in cellular compartments such as the cytoplasm, nucleus, or endoplasmic reticulum.

In the tertiary structure of water-soluble proteins, most hydrophobic side-chain groups are in the interior of the protein and away from water, while most polar side-chain groups are mostly kept on the exterior and therefore exposed to water. (The backbone amide groups, while polar and capable of forming hydrogen bonds, do not interact much with water because they are already engaged in hydrogen bonding with each other in α helices and β sheets.)

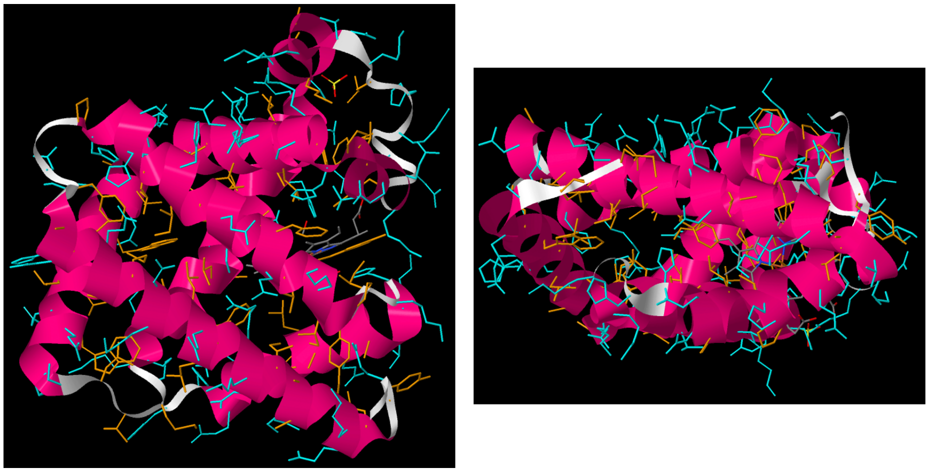


***Figure 12**. Front and side view of a myoglobin protein. The backbone is shown in ribbons only (α helices are in magenta). The side chains are shown in wire-frame. The hydrophobic side chains are colored orange, while the polar side chains are colored blue. (PDB: 6N03)*

The water-insoluble proteins include membrane channels, pumps, and receptors. These proteins are found in lipid bilayers. A description of how and why these proteins are associated with membranes is in Section D16.7.

One important determinant of tertiary structure in some proteins is the **disulfide bond**. It is similar to the cross-linking we've discussed for addition polymers. A protein can form disulfide bonds when cysteines in different parts of its strand are linked by a covalent bond between the sulfur atoms in their side-chains (Figure 13).

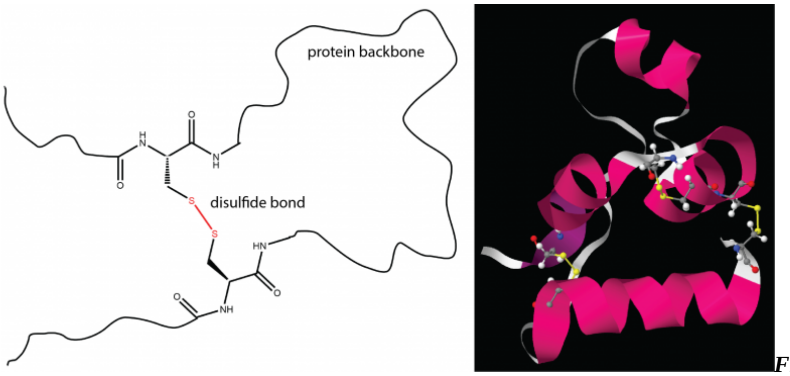


***Figure 13**. **Disulfide bonds.** Left: A disulfide bond (red) connects two cysteine side chains along the protein backbone. Right: Three disulfide bonds are shown in yellow. The backbone is shown as magenta ribbons and cysteines are shown as ball-and-stick models. The six cysteines in this protein form three S-S linkages. (PDB: 6RVA)*

Quaternary Structure

Quaternary structure arises when *more than one protein chain is present and the chains form a larger structure*. For example, the hemoglobin in your blood is composed of four chains (colored magenta, blue, aqua, and tan below) which form two subunits.

When oxygen binds to one subunit of hemoglobin, the interactions between the subunits change. In other words, oxygen binding affects the quaternary structure. Quaternary structure is the usual mechanism for the processes known as *allostery* (in which binding of a molecule at one site on a protein has effects at other sites far away from that site) and *cooperativity* (in which binding of a molecule at one site in a multi-subunit protein increases or decreases the likelihood that another molecule will bind at another site of the protein).

D15.7 Protein Folding and Denaturation

How do proteins fold into the complicated three-dimensional structures? This is a very active area of research in chemistry and biochemistry right now. The first hint came from the work of Christian Anfinsen on the protein ribonuclease, which breaks down RNA molecules. Anfinsen discovered that after treating ribonuclease with high concentrations of certain chemicals that cause proteins to unfold and lose their tertiary and secondary structure, the ribonuclease no longer broke down RNA. Moreover, if the chemicals were removed, the ribonuclease would spontaneously recover nearly all its RNA-hydrolyzing activity, without needing any other cellular components. Anfinsen concluded that the primary structure of a protein completely determines its three-dimensional structure at the secondary, tertiary, and quaternary levels.

Scientists are still trying to learn how the primary structure of a protein determines its other levels of structure. They have determined the primary forces that stabilize a protein's three-dimensional structure are:

- Sequestration of hydrophobic side-chains away from water (for example, in the interior of water-soluble proteins)
- Maximizing London dispersion interactions (minimizing open spaces) in the interior of proteins
- Maximizing hydrogen bonding (for example, in α-helices or β-sheets)
- Attractions between negatively and positively charged sites formed when acidic and basic side-chains lose and gain H^+ ions

The process that Anfinsen used is called **denaturation**, in which *proteins lose the quaternary, tertiary, and secondary structures which is present in their native state*. Proteins can be denatured by application of some external stress or compound such as a strong acid or base, a concentrated inorganic salt, an organic solvent (e.g., alcohol or chloroform), radiation, or heat. Denatured proteins can exhibit a wide range of characteristics, from conformational change and loss of solubility to aggregation due to the exposure of hydrophobic groups.

Protein folding is key to whether a protein can do its job correctly; it must be folded into the right shape to function. However, hydrogen bonds, which play a big part in folding, are weak compared to covalent bonds and thus can easily be affected by heat, acidity, varying salt concentrations, and other stresses. This is one reason why homeostasis is physiologically necessary in many life forms.

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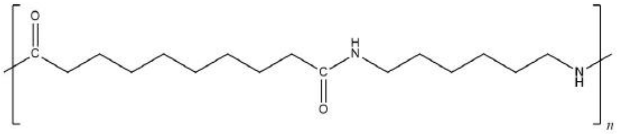
Day 15 Pre-class Podia Problem: Nylon

The repeating unit of nylon-6,10 has this structure.



Answer these questions:

1. Write the structures of two monomers that could be combined to form nylon-6,10.
2. List all the intermolecular forces that exist between polymer chains in nylon-6,10.
3. Depending on the orientation of adjacent polymer chains, intermolecular forces between nylon-6,10 chains might be stronger or weaker. Draw structures of two nylon-6,10 repeating units, one above and one below the structure given. Orient the structures you draw to maximize intermolecular forces.
4. Indicate in your drawing which types of intermolecular forces are important between which parts of the molecules. Also, write an explanation in words describing which forces are important where and why.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

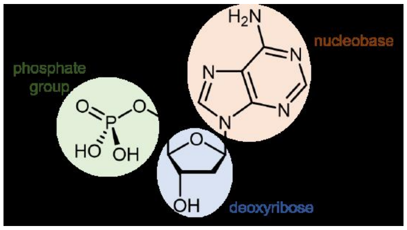
2.8: Day 16- DNA and Lipids

15

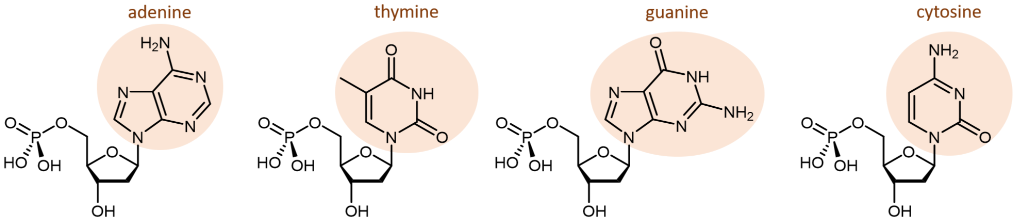
Day 16: DNA and Lipids

D16.1 DNA

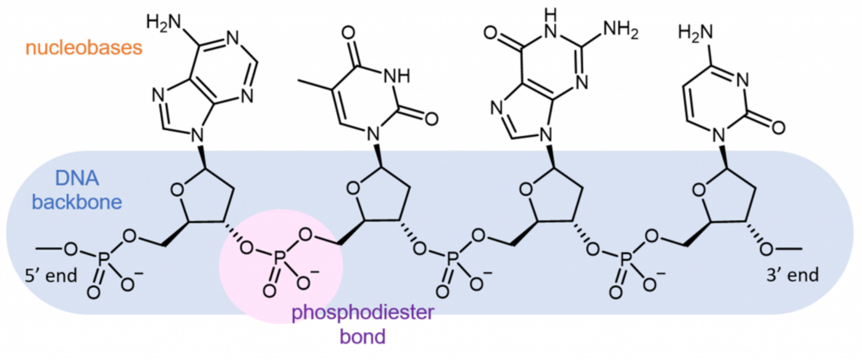
Deoxyribonucleic acid (**DNA**) consists of *two polymer chains that coil around each other, forming a double helix*. The monomer units of DNA strands are called nucleotides. A **nucleotide** consists of *a phosphate group and a nucleobase attached to a sugar (deoxyribose)*.



There are four different nucleobases found in DNA. They are called adenine (abbreviated A), thymine (T), guanine (G) and cytosine (C). The nucleotides containing those nucleobases are called deoxyadenosine monophosphate, deoxythymidine monophosphate, deoxyguanosine monophosphate, and deoxycytidine monophosphate (click on each name to see a rotatable molecular model).



The polymerization reaction forming a DNA strand is a condensation reaction between the phosphate group and deoxyribose (specifically the -OH group), which results in the formation of phosphodiester bonds joining the nucleotides. In organisms containing DNA the pH is about 7, and at that pH the phosphate groups are ionized. Thus, DNA is a huge polyatomic anion with one negative charge for each monomer unit along the chain. The negative charge is balanced by positive charges on metal ions, protein molecules, and other cations surrounding the DNA.



Each DNA polymer chain has a backbone of alternating sugar group and phosphodiester bond, with aromatic nitrogen-containing nucleobases forming side-chains bonded to the backbone.

A DNA strand has a free phosphate group at one end (called the 5′ end because the phosphate is attached to the carbon-5 position in the ribose) and a free hydroxyl (-OH) group at the other end (called the 3′ end because the hydroxyl is attached to the carbon-3 position in the ribose). By convention, the sequences are named from 5′ to 3′, and only the nucleobases are included in the name. For example, the molecule shown above is ATGC (not CGTA).

Two single strands of DNA combine to make the double-helix molecular anion (typically called just the DNA molecule). The strands run in opposite directions: at one end of the double helix is the 5′ end of one strand and the 3′ end of the other strand. The two strands wrap around each other to form two intertwined helixes. The rotating figure shows how the two helixes are oriented. Note that one of the gaps between the entwined strands is wider than the other gap. The two separate strands are held in this orientation by hydrogen bonding between nucleobases in the center of the molecule.

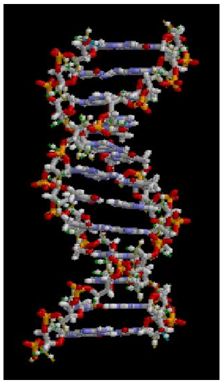


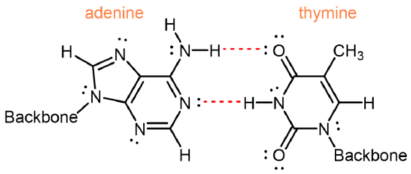
Figure 1. The DNA double helix. *The molecule is shown rotating around the axis of both helices. Source: Wikimedia commons.*

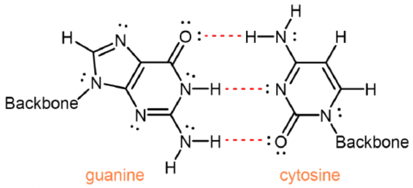
D16.2 Base Pairing

One of the most remarkable things about DNA is that the quantity of adenine always equals the quantity of thymine and the quantity of guanine always equals the quantity of cytosine. From one organism to another, the quantity of adenine can vary, but the quantity of thymine always varies the same way. These equalities imply that the nucleobases occur in pairs: adenine paired with thymine and guanine paired with cytosine. These *pairs of nucleobases* are called **complementary base pairs**.

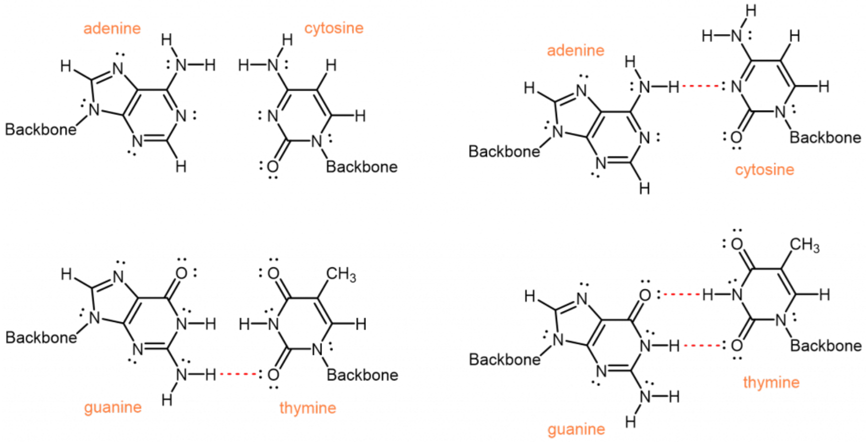
Out of six possible combinations, why are these two the complementary pairs? First, the nucleobases have different sizes: T and C have single rings and are smaller; A and G have double rings and are larger. If A and G paired, their larger size would force the double helix to bulge out. If T and C paired, their smaller size would cause pinching of the double helix. Only a pairing between a single-ringed and a double-ringed nucleobase has the proper consistent spacing.

This leaves four possible combinations: A-C, A-T, G-C and G-T. Of these, A-T and G-C pairs maximize the number of hydrogen bonds across the shared helical axis:





The A-C and G-T pairings, on the other hand, would have fewer hydrogen bonding interactions. To achieve any hydrogen-bonding, there would have to be awkward positioning of the nucleobases relative to each other.



Lined up nucleobases: little hydrogen-bonding

Offset nucleobases: a bit more hydrogen-bonding

Therefore, intermolecular interactions, specifically the efficient hydrogen-bonding, between adenine and thymine, and between guanine and cytosine, result in the specificity observed for the complementary base pairs.

Because of the nature of complementary base pairing, if you know the sequence of one strand of DNA, you can predict the sequence of the strand that will pair with, or “complement” it.

During DNA replication, the strands of the double helix of DNA first separate. Then, enzymes catalyze the synthesis of new DNA in the 5′ to 3′ direction, using the two original strands as models, or *templates*, for the complementary strands. Two complete DNA molecules, each an exact copy of the original, are the result.

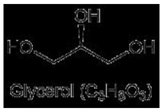
Because of the specificity of base pairing and a proofreading activity of the enzyme that synthesizes new DNA, less than one error in 100 million is incorporated into the new DNA strands. Thus genetic information is passed accurately on to the next generation.

D16.3 Lipids

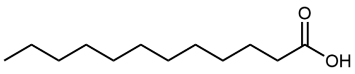
Fats and oils are part of a class of biomolecules called **lipids**, which are loosely defined as *biomolecules that are insoluble in water but soluble in organic solvents* like hexane or chloroform. Here, we discuss two important classes of lipids: glycerolipids and phospholipids. The molecular structures of lipids give rise to different intermolecular interactions that influence their physical properties and biological functions.

D16.4 Glycerolipids

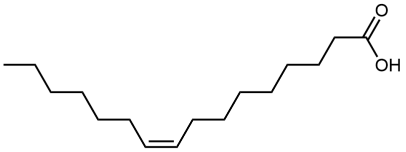
Glycerolipids are *composed of glycerol and fatty acids*. Glycerol has three carbon atoms, each of which has a hydroxyl (-OH) group bonded to it:



Fatty acids are *long, unbranched hydrocarbon chains with a carboxylic acid group at one end*.



n-dodecanoic acid (lauric acid)

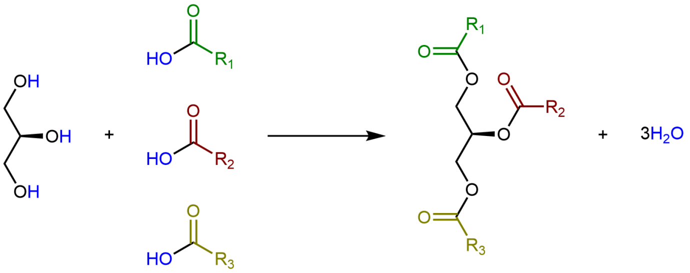


cis-D-hexadecanoic acid (palmitoleic acid)

Fatty acids are systematically named based on the number of carbon atoms and C=C double bonds in the chain. But their common names, such as lauric acid, are often used to identify them.

Note that there are only C-C single bonds in lauric acid; similar to hydrocarbons, such a fatty acid is a *saturated* fatty acid. In contrast, palmitoleic acid has a C=C double bond, i.e. it has one degree of *unsaturation*. The π bond can undergo addition of H_2 and form a saturated fatty acid. Lipids made from saturated and unsaturated fatty acids have different properties.

Glycerolipids are formed when three fatty acids are joined to glycerol. Catalyzed by enzymes, each hydroxyl group on glycerol can undergo condensation with the carboxylic acid group of a fatty acid, forming an ester linkage.



The lengths of the fatty acid chains (e.g. R_1, R_2, R_3) and the number of C=C double bonds within them determine the melting point of a glycerolipid. Longer chains have stronger London dispersion forces than shorter chains, leading to a higher melting point. Saturated chains can pack against each other regularly, giving rise to stronger London dispersion forces between the chains and higher melting points. Unsaturated chains, especially with *cis* double bonds, which force the chain to bend, cannot stack together as well, so the London dispersion forces are weaker.

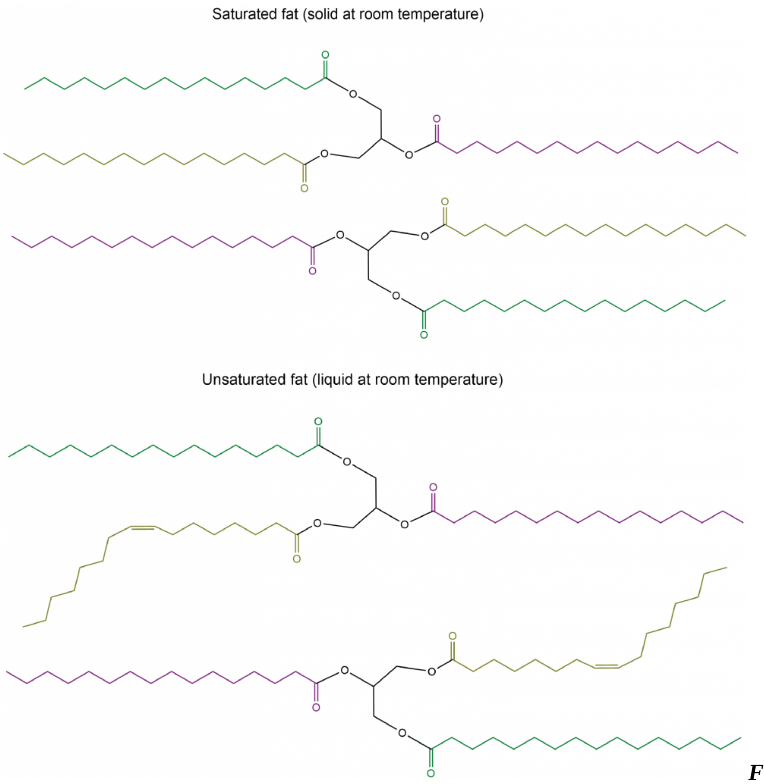


Figure 2. *Shown here are examples of saturated and unsaturated glycerolipid (two molecules of each), illustrating differences in packing of molecules in the solid state and consequently differences in London dispersion forces.*

Glycerolipids with a higher melting point that are usually solids at room temperature are called **fats** or **waxes**. Glycerolipids with a lower melting point that are usually liquids at room temperature are called **oils**.

An important role of glycerolipids is in energy storage. The carbon atoms in fatty acids are mostly involved in C-H bonds, and therefore can be oxidized and in the process release energy. In living organisms, this is carried out in a controlled manner via enzymes. But we can also burn fats and waxes (for example, in a candle) to obtain energy in the form of light.

D16.5 Phospholipids

If *one of the fatty acids in a glycerolipid is replaced by a hydrophilic phosphate group*, the result is a **phospholipid** molecule.

Below the line structure is a common, simplified way of representing a phospholipid molecule. The phosphate group, together with the polar ester groups, is often called *the hydrophilichead* of the molecule (red circle). The fatty-acid hydrocarbon chains are often called the *hydrophobic tails* of the molecule (black squiggly lines). *Molecules with both hydrophobic and hydrophilic parts* are called **amphiphiles** or **amphiphilic molecules**.

In an aqueous environment, such as a living cell, amphiphilic molecules spontaneously arrange into ordered structures. The most important of these is a **lipid bilayer**, *two layers of phospholipid molecules with the hydrophobic tails intermingled and the hydrophilic heads contacting the water*. As the diagram below shows, water is excluded from the center of the bilayer where the fatty acid tails are, while the polar head-groups have access to the water. Phospholipid bilayers form the basis for cell membranes and all the other organelle boundaries found in living cells. Membranes found in cells also contain many other components, such as free fatty acids, other lipids, and proteins.

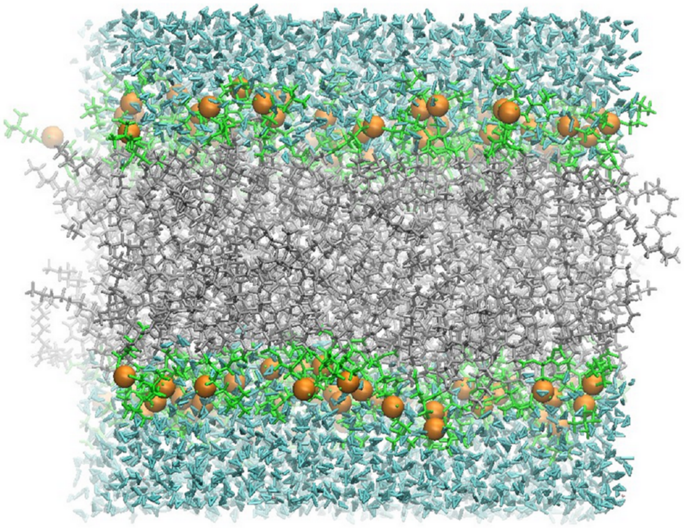


Figure 3. Lipid bilayer. *The blue areas at top and bottom represent water molecules. Orange spheres represent phosphate groups and green areas the glycerol parts of hydrophilic heads. The gray area in the center is hydrocarbon chains in the hydrophobic tails of the lipid molecules. The representation shows 128 lipid molecules. Source: "An Amber Lipid Force Field Tutorial: Lipid 14 Edition" by Benjamin D. Madej and Ross C. Walker, http://ambermd.org/tutorials/advance.../#Introduction.*

Since the center of the bilayer is nonpolar, only nonpolar molecules, such as O_2, CO and CO_2, can cross the bilayer. Ions, such as K^+, Na^+, and Cl^-, are completely blocked by bilayers. Because of the large number of atoms that would have to be rearranged to allow passage of large molecules, fatty acids, complex carbohydrates, proteins, and nucleic acids are also blocked by bilayers.

16.6 Proteins, Lipids, and Fatty Acids

Passage of large molecules or ions through lipid bilayers, can be controlled by protein molecules that are embedded in a bilayer and extend outside the bilayer on both sides. In these membrane-spanning proteins, side chains facing the lipid membranes are usually hydrophobic; side chains contacting the aqueous space on either side of the membrane can be polar.

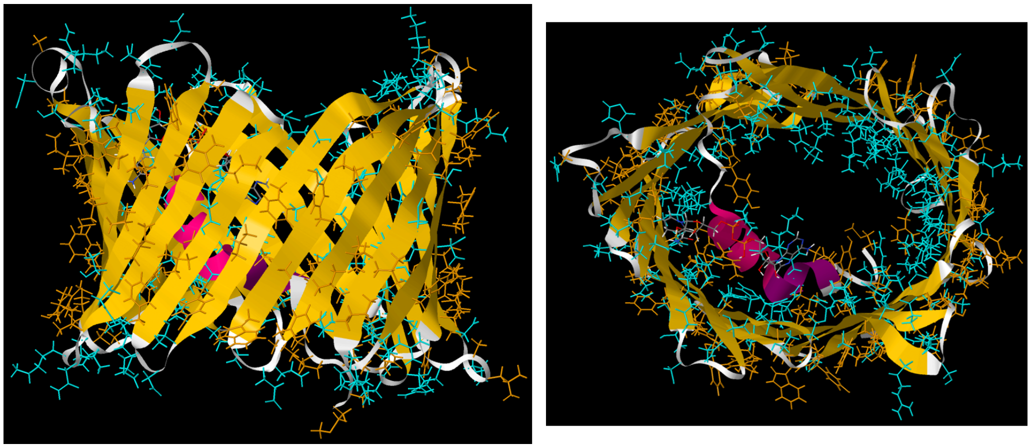
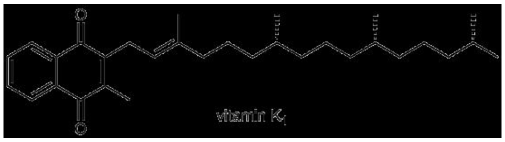


***Figure 4**. Front and side view of a membrane protein. The backbone is shown as ribbons (α-helices are in magenta, β-sheets are in yellow). The side chains are shown in wire-frame. The hydrophobic side chains are colored orange, while the polar side chains are colored blue. (PDB: 6TIR)*

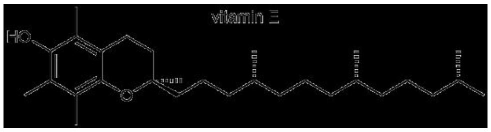
Many proteins are anchored to cell membranes by forming a covalent bond to a fatty acid. For example, the amine group (-NH_2) on the N-terminus of a protein or in a lysine side chain can undergo condensation with the carboxylic acid group (-COOH) on a fatty acid found in a cell membrane to form an amide linkage. Such a covalent bond keeps the protein associated with the membrane.

Several vitamins necessary for higher animal life are only soluble in lipids. These vitamins are composed almost entirely of carbon and hydrogen, meaning they are hydrophobic like the fatty acid tails of lipids. A diet completely lacking in fat will be deficient in these vitamins unless the vitamins are taken as pills.

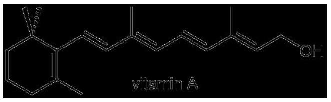
For example, vitamin K_1 is necessary for blood clotting:



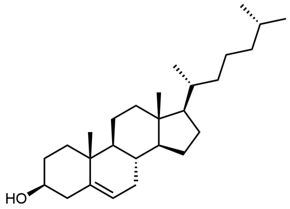
α-Tocopherol (Vitamin E) prevents the inappropriate oxidation of membrane lipids. Deficiency in Vitamin E also causes infertility in rats.



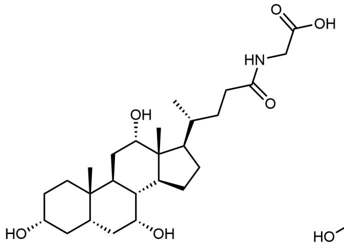
Retinol (Vitamin A) is necessary for normal juvenile growth. Vitamin A deficiency also leads to night blindness.



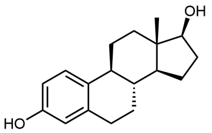
The four-ringed lipid **cholesterol** forms the basis for another class of lipids. Cholesterol is a building block for many important molecules used for various purposes in higher organisms. It is partially oxidized in the liver to bile salts, which act like detergents to solubilize fatty acids in foods and allow them to be absorbed by the body. Many hormones, including estrogens and testosterone, are also derived from cholesterol. The diagram below shows the structures of cholesterol, glycocholic acid (the most common bile acid), estradiol and testosterone (two well-known hormones that are derivatives of cholesterol). As you can see, all four are molecules are amphiphiles, since they have hydrophobic and hydrophilic regions.



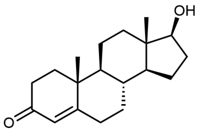
cholesterol



glycocholic acid

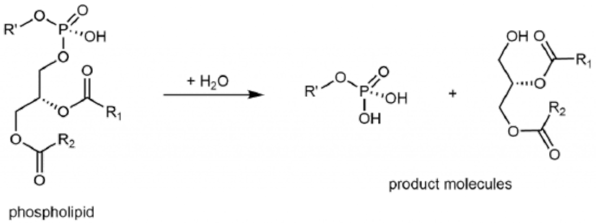


estradiol



testosterone

Lipids also serve a role in intracellular signaling. Some stimuli, such as the smell of bell peppers in olfactory receptor cells, activate an enzyme that breaks up phospholipids into smaller molecules. These molecules, derivatives of glycerol and fatty acids, then act on other enzymes in the cell.



Day 16 Pre-class Podia Problem: Polyfluoroalkyl Substances

The presence of per- and polyfluoroalkyl substances (PFASs) in the environment is a significant public health issue. Some sites in Wisconsin and many in Michigan and other states have been identified as being contaminated by these compounds. They've been dubbed "forever chemicals" because they don't degrade naturally. See the *Science* article at this link for more information. The *Science* article says that one of the problems of PFASs is the fact that some of the molecules involved have structures that enable water and airborne droplets to carry them long distances away from their sources.

1. One of the PFASs is perfluorooctanoic acid, which is used in the manufacture of teflon polymers. (Perfluoro means that all H atoms in a hydrocarbon chain have been replaced by F atoms.) Write a Lewis structure for perfluorooctanoic acid.

2. Consider the structure of perfluorooctanoic acid and the statement above that "some of the molecules involved have structures that enable water and airborne droplets to carry them long distances." Use models of molecular structure and intermolecular forces to construct an explanation of this fact.

3. Other perfluoroalkyl substances have longer chains of carbon atoms than perfluorooctanoic acid. In what type of body tissue would you expect to find these substances? Use models of molecular structure and intermolecular forces to answer the question and construct an explanation.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

CHAPTER OVERVIEW

3: Unit Three

3.1: Day 18- Reaction Rate

16

Day 18: Reaction Rate

D18.1 Reaction Rate

The **rate of a chemical reaction** is usually defined as *the change in concentration of a reactant or a product per unit time.* Rates can be determined by measuring the concentration of a reactant or product at each of a series of times after the reaction is started.

Often, it is easier to measure some property related to a substance's concentration instead. For example, for a reaction involving a colored reactant, light absorption can be measured at different times after the start of the reaction. Then the reactant's concentration at a given time can be calculated from the proportionality between light absorption and concentration.

Consider the decomposition reaction of cyclobutane to ethene in the gas phase:

$$C_4H_8(g) \longrightarrow 2\ C_2H_4(g)$$

The rate at which cyclobutane decomposes can be expressed in terms of the rate of change of its concentration:

$$\begin{aligned} \text{rate of decomposition of } C_4H_8 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[C_4H_8]_{t_2} - [C_4H_8]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[C_4H_8]}{\Delta t} \end{aligned}$$

In this equation, square brackets represent concentration in mol/L (M), so $\Delta[C_4H_8]$ represents the change in concentration of cyclobutane during the time interval Δt (that is, $t_2 - t_1$). The minus sign in front of the fraction is there because *reaction rate is defined to be positive*. The reactant concentration decreases as the reaction proceeds, making $\Delta[C_4H_8]$ a negative quantity, so a negative sign is needed to make the calculated rate positive.

Table 1 provides an example of data collected during the decomposition of C_4H_8.

Table 1. concentrations of cyclobutane measured at 40 °C

Time (s)	**$[C_4H_8]$ (M)**	**$\Delta[C_4H_8]$ (M)**	**Δt (s)**	**Rate of decomposition (M/s)**
0.0	0.240			
20.0	0.120	-0.120	20.0	0.00600
40.0	0.060	-0.060	20.0	0.0030
60.0	0.030	-0.030	20.0	0.0015
80.0	0.015	-0.015	20.0	0.00075

Notice that the reaction rate varies with time, decreasing as the reaction proceeds and $[C_4H_8]$ decreases. An **average rate** over a given time period can be calculated using the concentrations at the beginning and end of the period. For example, the average rate for the first and last 20-second period are:

$$\text{rate} = \frac{-\Delta[C_4H_8]}{\Delta t} = \frac{-(0.120\ \text{M} - 0.240\ \text{M})}{(20.0\ \text{s} - 0.00\ \text{s})} = 0.00600\ \frac{\text{M}}{\text{s}}$$

$$\text{rate} = \frac{-\Delta[C_4H_8]}{\Delta t} = \frac{-(0.015\ \text{M} - 0.030\ \text{M})}{(80.0\ \text{s} - 60.0\ \text{s})} = 0.00075\ \frac{\text{M}}{\text{s}}$$

The *rate of reaction atany specific time* is known as the **instantaneous rate**. The *instantaneous rate when the reaction starts (at t_0)*, is **the initial rate**. The instantaneous rate of a reaction may be determined one of two ways:

- If concentration changes can be measured over very short time intervals, then average rates over these very short time intervals provide reasonably good approximations of instantaneous rates.
- If we plot concentration vs. time, the instantaneous rate at any time *t* is given by the negative of the slope of a straight line that is tangent to the curve at that time (Figure 1).

Figure 1. *Graph of [C_4H_8] versus time. The reaction rate at any instant is equal to the negative of the slope of a line tangent to this curve at that time. Tangents are shown at t = 0 s (magenta; initial rate) and at t = 40 s (orange); click on "+" signs for more information.*

D18.2 Relative Rates of Reaction

The reaction rate can be expressed in terms of the change in concentration of any reactant or product, and therefore depends on the stoichiometry of the reaction. Let's use the ammonia decomposition reaction as an example:

$$2\ \mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\ \mathrm{H_2}(g)$$

From the balanced reaction, we can see that one N_2 molecule is produced for every two NH_3 molecules that have reacted. Therefore, the formation of N_2 is half as fast as disappearance of ammonia:

$$\text{rate} = \frac{\Delta[\mathrm{N_2}]}{\Delta t} = -\frac{1}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t}$$

The negative sign accounts for the fact that NH_3 (reactant) concentration is decreasing while N_2 (product) concentration is increasing. The fraction ½ accounts for the stoichiometry.

Similarly, because 3 mol H_2 forms during the time required for formation of 1 mol N_2:

$$\text{rate} = \frac{\Delta[\mathrm{N_2}]}{\Delta t} = \frac{1}{3}\frac{\Delta[\mathrm{H_2}]}{\Delta t}$$

Figure 2 plots concentrations vs. time for this reaction. At any time, the instantaneous rates for reactants and products are related by the reaction stoichiometry. For example, at 500 s the rate of H_2 production is three times greater than that for N_2 production.

Figure 2. *Concentrations of reactants and products during the reaction $2NH_3 \rightarrow N_2 + 3H_2$ as a function of time at 1100 °C. The rates of change of the three concentrations are related by the reciprocals of their stoichiometric coefficients. An example of this is shown by the different slopes (click on the "+" signs) of the tangents at t = 500 s.*

The rate of a reaction is therefore defined by taking the change in concentration per unit time of a reactant or product and multiplying by the reciprocal of the stoichiometric coefficient for that reactant or product. The reaction rate determined this way is the same regardless of which reactant or product is measured during an experiment. For a generic reaction:

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

where lower-case letters are stoichiometric coefficients and upper-case letters represent chemical formulas, the rate of the reaction is:

$$\text{rate} = -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t}$$

D18.3 Factors Affecting Reaction Rates

During a chemical reaction, reactant molecules are changed into product molecules. This involves changes in bonding (i.e. bonds broken and bonds formed), and typically this requires molecules to come into close contact; that is, atomic-scale particles must collide to react. Anything that affects the number and/or effectiveness of those collisions will affect the rate of reaction.

Chemical Nature of the Reacting Substances

Some substances react faster than others. For example, potassium and calcium, which are next to each other in the fourth row of the periodic table, both react with water to form H_2 gas and a basic solution. Yet calcium reacts at a moderate rate, whereas potassium reacts so rapidly that the reaction is almost explosive. One factor affecting these different rates is that the reactions involve loss of electrons from potassium or calcium atoms, and potassium has a smaller first ionization energy, making loss of an electron easier.

https://mediaspace.wisc.edu/id/1_jkttq85m

Video 1. *Different substances react at different rates. Left: reaction of potassium with water. Right: reaction of calcium with water. The reaction of potassium with water is faster. At the end of the video the calcium reaction is enlarged so that bubbles of* $H_2(g)$ *can be seen more easily.*

Temperature

Chemical reactions typically occur faster at higher temperatures. At higher temperatures atomic-scale particles move faster, so they collide harder and more often, both of which increase the probability that they will react. For example, methane (CH_4) does not react rapidly with air at room temperature, but strike a match and POP!

https://mediaspace.wisc.edu/id/1_c52zzadj

Video 2. *Temperature affects the rate of a chemical reaction. Natural gas coming out of a burner does not combust rapidly until its temperature is raised by a burning match.*

Concentrations

Reaction rates usually increase when the concentration of one or more of the reactants increases. In some cases, rates depend on the concentrations of products as well. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide (SO_2). Specifically, sulfur dioxide reacts with water vapor to produce sulfurous acid:

$$SO_2(g) + H_2O(g) \rightarrow H_2SO_3(aq)$$

Sulfurous acid then reacts with calcium carbonate:

$$CaCO_3(s) + H_2SO_3(aq) \rightarrow CaSO_3(aq) + CO_2(g) + H_2O(l)$$

The rate of the overall reaction depends on the concentration of sulfur dioxide in the air. In a more polluted atmosphere where the concentration of sulfur dioxide is higher, calcium carbonate deteriorates more rapidly (Figure 3).

Figure 3. *Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water as well as thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. (credit: James P Fisher III)*

In another example, a cigarette burns slowly in air, which contains about 21% oxygen by volume, but burns much more rapidly in pure oxygen, as shown in the video below.

https://mediaspace.wisc.edu/id/0_obzl1l3a

Video 3. *Higher concentration usually increases reaction rate. The flask contains pure oxygen, which reacts with paper and tobacco in the cigarette. The cigarette burns much faster in pure oxygen than in air, which contains about one-fifth the oxygen concentration.*

Presence and Concentration of a Catalyst

A **catalyst** is *a substance that increases the rate of a chemical reaction by providing an alternative reaction pathway but is not consumed by the reaction*. The greater the concentration of a catalyst the more the catalyst can speed up a reaction. How catalysts work will be discussed in detail later on in this course. Watch the video below to see how a catalyst can speed up the decomposition of hydrogen peroxide to oxygen and water.

https://mediaspace.wisc.edu/id/0_8ps7n4sa

Video 4. *Effect of a catalyst. Manganese dioxide catalyzes decomposition of aqueous hydrogen peroxide, forming water and oxygen. Until the* MnO_2 *is added there is no perceptible reaction. A rapid reaction occurs as soon as the* MnO_2 *is added to the aqueous solution of* H_2O_2*. The reaction is exothermic so the temperature goes up. The white cloud is water droplets that condense when heated water vapor cools after escaping from the soda bottle.*

Surface Area

The factors discussed so far apply to **homogeneous reactions**, *reactions that occur in a single phase* (solid, liquid, or gas). If a reaction occurs at a surface, an increase in surface area of the intersection of two phases (such as the surface of a solid in contact with a gas) can increase the rate. *Reactions that take place at a surface* are called **heterogeneous reactions**. A finely divided solid (like a powder) has more surface area available for reaction than one large solid piece of the same substance. For example, large pieces of wood smolder, smaller pieces burn rapidly, and sawdust burns explosively. The video below shows how large pieces of iron can be held in a burner flame for a long time and hardly react, whereas iron powder blown into the flame sparkles as the tiny particles burn.

https://mediaspace.wisc.edu/id/0_r05fieh4

Video 5. *Surface area affects the rate of a heterogeneous reaction. A bar of iron held in a flame does not oxidize perceptibly, but when the iron is powdered and blown into the flame from a plastic bottle, a rapid reaction with oxygen occurs.*

D18.4 Effect of Concentration: Rate Laws

Rate laws or **rate equations** are *mathematical expressions that relate the rate of a chemical reaction to the concentrations of reactants* (and sometimes products or catalysts). Often the rate of reaction is proportional to the concentration, or to a power of the concentration, of a substance involved in the reaction:

$$\text{rate} = k[\text{A}]^m[\text{B}]^n[\text{C}]^p\ldots$$

Here, k is the **rate constant**, *a proportionality constant independent of reactant concentrations that is specific for a particular reaction at a particular temperature*.

Each exponent, m, n, or p, defines the **order of a reaction** with respect to each reactant, A, B, or C. It is *the power to which a concentration must be raised to correctly calculate the rate*. For example, if $m = 1$, the reaction is *first-order* with respect to *A*; if $n = 2$, the reaction is *second-order* with respect to *B*; if $p = 0$, the reaction is *zeroth-order* with respect to *C*, which means that the rate of the reaction is not affected by the concentration of C, because $[\text{C}]^0 = 1$. The **overall reaction order** is the sum of the individual orders, $m + n + p + \ldots$ Reaction orders are usually positive integers, although they can be fractions or negative numbers.

Activity 1: Order of a Reaction and Rate Law

D18.5 Method of Initial Rates

The rate constant and the reaction orders must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. One way to do this is the **method of initial rates**. To use this method, *select two sets of rate data where all concentrations but one are the same and set up a ratio of the two rates and the two rate laws*. This will yield an equation that contains only one unknown: the reaction order of the substance whose concentration varies.

Activity 2: Rate Law from Initial Rates

Activity 3: Rate Law from Initial Rates, Mathematical Approach

D18.6 Reaction Order and Rate Constant Units

It is often true that, as in the last activity, the reaction orders in the rate law are different from the coefficients in the chemical equation for the reaction. It is important to note that *rate laws must be determined by experiment and are not reliably predicted by reaction stoichiometry.*

Reaction orders play a role in determining the units for the rate constant—the units for k are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate.

The units for the rate constant for common reaction orders are summarized below.

Overall Reaction Order (m+n+…)	Units of k ($M^{1-(m+n+\ldots)}s^{-1}$)
zeroth	M/s or M s^{-1}
first	1/s or s^{-1}

Overall Reaction Order (m+n+…)	Units of *k* ($M^{1-(m+n+\ldots)}s^{-1}$)
second	1/M s or M^{-1} s^{-1}
third	1/M^2 s or M^{-2} s^{-1}

Day 18 Pre-class Podia Problem: Determining a Rate Law

This Podia problem is based on *today’s pre-class* material; working through that material will help you solve the problem.

Consider these data for the hydrolysis of benzene sulfonyl chloride (abbreviated BSC) in aqueous solution containing fluoride ions at 15 °C. The concentration of BSC was 2×10^{-4} M in all trials and from other experiments where no fluoride ions were present the reaction is known to be first order in BSC. Determine the rate law for the overall reaction. Also determine numeric values for all rate constants and express them in appropriate units.

Trial	$[F^-]$ (M)	Initial Rate (M/s)
1	0	2.4×10^{-7}
2	0.5×10^{-2}	5.4×10^{-7}
3	2.0×10^{-2}	13.9×10^{-7}
4	5.0×10^{-2}	32.0×10^{-7}

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day’s material. We appreciate your comments.

3.2: Day 19- Integrated Rate Law

Instead of using the method of initial rates, you can use the **integrated rate law** method to determine the rate law and rate constant from experimental data. An integrated rate law relates the concentration of a reactant or product to the elapsed time of the reaction. Thus, it can be used to determine the concentration of a reactant or product present after a certain period of time or to estimate the time required for a reaction to proceed to a certain extent.

For a given rate equation, calculus can be used to derive an appropriate integrated rate law. If you are not familiar with calculus and integration, don't worry—you can still use the integrated rate law for a reaction without deriving it yourself.

For a generic reaction:

$$\mathrm{A} \longrightarrow \text{products}$$

The rate of the reaction can be expressed as:

$$\text{rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]^m$$

In calculus, the definition of a derivative is:

$$\frac{d[\mathrm{A}]}{dt} = \lim_{\Delta t \to 0} \frac{\Delta[\mathrm{A}]}{\Delta t}$$

So a rate law for the reaction can be written as:

$$\text{rate} = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^m$$

Rearranging gives:

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]^m} = k\ dt$$

Integrating both sides of this equation gives:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} -\frac{d[\mathrm{A}]}{[\mathrm{A}]^m} = \int_0^t k\ dt$$

Assuming that the reaction starts at t = 0, the right side integration simply becomes kt. And then multiplying both sides by -1 gives:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^m} = -kt$$

$[A]_0$ is the initial reactant concentration and $[A]_t$ is the reactant concentration at time t. The solution to the left side integration has a different mathematical form depending on the order of the reaction with respect to A (value of m). We will explore cases where m = 1, 2, and 0, in the next three sections.

D19.2 First-Order Reaction

When m = 1, the integrated rate law for the reaction "A ⟶ products" becomes:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^m} = \int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = \ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0 = -kt$$

This integrated rate law for a first order reaction can be alternatively expressed as:

$$\ln\left(\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0}\right) = -kt$$

It is easier to use this form of this equation when trying to calculate the time required for a reaction to proceed to a certain extent.

On the other hand, if you raise e (the base of the natural logarithm system) to the power of each side of the equation, it gives:

$$\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = e^{-kt} \quad \text{or} \quad [\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt}$$

It is easier to use this form when trying to determine the concentration of reactant left after a certain period of time.

The integrated rate law for a first order reaction can be rearranged to have a standard linear equation format:

$$\begin{aligned} \ln[\mathrm{A}]_t &= -kt + \ln[\mathrm{A}]_0 \\ y &= mx + b \end{aligned}$$

Hence, if a reaction "A ⟶ products" is first order in [A], a plot of "$\ln[A]_t$ vs. t" must give a straight line. The slope of such a plot would be $-k$ and the y-intercept would correspond to $\ln[A]_0$. If the plot is *not* a straight line, the reaction is *not* first order in *[A]*.

Activity 1: First-order Rate Constant from Graph

D19.3 Second-Order Reaction

When m = 2, the integrated rate law for the reaction "A ⟶ products" becomes:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^m} = \int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -\frac{1}{[\mathrm{A}]_t} - \left(-\frac{1}{[\mathrm{A}]_0}\right) = -kt$$

This integrated rate law for a second order reaction can be alternatively expressed as:

$$\frac{1}{[\mathrm{A}]_t} = kt + \frac{1}{[\mathrm{A}]_0}$$

The integrated rate law for second-order reaction also has a standard linear equation format:

$$\begin{aligned} \frac{1}{[\mathrm{A}]_t} &= kt + \frac{1}{[\mathrm{A}]_0} \\ y &= mx + b \end{aligned}$$

Hence, if a reaction "A ⟶ products" is second order in [A], a plot of

$$\frac{1}{[\mathrm{A}]_t}$$

vs t should be a straight line, where the slope equals k and the y-intercept is

$$\frac{1}{[\mathrm{A}]_0}$$

If the plot is *not* a straight line, then the reaction is *not* second order with respect to [A].

Activity 2: Order from Integrated Rate Law

D19.4 Zeroth-Order Reaction

The "A ⟶ products" reaction that is zeroth-order (m = 0) in [A] exhibits a constant reaction rate regardless of the concentration of A:

$$\text{Rate} = k[A]^0 = k$$

The integrated rate law for such a zeroth-order reaction is:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^m} = \int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = [\mathrm{A}]_t - [\mathrm{A}]_0 = -kt$$

This integrated rate law also has a standard linear equation format:

$$\begin{aligned}[\mathrm{A}]_t &= -kt + [\mathrm{A}]_0 \\ y &= mx + b\end{aligned}$$

A plot of $[A]_t$ vs t for a zeroth-order reaction is a straight line with a slope of $-k$ and a y-intercept of $[A]_0$.

Figure 1 shows two plots, both are for the decomposition reaction of ammonia. One reaction occurred on a hot tungsten (W) surface, while the other reaction occurred on a hot quartz (SiO_2) surface.

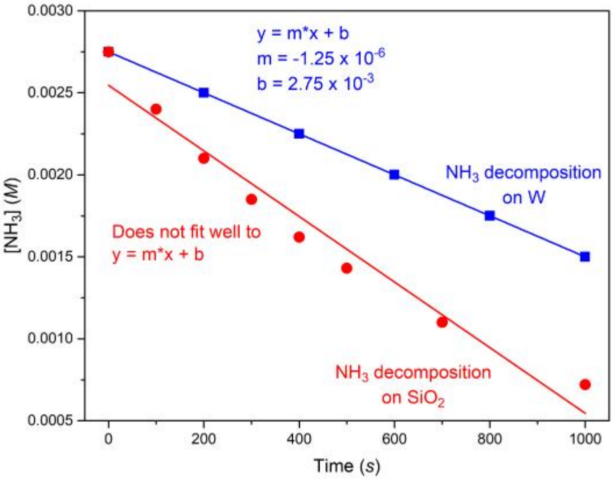


Figure 1. *The decomposition of NH_3 on a tungsten (W) surface is a zeroth-order reaction because the concentration data fit the equation $y = mx + b$. However, when data are collected for a quartz (SiO_2) surface, there is curvature: the reaction is not zeroth-order.*

We can see from this set of data that the reaction on tungsten is zeroth-order; the plot of $[NH_3]$ vs t is a straight line. From the slope, we find that the rate constant for this reaction under the experimental conditions is:

$$-\text{slope} = k = 1.25 \times 10^{-6}\,\frac{M}{s}$$

The decomposition on hot quartz, on the other hand, is not zeroth-order (analysis of the data shows that it is first order).

Equations for zeroth-, first-, and second-order reactions are summarized in Table 1.

Property	Zeroth-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	M/s	1/s	1/M s
integrated rate law	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$1/[A]_t = kt + 1/[A]_0$
linear plot	[A] vs. t	ln[A] vs. t	$1/[A]_t$ vs. t
relationship between slope of linear plot and rate constant	$k = -$slope	$k = -$slope	$k = +$slope

Table 1. Summary of Rate Laws for Zeroth-, First-, and Second-Order Reactions

D19.5 Flooding Method: Pseudo-Order Reaction

The integrated rate laws are quite useful when determining the reaction order and rate constant using all the data from a single experimental trial. However, thus far we have only considered example reactions involving one reactant, whereas most reactions involve two or more reactants. How can we use integrated rate laws to find the reaction order and rate constants for those reactions?

Let’s consider a generic reaction:

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products}$$

where:

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n$$

Flooding refers to *running a reaction that involves two or more reactants with a large excess of all but one reactant*. For example, we can run the reaction above with a *large excess* of B so that A is the *limiting reactant* by a significant amount. In that case, $[\text{B}]_0 >> [\text{A}]_0$, and the concentration of B would effectively remain constant during the course of the reaction. (If $[\text{B}]_0$ = 0.100 M and $[\text{A}]_0$ = 0.00100M, then at a time *t* when all the A has reacted, $[\text{B}]_t$ = (0.100-0.00100) M = 0.099 M, which is essentially no change in the concentration of B.)

Under this condition of $[\text{B}]_t \approx [\text{B}]_0$ = constant, the rate law becomes:

$$\text{Rate} = k[\text{A}]^m[B]_0{}^n = k_{\text{obs}}[\text{A}]^m$$

where k_{obs}, the rate constant we observe during the flooded experiment, is $k_{\text{obs}} = k[\text{B}]_0{}^n$. This new rate equation allows us to use the integrated rate laws we've just discussed to determine the reaction order with respect to [A], and also to determine k_{obs} and *k*. The order of the reaction, *m*, is called a **pseudo order** because it is *obtained under flooding conditions and is not necessarily the overall order of the reaction*. If *m* = 1, we say the reaction is pseudo first order and k_{obs} is called a pseudo-first-order rate constant.

Here is an example experiment: For trial 1, flood the reaction mixture with a large excess of reactant B

$$[B]_{0\,1}$$

and measure $[\text{A}]_t$ as the reaction progresses. Then plot $\ln[\text{A}]_t$ vs *t*. If the graph is a straight line, then the reaction is first-order with respect to [A]. (In this case, the flooded reaction a pseudo-first-order reaction.) The slope of this graph is

$$-k_{obs_1}$$

For trial 2, flood the reaction mixture with a *different* large excess of B

$$[B]_{0\,2}$$

The plot of $\ln[\text{A}]_t$ vs *t* has a different slope corresponding to

$$-k_{obs_2}$$

The ratio of the two k_{obs} allows us to determine *n*, the reaction order with respect to [B]:

$$\frac{k_{obs_2}}{k_{obs_1}} = \frac{k([B]_{0_2})^n}{k([B]_{0_1})^n} = \left(\frac{[B]_{0_2}}{[B]_{0_1}}\right)^n$$

In the above equation, all the variables aside from *n* are known or have been experimentally determined.

Finally, the actual rate constant for the reaction, *k*, can be determined from the relationship $k_{\text{obs}} = k[\text{B}]_0{}^n$. The data all trials should be averaged to get the best value of *k*.

Activity 3: Determining a Rate Constant Using Flooding

Day 19 Pre-class Podia Problem: Integrating a Rate Law

In Activity 1, earlier in today's work, data are given for the decomposition of hydrogen peroxide. Hydrogen peroxide decomposes to form oxygen and water. Write a balanced chemical equation for decomposition of hydrogen peroxide. How is the equation you wrote for hydrogen peroxide different from the chemical equation A → products that was used to derive the integrated rate law in Section D19.1?

Now define the rate of reaction for decomposition of hydrogen peroxide using the method given in Section D18.2 and derive the integrated first-order rate law, following the derivation in Sections D19.1 and D19.2. Use your mathematical work to show that the rate constant calculated in Activity 1 for the first-order decomposition of hydrogen peroxide is twice as big as it should be.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

3.3: Day 20- Rate of Radioactive Decay

D20.1 Radioactive Decay

Determining the rate law and rate constant of a reaction has numerous real world applications, one of which involves the rate of **radioactive decay**, *the spontaneous change of an unstable nuclide into a different nuclide*. (A nuclide is an atomic species of a specific isotope; all examples of a given nuclide have the same number of protons and the same number of neutrons.) The rate of radioactive decay allows scientists to learn about the histories of our world in geological and archaeological studies. Before we get to the kinetics of radioactive decay, let's first consider what reactions are involved in radioactive decay.

During a radioactive decay process, the unstable nuclide is called the *parent nuclide*; the nuclide that results from the decay is called the *daughter nuclide* (Figure 1). The daughter nuclide may be stable, or it may decay itself.

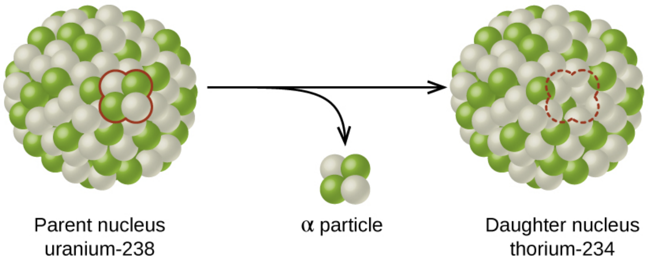


Figure 1. *A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle consists of two protons (green) and two neutrons (gray) that are removed from the uranium-238 nucleus.*

The atomic representations used when discussing radioactive decay reactions have two numbers written to the left of the atomic symbol, for example,

$$^{238}_{92}\mathrm{U}$$

and its isotope

$$^{235}_{92}\mathrm{U}$$

The subscript denotes the atomic number, *Z*, of the element (number of protons), and the superscript denotes the mass number, *A*, of the isotope (number of protons + number of neutrons). Both subscript and superscript are necessary for balancing nuclear equations.

D20.2 Types of Radioactive Decay

Experiments involving the interaction of radiation with a magnetic or electric field (Figure 2) indicated that one type of radioactive decay particle consists of positively charged and relatively massive **α particles**, which are high-energy helium nuclei

$$(^{4}_{2}\mathrm{He},\ \text{or}\ ^{4}_{2}\alpha)$$

A second type consists of negatively charged and much lighter **β particles**, which are high-energy electrons

$$(^{\ 0}_{-1}\beta,\ \text{or}\ ^{\ 0}_{-1}\mathrm{e})$$

A third consists of uncharged electromagnetic waves, **γ rays**, which are very high energy photons. (Note that for β particles, which do not contain any protons, the subscript denotes the charge of the particle.) These three types of radioactive decays are the most commonly observed ones.

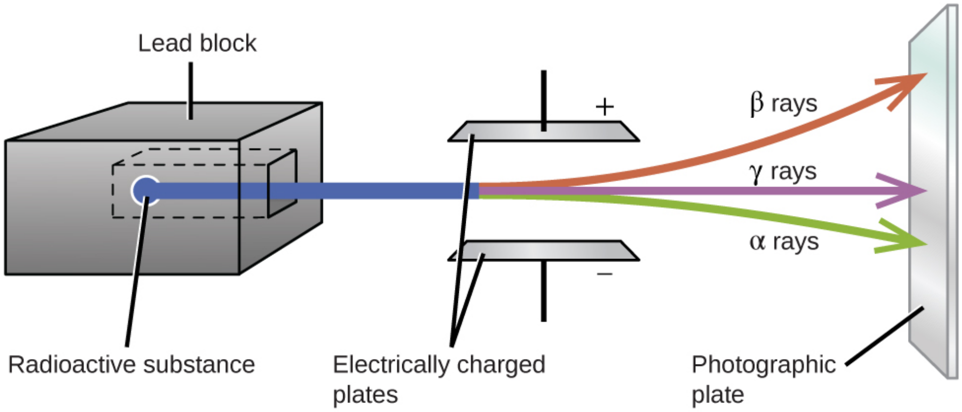


Figure 2. α particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. β particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. γ rays, which are unaffected by the electric field, must be uncharged.

α decay is the emission of an α particle from the nucleus. For example:

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\alpha + {}^{206}_{82}\text{Pb}$$

α decay occurs primarily in heavy nuclei (A > 200, Z > 83). The loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide. Note that the sum of protons (subscripts) on the product side is equal to that on the reactant side. The same is true for the mass number (superscripts). This nuclear reaction is balanced.

β decay is the emission of an electron from a nucleus. For example:

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\text{Xe}$$

Beta decay involves the conversion of a neutron into a proton and a β particle. The β particle emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Emission of a β particle does not change the mass number of the nuclide but does increase its number of protons and decrease its number of neutrons.

γ decay is the emission of a γ-ray photon from a nucleus. The energies of γ rays are quite high, in the range of 10^5-10^7 kJ/mol, so γ rays can easily break chemical bonds if they are absorbed by matter. (In comparison, x-rays have energies roughly 10 times smaller than γ rays.) Cobalt-60 is a nuclide that decays via β emission as well as γ emission:

$$^{60}_{27}\text{Co} \longrightarrow {}^{0}_{0}\gamma + {}^{0}_{-1}\beta + {}^{60}_{28}\text{Ni}^{*}$$

The asterisk (*) denotes that the nickel-60 produced in the above radioactive decay is in an excited state. It decays to its ground state with the emission of another γ photon:

$$^{60}_{28}\text{Ni}^{*} \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{28}\text{Ni}$$

There is no change in mass number or atomic number during γ emission unless it is accompanied by one of the other modes of decay.

Positron (β^+) decay is the emission of a positron, or antielectron, from a nucleus. In the process, a proton is converted into a neutron. For example:

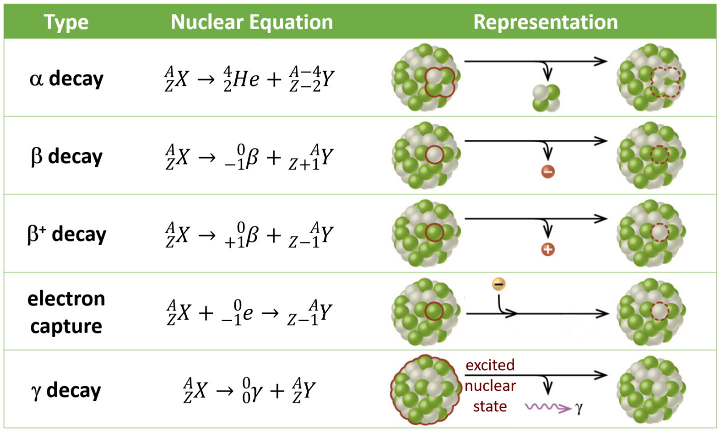
$$^{15}_{8}\text{O} \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}\text{N}$$

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus and transforms a proton into a neutron. For example:

$$^{40}_{19}\text{K} + {}^{0}_{-1}\text{e} \longrightarrow {}^{40}_{18}\text{Ar}$$

Electron capture has the same effect on the nucleus as does β^+ decay, and both are sometimes considered as a type of β decay.

The table below summarizes the various types of radioactive decay.



Type	Nuclear Equation	Representation
α decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$	
β decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}\beta + {}_{Z+1}^{A}Y$	
β⁺ decay	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}\beta + {}_{Z-1}^{A}Y$	
electron capture	${}^{A}_{Z}X + {}^{0}_{-1}e \rightarrow {}_{Z-1}^{A}Y$	
γ decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$	

D20.3 Half-Life of a Reaction

An important aspect of the kinetics of radioactive decay is the **half-life ($t_{½}$)** of the reaction, which is *the time required for the concentration of a reactant (e.g. the parent nuclide) to be reduced to half of its initial value.* In each succeeding half-life, the remaining concentration of the reactant is again halved.

The half-life of a reaction can be derived from the integrated rate law. Hence, there is a general equation for half-life for zeroth-order, first-order, and second-order reaction.

First-Order Reaction

The integrated rate law gives:

$$\begin{aligned} \ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) &= kt \\ t &= \ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) \times \frac{1}{k} \end{aligned}$$

When $t = t_{½}$:

$$[\mathrm{A}]_{t_{\frac{1}{2}}} = \frac{1}{2}[\mathrm{A}]_0$$

Therefore:

$$\begin{aligned} t_{\frac{1}{2}} &= \ln\left(\frac{[\mathrm{A}]_0}{\frac{1}{2}[\mathrm{A}]_0}\right) \times \frac{1}{k} \\ &= \ln(2) \times \frac{1}{k} \\ &= \frac{0.693}{k} \end{aligned}$$

The half-life of a first-order reaction is inversely proportional to the rate constant k: A fast reaction (larger k) has a shorter half-life; a slow reaction (smaller k) has a longer half-life. Moreover, the half-life is, conveniently, independent of the concentration of the reactant. Therefore, you do not need to know the initial concentration to calculate the rate constant from the half-life, or vice versa.

Second-Order Reactions

The integrated rate law is:

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt$$

When $t = t_{½}$,

$$[\mathrm{A}]_{t_{\frac{1}{2}}} = \frac{1}{2}[\mathrm{A}]_0$$

so:

$$\begin{aligned} \frac{1}{\frac{1}{2}[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0} &= kt_{\frac{1}{2}} \\ \frac{2}{[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0} &= kt_{\frac{1}{2}} \\ \frac{1}{[\mathrm{A}]_0} &= kt_{\frac{1}{2}} \end{aligned}$$

Therefore:

$$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$$

For a second-order reaction, $t_{½}$ is inversely proportional to the rate constant and the concentration of the reactant, and hence is not constant throughout the reaction. The half-life increases as the reaction proceeds due to decreasing concentration of reactant. Consequently, unlike the situation 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.

Zeroth-Order Reactions

For a zeroth-order reaction:

$$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0$$

When $t = t_{½}$,

$$[\mathrm{A}]_{t_{\frac{1}{2}}} = \frac{1}{2}[\mathrm{A}]_0$$

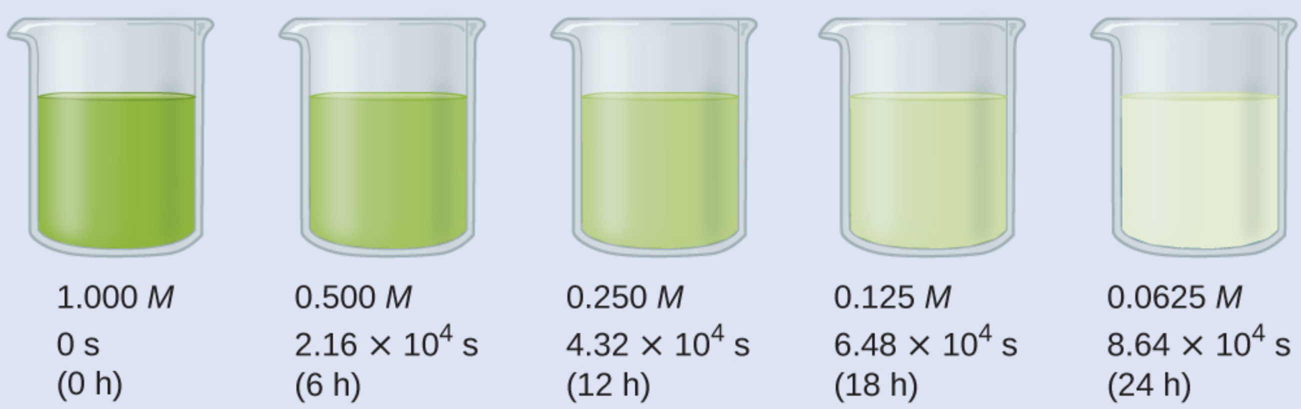
so:

$$\begin{aligned} \frac{[\mathrm{A}]_0}{2} &= -kt_{\frac{1}{2}} + [\mathrm{A}]_0 \\ kt_{\frac{1}{2}} &= \frac{[\mathrm{A}]_0}{2} \\ t_{\frac{1}{2}} &= \frac{[\mathrm{A}]_0}{2k} \end{aligned}$$

The half-life of a zeroth-order reaction is inversely proportional to the rate constant and directly proportional to the concentration of the reactant. Therefore, $t_{½}$ decreases as the reaction progresses and the reactant concentration decreases.

Activity 1: Half-life and Order from Concentration-Time Data

Some dyes can be decomposed by sunlight. The figure below shows the decomposition of an aqueous solution of a green dye in sunlight at 40 °C. Without making a plot/graph of the data, determine the order of the reaction and then calculate its rate constant.



Think. Write in your notebook. Then click for an explanation.

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D20.4 Radioactive Half-Lives

Radioactive decay occurs in atomic nuclei and therefore does not depend on chemical bonding or collisions of molecules. Therefore, most radioactive decay processes follow first-order kinetics, and have a characteristic, constant half-life. A radioactive isotope's half-life allows us to determine how long a sample of a useful isotope will be available, or how long a sample of an undesirable or dangerous isotope must be stored before it decays to a sufficiently low radiation level.

For example, coba source, both the amount of

$$\mathrm{Co}^{60}_{27}$$

and the intensity of the radiation emitted is cut in half every 5.27 years.

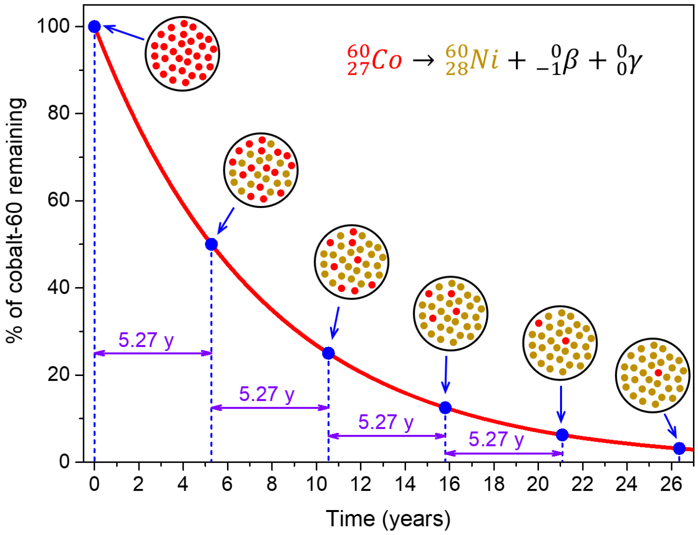


***Figure 3**. For cobalt-60 ($t_{½}$ = 5.27 years), 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.*

The *number of nuclear transformations per unit time* is called the **activity,** symbol ***A*,** of the radioactive sample. The activity of a sample can be measured with an instrument, such as a Geiger counter. The activity is directly proportional to the *number of radioactive nuclei present*, which is symbolized by *N*. The *rate constant for nuclear decay* is called the **decay constant,** symbol **λ**. Hence, the rate expression for radioactive decay becomes:

$$\text{Rate of radioactive decay} = A = \lambda N$$

This is analogous to the first-order rate law for a chemical reaction, X → products,

$$\text{Rate} = -\frac{\Delta[\mathrm{X}]}{\Delta t} = k[X]$$

but the rate is called the activity and the concentration of reactant is replaced by the number of radioactive nuclei. Because the radioactivity is defined in terms of the number of radioactive nuclei, the activity increases as the mass of a sample of radioactive material increases.

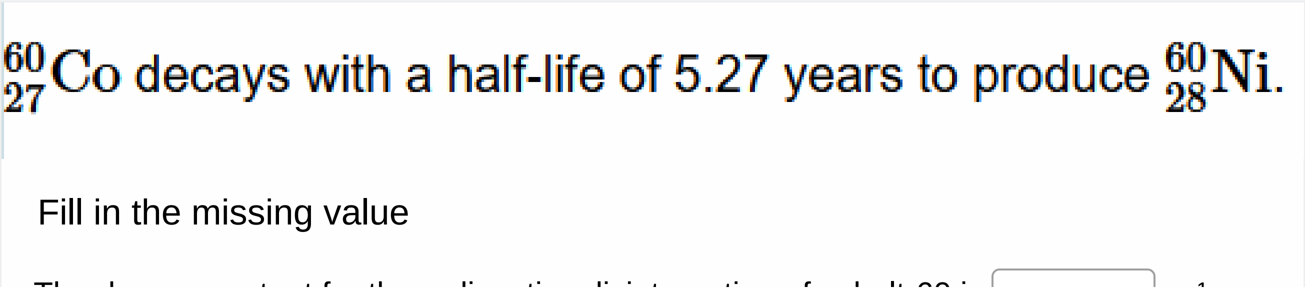
The other kinetic equations for first-order reactions similarly apply to radioactive decay, but with the radioactive-decay-specific symbols:

$$t_{\frac{1}{2}} = \frac{\ln(2)}{\lambda} = \frac{0.693}{\lambda}$$

$$\mathrm{N}_t = \mathrm{N}_0\left(e^{-\lambda t}\right) \quad \text{or} \quad t = -\frac{1}{\lambda}\ln\left(\frac{\mathrm{N}_t}{\mathrm{N}_0}\right)$$

Note that rather than concentration units (M or mol/L), N_0 and N_t have the units of moles or number of atoms.

Activity 2: Radioactive Decay and Half-life



$^{60}_{27}$Co decays with a half-life of 5.27 years to produce $^{60}_{28}$Ni.

Fill in the missing value

The decay constant for the radioactive disintegration of cobalt-60 is ______ y^{-1}.

Check

Solution

◉ ●

Fill in the missing value

The fraction of a sample of the cobalt-60 isotope that remains after 15.0 years is ______ %. (use 2 sig. figs.)

Check

Solution

◉ ●

Fill in the missing value

The time required for a sample of cobalt-60 to disintegrate to the extent that only 2.00% of the original number of nuclei remain is ______ years. (use 3 sig. figs.)

Check

Solution

● ●

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D20.5 Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for **radiometric dating**, *the process of determining an object's date of origin*. The objects of interest can be geological formations, archeological artifacts, or formerly living organisms. Radiometric dating has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilizations.

Radiometric Dating Using Carbon-14

Radiocarbon dating or *carbon-14 dating* can provide reasonably accurate dating of carbon-containing substances up to ~50,000 years old.

Naturally occurring carbon consists of three isotopes: ^{12}C, which constitutes 99% of the carbon on earth; ^{13}C, about 1% of the total; and 1 part per trillion (0.0000000001%) of ^{14}C. ^{14}C is formed in the upper atmosphere by the reaction of nitrogen atoms with neutrons:

$$^{14}_{7}\text{N} + {}^{1}_{0}\text{n} \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$$

All isotopes of carbon react with oxygen to produce CO_2. In the atmosphere, the ratio of $^{14}CO_2$ to $^{12}CO_2$ has been nearly constant for a long time, as shown by analysis of carbon-containing gas samples trapped in Greenland ice sheets.

The incorporation of $^{14}CO_2$ and $^{12}CO_2$ into plants is a regular part of photosynthesis. Therefore, a living plant is constantly exchanging carbon with its environment, meaning that the ^{14}C/^{12}C ratio found in a living plant is the same as the ^{14}C/^{12}C ratio in the atmosphere. But when a plant dies, the carbon exchange with the atomosphere stops. Because ^{12}C is a stable isotope and does not undergo radioactive decay, the amount of ^{12}C in the dead plant does not change. However, ^{14}C undergoes β decays with a half-life of 5730 years:

$$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\beta$$

Thus, the $^{14}C/^{12}C$ ratio gradually decreases after the plant dies, and this provides a measure of the time that has elapsed since the death of the plant. For example, if the $^{14}C/^{12}C$ ratio in a wooden object found in an archaeological site is half what it is in a living tree, this indicates that 5730 years have elapsed since the death of the tree from which the wooden object was made. Highly accurate determinations of $^{14}C/^{12}C$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

This process works for other organisms as well, since they also constantly exchange carbon (by eating plants or eating others that eat plants) until they die.

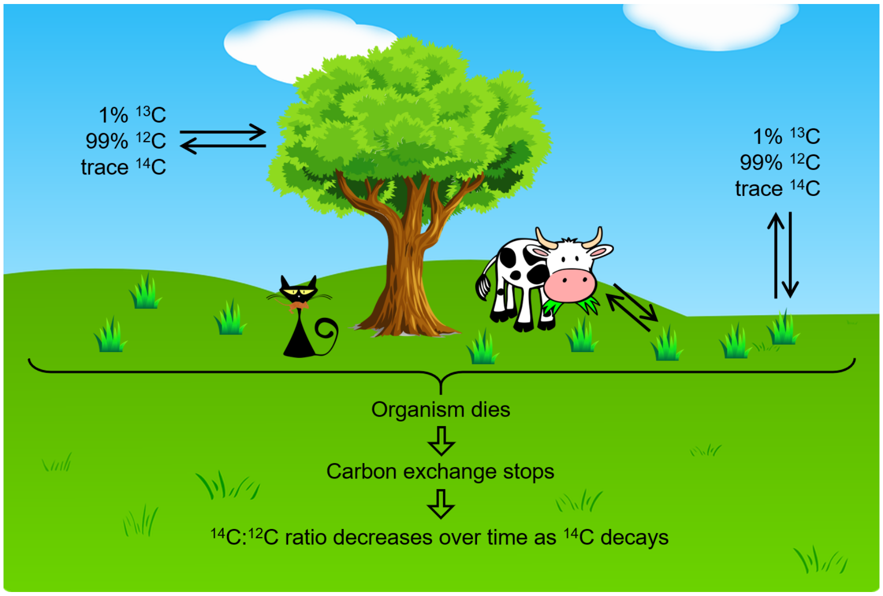
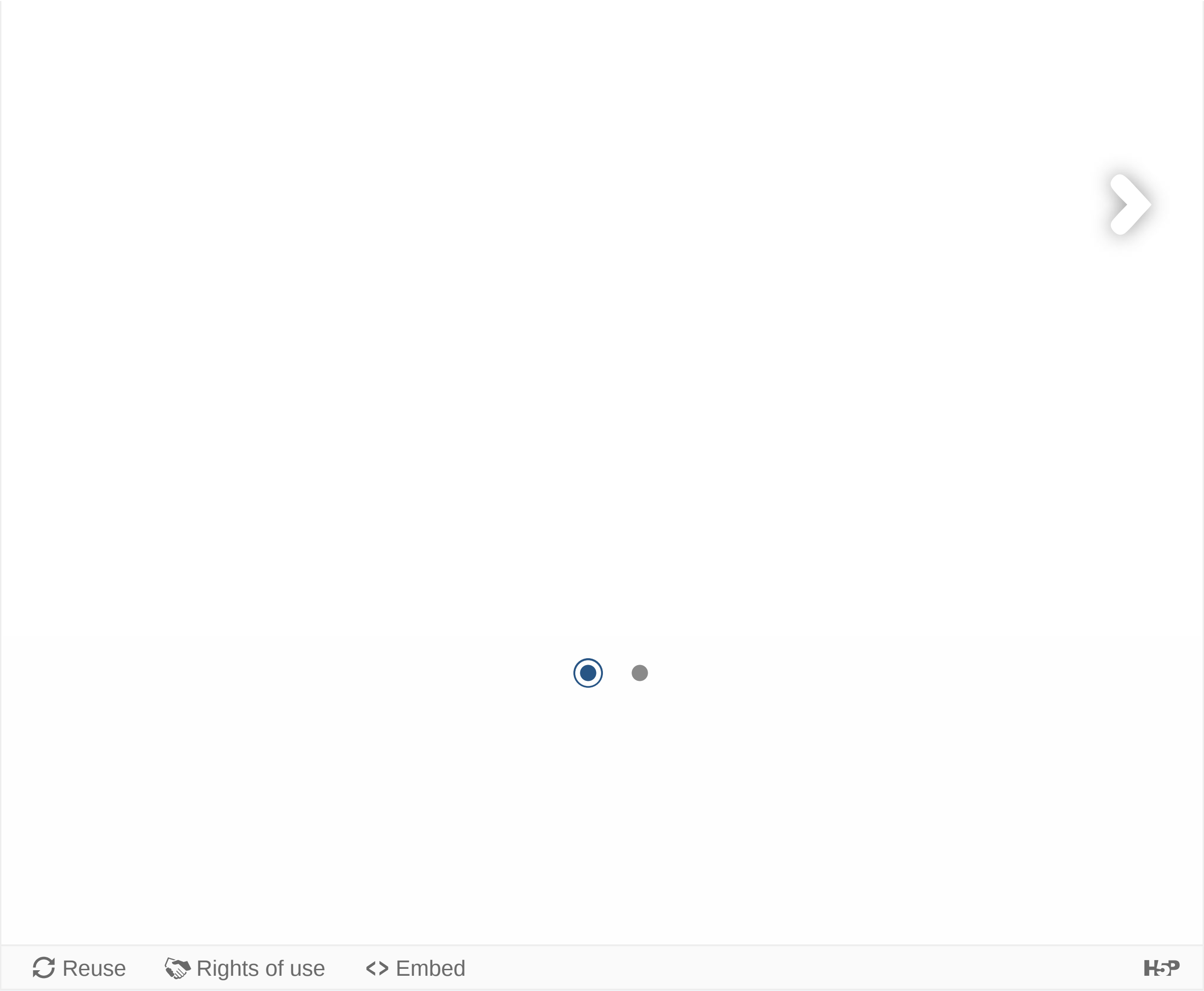


***Figure 4**. Along with the stable ^{12}C, radioactive ^{14}C is constantly exchanged by living plants and animals with the environment, and the $^{14}C/^{12}C$ ratio remains at a constant level within them while they are alive. After death, the ^{14}C that remains in the organism decays and the $^{14}C/^{12}C$ ratio begin to decrease. Comparing this ratio to the ratio in living organisms allows determination of how long ago the organism lived (and died).*

Activity 3: Radiocarbon Dating

The Dead Sea Scrolls are ancient Jewish religious manuscripts discovered in 1946 and 1947. The first radiocarbon dating of the scrolls was in 1950. A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls was found to have an activity of 10.8 disintegrations per minute per gram of carbon. If the initial carbon-14 activity was 13.6 disintegrations per min per gram of carbon, estimate when the Dead Sea Scrolls were written. (The half-life of carbon-14 is 5730 years)

Solution



The accuracy of radiocarbon dating assumes that the $^{14}C/^{12}C$ ratio in a living plant is the same now as it was in an earlier era, but this is not always valid. For example, right now, due to the increasing accumulation of CO_2 (largely $^{12}CO_2$) in the atmosphere, caused by combustion of fossil fuels in which essentially all of the ^{14}C has decayed, the $^{14}C/^{12}C$ ratio in our atmosphere is decreasing. This in turn affects the $^{14}C/^{12}C$ ratio in currently living organisms on the earth. Fortunately, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, more accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radiometric Dating Using Nuclides Other than Carbon-14

Radiometric dating using radioactive nuclides with half-lives longer than that of carbon-14 can date events older than 57,000 years ago.

For example, uranium-238 can be used to estimate the ages of some of the oldest rocks on earth. Since ^{238}U has a half-life of 4.5 billion years, it takes that amount of time for half of the original ^{238}U to decay by a series of nuclear reactions into ^{206}Pb. In a rock sample that does not contain appreciable qunatities of ^{208}Pb, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of $^{238}U/^{206}Pb$, we can determine the age of the rock. This assumes that all of the ^{206}Pb present came from the decay of ^{238}U. If there is ^{206}Pb from sources other than ^{238}U, which is often indicated by the co-presence of other lead isotopes in the sample, it is necessary to make adjustments in the calculations.

Potassium-argon dating uses a similar method. ^{40}K decays to form ^{40}Ar with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of ^{40}Ar gas that escapes is measured, determination of the $^{40}K/^{40}Ar$ ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (^{87}Rb decays into ^{87}Sr with a half-life of 48.8 billion years), operate on the same principle.

To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Day 20 Pre-class Podia Problem: Radiocarbon Dating

A sample of an igneous rock contains 9.58×10^{-5} g of ^{238}U, 2.51×10^{-5} g of ^{206}Pb, and a negligible quantity of ^{208}Pb. No other lead isotopes are detected. Determine the approximate time at which the rock was formed. (^{238}U decays into ^{206}Pb with a half-life of 4.5×10^{9} y.)

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

3.4: Day 21- Reaction Energy Diagram and Arrhenius Equation

D21.1 Factors that Affect the Rate Constant

Section D18.3 listed several factors that affect reaction rate: the chemical nature of the reactants; temperature; concentrations; catalysts; and, for heterogeneous reactions, surface area. The rate law, and the order of reaction with respect to each concentration in the rate law, indicate how rate depends on concentration. Chemical nature of reactants and temperature both affect the rate constant *k*. We will discuss catalysts and heterogeneous reactions later.

It appears obvious to say that different substances are likely to react at different rates. Thus a rate constant value applies to specific reactant and product molecules; that is, to a particular balanced chemical equation. Less obvious is that the rate "constant" is only constant at a given temperature; that is, a reaction has many different rate constants, each constant at a specified temperature. The value of the rate constant is determined by three main factors, the first two of which depend on temperature:

1. To react, molecules must come close enough to each other to exchange energy and perhaps to break and form bonds; that is, molecules must collide. The rate constant is proportional to the rate of collisions:

$$k \propto \frac{\text{number of collisions}}{\text{time}}$$

2. For a reaction to occur, there must be sufficient energy in the reactant molecule or molecules to allow electrons to rearrange (to break and/or form bonds). The smaller the energy required, the larger the rate constant is.
3. The reacting molecules must collide in an orientation that allows the reaction to proceed; that is, even though the molecules have enough energy, a collision is more likely to result in reaction when the molecules are arranged in certain ways.

Let's consider these factors in more detail.

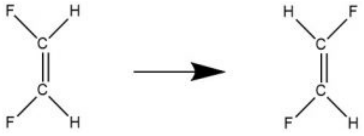
D21.2 Reaction Energy Diagrams

The rate of a chemical reaction depends on the energies of the reacting atoms and/or molecules. Bonds often need to be broken along the course of the reaction as new bonds are formed, and energy is required to break those bonds. Because energy is crucial for understanding the kinetics of a reaction, it is useful to diagram the energy changes that occur as a reaction proceeds.

Let's use a simple reaction as an example. Consider *cis*–*trans* isomerization—changing a *cis* isomer into a *trans* isomer or vice versa. We've learned before that these geometric isomers can be separated at room temperature because there is a barrier to rotation around an alkene double bond. This "barrier" is the energy needed to rotate around the double bond until the π bond is completely broken (when the two 2*p* AOs that form the π bond are oriented at 90° to each other).

Figure 1. *The π bonding orbital in ethene is shown. Move the slider to see the two 2p AOs from the two C atoms that overlap side-by-side to form the π bond. As the front C atom is rotated 90° relative to the back C atom, the* p-*orbital overlap is reduced to zero, breaking the π bond.*

For a *cis*–*trans* isomerization, the angle of rotation around the double bond is a good measure of the progress of the reaction. Figure 2 shows energy versus reaction progress for conversion of *cis*-1,2-difluoroethene to *trans*-1,2-difluoroethene.



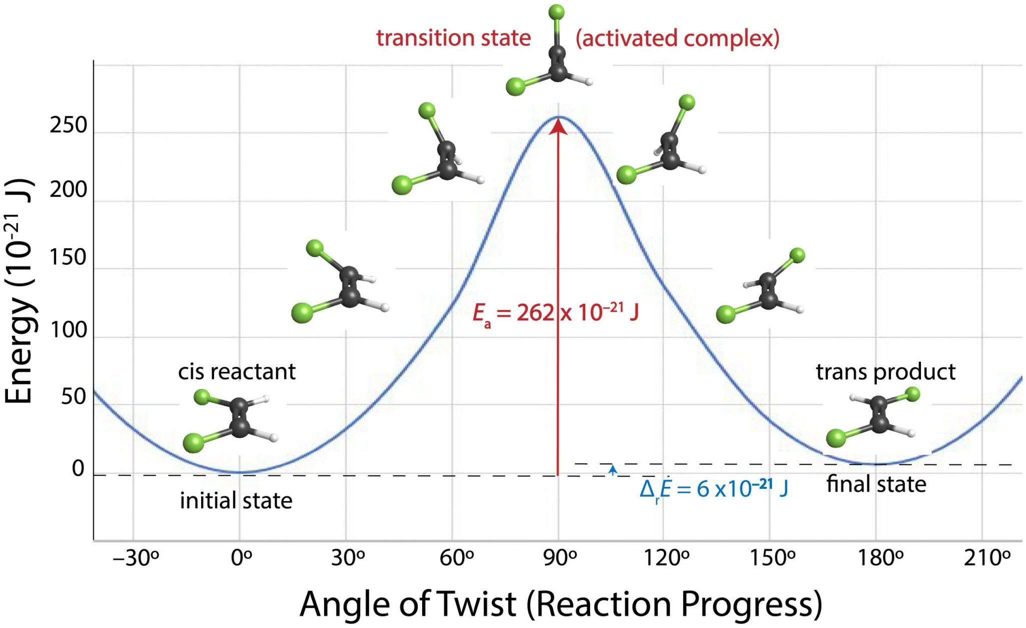


Figure 2. *Reaction energy diagram. At high temperatures, cis-1,2-difluoroethene can isomerize to trans-1,2-difluoroethene by rotation around the double bond. Energy increases with angle of twist up to 90 degrees and then decreases. The structure at 90-degree rotation is called a transition state or an activated complex. The maximum energy along the reaction progress scale is the activation energy,* E_a.

As one end of the molecule rotates relative to the other, energy increases because the π bond is partially broken. When the angle of rotation reaches 90° the π bond is completely broken and the energy of the molecule has increased by the bond energy of the π bond. Once the angle exceeds 90°, a new π bond begins to form and the molecule's energy decreases. Finally, when the angle of rotation is 180° the new π bond is completely formed and the molecule's energy has decreased almost to the same value it was initially. If a molecule does not have enough energy, which in this case is 262×10^{-21} J, the rotation cannot occur. Thus, only molecules whose energy is more than 262×10^{-21} J can react. As we shall see, at room temperature only a tiny fraction of all *cis*-1,2-difluoroethene molecules has this much energy, so rotation around the double bond is very slow at room temperature. Raising the temperature increases the fraction of molecules with enough energy to react and therefore increases the rate.

A diagram that shows energy as a function of reaction progress (such as Figure 2) is called a **reaction energy diagram**. In Figure 2, the reactant (*cis* isomer) and product (*trans* isomer) are connected by a single **transition state**, which is *a maximum on the reaction energy diagram.* The **transition-state structure** (or **activated complex**) is *the structure that corresponds to the transition state*. Because a transition-state structure has greater energy than either reactant molecule(s) or product molecule(s), it is unstable and exists for a very short time (typically < 10^{-15} s). This makes it very difficult to observe experimentally, unlike the stable reactant(s) and product(s).

The *difference in energy between the transition state and the reactant(s)* is the **activation energy** (**E_a**) of the reaction going forward (from reactant to product). If all other factors affecting the rate are the same, the greater the activation energy is, the slower the reaction is.

The *difference in energy between products and reactants* is the **reaction energy change, $\Delta_r E$**:

$$\Delta_r E = \sum E_{\text{products}} - \sum E_{\text{reactants}}$$

Figure 2 shows that the *cis–trans* isomerization of 1,2-difluoroethene has an activation energy of 262×10^{-21} J/molecule (or 158 kJ/mol) and a reaction energy change of $+6 \times 10^{-21}$ J/molecule (or +4 kJ/mol; the positive sign indicates that the *trans* isomer is slightly higher in energy than the *cis* isomer).

D21.3 Temperature and Maxwell-Boltzmann Distribution

How do we think about the energies available to each molecule in a reaction mixture, and how does the temperature of the system play into this?

For a collection of molecules, say a 1-L container of gaseous *cis*-1,2-difluoroethene at 1 bar, the average kinetic energy of all the molecules, KE_{avg}, is directly proportional to the observed temperature:

$$KE_{\text{avg}} = \frac{3}{2}RT$$

R is the gas constant, 8.314 J/K·mol.

But the individual molecules do not all have the same *KE* nor are they all traveling at the same velocity. Recall that the kinetic energy of a molecule of mass (m) and velocity (v) is:

$$KE = \tfrac{1}{2}mv^2$$

At any given temperature (or KE_{avg}), there is a distribution of individual molecular velocities (or kinetic energies). This distribution is known as the **Maxwell-Boltzmann distribution**. It shows *the fraction of molecules that have a particular velocity*. For example, Figure 3 shows the Maxwell-Boltzmann distribution for *cis*-1,2-difluoroethene gas at various temperatures.

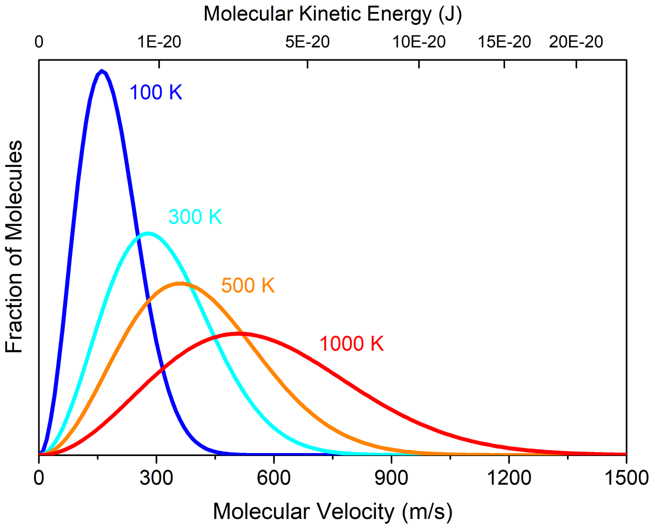


Figure 3. *The Maxwell-Boltzmann distribution for cis-1,2-difluoroethene gas at various temperatures. Each line shows the fraction of all molecules that has a specific velocity (bottom axis) or kinetic energy (top axis) at the given temperature. The area under the curve for each plot is the same; it is proportional to the total number of molecules in the given sample.*

The fraction of *cis*-1,2-difluoroethene molecules moving at 1200 m/s is much larger when the sample is at 1000 K (red curve) than at 100 K (blue curve). In general, if the temperature of a gas sample increases, its KE_{avg} increases, and the Maxwell-Boltzmann distribution shifts toward higher velocity.

Because the molecules are in constant motion, they will occasionally collide against each other. In a collision, energy can be transferred from one molecule to another, so that one molecule speeds up after the collision while the other slows down. Hence, even while the temperature of the sample and KE_{avg} remain constant, the kinetic energy of any given molecule is continually changing over time.

D21.4 Activation Energy and Temperature

A reaction will not proceed unless the kinetic energy available to the reactant(s) is at least as high as the activation energy (E_a). If the activation energy is much larger than the average kinetic energy of the reactants, $E_a >> KE_{\text{avg}}$, the reaction will occur slowly. This is the case when E_a is large (e.g., the transition state structure involves numerous covalent bonds breaking but few bonds forming) and/or when the temperature of the sample is low. On the other hand, if $E_a << KE_{\text{avg}}$, the reaction will likely proceed rapidly.

For example, Figure 2 indicates that the *cis–trans* isomerization reaction of *cis*-1,2-difluoroethene has $E_a = 262 \times 10^{-21}$ J/molecule, corresponding to the energy needed to break the π bond. At 500 K, the Maxwell-Boltzmann distribution (Figure 3, orange curve) shows that nearly all the molecules have KE $< 15 \times 10^{-20}$ J, that is, 150×10^{-21} J, much smaller than E_a. Very few reactant molecules have enough energy to reach the transition state.

Nevertheless, at 500 K, a very small fraction of the molecules is moving very fast ($v > 1200$ m/s). If such a rapidly moving molecule hits another molecule in a way that causes one carbon to start rotating around the other carbon, and if the hit is hard enough so that after the collision the second molecule has energy greater than E_a , that is, $> 262 \times 10^{-21}$ J/molecule, then the reaction can occur. But this happens very rarely at 500 K.

If the temperature increases, for example to 1000 K, then there is a larger fraction of molecules moving at sufficiently high speed, and more molecules can overcome the E_a barrier and change from a *cis* isomer into a *trans* isomer at any given time. Hence, the reaction is occurring faster (rate is higher). On the other hand, at room temperature (300 K), the fraction of molecules that can have sufficient energy to overcome the barrier is so small that the reaction can essentially be considered as not occurring (rate ≈ 0). Hence, at room temperature we can separate the *cis* and *trans* isomers and they are considered as different substances.

The fraction of reactant molecules with sufficient energy to react depends on the activation energy of the reaction and the temperature of the reaction mixture. The rate constant is proportional to the fraction of molecules with sufficient energy and that fraction involves an exponential (a power of e, the base of the natural logarithm system).:

$$k \propto e^{-E_a/RT}$$

Here, R is the ideal gas constant (as 8.314 J mol^{-1} K^{-1}), T is absolute temperature (in kelvins), and E_a is expressed in J/mol; hence units in the exponent cancel. This proportionality relationship tells us that k is larger when E_a is smaller as well as when T is larger. Hence, increasing the temperature of a reaction has a similar effect on reaction rate as lowering the reaction's activation energy. This is illustrated in Figure 4.

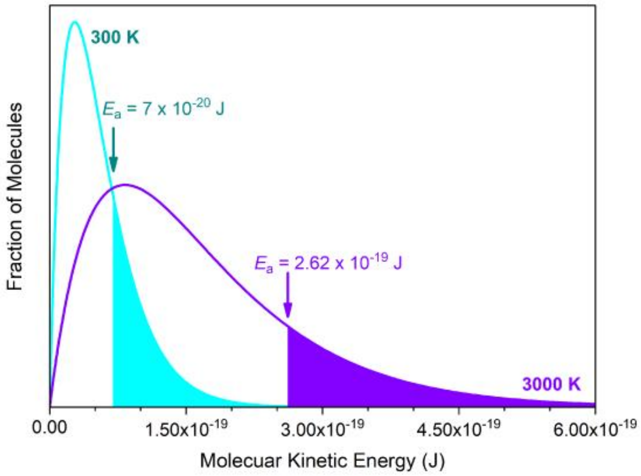


***Figure 4**. The Maxwell-Boltzmann distribution for cis-1,2-difluoroethene gas at 300 K (cyan) and 3000 K (violet). The shaded areas under the curves represent the number of molecules with energy greater than the activation energy.*

The number of *cis*-1,2-difluoroethene molecules exceeding the $E_a = 2.62 \times 10^{-19}$ J barrier at 3000 K (violet curve) is shaded in violet. This is the same fraction of molecules (shaded in cyan) that exceeds a lower $E_a = 7 \times 10^{-20}$ J barrier at room temperature (300K, cyan curve). This lower barrier, 7×10^{-20} J/molecule (or 40 kJ/mol), is typical for rotation around a C-C *single* bond (conformational isomers). Hence, we cannot separate one conformer from another at room temperature, because the reaction for converting between them has a fast rate at room temperature (conformers are not considered as distinct substances).

D21.5 Steric Factor

The **steric factor** is *the fraction of collisions energetic enough to react that actually results in reaction*. To see why some sufficiently energetic collisions do not always result in a reaction proceeding forward, consider this reaction:

$$CO(g) + O_2(g) \rightarrow CO_2(g) + O(g)$$

The reaction energy diagram is shown in Figure 5. In order to proceed forward, an O_2 molecule needs to collide with a CO molecule with sufficient energy to reach the transition state, where a new C=O double bond begins to form while the O=O double bond breaks and one of the C≡O π bonds also breaks.

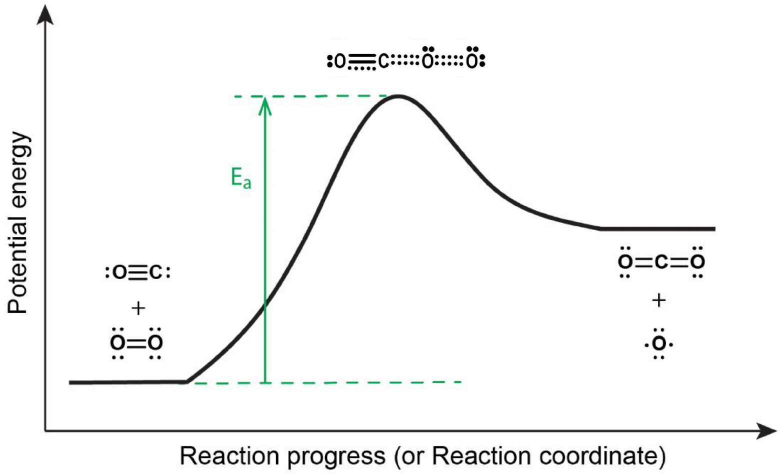


***Figure** 5. Reaction energy diagram for the CO(g) + O$_2$(g) → CO$_2$(g) + O(g) reaction. The activated complex or transition state (dotted lines indicate bonds being broken and formed) corresponds to the highest energy point along the reaction coordinate.*

Activity 1: Steric Factor

D21.6 Arrhenius Equation and Arrhenius Plot

Taking all that we have discussed above, the relationship between the activation energy, temperature, steric factor and the rate constant for a given reaction is summarized by the **Arrhenius equation** :

$$k = Ae^{-E_a/RT}$$

The constant A is called the **frequency factor** and it *depends on the rate at which collisions occur and the fraction of collisions that have the correct orientation (steric factor)*. The exponential term, $e^{-E_a/RT}$, is the fraction of the total number of collisions that has sufficient energy to overcome the activation-energy barrier of the reaction.

The Arrhenius equation describes quantitatively much of what we have already discussed about reaction rates. For example, for two similar reactions occurring at the same temperature, the reaction with the higher E_a has the smaller rate constant and hence is slower. Also, a change in conditions that increases the number of collisions with a favorable orientation results in an increase in A and, consequently, an increase in k.

If we take the natural logarithm of both sides of the Arrhenius equation, we have:

$$\ln(k) = \ln(A) + \left(-\frac{E_a}{RT}\right)$$

which has a standard linear equation format:

$$\begin{aligned} \ln(k) &= \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A) \\ y &= \quad m \quad\ x \qquad + b \end{aligned}$$

This provides a convenient way to experimentally determine E_a and A for a reaction. By measuring k at different temperatures and plotting ln(k) versus 1/T, we can obtain a straight line where slope = $-E_a/R$ and y-intercept = ln(A).

$_a$Activity 2: Determining E

You can estimate the activation energy without constructing the Arrhenius plot if the rate constant was determined at only two temperatures.

The slope of an Arrhenius plot is:

$$\text{Slope} = \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} = -\frac{E_a}{R}$$

Therefore:

$$\frac{\ln(k_1)-\ln(k_2)}{\frac{1}{T_1}-\frac{1}{T_2}}=-\frac{E_\text{a}}{R}$$

which can be rearranged as:

$$\ln\left(\frac{k_1}{k_2}\right)=-\frac{E_\text{a}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Day 21 Pre-class Podia Problem

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase:

$$2\ N_2O_5(g) \rightarrow 4\ NO(g) + 3\ O_2(g)$$

is 1.66 $M^{-1}s^{-1}$ at 650. K and 7.39 $M^{-1}s^{-1}$ at 700. K. Assuming this reaction obeys the Arrhenius equation, calculate the activation energy.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

3.5: Day 22- Elementary Reactions

D22.1 Elementary Reactions

A balanced equation for a chemical reaction indicates which substances react, which substances are produced when the reaction is over, and how the amounts of reactants and products are related. But it does not necessarily show what happens on the atomic scale as the reaction takes place. Although it is not obvious on the laboratory scale, most chemical reactions occur as a series of atomic-scale steps; that is, as a sequence of simpler reactions, each of which often involving collisions between molecules. *The step-by-step sequence of simple reactions by which an overall reaction occurs* is called a **reaction mechanism**.

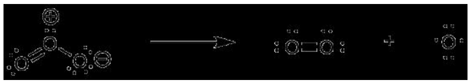
For example, ozone in the stratosphere protects Earth's surface from harmful ultraviolet radiation. Ultraviolet photons cause ozone molecules to decompose to oxygen molecules. The overall reaction equation is:

$$2\ \mathrm{O_3}(g) \xrightarrow{h\nu} 3\ \mathrm{O_2}(g)$$

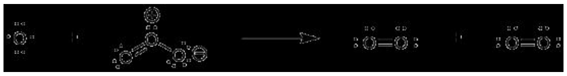
However, at the atomic scale this reaction does not involve collision and reaction between two O_3 molecules. Rather, there are two steps that occur one after the other:

$$\begin{array}{lll} \text{step 1:} & \mathrm{O_3}(g) & \xrightarrow{h\nu} \mathrm{O_2}(g) + \mathrm{O}(g) \\ \text{step 2:} & \mathrm{O}(g) + \mathrm{O_3}(g) & \longrightarrow 2\ \mathrm{O_2}(g) \\ \text{overall:} & 2\ \mathrm{O_3}(g) & \longrightarrow 3\ \mathrm{O_2}(g) \end{array}$$

In step 1, upon absorption of an UV photon, a bond breaks in an O_3 molecule producing an O_2 molecule and an O atom:



In step 2, the O atom formed in step 1 reacts with a second O_3 molecule, producing two O_2 molecules:



The overall reaction is the sum of the two steps. Write reactants from all steps to the left of a reaction arrow; write products from all steps to the right of the arrow; then cancel formulas that appear on both sides of the arrow. This gives

$$\mathrm{O_3}(g) + \cancel{\mathrm{O}(g)} + \mathrm{O_3}(g) \longrightarrow \mathrm{O_2}(g) + \cancel{\mathrm{O}(g)} + 2\mathrm{O_2}(g)$$

which is the overall reaction equation given above: $2\ O_3(g) \longrightarrow 3\ O_2(g)$. *An atom or molecule that is a product in an earlier step and reacts away in a later step of a reaction mechanism* is called a **reaction intermediate**.

Each step in a reaction mechanism is called an **elementary reaction**, which is *a chemical reaction that has only a single transition state*. An elementary reaction shows which atomic-scale particles collide, break apart, or rearrange their structures to form reaction products and/or intermediates.

The equation for an elementary reaction specifies exactly which atoms or molecules are involved in that reaction. For example, step 2 in the ozone decomposition reaction mechanism above states that one O atom reacts with one O_3 molecule and two O_2 molecules are formed. That is, for this elementary reaction to occur, one O atom must collide with (come very close to) one O_3 molecule.

In contrast, the overall reaction equation does not necessarily specify which atoms or molecules collide and react. Even though the overall ozone reaction is $2\ O_3(g) \longrightarrow 3\ O_2(g)$, two O_3 molecules do not have to collide for products to appear.

Because each elementary reaction has a single transition state, in an overall reaction that consists of several sequential elementary reaction steps there is a series of transition states, one for each step in the mechanism. For example, Figure 1 shows the overall reaction energy diagram for the ozone decomposition reaction.

***Figure 1**. Reaction energy diagram for the overall 2 $O_3(g)$ → 3 $O_2(g)$ reaction. This reaction proceeds via a mechanism consisting of two elementary reaction steps. Click on each + sign to identify each chemical species in the diagram.*

Note that although one of the O_3 molecules does not react until step 2, you still need to include it as a reactant in the reaction energy diagram. In other words, in a reaction energy diagram, all the atoms and molecules that are involved in the reaction are accounted for from the very beginning to the end. Hence, step 1 could be written $2\ O_3(g) \longrightarrow O_2(g) + O(g) + O_3(g)$, to emphasize that one O_3 molecule has not yet reacted, and step 2 becomes $O_2(g) + O(g) + O_3(g) \longrightarrow 3\ O_2(g)$. This is because there is a significant quantity of energy associated with each atom or molecule; to omit one, or suddenly add one in the middle of the diagram would change the energy (*y*-axis) a lot.

D22.2 Unimolecular Elementary Reactions

A **unimolecular elementary reaction** *involves the rearrangement of a single reactant molecule to produce one or more product molecules*. The isomerization of *cis*-1,2-difluoroethene (Section 21.2), step 1 in the mechanism for ozone decomposition given above, and many radioactive decay reactions (Day 20), are all examples of unimolecular elementary reactions.

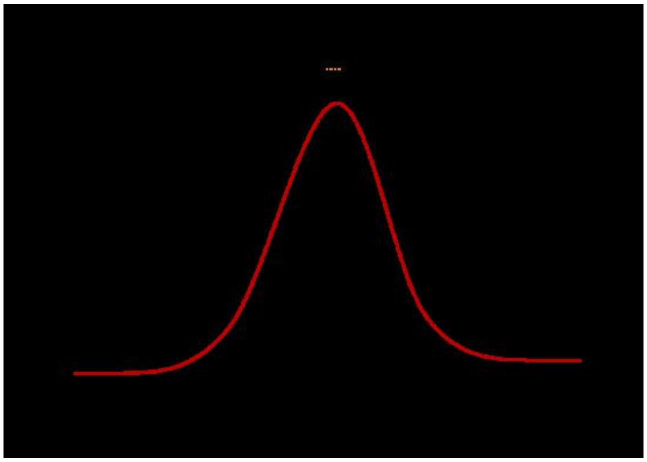


***Figure 2**. Reaction energy diagram of the cis-trans isomerization of cis-1,2-difluoroethene, an example of a unimolecular elementary reaction. In the transition state, the bond that is breaking (π bond) is shown as a dash and it is highlighted in orange.*

A general equation for a unimolecular elementary reaction is:

$$A \rightarrow \text{products}$$

Suppose that a 1.0-L flask contains 0.0010 mol of reactant A. The concentration of A is 0.0010 mol/1.0 L = 0.0010 M. At any given temperature a tiny fraction of the A molecules has enough energy to overcome the activation-energy barrier and react. If we add another 0.0010 mol A to the flask, the number of A molecules doubles and the concentration of A doubles to 0.0020 M. If the temperature remains the same, the fraction of molecules that has enough energy to react remains the same, but now there are twice as many molecules so the number of molecules reacting (and the rate of reaction) doubles; that is, the rate of reaction is directly proportional to the concentration of A. Thus, the rate equation for a unimolecular reaction is:

$$\text{rate} = k[A]$$

If a reaction is known to be a unimolecular elementary reaction, its reaction rate is directly proportional to the concentration of the reactant and the reaction is overall first-order. We see here that because an elementary reaction describes exactly the reaction that is occurring, **it is possible to determine the order of an elementary reaction solely by looking at the equation. This is true for all elementary reactions.**

D22.3 Bimolecular Elementary Reactions

The collision and reaction of two molecules or atoms in an elementary reaction is a **bimolecular elementary reaction**. There are two general types of bimolecular elementary reactions. In one type, the two reactants are different:

$$A + B \rightarrow \text{products}$$

The rate law for such a reaction is first-order in [A] and [B]:

$$\text{rate} = k[A][B]$$

In the other type of bimolecular elementary reaction, the two reactants are the same:

$$A + A \rightarrow \text{products or } 2\ A \rightarrow \text{products}$$

The rate law for such a reaction is second-order in [A]:

$$\text{rate} = k[A]^2$$

If a reaction is known to be a bimolecular elementary reaction, then its rate law can be derived by considering how concentration of each reactant affects the number of collisions. This is shown in Figure 3. Assuming that the fraction of collisions that results in reaction is the same in all three cases, the rate of reaction doubles when the number (and concentration) of each type of molecule doubles. The rate law derived from number of collisions agrees with the rate law derived from the reaction equation. A bimolecular reaction is overall second-order.

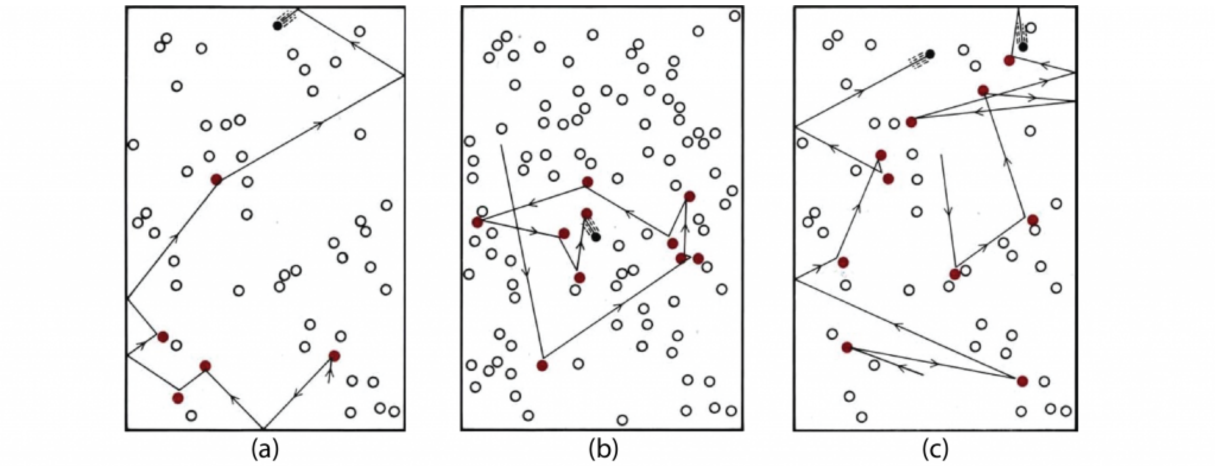


Figure 3. *The effect of concentration on the frequency of collisions for a bimolecular reaction. (a) A single black molecule moving among 50 white molecules traces the path shown and collides with 5 white molecules in 1 s. Each white molecule that has been struck by a moving black molecule is shown in color. (b) If the number of white molecules is doubled, the frequency of collisions rises to 10 per second. (c) Two black molecules moving among 50 white ones produce 10 collisions per second. The number of collisions can thus be seen to be proportional to both the concentration of white molecules and the concentration of black molecules.*

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. An example is the gas-phase reaction of 1,3-butadiene with ethene to form cyclohexene, shown in Figure 4.

$$C_4H_6(g) + C_2H_4(g) \rightarrow C_6H_{10}(g) \text{ rate} = k[C_4H_6][C_2H_4]$$

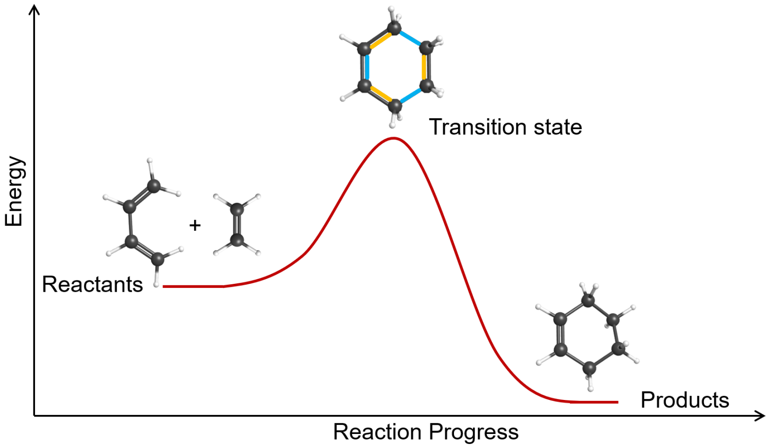


Figure 4. *The probable mechanism for the reaction of 1,3-butadiene with ethene to produce cyclohexene. In the transition state, bonds that are breaking (three π bonds) are shown in orange and bonds that are forming (one π bond and two σ bonds) are shown in cyan.*

Another example of a bimolecular elementary reaction is step 2 in the ozone decomposition mechanism given earlier:

$$O(g) + O_3(g) \rightarrow 2O_2(g) \text{ rate} = k[O][O_3]$$

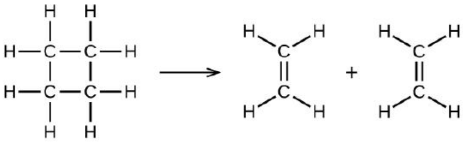
D22.4 Trimolecular Elementary Reactions

An **trimolecular** (or **termolecular**) **elementary reaction** involves *the simultaneous collision of three atoms or molecules*. Trimolecular elementary reactions are very unlikely, because the probability of three particles colliding simultaneously is less than 0.1% of the probability of two particles colliding. When a reaction involves three reactant molecules, it is much more likely for it to proceed via a multi-step mechanism involving unimolecular and/or bimolecular elementary reaction steps.

While there are rare examples of trimolecular elementary reaction occurring under certain conditions, in general, the individual steps in reaction mechanisms for gas-phase reactions are restricted to unimolecular and bimolecular reactions.

Day 22 Pre-class Podia Problem: Activated Complex (Transition State)

Consider the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, which occurs via a unimolecular elementary reaction:



1. Write the rate law for this reaction. Express the rate of reaction in terms of concentration. (Don't just write "rate =", use Δ*[A]*/Δ*t.)*

2. Describe in words which bonds must break and which bonds must form when this reaction occurs.

3. Based on your description in part 2, suggest a structure for the activated complex (transition state) for this reaction. Use dotted lines to indicate existing bonds that are partially broken or new bonds that are partially formed.

4. At the temperature of the kinetic study the reaction energy change, $\Delta_r E$ = – 300 kJ/mol. The activation energy, E_a = 261 kJ/mol. Use this information to draw a reaction energy diagram. Make the vertical axis scale as accurate as possible. Draw the structures of the reactant, the transition state, and the product molecules at appropriate positions on the diagram.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

3.6: Day 23- Reaction Mechanisms

D23.1 Multi-step Reactions and Rate-Determining Step

A valid mechanism for a multi-step reaction has these characteristics:

- The mechanism should consist of a series of unimolecular and/or bimolecular elementary reaction steps.
- The sum of the reaction steps should agree with the overall balanced reaction equation.
- The mechanism must agree with the experimentally observed rate law.

For elementary reactions, rate laws (and reaction order) can be derived directly from the stoichiometry of the chemical equations, but this is not true for a multi-step reaction where the balanced overall equation is not an elementary reaction. For some multi-step mechanisms, it is possible to derive the overall rate law from the known rate laws of the individual elementary steps. The overall rate law can also be determined from experimental data. If the experimental rate law agrees with the theoretical rate law (derived from the mechanism), the mechanism is a plausible theory for how the reaction occurs. Other experimental data can also support the plausibility of a mechanism. For example, if an intermediate proposed in the mechanism can be detected, that would support the mechanism.

Deriving rate law from a reaction mechanism can be a complex task. However, for many multi-step reactions, one elementary reaction step is *significantly slower* than the other steps, and this step limits the rate at which the overall reaction occurs. This *slowest step in a mechanism* is called the **rate-determining step** (or **rate-limiting step**), and it allows for some simplifying approximations.

As an example of a rate-determining step, consider the oxidation of iodide ions by hydrogen peroxide in aqueous solution:

$$2\ \mathrm{I^-}(aq) + \mathrm{H_2O_2}(aq) + 2\ \mathrm{H^+}(aq) \longrightarrow \mathrm{I_2}(aq) + \mathrm{H_2O}(l)$$

The currently accepted mechanism for this reaction has three steps. The third step occurs twice each time the first and second steps take place, so it is written twice. For simplicity the states of matter have been omitted.

$$\begin{array}{lllll}
\text{Step 1:} & \mathrm{H_2O_2} + \mathrm{I^-} & \xrightarrow{k_1} & \mathrm{HOI} + \mathrm{OH^-} & \text{Slow} \\
\text{Step 2:} & \mathrm{HOI} + \mathrm{I^-} & \xrightarrow{k_2} & \mathrm{I^2} + \mathrm{OH^-} & \text{Fast} \\
\text{Step 3:} & \mathrm{OH^-} + \mathrm{H^+} & \xrightarrow{k_3} & \mathrm{H_2O} & \text{Fast} \\
 & \mathrm{OH^-} + \mathrm{H^+} & \xrightarrow{k_3} & \mathrm{H_2O} &
\end{array}$$

The first step is labeled slow, which means that the rate constant k_1 is smaller than the other two rate constants. Steps 2 and 3 are labeled fast, because rate constants k_2 and k_3 are larger than k_1. Initially steps 2 and 3 cannot occur, because the concentration of one of their reactants is zero or very low. For example, the concentration of HOI is zero before the reaction begins because HOI is not a reactant in the overall reaction. Thus, step 2 cannot occur until there is some HOI available, which means that until step 1 produces some HOI and raises [HOI], step 2 has zero rate. No matter how big the rate constant for step 2 might be, step 2 cannot go any faster than step 1. *We say that the rate of step 2 is limited by the rate of step 1.* Similarly, step 3 cannot occur until steps 1 and 2 produce some $\mathrm{OH^-}$, so the rate of step 3 also limited by the rate of step 1. Thus, in this case, step 1 is the rate-limiting step.

Activity 1: Reaction Energy Diagram

D23.2 First Step is Rate-Determining

When the rate-determining step is the first step in a mechanism, the rate law for the overall reaction can be approximated as the rate law for the first step. The reaction of NO_2 and CO provides an illustrative example:

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$$

At temperatures below 225 °C, the experimentally observed rate law is:

$$\text{rate} = k[\mathrm{NO_2}]^2$$

This is consistent with a mechanism that involves these two elementary reaction steps:

$$\begin{array}{lllll}\text{Step 1:} & NO_2(g) + NO_2(g) & \xrightarrow{k_1} & NO_3(g) + NO(g) & \text{slow (larger } E_a) \\ \text{Step 2:} & NO_3(g) + CO(g) & \xrightarrow{k_2} & CO_2(g) + NO_2(g) & \text{fast (smaller } E_a) \\ \text{Overall:} & NO_2(g) + CO(g) & \longrightarrow & CO_2(g) + NO(g) & \end{array}$$

Both steps in this mechanism are bimolecular elementary reactions, and the sum of the two steps agrees with the overall reaction (the NO_3 that is formed in step 1 reacts away in step 2, and one of the NO_2 molecules that reacts in step 1 is reformed in step 2, so only one NO_2 molecule reacts overall).

Figure 1 shows the corresponding reaction energy diagram for this mechanism. $E_{a,1}$ is the activation energy for step 1, and it reflects the energy difference between the reactants and the first transition state. $E_{a,2}$ is the activation energy for step 2, and it reflects the energy difference between the intermediary minimum and the second transition state.

Figure 1. *Reaction energy diagram for the $NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$ reaction. Click on each "i" in the figure for additional information.*

With $E_{a,1}$ being much larger than $E_{a,2}$, step 1 has a smaller rate constant than step 2 ($k_1 < k_2$, assuming that the frequency factor (A) for the two steps are similar). However, step 2 cannot occur until step 1 produces some amount of NO_3 (NO_3 is a reaction intermediate, and therefore its concentration is zero at the beginning of the reaction). Because k_2 is larger, as soon as some NO_3 molecules are formed, they readily react away (step 2 reaction). Hence, the concentration of NO_3 is always very small, and the rate of step 2 cannot go faster than the rate of step 1.

Step 1 limits the rate of step 2, and is therefore the rate-determining step in this mechanism. Typically, the slowest reaction step is the one with the largest E_a and/or the highest energy transition state, as illustrated in Figure 1.

The stoichiometry of step 1, which is an elementary reaction, gives this rate law:

$$\text{rate}_1 = k_1[NO_2]^2$$

which can be approximated as the rate law for the overall reaction, and it is in agreement with the experimentally observed rate law.

D23.3 Equilibrium Approximation

When the rate-determining step is not the first step, the rate law can be approximated as the rate law for the rate-determining step. However, one or more of the reactants involved in the rate-determining step is a reaction intermediate formed from a previous step. Hence, the rate law for the rate-determining step includes the concentration of one or more reaction intermediates.

Experimentally, the concentration of a reaction intermediate is rarely measurable. (Even if it can be measured, the accuracy is usually low.) Therefore, experimentally determined rate laws are always expressed in terms of concentrations of reactants and/or products, for which accurate measurements are much easier to obtain.

In order to compare the theoretical rate law derived from the mechanism to the experimentally determined rate law, we must express the mechanism rate law only in terms of reactant and product concentrations, that is, we cannot simply use the rate law of the rate-determining step as is. If a preceding step that forms the reaction intermediate is at equilibrium, then we can make use of the **equilibrium approximation** to express the concentration of the intermediate in terms of concentrations of reactants.

For example, consider the following multi-step reaction:

$$2\ NO(g) + Cl_2(g) \longrightarrow 2\ NOCl(g)$$

The currently accepted mechanism for this reaction is:

$$\begin{array}{llcll}\text{Step 1:} & NO(g) + Cl_2(g) & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & NOCl_2(g) & \text{fast} \\ \text{Step 2:} & NOCl_2(g) + NO(g) & \xrightarrow{k_2} & 2NOCl(g) & \text{slow} \\ \text{Overall:} & 2NO(g) + Cl_2(g) & \longrightarrow & 2NOCl(g) & \end{array}$$

Figure 2. *Reaction energy diagram for the $2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$ reaction. Click on each "i" for more info.*

Step 2 is the rate-determining step, and its rate law is:

$$\text{rate}_2 = k_2\,[NOCl_2]\,[NO]$$

However, this rate law involves the concentration of an intermediate, $[NOCl_2]$, so it cannot be compared to experimental data. We need to express $[NOCl_2]$ in terms of concentrations of reactants.

Step 1 in this mechanism is much faster than step 2 and it is a reversible reaction. Reversible means that not only can NO and Cl_2 react to form $NOCl_2$, but $NOCl_2$ rapidly reacts to form NO and Cl_2. That is, step 1 can go forward with rate constant k_1 and backward with rate constant k_{-1}; this is represented by the two arrows pointing in opposite directions.

Because step 2 is slow, reaction of $NOCl_2$ with NO is much slower than reaction of $NOCl_2$ to form NO and Cl_2 (the reverse of step 1). Thus, when $NOCl_2$ molecules are formed, they are more likely to decompose back to NO and Cl_2 than to react in step 2. When enough $NOCl_2$ has formed, we can approximate that the rate of its decomposition (rate_{-1}) is equal to the rate at which it forms (rate_1) and step 1 is at *equilibrium* ($\text{rate}_1 = \text{rate}_{-1}$). This approximation allows us to express the rate laws of step 1 as:

rate_1	=	rate_{-1}
$k_1[NO][Cl_2]$	=	$k_{-1}[NOCl_2]$

This relationship can be rearranged to solve for the concentration of $NOCl_2$:

$$[\mathrm{NOCl_2}] = \left(\frac{k_1}{k_{-1}}\right)[\mathrm{NO}][\mathrm{Cl_2}]$$

And substituting this into the rate law for step 2, we have:

$$\text{rate}_2 = k_2[\mathrm{NOCl_2}][\mathrm{NO}] = k_2\left(\frac{k_1}{k_{-1}}\right)[\mathrm{NO}][\mathrm{Cl_2}][\mathrm{NO}] = \left(\frac{k_1k_2}{k_{-1}}\right)[\mathrm{NO}]^2[\mathrm{Cl_2}]$$

If we make:

$$k' = \frac{k_1k_2}{k_{-1}}$$

then the rate law for the overall reaction becomes:

$$\text{rate} = k'[NO]^2[Cl_2]$$

This rate law can be compared with experimental data to determine whether the proposed mechanism is a plausible one.

Activity 2: Rate Law from Mechanism

D23.4 Catalysts and Reaction Mechanisms

A **catalyst** *increases the rate of a reaction by altering the mechanism*, allowing the reaction to proceed via a pathway with lower activation energy than for the uncatalyzed reaction. A catalyzed mechanism must involve at least two steps, one where the catalyst interacts with a reactant to form an intermediate substance, and one where the intermediate then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product. Hence, the catalyst is involved in the reaction mechanism but *is not consumed by the reaction*.

An extremely important example of catalysis involves the catalytic destruction of ozone in Earth’s stratosphere, 10 to 40 km above the surface (Section D22.1). Stratospheric ozone intercepts ultraviolet radiation from the Sun that otherwise would reach Earth’s surface, damaging many forms of life including humans. The reaction mechanism for this process is

$$\begin{array}{llcl}
\text{Step 1: (fast)} & \mathrm{O_3}(g) & \xrightarrow{h\nu} & \mathrm{O_2}(g) + \mathrm{O}(g) \\
\text{Step 2: (slow)} & \mathrm{O_3}(g) + \mathrm{O}(g) & \longrightarrow & 2\ \mathrm{O_2}(g) \\
\text{Overall:} & 2\ \mathrm{O_3}(g) & \xrightarrow{h\nu} & 3\ \mathrm{O_2}(g)
\end{array}$$

In the first step, a photon of ultraviolet (UV) radiation with wavelength between 200 and 310 nm breaks a bond in the ozone molecule, forming O_2 and an O atom; the UV radiation is indicated by *hν* above the reaction arrow. In the second step the O atom from step 1 reacts with a second O_3 molecule to form two oxygen molecules; this second step has higher activation energy and is the rate-limiting step.

Ozone is formed in the stratosphere by short-wavelength UV photons (wavelength below 240 nm) that break the double bonds in O_2 molecules. The O atoms thus formed react with O_2 molecules to form O_3. The concentration of O_3 in the stratosphere is a small, constant value because the rate of formation of O_3 equals the rate at which it reacts away according to the mechanism above. Anything that speeds up the $2\ O_3 \rightarrow 3\ O_2$ reaction will reduce the concentration of ozone and allow more UV radiation to reach Earth’s surface.

One catalyst for the ozone decomposition reaction is chlorine atoms, which can be generated in the stratosphere from chlorofluorocarbon molecules, which at one time were used in air conditioners and cans of aerosol sprays. An example chlorofluorocarbon is CF_2Cl_2. An ultraviolet photon can break a C–Cl bond in CF_2Cl_2, producing Cl atoms, which react with ozone via this simplified mechanism:

Step 1: (slow)	$Cl(g) + O_3(g)$	$\longrightarrow$	$O_2(g) + ClO(g)$
Step 2: (fast)	$O_3(g) + ClO(g)$	$\longrightarrow$	$2\ O_2(g) + Cl(g)$
Overall:	$2\ O_3(g)$	$\longrightarrow$	$3\ O_2(g)$

Notice that Cl is a reactant in the first step and a product in the second step, so Cl participates in the mechanism but is not consumed by the overall reaction; that is, Cl is a catalyst. Because Cl is not reacted away, a single Cl atom can destroy as many as 100,000 O_3 molecules before the Cl atom reacts with something else and is removed from the stratosphere. Discovery of the catalytic effect of Cl atoms led to an international agreement, the Montreal Protocol, halting production of chlorofluorocarbons and banning their use. The Montreal Protocol now has 197 signatory countries—an essentially unanimous international agreement that is reversing the trend to lower ozone concentrations in the stratosphere and greater UV radiation at Earth’s surface.

Reactants or products can also be catalysts in a reaction. When a product catalyzes a reaction the reaction is called *autocatalytic*. An autocatalytic reaction can be dangerous because the reaction can “run away”; that is, it can speed up a lot as product is formed and produce products way too fast. An example of a reaction catalyzed by a reactant was in Day 23:

Step 1:	$NO_2(g) + NO_2(g)$	$\longrightarrow$	$NO_3(g) + NO(g)$
Step 2:	$NO_3(g) + CO(g)$	$\longrightarrow$	$CO_2(g) + NO_2(g)$
Overall:	$NO_2(g) + CO(g)$	$\longrightarrow$	$CO_2(g) + NO(g)$

The second NO_2 molecule in step 1 (highlighted in green) is a catalyst, because it is reformed as a product in step 2. This catalyzed reaction has the first step as the rate-determining step, which yields a reaction rate of:

$$\text{rate}_{\text{catalyzed}} = k_{\text{catalyzed}}[NO_2]^2$$

Without the catalytic action, this reaction ($NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$) would be a bimolecular elementary reaction (with only one transition state) with a rate law of:

$$\text{rate}_{\text{uncatalyzed}} = k_{\text{uncatalyzed}}[NO_2][CO]$$

Figure 3 shows the reaction energy diagrams of the catalyzed and uncatalyzed reactions. Because the reactants and products involved in both reactions are exactly the same, they are at the same energies (a catalyst has no effect on the relative energies of the reactants and products).

Figure 3. Reaction energy diagrams of catalyzed (green) and uncatalyzed (brown) $NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$ reaction. Click on each “i” for more info.

The transition states, and therefore the activation energies, of the two pathway differ. The lower E_a in the catalyzed pathway results in $k_{\text{catalyzed}} > k_{\text{uncatalyzed}}$, and the reaction proceeds almost entirely via the faster pathway.

In this particular example, 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). Other catalyzed reactions might have more than two steps. Usually there are more mechanistic steps in a catalyzed reaction than in the uncatalyzed mechanism.

Podia Question

The important industrial chemical hydrazine, N_2H_4, is produced by the Raschig process. Here is a proposed mechanism for the process:

Step 1 (slow): $NH_3(aq) + OCl^-(aq) \longrightarrow NH_2Cl(aq) + OH^-(aq)$

Step 2 (fast): $NH_2Cl(aq) + NH_3(aq) \longrightarrow N_2H_5^+(aq) + Cl^-(aq)$

Step 3 (fast): $N_2H_5^+(aq) + OH^-(aq) \longrightarrow N_2H_4(aq) + H_2O(l)$

1. Determine which is the rate-limiting step. Describe how this step limits the overall reaction rate.
2. Determine the overall reaction equation for the Raschig process.
3. Identify all reaction intermediates in the proposed mechanism.
4. Another student tells you that the reaction is second-order in ammonia and does not depend on any other concentration. The student says this is consistent with the mechanism written above. Explain why the student is, or is not, correct.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

3.7: Day 24- Enzymes and Enzyme Catalysis

22

Day 24: Enzymes and Enzyme Catalysis

D24.1 Enzymes

Millions of chemical reactions occur within each of our cells every minute. Without catalysts, many of these reactions proceed at an extremely slow rate. For example, the dissociation of carbonic acid that takes place in the lungs:

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$$

only proceeds at a rate of ~10^{-7} M/s at room temperature. However, CO_2 needs to be produced in our body at a much higher rate than this. While it's theoretically possible to accelerate the reaction by raising the temperature, unfortunately, most life is only compatible with a limited temperature range.

Biological catalysts, known as **enzymes**, are crucial for life as they can accelerate reactions by factors of 10^6-10^{20}. For example, the enzyme carbonic anhydrase accelerates the above reaction at room temperature by more than a million times the rate of the uncatalyzed reaction.

Like all catalysts, enzymes act by combining with reactant(s) and thereby forming lower energy transition states. *In an enzyme-catalyzed reaction, the reactant(s) with which the enzyme combines* is called the **substrate**(s). Unlike chemical catalysts, an enzyme's interactions with substrate molecules are often partly or entirely noncovalent; that is, the interactions involve hydrogen bonding, ionic attractions, or dipole-dipole attractions.

In addition, enzyme-catalyzed reactions are highly specific to a particular substrate or a particular category of substrate molecules. Enzymes are said to "recognize" the substrate, or class of substrates, for which the enzyme serves as a catalyst. Enzyme interactions with substrates are sometimes so specific that an enzyme does not recognize a molecule that differs from its preferred substrate by as little as a single methyl ($-CH_3$) group, and many enzymes will recognize one enantiomer but not its mirror image.

How do enzymes accelerate chemical reactions and achieve their specificity? The answer to both questions lies in how enzymes interact with their substrates. Typically an enzyme is a protein molecule—a macromolecule. Usually only part of the large enzyme molecule interacts with a substrate. *The part of an enzyme molecule that interacts with a substrate* is called the **active site**.

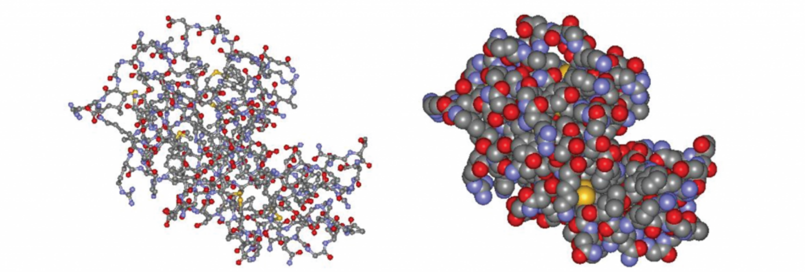


***Figure 1**. Structure of the enzyme lysozyme. Left: ball-and-stick structure. Right: space filling structure. Note the "cleft" in the middle of the right side of the molecule. Molecules whose reactions are catalyzed by lysozyme fit into the cleft, which is the active site of the enzyme. (Structures from http://lysozyme.co.uk.)*

In 1890, the chemist Emil Fischer proposed that the substrate fits into the enzyme's active site as a key fits into a lock. The key (substrate) has a specific molecular shape (arrangement of functional groups and other atoms) that allows it, and no other key, to fit into the lock (the enzyme).

In 1958, Daniel E. Koshland Jr. modified this lock-and-key model by proposing that binding of the substrate to the enzyme alters the configuration of both, providing a better fit. This *induced-fit* model explains both the large increase in reaction rates and the specificity of enzyme-catalyzed reactions:

- As the substrate interacts with the enzyme, the substrate is distorted (atoms are shifted, bonds are stretched, and reactive groups are brought close together) to a structure closer to the transition state of the reaction. This lowers the energy of the transition state, accelerating the reaction.

- Only molecules with the correct functional groups in the correct configurations are able to be induced to fit the active site of the enzyme.

For many years, it was believed that the only enzymes were proteins. Recently, however, several RNA enzymes have been discovered. These enzymes are called **ribozymes** and exhibit all the same features as protein enzymes (Figure 2).

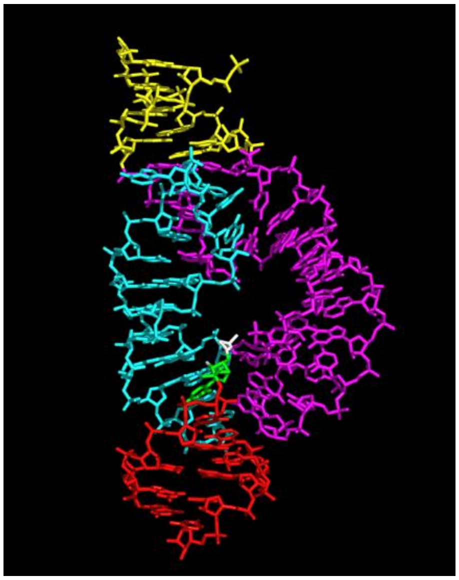


Figure 2. *An example ribozyme, known as hammerhead ribozyme, originally discovered in viruses.*

D24.2 Enzyme Kinetics: Michaelis-Menten Mechanism

The **Michaelis-Menten mechanism** is *a two-step reaction mechanism that applies to many enzyme-catalyzed reactions.* An enzyme (E) binds with a substrate (S) to form an enzyme-substrate complex (ES), which then separates to give the product (P) and regenerates the enzyme. The overall reaction is:

$$\mathrm{S} \rightarrow \mathrm{P}$$

with the simple two-step mechanism:

$$\begin{array}{lccc} \text{step 1: (fast)} & E+S & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & ES \\ \text{step 2: (slow)} & ES & \xrightarrow{k_2} & P+E \end{array}$$

The second step is rate determining. Enzyme kinetics studies are typically carried out by measuring the reaction rate as a function of the concentration of substrate and the concentration of enzyme. The rate of the catalyzed reaction can be measured by observing the rate of the production of the product:

$$rate = \frac{\Delta[P]}{\Delta t} = k_2[ES]$$

but ES is a reactive intermediate whose concentration is not easily determined. We need to express the reaction rate in terms of concentrations that are easily measured. This can be done by assuming that, *once the reactive intermediate, ES, forms, its concentration remains approximately constant throughout the rest of the reaction*; this is called the **steady-state approximation**. It differs from the equilibrium approximation we discussed in Section D23.3 in that it is not necessary to assume step 1 has reached equilibrium. The steady-state approximation is reasonable, because once [ES] builds up enough, the reactions that consume ES become faster and prevent the concentration from increasing further.

When the concentration of the enzyme-substrate complex reaches a steady state:

$$\frac{d[ES]}{dt} = 0$$

The ES complex is formed by the forward reaction in step 1, and is reacted away in the reverse reaction of step 1 and forward reaction of step 2. Summing the rates of these reactions:

$$\frac{d[ES]}{dt} = 0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

Rearranging the equation to solve for [ES] gives:

$$(k_{-1} + k_2)[ES] = k_1[E][S]$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$$

or:

$$[ES] = \frac{[E][S]}{K_M}$$

where K_M is the **Michaelis constant**:

$$K_M = \frac{k_{-1} + k_2}{k_1}$$

It is difficult to know the exact concentration of the free enzyme ([E]) at any given moment. However, we do know the total concentration of enzyme, $[E]_{total}$ (the enzyme must be either in its unreacted form (E) or combined with substrate (ES)):

$$[E]_{total} = [E] + [ES]$$

Substituting into the above equation gives:

$$[ES] = \frac{([E]_{\text{total}} - [ES])[S]}{K_M}$$

Rearranging the variables gives:

$$[ES] = \frac{[E]_{\text{total}}[S]}{K_M} - \frac{[ES][S]}{K_M}$$

$$\frac{[ES][S]}{K_M} + [ES] = \frac{[E]_{\text{total}}[S]}{K_M}$$

$$\left(\frac{[S] + K_M}{K_M}\right)[ES] = \frac{[E]_{\text{total}}[S]}{K_M}$$

$$[ES] = \left(\frac{[E]_{\text{total}}[S]}{K_M}\right)\left(\frac{K_M}{[S] + K_M}\right) = \frac{[E]_{\text{total}}[S]}{[S] + K_M}$$

Substituting the expression for $[ES]$ into the expression for the reaction rate in terms of [ES} gives

$$rate = \frac{\Delta[P]}{\Delta t} = \frac{k_2[E]_{\text{total}}[S]}{[S] + K_M}$$

or

$$rate = \frac{V_{\max}[S]}{[S] + K_M} \quad \text{Michaelis-Menten equation}$$

where $V_{max} = k_2[E]_{total}$ is the maximum rate the reaction can achieve. There are two limiting cases for this equation, depending on the relative sizes of $[S]$ and $K_{M.}$

If there is a lot of substrate, $[S] \gg K_M$, and therefore $[S] + K_M \approx [S]$. In this case the Michaelis-Menten equation becomes

$$\text{rate} = \frac{V_{\max}[S]}{[S]} = V_{\max} = k_2[E]_{\text{total}}$$

The reaction reaches its maximum rate, rate = V_{max}. The reaction rate depends only on $[E]_{\text{total}}$ and is independent of [S]. This happens when almost all of the enzyme molecules have a substrate molecule in the active site, which means that increasing the concentration of substrate can no longer increase the concentration of enzyme-substrate complex (and thus can no longer increase the rate).

If there is a very small concentration of substrate, $[S] \ll K_{\text{M}}$, we have $[S] + K_{\text{M}} \approx K_{\text{M}}$, and the Michaelis-Menten equation becomes first-order in $[S]$:

$$rate = \left(\frac{V_{\text{max}}}{K_M}\right)[S]$$

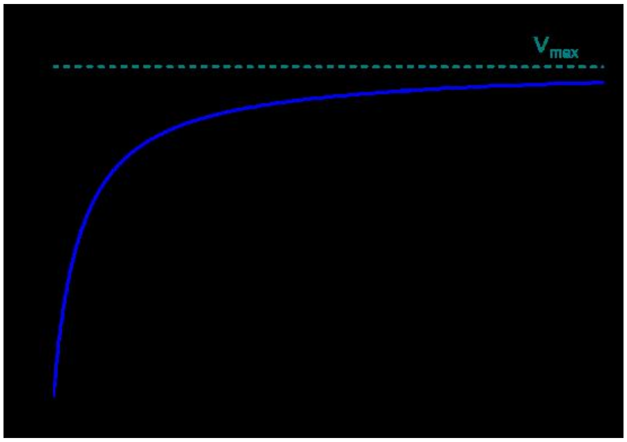


***Figure 3**. Reaction rate as a function of substrate concentration. At low [S], the reaction rate is first-order in [S]. As [S] increases, the rate approaches V_{max}.*

The Michaelis constant is an inverse measure of the substrate's affinity for the enzyme—a small K_{M} indicates high affinity, meaning that the rate approaches V_{max} more quickly. The value of K_{M} depends on both the enzyme and the substrate, as well as reaction conditions such as temperature and pH.

D24.3 Enzyme Denaturation and Inhibitors

Denaturation is a process in which *proteins lose their quaternary, tertiary and secondary structure* (see Section D15.6). Enzymes must be folded into the right 3D shape to function. But hydrogen bonds, which play a big part in protein folding, are rather weak, and it does not take much heat, acidity, or other stress to break some hydrogen bonds and denature the enzyme.

Hence, enzyme-catalyzed reactions exhibit an unusual temperature dependence. At relatively low temperatures, the reaction rate increases with temperature, as expected. However, at higher temperatures, the reaction rate drops dramatically due to denaturation of the enzyme, as shown in Figure 4.

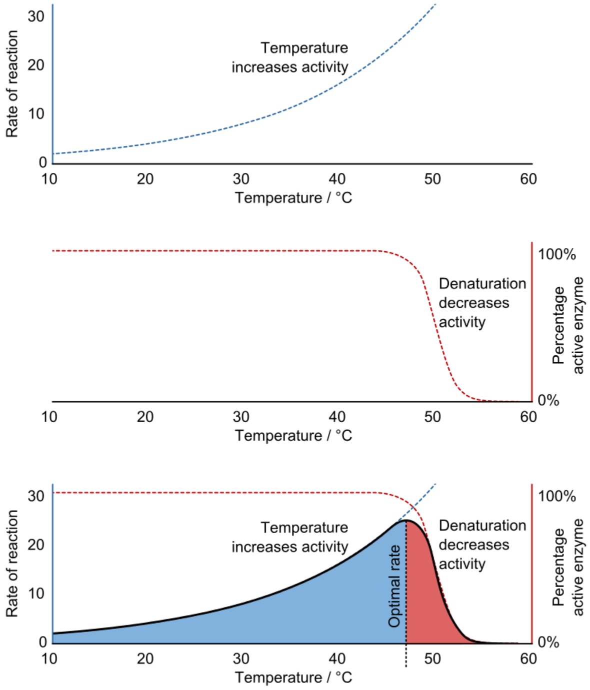


Figure 4. *Enzyme activity increases with temperature until the enzyme's structure unfolds (denaturation), so the largest rate of reaction is at an intermediate temperature. (CC-BY-SA-4.0; Thomas Shafee)*

Usually enzymes will not denature at temperatures typically encountered by the living organism in which they are found. As a result, enzymes from bacteria living in high-temperature environments such as hot springs are prized by industrial users for their ability to function at high temperatures.

An **inhibitor** (I) *interacts with an enzyme to decreases the enzyme's catalytic efficiency*. An **irreversible inhibitor** covalently binds to the enzyme's active site, *producing a permanent loss in catalytic efficiency* even if the inhibitor's concentration is later decreased. A **reversible inhibitor** forms a noncovalent complex with the enzyme, *resulting in a temporary decrease in catalytic efficiency*. Reducing the concentration of a reversible inhibitor returns the enzyme's catalytic efficiency to its normal level.

There are several kinds of reversible inhibition. In **competitive inhibition** *the substrate and the inhibitor compete for the same active site on the enzyme*. Because the substrate cannot bind to an enzyme–inhibitor complex (EI), the concentration of enzyme available to form enzyme-substrate complex is lower and the enzyme-catalyzed reaction is slower. With **uncompetitive inhibition** *the inhibitor binds to the enzyme-substrate complex but not to the active site*, forming an enzyme–substrate–inhibitor (*ESI*) complex. The formation of an *ESI* complex decreases catalytic efficiency because some of the enzyme-substrate complex has reacted with inhibitor. This reduces the concentration of ES, which reduces the rate of the rate-limiting step in the mechanism. Finally, in **noncompetitive inhibition** the *inhibitor binds to both the enzyme itself and the enzyme–substrate complex at a site different from the active site. As in uncompetitive inhibition*, this forms an inactive *ESI* complex and reduces the concentration of ES.

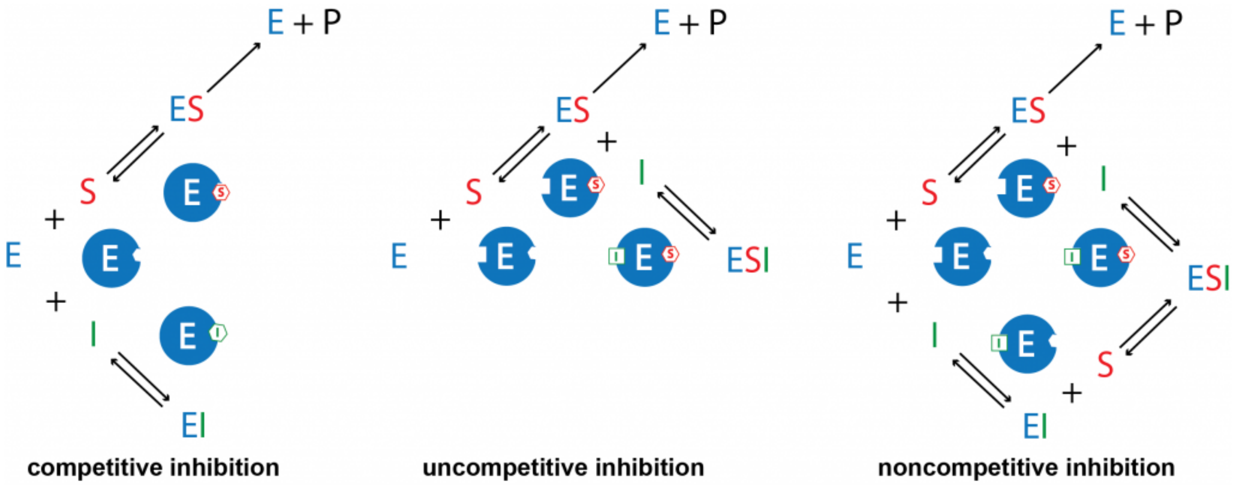


***Figure** 5. Mechanisms for the reversible inhibition of enzyme catalysis. E: enzyme, S: substrate, P: product, I: inhibitor, ES: enzyme–substrate complex, EI: enzyme–inhibitor complex, ESI: enzyme–substrate–inhibitor complex.*

Podia Question

Consider the reaction mechanism for Michaelis-Menten enzyme kinetics in Section D24.2:

1. Draw a reaction energy diagram for this reaction. If you need to make any assumptions to draw the diagram, describe each assumption. Also, describe which parts of the diagram you can draw definitively given the information in Section D24.2.

2. Suppose that a reversible, competitive inhibitor is present during the enzyme-catalyzed reaction. How does the presence of this inhibitor affect the reaction energy diagram?

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

3.8: Day 25- Homogeneous and Heterogeneous Catalysis

23

Day 25: Homogeneous and Heterogeneous Catalysis

D25.1 Homogeneous Catalysis

Reactions that are facilitated by catalysts can be divided into two major classes: homogeneous catalysis and heterogeneous catalysis. A **homogeneous catalyst** is *present in the same phase as the reactants*. Gas-phase reactions and reactions in solution are homogeneous reactions and we have already discussed several examples where catalyst and reactants are all in the same phase. Here is one more.

In Section D13.5 we described condensation reactions and hydrolysis reactions that occur in aqueous solutions. (Hydrolysis is the reverse of a condensation that produces water as the small molecule.) We also mentioned that condensation and hydrolysis can be catalyzed by strong acids (that is, by H^+ ions). This is a homogeneous catalytic reaction because reactants, products, and catalyst are all in aqueous solution.

An example of ester hydrolysis is the acid-catalyzed decomposition of methyl acetate to form acetic acid and methanol. The reaction mechanism is shown in Figure 1.

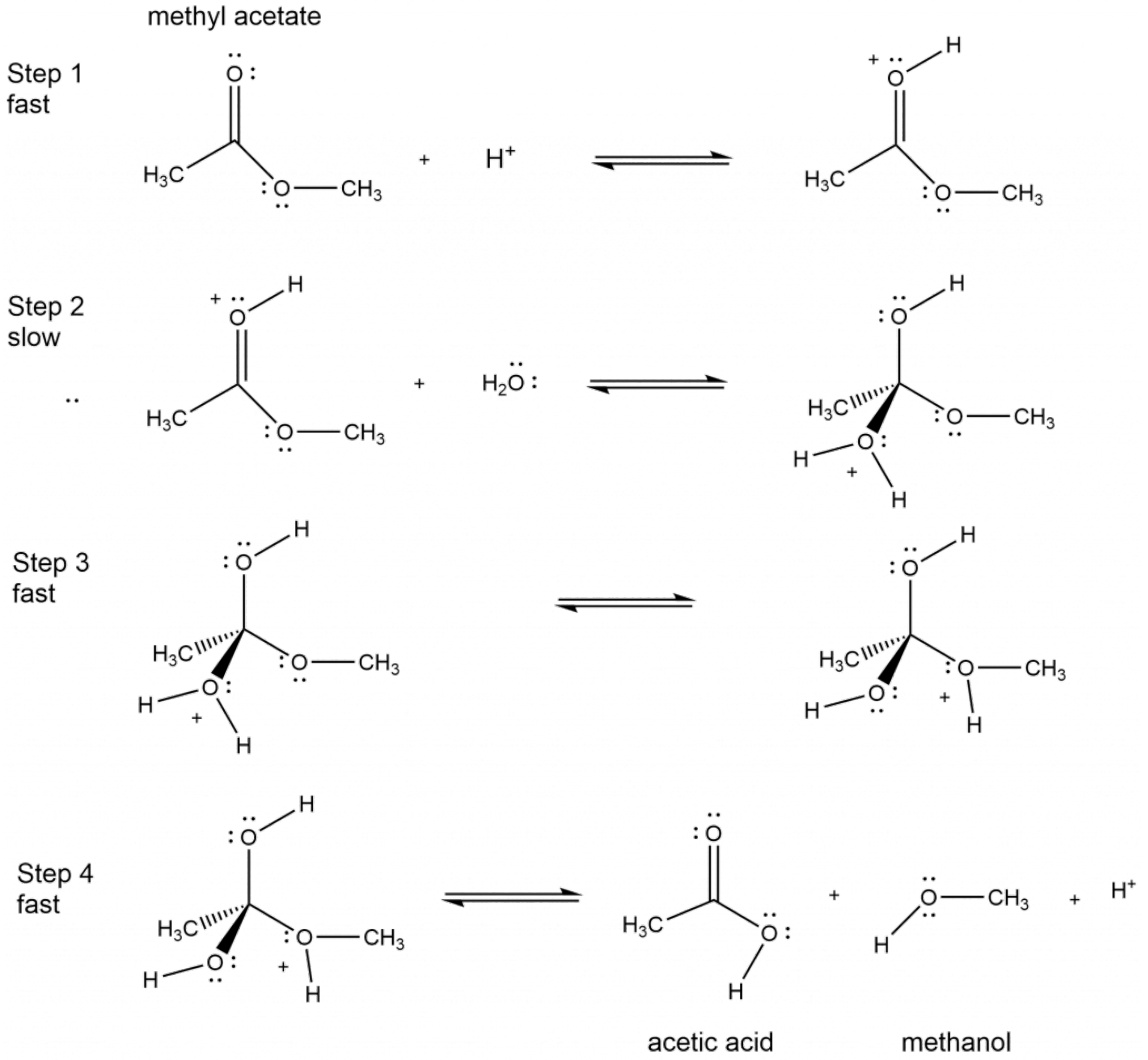


Figure 1. Mechanism of acid-catalyzed hydrolysis of methyl acetate to form acetic acid and methanol.

Activity 1: Analyzing a Reaction Mechanism

D25.2 Heterogeneous Catalysts

A **heterogeneous catalyst** is *present in a different phase from the reactants*. Such catalysts are usually solids, and often function by furnishing an active surface upon which one or more steps in the reaction can occur.

A heterogeneous catalytic reaction has at least four steps in its reaction mechanism:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)
3. Reaction of the adsorbed reactant(s)
4. Diffusion of the product(s) 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. But the overall rate of the reaction is still faster than it would be without the catalyst. Figure 1 illustrates the reaction of alkenes with hydrogen on a nickel catalyst.

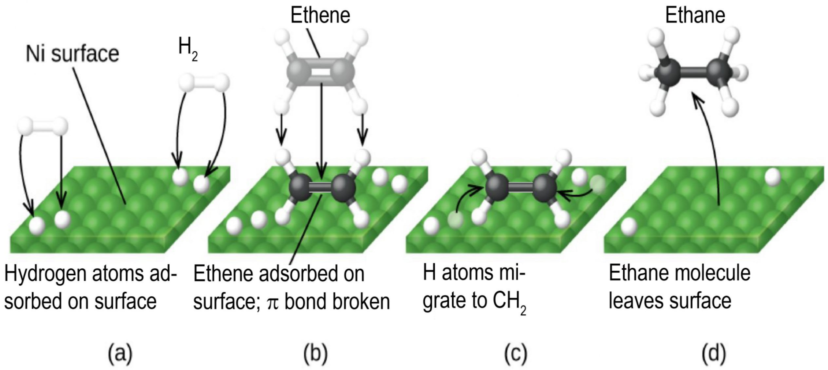


***Figure 2**. There are four steps in the catalytic hydrogenation of ethene on a nickel surface, $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethene is adsorbed on the surface, breaking the π bond and forming Ni–C bonds. (c) H atoms diffuse across the surface and form new C–H bonds when they reach ethene molecules. (d) The saturated carbon atoms in C_2H_6 molecules can no longer bond to the surface so the ethane molecules escape from the surface.*

The uncatalyzed $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$ reaction would necessitate a transition state where the C=C π bond and the H-H σ bond are breaking while the C-H σ bonds form. Such a transition state is so high in energy that without a catalyst, H_2 is considered as being unreactive towards alkenes under most conditions.

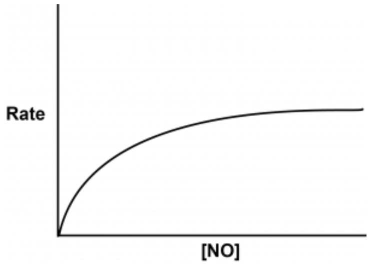
Nickel is a catalyst often used in the hydrogenation of polyunsaturated fats and oils to produce saturated fats and oils. Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles.

Podia Question

Platinum metal is a heterogeneous catalyst for this reaction:

$$2\ NO(g) \rightarrow N_2(g) + O_2(g)$$

The reaction rate varies with concentration of NO as shown in the graph.



Explain each of these observations. Include in your explanation an atomic-level description of NO molecules, the platinum surface, and how the two interact.

- The graph is linear with positive slope at low concentrations of NO.
- The graph is horizontal at high concentrations of NO.

Suggest an experiment that could be done to support or contradict your explanation of the horizontal graph. Describe the hypothesis you propose for what will happen in the experiment if your explanation is correct; also describe what experimental results would contradict your hypothesis.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

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platform.

CHAPTER OVERVIEW

4: Unit Four

4.1: Day 27- Thermochemistry and Enthalpy

24

Day 27: Thermochemistry and Enthalpy

D27.1 Energy, Temperature, and Heat

Thermal energy is *kinetic energy associated with the random motion of atoms and molecules*. When thermal energy is transferred into an object, its atoms and molecules move faster on average (higher $KE_{average}$), the object's temperature increases, and we say that the object is "hotter". When thermal energy is transferred out of an object, its atoms and molecules move more slowly on average (lower $KE_{average}$), the object's temperature decreases, and we say that the object is "colder".

Heating (or **heat**), represented by ***q***, is the *transfer of thermal energy between two bodies at different temperatures* (Figure 1).

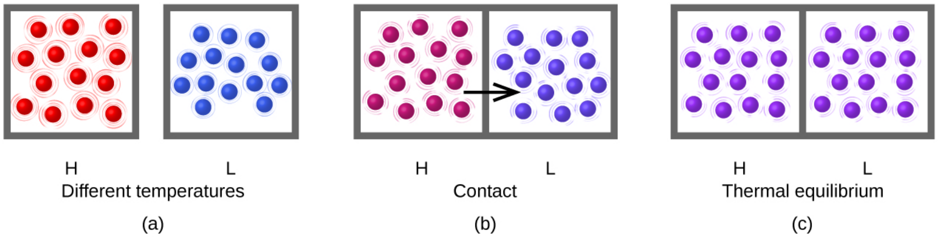


Figure 1. *(a) Two samples of matter are initially at different temperatures, higher (H) and lower (L). (b) When the two samples come into contact, collisions between molecules result in transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two samples reach "thermal equilibrium" when both are at the same temperature, and their molecules have the same average kinetic energy. The hotter sample has heated the cooler sample by transfer of energy.*

The **heat capacity (*C*)** of an object is *the heating required when the object's temperature changes by 1 °C*. (Because 1 K is the same size as 1 °C, ΔT has the same numeric value whether expressed in K or °C.*)* It typically has units of J/°C. Heat capacity depends on both the type and the quantity of substance, and therefore is an *extensive property*—its value is proportional to the quantity of the substance.

The **specific heat capacity (*c*)** of a substance is *the heating required to raise the temperature of 1 g of a substance by 1 °C*. It typically has units of J/g·°C. Specific heat capacity depends only on the type of substance and therefore is an *intensive property*. The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and typically has units of J/mol·°C.

Specific heat capacities of some common substances are listed in Table 1.

Substance	Symbol (*state*)	Specific Heat Capacity (J/g·°C)
helium	He(*g*)	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040
oxygen	$O_2(g)$	0.918
aluminum	Al(*s*)	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	Ar(*g*)	0.522
iron	Fe(*s*)	0.449
copper	Cu(*s*)	0.385

Substance	Symbol (*state*)	Specific Heat Capacity (J/g·°C)
lead	Pb(*s*)	0.130
gold	Au(*s*)	0.129
silicon	Si(*s*)	0.712

Table 1. Specific Heat Capacities of Common Substances at 25 °C and 1 bar

If we know the mass, *m*, of a sample and its specific heat capacity, *c*, we can calculate the heat transferred to or from the sample by measuring the temperature change during heating or cooling:

$$q = m \cdot c \cdot \Delta T = m \cdot c \cdot (T_{\text{final}} - T_{\text{initial}})$$

The sign of ΔT tells us whether the substance is being heated (positive value for q) or cooled (negative q).

D27.2 Calorimetry

Calorimetry is *an experimental technique used to quantitatively measure heat transfer of energy*. Energy is exchanged with a **calorimeter**, *a device with known heat capacity that therefore can relate ΔT to q*. A calorimeter must be insulated thermally so that energy does not transfer beyond its physical boundaries. In calorimetry it is useful to define a **system**, *the substance(s) undergoing the chemical or physical change*, and **the surroundings**, *everything else that can exchange energy with the system*.

For example, if we place a piece of hot metal (M) into cool water (W), heat transfer of energy occurs from metal to water until the two substances reach the same temperature (Figure 2).

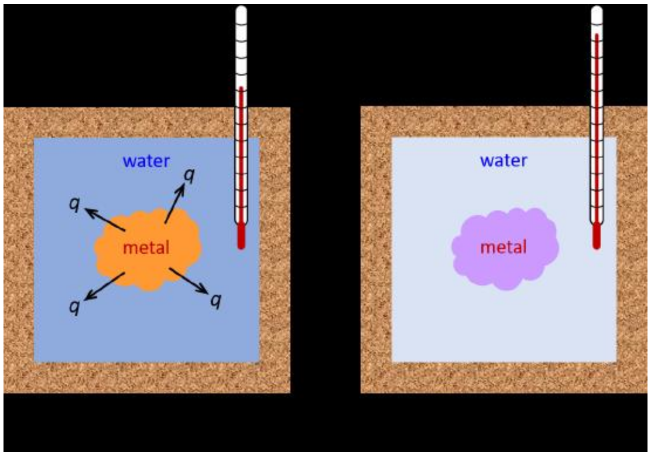


Figure 2. *In a simple calorimetry process, (a) there is heat transfer of energy, q, from the hot metal to the cool water, until (b) both are at the same temperature.*

If this occurs in a well insulated calorimeter, this heat transfer would ideally occur only between the two substances. Thus, the magnitude of q is the same for both substances.

$$q_M + q_W = 0$$

The arithmetic sign of q is determined by whether the substance loses or gains energy. In our example, energy is transferred from the metal (q_M is negative) to the water (q_W is positive).

The same principles apply when we apply calorimetry to determine the heat transfer of energy involved in chemical reactions:

$$q_{\text{reaction}} + q_{\text{surroundings}} = 0$$

Here, q_{reaction} is defined as the change in energy of all atoms present in reactants and products.

A reaction in which there is *heat transfer from the reacting substances to their surroundings* (a reaction that heats the surroundings) is an **exothermic reaction**. For example, the combustion reaction that occurs in the flame of a lit match is exothermic. A reaction in which there is *heat transfer from the surroundings to the system* (a reaction that cools the surroundings) is an **endothermic reaction**. For example, when the substances in a cold pack (water and a salt such as ammonium nitrate) are mixed, the resulting process transfers energy from the surroundings, making the surroundings colder.

If the heat capacity of a calorimeter is too large to neglect or if we require more accurate results, then we must take into account energy transferred to or from the calorimeter as well as energy transfers within the the calorimeter. For example, *a type of calorimeter that operates at constant volume*, colloquially known as a **bomb calorimeter** because it involves a strong, steel container that will not explode when an exothermic reaction occurs inside it (the "bomb"). Bomb calorimetry is used to measure energy transfers for reactions such as combustion reactions. The reaction occurs inside the bomb (Figure 3), which is immersed in a water bath and the temperature change of the water bath is measured. Energy has to be transferred to the bomb so the bomb can heat the water, so you need to account for the heat capacity of the bomb as well as the water. That is,

$$q_{\text{reaction}} = -[q_{\text{water}} + q_{\text{bomb}}]$$

Figure 3. *Reactants are added to the stainless steel "bomb", which is then placed into a water bath inside the calorimeter. Reaction is initiated by brief electric heating and both the bomb and the surrounding water exchange energy with the reaction system. The calorimeter is well insulated so the only energy transfers are between the reaction, the bomb, and the water. The heat transfer of energy can be calculated from the temperature change of bomb and water.*

D27.3 Enthalpy

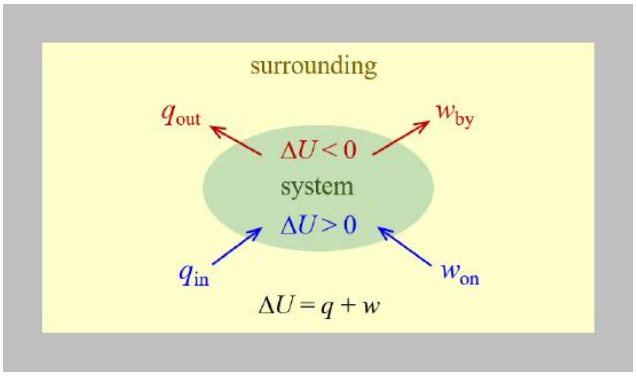
Chemical thermodynamics deals with *the relationships between heat, work, and other means of energy transfer in the context of chemical and physical processes*. **Work**, represented by ***w***, is *a process that transfers kinetic energy to or from a macroscopic object.* When a golf club strikes a golf ball, for example, the club does work on the ball, accelerating the ball to a high speed.

Substances act as reservoirs of energy. *The total of all possible kinds of energy present in a substance* is called the **internal energy (*U*)**. (The symbol U, instead of E, represents a sum over several different kinds of energy within the substance.) Energy is transferred into a system when it is heated (q) by the surroundings or when the surroundings does work (w) on the system. For example, energy can be transferred into room-temperature metal wire if it is immersed in hot water (the water heats the wire), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w$$

assuming there are no energy transfers other than heat and work. This is one version of the **first law of thermodynamics**, *the law of conservation of energy*. The equation shows that the internal energy of a system changes through heat transfer into or out of the system (positive q is heat transfer in; negative q is heat transfer out) or work done on or by the system. The work, w, is positive if it is done on the system (increases the system's internal energy) and negative if it is done by the system. This is summarized in the figure below.



Chemists ordinarily use a property known as **enthalpy (*H*)** to describe the thermodynamics of chemical and physical processes. Enthalpy is defined by this equation:

$$H = U + PV$$

where P is pressure and V is volume. Enthalpy is closely related to energy, differing by the quantity PV.

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 that take place at atmospheric pressure), the **enthalpy change (Δ*H*)** is:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V$$

(where P is factored out of $\Delta(PV)$ because P is constant).

The mathematical product $P\Delta V$ represents pressure-volume work, also called expansion work. For example, consider a gas (the system) confined in a cylinder by a piston, as shown in the figure. The pressure exerted by the gas results from many collisions of gas molecules with the bottom of the piston and the walls of the cylinder. If the pressure of the gas causes the piston to move upward, the gas does work on the piston (part of the surroundings). This reference shows that the work done by the system on the surroundings equals $P\Delta V$. Work done *by* the system is the negative of w, which is defined as work done *on* the system, so

$$P\Delta V = -w$$

Substituting yields:

ΔH	=	$\Delta U + P\Delta V$
	=	$(q_P + w) - w$
	=	q_P

where q_p is the heat of reaction under constant pressure. Therefore, 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 transfer of energy (q_p) equals the enthalpy change (ΔH) for the process.

The heat transfer to the surroundings when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, because the reaction occurs at the essentially constant pressure of the atmosphere. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q_p = \Delta H$, which makes enthalpy the most convenient choice for determining heat transfer of energy as a result of a chemical reaction. The enthalpy change for a chemical reaction is symbolized $\Delta_r H$, where the subscript **r** indicates that the change is for a **r**eaction.

On the other hand, the heat transfer of energy by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. In a constant-volume system $w = 0$ and $\Delta U = q_v + w = q_v$, where the subscript v indicates constant volume.

D27.4 Standard-state Reaction Enthalpy Change, $\Delta_r H°$

Heat effects of a chemical reaction are summarized in **thermochemical expressions**, *balanced chemical equations together with values of* $\Delta_r H°$*, the standard-state reaction enthalpy change, and a temperature*. The **standard-state reaction enthalpy change,** $\boldsymbol{\Delta_r H°}$**,** is *the standard-state enthalpy of pure, unmixed products minus the standard-state enthalpy of pure, unmixed reactants*; that is, the enthalpy change for the reaction under standard-state conditions.

$$\Delta_r H° = H°(\text{products}) - H°(\text{reactants})$$

A **standard state** is *a commonly accepted set of conditions used as a reference point*. For chemists, the standard state refers to substances under a pressure of *1* bar and solutions at a concentration of *1* mol/L (1 M). (Note that some thermochemical tables may list values with a standard state of 1 atm. Because 1 bar = 0.987 atm, thermochemical values are nearly the same under both sets of standard conditions; however, for accurate work the standard state should be checked.)

The standard state does not specify a temperature. Because $\Delta_r H°$ can vary with temperature, temperature is typically specified in a thermochemical expression.

We will include a superscript "°" to designate standard state. Thus, the symbol $\Delta_r H°_{298\text{ K}}$ indicates an enthalpy change for a process occurring under standard-state conditions and at 298 K.

For example, consider this thermochemical expression:

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)\ \Delta_r H° = 8.031 \times 10^{-22}\text{ kJ} = -483.6\text{ kJ/mol (25 °C)}$$

This refers to reaction of two molecules of hydrogen with 1 molecule of oxygen to form two molecules of water, all in the gas phase at 1 bar pressure. If this reaction equation took place once, the two hydrogen molecules and the one oxygen molecule would react to form two water molecules and 8.031×10^{-22} kJ would be transferred to the surroundings. Because we are interested in laboratory-scale reactions, where moles of reactants are involved, $\Delta_r H°$ is always reported per mole of reaction rather than for a single reaction event. A mole of reaction involves a chemical reaction equation happening 6.022×10^{23} times; in this case that is 2 mol $H_2(g)$ reacting with 1 mol $O_2(g)$ to give 2 mol $H_2O(g)$. The heat transfer of energy to the surroundings is then 8.031×10^{-22} kJ $\times\ 6.022 \times 10^{23}$ mol^{-1} = 483.6 kJ/mol. Because the energy transfer is from system to surroundings, the sign is negative and $\Delta_r H° = -483.6$ kJ/mol.

These conventions apply to thermochemical expressions:

1. In a thermochemical expression, the listed $\Delta_r H°$ value indicates the heat transfer of energy for the coefficients in the chemical equation. If the coefficients are multiplied by some factor, $\Delta_r H°$ must be multiplied by that same factor. In other words, $\Delta_r H°$ is an extensive property. For example:

	$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)$	$\Delta_r H° = -483.6$ kJ/mol
two-fold increase:	$4\ H_2(g) + 2\ O_2(g) \longrightarrow 4\ H_2O(g)$	$\Delta_r H° = 2(-483.6$ kJ/mol$) = -967.2$ kJ/mol
two-fold decrease:	$H_2(g) + ½\ O_2(g) \longrightarrow H_2O(g)$	$\Delta_r H° = ½(-483.6$ kJ/mol$) = -241.8$ kJ/mol

2. $\Delta_r H°$ of a reaction depends on the physical state of the reactants and products (whether we have gases, liquids, solids, or aqueous solutions), so physical states must be shown.
3. A negative $\Delta_r H°$ indicates an exothermic reaction; a positive $\Delta_r H°$ indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its $\Delta_r H°$ is changed. (A process that is endothermic when reactants change into products is exothermic when products change into reactants).

Be sure to take both stoichiometry and limiting reactants into account when determining the $\Delta_r H°$ for a chemical reaction.

D27.5 Bond Enthalpy and Reaction Enthalpy Change

The enthalpy change for a gas-phase chemical reaction, $\Delta_r H$, equals the sum of the enthalpy required to break each of the bonds in the reactant molecules (energy *in*, *positive* sign) plus the sum of the enthalpy released when each of the bonds in the product molecules forms (energy *out*, *negative* sign). This can be expressed mathematically as:

$$\Delta_r H = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}}$$

Because the bond enthalpy values provided in the Appendix are averaged over many different molecules for each type of bond, this calculation is not exact, but it provides a good estimate for the enthalpy change of any specific reaction. Also, bond enthalpy calculations assume that all molecules are far from each other (which means that reactants and products must be in the gas phase). Additional enthalpy changes occur when a gas condenses to a liquid or solid or dissolves into a solution; these transformations are not accounted for by bond enthalpies.

Consider this balanced reaction:

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

One H–H bond (436 kJ/mol) and one Cl–Cl bond (242 kJ/mol) are broken; two H-Cl bonds (431 kJ/mol each) are formed. Representing bond enthalpies by D_{bond}, we have:

$$\Delta_r H = \sum E_{\text{bonds broken}} - \sum E_{\text{bonds formed}} = [D_{\text{H-H}} + D_{\text{Cl-Cl}}] - [D_{\text{H-Cl}} + D_{\text{H-Cl}}]$$

$$\Delta_r H = [436\text{ kJ/mol} + 242\text{ kJ/mol}] - 2(431\text{ kJ/mol}) = -184\text{ kJ/mol}$$

There are the same number of bonds formed as were broken. Because the bonds in the products are stronger than those in the reactants, the reaction has a net release (negative sign) of about 184 kJ for every mole of reaction as written. The energy released increases the temperature of the surroundings (the reaction is *exo*thermic).

Here are two general rules to predict whether a chemical reaction releases energy (is exothermic):

- If there are more bonds in the product molecules than in the reactant molecules and the bonds have about the same strength, the reaction is exothermic.
- If there are stronger bonds in the product molecules than in the reactant molecules and the number of bonds is the same in reactants and products, the reaction is exothermic.

Check Your Learning

D27.6 Hess's Law

The enthalpy change for a particular reaction is the same regardless of which or how many steps the reaction is carried out in. This conveniently allows us to calculate the heat transfer for a chemical change from other experimentally determined enthalpy changes. This type of calculation usually involves **Hess's law**: *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.*

For example, we can think of this reaction occurring in a single step:

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ \Delta_r H° = -394\text{ kJ/mol}$$

or in a two-step process:

step 1:	$C(s) + ½O_2(g)$	$\longrightarrow$	$CO(g)$	$\Delta_r H° = -111$ kJ/mol
step 2:	$CO(g) + ½O_2(g)$	$\longrightarrow$	$CO_2(g)$	$\Delta_r H° = -283$ kJ/mol

According to Hess's law, the $\Delta_r H°$ of the one-step reaction equals the sum of the $\Delta_r H°$ of the two steps in the two-step reaction:

step 1:	$C(s) + ½O_2(g)$	$\longrightarrow$	$CO(g)$	$\Delta_r H° = -111$ kJ/mol
step 2:	$CO(g) + ½O_2(g)$	$\longrightarrow$	$CO_2(g)$	$\Delta_r H° = -283$ kJ/mol
Sum:	$C(s) + O_2(g)$	$\longrightarrow$	$CO_2(g)$	$\Delta_r H° = -394$ kJ/mol

This concept is illustrated in Figure 4.

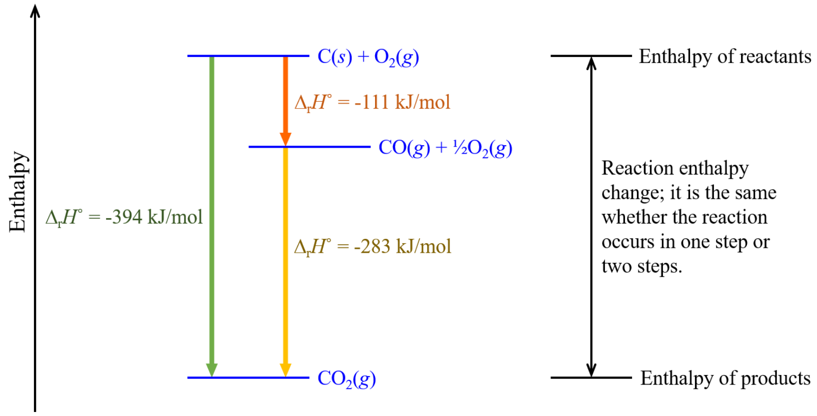


Figure 4. *Enthalpy values based on one mole of reaction: $C(s) + O_2(g) \longrightarrow CO_2(g)$. The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. For an exothermic process, the products are at lower enthalpy than the reactants.*

D27.7 Standard Enthalpy of Formation

Standard enthalpy of formation, $\Delta_f H°$, is *the enthalpy change for a reaction in which exactly one mole of a pure substance in a specified state (s, l, or g) is formed from free elements in their most stable states under standard-state conditions*. $\Delta_f H°$ is also referred to as the *standard heat of formation*.

For example, $\Delta_f H°$ of $CO_2(g)$ at 25 °C is −393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)\ \Delta_f H° = -393.5\ \text{kJ/mol}\ (25\ °C)$$

The gaseous reactant and product are at a pressure of 1 bar, the carbon is present as graphite, which is the most stable form of carbon under standard conditions.

For nitrogen dioxide, $NO_2(g)$, $\Delta_f H°$ is 33.2 kJ/mol at 25 °C:

$$½N_2(g) + O_2(g) \longrightarrow NO_2(g)\ \Delta_f H° = +33.2\ \text{kJ/mol}\ (25\ °C)$$

A reaction equation with ½ mole of N_2 and 1 mole O_2 is appropriate in this case because the standard enthalpy of formation always refers to formation of 1 mol $NO_2(g)$.

By definition, the standard enthalpy of formation of an element in its most stable form is 0 kJ/mol under standard conditions. A table of $\Delta_f H°$ values for many common substances can be found in the Appendix.

Hess's law can be used to determine the $\Delta_r H°$ of any reaction if the $\Delta_f H°$ of the reactants and products are available. In other words, we can think of any reaction as occurring via step-wise decomposition of the reactants into their component elements followed by re-combination of the elements to give the products. (Almost no reaction would actually occur via such a mechanism because some of the reactions would have large activation-energy barriers and consequently very small rates, but we can imagine such a path for the sole purpose of using Hess's law to calculate $\Delta_r H°$.)

The $\Delta_r H°$ of the overall reaction is therefore equal to:

$$\Delta_r H° = \sum \Delta_f H°(\text{products}) - \sum \Delta_f H°(\text{reactants})$$

Activity 1: Applying Hess's Law to Standard Formation Enthalpies

Podia Question

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$(i)\ \text{ClF}(g) + \text{F}_2(g) \longrightarrow \text{ClF}_3(g) \qquad \Delta_r H^\circ = ?$$

Use the reactions here to determine the $\Delta_r H°$ for reaction *(i)*:

$$(ii)\ 2\text{OF}_2(g) \longrightarrow \text{O}_2(g) + 2\text{F}_2(g) \qquad \Delta_r H^\circ_{(ii)} = -49.4\ \text{kJ/mol}$$

$$(iii)\ 2\text{ClF}(g) + \text{O}_2(g) \longrightarrow \text{Cl}_2\text{O}(g) + \text{OF}_2(g) \qquad \Delta_r H^\circ_{(iii)} = +205.6\ \text{kJ/mol}$$

$$(iv)\ \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \qquad \Delta_{\mathrm{r}}H^\circ{}_{(iv)} = +266.7\ \mathrm{kJ/mol}$$

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

4.2: Day 28- Entropy, Gibbs Free Energy

25

Day 28: Entropy, Gibbs Free Energy

D28.1 Entropy and Microstates

An important goal of chemical thermodynamics is to predict whether reactants are changed to products or products are changed to reactants. For a given reaction, such a prediction requires knowledge of specific conditions of temperature and of concentrations or partial pressures of reactants and products. *When reactants change to products* we say that the reaction is **spontaneous**, or **spontaneous in the forward direction**. *When products change to reactants*, we say the reaction is **not spontaneous**, or that it is **spontaneous in the reverse direction**. In this context, the word "spontaneous" does not imply that the reaction is fast or slow, just that reactants change to products. Even if it takes millions of years for a process to occur, if there is an overall change of reactants to products we call the process spontaneous.

It is useful to define parallel terms that relate to a convenient reference point—standard-state conditions. *If, when all substances are at the standard-state pressure of 1 bar or at the standard-state concentration of 1 M, reactants change to products*, we call a reaction **product-favored**. In contrast, *if products change to reactants under standard-state conditions*, a process is **reactant-favored**. That is, a product-favored process is spontaneous under the specific conditions of standard-state pressures or concentrations and a reactant-favored process is not spontaneous under those specific conditions..

Deciding whether a process is spontaneous requires knowledge of the system's enthalpy change, but that is not sufficient. It also requires knowledge of change in another property: entropy. (Similarly, deciding whether a process is product-favored requires knowledge of the system's standard enthalpy change and standard entropy change.) The **entropy change, Δ*S*,** at constant temperature is defined as:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

Here, q_{rev} is the heat transfer of energy for a **reversible process**, *a theoretical process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change in some condition*. An example of a reversible process is melting water at 0 °C and 1 bar, where liquid water and ice are at equilibrium. Raising the temperature a tiny bit causes the ice to melt; lowering the temperature a tiny bit reverses the process, causing liquid water to freeze.

On a molecular scale, the entropy of a system can be related to the number of possible microstates (W). A **microstate** is *a specific configuration of the locations and energies of the atoms or molecules that comprise a system*. The relationship is:

$$S = k_{\text{B}} \cdot \ln(W)$$

where k_{B} is the Boltzmann constant with a value of 1.38×10^{-23} J/K.

Similar to enthalpy, the change in entropy for a process is the difference between its final (S_{f}) and initial (S_{i}) values:

$$\Delta S = S_{\text{f}} - S_{\text{i}} = k_{\text{B}} \cdot \ln(W_{\text{f}}) - k_{\text{B}} \cdot \ln(W_{\text{i}}) = k_{\text{B}} \cdot \ln\left(\frac{W_{\text{f}}}{W_{\text{i}}}\right)$$

For processes involving an increase in the number of microstates, $W_{\text{f}} > W_{\text{i}}$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_{\text{f}} < W_{\text{i}}$, yield a decrease in system entropy, $\Delta S < 0$.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, suppose four atoms, one atom each of He, Ne, Ar, and Kr, are distributed among two boxes as illustrated in Figure 1. There are $2^4 = 16$ different microstates. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system exists as a given distribution is proportional to the number of microstates within the distribution. Because entropy increases logarithmically with the number of microstates, *the most probable distribution is the one of greatest entropy*.

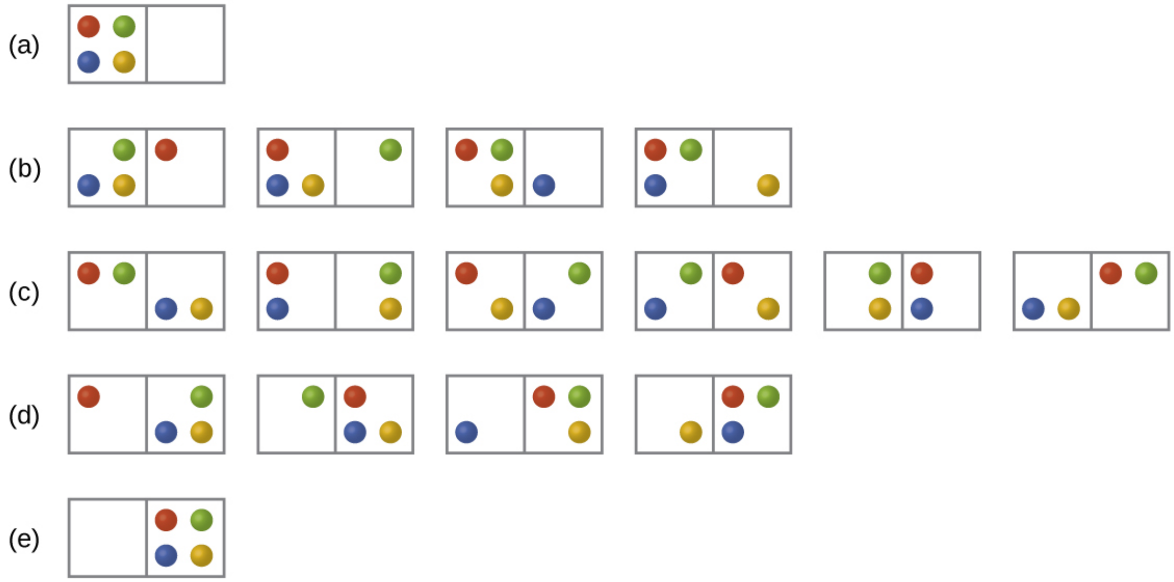


Figure 1. *The sixteen microstates associated with placing four distinguishable particles in two boxes are shown. The microstates are collected into five distributions—(a) 4,0, (b) 3,1, (c) 2,2, (d)1,3, and (e) 0,4—based on the numbers of particles in each box.*

For the system in Figure 1, the most probable distribution is (c), where the particles are evenly distributed between the boxes. The probability of finding the system in this configuration is $\frac{6}{16}$ or 37.5%. The least probable configuration of the system is distributions (a) and (e), where all four particles are in one box, and each distribution has a probability of $\frac{1}{16}$.

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic system typically consists of moles of particles ($N \approx 10^{23}$), and the corresponding number of microstates is staggeringly huge. Regardless of the number of particles in a system, the distributions with uniform dispersal of particles between the boxes have the greatest number of microstates and are the most probable.

Activity 1: Entropy Change and Microstates

Consider another system as shown in Figure 2. This system consists of two objects, **AB** and **CD**, and two units of energy (represented as "*"). Distribution (a) shows the three microstates possible for the initial state of the system, where both units of energy are contained within the hot **AB** object. If one energy unit is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates.

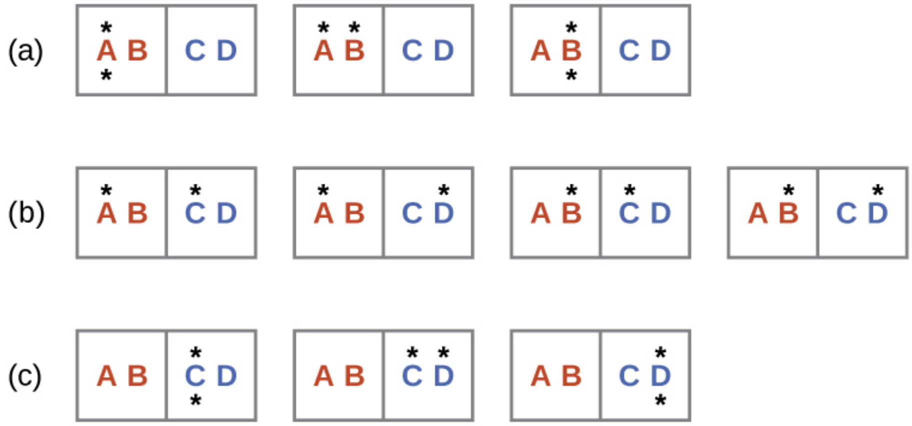


Figure 2. *This shows a microstate model describing the heat transfer of energy from a hot object to a cold object. (a) Before the heat transfer occurs, the* ***AB*** *object contains both units of energy and the distribution has three microstates. (b) If the heat transfer results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.*

Hence, we may describe this system by a total of ten microstates. The probability that there is no heat transfer of energy when the two objects are brought into contact (the system remains in distribution (a)) is 30%. It is much more likely for heat transfer to occur and yield either distribution (b) or (c), the combined probability being 70%. The most likely result, with 40% probability, is heat transfer to yield the uniform dispersal of energy represented by distribution (b).

This simple example supports the common observation that placing hot and cold objects in contact results in heat transfer that ultimately equalizes the objects' temperatures. Such a process is characterized by an increase in system entropy.

D28.2 Predicting the Sign of Δ*S*

The relationships between entropy, microstates, and matter/energy dispersal make it possible for us to assess relative entropies of substances and predict the sign of entropy changes for chemical and physical processes.

Consider the phase changes illustrated in Figure 3. In the solid phase, the molecules are restricted to nearly fixed positions relative to each other and only oscillate a little about these positions; the number of microstates (W_{solid}) is relatively small. In the liquid phase, the molecules can move over and around each other, though they remain in relatively close proximity. This increased freedom of motion results in a greater variation in possible particle locations, $W_{liquid} > W_{solid}$. As a result, $S_{\text{liquid}} > S_{\text{solid}}$ and the process of melting is characterized by an increase in entropy, $\Delta S > 0$.

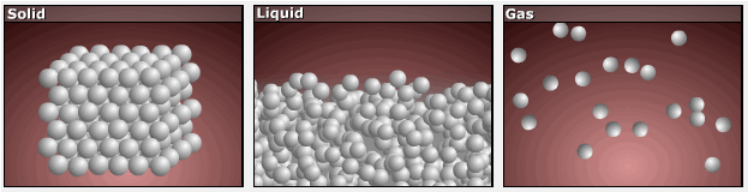


Figure 3. *The entropy of a substance increases (ΔS > 0) as it transforms from solid, to liquid, and then to gas. (Source: quantum casino)*

Solids and liquids have surfaces that define their volume, but in the gas phase the molecules occupy the entire container; therefore, for the same sample, each molecule in a gas can be found in many more locations (and there are many more microstates) than in the liquid or solid phase. Consequently, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$, and the processes of vaporization and sublimation involve increases in entropy, $\Delta S > 0$.

We have already discussed that the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature results in more extensive vibrations of the particles in solids and more rapid movements of the particles in liquids and gases. At higher temperatures, the Maxwell-Boltzmann distribution of molecular kinetic energies is also broader than at lower temperatures; that is, there is a greater range of energies of the particles. Thus, *the entropy for any substance increases with temperature* (Figure 4).

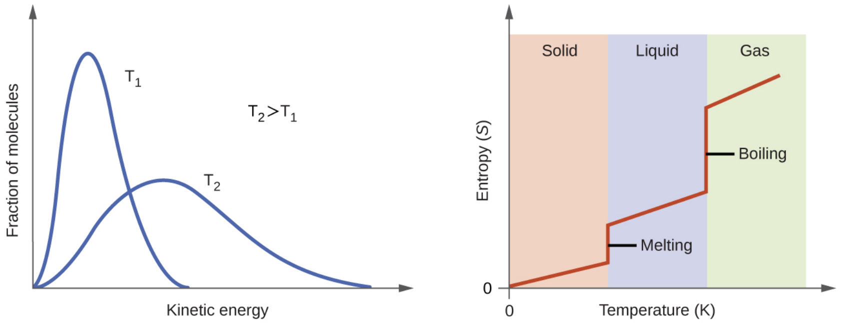


Figure 4. *Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.*

The entropy of a substance is also influenced by the structure of the particles that comprise the substance. For atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms. For heavier atoms the energy levels corresponding to movement from one place to another are closer together, which means that at a given temperature there are more occupied energy levels and more microstates. For molecules, greater number of atoms (regardless of their masses) within a molecule gives rise to more ways in which the molecule can vibrate, which increases the number of possible microstates. Thus, *the more atoms there are in a molecule the greater the entropy is.*

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of different particle types is greater due to the additional orientations and interactions that are possible. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. All other things being equal, the process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

D28.3 Second Law of Thermodynamics

The second law of thermodynamics enables predictions of whether a process, such as a chemical reaction, is spontaneous and whether the process is product-favored.

In thermodynamic models, the system and surroundings comprise everything (in other words, the universe), and so

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

To illustrate this relation, consider the process of heat transfer between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and energy transfers from the hotter object to the cooler object. *This is always observed to occur.* Designating the hotter object as the system and invoking the definition of entropy yields:

   $$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \qquad \text{and} \qquad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

   The arithmetic signs of q_{rev} denote the loss of energy by the system and the gain of energy by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, ΔS_{surr} is positive and its magnitude is greater than the magnitude of ΔS_{sys}. Thus, ΔS_{sys} and ΔS_{surr} sum to a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and energy transfers from the cooler object to the hotter object. *This is never observed to occur.* Again designating the hotter object as the system:

   $$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \qquad \text{and} \qquad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

   The magnitude of ΔS_{surr} is again greater than that for ΔS_{sys}, but in this case, the sign of ΔS_{surr} is negative, yielding a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.* (Note also that possibility 1, which is the reverse of this process, always occurs.)
3. The temperature difference between the objects is infinitesimally small, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the heat transfer is thermodynamically reversible. In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to the **second law of thermodynamics**: *all changes that take place of their own accord (are spontaneous) involve an increase in the entropy of the universe.*

$\Delta S_{\text{univ}} > 0$	spontaneous (takes place of its own accord)
$\Delta S_{\text{univ}} < 0$	not spontaneous (reverse reaction would occur)
$\Delta S_{\text{univ}} = 0$	system is at equilibrium

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat transfer of energy to or from the surroundings as a result of some process is a nearly infinitesimal fraction of its total thermal energy. For example, combustion of a hydrocarbon fuel in air involves heat transfer from a system (the fuel and oxygen molecules reacting to form carbon dioxide and water) to surroundings that are significantly more massive (Earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + q_{\text{surr}}/T$$

We can use this equation to predict whether a process is spontaneous.

Activity 2: Enthalpy, Entropy, and Spontaneous Reactions

D28.4 Third Law of Thermodynamics

Consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical molecule comprising the crystal ($W = 1$). According to the Boltzmann equation, the entropy of this system is zero:

$$S = k_B \cdot \ln(W) = k_B \cdot \ln(1) = 0$$

This limiting condition for a system's entropy represents the **third law of thermodynamics**: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Starting with zero entropy at absolute zero, it is possible to make careful calorimetric measurements (q_{rev}/T) to determine the temperature dependence of a substance's entropy and to derive absolute entropy values at higher temperatures. (Note that, unlike enthalpy values, the third law of thermodynamics identifies a zero point for entropy; thus, there is no need for formation enthalpies and every substance, including elements in their most stable states, has an absolute entropy.) **Standard entropy ($S°$)** values are *the absolute entropies per mole of substance at a pressure of 1 bar or a concentration of 1 M.* The **standard entropy change ($\Delta_r S°$)** for any chemical process may be computed from the standard entropy of its reactant and product species:

$$\Delta_r S° = \sum S°(\text{products}) - \sum S°(\text{reactants})$$

The thermodynamics table in the appendix lists standard entropies of select compounds at 298.15 K.

Suppose an exothermic chemical reaction takes place at constant atmospheric pressure. There is a heat transfer of energy from the reaction system to the surroundings, $q_{surr} = -q_{sys}$. The heat transfer for the system is the enthalpy change of the reaction because, at constant pressure, $\Delta_r H° = q$ (Section D27.3). Because the energy transfer to the surroundings is reversible, the entropy change for the surroundings can also be expressed as:

$$\Delta S_{surr} = \frac{q_{rev}}{T} = \frac{q_{surr}}{T} = \frac{-q_{sys}}{T} = \frac{-\Delta H_{sys}}{T} = \frac{-\Delta_r H°}{T}$$

The same reasoning applies to an endothermic reaction: q_{sys} and q_{surr} are equal but have opposite sign.

Also, for a chemical reaction system, $\Delta S_{sys} = \Delta_r S°$ (the standard entropy change for the reaction). Hence, ΔS_{univ} can be expressed as:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta_r S° - \Delta_r H°/T$$

The convenience of this equation is that, for a given reaction, ΔS_{univ} can be calculated from thermodynamics data for the system only. That is, from data found in the Appendix.

D28.5 Gibbs Free Energy

A new thermodynamic property was introduced in the late 19th century by American mathematician Josiah Willard Gibbs. The property is called the **Gibbs free energy (G)** (or simply the *free energy*), and is defined in terms of a system's enthalpy, entropy, and temperature:

$$G_{sys} = H_{sys} - TS_{sys}$$

The **change in Gibbs free energy (ΔG)** at constant temperature may be expressed as:

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

ΔG is related to whether a process is spontaneous. This relationship can be seen by comparing to the second law of thermodynamics:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{univ} = \Delta S_{sys} - \Delta H_{sys}/T$$

Multiplying both sides of this equation by $-T$, and rearranging, yields:

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

Which can be compared to the equation:

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Hence:

$$\Delta G_{\text{sys}} = -T\Delta S_{\text{univ}}$$

For a process that is spontaneous, ΔS_{univ} must be positive. Because thermodynamic temperature is always positive (values are in kelvins), ΔG must be negative for a process that proceeds forward of its own accord.

$\Delta S_{\text{univ}} > 0$	$\Delta G_{sys} < 0$	spontaneous (takes place of its own accord)
$\Delta S_{\text{univ}} < 0$	$\Delta G_{sys} > 0$	not spontaneous (reverse reaction would occur)
$\Delta S_{\text{univ}} = 0$	$\Delta G_{sys} = 0$	at equilibrium

D28.6 Calculating ΔG°

A convenient and common approach to calculate $\Delta_r G°$ for reactions is by using standard state thermodynamic data. One method involves determining the $\Delta_r H°$ and $\Delta_r S°$ first, then using the equation:

$$\Delta_r G° = \Delta_r H° - T\Delta_r S°$$

It is also possible to use the **standard Gibbs free energy of formation** ($\Delta_f G°$) of the reactants and products involved in the reaction to calculate $\Delta_r G°$. $\Delta_f G°$ is the *Gibbs free energy change that accompanies the formation of one mole of a substance from its elements in their standard states*. It is by definition zero for the most stable form of an elemental substance under standard state conditions.

For a generic reaction:

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D}$$

$\Delta_r G°$ from $\Delta_f G°$ would be:

$$\Delta_r G° = \sum \Delta_f G°(\text{products}) - \sum \Delta_f G°(\text{reactants}) = [x\Delta_f G°(\text{C}) + y\Delta_f G°(\text{D})] - [m\Delta_f G°(\text{A}) + n\Delta_f G°(\text{B})]$$

Podia Question

Use data from the Appendix to calculate $\Delta_r S°$ for this reaction at 298 K:

$$2\ \text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\ \text{NO}_2\text{(g)}$$

colorless gas colorless gas → red-brown gas

Predict whether the reaction is product-favored (spontaneous under standard-state conditions) or reactant-favored (not spontaneous under standard-state conditions).

After making your prediction, watch this video where NO(g) is added to O_2(g) in a flask:

https://mediaspace.wisc.edu/id/1_5g4s60ey

Does the video validate your prediction? Explain why or why not.

If the video does not validate your prediction, try to figure out why your prediction did not work and re-do it in a different way.

If the video does validate your prediction, explain what thermodynamic aspect of the reaction accounts for the observations in the video.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

4.3: Day 29- Gibbs Free Energy, Chemical Equilibrium

26

Day 29: Gibbs Free Energy, Chemical Equilibrium

D29.1 Temperature Dependence of Gibbs Free Energy

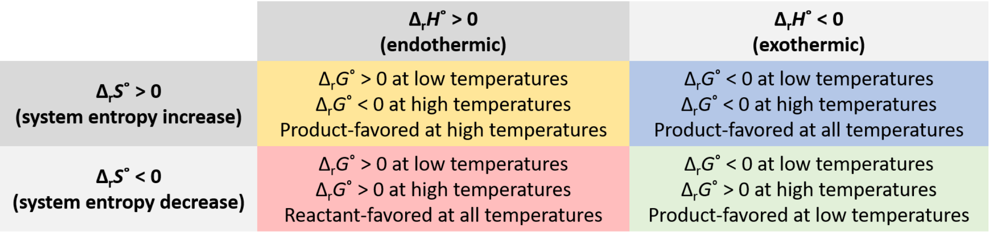
Whether a reaction is product-favored, that is, whether the reactants are converted to products under standard-state conditions, is reflected in the arithmetic sign of its $\Delta_r G°$. This equation

$$\Delta_r G° = \Delta_r H° - T\Delta_r S°$$

shows that the sign of $\Delta_r G°$ depends on the signs of $\Delta_r H°$ and $\Delta_r S°$, and, in some cases, the absolute temperature (which can only have positive values). Four possibilities exist:

1. **Both $\Delta_r H°$ and $\Delta_r S°$ are positive**—an endothermic process with an increase in system entropy. $\Delta_r G°$ is negative if $T\Delta_r S° > \Delta_r H°$, and positive if $T\Delta_r S° < \Delta_r H°$. Such a process is *product-favored at high temperatures and reactant-favored at low temperatures.*
2. **Both $\Delta_r H°$ and $\Delta_r S°$ are negative**—an exothermic process with a decrease in system entropy. $\Delta_r G°$ is negative if $|T\Delta_r S°| < |\Delta_r H°|$ and positive if $|T\Delta_r S°| > |\Delta_r H°|$. Such a process is *product-favored at low temperatures and reactant-favored at high temperatures.* (Remember that $|T\Delta_r S°|$ represents the magnitude of $T\Delta_r S°$, ignoring mathematical sign.)
3. **$\Delta_r H°$ is positive and $\Delta_r S°$ is negative**—an endothermic process that with a decrease in system entropy. $\Delta_r G°$ is positive regardless of the temperature. Such a process is *reactant-favored at all temperatures.*
4. **$\Delta_r H°$ is negative and $\Delta_r S°$ is positive**—an exothermic process with an increase in system entropy. $\Delta_r G°$ is negative regardless of the temperature. Such a process is *product-favored at all temperatures.*

These four scenarios are summarized in Figure 1.



	$\Delta_r H° > 0$ (endothermic)	**$\Delta_r H° < 0$ (exothermic)**
$\Delta_r S° > 0$ (system entropy increase)	$\Delta_r G° > 0$ at low temperatures $\Delta_r G° < 0$ at high temperatures Product-favored at high temperatures	$\Delta_r G° < 0$ at low temperatures $\Delta_r G° < 0$ at high temperatures Product-favored at all temperatures
$\Delta_r S° < 0$ (system entropy decrease)	$\Delta_r G° > 0$ at low temperatures $\Delta_r G° > 0$ at high temperatures Reactant-favored at all temperatures	$\Delta_r G° < 0$ at low temperatures $\Delta_r G° > 0$ at high temperatures Product-favored at low temperatures

Figure 1. *There are four possible combinations of signs of $\Delta_r H°$ and $\Delta_r S°$. For two combinations, whether a process is reactant-favored or product-favored depends on temperature.*

Activity 1: Temperature and Product-favored or Reactant-favored Reactions

Figure 2 illustrates the four scenarios graphically, where $\Delta_r G°$ is plotted versus temperature:

$\Delta_r G°$	=	$-\Delta_r S°(T)$	+	$\Delta_r H°$
y	=	m(x)	+	b

Figure 2. *These plots show the variation in $\Delta_r G^o$ with temperature for the four possible combinations of arithmetic sign for $\Delta_r G^o$. Click on each "+" for more information.*

For most reactions, neither $\Delta_r H°$ nor $\Delta_r S°$ change significantly as temperature changes. Thus, in Figure 2, the lines representing $\Delta_r G°$ are linear because the slope of each line ($-\Delta_r S°$) is the same at all temperatures. The orange and green plots (representing examples of scenario 1 and 2, respectively) cross from product-favored to reactant-favored (as reflected by the sign of $\Delta_r G°$) at a temperature that is characteristic of the specific process. This temperature is represented by the *x*-intercept, the value of *T* for which $\Delta_r G°$ is zero:

$$\Delta_r G° = 0 = \Delta_r H° - T\Delta_r S°$$

$$T_{\Delta_r G°=0} = \frac{\Delta_r H°}{\Delta_r S°}$$

Hence, saying a process is product-favored at “high” or “low” temperatures is simply indicating whether the temperature is above or below $T_{\Delta_r G^\circ=0}$. These relative terms are reaction-specific, that is, what is a “high” temperature for one reaction may very well be a “low” temperature for another reaction.

D29.2 Chemical Equilibrium

A chemical reaction is usually written with a single arrow, which suggests it proceeds in one direction, the direction of the arrow. But all chemical reactions are reversible, and both the forward and reverse reaction occur simultaneously. When reactions involve gases or solutions, where concentrations change as the reaction proceeds, the reaction eventually reaches a *dynamic* chemical equilibrium.

In a **chemical equilibrium**, *the forward and reverse reactions occur at the same rates, and the concentrations of products and reactants remain constant over time*. This implies that, if a reaction occurs in a closed system so that the products cannot escape, the reaction often does not yield 100% 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.

For example, when we place a sample of dinitrogen tetraoxide (N_2O_4, a colorless gas) in a glass vessel, the color becomes darker as N_2O_4 is converted to nitrogen dioxide (NO_2, a red-brown gas) by the reaction:

$$N_2O_4(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2NO_2(g)$$

Activity 2: Reaction Energy Diagram

At the beginning of this reaction, there is pure N_2O_4. As soon as the forward reaction produces some NO_2, at rate = $k_f[N_2O_4]_t$, the reverse reaction begins to occur at rate = $k_r[NO_2]_t^2$, and NO_2 starts to react to form N_2O_4. (The subscripts, *t*, indicate a time before equilibrium is reached.) As the reaction proceeds, the rate of the forward reaction decreases as $[N_2O_4]_t$ decreases and the rate of the reverse reaction increases as $[NO_2]_t$ increases. When the system reaches equilibrium, both N_2O_4 and NO_2 are present.

Figure 3. *A container of $N_2O_4(g)$ reacts toward equilibrium at 75°C. Colorless N_2O_4 converts to brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2. Once equilibrium has been reached, there is no further darkening of color.*

At equilibrium, $[N_2O_4]$ and $[NO_2]$ no longer change over time because the rate of NO_2 formation is exactly equal to the rate of NO_2 consumption, and the rate of N_2O_4 formation is exactly equal to the rate of N_2O_4 consumption. *Chemical equilibrium is a dynamic process*: the numbers of reactant and product molecules remain constant, but the forward and reverse reactions do not stop.

We use the ⇌ arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. When we wish to speak about one particular aspect of a reversible reaction, we use a single arrow. For example, when the reaction in Figure 3 is at equilibrium, the rate of the forward reaction:

$$N_2O_4(g) \rightarrow 2\ NO_2(g)$$

is equal to the rate of the reverse reaction:

$$2\ NO_2(g) \rightarrow N_2O_4(g)$$

An equilibrium can be established for a physical change as well as for a chemical reaction. For example:

$$Br_2(l) \rightleftharpoons Br_2(g)$$

Figure 4 shows a sample of liquid Br_2 at equilibrium with Br_2 vapor in a closed container. When we pour liquid Br_2 into an empty bottle in which there is no bromine vapor, some liquid evaporates: the amount of liquid decreases and the amount of vapor increases. If we seal the container so no vapor escapes, the amount of liquid and vapor will eventually stop changing; at that point an equilibrium between the liquid and the vapor has been established. If the container were not sealed, the bromine vapor would escape and no equilibrium would be reached.

Figure 4. *Sample of bromine in a sealed glass tube. Liquid bromine is in the bottom of the tube with gaseous bromine above it.*

D29.3 Concentration Equilibrium Constants

A concentration **equilibrium constant (K_c)** is *a ratio of equilibrium concentrations of products and reactants that is constant for a given reaction at a given temperature*. For example, consider this generic reversible reaction:

$$m\,\mathrm{A} + n\,\mathrm{B} \rightleftharpoons x\,\mathrm{C} + y\,\mathrm{D}$$

For this reaction, the concentration equilibrium constant, K_c, is:

$$K_c = \frac{[\mathrm{C}]_e{}^x\ [\mathrm{D}]_e{}^y}{[\mathrm{A}]_e{}^m\ [\mathrm{B}]_e{}^n}$$

This mathematical expression is called the equilibrium constant expression. The “[…]$_e$” expression indicates explicitly *equilibrium* concentration of a reactant or product.

As a reaction approaches equilibrium, concentrations of reactants and products need to change until the rates of forward and reverse reactions are equal. Therefore, only substances whose concentrations can change as a reaction occurs are included in an equilibrium constant expression. For example, consider the following reaction at equilibrium:

$$2\ \mathrm{HgO}(s) \rightleftharpoons 2\ \mathrm{Hg}(l) + \mathrm{O_2}(g)\ K_c = [\mathrm{O_2}]_e$$

Because HgO is a pure solid, the number of HgO formula units in a given volume of HgO is the same throughout the reaction; it depends only on the density of HgO at the temperature of the reaction. Similarly, the number of Hg atoms per unit volume of pure Hg(*l*) is constant throughout the reaction. Thus, these concentrations are not included in the K_c expression. It is necessary for *some* HgO(s) and *some* Hg(*l*) to be present for the equilibrium to be maintained, but the quantity of each does not matter.

In general, K_c expressions do not contain terms for pure solids or pure liquids. In addition, for dilute solutions, the concentration of solvent remains constant throughout an equilibrium reaction and is also not included in the K_c expression, even though the solvent may appear in the reaction equation.

A **homogeneous equilibrium** is one in which *all of the reactants and products are present in a single phase*. Examples of homogeneous equilibria are reactions in the gas phase and reactions in liquid solutions. For example:

$$\mathrm{C_2H_2}(g) + 2\ \mathrm{Br_2}(g) \rightleftharpoons \mathrm{C_2H_2Br_4}(g)$$

$$K_c = \frac{[\mathrm{C_2H_2Br_4}]_e}{[\mathrm{C_2H_2}]_e[\mathrm{Br_2}]_e{}^2}$$

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq)$$

$$K_c = \frac{[\mathrm{I_3^-}]_e}{[\mathrm{I_2}]_e[\mathrm{I^-}]_e}$$

$$\mathrm{Hg_2{}^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\ \mathrm{H_3O^+}(aq) \rightleftharpoons 2\ \mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + 4\mathrm{H_2O}(l)$$

$$K_c = \frac{[\mathrm{Hg^{2+}}]_e{}^2[\mathrm{HNO_2}]_e}{[\mathrm{Hg_2^{2+}}]_e[\mathrm{NO_3^-}]_e[\mathrm{H_3O^+}]_e{}^3}$$

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq)$$

$$K_c = \frac{[H_3O^+]_e[F^-]_e}{[HF]_e}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_c = \frac{[NH_4^+]_e[OH^-]_e}{[NH_3]_e}$$

In the aqueous equilibrium systems, $H_2O(l)$ is the solvent. Its concentration does not appear in the K_c expression.

A **heterogeneous equilibrium** is a system in which *reactants and products are found in two or more phases*. Some heterogeneous equilibria involve chemical changes, for example:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)\ K_c = [Pb^{2+}]_e[Cl^-]_e^2$$

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

$$K_c = \frac{1}{[CO_2]_e}$$

$$C(s) + 2S(g) \rightleftharpoons CS_2(g)$$

$$K_c = \frac{[CS_2]_e}{[S]_e^2}$$

Other heterogeneous equilibria involve phase changes, for example:

$$Br_2(l) \rightleftharpoons Br_2(g)\ K_c = [Br_2(g)]_e$$

Working with K_c

When all the coefficients in a balanced chemical equation are multiplied by some factor *n*, then the new K_c is the original K_c raised to the nth power. For example:

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

$$K_{c,1} = \frac{[N_2O_4]_e}{[NO_2]_e^2}$$

$$NO_2(g) \rightleftharpoons \tfrac{1}{2}\ N_2O_4(g)$$

$$K_{c,2} = \frac{[N_2O_4]_e^{1/2}}{[NO_2]_e} = (K_{c,1})^{1/2}$$

When a reaction's direction is reversed, the K_c for the new reaction is the reciprocal (inverse) of the original reaction K_c. For example:

$$A + 2B \rightleftharpoons AB_2$$

$$K_{c,1} = \frac{[AB_2]_e}{[A]_e[B]_e^2}$$

$$AB_2 \rightleftharpoons A + 2B$$

$$K_{c,2} = \frac{[A]_e[B]_e^2}{[AB_2]_e} = \frac{1}{K_{c,1}}$$

When two reactions occur sequentially to yield a new overall reaction, the K_c for the overall reaction is the product of the K_c values for the individual steps. For example:

$$A + C \rightleftharpoons AC$$

$$K_{c,1} = \frac{[AC]_e}{[A]_e[C]_e}$$

$$\mathrm{AC} + \mathrm{C} \rightleftharpoons \mathrm{AC_2}$$

$$K_{c,2} = \frac{[\mathrm{AC_2}]_e}{[\mathrm{AC}]_e[\mathrm{C}]_e}$$

$$\mathrm{A} + 2\mathrm{C} \rightleftharpoons \mathrm{AC_2}$$

$$K_{c,3} = \frac{[\mathrm{AC_2}]_e}{[\mathrm{A}]_e[\mathrm{C}]_e{}^2} = K_{c,1} \times K_{c,2}$$

D29.4 Equilibrium Constant and Partial Pressure

Reactions in which all reactants and products are in the gas phase are another class of homogeneous equilibria. In these cases, the partial pressure of each gas can be used instead of its concentration in the equilibrium constant equation. At constant temperature, the partial pressure of a gas is directly proportional to its molar concentration (c), which is the amount of a substance (moles) per unit volume (liters): $c = n/V$. This proportionality of pressure and concentration can be derived from the ideal gas equation:

$$\begin{aligned} PV &= nRT \\ P &= \left(\frac{n}{V}\right) RT \\ P &= cRT \end{aligned}$$

For an example, consider the following reaction:

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g)$$

We can write the equilibrium constant, K_p, using the equilibrium partial pressures of the gases, by following the same guidelines as for K_c expressions:

$$K_\mathrm{p} = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}}$$

The two equilibrium constants, K_c and K_p, are directly related to each other. For the generic gas-phase reaction:

$$m\,\mathrm{A} + n\,\mathrm{B} \rightleftharpoons x\,\mathrm{C} + y\,\mathrm{D}$$

$$\begin{aligned} K_\mathrm{p} &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \\ &= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} \\ &= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \\ &= K_\mathrm{c}(RT)^{(x+y)\,-\,(m+n)} \\ K_\mathrm{p} &= K_\mathrm{c}(RT)^{\Delta n} \end{aligned}$$

where 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 (that is, the change in amount of gas between the reactants and the products).

Note that the gas constant, R, can be expressed in different units. Use the R value and associated units that match the partial pressure units used in the K_p expression.

For heterogeneous equilibria that involve gases, equilibrium constants can also be expressed using partial pressures instead of concentrations. Two examples are:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s)$$

$$K_p = \frac{1}{P_{CO_2}}$$

$$C(s) + 2\ S(g) \rightleftharpoons CS_2(g)$$

$$K_p = \frac{P_{CS_2}}{(P_S)^2}$$

D29.5 Calculations Involving Equilibrium Constants

One way to determine the value for an equilibrium constant is to measure the concentrations (or partial pressures) of all reactants and all products at equilibrium.

Exercise 5: Calculating an Equilibrium Constant

Calculate the equilibrium constant K_c for the decomposition of PCl_5 at 250 °C.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At equilibrium, $[PCl_5]_e = 4.2 \times 10^{-5}$ M, $[PCl_3]_e = 1.3 \times 10^{-2}$ M, $[Cl_2]_e = 3.9 \times 10^{-3}$ M

A known equilibrium constant can be used to calculate an unknown equilibrium concentration, provided the equilibrium concentrations of all other reactants and products are known.

D29.6 Equilibrium Constants and Product-favored Reactions

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A very large value for K_c ($K_c >> 1$) indicates that product concentrations are much larger than reactant concentrations when equilibrium has been achieved: nearly all reactants have been converted into products. If K_c is large enough, the reaction has gone essentially to completion when it reaches equilibrium.

Earlier we defined a product-favored reaction as one that proceeds spontaneously in the forward direction when all concentrations (or partial pressures) have the standard-state value of 1 M. If $K_c > 1$,so that the concentrations of products are greater than the concentrations of reactants, then when all concentrations are 1 M the reaction needs to produce greater concentrations of products to reach equilibrium. That is, the reaction needs to proceed in the forward direction. Thus, **$K_c > 1$ (or $K_p > 1$) means that a reaction is product-favored**.

A very small value of K_c, ($K_c << 1$) indicates that equilibrium is achieved when only a small fraction of the reactants has been converted into products. Such a reaction is reactant-favored. If K_c is small enough, essentially no reaction has occurred when equilibrium is reached. When $K_c \approx 1$, both reactant and product concentrations are significant and it is necessary to use the equilibrium constant to calculate equilibrium concentrations.

By an argument similar to the one in the next to last paragraph above, **$K_c < 1$ (or $K_p < 1$) means that a reaction is reactant-favored**.

Podia Question

One way to remove silver oxide tarnish from silver is to heat the silver to a high temperature.

https://mediaspace.wisc.edu/id/0_p9myzb11

The reaction is:

$$2\ Ag_2O \rightarrow 4\ Ag(s) + O_2(g)$$

At 298 K, the reaction is reactant-favored. Obtain data from the Appendix and determine at what temperature the reaction becomes product-favored. What assumptions need to be made to solve this problem?

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

4.4: Day 30- ICE Table, Reaction Quotient, Le Châtelier’s Principle

27

Day 30: ICE Table, Reaction Quotient, Le Chatelier’s Principle

D30.1 ICE Table

An **ICE table** (for ***I****nitial concentration,* ***C****hange in concentration, and* ***E****quilibrium concentration*) is a good methodology for calculating an equilibrium constant from experimental data. ICE tables also help to solve many other types of equilibrium problems.

An ICE table begins with the balanced reaction equation, using the reactants and products as column headings. The second row lists the initial concentrations of the reactants and products; these can usually be obtained from experimental data based on the assumption that no reaction has yet taken place. The third row is the change in concentration that occurs as the system proceeds toward equilibrium; this row is derived from the stoichiometry of the reaction. The last row is the sum of the first two rows, which yields the equilibrium concentrations.

For example, consider determining the equilibrium constant for the reaction:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

If a solution initially has $[I_2]_0 = [I^-]_0 = 1.000 \times 10^{-3}$ M and no triiodide ions ([I3−] = 0), and then reacts to give an equilibrium concentration of $[I_2]_e = 6.61 \times 10^{-4}\ M$, we can use an ICE table to determine the equilibrium constant for the reaction. First, write the balanced reaction at the top of the table. The next row gives the initial concentrations.

	$I_2(aq)$	+	$I^-(aq)$	$\leftrightharpoons$	$I_3^-(aq)$
Initial concentration (*M*)	1.000×10^{-3}		1.000×10^{-3}		0
Change in concentration (*M*)	$-x$		$-x$		$+x$
Equilibrium concentration (*M*)	$(1.000 \times 10^{-3}) - x$		$(1.000 \times 10^{-3}) - x$		x

In the “Change” row, the mathematical sign indicates the direction of change: the sign is positive when the concentration increases as the reaction proceeds toward equilibrium, and negative when the concentration decreases. For example, because the reaction starts with no I_3^-, $[I_2]_t$ must decrease as the reaction proceeds, so its (unknown) change in concentration is “-*x*“. In general, *x* is also multiplied by the stoichiometric coefficient, but in this case, all coefficients are 1, so that is not obvious.

Using the information that $[I_2]_e = 6.61 \times 10^{-4}\ M$, we can solve for *x*:

$(1.000 \times 10^{-3}) - x$	=	$6.61 \times 10^{-4}\ M$
x	=	$3.39 \times 10^{-4}\ M$

and then calculate the equilibrium constant K_c:

$$\begin{aligned} K_c &= \frac{[\mathrm{I_3^-}]_e}{[\mathrm{I_2}]_e[\mathrm{I^-}]_e} \\ &= \frac{x}{\{(1.00 \times 10^{-3}) - x\}\{(1.00 \times 10^{-3}) - x\}} \\ &= \frac{3.39\ \times\ 10^{-4}\ M}{(6.61\ \times\ 10^{-4}\ M)(6.61\ \times\ 10^{-4}\ M)} \\ &= 776\ \mathrm{M}^{-1} \text{ reported without units as } 776 \end{aligned}$$

Activity 1: Calculating Equilibrium Concentrations I

Activity 2: Calculating Equilibrium Concentrations II

D30.2 “All-Reactant” or “All-Product” Starting Point

The same equilibrium concentrations are achieved whether a reaction begins with only reactants present or only products present. Let’s use an example to consider this in further detail. HF is a deadly, but weak, acid. It ionizes partially in water :

$$\text{HF}(aq) \rightleftharpoons \text{H}^{+}(aq) + \text{F}^{-}(aq)\ K_c = 6.80 \times 10^{-4}$$

What are the equilibrium concentrations of the various aqueous species in a solution of 0.150-M HF?

One way to determine these equilibrium concentrations is to start with only reactants. This is called the “all-reactant” starting point.

Activity 3: All-reactant Starting Point

Alternatively, we could solve the problem assuming that all the HF ionizes first, and then the system comes to equilibrium. This is called the “all-product” starting point.

Activity 4: All-product Starting Point

The two approaches give the same results, and show that starting with all products leads to the same equilibrium conditions as starting with all reactants. Note that this is true only if the temperature is the same and the same total number of atoms of each kind is present in both cases. Here we either started with all reactants, 0.150-M HF (which contains 0.150 mol/L H and 0.150 mol/L F), or with all products, 0.150–M H^+ and 0.150-M F^- (which also contains 0.150 mol/L H and 0.150 mol/L F). Had we started with 0.140-M H^+ and 0.160-M F^-, the equilibrium concentrations would not be the same.

For the ionization of HF(aq) the equilibrium constant is small: $K_c = 6.80 \times 10^{-4}$. That is, the ionization of HF(aq) is reactant-favored. In Activity 3 the change in concentration, $x_3 = 0.00977$, while in Activity 4 the change in concentration, $x_4 = 0.140$. Because the process is reactant-favored, the all-reactant initial concentrations are much closer to the equilibrium concentrations than the all-product initial concentrations. Therefore the all-reactants situation involves only small changes in concentrations to reach equilibrium. Recognizing this allows making approximations that can significantly simplify the calculations in equilibrium problems.

We know that when $K_c << 1$, the equilibrium is significantly reactant-favored, and when $K_c >> 1$, the equilibrium is significantly product-favored. If the ICE table can be set up so that the “initial” concentrations are close to equilibrium (either all-reactant or all-product, depending on the size of K_c), then any change in concentration that is small compared to the initial concentrations can be neglected. “Small” is defined as resulting in an error that does not change the answer within the the number of significant figures involved.

Activity 5: Solving an Aqueous Equilibrium Problem

D30.3 Reaction Quotient

Starting with only reactants present means that the reaction must initially be spontaneous left to right, even if only very small concentrations of products are present when equilibrium is reached. Starting with only products present requires that the reaction go from right to left. Which direction does a reaction go when both reactants and products are present but the reaction is not at equilibrium? The reaction quotient can answer this question.

For a generic reaction,

$$m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$$

the **reaction quotient (*Q*)** is defined as:

$$Q_c = \frac{[\text{C}]_t{}^x [\text{D}]_t{}^y}{[\text{A}]_t{}^m [\text{B}]_t{}^n}$$

In Q_c the subscript “c” indicates Q is in terms of concentrations; for a gas-phase reaction we could write Q_p similarly in terms of partial pressures.

The concentrations are represented by "[…]$_t$" to emphasize that Q_c for a reaction depends on the concentrations present *at the time when* Q_c *is determined*; this is usually not at equilibrium. When only reactants are present, $Q_c = 0$. As the reaction proceeds, Q_c increases because product concentrations increase and reactant concentrations decrease (Figure 1). When the reaction reaches equilibrium, Q_c no longer changes over time because the concentrations no longer change, and, at equilibrium, $Q_c = K_c$:

$$Q_c(\text{at equilibrium}) = \frac{[\mathrm{C}]_e{}^x[\mathrm{D}]_e{}^y}{[\mathrm{A}]_e{}^m[\mathrm{B}]_e{}^n} = K_c$$

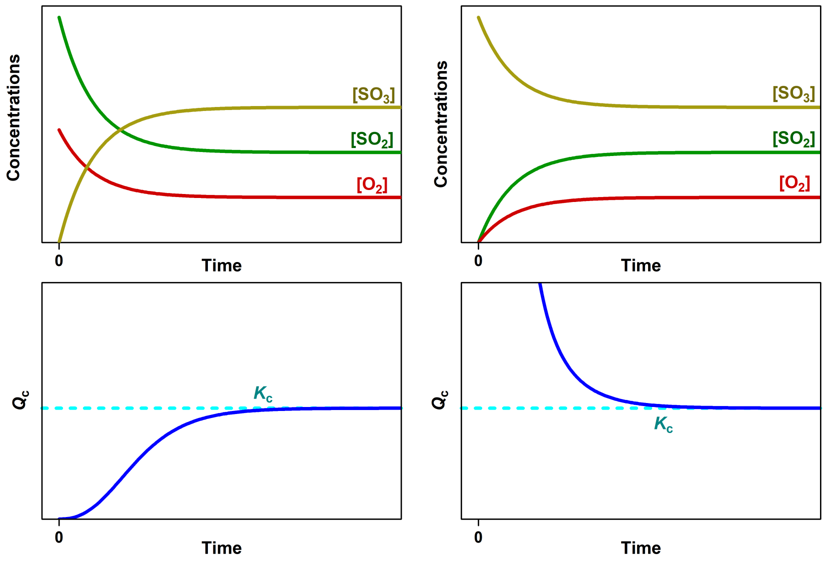


Figure 1. *(Left) The change in the concentrations of reactants and products is depicted as the 2* $SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$ *reaction approaches equilibrium. The graph below shows the change in* Q_c *as the reaction approaches equilibrium. (Right) The change in concentrations of reactants and products is depicted as the reverse reaction 2* $SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$ *approaches equilibrium. The graph below shows the change in* Q_c *as the reaction approaches equilibrium.*

A system that is not at equilibrium proceeds spontaneously in the direction that establishes equilibrium (Q_c changes until it equals K_c). Hence, we can predict directional shifts of a reaction by comparing Q_c to K_c: **when $Q_c < K_c$, the reaction proceeds spontaneously from left to right (to the product side); when $Q_c > K_c$, the reaction proceeds spontaneously to the left (reactant side).**

For example, for the water-gas shift reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)\ K_c = 0.64\ T = 800\ °C$$

different starting mixtures of CO, H_2O, CO_2, and H_2 react (and the concentrations of reactants and products change) until the compositions reach the same value of Q_c; that is, until $Q_c = K_c$ (Figure 2).

Figure 2. *Concentrations of four different mixtures are shown before and after reaching equilibrium at 800 °C for the water gas shift reaction:* $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$.

It is important to recognize that Q_c reaches the same equilibrium value (K_c) whether the reaction starts from all reactants, from all products, or from a mixture of both. In fact, one technique to determine whether a reaction is truly at equilibrium is to start with only reactants in one experiment and start with only products in another. If the same value of the reaction quotient is observed when the concentrations have stopped changing in both experiments, then it is highly likely that the system has reached equilibrium.

D30.4 **Le Chatelier's principle:** Change in Concentration

Le Chatelier's principle states that *when a chemical system is at equilibrium and conditions are changed so that the reaction quotient, Q, changes, the chemical system will react to achieve new equilibrium concentrations or partial pressures; reaction occurs in a way that partially counteracts the change in conditions.* To establish the new equilibrium, the reaction proceeds in the forward direction if $Q < K$ or in the reverse direction if $Q > K$, until Q is again equal to K.

For a chemical system at equilibrium at constant temperature, if the concentration of a reactant or a product is changed, therefore changing Q, the system is no longer at equilibrium because $Q \neq K$. The concentrations of all reaction species will then undergo additional changes until the system reaches a new equilibrium with a different set of equilibrium concentrations. We say that the equilibrium shifts in a direction (forward or reverse) that partially counteracts the change.

For example, consider the chemical reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_c = 50.0 \text{ at } 400\ °C$$

A mixture of gases at 400 °C with $[H_2]_{e1} = 0.221\ M$, $[I_2]_{e1} = 0.290\ M$, and $[HI]_{e1} = 1.790\ M$ is at equilibrium in a closed container. For this mixture, $Q_c = K_c = 50.0$. If additional H_2 is introduced into the container quickly such that $[H_2]$ doubles before it begins to react (that is, the new $[H_2]_t = 0.442\ M$), Q_c is now ½ of K_c:

$$Q_c = \frac{[\mathrm{HI}]_t{}^2}{[\mathrm{H}_2]_t[\mathrm{I}_2]_t} = \frac{(1.790M)^2}{(0.442M)(0.290M)} = 25.0 = \frac{1}{2}K_c$$

The reaction then proceeds in the forward direction to reach a new equilibrium. Experimental measurements show that at the new equilibrium $[H_2]_{e2} = 0.362\ M$, $[I_2]_{e2} = 0.210\ M$, and $[HI]_{e2} = 1.950\ M$. Notice that $[H_2]_{e2}$ (0.362 M) is less than the doubled concentration (0.442 M) but more than $[H_2]_{e1}$ (0.221 M). The equilibrium has shifted to *partially counteract* the change in H_2 concentration. Because of the shift, the concentration of the other reactant decreases and the concentration of the product increases. To verify that these new concentrations are equilibrium concentrations, calculate Q:

$$Q_c = \frac{(1.950M)^2}{(0.362M)(0.210M)} = 50.0 = K_c$$

Another way to think about the shift in equilibrium is to recall that at equilibrium, $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$. The forward reaction is first-order in H_2, so doubling the concentration of H_2 doubles $\text{rate}_{\text{forward}}$, making $\text{rate}_{\text{forward}} > \text{rate}_{\text{reverse}}$. As the equilibrium shifts, the concentrations of both reactants decrease and the concentration of product increases until new equilibrium concentrations are reached, where forward and reverse reactions have reached new, but equal, rates.

Figure 3 illustrates graphically the effect of adding H_2 to the reaction at equilibrium.

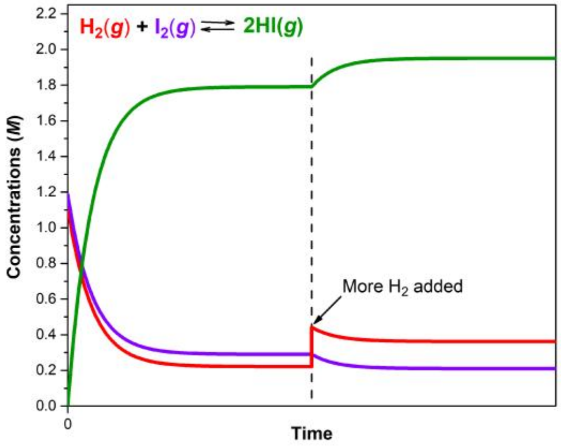


Figure 3. *A mixture of $H_2(g)$ and $I_2(g)$ reacts to reach the equilibrium of $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. Then $H_2(g)$ is added (at dashed vertical line). The reaction proceeds toward the products until a new equilibrium is achieved.*

D30.5 **Le Chatelier's Principle:** Change in Pressure or Volume

Changes in pressure have a measurable effect on equilibrium in systems involving gases if the chemical reaction produces a change in the total number of gas molecules (that is, if the number of gas molecules on the reactant side differs from the product side). The overall change in pressure must affect partial pressures of reactants and/or products: adding an inert gas that is not a reactant or product changes the total pressure but not the partial pressures of the gases in the equilibrium constant expression, and therefore does not perturb the equilibrium.

Consider what happens when the volume decreases for this equilibrium:

$$2\ NO(g) + O_2(g) \rightleftharpoons 2\ NO_2(g)$$

Decreasing the volume increases the total pressure and increases the partial pressure of each gas. The equilibrium shifts to partially counteract the increase in pressure. Formation of additional NO_2 decreases the total number of gaseous molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 react away. This reduces the total pressure exerted by the system and partially counteracts increased pressure. LeChatelier's principle predicts that the equilibrium shifts to the right, toward products.

We can also look at this by considering Q_c. Reducing the system volume increases the partial pressure (or concentration) of all gaseous species. If the volume is reduced by half, then each partial pressure becomes twice what it was for the previous equilibrium:

$$Q_c = \frac{[\mathrm{NO_2}]_t{}^2}{[\mathrm{NO}]_t{}^2[\mathrm{O_2}]_t} = \frac{(2[\mathrm{NO_2}]_{e1})^2}{(2[\mathrm{NO}]_{e1})^2)(2[\mathrm{O_2}]_{e1})} = \frac{1}{2}K_c$$

Because $Q_c < K_c$, the reaction proceeds toward the product side (forming additional NO_2) to re-establish equilibrium.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$$

Because there is no change in the total number of gaseous molecules in the system during reaction, a change in pressure does not shift the equilibrium towards either reactant or product side.

For reactions in solution, changing the solution volume changes the concentrations of all reaction species. Therefore, when solvent is added (the solution is diluted), the equilibrium shifts toward the side with more solute particles, partially compensating for the dilution of total concentration. If solvent is removed (by evaporation, for example) so that all solute concentrations increase, the equilibrium shifts toward the side with fewer solute particles, decreasing the total concentration of solute particles.

For example, when enough water is added to this equilibrium to double the solution volume:

$$C_2H_2(aq) + 2\ Br_2(aq) \rightleftharpoons C_2H_2Br_4(aq)$$

the concentration of each solute is halved compared to the initial equilibrium concentration. Hence:

$$Q_c = \frac{\frac{1}{2}[\mathrm{C_2H_2Br_4}]_{e1}}{\left(\frac{1}{2}[\mathrm{C_2H_2}]_{e1}\right)\left(\frac{1}{2}[\mathrm{Br_2}]_{e1}\right)^2} = 4K_c$$

Because $Q_c > K_c$ the reaction proceeds toward the reactant side (the side with more solute particles) as equilibrium is re-established.

Podia Question

This question explores Le Chatelier's principle applied to the equilibrium between hydrogen, nitrogen, and ammonia:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)\ K_p = 5.8 \times 10^6\ \text{atm}^{-2} \text{ at } 25\ °C$$

a) Write the expression for K_p for this reaction.

b) Predict the effect on the equilibrium (at 25 °C) of an increase in each partial pressure:
i) P_{N2}
ii) P_{H2}

c) Suppose that 0.245 mol N_2, 0.00145 mol H_2, and 0.162 mol NH_3 occupy a 10.0-L volume; the partial pressures are P_{N2}= 0.600 atm, P_{H2}= 0.00356 atm, and P_{NH3}= 0.396 atm and the total pressure is 1.00 atm. Is the system at equilibrium? If not, in which direction would the reaction shift to reach equilibrium? Show a calculation to support your answer.

d) Suppose the total pressure is kept constant and that 0.010 mol N_2 is added to the system described in part c so that the total amount of N_2 is 0.255 mol and the total amount of all gases is 0.418 mol. If the total pressure stays constant, what must happen to the volume? Why?

e) Based on the ideal gas law it is possible to calculate the new volume of the mixture of gases and to calculate the partial pressures of the constituent gases. The partial pressures are P_{N2} = 0.610 atm, P_{H2} = 0.00347 atm, and P_{NH3} = 0.388 atm. Is the system at equilibrium? If not, in which direction does the reaction shift to reach equilibrium? Show a calculation to support your answer.

f) Does your answer in part (e) agree with your first answer in part b? Explain why or why not.

g) Have you discovered an exception to Le Chatelier’s principle? Explain why or why not.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day’s material. We appreciate your comments.

4.5: Day 31- Le Châtelier’s Principle, Equilibrium and Gibbs Free Energy

28

Day 31: Le Chatelier’s Principle, Equilibrium and Gibbs Free Energy

D31.1 Le Chatelier’s Principle: Change in Temperature

When a chemical reaction is at equilibrium and the temperature changes, the reaction’s equilibrium constant is different at the new temperature. Le Chatelier’s principle can be used to predict which direction an equilibrium shifts and hence whether increasing temperature increases or decreases K. Remember that, according to Le Chatelier’s principle, an equilibrium shifts in a direction that partially counteracts the change in conditions.

Consider the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)\ \Delta_r H° = 180.5\text{ kJ/mol at 25 °C}$$

As shown by the enthalpy change, this reaction is endothermic: when the reaction takes place in the forward direction, the temperature is lowered. Because enthalpy change does not vary significantly with temperature, the forward reaction is endothermic at all temperatures where all reactants and products are in the gas phase. The reverse reaction is always exothermic.

Suppose that the reaction is at equilibrium at a particular temperature and the temperature is suddenly increased. To partially compensate for the temperature increase, the reaction shifts toward products (the endothermic direction), which lowers the temperature a bit. Thus, when equilibrium is reached at the higher temperature, the concentration of NO is larger and the concentrations of N_2 and O_2 are lower. This results in a larger value for K_c at the higher temperature.

If the temperature of the reaction is suddenly lowered, the reaction shifts to partially raise the temperature—in the exothermic direction. In this case, the shift is from products to reactants. Thus, at a lower temperature the concentrations of reactants are larger, the concentrations of products are smaller, and the equilibrium constant is smaller.

Summarizing,

- An increase in temperature shifts an equilibrium in the endothermic direction (the direction with positive $\Delta_r H°$) because the endothermic reaction partially counteracts the increase in temperature
- A decrease in temperature shifts an equilibrium in the exothermic direction (the direction with negative $\Delta_r H°$) because the exothermic reaction partially counteracts the decrease in temperature.
- The different concentrations in the new equilibrium system (after the shift resulting from the temperature change) correspond to a different value for the equilibrium constant.
- The larger the magnitude of $\Delta_r H°$ is the larger the shift in the equilibrium is and the greater the change in the equilibrium constant is.

D31.2 Catalysts and Equilibrium

A catalyst speeds up the rate of a reaction, allowing the equilibrium to be reached more quickly (by speeding up both forward and reverse reactions). Hence, catalysts influence the kinetics of a reaction. However, a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

D31.3 Gibbs Free Energy and Equilibrium

The standard Gibbs free energy change for a reaction indicates whether a reaction is product-favored at equilibrium ($\Delta_r G° < 0$) or reactant-favored at equilibrium ($\Delta_r G° > 0$). A strongly product-favored reaction (large negative $\Delta_r G°$) has a large equilibrium constant ($K >> 1$) and a strongly reactant-favored reaction (large positive $\Delta_r G°$) has a very small equilibrium constant ($K << 1$, a very small fraction because K cannot be negative). These qualitative statements suggest that there may be a quantitative relationship between the equilibrium constant and $\Delta_r G°$ for a given reaction.

The reaction quotient, Q, was introduced as a convenient measure of the status of a reaction. When $Q < K$, the reaction proceeds spontaneously in the forward direction until equilibrium is reached ($Q = K$). Conversely, if $Q > K$, the reaction proceeds spontaneously in the reverse direction until equilibrium is achieved.

The relationship between $\Delta_r G°$, Q, and K is illustrated graphically in Figure 1 in graphs of G vs. reaction progress. In each graph, on the far left, the system is all reactants and $Q = 0$. On the far right, the system is all products and $Q = \infty$. The slope at any point on each graph is Δ_rG/Δ(reaction progress). Because Δ(reaction progress) is always positive, the sign of the slope is the sign of Δ_rG.

In the light cyan region where $Q < K$, the slope of the plot is negative, corresponding to negative Δ_rG, which predicts spontaneous forward reaction. In the light pink region where $Q > K$, the slope is positive, corresponding to positive Δ_rG which predicts spontaneous reverse reaction. Where the slope is zero (bottom of the curve), $\Delta_rG = 0$, and the system is at equilibrium *with* $Q = K$. Hence, we can think of reaction progress as rolling down the sides of a Gibbs free energy valley, with equilibrium at the bottom (minimum *G*).

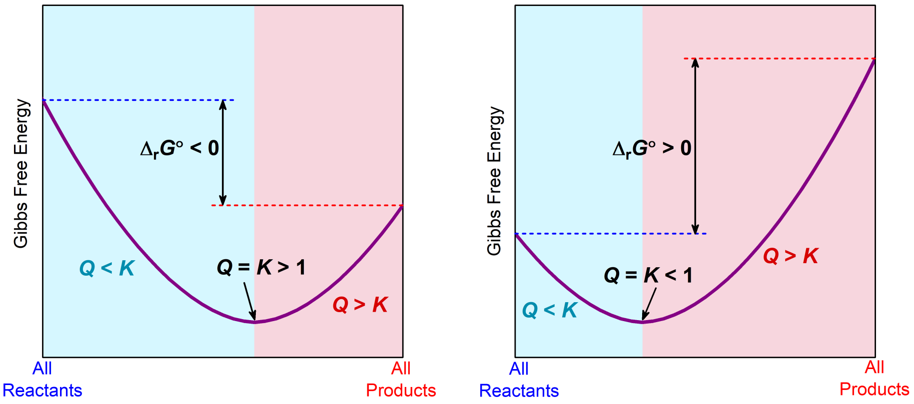


***Figure 1**. These plots show the Gibbs free energy (G) versus reaction progress for systems whose standard Gibbs free energy changes (ΔG°) are negative (left), and positive (right). One end of the x-axis represents all reactants, the other end all products. Non-equilibrium systems proceed spontaneously in whatever direction is necessary to minimize Gibbs free energy and establish equilibrium.*

Where equilibrium lies along the reaction progress depends on the sign of $\Delta_rG°$. When $\Delta_rG° < 0$, the equilibrium (minimum in the curve) is further to the right, indicating that there are more products than reactants when equilibrium is reached. When $\Delta_rG° > 0$, the equilibrium is further to the left, indicating that reactants predominate.

The Gibbs free energy change at any point along the reaction progress involves adjusting $\Delta_rG°$ by the factor RT(ln*Q*):

$$\Delta_rG = \Delta_rG° + RT(\ln Q)$$

At equilibrium, $Q = K$ and $\Delta_rG = 0$, therefore:

$$0 = \Delta_rG° + RT(\ln K°)$$

$$\Delta_rG° = -RT(\ln K°) \text{ or } K° = e^{-\Delta_rG°/RT}$$

Note that in these last equations the equilibrium constant is represented by *K*°. The **standard equilibrium constant**, ***K*°**, is *either the concentration equilibrium constant (K_c) with each concentration divided by the standard-state concentration of 1 M or the pressure equilibrium constant (K_p) with each pressure divided by the standard-state pressure of 1 bar*. Hence, *K*° is truly unitless. Dividing by the standard-state concentration or pressure means that if concentrations in K_c are expressed in M (mol/L) the numerical values of *K*° and K_c are the same. Similarly, if partial pressures in K_p are expressed in bar, the numerical values of *K*° and K_p are the same.

K°	$\Delta_rG°$	
> 1	< 0	Product-favored at equilibrium.
< 1	> 0	Reactant-favored at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.

D31.4 Effect of Temperature

Recall that:

$$\Delta_rG° = \Delta_rH° - T\Delta_rS°$$

Therefore:

$$-RT(\ln K^\circ) = \Delta_r H^\circ - T\Delta_r S^\circ$$

This equation can be used to calculate K° at different temperatures, if we assume that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ for a reaction have the same values at all temperatures. This is a good, but not perfect, assumption and we will use it in this course unless specified otherwise. It is not a good assumption if there is a phase change for a reactant or a product within the temperature range of interest.

Dividing both sides of the equation by -RT gives:

$\ln K^\circ =$	$-\Delta_r H^\circ/RT$	+	$\Delta_r S^\circ/R$
$y =$	mx	+	b

A plot of lnK° vs. 1/T is called a **van't Hoff plot**. The graph has

$$\text{slope} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T}\right)$$

and

$$\text{intercept} = \frac{\Delta_r S^\circ}{R}$$

If the concentrations of reactants and products are measured at various temperatures so that K° can be calculated at each temperature, both the reaction entropy change and enthalpy change can be obtained from a van't Hoff plot.

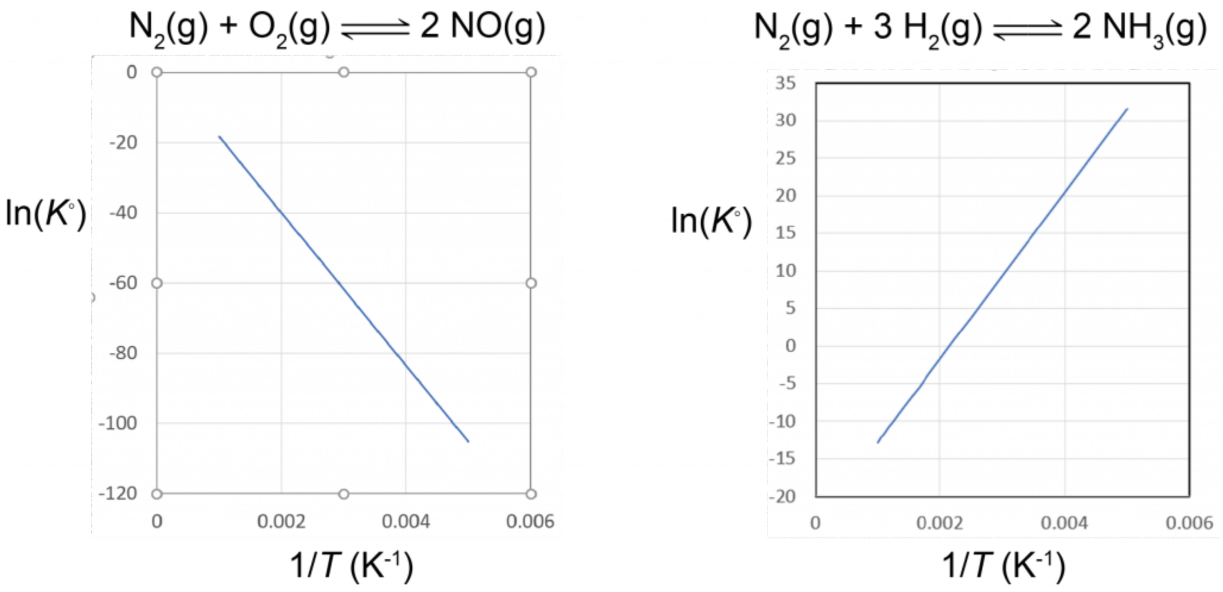


***Figure 2**. Van't Hoff plots. The reaction $N_2 + O_2 = 2\ NO$ has $\Delta_r H^\circ = 180.5$ kJ/mol; for this endothermic reaction, as T increases (smaller 1/T) the equilibrium constant increases. The reaction $N_2 + 3\ H_2 = 2\ NH_3$ has $\Delta_r H^\circ = -92.2$ kJ/mol; for this exothermic reaction, as T increases (smaller 1/T) the equilibrium constant decreases.*

Based on the equation for the van't Hoff plot, an exothermic reaction ($\Delta_r H^\circ < 0$) has K° decreasing with increasing temperature, and an endothermic reaction ($\Delta_r H^\circ > 0$) has K° increasing with increasing temperature. This quantitative result agrees with the qualitative predictions made by applying Le Chatelier's principle. It also shows that the magnitude of $\Delta_r H^\circ$ dictates how rapidly K° changes as a function of temperature. In contrast, $\Delta_r S^\circ$ affects the magnitude of K° but not its temperature dependence.

For example, suppose that K°_1 and K°_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively:

$$\ln K_1^\circ = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1}\right) + \frac{\Delta_r S^\circ}{R}$$

$$\ln K_2^\circ = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2}\right) + \frac{\Delta_r S^\circ}{R}$$

Subtracting the two equations yields:

$$\begin{aligned}\ln \mathrm{K}_2^\circ - \ln \mathrm{K}_1^\circ &= \left(-\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2}\right)+\frac{\Delta_r S^\circ}{R}\right)-\left(-\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1}\right)+\frac{\Delta_r S^\circ}{R}\right)\\ \ln\frac{K_2^\circ}{K_1^\circ} &= -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\\ &= \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\end{aligned}$$

Thus calculating $\Delta_r H°$ from tabulated $\Delta_f H°$ and measuring the equilibrium constant at one temperature allows us to calculate the equilibrium constant at any other temperature (assuming that $\Delta_r H°$ and $\Delta_r S°$ are independent of temperature).

Podia Question

Ammonium nitrate is an important fertilizer that supplies nitrogen to crops. It also can be used as an explosive to remove tree stumps from farm fields or in terrorist bombings. There are two reactions that can occur to produce the explosive effect. At lower temperatures ammonium nitrate decomposes to form dinitrogen monoxide and water vapor, but at higher temperatures it decomposes explosively to form nitrogen, water vapor, and oxygen. The reaction equations and thermodynamic parameters at 298 K are

(1) $NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(g)$ $\Delta_r H° = -36.026$ kJ/mol $\Delta_r S° = 446.42$ J K^{-1} mol^{-1}

(2) $NH_4NO_3(s) \rightarrow N_2(g) + ½\ O_2(g) + 2\ H_2O(g)$ $\Delta_r H° = -118.076$ kJ/mol $\Delta_r S° = 520.749$ J K^{-1} mol^{-1}

a) Which of the reactions is(are) product-favored at room temperature? Which of the reactions is(are) product-favored at 1000 K? Explain briefly.

b) Is there a temperature below which one of the reactions is more product-favored and above which the other reaction is more product favored? If there is such a temperature for these two reactions, determine what that temperature is.

c) Given your results, write an appropriate scientific explanation of the fact that nitrogen and oxygen are produced explosively at higher temperatures but dinitrogen monoxide is produced at lower temperatures.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

4.6: Day 32- Gibbs Free Energy and Work, Kinetic Metastability

29

Day 32: Gibbs Free Energy and Work, Kinetic Metastability

D32.1 Gibbs Free Energy and Work

Recall that when we we talk about kinetics of a reaction, we are concerned with the rate of the reaction: how fast it goes from reactants to products. When we talk about the thermodynamics of a reaction, we are concerned primarily with the difference in energy between reactants and products, but not with the mechanism by which reactants change into products.

When *the Gibbs free energy of the products is lower than that of the reactants*, a reaction is said to be **exergonic**. Conversely, an **endergonic** reaction is *one in which the products are higher in Gibbs free energy than the reactants.*

When there is a *decrease in Gibbs free energy* as a reaction occurs, $\Delta_r G$ equals the maximum *useful work* that can be *done by the reaction system*. $\Delta_r G = -w_{\text{max}}$. (The negative sign reflects the fact that w is defined as work done *on* the system.) Conversely, if a reaction has positive $\Delta_r G$, work must be done on the system to force the reaction to occur. The minimum work that must be done is given by $\Delta_r G$.

Activity 1: Exergonic and Endergonic Reactions

When considering a reaction under standard-state conditions the relevant thermodynamic quantity is $\Delta_r G°$. If a reaction is exergonic under standard-state conditions, $\Delta_r G° < 0$.

Coupled Reactions

One way to allow a reactant-favored process to occur is to couple it with a reaction that is product-favored. For example, consider the recovery of aluminum from alumina (Al_2O_3) ore:

$$Al_2O_3(s) \rightarrow 2\ Al(s) + 3/2\ O_2(g)\ \ \Delta_r G°\ (298\ K) = 1576.4\ kJ/mol$$

At least 1576.4 kJ of work must be done to change 1 mol Al_2O_3(s) into 2 mol Al(s) and 1.5 mol O_2(g) (at 1 bar). In a modern aluminum manufacturing plant, this work is supplied electrically and the electricity is often provided by burning coal. Assuming coal to be mainly carbon, the combustion reaction is:

$$C(s) + O_2(g) \rightarrow CO_2(g)\ \ \Delta_r G°\ (298\ K) = -394.4\ kJ/mol$$

Thus the $\Delta_r G°$ values indicate that, under standard-state conditions and ideal 100% efficiency, at least four moles of carbon/coal must burn to process each mole of Al_2O_3 ore. (In practice the aluminum smelting process is only 17% efficient, so it is necessary to burn nearly 6 times the theoretical amount of coal.) **Coupled reactions** *occur simultaneously and there is a means of exchanging energy between them*. The energy exchange occurs via the electric power grid in this specific case.

In other words, a reaction that is endergonic under standard-state conditions can be *coupled* to a separate exergonic reaction that *drives* the endergonic reaction (the thermodynamically unfavorable one) to occur. The $\Delta_r G°$ values for the two coupled reactions are summed to yield the overall $\Delta_r G°$. For this example, multiply the second reaction by 4, add the reaction equations, and apply Hess's Law, gives:

$$Al_2O_3(s) + 4\ C(s) + 4\ O_2(g) \rightarrow 2\ Al(s) + 3/2\ O_2(g) + 4\ CO_2(g)\ \ \Delta_r G°(298\ K) = -1.2\ kJ/mol$$

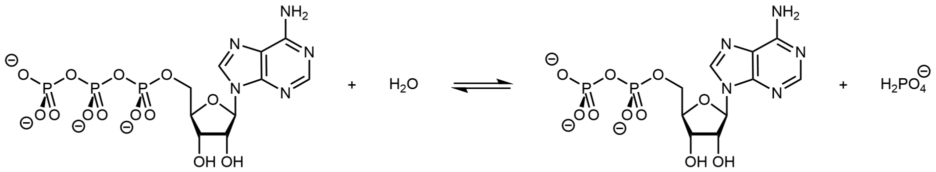
The overall reaction now has a negative $\Delta_r G°$ and is product-favored.

Under non-standard-state conditions a reaction with $\Delta_r G < 0$ can drive a reaction with $\Delta_r G > 0$, provided energy can be transferred from one to the other.

D32.2 Gibbs Free Energy in Biological Systems

Biological organisms often couple the product-favored hydrolysis of ATP (adenosine triphosphate) to a reactant-favored reaction. Thus ATP hydrolysis reaction can be used to drive a necessary, but thermodynamically unfavorable, reaction.

$$ATP + H_2O \rightleftharpoons ADP + H_2PO_4^-\ \ \Delta_r G° = -30.5\ kJ/mol$$



The triphosphate part of ATP is an inorganic ester. It can be formed by condensation reaction of ADP and $H_2PO_4^-$ with water formed as a byproduct (the reverse of the reaction shown above). ATP can be made available in an organism where an endergonic reaction needs to occur. Its hydrolysis can then be coupled with the endergonic reaction to yield a thermodynamically favorable overall reaction.

For example, ATP hydrolysis can be used to drive condensation reactions of amino acids to generate proteins as graphically illustrated by Figure 1.

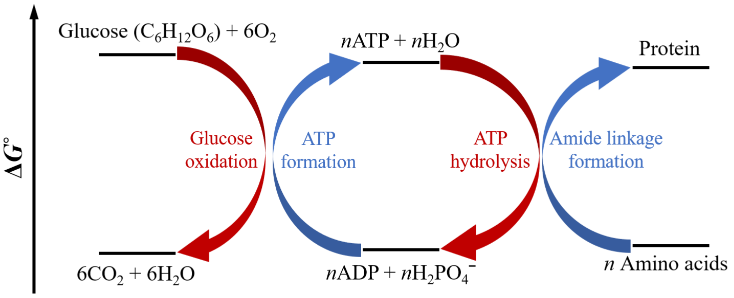


Figure 1. *Exergonic reactions like burning of glucose drive ATP synthesis. The ATP molecules are used to power other endergonic reactions like protein synthesis.*

Figure 1 shows ATP formation being initially coupled to the glucose oxidization reaction:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O\ \ \Delta_rG° = -2880\ \text{kJ/mol}$$

which has close to 100x greater capability to do work than the hydrolysis of a single ATP. Hence, the equilibrium for this reaction so strongly favors the products that a single arrow is typically used in the chemical equation as it is essential irreversible. It may not be surprising that glucose and all sugars are very energetic molecules since they are the primary energy source for life.

D32.3 Kinetic Metastability

At a given temperature, the rate law and rate constant can be used to determine how rapidly reactants are converted to products. The equilibrium constant expression and the value of $K°$, on the other hand, can be used to determine the equilibrium concentrations of products relative to reactants. In other words, *kinetics describes how fast equilibrium is reached, and thermodynamics describes where the equilibrium lies*. However, there is not necessarily a correlation between a fast reaction and one that is product-favored at equilibrium. Both kinetics and thermodynamics are needed to characterize a chemical reaction because a useful reaction usually is one where significant quantities of products can be produced in a short time.

On the other hand, it is often true that a substance is valuable for some purpose when it is stable and does not change into some other substance. For example, iron and steel are useful for making automobiles and constructing buildings precisely because they are stable. When discussing the concept of stability, it is useful to distinguish between thermodynamic stability and kinetic metastability.

Consider a generic reaction:

$$A \rightleftharpoons B\ \ \Delta_rG° < 0$$

Here product B has lower $\Delta_fG°$ than reactant A so that $\Delta_rG°$ of the forward reaction is negative. *When a reaction favors products at equilibrium*, we say that products are **thermodynamically stable** relative to reactants. In the example above, product B is thermodynamically stable compared to reactant A. However, if the activation-energy barrier (E_a) is high, at a given temperature the reaction could proceed very slowly, and reactant A would be described as being *inert* (unreactive). We say that compound A is **kinetically metastable** (or *kinetically stable*) relative to compound B.

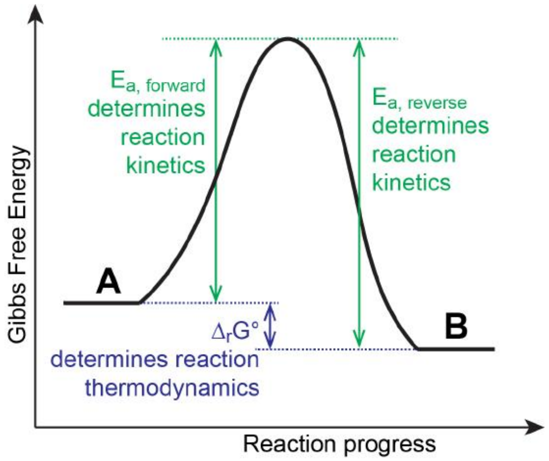


Figure 2*. Reaction coordinate diagram showing kinetic and thermodynamic relationships.*

Notice that stability (and metastability) are defined by comparing one substance with another. It is possible that some other substance, say C, is even more stable than B and therefore B is thermodynamically unstable relative to C.

For example, diamond and graphite are two compounds composed solely of carbon atoms. The title of an old James Bond film, and an even older advertising slogan, says, “Diamonds Are Forever.” This implies some stability: we don’t expect the diamond in a ring to change anytime soon.

$$\text{C(s, diamond)} \longrightarrow \text{C(s, graphite)} \quad \Delta_r G° = -2.9 \text{ kJ/mol}$$

Diamond is *kinetically metastable*. Thermodynamics says it should change to graphite, but the change is so slow as to be essentially undetectable at day-to-day temperatures in a human lifetime. The fact that diamond exists is due to a very large activation-energy barrier for conversion of diamond to graphite; diamond would convert to graphite at temperatures of >4500 K.

This very large E_a, as well as the facts that diamond is the hardest known solids and graphite is one of the softest, can be explained by differences in the way the atoms are bonded. In diamond, every carbon atom has sp^3 hybridization and each sp^3 carbon is bonded to 4 other sp^3 carbon atoms at the corners of a tetrahedron. In graphite, every carbon atom has sp^2 hybridization and each sp^2 carbon is bonded to 3 other sp^2 carbon atoms in planar sheets of connected benzene rings. Because the sheets can slide past one another relatively easily, graphite is soft and slippery.

Conversion of diamond to graphite requires breaking numerous C−C single bonds with bond energy of 356 kJ/mol. There is no easy mechanism for this conversion and so transforming diamond into graphite, or vice versa, requires almost as much energy as destroying the entire crystal lattice and rebuilding it. Therefore, once diamond is formed, it cannot convert back to graphite under normal conditions because E_a is too high: diamond is said to be *metastable* because its stability depends on kinetics, not thermodynamics.

D32.4 Haber-Bosch Process

The interplay of thermodynamics and kinetics is illustrated in the industrial synthesis of ammonia. It became possible to manufacture ammonia in useful quantities in the early 20th century after the factors that influence this reaction equilibrium were understood:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad \Delta_r H° = -92.2 \text{ kJ/mol}$$

Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. It plays a vital role in the global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for enhancing 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.

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, which shifts the reaction equilibrium towards the product side, increasing the concentration and partial pressure of ammonia.

At low temperatures, the rate of formation of ammonia is slow so equilibrium would be achieved more quickly at higher temperatures. However, the reaction is exothermic. Increasing the temperature to increase the rate shifts the equilibrium in the endothermic direction and lowers the product yield.

Part of the slower rate caused 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.

Ammonia, the reaction product, has a higher boiling point than the reactants, nitrogen and hydrogen; thus, ammonia can be condensed to a liquid at temperatures where N_2 and H_2 remain gases. Condensing ammonia by refrigeration of the gaseous mixture removes product, shifting the equilibrium to the right.

Exercise 5: Intermolecular Forces and Boiling Point

Ammonia has a higher boiling point than nitrogen and hydrogen because of intermolecular forces.

In the commercial production of ammonia, conditions are typically 400 – 500 °C and 150–250 bar. The catalyst consists of Fe_3O_4 mixed with KOH, Al_2O_3, and SiO_2. This gives the best compromise among rate, product yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure 3).

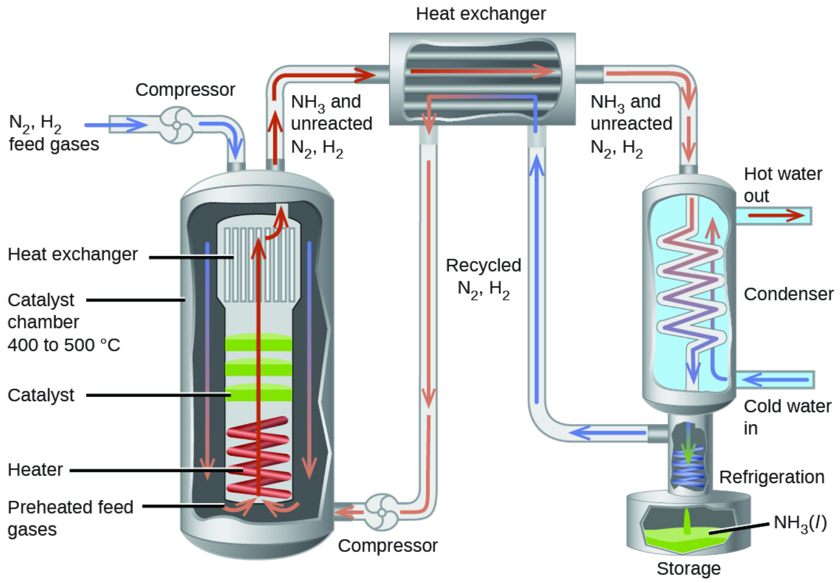
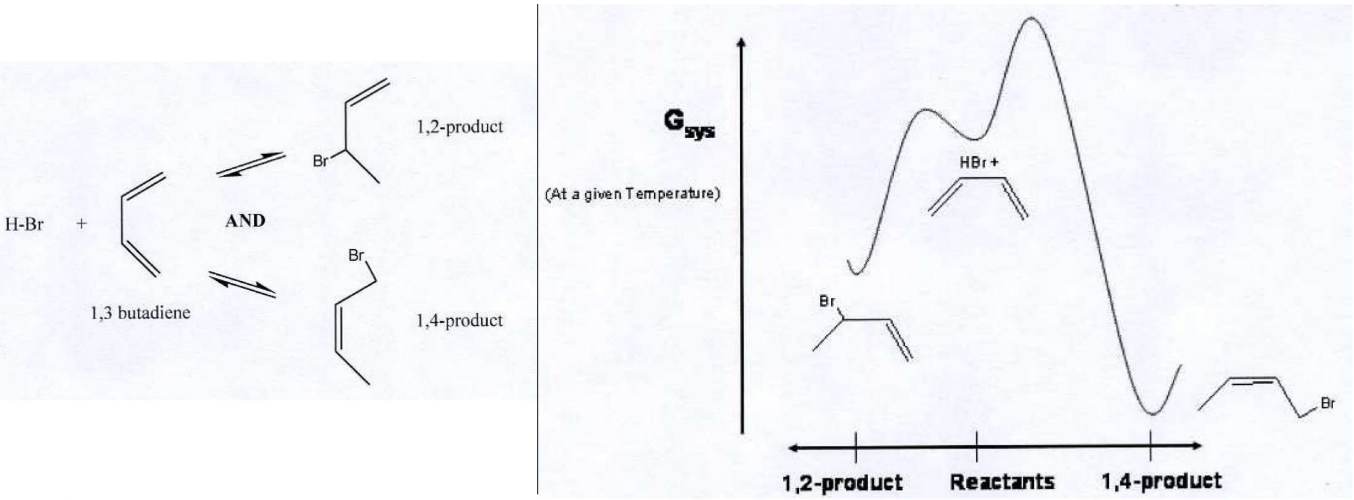


Figure 3. *Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant. Heat exchangers are used to pre-heat reactants and to cool the equilibrium mixture prior to refrigeration to condense ammonia.*

Podia Question

Consider the addition of HBr to 1,3-butadiene. Two products are possible: 1,2-product and 1,4-product (see left side of figure).



On the right side of the figure is a diagram showing Gibbs free energy as a function of reaction progress. On the horizontal axis reactants are in the middle. The 1,2-product is reached by moving left. The 1,4-product is reached by moving right.

1. Write an explanation in scientifically appropriate language for the fact that at lower temperatures the reaction produces mainly 1,2-product while at higher temperatures the reaction produces mainly 1,4-product. If any assumptions need to be made, say what they are.

2. A student says that at lower temperatures the 1,2-product is kinetically metastable compared with the 1,4-product. Is this a correct statement? Why or why not?

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

4.7: Day 33- Acids and Bases

30

Day 33: Acids and Bases

We will apply the knowledge we learned so far, e.g. thermodynamics, kinetics, molecular structure, etc., to explore two prevalent types of chemical reactions: acid-base reactions and redox/electrochemical reactions.

D33.1 Definition of Acids and Bases

According to the **Brønsted-Lowry acid-base definition**, *a chemical species that donates a proton (hydrogen ion,* H^+*) to another chemical species is called an acid and a chemical species that accepts a proton is a base*. (Recall that when a H atom loses an electron, only the proton in the nucleus remains, so a proton is a H^+ ion.) An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

The *chemical species that remains after an acid has donated a proton* is called the **conjugate base** of that acid. Consider these examples of the generic reaction *acid* + $H_2O \rightleftharpoons$ *conjugate base* + H_3O^+:

$$\mathrm{HF} + \mathrm{H_2O} \rightleftharpoons \mathrm{F^-} + \mathrm{H_3O^+}$$
$$\mathrm{H_2SO_4} + \mathrm{H_2O} \rightleftharpoons \mathrm{HSO_4^-} + \mathrm{H_3O^+}$$
$$\mathrm{HSO_4^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{SO_4^{2-}} + \mathrm{H_3O^+}$$
$$\mathrm{NH_4^+} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_3} + \mathrm{H_3O^+}$$

Similarly, *the chemical species that forms after a base accepts a proton* is called the **conjugate acid** of that base. Consider the following examples of the generic reaction *base* + $H_2O \rightleftharpoons$ *conjugate acid* + OH^-:

$$\mathrm{NH_3} + \mathrm{H_2O} \rightleftharpoons \mathrm{NH_4^+} + \mathrm{OH^-}$$
$$\mathrm{S^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{HS^-} + \mathrm{OH^-}$$
$$\mathrm{CO_3^{2-}} + \mathrm{H_2O} \rightleftharpoons \mathrm{HCO_3^-} + \mathrm{OH^-}$$
$$\mathrm{F^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{HF} + \mathrm{OH^-}$$

From these examples, we can see that the conjugate acid and conjugate base are paired: the conjugate base of an acid has that acid as its conjugate acid. For instance, NH_3 is the conjugate base of NH_4^+, while NH_4^+ is the conjugate acid of NH_3. Similarly, F^- is the conjugate base of HF, while HF is the conjugate acid of F^-.

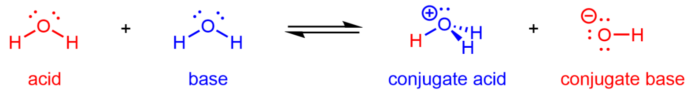
You may have noticed in earlier sections that we wrote $H^+(aq)$ to represent hydrogen ions in aqueous solution, while in the preceding reactions we have written H_3O^+. A H^+ ion, a proton, is much smaller than any other cation and therefore is a highly concentrated positive charge that strongly attracts water-molecule dipoles and forms strong hydrogen bonds. Thus, when a Brønsted-Lowry acid transfers a proton to water, more than a single water molecule accepts the proton. Experiments show that as many as six water molecules may be involved, which would make the formula of $H^+(aq)$ $H_{13}O_6^+$, but the structure changes continually as water molecules move about in the liquid. For Brønsted-Lowry acid-base reactions, we will use $H_3O^+(aq)$ to emphasize that a proton has been transferred to water and to represent the more complicated actual structure. In general, $H^+(aq)$ is appropriate to represent a proton surrounded by many water molecules.

Finally, Brønsted-Lowry acid-base reactions are very fast. Their equilibrium is established quickly and this equilibrium is an important aspect when we consider acid and base strengths later.

D33.2 Autoionization of Water

In the example reactions above, there are also two other conjugate acid-base pairs: H_2O is the conjugate base of its conjugate acid H_3O^+, and H_2O is the conjugate acid of its conjugate base OH^-. (However, note that H_3O^+ is not the conjugate acid of OH^-; these two species are not a conjugate acid-base pair because their structures do not differ by a single H^+.)

Hence, H_2O can react as an acid or a base depending on the other species involved in the reaction. In pure water, H_2O acts as both acid and base—a very small fraction of water molecules donate protons to other water molecules:



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 10^9 molecules are ionized at 25 °C. The $[H_3O^+]_e$ and $[OH^-]_e$ give an **autoionization constant for water, K_w** $= 1.0 \times 10^{-14}$ at 25 °C. Because it is the mathematical product of concentrations of two ions, it is also called the ion-product constant for water.

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \; K_w = [H_3O^+]_e[OH^-]_e = 1.0 \times 10^{-14} \text{ at } 25\ °C$$

Activity 1: Autoionization of Water

Water is an example of an **amphiprotic** chemical species *a molecule that could either gain a proton or lose a proton in an acid-base reaction*. Amphiprotic species are also **amphoteric**, 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 definition). For example, the bicarbonate ion is also amphoteric:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Activity 2: Amphiprotic Species

D33.3 pH and pOH

The concentrations of H_3O^+ and OH^- in a solution are important for the solution's acid-base properties and often affect the chemical behaviors of other solutes. A solution is **neutral** if its $[H_3O^+]_e = [OH^-]_e$; **acidic** if its $[H_3O^+]_e > [OH^-]_e$; and **basic** if its $[H_3O^+]_e < [OH^-]_e$.

A common means of expressing values that span many orders of magnitude is to use a logarithmic scale. One such scale is based on the p-function:

$$pX = -\log X$$

where "X" is the quantity of interest and "log" is the base-10 logarithm. The **pH** of a solution is therefore defined as:

$$\text{pH} = -\log\left(\frac{[\text{H}_3\text{O}^+]_e}{mol/L}\right)$$

The reason for dividing by the units "mol/L" (M) is that $[H_3O^+]$ has units of mol/L and taking the logarithm of a unit makes no sense. From here on we will assume that you are aware that only the numeric value of a concentration (or other quantity) needs to be used as the argument of a logarithm and we will not explicitly divide by the units.

If a pH value is known, the concentration of hydronium ions can be calculated:

$$[H_3O^+]_e = 10^{-pH}$$

Here we assume that you know that units are required for the concentration obtained from this equation and the units are mol/L. Similarly, the hydroxide ion concentration may be expressed as **pOH**:

$$pOH = -\log[OH^-]_e \text{ and } [OH^-]_e = 10^{-pOH}$$

Finally, the relation between pH and pOH can be derived from the K_w expression:

K_w	=	$[H_3O^+]_e[OH^-]_e$
$-\log(K_w)$	=	$-\log([H_3O^+]_e[OH^-]_e)$
pK_w	=	$-\log([H_3O^+]_e) + (-\log([OH^-]_e))$
pK_w	=	pH + pOH

At 25 °C:

$$pK_w = 14 = pH + pOH$$

Therefore, at this temperature:

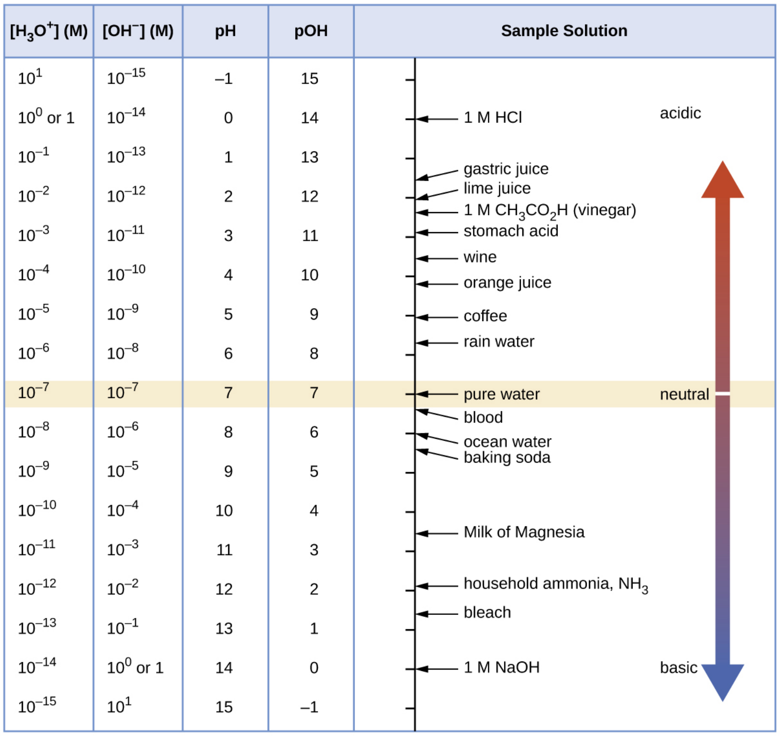
Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	< 7
neutral	$[H_3O^+] = [OH^-]$	7
basic	$[H_3O^+] < [OH^-]$	> 7

Because K_w is temperature dependent, the correlations between pH values and the acidic/neutral/basic adjectives are different at different temperatures. For example, $[H_3O^+]$ in pure water at 80 °C is 4.9×10^{-7} M, which corresponds to pH and pOH values of:

$$pH = -\log[H_3O^+]_e = -\log(4.9 \times 10^{-7}) = 6.31$$
$$pOH = -\log[OH^-]_e = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, neutral solutions have pH = pOH = 6.31, acidic solutions have pH < 6.31 and pOH > 6.31, and basic solutions have pH > 6.31 and pOH < 6.31. This distinction can be important when studying certain processes that occur at temperatures other than 25 °C, such as acid-base reactions in the human body where temperatures are typically 37 °C.

Unless otherwise noted, references to pH values are presumed to be those at 25 °C. Figure 1 shows the relationships among $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties for some common substances.



$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH
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 1. *The pH and pOH values of some common substances at 25 °C are shown in this chart.*

Activity 3: pH and Relative Strengths of Acids

The acidity of a solution is typically determined by measuring its pH. The pOH of a solution is not usually measured, but it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 2), or visually estimated using colored indicators (Figure 3).

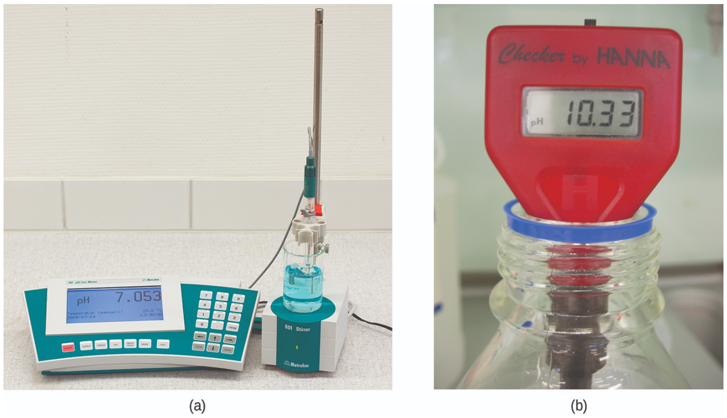


Figure 2. *(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)*

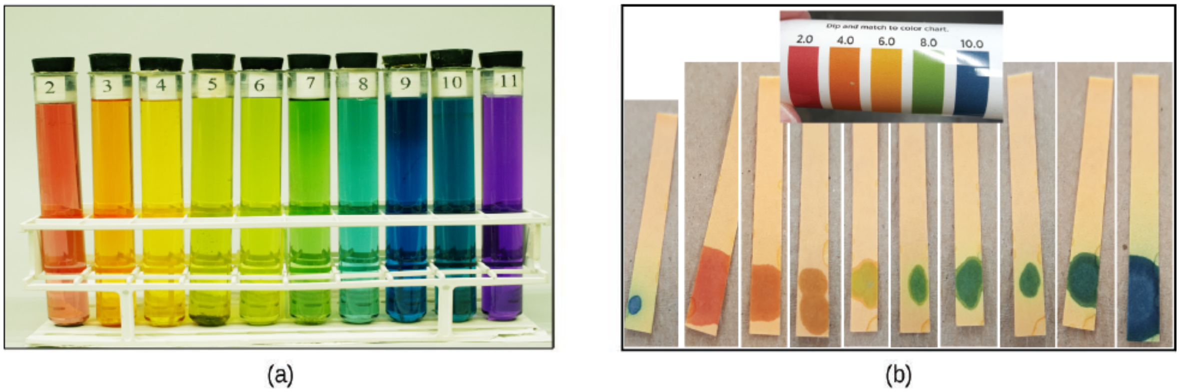


Figure 3. *A universal indicator is a mixture of indicators that assumes a different color at different pH values. (a) A universal indicator has been added to solutions in ten test tubes, each with the pH shown at the top of each tube. (b) pH paper contains a different universal indicator that gives different colors when moistened with solutions of differing pH values. The scale at the top shows colors for even-numbered pH values from 2 to 10.*

D33.4 Acid Constant K_a and Base Constant K_b

The relative strengths of acids and bases may be determined by comparing the equilibrium constants for their ionization reactions. For the reaction of a generic acid, HA, in water:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

we write the **acid ionization constant (K_a)** expression as:

$$K_a = \frac{[H_3O^+]_e[A^-]_e}{[HA]_e}$$

(Although water is a reactant in the reaction, it is also the solvent with its phase indicated as “*l*“, so we do not include $[H_2O]$ in the expression.)

An acid with a larger K_a would have a larger concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA. Thus a stronger acid, which ionizes to a greater extent, has a larger ionization constant than a weaker acid.

For example, these data on acid ionization constants:

$CH_3COOH(aq) + H_2O(l)$	$\rightleftharpoons$	$CH_3COO^-(aq) + H_3O^+(aq)$	$K_a = 1.8 \times 10^{-5}$
$HNO_2(aq) + H_2O(l)$	$\rightleftharpoons$	$NO_2^-(aq) + H_3O^+(aq)$	$K_a = 7.4 \times 10^{-4}$
$HSO_4^-(aq) + H_2O(l)$	$\rightleftharpoons$	$SO_4^{2-}(aq) + H_3O^+(aq)$	$K_a = 1.1 \times 10^{-2}$

indicate that the order of acid strength is: acetic acid (CH_3COOH) is a weaker acid than nitrous acid (HNO_2) which is itself weaker than hydrogen sulfate ion (HSO_4^-).

We can consider the strength of a base (B) similarly by considering the extend that it will form hydroxide ions in an aqueous solution:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

where the **base ionization constant (K_b)** expression is:

$$K_\mathrm{b} = \frac{[\mathrm{HB}^+]_e[\mathrm{OH}^-]_e}{[\mathrm{B}]_e}$$

A stronger base ionizes to a greater extent than does a weaker base. Therefore, a stronger base has a larger K_b than a weaker base.

Notice that K_a and K_b provide a quantitative measure of acid and base strengths—significantly more accurate than qualitative descriptions of “strong acid” or “weak acid”.

Consider the ionization reactions for a conjugate acid base pair, HA and A^-:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{[\mathrm{H_3O}^+]_e[\mathrm{A}^-]_e}{[\mathrm{HA}]_e}$$

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

$$K_b = \frac{[\mathrm{HA}]_e[\mathrm{OH}^-]_e}{[\mathrm{A}^-]_e}$$

Adding these two chemical equations yields the equation for the autoionization of water:

$$\cancel{HA(aq)} + H_2O(l) + \cancel{A^-(aq)} + H_2O(l) \rightleftharpoons \cancel{A^-(aq)} + H_3O^+(aq) + \cancel{HA(aq)} + OH^-(aq)$$

When two equilibria sum to a third equilibrium, the product of the first two equilibrium constants equals the third equilibrium constant:

$$K_\mathrm{a} \times K_\mathrm{b} = \frac{[\mathrm{H_3O}^+]_e[\mathrm{A}^-]_e}{[\mathrm{HA}]_e} \times \frac{[\mathrm{HA}]_e[\mathrm{OH}^-]_e}{[\mathrm{A}^-]_e} = [\mathrm{H_3O}^+]_e[\mathrm{OH}^-]_e = K_\mathrm{w}$$

For example, at 25 °C, K_a of acetic acid (CH_3COOH) is 1.8×10^{-5} M, and K_b of its conjugate base, acetate anion (CH_3COO^-), is 5.6×10^{-10} M. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}\ \mathrm{M}) \times (5.6 \times 10^{-10}\ \mathrm{M}) = 1.0 \times 10^{-14} = K_w$$

This relationship tells us that stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases.

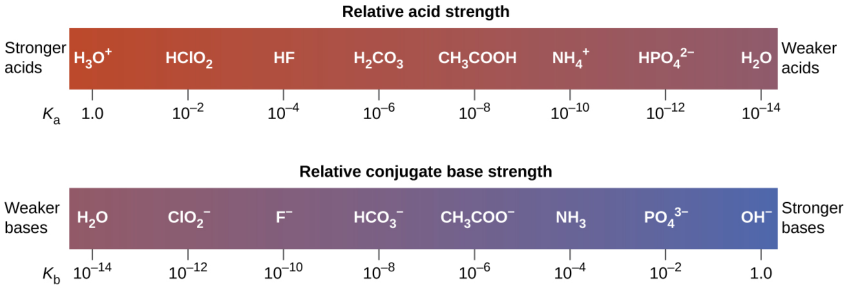
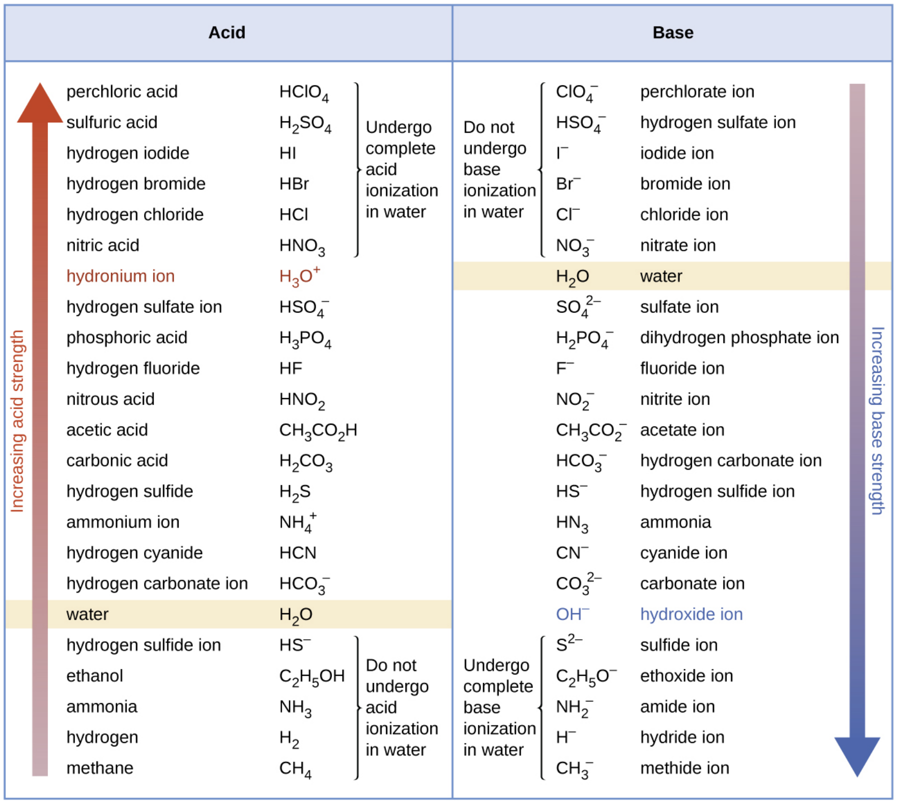


Figure 4. *This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution. Conjugate acids are above their conjugate bases.*



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^+			HN_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. *The chart shows the relative strengths of conjugate acid-base pairs. The acid and base in a given row are conjugate to each other.*

Although “strong” and “weak” are relative terms, generally, we refer to acids stronger than H_3O^+ as strong acids, and bases stronger than OH^- as strong bases. Because strong acids and strong bases are completely ionized in aqueous solutions, the concentration of nonionized acid or base is essentially zero. For example, in a 0.10-M solution of HCl, $[HCl]_e = 0$, $[H_3O^+]_e = 0.10$ M, and $[Cl^-]_e = 0.10$ M.

A consequence of this complete ionization is that in aqueous solution there is no way to tell whether one strong acid is stronger than another: HCl, HBr, and HI all are completely ionized. This is known as the *leveling effect of water*. However, when dissolved in some other solvents, these acids do not ionize completely. The extent of ionization increases in the order HCl < HBr < HI, and so HI is the strongest of these acids. Water exerts a similar leveling effect on strong bases.

Many acids and bases are considered “weak”. A solution of a weak acid in water is a equilibrium mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid.

Activity 4: Determining Ka

Activity 5: Using Ka to Calculate Concentrations

The **percent ionization** of a weak acid is another measure of the strength of an acid, HA:

$$\text{percent ionization} = \frac{[\mathrm{H_3O^+}]_e}{[\mathrm{HA}]_0} \times 100\%$$

A stronger acid, with a higher K_a, has higher percent ionization than a weaker acid (for the same concentration).

The percent ionization for a solution of a weak acid increases with decreasing acid concentration; this can be seen by applying Le Chatelier’s principle to the ionization equilibrium:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

Increasing the solution volume for a given quantity of HA added causes the equilibrium to shift to the product side to partially counteract the decrease in total solute concentration.

D33.5 Acid Strength and Molecular Structure

Acid-base reactions, like many other chemical reactions, involve breaking and forming bonds. Hence, we can use our chemical understanding of molecular structure and stability to understand what makes some acids stronger than others.

We know that an equilibrium favors the thermodynamically more stable side of the reaction, and that the magnitude of the equilibrium constant reflects the energy difference ($\Delta_r G°$) between the reactants and products. Therefore, in an acid-base equilibrium, the equilibrium always favors the side with weaker acid and base (these are the more stable species). Consequently, anything that stabilizes the conjugate base of an acid will necessarily make that acid stronger, and anything that stabilizes the acid will make it a weaker acid. This idea is illustrated in Figure 6.

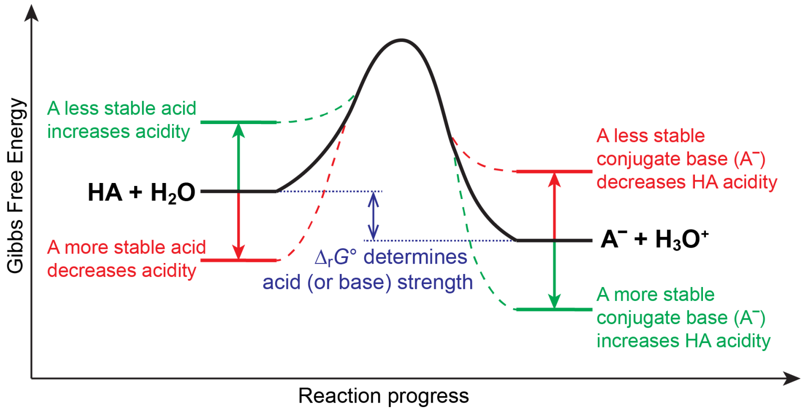


Figure 6*. Acid (or base) strength is dependent on the thermodynamics of the acid-base reaction.*

Bond Strength

Let’s consider a generic acid:

$$HA \rightleftharpoons A^- + H^+$$

In general, the stronger the H–A bond is, the more stable the HA molecule is, and the less acidic the substance is. This effect is illustrated by the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Enthalpy (kJ/mol)	566	431	366	299
pK_a	3.2	−6.1	−8.9	−9.3

Note that the “bond enthalpy” values are associated with a different bond breaking reaction, which produces a hydrogen atom instead of a hydrogen ion:

$$HA \rightleftharpoons A\cdot + H\cdot$$

Nonetheless, bond strengths correlate with acid strength. As you go down the halide group, the overlap between the hydrogen 1*s* orbital and the valence orbital of the halogen atom decreases, and the H-X bond enthalpy decreases, indicating weaker bonds. As a result, HX acid strength increases as you go down the group.

A similar trend is observed for other groups. For example, for group 16:

	$H_2A \rightleftharpoons HA^- + H^+$			
	H_2O	**H_2S**	**H_2Se**	**H_2Te**
pK_a	14.0	*7.0*	3.9	2.6

Stabilizing the Excess Charge on Conjugate Base

Electronegativity

When the conjugate base is negatively charged, factors that stabilize the excess negative charge on the conjugate base favor the dissociation of the acid and make the acid a stronger acid. For example, the relative acidity of the acids with second row elements is:

	$H_nA \rightleftharpoons H_{n-1}A^- + H^+$			
	CH_4	NH_3	H_2O	HF
pK_a	50	*36*	14.0	3.2

Consider the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the extra negative charge in the F^- anion than carbon can stabilize the extra negative charge in the CH_3^- anion. Consequently, HF can dissociate and form H^+ and F^- to a much greater extent than CH_4 can form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the acids as well: as the electronegativity of A in H_nA increases, the A–H bond becomes more polar, favoring dissociation to form $H_{n-1}A^-$ and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the A–H bond in the acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

Electron Delocalization

The pK_a values of some carboxylic acids are shown in Figure 7.

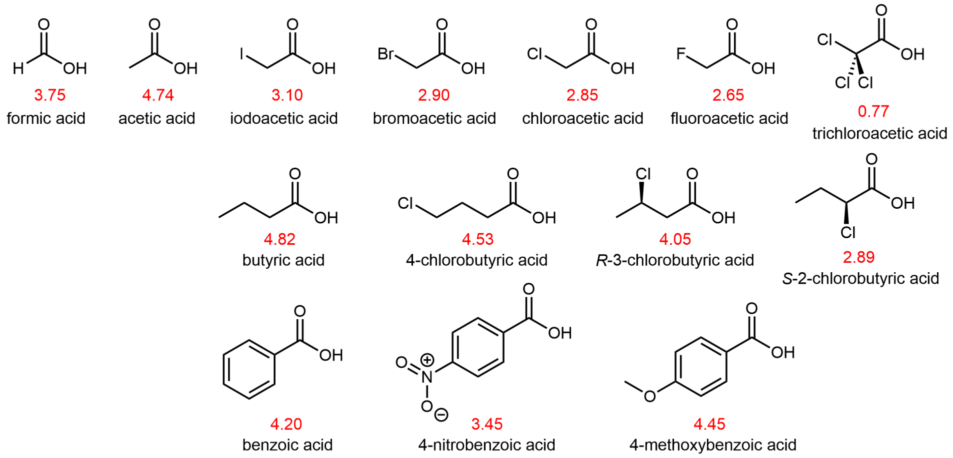


Figure 7. *Line drawings of select carboxylic acid molecules, along with their pK_a values (in red) and their names.*

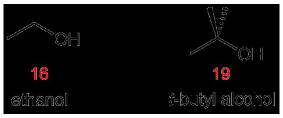
The bond that breaks in a carboxylic acid is the O–H bond:

$$R\text{-}COOH \rightleftharpoons R\text{-}COO^- + H^+$$

An O–H bond also breaks when an alcohol acts as an acid in an acid-base reaction:

$$R\text{-}OH \rightleftharpoons R\text{-}O^- + H^+$$

However, when we compare the carboxylic acid pK_a's with those of comparable alcohols, such as:



it is clear that carboxylic acids are stronger acids than alcohols by over ten orders of magnitude. Why should the presence of a carbonyl group adjacent to a hydroxyl group have such a profound effect on the acidity of the hydroxyl proton?

Both the carboxylic acid and its conjugate base, carboxylate anion, are stabilized by having additional resonance structures that delocalize electron densities. However, the stabilization in carboxylate anion is much greater because the two major resonance structures have equal contributions to the resonance hybrid, and the extra electron density (negative charge) is shared equally between the two oxygen atoms, which have high electronegativity. This stabilization leads to a markedly increased acidity of carboxylic acids.

***Figure 8**. Greater resonance stabilization of carboxylate ion compared to carboxylic acid results in increased acid strength. Click on each "i" for more information.*

Inductive Effect

Atoms (or groups of atoms) in a molecule that are not directly bonded to the acidic H can also influence the molecule's acidity. They can do so via an **inductive effect**, that is, they *induce a polarization in the distribution of electrons within the molecule*. This can be seen by studying the structures in Figure 7 above. Electronegative substituents (F, Cl, Br, I) near the carboxyl group act to increase the acidity of the carboxylic acid. For example, fluoroacetic acid, CH_2FCOOH, is significantly more acidic than acetic acid, CH_3COOH.

The magnitude of the inductive effect depends on both the nature and the number of halogen substituents, as shown by the pK_a values for several acetic acid derivatives:

	CH_3COOH	$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH	CF_3COOH
pK_a	4.74	*2.85*	1.35	0.77	0.52

Fluorine, which is more electronegative than chlorine, causes a larger inductive effect as it draws electron density away from the acidic proton in the carboxyl group. Moreover, having three halogens causes a larger inductive effect than having two or one. Note that inductive effects can be quite significant. For instance, replacing the $–CH_3$ group of acetic acid by a $–CF_3$ group results in a almost 10,000-fold increase in acidity.

In another example, the acidity of hypohalous acids ($HOX \rightleftharpoons OX^- + H^+$) varies by about three orders of magnitude due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	2.73	7.2
HOBr	2.64	8.5
HOI	2.11	10.5

As the electronegativity of X increases, the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond, enhancing ionization of hydrogen as H^+ and making the acid stronger.

Oxoacids

The acidity of oxoacids, with the general formula $HOXO_n$ (with n = 0−3), depends strongly on the number of terminal oxygen atoms attached to the central atom X (Figure 8) due to both an inductive effect and increased stabilization of the conjugate base.

Because oxygen is the second most electronegative element, adding terminal oxygen atoms (oxygen atoms only bonded to the central atom) causes electron densities to be drawn away from the O–H bond, thereby increasing the strength of the acid. Figure 9 shows how the H atom becomes steadily more blue from HClO to $HClO_4$, making it easier for the acid to lose the hydrogen as an H^+ ion.

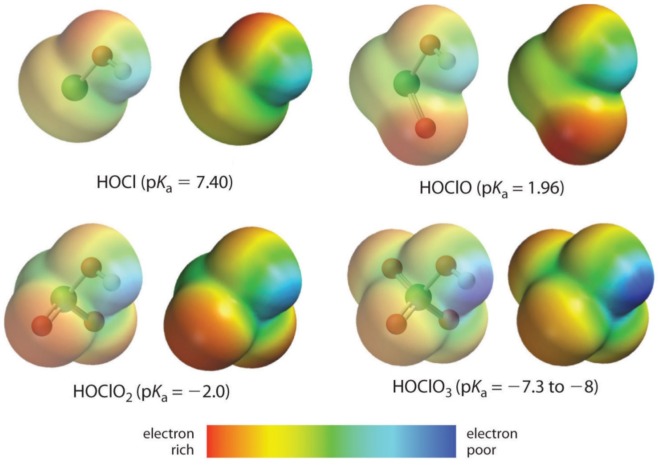
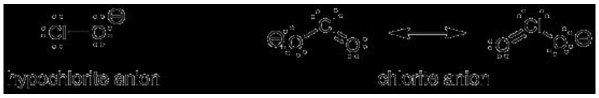


Figure 9: *The relationship between the acid strengths of the oxoacids of chlorine and the electron density on H in the O–H unit. These electrostatic potential maps show how the electron density on H decreases (darker blue color) as the number of terminal oxygen atoms increases. Blue corresponds to low electron densities, whereas red corresponds to high electron densities. Source: Chlorine oxoacids pKa values from J. R. Bowser, Inorganic Chemistry (Pacific Grove, CA: Brooks-Cole, 1993).*

Also important is the effect of electron delocalization that stabilizes the extra negative charge in the conjugate base. For example, in the chlorite anion (ClO_2^-), the excess electron density is delocalized equally over both oxygen atoms, whereas in the hypochlorite ion (ClO^-), the negative charge is largely localized on a single oxygen atom:



As a result of this stabilization of the conjugate base, as well as additional inductive effect, chlorous acid is more than 200,000 times stronger than hypochlorous acid.

The inductive effect is additionally responsible for the trend in the acidities of oxoacids that have the same number of oxygen atoms as we go across a row of the periodic table. For example, H_3PO_4 is a weak acid, H_2SO_4 is a strong acid, and $HClO_4$ is one of the strongest acids known. The number of *terminal* oxygen atoms increases steadily across the row, consistent with the observed increase in acidity. In addition, the electronegativity of the central atom increases steadily from P to S to Cl, which causes more electron densities to be drawn from OH group to the central atom, weakening the O–H bond and increasing the strength of the oxoacid.

Podia Question

Arrange these acids in order of decreasing acid strength (smallest pK_a first, largest pK_a last). Analyze the factors that affect the strength of each acid and based on that analysis explain the order of acidity.

$$CH_3CH_2OH\ CF_3COOH\ HOClO_3\ CH_2BrCOOH\ HOClO_2$$

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

4.8: Day 34- Acid-Base Reactions

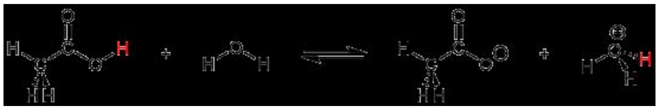
31

Day 34: Acid-Base Reactions

D34.1 Polyprotic Acids

We can classify acids by the number of protons per molecule that they can donate in an acid-base reaction. *Acids that contain one ionizable hydrogen atom per molecule* are called **monoprotic acids**. Examples are HCl, HNO_3, CH_3COOH, and HCN.

Even though it contains four hydrogen atoms, acetic acid is also monoprotic because only the hydrogen atom from the carboxyl group (-COOH) reacts with bases:



The three hydrogen atoms in the methyl group are not reactive (the C–H bonds are similar those in alkanes, which are unreactive).

In the same vein, **monoprotic bases** are *bases that accept a single proton*.

Diprotic acids *contain two ionizable hydrogen atoms per molecule*. The dissociation of the first H^+ always takes place to a greater extent than the dissociation of the second H^+. For example, sulfuric acid ionizes in two steps:

$H_2SO_4(aq) + H_2O(l)$	⇌	$HSO_4^-(aq) + H_3O^+(aq)$	$K_{a,1} > 10^2$
$HSO_4^-(aq) + H_2O(l)$	⇌	$SO_4^{2-}(aq) + H_3O^+(aq)$	$K_{a,2} = 1.1 \times 10^{-2}$

This *stepwise ionization* occurs for all polyprotic acids.

A solution of a weak diprotic acid contains a mixture of acids. For example, when carbonic acid loses one H^+, it yields hydronium ions and bicarbonate ions in small quantities:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$K_{\text{a, }H_2CO_3} = \frac{[H_3O^+]_e[HCO_3^{\ -}]_e}{[H_2CO_3]_e} = 4.3 \times 10^{-7}$$

The bicarbonate ion can lose an H^+ to form hydronium ions and carbonate ions in even smaller quantities:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

$$K_{\text{a, }HCO_3^-} = \frac{[H_3O^+]_e[CO_3^{\ 2-}]_e}{[HCO_3^{\ -}]_e} = 4.7 \times 10^{-11}\ \text{M}$$

$K_a(H_2CO_3)$ is larger than $K_a(HCO_3^-)$ by about four orders of magnitude (10^4 times larger), so H_2CO_3 is the dominant producer of H_3O^+ in the solution. This means that the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

If $K_{a,1}$ of a weak diprotic acid at least 20 times larger than $K_{a,2}$, 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.

Activity 1: Ionization of a Diprotic Acid

A **triprotic acid** is an acid that has *three protons that undergo stepwise ionization*: Phosphoric acid is an example:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)\ K_{a,1} = 7.2 \times 10^{-3}\ \text{M}$$
$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)\ K_{a,2} = 6.3 \times 10^{-8}\ \text{M}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq) \quad K_{a,3} = 4.6 \times 10^{-13}\ M$$

Again, the differences in the ionization constants of these reactions tell us that the degree of ionization is significantly weaker in each successive step. This is a general characteristic of polyprotic acids. Here, because the successive ionization constants differ by a factor of 10^5-10^6, the calculations of equilibrium concentrations in a solution of H_3PO_4 can be broken down into a series of parts, similar to activity 1.

Polyprotic bases can accept more than one H^+. The carbonate ion is an example of a **diprotic base**, because it can accept up to two protons. Solutions of alkali metal carbonates (e.g. K_2CO_3) are quite alkaline, due to the reactions:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

D34.2 Acid-Base Reactions

Mixing a solution of an acid with a solution of a base results in an acid-base neutralization reaction that produces a salt and water. The thermodynamics of an acid-base reaction dictates that the side with the weaker acid and weaker base is favored. In other words, if the weaker acid and weaker base are on the left side of an equilibrium reaction, the reaction is reactant-favored at equilibrium; if the weaker acid and weaker base are on the right side, the reaction is product-favored at equilibrium. Strengths of acids and bases are quantitatively comparable by their K_a and K_b values, which can be obtained from a reference table.

A strong acid reacts with a strong base to form a neutral solution (containing equal concentrations of H_3O^+ and OH^-) provided that *stoichiometrically equivalent quantities* of acid and base are mixed. For example:×

$$HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$$

The salt formed, NaCl(aq), consists of $Na^+(aq)$ and $Cl^-(aq)$, each of which has negligible acid or base strength. Hence, this equilibrium heavily favors the product side and goes essentially to completion. (Note that any soluble salt consists of aqueous ions, so the formula NaCl(aq) represents an aqueous solution consisting of the same number of $Na^+(aq)$ and $Cl^-(aq)$ ions.) If the mixture has an excess of one of the reactants, then the concentration of leftover acid (HCl) or base (NaOH) determines the pH of the solution.

A weak acid reacts with a strong base to form a salt that contains the conjugate base of the weak acid, which is usually a weak base. For example, the reaction of acetic acid with sodium hydroxide forms sodium acetate:

$$CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3COONa(aq) + H_2O(l)$$

The equilibrium of this reaction favors the product side, and the reaction can be approximated as going to completion. Mixing stoichiometrically equivalent amounts of reactants gives a solution containing $Na^+(aq)$, which has no effect on the pH of the solution, and $CH_3COO^-(aq)$, the conjugate base of acetic acid. Because the acetate anion is a weak base, the solution pH is >7 after acetic acid reacts stoichiometrically with a strong base. The weak-base reaction is:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

The equilibrium constant for this reaction is the ionization constant, K_b, for the acetate anion. (Some reference tables only report ionization constants for acids; K_b can be calculated from K_w and K_a of the conjugate acid—acetic acid in this case.) Generalizing this example, when a strong base reacts stoichiometrically with a weak acid, the solution that results is basic.

A strong acid reacting with a weak base forms a salt containing the conjugate acid of the weak base, which is usually a weak acid. For example, the reaction of HCl with ammonia forms ammonium chloride:

$$NH_3(aq) + HCl(aq) \rightleftharpoons NH_4Cl(aq)$$

The equilibrium of this reaction favors the product side, and the reaction can be approximated as going to completion. Mixing stoichiometrically equivalent amounts of reactants gives a solution that contains $Cl^-(aq)$, which is the conjugate base of a strong acid and has no effect on the pH of the solution, and $NH_4^+(aq)$, the conjugate acid of ammonia. Because the ammonium ion is a weak acid, the solution pH would be <7 after ammonia reacts stoichiometrically with a strong acid. The reaction is:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

The equilibrium constant for this reaction is the ionization constant, K_a, for the acid NH_4^+. Generalizing this example, when a weak base reacts stoichiometrically with a strong acid, the solution that results is acidic.

Activity 2: pH of an Ammonium Salt

To predict the pH of a solution resulting from the reaction between **a weak acid and a weak base**, we must know both the K_a of the weak acid and the K_b of the weak base. If $K_a > K_b$, the solution is acidic; if $K_b > K_a$, the solution is basic.

D34.3 Reaction Between Amphiprotic Species

Acid-base reactions can also occur between two amphiprotic species. For example, mixing a solution containing hydrogen sulfate ions (HSO_4^-) and a solution containing hydrogen carbonate ions (HCO_3^-) results in an acid-base reaction. However, if both reactants can act as either an acid or a base, which reactant is the acid and which is the base? In the example mixture, there are two possibilities:

$$\text{possibility I: } HSO_4^-(aq) + HCO_3^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2CO_3(aq)$$

$$\text{possibility II: } HSO_4^-(aq) + HCO_3^-(aq) \rightleftharpoons H_2SO_4(aq) + CO_3^{2-}(aq)$$

Qualitatively, a product-favored acid-base reaction involves a stronger acid reacting with a stronger base to form a weaker acid and a weaker base. Acid and base strengths are comparable by K_a and K_b values.

In possibility I the acids are HSO_4^- ($K_a = 1.1 \times 10^{-2}$) and H_2CO_3 ($K_a = 4.3 \times 10^{-7}$) and the bases are HCO_3^- ($K_b = 2.3 \times 10^{-8}$) and SO_4^{2-} ($K_b = 9.1 \times 10^{-13}$). The stronger acid and the stronger base are on the left side of the equation so this reaction is product-favored.

On the other hand, possibility II is reactant-favored because it produces H_2SO_4, a strong acid, and CO_3^{2-}, a weak base with a relatively large $K_b = 2.1 \times 10^{-4}$ (significantly larger than the K_b for HSO_4^-).

Quantitatively, we can make use of the ionization constants to determine which reaction occurs. In possibility I,

$$HSO_4^-(aq) + \cancel{H_2O(l)} \rightleftharpoons SO_4^{2-}(aq) + \cancel{H_3O^+(aq)}$$

$$K_1 = K_{a,\ HSO_4^-} = 1.1 \times 10^{-2}$$

$$HCO_3^-(aq) + \cancel{H_3O^+(aq)} \rightleftharpoons H_2CO_3(aq) + \cancel{H_2O(l)}$$

$$K_2 = \frac{1}{K_{a,\ H_2CO_3}} = \frac{1}{4.3 \times 10^{-7}}$$

The sum of these two equilibria gives the overall reaction for possibility I: $HSO_4^-(aq) + HCO_3^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2CO_3(aq)$, and the total equilibrium constant is:

$$K_{\text{total, possibility I}} = K_1 \times K_2 = \frac{1.1 \times 10^{-2}}{4.3 \times 10^{-7}} = 2.6 \times 10^4$$

Clearly possibility I is product-favored at equilibrium because the equilibrium constant is much greater than 1.

In possibility II,

$$HSO_4^-(aq) + \cancel{H_3O^+(aq)} \rightleftharpoons H_2CO_3(aq) + \cancel{H_2O(l)}$$

$$K_1 = \frac{1}{K_{a,\ H_2SO_4}} \leq \frac{1}{20}$$

$$HCO_3^-(aq) + \cancel{H_2O(l)} \rightleftharpoons CO_3^{2-}(aq) + \cancel{H_3O^+(aq)}$$

$$K_2 = K_{a,\ HCO_3^-} = 4.7 \times 10^{-11}$$

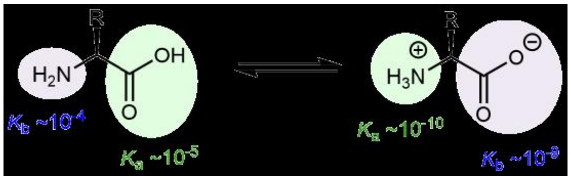
(K_a for H_2SO_4 is too large to measure in aqueous solution but is greater than K_a for HNO_3, which is ≅20, so the value 20 is a minimum for K_a for H_2SO_4.) The sum of these two equilibria gives the overall reaction for possibility II: $HSO_4^-(aq) + HCO_3^-(aq) \rightleftharpoons H_2SO_4(aq) + CO_3^{2-}(aq)$, and the total equilibrium constant is:

$$K_{\text{total, possibility II}} = K_1 \times K_2 = \frac{4.7 \times 10^{-11}}{20} = 2 \times 10^{-12}$$

Possibility II is heavily reactant-favored at equilibrium. Therefore, of the two possibilities, the reaction that proceeds (and produces products) is possibility I, where HSO_4^- acts as an acid and HCO_3^- acts as a base.

D34.4 Amino Acids

Amino acids are amphiprotic because each amino acid molecule contains a carboxylic acid group that can donate a proton and an amine group that can accept a proton. Carboxylic acids are moderately acidic, many with K_a of ~10^{-5}. Organic amines are somewhat basic, many with K_b of ~10^{-4}. This combination creates an interesting situation, where an acid-base reaction is possible within a single amino acid molecule:



The carboxylic acid group, with K_a = ~10^{-5}, is a stronger acid than the protonated amine group, with $K_a = K_w/K_b$(amine) = $10^{-14}/10^{-4}$ = ~10^{-10}. The amine group (K_b = ~10^{-4}) is a stronger base than the carboxylate anion (K_b = ~10^{-9}). The stronger acid and stronger base are on the left side so this reaction is product-favored at pH = ~7. Hence, at the pH of a typical living organism, the amino acid is a **zwitterion** (German for "double ion"). A zwitterion is a species with no overall electrical charge but with separate parts that are positively and negatively charged.

The formation of a zwitterion is analogous to the acid-base reaction between methylamine ($K_b = 4.4 \times 10^{-4}$) and acetic acid ($K_a = 1.8 \times 10^{-5}$):

$$CH_3NH_2(aq) + CH_3COOH(aq) \rightleftharpoons CH_3NH_3^+(aq) + CH_3COO^-(aq)$$

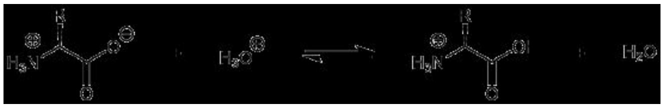
where the equilibrium favors products because:

$$K_{total} = \frac{1.8 \times 10^{-5}}{2.3 \times 10^{-11}} = 7.8 \times 10^5$$

Increasing the pH of an amino acid solution by adding hydroxide ions can remove the hydrogen ion from the -NH_3^+ group:

The product molecule is no longer a zwitterion. Instead, it is an anion with an overall charge of -1.

Similarly, decreasing the pH by adding strong acid to an amino acid solution protonates the -COO^- part of the zwitterion:



Again, the product molecule is not a zwitterion, but a cation with an overall charge of +1.

Podia Question

Write a clear, concise explanation in scientifically appropriate language for each of these correct statements.

1. When a polyprotic acid donates a hydrogen ion, the species that remains is usually a much weaker acid than was the original polyprotic acid.

2. When trichloroacetic acid reacts with hydrogen carbonate ion the equilibrium is significantly more product-favored than when acetic acid reacts with hydrogen carbonate ion.

3. When a strong base reacts with a weak acid in stoichiometrically equivalent quantity, the pH of the solution is above 7.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

CHAPTER OVERVIEW

5: Unit Five

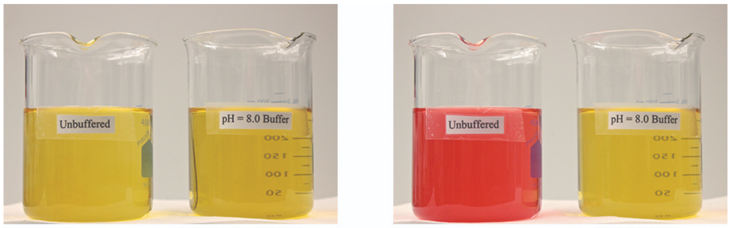
5.1: Day 36- Buffer Solutions

32

Day 36: Buffer Solutions

D36.1 Buffer Solutions

A mixture of a weak acid and its conjugate base, such as acetic acid and sodium acetate ($CH_3COOH + CH_3COONa$), or a mixture of a weak base and its conjugate acid, such as ammonia and ammonium chloride ($NH_3 + NH_4Cl$), is a buffer solution. A **buffer solution** *resists changes in pH when small amounts of a strong acid or a strong base are added* (Figure 1).



(a) (b)

Figure 1. *(a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8), showing the yellow color of the indicator methyl orange. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution pH has not changed detectably. The unbuffered solution has become acidic, as indicated by the red color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)*

A solution of equal concentrations of CH_3COOH and CH_3COONa is slightly acidic because the $K_{a,\text{acetic acid}} > K_{b,\text{ acetate anion}}$. When a strong base, such as NaOH, is added to this solution, the OH^- anions react with the few H_3O^+ cations, decreasing concentrations of H_3O^+. This shifts the following equilibrium to the right:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

restoring H_3O^+ concentration to almost the value it had before the NaOH was added. The net effect of most of the added NaOH is to convert some of the weak acid, CH_3COOH, to a weak base, CH_3COO^-:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

Hence, there is only a minimal decrease in H_3O^+ concentration.

When a strong acid, such as HCl, is added, the net effect of most of the added H_3O^+ is to convert acetate anions to acetic acid molecules:

$$CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$

And again, there is only a minimal increase in H_3O^+ concentration.

As illustrated in Figure 2, a buffer solution can moderate changes to pH because it consists of a weak acid that can react with added strong base as well as a weak base that can react with added strong acid.

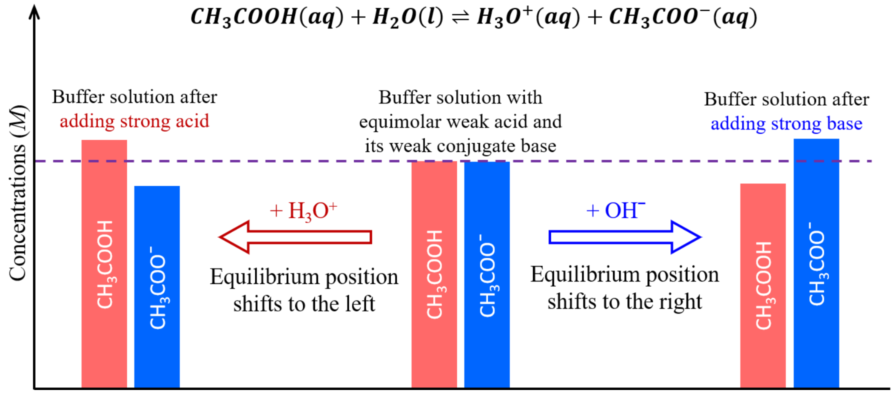


Figure 2. *When a strong acid (producing H_3O^+) is added to a buffer solution, the weak base is converted to its weak conjugate acid. When a strong base (producing OH^-) is added to a buffer solution, the weak acid is converted to its weak conjugate base.*

The weak base and weak acid in a buffer solution are typically a conjugate acid-base pair, which maintains one dynamic equilibrium that responds to additions of other acids and bases. If they are not a conjugate acid-base pair, then there would be two dynamic equilibria at play, which significantly complicates the buffering actions.

Activity 1: pH of a Buffer Solution

D36.2 Henderson-Hasselbalch Equation

The ionization constant expression for a weak acid HA is:

$$K_a = \frac{[\mathrm{H_3O^+}]_e[\mathrm{A^-}]_e}{[\mathrm{HA}]_e}$$

Rearranging gives:

$$[\mathrm{H_3O^+}]_e = K_a \times \frac{[\mathrm{HA}]_e}{[\mathrm{A^-}]_e}$$

Taking the negative logarithm of both sides, we have:

$$\begin{aligned} -\log[\mathrm{H_3O^+}]_e &= -\log K_a - \log\frac{[\mathrm{HA}]_e}{[\mathrm{A^-}]_e} \\ \mathrm{pH} &= \mathrm{p}K_a - \log\frac{[\mathrm{HA}]_e}{[\mathrm{A^-}]_e} \\ \mathrm{pH} &= \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]_e}{[\mathrm{HA}]_e} \end{aligned}$$

It is much more convenient to deal with the initial concentrations of the weak acid and weak base when preparing a buffer solution. (The initial concentration is the amount of weak acid and weak base added to the solution mixture divide by the volume.) Therefore:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]_0 + x}{[\mathrm{HA}]_0 - x}$$

“x” is the increase in concentration of H_3O^+ as the solution reaches equilibrium (see activity 1 above) and $[HA]_0$ and $[A^-]_0$ are the concentration of HA and A^- before any reaction occurs. When the approximation that x is at least 100 times smaller than the concentrations of HA and A^- is valid, we have the **Henderson-Hasselbalch equation**:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]_0}{[\mathrm{HA}]_0}$$

Note that when $[A-]_0 = [HA]_0$, pH = $\mathrm{p}K_\mathrm{a}$ + log(1) = $\mathrm{p}K_\mathrm{a}$.

The Henderson-Hasselbalch equation can be used to calculate the buffer solution pH, given the K_a and the initial concentrations, or it can be used to determine the ratio of initial concentrations of weak acid and base required to achieve a desired pH.

The Henderson-Hasselbalch equation applies only to buffer solutions in which the ratio

$$\frac{[\mathrm{A^-}]_0}{[\mathrm{HA_0}]}$$

is between 0.1 and 10. If enough strong acid or strong base is added to the buffer solution to exceed this range, the pH begins to change significantly (in other words, the solution is no longer a buffer solution).

D36.3 Selection of a Suitable Buffer

A buffer solution moderates changes in pH because it contains both a weak acid that can react with added strong base and a weak base that can react with added strong acid. This leads to several criteria for selecting a suitable buffer solution for a given purpose.

1. *The pK_a of the weak acid in the buffer should be close to the desired pH of the buffer solution.* According to the Henderson-Hasselbalch equation, if the concentrations of weak acid and weak base are equal, the pH of the buffer solution equals the pK_a of the weak acid involved.
2. *A buffer solution should have approximately equal concentrations of the weak acid and weak base.* A

$$\frac{[\text{A}^-]_0}{[\text{HA}_0]}$$

ratio of >10 or <0.1 makes for a poor buffer solution. Figure 3 shows how the pH of an acetic acid-acetate ion buffer increases as strong base is added. The initial pH is pK_a = 4.74. When pH reaches 5.74, a change of 1 pH unit, the ratio

$$\frac{[\text{acetic acid}]}{[\text{acetate anion}]} = 0.11 = 11\%$$

After that the pH increases more rapidly and the solution no longer provides significant buffering.

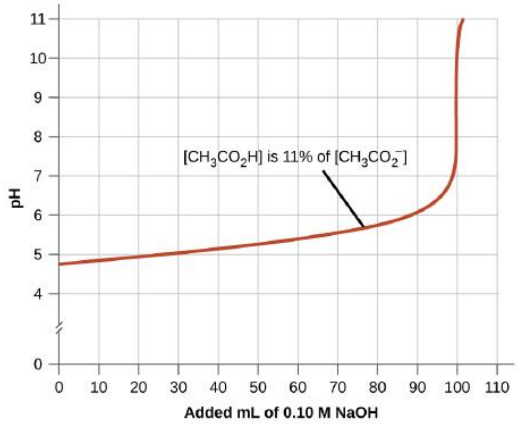


Figure 3. *The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, [CH_3COOH] = [CH_3COO^-] = 0.10 M.*

1. *The larger the amounts (mol) of weak acid and weak base are the greater is the amount (mol) of strong base or strong acid that can be added before there is a significant change in pH .*

When designing a buffer system, look for weak conjugate acid-base pairs that have pK$_\text{a}$ of the weak acid near the desired pH. Then adjust the ratio of the weak base to weak acid concentrations to achieve the exact pH desired. Make certain that the concentrations of weak base and weak acid are large enough to react with the quantities of acid or base that might be added to the buffer solution.

Activity 2: Preparing a Buffer Solution with a Desired pH

D36.4 Buffer Capacity

We can see how a buffer solution works by comparing quantitatively the pH of a buffered solution with the pH of a unbuffered solution upon addition of a strong acid or base.

Activity 3: Calculating pH Change for a Buffer Solution

Activity 4: pH Change in an Unbuffered Solution

We can see from the above activities that the change in pH is much more significant in the unbuffered solution compared to the buffered solution.

However, buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 4). For example, if we add sufficient strong base to a buffer that all the weak acid has reacted, no more buffering action toward the base is possible. Similarly, if we add an excess of strong acid, the weak base would all be reacted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to react away all the weak acid or base in a buffer to make significant change in pH: buffering action diminishes rapidly as a given component nears depletion. This was seen in Figure 3 in the above section, where reducing the concentration of weak acid to 11% of the concentration of weak base caused a change of 1 pH unit. The curve in Figure 3 goes up rapidly after that, indicating that the buffer has been “broken” and no longer resists changes in pH.

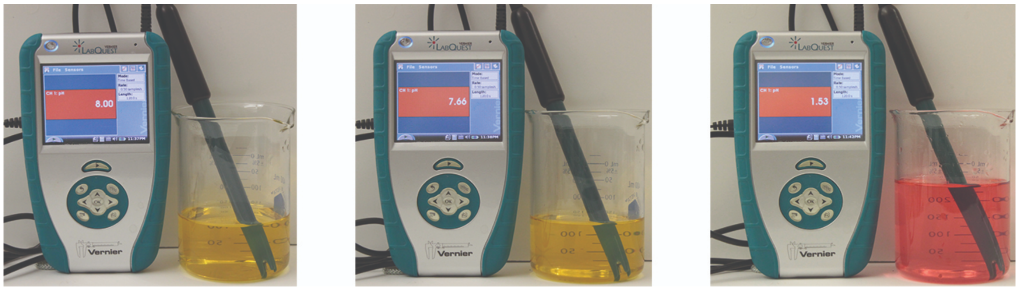


Figure 4. Adding acid to a buffer solution. *The color of the indicator (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little effect on the pH of the buffer (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)*

The **buffer capacity** is *the amount (mol) of acid or base that can be added to a given volume of a buffer solution before the pH changes by ±1 from the pK_a of the weak acid.* (Recall that if equal concentrations of weak acid and conjugate base are in a buffer solution, pH = pK_a.)

Buffer capacity depends on the amount (mol) of weak acid and its conjugate base that are in a buffer mixture. For example, a 1 L solution of 1.0 *M* CH_3COOH and 1.0 *M* CH_3COONa has a greater buffer capacity than a 1 L solution of 0.10 *M* CH_3COOH and 0.10 *M* CH_3COONa, even though both solutions have the same pH. The first solution has more buffer capacity because it contains more moles of acetic acid and acetate ion.

It takes 0.82 mol HCl to change the buffer pH from 4.74 to 3.74 in the first solution:

$$\begin{aligned}
3.74 &= 4.74 + \log\frac{[\mathrm{CH_3COO^-}]_0}{[\mathrm{CH_3COOH}]_0} \\
10^{3.74-4.74} &= \frac{[\mathrm{CH_3COO^-}]_0}{[\mathrm{CH_3COOH}]_0} \\
0.10 &= \frac{(1.0\ \mathrm{mol} - x)/(1\ \mathrm{L})}{(1.0\ \mathrm{mol} + x)/(1\ \mathrm{L})} \\
0.10(1.0\ \mathrm{mol} + x) &= 1.0\ \mathrm{mol} - x \\
1.1x &= 0.90 \\
x &= 0.82\ \mathrm{mol}
\end{aligned}$$

On the other hand, for the solution where the concentrations of weak acid and conjugate base are 0.10 M, it takes only one-tenth as much HCl, 0.082 mol HCl, to change the buffer pH from 4.74 to 3.74:

$$\frac{[\mathrm{CH_3COO^-}]_0}{[\mathrm{CH_3COOH}]_0} = 10^{-1} = 0.1 = \frac{0.1\ \mathrm{mol} - x}{0.1\ \mathrm{mol} + x} \qquad x = 0.082\ \mathrm{mol}$$

If a buffer solution does not have equal concentrations of weak acid and weak base, the buffer capacity when strong acid is added is different from the buffer capacity when strong base is added.

Podia Question

A solution is prepared by adding 50.0 mL 0.50-M acetic acid and 50.0 mL 0.30-M NaOH to a beaker and stirring. Is this solution a buffer solution? If so, calculate the pH of the buffer. If not, explain why the solution does not resist change in pH when 1.0 mL 0.5-M HCl is added.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day’s material. We appreciate your comments.

5.2: Day 37- Acid-Base Titration

33

Day 37: Acid-Base Titration

D37.1 Titration

At this point, you have already carried out several titration experiments in lab. In a **titration**, *one solution is added to a second solution in a way that allows the quantity of each solution to be measured accurately*. Typically, one solution is added from a **buret**, *a calibrated glass tube with a stopcock at the bottom*. The buret allows additions of very small increments of volume of solution and determination of the total volume added. The *solution added from the buret* is the **titrant.** Titrant is added to a carefully measured volume of a second solution in a flask or beaker.

A chemical reaction occurs between solutes in the two solutions, and w*hen just enough titrant has been added for complete reaction with the second solution*, the **equivalence point** of the titration has been reached. From the balanced chemical equation for the titration reaction, the volume of each solution at the equivalence point, and the concentration of one of the two solutions, the concentration of the other solution can be determined.

The equivalence point of a titration may be detected visually if there is a color change that accompanies the completion of the reaction. Typically, a special dye called an **indicator** is *added to the solution being titrated to provide a color change at or very near the equivalence point*. Equivalence points may also be detected by measuring a solution property that changes in a predictable way during the course of the titration, such as pH.

Regardless of the approach taken to detect a titration's equivalence point, *the measured total volume of titrant added* is called the **end point**. A properly designed titration typically ensure that the difference between the equivalence point and the end point is negligible.

Although any type of chemical reaction may serve as the basis for a titration analysis, precipitation, acid-base, and oxidation-reduction titrations are most common.

D37.2 Titration Curves

Titration is effective in quantitatively analyzing a solution's acid (or base) concentration because pH changes rapidly near the equivalence point. In other words, there is a large observable change accompanying a small addition of titrant, which minimizes experimental uncertainty. For example, an acid-base indicator generally changes color over a range of about 2 pH units, so if pH increases (or decreases) by 2 or more pH units when 0.01 mL of titrant is added at the equivalence point, the color change would effectively signal the end point of the titration.

Figure 1 shows a **titration curve**, *a graph of pH as a function of volume of titrant*, for the titration of a 50.00-mL sample of 0.100-M hydrochloric acid with 0.100-M sodium hydroxide.

Figure 1. *Titration curve for the titration of 50.00 mL of 0.100-M HCl (strong acid) with 0.100-M NaOH (strong base) has the equivalence point at pH = 7.00. Click on "i" for more information.*

Now consider the titration of 50.00 mL of 0.100-*M* acetic acid (a weak acid) with 0.100-*M* sodium hydroxide (Figure 2). Comparing Figure 2 to Figure 1, we see that although the initial volumes and concentrations of the acids (acetic acid vs. HCl) are the same, the pH for acetic acid begins at a higher value and the titration curve maintains higher pH values up to the equivalence point. This is because, unlike HCl, acetic acid is only partially ionized.

Figure 2. *Titration curve for the titration of 50.00 mL of 0.100-M CH_3COOH (weak acid) with 0.100-M NaOH (strong base) has an equivalence point at pH = 8.72. Move the slider to the right for overlay of Figure 1 and Figure 2 titration curves.*

The pH at the equivalence point is also higher (8.72 rather than 7.00) due to the presence of acetate anion, a weak base that raises the pH:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

After the equivalence point, the two curves (Figure 1 and Figure 2) are identical because the pH depends on the excess hydroxide ion from NaOH added in both cases.

Activity 1: Titration Equivalence Point

The **midpoint** of a titration is when we have *added half the volume of titrant needed to reach the equivalence point*. As part (b) in the above exercise shows, when titrating a weak acid with a strong base, the pH of the solution equals the pK_a of the weak acid at the midpoint because we have added half the amount of strong base needed to react with all the weak acid. Therefore, according to the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{weak base}]_0}{[\text{weak acid}]_0} = \text{p}K_a + \log(1) = \text{p}K_a + 0 = \text{p}K_a$$

Activity 2: Titration of a Weak Base with a Strong Acid

D37.3 Acid-Base Indicators

Acid-base indicators are *substances with intense colors that change color when [H_3O^+] reaches a particular value*. Acid-base indicators are either weak organic acids or weak organic bases and can be used to determine the pH of a solution. For example, phenolphthalein is colorless in an aqueous solution with pH < 8.3 ([H_3O^+] > 5.0 × 10^{-9}*M*), and turns red or pink when pH > 8.3.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use “HIn” as a simple representation for the complex methyl orange molecule:

$$\begin{array}{ccccccc} \text{HIn}(aq) & + & \text{H}_2\text{O}(l) & \leftrightharpoons & \text{H}_3\text{O}^+(aq) & + & \text{In}^-(aq) \\ \text{red} & & & & & & \text{yellow} \end{array}$$

$$K_\text{a} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = 4.0 \times 10^{-4}$$

When we add acid to a solution of methyl orange, the increased [H_3O^+] shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier’s principle. If we add base, the equilibrium shifts towards the anionic yellow form. The overall color of the solution is the visible result of the ratio of the concentrations of the two species, In^- and HIn. If most of the indicator is present as In^-, then we see the color yellow. If most is present as HIn, then we see the color red. We can rearrange the equation for K_a and write:

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_\text{a}}{[\text{H}_3\text{O}^+]}$$

When [H_3O^+] = $K_{a,HIn}$, 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 color. When [H_3O^+] increases to 8 × 10^{-4} *M* (pH = 3.1), the solution turns red. No change in color is visible for further increase in [H_3O^+]. When [H_3O^+] decreases to 4 × 10^{-5} *M* (pH = 4.4), most of the indicator is in the yellow ionic form, and further decrease in [H_3O^+] does not produce a visible color change. The pH range of 3.1 – 4.4 is the **color-change interval** of methyl orange, *the range of pH values over which the color change takes place*.

There are many different acid-base indicators. Their color changes have a wide range of pH values (Figure 3). Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pH values.

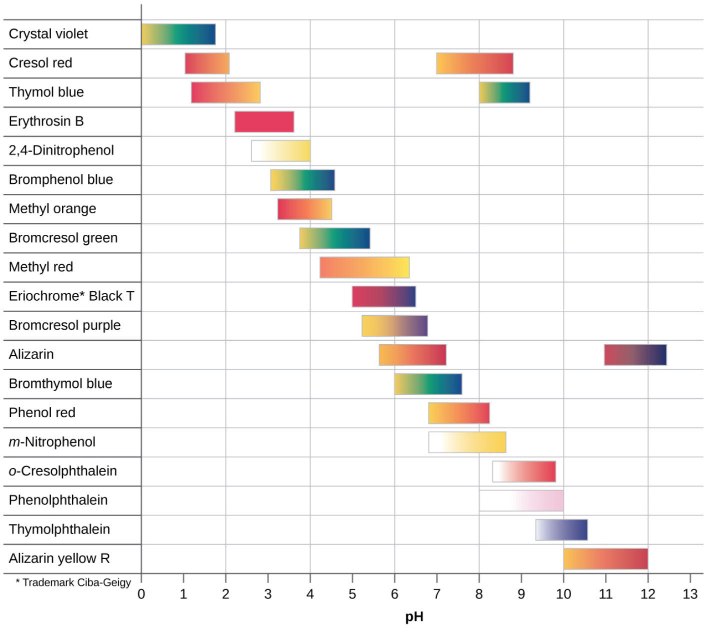


Figure 3. *This chart illustrates the ranges of color change for several acid-base indicators.*

Titration curves can help us select an indicator that will provide a sharp color change at the equivalence point. The best selection is an indicator with a color change interval that brackets the pH at the equivalence point of the titration. (We can also base our choice of indicator on the calculated pH at the equivalence point.)

The color change intervals of three indicators are shown in Figure 4. The steep section of the titration curves of both the titration of HCl and of CH_3COOH are located in the color-change interval of phenolphthalein. We can use it for titrations of either acid.

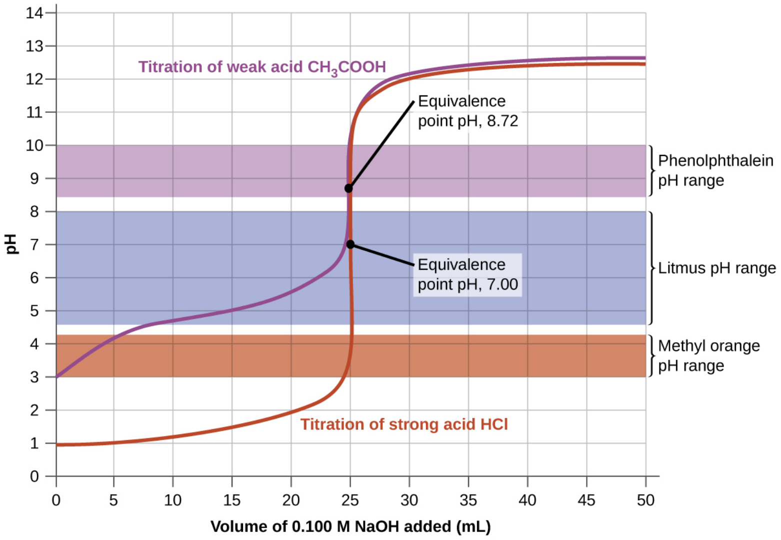


Figure 4. *The graph shows a titration curve for the titration of 25.00 mL of 0.100 M* CH_3COOH *(weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.*

Litmus is a suitable indicator for the HCl titration. However, we should not use it for the CH_3COOH titration because the pH is within the color-change interval of litmus when only 8 mL of NaOH has been added, and it does not leave the range until 25 mL has been added. The color change would be very gradual, taking place during the addition of 17 mL of NaOH, making litmus useless as an indicator of the equivalence point.

We can use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color during the addition of 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein. Methyl orange would be completely useless as an indicator for the CH_3COOH titration. Its color change is completed long before the equivalence point is reached and hence provides no indication of the equivalence point.

D37.4 Titration of Polyprotic Acids and Bases

When a polyprotic acid is titrated, there are usually multiple equivalence points. For example, when H_2SO_3 is titrated with NaOH, there are two equivalence points corresponding to the two acidic protons from the H_2SO_3 molecule. There are also as many midpoints as there are equivalence points.

When a strong monoprotic base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic proton ($K_{a,1}$) is titrated first, followed by the next most acidic ($K_{a,2}$), and so forth. If the K_a values differ by at least three orders of magnitude, then the overall titration curve will show well-resolved “steps” corresponding to the titration of each acidic proton.

Consider the titration of a generic weak polyprotic acid H_3A with NaOH as shown in Figure 5. The first equivalence point correspond to the point where 1 mole of NaOH has been added per mole of H_3A in the solution being titrated. As more titrant is added, the titration curve crosses another midpoint and reaches the second equivalence point, corresponding to a total of 2 moles of NaOH being added per mole of H_3A in the solution. The titration is finally complete when all three equivalence points have been reached.

Figure 5: *Titration of a weak polyprotic acid by a strong base. Move the slider to see the different stages of titration. .*

It is not always possible to detect all of the equivalence points in the titration of a polyprotic acid. An actual titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 6. It shows two well-defined steps: the first midpoint corresponds to p$K_{a,1}$, and the second midpoint corresponds to p$K_{a,2.}$ Because HPO_4^{2-} is such a weak acid, p$K_{a,3}$ has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

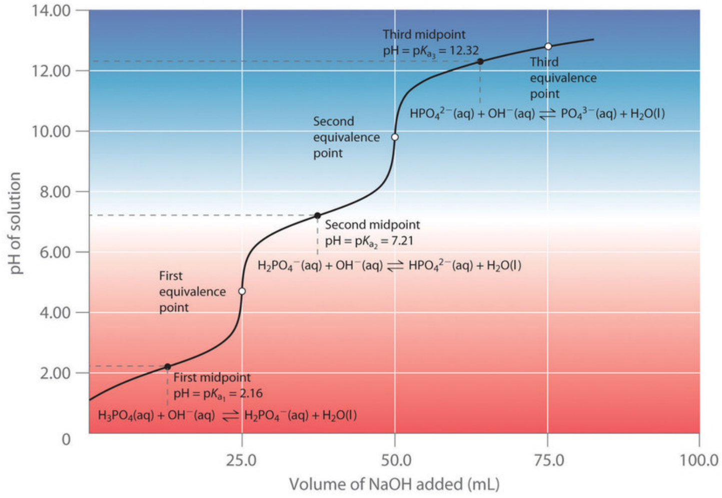


Figure 6*: Titration Curve for Phosphoric Acid. The curve for the titration of 25.0 mL of 0.100-M H_3PO_4 solution with 0.100-M NaOH. Species in solution at each midpoint are shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^-$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (This is because the maximum pH that can be achieved with 0.100-M NaOH is 13.)*

The titration curve for the reaction of a polyprotic base with a strong acid is inverted on the pH scale. The initial pH is high; as acid is added, the pH decreases in steps if the successive pK_b values are well separated.

Podia Question

Draw the structure of the amino acid alanine at pH = 2.

Sketch a titration curve for titration of a solution of alanine starting at pH = 2 and ending at pH = 13. The concentration of alanine is 0.100 M and there is 25.00 mL initially, at pH = 2. This solution is titrated with 0.100-M NaOH. pK_a values for alanine are 2.85 and 9.87. No calculations are required, but the curve should be as accurate as possible.

There are two equivalence points and two midpoints in this titration. Label each midpoint with the volume and pH. Explain how you determined the pH at each midpoint.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day’s material. We appreciate your comments.

5.3: Day 38- Oxidation-Reduction Reactions, Voltaic Cells

34

Day 38: Oxidation-Reduction Reactions, Voltaic Cells

D38.1 Oxidation-reduction Reactions and Electrochemistry

Electrochemistry deals with *chemical reactions that involve transfer of electron density*; in other words, the reactions either produce electricity or are caused by passage of electrical current through matter. These reactions are called **oxidation-reduction** (abbreviated **redox**) reactions.

Here's a brief list of units and definitions used when discussing redox reactions and their applications.

- The *SI unit of electric charge* is the **coulomb**, **C**.
  - The elementary unit of charge is the charge of a single electron, which is equal to 1.602×10^{-19} C.
- Movement of electrons (or ions) carries electric charges from one place to another, and *the quantity of such charge transferred per unit time* is the electric **current**.
  - Current has the SI unit **ampere**, **A**, which is the *transfer of one coulomb per second* (1 A = 1 C/s).
- Typically, *electric current flows in a closed path*, called an electric **circuit**.
  - It is necessary to maintain a closed circuit for current to flow. If the circuit is open, current will not flow.
- **Electrical potential**, SI unit **volt**, **V**, is *the ability of an electric field to do work on a charge*.
  - A flow of charge is caused by an electrical potential *difference* between two points in the circuit.
- When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule of energy (1 J = 1 C × 1 V).
- **Electric power** is *the quantity of energy transferred per unit time* and is measured in **watts, W** (1 W = 1 J / 1 s).

D38.2 Redox Reactions and Oxidation Number

Some redox reactions involve transfer of electrons between reactant atoms to yield ionic products. For example, formation of a crystal lattice of sodium chloride (a lattice of Na^+ ions and Cl^- ions) requires transfer of electrons from sodium atoms to chlorine atoms:

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

It is useful to consider the electron transfer as two concurrent processes. The processes are called **half-reactions**, *one in which electrons are lost and one in which electrons are gained*. The half-reactions for reaction of sodium with chlorine are:

$2Na(s)$	$\longrightarrow$	$2Na^+(s) + 2e^-$
$Cl_2(g) + 2e^-$	$\longrightarrow$	$2Cl^-(s)$

The half-reactions allow us to see that the number of electrons lost equals the number of electrons gained—we cannot create or destroy electrons in a chemical reaction. The half-reactions also show which species gains electrons (Cl atoms in Cl_2) and which species loses electrons (Na atoms). The species that loses electrons is said to be oxidized and the *loss of electrons* is called **oxidation**; the species that gains electrons is said to be reduced and the *gain of electrons* is called **reduction**.

The *species that causes reduction to occur* is called the **reducing agent** (or **reductant**). In this reaction sodium is the reducing agent because it causes Cl_2 to gain electrons. The *species that causes oxidation to occur* is called the **oxidizing agent** (or **oxidant**). In this reaction chlorine functions as an oxidant, causing sodium to lose electrons.

Some redox processes do not involve obvious transfer of electrons because no ions are involved in the reaction. For example:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

To systematically classify redox reactions of all types, we define **oxidation number** (or **oxidation state**) of an element in a compound as *the charge its atoms would possess if the compound was ionic, that is, if all electrons in each polar covalent bond were assigned to the more electronegative atom*.

The steps below can be used to assign oxidation numbers to each element in a compound.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monoatomic ion is equal to the ion's charge.
3. The sum of oxidation numbers over all atoms in a neutral compound is zero.
4. The sum of the oxidation numbers over all atoms in a polyatomic ion equals the ion's charge. If a compound includes more than one polyatomic ion, the oxidation number of an atom in one ion can differ from the oxidation number in the other polyatomic ion.
5. Atoms of some elements have the same oxidation number in almost all compounds.
    a. Fluorine always has oxidation number −1 when present in a compound
    b. Atoms of alkali metals (Li, Na, K, Rb, Cs) have oxidation number +1 in nearly all compounds
    c. Atoms of alkaline earth metals (Be, Mg, Ca, Sr, Ba) have oxidation number +2 in nearly all compounds
    d. Hydrogen has oxidation number +1 when combined with nonmetals, −1 when combined with metals
6. Apply these two rules only if rules 1-5 have not determined all oxidation numbers.
    a. Oxygen has oxidation number −2 unless rules 1-5 have already given O a different oxidation number
    b. In binary compounds of nonmetals, the more electronegative element is given a negative oxidation number equal to the charge on its monoatomic ion; for example in PCl_3, the more electronegative Cl is assigned oxidation number −1 and P is assigned +3 (by rule 3).

Activity 1

Using oxidation numbers we can identify redox reactions by looking for one or more elements whose oxidation numbers change during the course of the reaction. *When its oxidation number increases, an element has been oxidized; when its oxidation number decreases, the element has been reduced.*

In this reaction

$$2\ Na(s) + Cl_2(g) \longrightarrow 2\ NaCl(s)$$

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 this reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2\ HCl(g)$$

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).

Several subclasses of redox reactions can be identified. One example is combustion reactions in which the reductant (fuel) and oxidant (often, O_2) react vigorously and produce significant temperature increase, often in the form of a flame. Another class of redox reaction is a rocket propellant reaction such as this one in which solid aluminum is oxidized by ammonium perchlorate:

$$10\ Al(s) + 6\ NH_4ClO_4(s) \longrightarrow 4\ Al_2O_3(s) + 2\ AlCl_3(s) + 12\ H_2O(g) + 3\ N_2(g)$$

Exercise 4: Recognizing Oxidizing and Reducing Agents

For the reaction below, identify which species is oxidized and which is reduced, and identify the oxidizing agent and the reducing agent.

$$8\ H^+(aq) + MnO_4^-(aq) + 5\ Fe^{2+}(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

[Enter your answers without subscripts, superscripts, or states, and put charges in parentheses. For example, $SO_4^{2-}(aq)$ would be entered as SO4(2-).]

D38.3 Balancing Redox Reactions

Redox reactions frequently occur in aqueous solutions, which can be acidic, basic, or neutral. Moreover, H_2O molecules may actively participate in the reaction, and depending on the conditions, H_3O^+ (present under acidic conditions) and OH^- (present under basic conditions) may also be a reactant or a product.

Half-reactions make it easier to balance redox reactions because you can balance the oxidation half-reaction separately from the reduction half-reaction, and make certain that the number of electrons lost in the oxidation process equals the number of electrons gained in the reduction process.

We will balance an example redox reaction in acidic solution and one in basic solution to illustrate the process of balancing redox reactions, and highlight how the nature of the solution can play a role. (A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.)

Acidic Solution

Consider the unbalanced reaction:

$$MnO_4^-(aq) + Fe^{2+}(aq) \longrightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$$

where iron underwent oxidation because Fe^{2+} has lost an electron to become Fe^{3+}, and manganese underwent reduction because it gained five electrons to change from an oxidation state of +7 to an oxidation state of +2.

Oxidation (unbalanced):	$Fe^{2+}(aq)$	$\longrightarrow$	$Fe^{3+}(aq)$
Reduction (unbalanced):	$MnO_4^-(aq)$	$\longrightarrow$	$Mn^{2+}(aq)$

For redox reactions, it is a useful simplification to represent $H_3O^+(aq)$ as $H^+(aq)$—where there is a need for balancing O atoms, we can involve $H_2O(l)$, and then use $H^+(aq)$ to balance the H atoms.

For instance, in the above reduction half-reaction, there are four O atoms on the left side and none on the right side. To balance the elements, we can add 4 $H_2O(l)$ to the product side, and then to balance H atoms, add 8 $H^+(aq)$ to the reactant side:

$$\text{Reduction (charge not balanced): } MnO_4^-(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

Once the atoms have been balanced, we need to balance the electric charge for each half-reaction. For the oxidation half-reaction, the total charge on the left side is +2 and the total charge on the right side is +3, so charge is unbalanced. We use electrons to balance the charge. *Adding* a single electron on the right side gives a balanced oxidation half-reaction:

$$\text{Oxidation (balanced): } Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$

In oxidation half-reactions, electrons appear on the right side of the equation. Because iron is oxidized, iron is the reducing agent in this redox reaction.

You should always check that the half-reaction is balanced for the number of atoms of each element and the total charge:

Fe:	(1 atom in Fe^{2+})·(1 Fe^{2+}) = 1	$\longrightarrow$	(1 atom in Fe^{3+})·(1 Fe^{3+}) = 1	1 = 1 ✓
Charge:	1·(+2) = +2	$\longrightarrow$	1·(+3) + 1·(-1) = +2	+2 = +2 ✓

If the atoms and charges are balanced, then the half-reaction itself is balanced.

For the reduction half-reaction, we have balanced the atoms but not the charge. The total charge on the reactant-side is +7, the total charge on the product-side is +2. Therefore, it is necessary to add five electrons to the left side to achieve charge balance:

$$\text{Reduction (balanced): } MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$$

In all reduction half-reactions, electrons appear on the left side. The species that was reduced, MnO_4^-, is the oxidizing agent in this redox reaction.

Again, check that the half-reaction is balanced for the number of atoms of each element and the total charge:

Mn:	(1 atom in MnO_4^-)·(1 MnO_4^-) = 1	$\longrightarrow$	(1 atom in Mn^{2+})·(1 Mn^{2+}) = 1	1 = 1 ✓
O:	(4 atoms in MnO_4^-)·(1 MnO_4^-) = 4	$\longrightarrow$	(1 atom in H_2O)·(4 H_2O) = 4	4 = 4 ✓

H:	(1 atom in H^+)·(8 H^+) = 8	⟶	(2 atoms in H_2O)·(4 H_2O) = 8	8 = 8 ✓
Charge:	1·(-1) + 8·(+1) + 5·(-1) = +2	⟶	1·(+2) + 4·(0) = +2	+2 = +2 ✓

We now have two balanced half-reactions:

Oxidation:	$Fe^{2+}(aq)$	⟶	$Fe^{3+}(aq) + e^-$
Reduction:	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	⟶	$Mn^{2+}(aq) + 4H_2O(l)$

The key to combining the half-reactions is the electrons: the number of electrons generated by the oxidation half-reaction must equal the number of electrons consumed by the reduction half-reaction. Here, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five. Therefore, it is necessary to first multiply the oxidation half-reaction by five and the reduction half-reaction by one, then sum the resulting half-reactions:

Oxidation:	$5 \times (Fe^{2+}(aq)$	⟶	$Fe^{3+}(aq) + e^-)$
Reduction:	$MnO_4^-(aq) + 8\ H^+(aq) + 5e^-$	⟶	$Mn^{2+}(aq) + 4\ H_2O(l)$
overall:	$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq)$	⟶	$5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$

This is the overall balanced equation in acidic solution. Electrons do not appear in the overall reaction equation because all electrons lost in the oxidation half-reaction are gained in the reduction half-reaction. On each side of the overall equation there should be the same number of atoms of each element and the same total electric charge. Be sure to carefully check each side to verify everything has been balanced correctly.

Basic Solution

The simplest way to balance redox reaction in basic solution is to start with the balanced equation in acidic solution, then "convert" $H^+(aq)$ to $OH^-(aq)$ (there is an excess of OH^- ions instead of H_3O^+ ions in basic solutions). For example, when balancing the following reaction in basic solution:

$$MnO_4^-(aq) + Cr(OH)_3(s) \longrightarrow MnO_2(s) + CrO_4^{2-}(aq)$$

start by collecting the species given into unbalanced oxidation and reduction half-reactions:

Oxidation (unbalanced):	$Cr(OH)_3(s)$	⟶	$CrO_4^{2-}(aq)$
Reduction (unbalanced):	$MnO_4^-(aq)$	⟶	$MnO_2(s)$

For the oxidation half-reaction, we can add one H_2O molecule to the left side to balance oxygen atoms, and then balance hydrogen atoms with five $H^+(aq)$ on the right side (again, we do the initial balancing by assuming acidic solution):

$$\text{Oxidation (charge not balanced): } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5H^+(aq)$$

The left side of the equation has a total charge of 0, and the right side a total charge of +3. Adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{Oxidation (balanced): } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5H^+(aq) + 3e^-$$

Checking the half-reaction:

Cr:	(1 atom in $Cr(OH)_3$)·(1 $Cr(OH)_3$) = 1	⟶	(1 atom in CrO_4^{2-})·(1 CrO_4^{2-}) = 1	1 = 1 ✓
O:	(3 atoms in $Cr(OH)_3$)·(1 $Cr(OH)_3$) + (1 atom in H_2O)·(1 H_2O) = 4	⟶	(4 atoms in CrO_4^{2-})·(1 CrO_4^{2-}) = 4	4 = 4 ✓

H:	(3 atoms in $Cr(OH)_3$)·(1 $Cr(OH)_3$) + (2 atoms in H_2O)·(1 H_2O) = 5	⟶	(1 atom in H^+)·(5 H^+) = 5	5 = 5 ✓
Charge:	1·(0) + 1·(0) = 0	⟶	1·(-2) + 5·(+1) + 3·(-1) = 0	0 = 0 ✓

For the reduction half-reaction, we need two H_2O molecules on the right to balance oxygen atoms. Then to balance hydrogen atoms, we need to add four H^+(aq) on the left:

$$\text{Reduction (charge not balanced): } MnO_4^-(aq) + 4H^+(aq) \longrightarrow MnO_2(s) + 2H_2O(l)$$

Then add three electrons to the left side to balance the charge:

$$\text{Reduction (balanced): } MnO_4^-(aq) + 4H^+(aq) + 3e^- \longrightarrow MnO_2(s) + 2H_2O(l)$$

Make sure to check the half-reaction:

Mn:	(1 atom in MnO_4^-)·(1 MnO_4^-) = 1	⟶	(1 atom in MnO_2)·(1 MnO_2) = 1	1 = 1 ✓
O:	(4 atoms in MnO_4^-)·(1 MnO_4^-) = 4	⟶	(2 atoms in MnO_2)·(1 MnO_2) + (1 atom in H_2O)·(2 H_2O) = 4	4 = 4 ✓
H:	(1 atom in H^+)·(4 H^+) = 4	⟶	(2 atoms in H_2O)·(2 H_2O) = 4	4 = 4 ✓
Charge:	1·(-1) + 4·(+1) + 3·(-1) = 0	⟶	1·(0) + 2·(0) = 0	0 = 0 ✓

Collecting what we have so far:

Oxidation:	$Cr(OH)_3(s) + H_2O(l)$	⟶	$CrO_4^{2-}(aq) + 5H^+(aq) + 3e^-$
Reduction:	$MnO_4^-(aq) + 4H^+(aq) + 3e^-$	⟶	$MnO_2(s) + 2H_2O(l)$

In this case, both half-reactions involve the same number of electrons, and therefore we can simply add the two half-reactions together and simplify:

$Cr(OH)_3(s) + H_2O(l) + MnO_4^-(aq) + 4\ H^+(aq) + 3\ e^-$	⟶	$CrO_4^{2-}(aq) + 5\ H^+(aq) + 3\ e^- + MnO_2(s) + 2\ H_2O(l)$
$Cr(OH)_3(s) + MnO_4^-(aq)$	⟶	$CrO_4^{2-}(aq) + H^+(aq) + MnO_2(s) + H_2O(l)$

This is the balanced redox equation in an acidic solution. To "convert" to basic solution, add OH^-(aq) to both sides of the equation to "react" with all the H^+(aq). This converts H^+(aq) to $H_2O(l)$ on one side and adds OH^-(aq) on the other side:

$Cr(OH)_3(s) + MnO_4^-(aq) + OH^-(aq)$	⟶	$CrO_4^{2-}(aq) + H^+(aq) + OH^-(aq) + MnO_2(s) + H_2O(l)$
$Cr(OH)_3(s) + MnO_4^-(aq) + OH^-(aq)$	⟶	$CrO_4^{2-}(aq) + MnO_2(s) + 2H_2O(l)$

This is the balanced equation in basic solution. Checking each side of the equation:

Cr:	(1 atom in $Cr(OH)_3$)·(1 $Cr(OH)_3$) = 1	⟶	(1 atom in CrO_4^{2-})·(1 CrO_4^{2-}) = 1	1 = 1 ✓
Mn:	(1 atom in MnO_4^-)·(1 MnO_4^-) = 1	⟶	(1 atom in MnO_2)·(1 MnO_2) = 1	1 = 1 ✓

O:	(3 in $Cr(OH)_3$)·(1) + (4 in MnO_4^-)·(1) + (1 in OH^-)·(1) = 8	⟶	(4in CrO_4^{2-})·(1) + (2 in MnO_2)·(1) + (1 in H_2O)·(2) = 8	8 = 8 ✓
H:	(3 in $Cr(OH)_3$)·(1) + (1 in OH^-)·(1) = 4	⟶	(2 atoms in H_2O)·(2 H_2O) = 4	4 = 4 ✓
Charge:	1·(0) + 1·(-1) + 1·(-1) = -2	⟶	1·(-2) + 1·(0) + 2·(0) = -2	-2 = -2 ✓

D38.4 Introduction to Voltaic Cells

A **voltaic cell** (or **galvanic cell**) is *an electrochemical cell in which a spontaneous redox reaction produces an electric current.* Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate.

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When the copper metal contacts the silver nitrate solution, silver metal begins to form on the copper surface and Cu^{2+} ions pass into the solution (indicated by the blue-green color of the solution). The net ionic equation for the reaction is:

$$Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

which may be split into its two half-reactions that sum to the overall reaction:

Oxidation:	$Cu(s)$	⟶	$Cu^{2+}(aq) + 2\,e^-$
Reduction:	$2\,Ag^+(aq) + 2\,e^-$	⟶	$2\,Ag(s)$

The half-reactions make clear that two electrons are transferred from a copper atom, which forms a Cu^{2+} ion. Each of the two electrons is then transferred to one Ag^+ ion, which forms a silver atom. Because a flow of electrons constitutes an electric current, this electron transfer can generate an electric current if we devise a way to carry out the two half-reactions in separate vessels and connect them with a metal (electrically conductive) wire. This is in essence how a voltaic cell is designed. Figure 1 shows one way to do this.

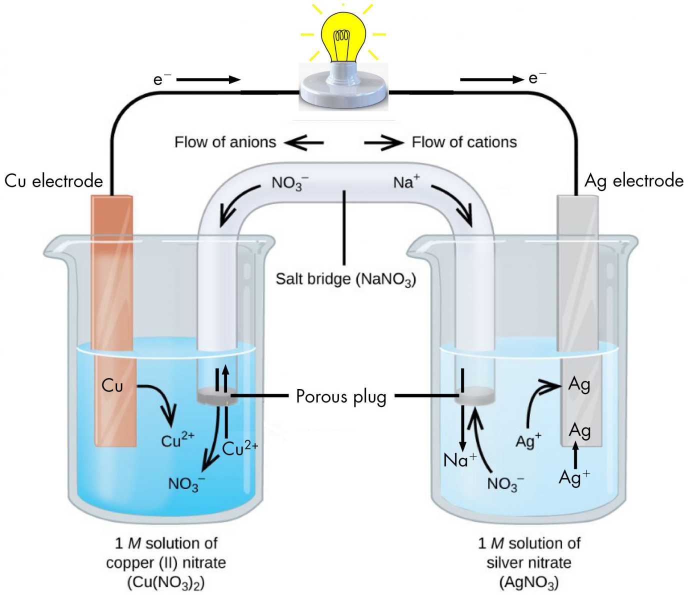


Figure 1. *In this typical voltaic cell, each half-reaction occurs in a separate beaker. Electrons generated when a copper atom becomes a Cu^{2+} ion (left beaker) flow through an external wire and combine with Ag^+ ions at the surface of the silver strip (right beaker). The flow of electrons can do electrical work, such as lighting a light bulb.*

The beaker on the left contains a 1-M solution of copper(II) nitrate [$Cu(NO_3)_2$] with a strip of copper metal partially submerged in the solution. The copper strip is an **electrode**, *a means for conducting electrons into or out of the solution*. At the surface of the copper strip, the oxidation half-reaction occurs:

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2\ e^{-}$$

The flow of electrons (electric current) passes out of the solution via the copper strip, flows through the light bulb, and moves into the silver strip in the beaker on the right. In the right-hand beaker, the reduction half-reaction occurs near the surface of the silver strip:

$$2Ag^{+}(aq) + 2\ e^{-} \longrightarrow 2Ag(s)$$

Thus, with the two half-reactions occurring in separate beakers, an electric current can be generated. *The container in which each half-reactions occurs* is called a **half-cell**.

If this were all that happened, the electric current would not flow for long. In the left-hand beaker, one Cu^{2+} ion is added to the solution for every two electrons conducted into the external wire. This means that the solution is continuously accumulating excess positive ions as the reaction occurs and an electric charge is building up. Such a charge build up would prevent further oxidation reaction from occurring. This can be mitigated if some positive ions move out of the beaker or some negative ions move into the beaker. A similar issue is occurring in the right-hand beaker, where Ag^{+} ions are being removed from the solution. Balancing total ionic charges requires either negative ions move out of the right-hand solution or positive ions move in.

This balancing of ion charges in the two separated half-reactions is maintained by the **salt bridge**, *a solution of a salt that does not mix with either half-cell solution but allows ions to pass into or out of the half-cells*. By allowing ions to conduct charge into or out of the half-cells, the salt bridge completes the electrical circuit involving the two half-cells. Without it, current cannot flow for more than an instant. Notice that negative ions in the salt bridge move in the same direction as electrons around the circuit and positive ions move in the opposite direction.

The *half-cell in which oxidation occurs* is called the **anode**. The *half-cell in which reduction occurs* is called the **cathode**. It is easy to remember that the **a**node involves **o**xidation because both words begin with vowels. It is easy to remember that the **c**athode involves **r**eduction because both words begin with consonants. These definitions, anode/oxidation and cathode/reduction, are true for any electrochemical cell, not just a voltaic cell.

Podia Question

Make a diagram of a voltaic cell that generates electric current from this product-favored chemical reaction:

$$Fe(s) + Cu(NO_3)_2(aq) \rightarrow Fe(NO_3)_2(aq) + Cu(s)$$

Choose an appropriate salt solution for the salt bridge. Make sure that the oxidation half-reaction is in the left-hand beaker. Label each electrode with an element symbol. Label the anode half-cell and the cathode half-cell. Label the direction of movement of electrons, positive ions, and negative ions in the electrical circuit.

As this voltaic cell operates, one electrode gains mass and one electrode loses mass. Identify which electrode gains mass. Explain why that electrode gains mass and why the other electrode loses mass.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

5.4: Day 39- Voltaic Cells, Half-Cell Potentials

35

Day 39: Voltaic Cells, Half-Cell Potentials

D39.1 Voltaic Cell Potential

When a voltaic cell is connected to a load, such as a light bulb, an electric current flows because there is a difference in electrical potential between the two electrodes. That electrical potential difference can be measured with a potentiometer (that is, a voltmeter). For an accurate measurement, the voltmeter must have a very high resistance so that no current flows; otherwise the voltage would drop from its highest possible value.

The voltaic cell shown in Figure 1, involves the spontaneous reaction

$$\text{Cu(s)} + 2\ \text{Ag}^{+}\text{(aq)} \longrightarrow \text{Cu}^{2+}\text{(aq)} + 2\ \text{Ag(s)}$$

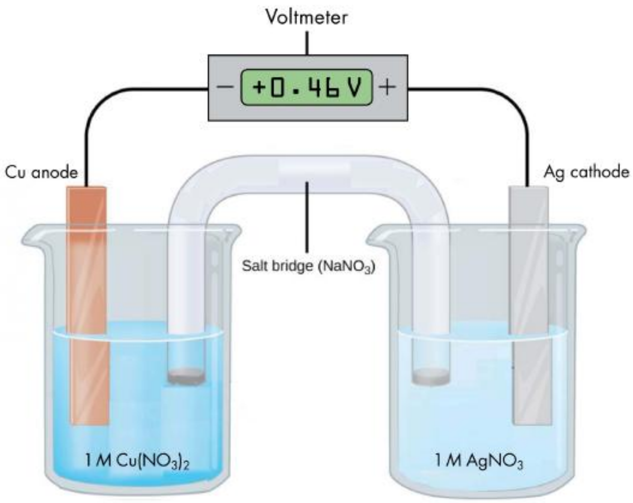


Figure 1. *In this voltaic cell, an electrical potential difference between the electrodes is being measured with a voltmeter. When the concentrations of both solutions are 1 M, the potential difference for this cell is 0.46 V.*

According to the reaction equation, copper loses electrons and is oxidized to copper(II) ions, so the half-cell with the copper electrode in Figure 1 is the anode. According to the reaction equation, silver ions gain electrons and are reduced to silver, so the half-cell with the silver electrode is the cathode. The copper electrode is more negative than the silver electrode.

When the more negative copper electrode is connected to the negative terminal of the voltmeter and the more positive silver electrode is connected to the positive terminal of the voltmeter, the meter reads +0.46 V. This reading is called the **cell potential, E_{cell}**. It is *a measure of the energy per unit charge available from a redox reaction* (V = J/C). A positive cell potential indicates how much electrical work a spontaneous reaction in a voltaic cell can do per unit electric charge moving though the circuit.

Under standard-state conditions (1 bar or 1 M, such as the 1-M concentrations in Figure 1), the cell potential is the standard cell potential, E°_{cell} (pronounced “E-standard-cell”). Thus, based on the voltmeter reading, $E^{\circ}_{\text{cell}}=0.46\ \text{V}$

A meter like the one in Figure 1 measures the difference in electrical potential between its positive terminal and its negative terminal. Because the positive meter terminal is on the right, the cell potential is the difference in electrical potential between the right-hand half-cell and the left-hand half-cell, and we can write,

$$E_{\text{cell}} = E_{\text{right half-cell}} - E_{\text{left half-cell}}$$

In Figure 1, all concentrations are 1 M (standard-state conditions), so we can also write,

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{right half-cell}} - E^{\circ}_{\text{left half-cell}}$$

If the wire connections are reversed, a typical voltmeter would read −0.46 V. This provides an experimental way to determine which half-cell is the cathode and which is the anode: a positive voltmeter reading indicates that the meter’s negative terminal is connected to the anode and the positive terminal is connected to the cathode; a negative voltmeter reading indicates the negative terminal is connected to the cathode and the positive terminal is connected to the anode.

The cell potential of a voltaic cell depends on the substances in each half-cell and the concentrations of solutions and partial pressures of gases involved in the half-cell. The half-cell potential does not depend on whether a half-reaction is occurring or on the direction in which the half-reaction goes. That is, the potential of the half cell involving silver ions and silver is the same whether silver is oxidized to silver ions or silver ions are reduced to silver.

A salt bridge must be present to complete an electric circuit. In the salt bridge when the cell generates electric current, *an*ions move toward the *an*ode and *cat*ions move toward the *cat*hode.

D39.2 Cell Notation

Drawing a diagram, like Figure 1 above, to define a voltaic cell takes a lot of time. **Cell notation** is *an abbreviation that summarizes the important information about a voltaic cell*. In cell notation, a vertical line, |, denotes a phase boundary and a double line, ||, a salt bridge. The anode electrode is written to the left, followed by the anode solution, then the salt bridge, then the cathode solution, and, finally, the cathode electrode to the right. Figure 2 shows how the cell notation for a voltaic cell relates to various components of the cell.

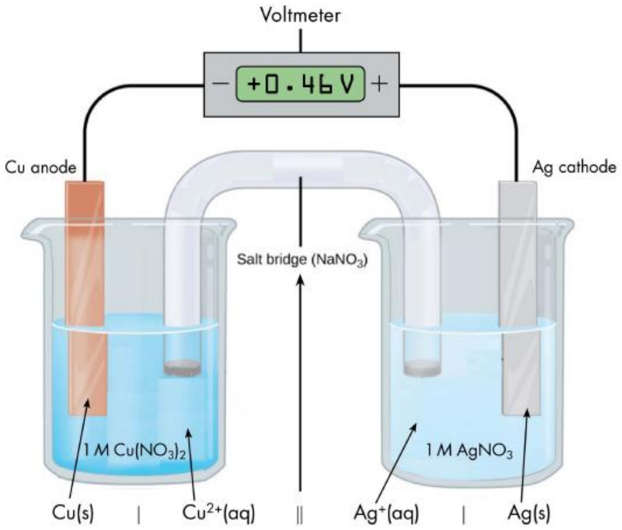


Figure 2. *The cell notation, Cu(s) | Cu^{2+}(aq) || Ag^+(aq) | Ag(s), is related to the diagram of the voltaic cell.*

Note that spectator ions, such as NO_3^-, are not included in the cell notation, and if there are coefficients in a half-reaction the coefficients are not included (that is, the coefficients of 2 in the silver half-reaction are do not appear in the cell notation). When known, the initial concentrations of ions are usually included in the cell notation, so a more complete cell notation for the cell in Figure 2 is Cu(s) | Cu^{2+}(aq, 1 M) || Ag^+(aq, 1 M) | Ag(s).

Some redox reactions involve species that are poor conductors of electricity, such as gases or ionic solids. For such substances, an inert electrode, that does not participate in the reactions, is used. An example of such a voltaic cell is shown in Figure 3.

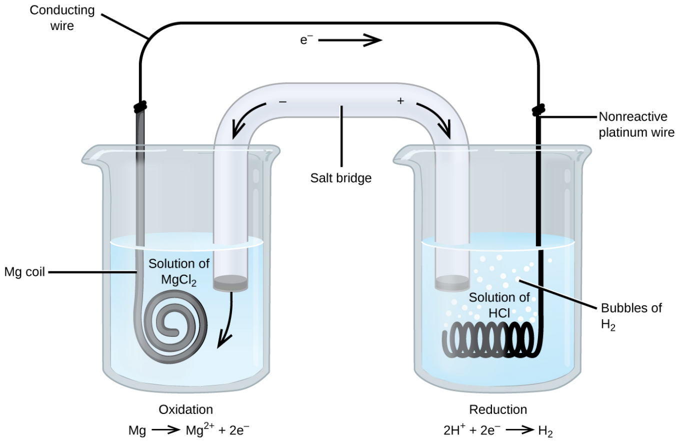


Figure 3. *The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive (inert) platinum wire conducts electrons into the right beaker.*

The redox reaction involved is:

Oxidation (anode):	$Mg(s)$	⟶	$Mg^{2+}(aq) + 2e^-$
Reduction (cathode):	$2H^+(aq) + 2e^-$	⟶	$H_2(g)$
overall:	$Mg(s) + 2H^+(aq)$	⟶	$Mg^{2+}(aq) + H_2(g)$

This voltaic cell uses an inert platinum wire for the cathode, so the cell notation is:

$$Mg(s) \mid Mg^{2+}(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$$

The magnesium electrode is an **active electrode** because it *participates in the redox reaction*. **Inert electrodes**, like the platinum electrode in Figure 3, *do not participate in the redox reaction* but must be present so that there is a complete electrical circuit. Platinum and gold are among the least reactive metals so they are good choices for inert electrodes. Graphite, also inert to many chemical reactions, is another common option.

D39.3 Standard Half-Cell Potentials

The cell potential in Figure 1 (+0.46 V) results from the *difference* in the electrical potential between the half-cells. It is not possible to measure directly the potential of a single half-cell; one half-cell has to be connected to another half-cell to measure a voltage.

However, it is useful to tabulate potentials for individual half-cells, such that the potential for a voltaic cell constructed from any two half-cells can be calculated from the values in the table. To create such a table, all half-cell potentials need to be measured relative to the same reference half-cell. That half-cell is the **standard hydrogen electrode (SHE)** (Figure 4), which consists of hydrogen gas at 1 bar pressure bubbling through a 1 M $H^+(aq)$ solution (platinum is used as the inert electrode):

$$2\,H^+(aq, 1\,M) + 2\,e^- \rightleftharpoons H_2(g, 1\,bar)\ E° = 0\ V$$

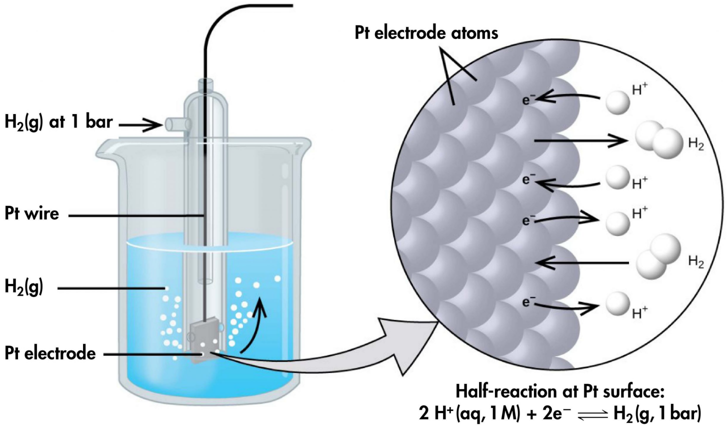


Figure 4. *Hydrogen gas at 1 bar is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with* H^+ *in solution to produce hydrogen gas.*

If a cell is set up with the SHE on the left and the half-cell whose potential we want to measure on the right, with all concentrations 1 M and all gas partial pressures 1 bar, then the reading on the voltmeter is ***E*°**, the **standard half-cell potential**, for the half-cell on the right. (Unless specified, the temperature is typically assumed to be 25 ºC.) For highly accurate measurements the voltmeter must not allow any current to flow; that is, no chemical reaction takes place.

For example, a voltaic cell consisted of a SHE and a Cu^{2+} | Cu(s) half-cell (Figure 5) can be used to determine the standard half-cell potential for Cu^{2+} | Cu(s).

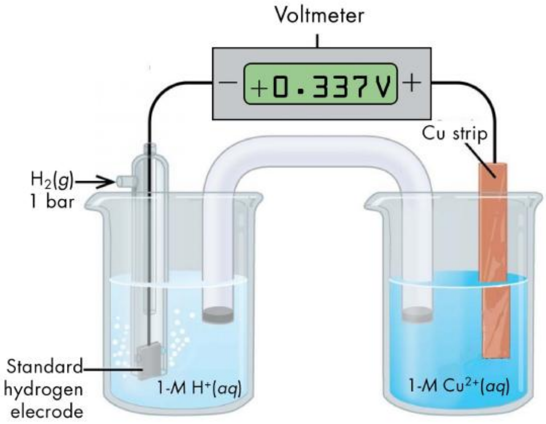


Figure 5. *A voltaic cell involving the standard hydrogen electrode can be used to determine the standard half-cell potential of* Cu^{2+} *| Cu(s).*

The cell notation for this voltaic cell is:

$$\mathrm{Pt}(s)\mid \mathrm{H_2(g,\ 1\ bar)}\mid \mathrm{H^+(aq,\ 1\ M)}\parallel \mathrm{Cu^{2+}(aq,\ 1\ M)}\mid \mathrm{Cu(s)}$$

As we noted in Section D39.1, the cell potential, $E°_{\mathrm{cell}}$, measured by the voltmeter, is the difference between the potential of the right-hand half-cell and the left-hand half-cell:

$$E°_{\mathrm{cell}} = E°_{\mathrm{right\ half\text{-}cell}} - E°_{\mathrm{left\ half\text{-}cell}}$$

From the measured $E°_{\mathrm{cell}}$ = +0.337 V and the defined potential of zero for the Pt(*s*) | H_2(g, 1 bar) | H^+(aq, 1 M) half-cell, we can calculate *E*° of the Cu^{2+}(aq, 1 M) | Cu(s) half-cell:

$$+0.337\ \mathrm{V} = E°_{\mathrm{Cu^{2+}|Cu}} - E°_{\mathrm{H^+|H_2}} = E°_{\mathrm{Cu^{2+}|Cu}} - 0 = E°_{\mathrm{Cu^{2+}|Cu}}$$

Sometimes, when a cell is set up with the SHE on the left, the reading on the voltmeter is negative. That is, for some half-cells the standard half-cell potential is lower than the potential for the Pt(*s*) | H_2(g, 1 bar) | H^+(aq, 1 M) half-cell. Consider the cell shown in Figure 6, with cell notation

$$\text{Pt}(s) \mid \text{H}_2(\text{g, 1 bar}) \mid \text{H}^+(\text{aq, 1 M}) \parallel \text{Zn}^{2+}(\text{aq, 1 M}) \mid \text{Zn(s)}$$

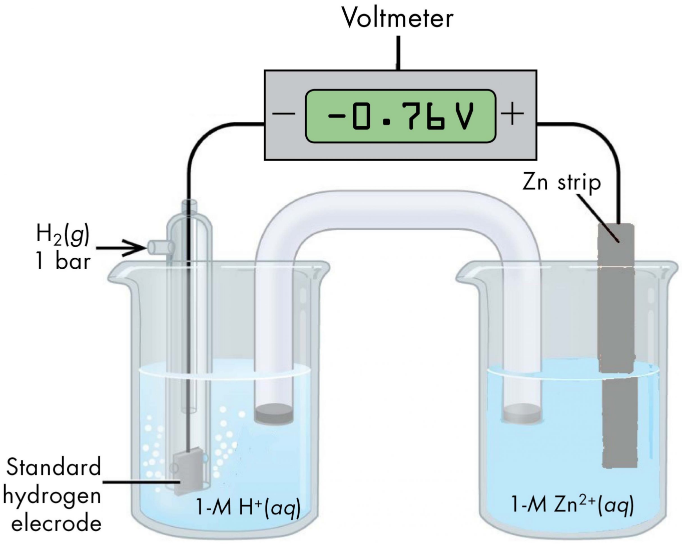


Figure 6. *This voltaic cell can be used to determine the standard half-cell potential of the Zn^{2+}(aq, 1 M) | Zn(s) half-cell. The SHE on the left has a standard half-cell potential of zero.*

Following the same reasoning as for the Cu^{2+}(aq, 1 M) | Cu(s) half-cell, $E°$ of the Zn^{2+}(aq, 1 M) | Zn(s) half-cell can be calculated.

$$E°_{\text{cell}} = E°_{\text{right half-cell}} - E°_{\text{left half-cell}}$$

$$-0.76\text{ V} = E^{\circ}_{\text{Zn}^{2+}|\text{Zn}} - E^{\circ}_{\text{H}^+|\text{H}_2} = E^{\circ}_{\text{Zn}^{2+}|\text{Zn}} - 0 = E^{\circ}_{\text{Zn}^{2+}|\text{Zn}}$$

It may seem strange that the standard half-cell potential is negative. This just reflects the fact that the electrical potential of the Zn^{2+}(aq, 1 M) | Zn(s) half-cell is smaller than the electrical potential of the Pt(s) | H$_2$(g, 1 bar) | H$^+$(aq, 1 M) half-cell. The potential of a half-cell depends only on the composition of the half-cell and does not depend on the direction of either a half-reaction or an overall reaction.

The standard hydrogen electrode is rather dangerous because H$_2$(g) is very flammable. Hence, it is rarely used in the laboratory. Its main significance is that it establishes the “zero” for standard half-cell potentials. Most standard half-cell potentials are measured by setting up a voltaic cell with one half-cell of known standard potential and one half-cell of unknown (to be measured) standard potential.

D39.4 Using Standard Half-Cell Potentials

Based on the methods described in the preceding section, standard half-cell potentials have been determined for many half-cells. The table below gives half-cell potentials for selected half-cells. Click on the table to open a version that can be enlarged or printed.

Standard Half-Cell Potentials in Aqueous Solution at 25 °C

Reduction Half-Reaction			Half-Cell	E° (V)
$F_2(g) + 2\ e^-$	→	$2\ F^-(aq)$	$F_2(g)\,|\,F^-(aq)\,|\,Pt$	+2.87
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^-$	→	$2\ H_2O(\ell)$	$H_2O_2(aq), H^+(aq), H_2O\ (\ell)\,|\,Pt$	+1.763
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	→	$PbSO_4(s) + 2\ H_2O(\ell)$	$PbO_2(s)\,|\,SO_4^{2-}(aq), H^+(aq)\,|\,PbSO_4(s)\,|\,Pb$	+1.690
$Au^{3+}(aq) + 3\ e^-$	→	$Au(s)$	$Au^{3+}(aq)\,|\,Au(s)$	+1.52
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$	→	$Mn^{2+}(aq) + 4\ H_2O(\ell)$	$MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)\,|\,Pt$	+1.51
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^-$	→	$2\ Cr^{3+}(aq) + 7\ H_2O(\ell)$	$Cr_2O_7^{2-}(aq), H^+(aq), Cr^{3+}(aq)\,|\,Pt$	+1.36
$Cl_2(g) + 2\ e^-$	→	$2\ Cl^-(aq)$	$Cl_2(g)\,|\,Cl^-(aq)\,|\,Pt$	+1.358
$O_2(g) + 4\ H^+(aq) + 4\ e^-$	→	$2\ H_2O(\ell)$	$O_2(g)\,|\,H^+(aq)\,|\,Pt$	+1.229
$Br_2(\ell) + 2\ e^-$	→	$2\ Br^-(aq)$	$Br_2(\ell)\,|\,Br^-(aq)\,|\,Pt$	+1.066
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^-$	→	$NO(g) + 2\ H_2O(\ell)$	$NO_3^-(aq), H^+(aq)\,|\,NO(g)\,|\,Pt$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\ e^-$	→	$Cl^-(aq) + 2\ OH^-(aq)$	$OCl^-(aq), Cl^-(aq), OH^-(aq)\,|\,Pt$	+0.89
$Hg^{2+}(aq) + 2\ e^-$	→	$Hg(\ell)$	$Hg^{2+}(aq)\,|\,Hg(\ell)$	+0.8535
$Ag^+(aq) + e^-$	→	$Ag(s)$	$Ag^+(aq)\,|\,Ag(s)$	+0.7991
$Hg_2^{2+}(aq) + 2\ e^-$	→	$2\ Hg(\ell)$	$Hg_2^{2+}(aq)\,|\,Hg(\ell)$	+0.7960
$Fe^{3+}(aq) + e^-$	→	$Fe^{2+}(aq)$	$Fe^{3+}(aq), Fe^{2+}(aq)\,|\,Pt$	+0.771
$I_2(s) + 2\ e^-$	→	$2\ I^-(aq)$	$I_2(s)\,|\,I^-(aq)\,|\,Pt$	+0.535
$O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	→	$4\ OH^-(aq)$	$O_2(g)\,|\,OH^-(aq)\,|\,Pt$	+0.401
$Cu^{2+}(aq) + 2\ e^-$	→	$Cu(s)$	$Cu^{2+}(aq)\,|\,Cu(s)$	+0.340
$Sn^{4+}(aq) + 2\ e^-$	→	$Sn^{2+}(aq)$	$Sn^{4+}(aq), Sn^{2+}(aq)\,|\,Pt$	+0.15
$2\ H^+(aq) + 2\ e^-$	→	$H_2(g)$	$H^+(aq)\,|\,H_2(g)\,|\,Pt$	0
$Sn^{2+}(aq) + 2\ e^-$	→	$Sn(s)$	$Sn^{2+}(aq)\,|\,Sn(s)$	-0.1375
$Ni^{2+}(aq) + 2\ e^-$	→	$Ni(s)$	$Ni^{2+}(aq)\,|\,Ni(s)$	-0.25
$PbSO_4(s) + 2\ e^-$	→	$Pb(s) + SO_4^{2-}(aq)$	$PbSO_4(s)\,|\,SO_4^{2-}(aq)\,|\,Pb(s)$	-0.3505
$Cd^{2+}(aq) + 2\ e^-$	→	$Cd(s)$	$Cd^{2+}(aq)\,|\,Cd(s)$	-0.403
$Fe^{2+}(aq) + 2\ e^-$	→	$Fe(s)$	$Fe^{2+}(aq)\,|\,Fe(s)$	-0.44
$Zn^{2+}(aq) + 2\ e^-$	→	$Zn(s)$	$Zn^{2+}(aq)\,|\,Zn(s)$	-0.763
$2\ H_2O(\ell) + 2\ e^-$	→	$H_2(g) + 2\ OH^-(aq)$	$H_2O\ (\ell), OH^-(aq)\,|\,H_2(g)\,|\,Pt$	-0.8277
$Al^{3+}(aq) + 3\ e^-$	→	$Al(s)$	$Al^{3+}(aq)\,|\,Al(s)$	-1.676
$Mg^{2+}(aq) + 2\ e^-$	→	$Mg(s)$	$Mg^{2+}(aq)\,|\,Mg(s)$	-2.356
$Na^+(aq) + e^-$	→	$Na(s)$	$Na^+(aq)\,|\,Na(s)$	-2.714
$K^+(aq) + e^-$	→	$K(s)$	$K^+(aq)\,|\,K(s)$	-2.925
$Li^+(aq) + e^-$	→	$Li(s)$	$Li^+(aq)\,|\,Li(s)$	-3.045

***Figure 7**. Standard half-cell potentials in aqueous solutions at 25 °C, in volts versus the standard hydrogen electrode (highlighted in peach). Half-cell reactions in basic solutions are highlighted in blue. (Data from Bard, A. J., Parsons, R., and Jordan, J. Standard Potentials in Aqueous Solution. New York: Marcel Dekker: 1985. International Union of Pure and Applied Chemistry Commission on Electrochemistry and Electroanalytical Chemistry.)*

There are several important aspects to note:

- The oxidizing agent is on the left (reactant) side of a reduction half-reaction equation.
- The **strongest oxidizing agents** (the substances most easily reduced) have the largest positive $E°$ values and **are at the top of the table**. (For example, $F_2(g)$ is a very strong oxidizing agent.)
- The reducing agent is on the right (product) side of a reduction half-reaction equation.
- The **strongest reducing agents** (the substances most easily oxidized) have the most negative $E°$ values and **are at the bottom of the table**. (For example, Li(s) and K(s) are very strong reducing agents.)
- **A redox reaction is product-favored when a stronger oxidizing agent reacts with a stronger reducing agent**. This results in a positive value for $E°_{cell}$ when the oxidation half-reaction is combined with the reduction half-reaction.
- **Half-cell reactions are reversible** and the direction a half-cell reaction goes depends on the potential of the other half-cell to which it is connected in a cell.

The table of standard half-cell potentials can be used to determine the $E°_{cell}$ for any voltaic cell and predict whether a specific redox reaction is product-favored. For example, for the cell:

$$\text{Cu(s)} \mid \text{Cu}^{2+}\text{(aq, 1 M)} \parallel \text{Ag}^{+}\text{(aq, 1 M)} \mid \text{Ag(s)}$$

$$E°_{cell} = E°_{\text{right half-cell}} - E°_{\text{left half-cell}} = E°_{\text{Ag}^+|\text{Ag}} - E°_{\text{Cu}^{2+}|\text{Cu}} = 0.7991\text{ V} - 0.340\text{ V} = 0.459\text{ V}$$

Because the value of $E°_{cell}$ is positive, the redox reaction corresponding to this cell notation is product-favored and the voltaic cell can produce electrical energy. The overall reaction can be obtained from the cell notation by writing the oxidation and the reduction half-reactions, multiplying each half-reaction by an appropriate number to balance electrons, and summing the two half-reactions:

Oxidation (left):	Cu(s)	⟶	$Cu^{2+}(aq) + 2e^-$	$E°_{anode} = +0.340$ V
Reduction (right):	$2 \times (Ag^+(aq) + e^-$	⟶	Ag(s))	$E°_{cathode} = +0.7991$ V
Overall:	$Cu(s) + 2Ag^+(aq)$	⟶	$Cu^{2+}(aq) + 2Ag(s)$	$E°_{cell} = +0.459$ V

Note that:

- Even though the reduction half-reaction is multiplied by 2, the $E°_{cathode}$ is not multiplied by 2 when $E°_{cell}$ is calculated. This is because electrical potential is a ratio of energy per coulomb of charge transferred (V = J/C). If the half-reaction is doubled, both energy and charge transferred are doubled, leaving the ratio constant.
- The oxidation half-reaction is the reverse of the reaction as shown in the half-cell potential table, but $E°_{right}$ is not multiplied by -1 . The cell potential does not depend on the direction of a half-reaction; it depends only on the composition of the half-cell.

$E°$ for many half-cells are included in the appendix. Tables like these make it possible to determine the $E°_{cell}$ for many redox reactions. Moreover, by comparing the standard potentials, we can discern which species is easier to reduce/harder to oxidize/is a stronger oxidizing agent (higher/more positive $E°$) and which species is easier to oxidize/harder to reduce/is a stronger reducing agent (lower/more negative $E°$).

Podia Question

Use data from the table of standard half-cell potentials to determine whether this redox reaction is product-favored.

$$2\ NO_3^-(aq) + 8\ H^+(aq) + 3\ Cd(s) \rightleftharpoons 2\ NO(g) + 3\ Cd^{2+}(aq) + 4\ H_2O(l)$$

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

5.5: Day 40- Thermodynamic Properties of Voltaic and Electrolytic Cells

36

Day 40: Thermodynamic Properties of Voltaic and Electrolytic Cells

D40.1 Relationships among $\Delta_r G°$, $K°$, and $E°_{cell}$

A redox reaction can be described in terms of $\Delta_r G°$ and $K°$, and these thermodynamic variables can be related to $E°_{cell}$ because they all describe whether the redox reaction is reactant-favored or product-favored at equilibrium.

In a voltaic cell, the difference in Gibbs free energy between products and reactants allows the cell to do electrical work. We represent electrical work done by the cell as w_{elec}.

$$w_{elec}\text{ (J)} = \text{charge transferred (C)} \times \text{potential difference (V)}$$

The charge of 1 mol electrons is known as the **Faraday's constant** (F):

$$F = \frac{6.0221\ \times\ 10^{23}\ \text{e}^-}{\text{mol}} \times \frac{1.6022\ \times\ 10^{-19}\ \text{C}}{\text{e}^-} = 96485\ \frac{\text{C}}{\text{mol}} = 96485 \frac{\text{J}}{\text{V·mol}}$$

Hence, the total quantity of charge transferred per mole of a redox reaction is:

$$\frac{\text{total charge transferred}}{\text{mole of reaction}} = (\text{number of e}^-\ \text{transferred})\ \times\ F = n\ \times\ F$$

In this equation, ***n*** is *the number of electrons transferred in the balanced redox reaction*, which can be obtained from the balanced half-reactions that are added to produce the overall redox reaction. For example, in the reaction:

$$2\ \text{Au}^{3+}(aq) + 3\ \text{Zn}(s) \rightarrow 3\ \text{Zn}^{2+}(aq) + 2\ \text{Au}(s)$$

6 e^- are transferred because each half-reaction, after multiplying by a factor to balance electrons, involves 6 e^-:

Oxidation:	$3 \times (\text{Zn}(s)$	$\longrightarrow$	$\text{Zn}^{2+}(aq) + 2e^-)$
Reduction:	$2 \times (\text{Au}^{3+}(aq) + 3e^-$	$\longrightarrow$	$\text{Au}(s))$
Overall:	$2\ \text{Au}^{3+}(aq) + 3\ \text{Zn}(s)$	$\longrightarrow$	$3\ \text{Zn}^{2+}(aq) + 2\ \text{Au}(s)$

When this redox reaction happens once, 6 e^- are transferred. When a mole of this reaction takes place, 6 moles of e^- are transferred; that is, 6 mol × 96485 C/mol = 578910 C are transferred. Hence, we have:

w_{elec}	=	charge transferred × potential difference
w_{elec}	=	$(nF) \times (E_{cell})$

If we operate a voltaic cell such that the maximum possible electrical work, w_{elec}, is done and the only work done is electrical work, then:

$$\Delta_r G = -w_{max} = -w_{elec} = -\text{nFE}_{cell}$$

The negative sign makes sense because a positive E_{cell} indicates a spontaneous redox reaction while for $\Delta_r G$, a negative value indicates a spontaneous reaction.

If all the reactants and products are in their standard states, then the equation becomes:

$$\Delta_r G° = -nFE°_{cell}$$

This equation also links standard cell potentials to equilibrium constants, since:

$$-nFE°_{cell} = \Delta_r G° = -RT\ln K°$$

Therefore:

$$E^\circ_{cell} = \frac{RT}{nF}\ \ln\ K^\circ$$

Thus, if any one of $\Delta_rG°$, $K°$, or $E°_{\text{cell}}$ is known or can be calculated for a redox reaction, the other two quantities can be determined using the relationships shown in Figure 1. Moreover, any of the three quantities can be used to determine whether a reaction is product-favored at equilibrium.

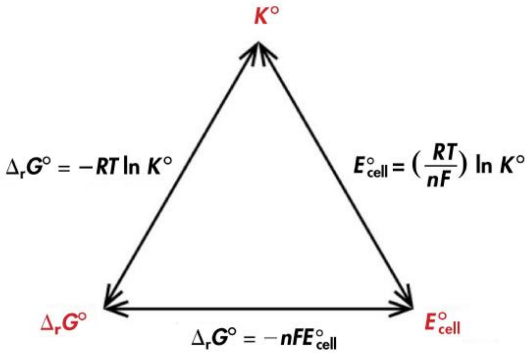


Figure 1. *The relationships between* Δ_rG°, K°, *and* E°_{cell}.

D40.2 Nernst Equation

Now that the connection has been made between standard Gibbs free energy change and standard cell potentials, we can consider the situation under nonstandard conditions. Recall that Δ_rG is related to $\Delta_rG°$ by the reaction quotient, Q, and a similar relationship can be applied to cell potentials:

Δ_rG	=	$\Delta_rG° + RT \ln Q$
$-nFE_{\text{cell}}$	=	$-nFE°_{\text{cell}} + RT\ln Q$

Rearranging the variables gives the **Nernst equation**:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

The Nernst equation can be used to calculate the cell potential at concentrations or partial pressures that differ from standard conditions, which is often the case for voltaic cells.

Activity 1: Is a Redox Reaction Spontaneous?

D40.3 Concentration Cells

A **concentration cell** is a special type of voltaic cell *where the electrodes are the same material but the half-cells have different concentrations of soluble species*. Because one or both half-cells are not under standard-state conditions, the half-cell potentials are unequal, and there is a potential difference between the half-cells. That potential difference can be calculated using the Nernst equation.

For example, consider this concentration cell at 25°C:

$$\text{Zn}(s) \mid \text{Zn}^{2+}(\text{aq, 0.10 M}) \parallel \text{Zn}^{2+}(\text{aq, 0.50 M}) \mid \text{Zn}(s)$$

The standard cell potential is 0 V because the anode and cathode involve the same reaction; however, the process is spontaneous because if equal volumes of the two half-cell solutions were mixed, the concentration of Zn^{2+} would change to the average of the initial concentrations, namely, to 0.30 M. The cell can do work because the concentrations of Zn^{2+} change.

Oxidation:	Zn(s)	⟶	Zn^{2+}(aq, 0.10 M) + $2e^-$	$E°_{\text{left half-cell}}$ = -0.763 V
Reduction :	Zn^{2+}(aq, 0.50 M) + $2e^-$	⟶	Zn(s)	$E°_{\text{right half-cell}}$ = -0.763 V

Overall:	Zn^{2+}(aq, 0.50 M)	$\longrightarrow$	Zn^{2+}(aq, 0.10 M)	$E°_{cell}$ = 0 V

The Nernst equation verifies that the process is spontaneous at the given conditions, because it shows that $E_{cell} > 0$ V:

$$E_{\text{cell}} = 0\text{ V} - \frac{\left(8.314 \frac{\text{J}}{\text{K}\cdot\text{mol}}\right)(298.15\text{ K})}{(2)\left(96485 \frac{\text{J}}{\text{V}\cdot\text{mol}}\right)} \ln\left(\frac{0.10\text{ M}}{0.50\text{ M}}\right) = +0.021\text{ V}$$

In a concentration cell, the standard cell potential ($E°_{cell}$) is always zero. In order to have a spontaneous forward reaction, and hence have a positive cell potential (E_{cell}), the reaction quotient Q must be less than 1 (when $Q < 1$, $\ln(Q) < 0$). As the reaction proceeds, the concentrations change, Q approaches 1 and E_{cell} approaches 0 V.

Podia Question

The gravity cell, a variant of the Daniell cell, was described in Exercise 3 in Day 39. The cell involves oxidation of Zn(s) by Cu^{2+}(aq). Suppose a gravity cell is constructed with 1.00 L saturated copper(II) sulfate in the bottom and 1.00 L 0.100-M zinc sulfate in the top. (There is no solid copper(II) sulfate in the cell. Assume a temperature of 25 °C.)

Write half-reactions for the overall reaction that powers the gravity cell and label them as oxidation and reduction.

Write the balanced overall cell reaction.

Calculate the standard cell potential.

Calculate the cell potential under the initial (nonstandard) conditions. The solubility of $CuSO_4•5H_2O$ in water is 32 g/100 mL.

Calculate the cell potential after 99% of the copper(II) ions in the bottom cell solution has reacted. (Assume there is an excess of Zn(s).)

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

5.6: Day 41- Electrolysis; Commercial Batteries

37

Day 41: Electrolysis; Commercial Batteries

D41.1 Electrolysis

In an **electrolytic cell**, *supplied electrical energy causes a nonspontaneous redox reaction to occur in a process known as* **electrolysis**. An electrolytic cell is the opposite of a voltaic cell, where a spontaneous redox reaction produces electrical energy.

For example, consider electrolysis of molten sodium chloride. A simplified diagram of the electrolytic cell used for commercial manufacture of sodium metal and chlorine gas is shown in Figure 1. In the molten salt, sodium ions move toward the cathode and chloride ions move toward the anode (note that negative ions move through the circuit in the same overall direction as electrons). A porous screen allows movement of ions but not mixing of the product sodium metal and chlorine gas, which would react spontaneously upon contact.

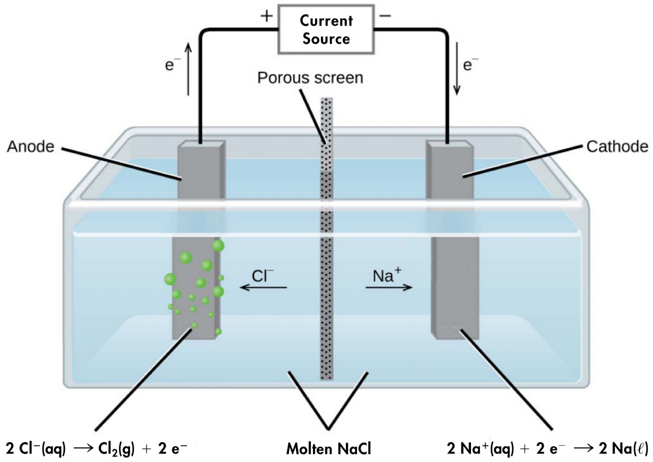


Figure 1. *Passing an electric current through NaCl(l) decomposes the molten salt into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous re-formation of sodium chloride.*

An external source of electric current forces electrons into the electrode in the cathode compartment, forcing the reduction half-reaction to occur:

$$\text{Reduction (cathode): } 2 \times (\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)\ )\ E^\circ_{\text{Na}^+|\text{Na}} = -2.714\text{ V}$$

(At the temperature of molten NaCl, sodium is a liquid, so $E^\circ_{\text{Na}^+|\text{Na}(s)} = -2.714$ V is an approximation. $E^\circ_{\text{Na}^+|\text{Na}(l)}$ for liquid sodium is not available in the appendix.)

In the anode compartment, the oxidation half-reaction occurs:

$$\text{Oxidation (anode): } 2\ \text{Cl}^-(aq) \longrightarrow \text{Cl}_2(g) + 2e^-\ E^\circ_{\text{Cl}_2|\text{Cl}^-} = +1.358\text{ V}$$

The electrons formed here are conducted through a wire to the the positive side of the voltage source, completing the electric circuit.

We can calculate E°_{cell} for this electrolysis cell using the same method we used for voltaic cells; that is,

$$E^\circ_{\text{cell}} = E^\circ_{\text{right half-cell}} - E^\circ_{\text{left half-cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -2.714\text{ V} - (+1.358\text{ V}) = -4.072\text{ V}$$

The overall reaction is:

$$\text{Overall: } 2\ \text{Na}^+(aq) + 2\ \text{Cl}^-(aq) \longrightarrow 2\ \text{Na}(s) + \text{Cl}_2(g)\ E^\circ_{\text{cell}} = -4.072\text{ V}$$

The negative E°_{cell} indicates that this reaction is strongly reactant-favored, and under standard-state conditions, the power supply must provide at least 4.1 V to cause the electrolysis reaction to occur. In practice, the applied voltages are higher due to inefficiencies in the process itself and also to help increase the rate of reaction.

With the transition from fossil fuels to renewable energy supplies, an important application of electrolysis is the “splitting” of water into hydrogen gas and oxygen gas (Figure 2). Electric energy from solar panels or wind turbines can be used to synthesize hydrogen for use as a fuel. For current to pass through the solution efficiently, there must be ions present. Hence, acid is typically added to the reaction solution to increase the concentration of ions in solution.

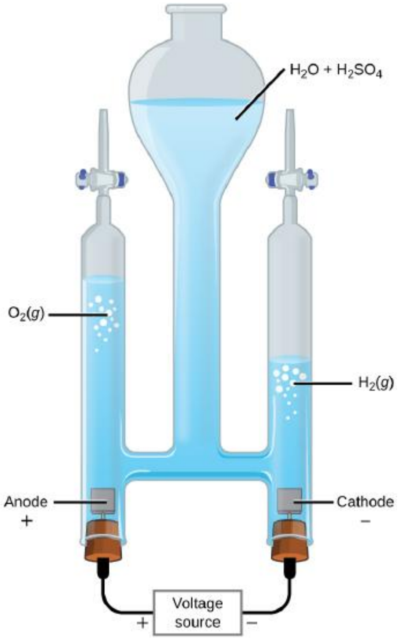


Figure 2. *Water decomposes into oxygen gas and hydrogen gas during electrolysis. Sulfuric acid is added to increase the concentration of* H^+ *ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, because the reaction produces 2 mol* H_2 *per 1 mol* O_2*.*

In 1-M acidic solution:

Oxidation (anode):	$2H_2O(l)$	$\longrightarrow$	$O_2(g) + 4H^+(aq) + 4e^-$	$E°_{anode} = +1.229$ V
Reduction (cathode):	$2 \times (2H^+(aq) + 2e^-$	$\longrightarrow$	$H_2(g))$	$E°_{cathode} = 0$ V
Overall:	$2H_2O(l)$	$\longrightarrow$	$O_2(g) + 2H_2(g)$	$E°_{cell} = -1.229$ V

At least 1.229 V is required to make this reactant-favored process occur in 1-M acidic solution.

Finally, consider what occurs during the electrolysis of 1-M aqueous potassium iodide solution at 25 °C. Present in the solution are $H_2O(l)$, $K^+(aq)$, and $I^-(aq)$. This example differs from the previous examples because more than one species can be oxidized and more than one species can be reduced.

Considering the anode first, the possible oxidation reactions are

(i)	$2I^-(aq)$	$\longrightarrow$	$I_2(s) + 2e^-$	$E°_{anode} = +0.535$ V
(ii)	$2H_2O(l)$	$\longrightarrow$	$O_2(g) + 4H^+(aq) + 4e^-$	$E°_{anode} = +1.229$ V

(Oxidation of K^+ to K^{2+} is not considered because K^+ has a noble-gas electron configuration and a very high ionization energy, making it very difficult to oxidize. Although I_2 is generated in aqueous solution, we approximate the $E°$ by using the value for $I_2(s)$.)

Because $E°_{cell} = E°_{cathode} - E°_{anode}$, the more positive the anode half-cell potential is, the more negative the cell potential would be. Therefore, iodide should be oxidized at the anode because it has a less positive half-cell potential. However, the pH of a 1-M KI solution is 7, so $[H^+]$ is far from standard-state conditions. Assuming that O_2 is produced at 1 bar, applying the Nernst equation to half-reaction (ii) gives:

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF}\ln\left(\frac{1}{[\mathrm{O_2}][\mathrm{H^+}]^4}\right)\\ &= 1.229\text{ V} - \frac{\left(8.314\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\right)(298.15\text{ K})}{4\left(96485\frac{\mathrm{J}}{\mathrm{V\cdot mol}}\right)}\ln\left(\frac{1}{(1)(1\times10^{-7})^4}\right)\\ &= 1.229\ \text{ V} - 0.414\text{ V} = 0.815\text{ V}\end{aligned}$$

(Note that the reaction given in the standard half-cell potential table is the reduction reaction “$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$ $E^\circ = +1.229$ V”, hence reaction quotient Q is expressed in accordance to the given reaction.)

The Nernst equation shows that $E_{\text{anode}} = +0.815$ V for reaction (ii) at pH = 7, which is still higher than E°_{anode} for reaction (i). Therefore, reaction (i) is the process that occurs at the anode and I_2 forms as a product.

Now consider the possible reactions at the cathode (reduction of I^- is not considered because I^- has a noble-gas electron configuration and it is not energetically favorable to add more electrons):

(iii)	$2H_2O(l) + 2e^-$	$\longrightarrow$	$H_2(g) + 2OH^-(aq)$	$E^\circ_{\text{cathode}} = -0.8277$ V
(ii)	$K^+(aq) + e^-$	$\longrightarrow$	$K(s)$	$E^\circ_{\text{cathode}} = -2.925$ V

For half-reaction (iii), we again need to apply the Nernst equation to calculate E at pH = 7, assuming H_2 is produced at 1 bar:

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF}\ln\left(\frac{[\mathrm{H_2}][\mathrm{OH^-}]^2}{1}\right)\\ &= -0.8277\text{ V} - \frac{\left(8.314\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\right)(298.15\text{ K})}{4\left(96485\frac{\mathrm{J}}{\mathrm{V\cdot mol}}\right)}\ln\left(\frac{(1)(1\times10^{-7})^4}{1}\right)\\ &= -0.8277\ \text{ V} - (-0.4141\text{ V}) = -0.4136\text{ V}\end{aligned}$$

Hence, reduction of water, with $E_{\text{cathode}} = -0.4136$ V at pH = 7, is much more likely to occur than reduction of $K^+(aq)$ with $E^\circ_{\text{cathode}} = -2.925$ V. (This conclusion is supported by the fact that potassium metal reacts vigorously with water to generate $K^+(aq)$, hydrogen gas, and hydroxide ions, so if K(s) formed it would immediately react with water.)

The overall reaction is then:

Oxidation (anode):	$2I^-(aq)$	$\longrightarrow$	$I_2(s) + 2e^-$	$E^\circ_{\text{anode}} = +0.535$ V
Reduction (cathode):	$2H_2O(l) + 2e^-$	$\longrightarrow$	$H_2(g) + 2OH^-(aq)$	$E_{\text{cathode}} = -0.4136$ V
Overall:	$2H_2O(l) + 2I^-(aq)$	$\longrightarrow$	$H_2(g) + I_2(s) + 2OH^-(aq)$	$E_{\text{cell}} = -0.949$ V

Electroplating

An important use for electrolytic cells is **electroplating**, which results in a thin coating of metal on top of a conducting surface. Metals typically used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. As an example of electroplating, consider how silver-plated tableware is produced (Figure 3).

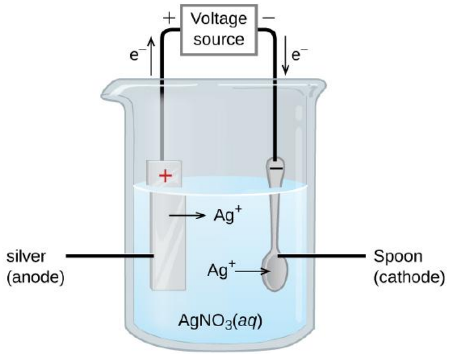


Figure 3. *The metal spoon is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When electric current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the spoon.*

The anode consists of a silver electrode. The cathode is a spoon made from a less expensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential from the voltage source is increased, current flows. Silver metal is lost at the anode as it goes into solution:

anode: $Ag(s) \longrightarrow Ag^+(aq) + e^-$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon:

cathode: $Ag^+(aq) + e^- \longrightarrow Ag(s)$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the electroplated object depends on the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The quantity of current that flows in an electrolytic cell is dictated by the amount (mol) of electrons transferred in a redox reaction, which is in turn related to quantities of reactants and products via reaction stoichiometry. Recall that current, *I*, is related to the total charge, *Q*:

$$I = \frac{Q}{t} \quad \left(\text{SI units: } A = \frac{C}{s}\right)$$

Hence:

$Q = (\text{amount } e^- \text{ transferred}) \times F = I \times t$

where *F* is the Faraday constant.

D41.2 Commercial Batteries

Many of the devices we use every day, such as laptops and smartphones, are powered by batteries. A **battery** is *an electrochemical cell or series of cells that produces an electric current.* In principle, any voltaic cell can be used as a battery. An ideal battery would never run down/drain, produce a constant voltage, and be capable of withstanding environmental extremes of temperature and humidity. Real batteries strike a balance between ideal characteristics and practical limitations.

For example, the mass of a car-starter battery is about 18 kg or ~1% of the mass of an average car. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be completely impractical because of its mass and size. Thus, no single battery is "best" and different batteries are selected for particular applications, keeping things like its mass, cost, reliability, and current capacity in mind.

There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

D41.3 Primary Batteries

Primary batteries are *single-use batteries that cannot be recharged.*

Zinc-Carbon Battery

A common primary battery is the **dry cell** (Figure 4), which is *a zinc-carbon battery*. The zinc serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small quantity of water.

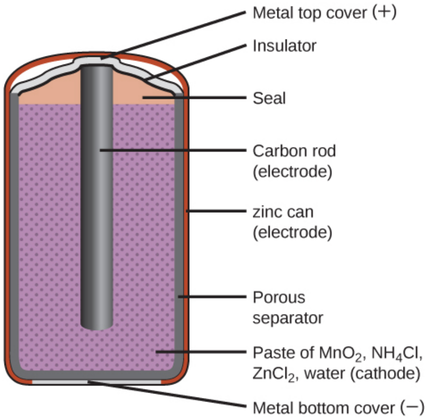


Figure 4. *A cross section of a flashlight battery, a zinc-carbon dry cell.*

The reaction at the anode can be represented as the oxidation of zinc:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\ e^{-} \quad E°_{anode} = -0.763\ V$$

The reaction at the cathode is more complicated, in part because more than one reduction reaction is occurring. The series of reactions that occurs at the cathode is approximately:

$$2MnO_2(s) + 2NH_4Cl(aq) + 2e^{-} \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2Cl^{-}(aq)$$

The overall reaction for the zinc–carbon battery can be represented as:

$$2MnO_2(s) + 2\ NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l) + 2\ Cl^{-}(aq) + Zn^{2+}(aq)$$

The cell potential is about 1.5 V initially, and decreases as the battery is used. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.

The voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage. However, larger batteries can deliver more moles of electrons and will therefore last longer if powering the same device.

Alkaline Battery

Alkaline batteries (Figure 5) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells, and are manufactured to be their exact replacements. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide.

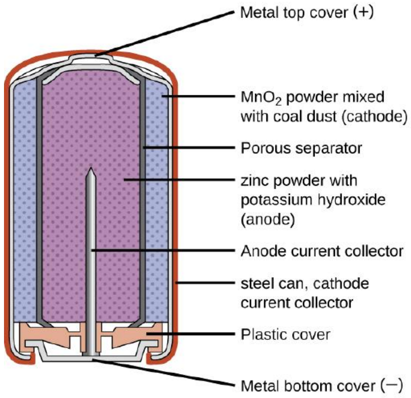


Figure 5. *Alkaline batteries were designed as direct replacements for zinc-carbon batteries.*

The reactions are:

Oxidation (anode):	$Zn(s) + 2OH^-(aq)$	⟶	$ZnO(s) + H_2O(l) + 2e^-$	$E°_{anode} = -1.28\ V$
Reduction (cathode):	$2MnO_2(s) + H_2O(l) + 2e^-$	⟶	$Mn_2O_3(s) + 2OH^-(aq)$	$E°_{cathode} = +0.15\ V$
overall:	$Zn(s) + 2MnO_2(s)$	⟶	$ZnO(s) + Mn_2O_3(s)$	$E°_{cell} = +1.43\ V$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries sometimes leak potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

D41.4 Secondary Batteries

Secondary batteries are *rechargeable; that is, the reaction that powers the battery can be reversed so that the original reactants can be regenerated*. Secondary batteries are found in smartphones, electronic tablets, automobiles, and many other devices.

Lead-Acid Battery

The **lead-acid battery** (Figure 6) is the type of secondary battery used to start gasoline-powered automobiles. It is inexpensive and capable of producing the high current required by the starter motors when starting a car. They are heavy because of lead's high density, they contain highly corrosive concentrated sulfuric acid, and must be disposed of properly to avoid lead-poisoning hazards. But they can produce a lot of current in a short time so for certain applications they are the best choice.

The reactions for a lead acid battery are:

Oxidation (anode):	$Pb(s) + HSO_4^-(aq)$	⟶	$PbSO_4(s) + H^+(aq) + 2e^-$
Reduction (cathode):	$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^-$	⟶	$PbSO_4(s) + 2H_2O(l)$
overall:	$Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$	⟶	$2PbSO_4(s) + 2H_2O(l)$

Each cell produces 2.05 V, so six cells can be connected in series to produce a 12-V car battery.

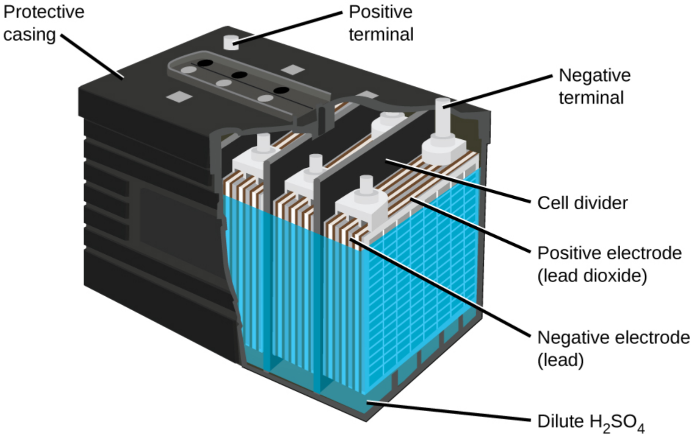


Figure 6. *The lead acid battery in an automobile consists of six cells connected in series to give 12 V. The low cost and high current output makes the battery suitable for providing power for a car's starter motor.*

In each cell, the lead electrodes are immersed in sulfuric acid. The anodes are spongy lead metal and the cathodes are lead impregnated with lead oxide. As the battery is discharged, a powder of $PbSO_4$ forms on the electrodes. When a lead-acid battery is recharged by a car's alternator, electrons are forced to flow in the opposite direction which reverses the reactions at anode and cathode, in other words, the cell undergoes electrolysis reactions to replenish the substances that have reacted away.

Practically, the concentrated sulfuric acid becomes quite viscous when the temperature is low, inhibiting the flow of ions between the plates and reducing the current that can be delivered. This effect is well-known to anyone who has had difficulty starting a car in cold weather. These batteries also tend to slowly self-discharge, so a car left idle for several weeks might be unable to start. And after thousands of discharge-charge cycles, $PbSO_4$ that does not get converted to PbO_2 gradually changes to an inert form which limits the battery capacity. Also, “fast” charging causes rapid evolution of potentially explosive H_2 gas from the water in the electrolyte (electrolysis of water); the gas bubbles form on the lead surface and can tear PbO_2 off the electrodes. Eventually enough solid material accumulates at the bottom of the electrolyte to short-circuit the battery, leading to its permanent demise.

Lithium Ion Battery

Lithium ion batteries (Figure 7) are among the most popular rechargeable batteries and are used in many portable electronic devices because their advantages outweigh the disadvantage of higher cost. In a typical Li-ion battery the reactions are:

Oxidation (anode):	$LiCoO_2$	$\longrightarrow$	$Li_{1\text{-}x}CoO_2 + xLi^+ + xe^-$
Reduction (cathode):	$xLi^+ + xC_6 + xe^-$	$\longrightarrow$	$xLiC_6$
overall:	$LiCoO_2 + xC_6$	$\longrightarrow$	$Li_{1\text{-}x}CoO_2 + xLiC_6$

(x is no more than about 0.5.) The battery voltage is about 3.7 V.

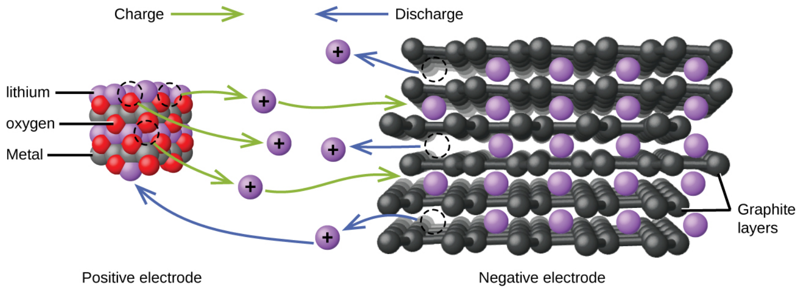


Figure 7. *In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.*

Lithium batteries are popular because they can provide a large amount of current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

D41.5 Fuel Cells

Suppose a voltaic cell is constructed such that the substance that is oxidized at the anode and the substance that is reduced at the cathode (the reactants in the overall redox reaction) are both supplied continuously. Such a battery would never run down because reactant concentrations or partial pressures would never decrease. Such a device is a **fuel cell**, which *produces electricity as long as fuel is available*. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure 8).

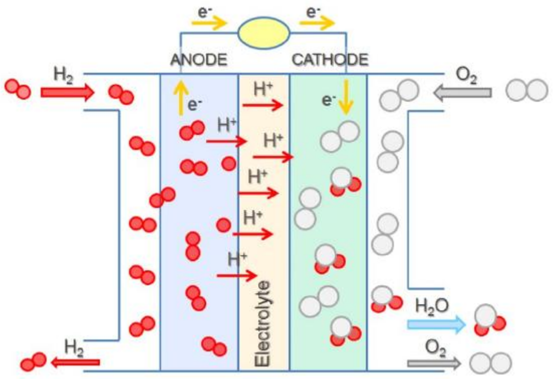


Figure 8. *In this schematic of a hydrogen-oxygen proton-exchange fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.*

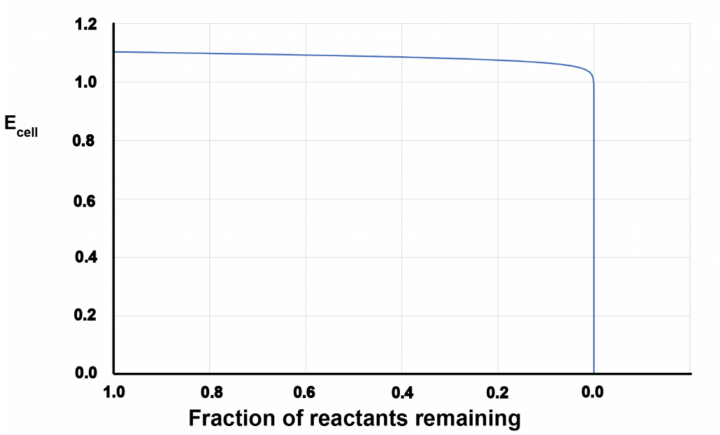
In a hydrogen-oxygen proton-exchange fuel cell, the cell potential is about 1 V, and the reactions involved are:

Oxidation (anode):	$2 \times (H_2(g)$	$\longrightarrow$	$2H^+(aq) + 2e^-)$
Reduction (cathode):	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow$	$2H_2O(l)$
overall:	$O_2(g) + 2H_2(g)$	$\longrightarrow$	$2H_2O(l)$

The efficiency of fuel cells is typically about 40-60%, which is higher than the typical internal combustion engine (25-35%). Moreover, in the case of the hydrogen fuel cell, nearly pure water is produced as exhaust. Currently, fuel cells are comparably more expensive and contain features that may cause a higher failure rate.

Podia Question

Consider this graph, which shows cell potential on the vertical axis and fraction of reactants remaining (battery life remaining) on the horizontal axis for a commercial battery.



- Write an explanation in appropriate scientific language for why the graph has the shape it has.
- Describe why the shape of this graph is a positive feature when batteries power devices such as smartphones and laptop computers.

Two days before the next whole-class session, this Podia question will become live on Podia, where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use this link to report them. A similar link will be included in each day's material. We appreciate your comments.

CHAPTER OVERVIEW

6: Appendix

6.1: Atomic Weights

Atomic Weights

John Moore, Jia Zhou, and Etienne Garand

[2016. Scaled to an atomic weight of 12 for carbon-12 (^{12}C), where ^{12}C is a neutral atom in its nuclear and electronic ground state, having the result that atomic weight values are dimensionless.]

The atomic weights of many elements are not invariant, but depend on the origin and treatment of the material. The standard atomic weights apply to elements of natural terrestrial origin. Although the atomic weights of some elements in some naturally occurring materials may differ from given values because of a variation in the mole fractions of an element's stable isotopes, the last significant figure of each tabulated value is considered reliable to ±1 except for zinc, which is ±2. For twelve of these elements, both a conventional atomic weight and an atomic weight interval is given with the symbol [a, b] to denote the set of atomic weight values in normal materials; thus, a ≤ atomic weight ≤ b. For lithium, the conventional atomic weight is only three digits because of the large variation found in lithium-bearing reagents.

Atomic Number	Element Name	Symbol	Standard Atomic Weight	Conventional Atomic Weight
1	hydrogen	H	[1.007, 1.009]	1.008
2	helium	He	4.003	
3	lithium	Li	[6.938, 6.997]	6.94
4	beryllium	Be	9.012	
5	boron	B	[10.80, 10.83]	10.81
6	carbon	C	[12.00, 12.02]	12.01
7	nitrogen	N	[14.00, 14.01]	14.01
8	oxygen	O	[15.99, 16.00]	16.00
9	fluorine	F	19.00	
10	neon	Ne	20.18	
11	sodium	Na	22.99	
12	magnesium	Mg	[24.30, 24.31]	24.31
13	aluminium (aluminum)	Al	26.98	
14	silicon	Si	[28.08, 28.09]	28.09
15	phosphorus	P	30.97	
16	sulfur	S	[32.05, 32.08]	32.06
17	chlorine	Cl	[35.44, 35.46]	35.45
18	argon	Ar	39.95	
19	potassium	K	39.10	
20	calcium	Ca	40.08	
21	scandium	Sc	44.96	
22	titanium	Ti	47.87	
23	vanadium	V	50.94	

Atomic Number	Element Name	Symbol	Standard Atomic Weight	Conventional Atomic Weight
24	chromium	Cr	52.00	
25	manganese	Mn	54.94	
26	iron	Fe	55.85	
27	cobalt	Co	58.93	
28	nickel	Ni	58.69	
29	copper	Cu	63.55	
30	zinc	Zn	65.38	
31	gallium	Ga	69.72	
32	germanium	Ge	72.63	
33	arsenic	As	74.92	
34	selenium	Se	78.97	
35	bromine	Br	[79.90, 79.91]	79.90
36	krypton	Kr	83.80	
37	rubidium	Rb	85.47	
38	strontium	Sr	87.62	
39	yttrium	Y	88.91	
40	zirconium	Zr	91.22	
41	niobium	Nb	92.91	
42	molybdenum	Mo	95.95	
43	technetium*	Tc		
44	ruthenium	Ru	101.1	
45	rhodium	Rh	102.9	
46	palladium	Pd	106.4	
47	silver	Ag	107.9	
48	cadmium	Cd	112.4	
49	indium	In	114.8	
50	tin	Sn	118.7	
51	antimony	Sb	121.8	
52	tellurium	Te	127.6	
53	iodine	I	126.9	
54	xenon	Xe	131.3	
55	caesium (cesium)	Cs	132.9	
56	barium	Ba	137.3	
57	lanthanum	La	138.9	

Atomic Number	Element Name	Symbol	Standard Atomic Weight	Conventional Atomic Weight
58	cerium	Ce	140.1	
59	praseodymium	Pr	140.9	
60	neodymium	Nd	144.2	
61	promethium*	Pm		
62	samarium	Sm	150.4	
63	europium	Eu	152.0	
64	gadolinium	Gd	157.3	
65	terbium	Tb	158.9	
66	dysprosium	Dy	162.5	
67	holmium	Ho	164.9	
68	erbium	Er	167.3	
69	thulium	Tm	168.9	
70	ytterbium	Yb	173.1	
71	lutetium	Lu	175.0	
72	hafnium	Hf	178.5	
73	tantalum	Ta	180.9	
74	tungsten	W	183.8	
75	rhenium	Re	186.2	
76	osmium	Os	190.2	
77	iridium	Ir	192.2	
78	platinum	Pt	195.1	
79	gold	Au	197.0	
80	mercury	Hg	200.6	
81	thallium	Tl	[204.3, 204.4]	204.4
82	lead	Pb	207.2	
83	bismuth*	Bi	209.0	
84	polonium*	Po		
85	astatine*	At		
86	radon*	Rn		
87	francium*	Fr		
88	radium*	Ra		
89	actinium*	Ac		
90	thorium*	Th	232.0	
91	protactinium*	Pa	231.0	

Atomic Number	Element Name	Symbol	Standard Atomic Weight	Conventional Atomic Weight
92	uranium*	U	238.0	
93	neptunium*	Np		
94	plutonium*	Pu		
95	americium*	Am		
96	curium*	Cm		
97	berkelium*	Bk		
98	californium*	Cf		
99	einsteinium*	Es		
100	fermium*	Fm		
101	mendelevium*	Md		
102	nobelium*	No		
103	lawrencium*	Lr		
104	rutherfordium*	Rf		
105	dubnium*	Db		
106	seaborgium*	Sg		
107	bohrium*	Bh		
108	hassium*	Hs		
109	meitnerium*	Mt		
110	darmstadtium*	Ds		
111	roentgenium*	Rg		
112	copernicium*	Cn		
113	nihonium*	Nh		
114	flerovium*	Fl		
115	moscovium*	Mc		
116	livermorium*	Lv		
117	tennessine*	Ts		
118	oganesson*	Og		

*Element has no stable isotopes, only radioactive isotopes, and an atomic weight cannot be determined. However, four such elements (Bi, Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these a standard atomic weight is tabulated.

6.2: Elemental Abundances

Elemental Abundances

John Moore, Jia Zhou, and Etienne Garand

Elemental Abundance in Solar System

Atom	Atomic No.	Abundance* (atoms/10^6 atoms Si)	Log(abund)
H	1	27900000000	10.45
He	2	2720000000	9.43
Li	3	57.1	1.76
Be	4	0.73	-0.14
B	5	21.2	1.33
C	6	10100000	7
N	7	313000	5.5
O	8	23800000	7.38
F	9	843	2.93
Ne	10	3440000	6.54
Na	11	57400	4.76
Mg	12	1074000	6.03
Al	13	84900	4.93
Si	14	1000000	6
P	15	10400	4.02
S	16	515000	5.71
Cl	17	5240	3.72
Ar	18	101000	5
K	19	3770	3.58
Ca	20	61100	4.79
Sc	21	34.2	1.53
Ti	22	2400	3.38
V	23	293	2.47
Cr	24	13500	4.13
Mn	25	9550	3.98
Fe	26	900000	5.95
Co	27	2250	3.35
Ni	28	49300	4.69
Cu	29	522	2.72
Zn	30	1260	3.1
Ga	31	37.8	1.58
Ge	32	119	2.08
As	33	6.56	0.82
Se	34	62.1	1.79
Br	35	11.8	1.07

Atom	Atomic No.	Abundance* (atoms/10^6 atoms Si)	Log(abund)
Kr	36	45	1.65
Rb	37	7.09	0.85
Sr	38	23.5	1.37
Y	39	4.64	0.67
Zr	40	11.4	1.06
Nb	41	0.698	-0.16
Mo	42	2.55	0.41
Tc	43		
Ru	44	1.86	0.27
Rh	45	0.344	-0.46
Pd	46	1.39	0.14
Ag	47	0.486	-0.31
Cd	48	1.61	0.21
In	49	0.184	-0.74
Sn	50	3.82	0.58
Sb	51	0.309	-0.51
Te	52	4.81	0.68
I	53	0.9	-0.05
Xe	54	4.7	0.67
Cs	55	0.372	-0.43
Ba	56	4.49	0.65
La	57	0.446	-0.35
Ce	58	1.136	0.06
Pr	59	0.1669	-0.78
Nd	60	0.8279	-0.08
Pm	61		
Sm	62	0.2282	-0.64
Eu	63	0.0973	-1.01
Gd	64	0.33	-0.48
Tb	65	0.0603	-1.22
Dy	66	0.3942	-0.4
Ho	67	0.0889	-1.05
Er	68	0.2508	-0.6
Tm	69	0.0378	-1.42
Yb	70	0.2479	-0.61
Lu	71	0.0367	-1.44
Hf	72	0.154	-0.81
Ta	73	0.0207	-1.68
W	74	0.133	-0.88

Atom	Atomic No.	Abundance* (atoms/10^6 atoms Si)	Log(abund)
Re	75	0.0517	-1.29
Os	76	0.675	-0.17
Ir	77	0.661	-0.18
Pt	78	1.34	0.13
Au	79	0.187	-0.73
Hg	80	0.34	-0.47
Tl	81	0.184	-0.74
Pb	82	3.15	0.5
Bi	83	0.144	-0.84
Po	84		
At	85		
Rn	86		
Fr	87		
Ra	88		
Ac	89		
Th	90	0.0335	-1.47
Pa	91		
U	92	0.009	-2.05
Np	93		
Pu	94		
Am	95		
Cm	96		
Bk	97		
Cf	98		
Es	99		
Fm	100		
Md	101		
No	102		
Lr	103		

*Anders, Edward; Grevesse; Nicolas, Geochimica et Cosmochimica Acta 1989, 53, 197-214.

Elemental Abundance in Earth Crust

Atom	Atomic No.	Abundance*
H	1	6.2
He	2	0
Li	3	4.1
Be	4	3.2
B	5	4
C	6	6.7
N	7	4.3

Atom	Atomic No.	Abundance*
O	8	8.67
F	9	5.8
Ne	10	0
Na	11	7.36
Mg	12	7.51
Al	13	7.92
Si	14	8.43
P	15	6
S	16	5.8
Cl	17	5.3
Ar	18	1
K	19	6.96
Ca	20	7.72
Sc	21	4.5
Ti	22	6.7
V	23	5.4
Cr	24	5.3
Mn	25	6.1
Fe	26	7.84
Co	27	4.5
Ni	28	5
Cu	29	4.9
Zn	30	4.9
Ga	31	4.3
Ge	32	3.2
As	33	3.4
Se	34	1.7
Br	35	3.4
Kr	36	-1
Rb	37	4.5
Sr	38	5.4
Y	39	4.3
Zr	40	5
Nb	41	4
Mo	42	3
Tc	43	
Ru	44	0
Rh	45	-1
Pd	46	0

Atom	Atomic No.	Abundance*
Ag	47	1.9
Cd	48	2
In	49	1.7
Sn	50	3.4
Sb	51	2.3
Te	52	-1
I	53	2.7
Xe	54	-2
Cs	55	3
Ba	56	5.4
La	57	4.2
Ce	58	4.5
Pr	59	3.6
Nd	60	4.2
Pm	61	
Sm	62	3.5
Eu	63	3
Gd	64	3.5
Tb	65	2.8
Dy	66	3.6
Ho	67	2.9
Er	68	3.3
Tm	69	2.5
Yb	70	3.3
Lu	71	2.5
Hf	72	3.5
Ta	73	3
W	74	3
Re	75	-0.3
Os	76	-1
Ir	77	-1
Pt	78	0
Au	79	0.5
Hg	80	2
Tl	81	2.6
Pb	82	3.9
Bi	83	-1
Po	84	
At	85	

Atom	Atomic No.	Abundance*
Rn	86	
Fr	87	
Ra	88	-4
Ac	89	
Th	90	3.6
Pa	91	-5
U	92	3
Np	93	
Pu	94	
Am	95	
Cm	96	
Bk	97	
Cf	98	
Es	99	
Fm	100	
Md	101	
No	102	
Lr	103	

*log(mass fraction in ppb, that is µg/kg)

6.3: Electron Configuration

Electron Configuration

John Moore, Jia Zhou, and Etienne Garand

Ground State Electron Configuration of Atoms

Atomic No.	Element	Configuration
1	H	$1s^{1}$
2	He	$1s^{2}$
3	Li	[He] $2s^{1}$
4	Be	[He] $2s^{2}$
5	B	[He] $2s^{2}2p^{1}$
6	C	[He] $2s^{2}2p^{2}$
7	N	[He] $2s^{2}2p^{3}$
8	O	[He] $2s^{2}2p^{4}$
9	F	[He] $2s^{2}2p^{5}$
10	Ne	[He] $2s^{2}2p^{6}$
11	Na	[Ne] $3s^{1}$
12	Mg	[Ne] $3s^{2}$
13	Al	[Ne] $3s^{2}3p^{1}$
14	Si	[Ne] $3s^{2}3p^{2}$
15	P	[Ne] $3s^{2}3p^{3}$
16	S	[Ne] $3s^{2}3p^{4}$
17	Cl	[Ne] $3s^{2}3p^{5}$
18	Ar	[Ne] $3s^{2}3p^{6}$
19	K	[Ar] $4s^{1}$
20	Ca	[Ar] $4s^{2}$
21	Sc	[Ar] $3d^{1}4s^{2}$
22	Ti	[Ar] $3d^{2}4s^{2}$
23	V	[Ar] $3d^{3}4s^{2}$
24	Cr	[Ar] $3d^{5}4s^{1}$
25	Mn	[Ar] $3d^{5}4s^{2}$
26	Fe	[Ar] $3d^{6}4s^{2}$
27	Co	[Ar] $3d^{7}4s^{2}$
28	Ni	[Ar] $3d^{8}4s^{2}$
29	Cu	[Ar] $3d^{10}4s^{1}$
30	Zn	[Ar] $3d^{10}4s^{2}$
31	Ga	[Ar] $3d^{10}4s^{2}4p^{1}$
32	Ge	[Ar] $3d^{10}4s^{2}4p^{2}$
33	As	[Ar] $3d^{10}4s^{2}4p^{3}$
34	Se	[Ar] $3d^{10}4s^{2}4p^{4}$
35	Br	[Ar] $3d^{10}4s^{2}4p^{5}$

Atomic No.	Element	Configuration
36	Kr	$[Ar]\ 3d^{10}4s^{2}4p^{6}$
37	Rb	$[Kr]\ 5s^{1}$
38	Sr	$[Kr]\ 5s^{2}$
39	Y	$[Kr]4d^{1}5s^{2}$
40	Zr	$[Kr]\ 4d^{2}5s^{2}$
41	Nb	$[Kr]\ 4d^{4}5s^{1}$
42	Mo	$[Kr]\ 4d^{5}5s^{1}$
43	Tc	$[Kr]\ 4d^{5}5s^{2}$
44	Ru	$[Kr]\ 4d^{7}5s^{1}$
45	Rh	$[Kr]\ 4d^{8}5s^{1}$
46	Pd	$[Kr]\ 4d^{10}$
47	Ag	$[Kr]\ 4d^{10}5s^{1}$
48	Cd	$[Kr]\ 4d^{10}5s^{2}$
49	In	$[Kr]\ 4d^{10}5s^{2}5p^{1}$
50	Sn	$[Kr]\ 4d^{10}5s^{2}5p^{2}$
51	Sb	$[Kr]\ 4d^{10}5s^{2}5p^{3}$
52	Te	$[Kr]\ 4d^{10}5s^{2}5p^{4}$
53	I	$[Kr]\ 4d^{10}5s^{2}5p^{5}$
54	Xe	$[Kr]\ 4d^{10}5s^{2}5p^{6}$
55	Cs	$[Xe]\ 6s^{1}$
56	Ba	$[Xe]\ 6s^{2}$
57	La	$[Xe]\ 5d^{1}6s^{2}$
58	Ce	$[Xe]\ 4f^{1}5d^{1}6s^{2}$
59	Pr	$[Xe]\ 4f^{3}6s^{2}$
60	Nd	$[Xe]\ 4f^{4}6s^{2}$
61	Pm	$[Xe]\ 4f^{5}6s^{2}$
62	Sm	$[Xe]\ 4f^{6}6s^{2}$
63	Eu	$[Xe]\ 4f^{7}6s^{2}$
64	Gd	$[Xe]\ 4f^{7}5d^{1}6s^{2}$
65	Tb	$[Xe]\ 4f^{9}6s^{2}$
66	Dy	$[Xe]\ 4f^{10}6s^{2}$
67	Ho	$[Xe]\ 4f^{11}6s^{2}$
68	Er	$[Xe]\ 4f^{12}6s^{2}$
69	Tm	$[Xe]\ 4f^{13}6s^{2}$
70	Yb	$[Xe]\ 4f^{14}6s^{2}$
71	Lu	$[Xe]\ 4f^{14}5d^{1}6s^{2}$
72	Hf	$[Xe]\ 4f^{14}5d^{2}6s^{2}$
73	Ta	$[Xe]\ 4f^{14}5d^{3}6s^{2}$
74	W	$[Xe]\ 4f^{14}5d^{4}6s^{2}$
75	Re	$[Xe]\ 4f^{14}5d^{5}6s^{2}$

Atomic No.	Element	Configuration
76	Os	[Xe] $4f^{14}5d^{6}6s^{2}$
77	Ir	[Xe] $4f^{14}5d^{7}6s^{2}$
78	Pt	[Xe] $4f^{14}5d^{9}6s^{1}$
79	Au	[Xe] $4f^{14}5d^{10}6s^{1}$
80	Hg	[Xe] $4f^{14}5d^{10}6s^{2}$
81	Tl	[Xe] $4f^{14}5d^{10}6s^{2}6p^{1}$
82	Pb	[Xe] $4f^{14}5d^{10}6s^{2}6p^{2}$
83	Bi	[Xe] $4f^{14}5d^{10}6s^{2}6p^{3}$
84	Po	[Xe] $4f^{14}5d^{10}6s^{2}6p^{4}$
85	At	[Xe] $4f^{14}5d^{10}6s^{2}6p^{5}$
86	Rn	[Xe] $4f^{14}5d^{10}6s^{2}6p^{6}$
87	Fr	[Rn] $7s^{1}$
88	Ra	[Rn] $7s^{2}$
89	Ac	[Rn] $6d^{1}7s^{2}$
90	Th	[Rn] $6d^{2}7s^{2}$
91	Pa	[Rn] $5f^{2}6d^{1}7s^{2}$
92	U	[Rn] $5f^{3}6d^{1}7s^{2}$
93	Np	[Rn] $5f^{4}6d^{1}7s^{2}$
94	Pu	[Rn] $5f^{6}7s^{2}$
95	Am	[Rn] $5f^{7}7s^{2}$
96	Cm	[Rn] $5f^{7}6d^{1}7s^{2}$
97	Bk	[Rn] $5f^{9}7s^{2}$
98	Cf	[Rn] $5f^{10}7s^{2}$
99	Es	[Rn] $5f^{11}7s^{2}$
100	Fm	[Rn] $5f^{12}7s^{2}$
101	Md	[Rn] $5f^{13}7s^{2}$
102	No	[Rn] $5f^{14}7s^{2}$
103	Lr	[Rn] $5f^{14}7s^{2}7p^{1}$
104	Rf	[Rn] $5f^{14}6d^{2}7s^{2}$
105	Db	[Rn] $5f^{14}6d^{3}7s^{2}$
106	Sg	[Rn] $5f^{14}6d^{4}7s^{2}$
107	Bh	[Rn] $5f^{14}6d^{5}7s^{2}$
108	Hs	[Rn] $5f^{14}6d^{6}7s^{2}$
109	Mt	[Rn] $5f^{14}6d^{7}7s^{2}$
110	Ds	[Rn] $5f^{14}6d^{9}7s^{1}$
111	Rg	[Rn] $5f^{14}6d^{10}7s^{1}$
112	Cn	[Rn] $5f^{14}6d^{10}7s^{2}$
113	—	[Rn] $5f^{14}6d^{2}7s^{2}7p^{1}$
114	Fl	[Rn] $5f^{14}6d^{2}7s^{2}7p^{2}$
115	—	[Rn] $5f^{14}6d^{2}7s^{2}7p^{3}$

Atomic No.	Element	Configuration
116	Lv	[Rn] $5f^{14}6d^{2}7s^{2}7p^{4}$
117	—	[Rn] $5f^{14}6d^{10}7s^{2}7p^{5}$
118	—	[Rn] $5f^{14}6d^{10}7s^{2}7p^{6}$

All electron configurations in this table are from experimental determinations except for elements 103-118, which are predicted theoretically. For elements 103-118, only a few atoms can be produced at a time and it is very difficult to determine electron configurations.

6.4: Radius

Radius

John Moore, Jia Zhou, and Etienne Garand

Atomic Radius

Atom	Atomic No.	Atomic Radius (pm)
H	1	37
He	2	31
Li	3	157
Be	4	112
B	5	86
C	6	77
N	7	74
O	8	74
F	9	72
Ne	10	68
Na	11	191
Mg	12	160
Al	13	143
Si	14	117
P	15	110
S	16	104
Cl	17	99
Ar	18	91
K	19	235
Ca	20	197
Sc	21	164
Ti	22	147
V	23	135
Cr	24	129
Mn	25	137
Fe	26	126
Co	27	125
Ni	28	125
Cu	29	126
Zn	30	137

Atom	Atomic No.	Atomic Radius (pm)
Ga	31	153
Ge	32	130.5
As	33	121
Se	34	117
Br	35	114
Kr	36	108
Rb	37	250
Sr	38	215
Y	39	182
Zr	40	160
Nb	41	147
Mo	42	140
Tc	43	135
Ru	44	134
Rh	45	134
Pd	46	137
Ag	47	144
Cd	48	152
In	49	167
Sn	50	149
Sb	51	151
Te	52	137
I	53	133
Xe	54	126
Cs	55	272
Ba	56	224
La	57	188
Ce	58	182
Pr	59	181
Nd	60	180
Pm	61	179
Sm	62	179
Eu	63	206
Gd	64	178

Atom	Atomic No.	Atomic Radius (pm)
Tb	65	177
Dy	66	176
Ho	67	175
Er	68	174
Tm	69	173
Yb	70	194
Lu	71	172
Hf	72	159
Ta	73	147
W	74	141
Re	75	137
Os	76	135
Ir	77	136
Pt	78	139
Au	79	144
Hg	80	155
Tl	81	171
Pb	82	175
Bi	83	182
Po	84	174
At	85	166
Rn	86	159
Fr	87	
Ra	88	
Ac	89	
Th	90	180
Pa	91	163
U	92	156
Np	93	156
Pu	94	164
Am	95	173
Cm	96	155
Bk	97	170
Cf	98	

Atom	Atomic No.	Atomic Radius (pm)
Es	99	
Fm	100	
Md	101	
No	102	
Lr	103	

Wells, A. F. Structural Inorganic Chemistry, 5th ed., Clarendon: Oxford, 1984, p 289 and 1288.
Slater, J. C. J. Chem. Phys. 1964, 41, 3199.
Clementi, E; Raimondi, D. L.; Reinhardt, W. P. J. Chem. Phys. 1967, 47(4), 1300-1307.

Ionic Radius

Ion Species	Atomic No.	Ionic Radius (pm)
H +1	1	
He	2	
Li +1	3	90
Be +2	4	59
B +3	5	41
C +4	6	30
N -3	7	
N +3	7	30
N +5	7	27
O -2	8	126
F -1	9	119
F +7	9	22
Ne	10	
Na +1	11	116
Mg +2	12	86
Al +3	13	67.5
Si +4	14	54
P +3	15	58
P +5	15	52
S -2	16	170
S +4	16	51
S +6	16	43
Cl -1	17	167
Cl +5	17	
Cl +7	17	41

Ion Species	Atomic No.	Ionic Radius (pm)
Ar	18	
K +1	19	152
Ca +2	20	114
Sc +3	21	88.5
Ti +2	22	100
Ti +3	22	81
Ti +4	22	74.5
V +2	23	93
V +3	23	78
V +4	23	72
V +5	23	68
Cr +2	24	94
Cr +3	24	75.5
Cr +4	24	69
Cr +5	24	63
Cr +6	24	58
Mn +2	25	97
Mn +3	25	78.5
Mn +4	25	67
Mn +5	25	
Mn +6	25	
Mn +7	25	60
Fe +2	26	92
Fe +3	26	78.5
Fe +4	26	72.5
Fe +6	26	
Co +2	27	88.5
Co +3	27	75
Co +4	27	67
Ni +2	28	83
Ni +3	28	74
Ni +4	28	62
Cu +1	29	91
Cu +2	29	87

Ion Species	Atomic No.	Ionic Radius (pm)
Cu +3	29	68
Zn +2	30	88
Ga +3	31	76
Ge +2	32	87
Ge +4	32	67
As +3	33	72
As +5	33	60
Se -2	34	184
Se +4	34	64
Se +6	34	56
Br -1	35	182
Br +3	35	
Br +5	35	
Br +7	35	53
Kr	36	
Rb +1	37	166
Sr +2	38	132
Y +3	39	104
Zr +4	40	86
Nb +3	41	86
Nb +4	41	82
Nb +5	41	78
Mo +3	42	83
Mo +4	42	79
Mo +5	42	75
Mo +6	42	73
Tc +4	43	78.5
Tc +5	43	74
Tc +7	43	70
Ru +3	44	82
Ru +4	44	76
Ru +5	44	70.5
Ru +7	44	
Ru +8	44	

Ion Species	Atomic No.	Ionic Radius (pm)
Rh +3	45	80.5
Rh +4	45	74
Rh +5	45	69
Pd +1	46	
Pd +2	46	100
Pd +3	46	90
Pd +4	46	75.5
Ag +1	47	129
Ag +2	47	108
Ag +3	47	89
Cd +2	48	109
In +3	49	94
Sn +4	50	83
Sb +3	51	90
Sb +5	51	74
Te -2	52	207
Te +4	52	111
Te +6	52	70
I -1	53	206
I +5	53	
I +7	53	67
Xe +8	54	62
Cs +1	55	181
Ba +2	56	149
La +3	57	117.2
Ce +3	58	115
Ce +4	58	101
Pr +3	59	113
Pr +4	59	99
Nd +2	60	
Nd +3	60	112.3
Pm +3	61	111
Sm +2	62	
Sm +3	62	109.8

Ion Species	Atomic No.	Ionic Radius (pm)
Eu +2	63	131
Eu +3	63	108.7
Gd +3	64	107.8
Tb +3	65	106.3
Tb +4	65	90
Dy +2	66	121
Dy +3	66	105.2
Ho +3	67	104.1
Er +3	68	103
Tm +2	69	117
Tm +3	69	102
Yb +2	70	116
Yb +3	70	100.8
Lu +3	71	100.1
Hf +4	72	85
Ta +3	73	86
Ta +4	73	82
Ta +5	73	78
W +4	74	80
W +5	74	76
W +6	74	74
Re +4	75	77
Re +5	75	72
Re +6	75	69
Re +7	75	67
Os +4	76	77
Os +5	76	71.5
Os +6	76	68.5
Os +7	76	66.5
Os +8	76	
Ir +3	77	82
Ir +4	77	76.5
Ir +5	77	71
Pt +2	78	94

Ion Species	Atomic No.	Ionic Radius (pm)
Pt +4	78	76.5
Pt +5	78	71
Au +1	79	151
Au +3	79	99
Au +5	79	71
Hg +1	80	133
Hg +2	80	116
Tl +1	81	164
Tl +3	81	102.5
Pb +2	82	133
Pb +4	82	91.5
Bi +3	83	117
Bi +5	83	90
Po +4	84	108
Po +6	84	81
At +7	85	76
Rn	86	
Fr +1	87	194
Ra +2	88	
Ac+3	89	126
Th +4	90	108
Pa +3	91	118
Pa +4	91	104
Pa +5	91	92
U +3	92	116.5
U +4	92	103
U +5	92	90
U +6	92	87
Np +2	93	124
Np +3	93	115
Np +4	93	101
Np +5	93	89
Np +6	93	86
Np +7	93	85

Ion Species	Atomic No.	Ionic Radius (pm)
Pu +3	94	114
Pu +4	94	100
Pu +5	94	88
Pu +6	94	85
Am +2	95	
Am +3	95	111.5
Am +4	95	99
Cm +3	96	111
Cm +4	96	99
Bk +3	97	110
Bk +4	97	97
Cf +3	98	109
Cf +4	98	96.1
Es	99	
Fm	100	
Md	101	
No +2	102	124
Lr	103	

Shannon, R. D. Acta Cryst. 1976, A32, 751-767.

6.5: Ionization Energies

Ionization Energies

John Moore, Jia Zhou, and Etienne Garand

Ionization Energy

Atom	Atomic No.	IE$_1$ (kJ/mol)	IE$_2$ (kJ/mol)	IE$_3$ (kJ/mol)	IE$_4$ (kJ/mol)	IE$_5$ (kJ/mol)	IE$_6$ (kJ/mol)	IE$_7$ (kJ/mo
H	1	1311.7						
He	2	2371.6	5248.8					
Li	3	520.1	7296.1	11811.7				
Be	4	899.2	1756.6	14844.3	21000.7			
B	5	800.4	2426.5	3658.7	25018.5	32817.3		
C	6	1086.8	2351.9	4618.2	6221.0	37820.9	47262.4	
N	7	1402.9	2856.4	4575.9	7472.8	9442.3	53252.7	64339.3
O	8	1313.6	3391.1	5300.3	7467.4	10987.1	13322.7	71313.7
F	9	1681.0	3375.1	6050.4	8416.4	11020.0	15159.5	17863.2
Ne	10	2080.1	3962.7	6175.1	9374.5	12195.7	15236.0	
Na	11	495.7	4562.8	6913.2	9540.5	13372.9	16630.2	20111.8
Mg	12	737.5	1450.2	7730.4	10544.9	13626.6	18029.3	21739.1
Al	13	577.4	1816.1	2744.0	11574.4	14836.6	18372.7	23342.7
Si	14	786.3	1576.6	3228.4	4354.4	16087.0	19790.1	23775.0
P	15	1011.8	1895.9	2909.6	4954.9	6272.2	21266.7	25405.6
S	16	999.3	2257.8	3377.0	4562.8	6995.2	8493.5	27111.4
Cl	17	1255.3	2296.4	3849.8	5162.0	6541.7	9330.1	11025.4
Ar	18	1520.1	2664.9	3946.3	5768.9	7236.4	8809.1	11964.2
K	19	418.6	3069.2	4438.3	5876.0	7975	9619.6	11385.3
Ca	20	589.6	1145.3	4941.0	6464.5	8142.4	10496	12350.1
Sc	21	632.9	1243.7	2388.0	7130.3	8876.7	10719.5	13314
Ti	22	659.0	1315.1	2715.1	4172.0	9629.2	11578.2	13585.1
V	23	650.3	1370.1	2865.6	4631.3	6290.8	12437.0	14569.3
Cr	24	652.5	1591.0	2986.2	4785.7	7043.4	8741.6	15543.8
Mn	25	717.1	1509.0	3250.6		7332.9		11504.9
Fe	26	762.2	1561.1	2956.3				
Co	27	758.4	1645.1	3231.3				
Ni	28	736.5	1751.2	3488.9				

Cu	29	745.3	1957.7	3553.6				
Zn	30	906.1	1732.9	3830.5				
Ga	31	578.9	1981.8	2962.1	6194.4	8299	10874	13585
Ge	32	760.3	1537.0	3300.8	4409.4	9011.7	11183	13981
As	33	946.5	1949.0	2730.5	4833.9	6040.0	12301.9	14183
Se	34	940.7	2074.4	3087.5	4139.2	7053.1	7882.9	14955.2
Br	35	1142.4	2084.1	3463.8				
Kr	36	1350.4	2369.7	3560.3				
Rb	37	402.9	2653.3	3859.4				
Sr	38	549.2	1063.9	0.0	5499.7		31261.3	
Y	39	627.2	1196.4	3762.9		7429.4		36085.5
Zr	40	670.6	1353.7	2392.8	3277.6		9552.0	
Nb	41	653.2	1350.8	2711.2	3695.4	4824.3	9938.0	12060.7
Mo	42	685.0	1558.2	2617.6	4476.9	5904.9	6561.0	12157.2
Tc	43	702.4	1472.4	0.0				
Ru	44	710.5	1617.1	2746.0				
Rh	45	719.8	1743.5	2995.9				
Pd	46	803.7	1873.7	3176.3				
Ag	47	730.8	2072.5	3359.6				
Cd	48	867.5	1631.0	3615.3				
In	49	558.2	1819.7	2704.5	5248.8			
Sn	50	708.4	1411.4	2941.8	3928.9	6975.9		
Sb	51	833.5	1592.0	2441.1	3193.7	5403.2	10420.4	
Te	52	869.3	1794.6	2991.0	3666.4	5789.1	6946.9	13218.5
I	53	1008.7	1841.9	0.0				
Xe	54	1170.1	2045.5	3097.2				
Cs	55	375.6	2421.8	0.0				
Ba	56	502.7	964.9	0.0				
La	57	538.1	1067.1	1850.3	4819.4			
Ce	58	527.4	1046.9	1948.8	3546.6			
Pr	59	523.1	1017.9	2086.4	3761.0	5550.8		
Nd	60	529.6	1035.3	2132.3	3899.0	5789.1		
Pm	61	535.9	1051.7	2151.6	3965.5	5952.2		
Sm	62	543.3	1068.1	2257.8	3994.5	6045.8		
Eu	63	546.7	1084.6	2404.4	4110.3	6100.8		

Gd	64	592.5	1166.5	1990.5	4245.4	6248.4		
Tb	65	564.6	1111.5	2114.0	3839.2	6412.4		
Dy	66	571.9	1126.0	2199.9	4001.2	5989.8		
Ho	67	580.6	1138.5	2203.7	4100.6	6168.3		
Er	68	588.7	1151.1	2194.1	4115.1	6281.2		
Tm	69	596.7	1162.6	2284.8	4119.0	6312.1		
Yb	70	603.4	1175.6	2415.0	4220.3	6327.5		
Lu	71	523.5	1341.1	2022.3	4360.2	6444.3		
Hf	72	641.6	1437.6	2248.1	3215.9	6595.4		
Ta	73	760.3				4657.6		
W	74	770.0						
Re	75	759.3						
Os	76	839.4						
Ir	77	868.4						
Pt	78	868.4	1790.8					
Au	79	889.6	1977.9					
Hg	80	1006.3	1809.2	3299.8				
Tl	81	589.1	1970.2	2875.3	4891.8			
Pb	82	715.4	1450.0	3080.8	4082.3	6638.2		
Bi	83	703.1	1609.4	2466.2	4370.8	5403.2	8519.7	
Po	84	813.4						
Rn	86	1036.8						
Fr	87	393.0						
Ra	88	509.2	978.7					
Ac	89	498.8	1167.5					
Th	90	586.6						
Pa	91	568.3						
U	92	583.7						
Np	93	597.2						
Pu	94	584.7						
Am	95	578.2						
Cm	96	580.8						
Bk	97	601.1						
Cf	98	607.9						
Es	99	619.4						

Fm	100	627.2						
Md	101	634.9						
No	102	641.6						
Lr	103	478.6						

C. E. Moore, Ionization Potentials and Limits Derived from the Analyses of Optical Spectra, NSRDS-NBS 34, National Bureau of Standards, Washington, DC, 1970.

For elements 57-72, values were obtained from Martin, W. C.; Hagan, Lucy; Reader, Joseph; Sugar, Jack J. Phys. Chem. Ref. Data, 1974, 3, 771-779.

For elements 59-73, fifth IEs came from Sugar, Jack J. Opt. Soc. Am. 1975, 65, 1366-1367.

For Lr see C&EN, Volume 93 Issue 15 | p. 8 | News of The Week, Issue Date: April 13, 2015 | Web Date: April 9, 2015 Lawrencium Ionization Energy Measured.

*Values for La, Hf, and Lr have been overwritten with more recent data

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6.6: Electron Affinity

Electron Affinity

John Moore, Jia Zhou, and Etienne Garand

Electron Affinity

Atom	Atomic No.	1st Electron Affinity (kJ/mol)
H	1	-72.77
He	2	48.24
Li	3	-59.63
Be	4	48.24
B	5	-26.73
C	6	-121.85
N	7	6.75
O	8	-140.98
F	9	-327.95
Ne	10	115.78
Na	11	-52.87
Mg	12	38.59
Al	13	-42.55
Si	14	-133.63
P	15	-72.03
S	16	-200.41
Cl	17	-348.99
Ar	18	96.49
K	19	-48.38
Ca	20	-2.37
Sc	21	-18.14
Ti	22	-7.62
V	23	-50.65
Cr	24	-64.26
Mn	25	115.78
Fe	26	-15.73
Co	27	-63.78
Ni	28	-111.54
Cu	29	-118.48
Zn	30	57.89
Ga	31	-28.95
Ge	32	-115.78
As	33	-78.15
Se	34	-194.97
Br	35	-324.67

Atom	Atomic No.	1st Electron Affinity (kJ/mol)
Kr	36	96.49
Rb	37	-46.88
Sr	38	48.24
Y	39	-29.62
Zr	40	-41.10
Nb	41	-86.16
Mo	42	-71.98
Tc	43	-53.07
Ru	44	-101.31
Rh	45	-109.70
Pd	46	-53.74
Ag	47	-125.62
Cd	48	67.54
In	49	-28.95
Sn	50	-115.78
Sb	51	-103.24
Te	52	-190.15
I	53	-295.16
Xe	54	77.19
Cs	55	-45.51
Ba	56	28.95
La	57	-48.24
Ce	58	
Pr	59	
Nd	60	
Pm	61	
Sm	62	
Eu	63	
Gd	64	
Tb	65	
Dy	66	
Ho	67	
Er	68	
Tm	69	
Yb	70	
Lu	71	0.00
Hf	72	-9.65
Ta	73	-31.07
W	74	-78.64
Re	75	-14.47

Atom	Atomic No.	1st Electron Affinity (kJ/mol)
Os	76	-106.13
Ir	77	-151.00
Pt	78	-205.32
Au	79	-222.75
Hg	80	48.24
Tl	81	-19.30
Pb	82	-35.12
Bi	83	-91.28
Po	84	-183.32
At	85	-270.16
Rn	86	67.54
Fr	87	
Ra	88	
Ac	89	
Th	90	
Pa	91	
U	92	
Np	93	
Pu	94	
Am	95	
Cm	96	
Bk	97	
Cf	98	
Es	99	
Fm	100	
Md	101	
No	102	
Lr	103	

Anderson, T.; Haugen, H. K.; and Hotop, W.. J. Phys. Chem. Ref. Data 1999, 28(6), 1526-1527.
Bratsch, Steven G.; Lagowski, J. J. Polyhedron 1986, 5, 1763-1770. Note that in this table the convention is that EA = ΔE when an electron is added to an atom to form a negative ion.

6.7: Common Polyatomic Ions

38

Common Polyatomic Ions

John Moore, Jia Zhou, and Etienne Garand

Polyatomic Ions (common)

Cations	
NH_4^+	Ammonium
Hg_2^{2+}	Mercury(I)
Anions (1-)	
OH^-	Hydroxide
HSO_4^-	Hydrogen sulfate
CH_3COO^-	Acetate
ClO^-	Hypochlorite
ClO_2^-	Chlorite
ClO_3^-	Chlorate
ClO_4^-	Perchlorate
NO_2^-	Nitrite
NO_3^-	Nitrate
MnO_4^-	Permanganate
$H_2PO_4^-$	Dihydrogen phosphate
CN^-	Cyanide
HCO_3^-	Hydrogen carbonate
SCN^-	Thiocyanate
Anions (2-)	
O_2^{2-}	Peroxide
SO_3^{2-}	Sulfite
SO_4^{2-}	Sulfate
$S_2O_3^{2-}$	Thiosulfate
$Cr_2O_7^{2-}$	Dichromate
CrO_4^{2-}	Chromate
CO_3^{2-}	Carbonate
HPO_4^{2-}	Monohydrogen phosphate
$C_2O_4^{2-}$	Oxalate
Anions (3-)	
PO_4^{3-}	Phosphate
AsO_4^{3-}	Arsenate

6.8: Bond Enthalpy and Length

Bond Enthalpy and Length

John Moore, Jia Zhou, and Etienne Garand

Average Bond Enthalpy (Scroll down for average bond length.)

In kJ/mol

	I	Br	Cl	S	P	Si	F	O	N	C	H
H	299	366	431	347	322	323	566	467	391	416	436
C	213	285	327	272	264	301	485	358	285	346	
N	-	-	193	-	~200	335	272	201	160		
O	201	-	205	-	~340	368	190	146			
F	-	238	255	326	490	582	158				
Si	234	310	391	226	-	226					
P	184	264	319	-	209						
S	-	213	255	226		**Multiple Bonds**			**Multiple Bonds**		
Cl	209	217	242			N=N		418	C=C		598
Br	180	193				N≡N		946	C≡C		813
I	151					C=N		616	C=O in CO_2		803
						C≡N		866	C=O carbonyl		695
						N=O		607	C≡O		1073
						O=O in O_2		498	N≡O		632

Data from Cotton, F.A., Wilkinson, G. and Gaus, P.L., Basic Inorganic Chemistry, 3rd ed., New York: Wiley, 1995. Corrected values for C-C, and C-O from Cottrell, T.L., The Strengths of Chemical Bonds, 2ed., London:Butterworths, 1958.

Average Bond Length

In picometers, (pm)

	I	Br	Cl	S	P	Si	F	O	N	C	H
H	161	142	127	132	138	145	92	94	98	110	74
C	210	191	176	181	187	194	141	143	147	154	
N	203	184	169	174	180	187	134	136	140		
O	199	180	165	170	176	183	130	148			
F	197	178	163	168	174	181	128				
Si	250	231	216	221	227	234					
P	243	224	209	214	220						
S	237	218	203	208		**Multiple Bonds**			**Multiple Bonds**		
Cl	232	213	200			N=N		120	C=C		134

Br	247	228				N≡N	110	C≡C	121
I	266					C=N	127	C=O in CO_2	116
						C≡N	115	C=O carbonyl	121
						N=O	115	C≡O	113
						O=O in O_2	121	N≡O	115

6.9: Electronegativity

39

Electronegativity

John Moore, Jia Zhou, and Etienne Garand

Electronegativity

Atom	Atomic No.	Electronegativity
H	1	2.2
He	2	
Li	3	1.0
Be	4	1.6
B	5	2.1
C	6	2.6
N	7	3.1
O	8	3.5
F	9	4.0
Ne	10	
Na	11	1.0
Mg	12	1.3
Al	13	1.6
Si	14	1.9
P	15	2.2
S	16	2.6
Cl	17	3.2
Ar	18	
K	19	0.8
Ca	20	1.0
Sc	21	1.4
Ti	22	1.6
V	23	1.7
Cr	24	1.7
Mn	25	1.6
Fe	26	1.9
Co	27	1.9
Ni	28	1.9
Cu	29	1.9
Zn	30	1.7
Ga	31	1.8
Ge	32	2.0
As	33	2.2
Se	34	2.6

Atom	Atomic No.	Electronegativity
Br	35	3.0
Kr	36	3.4
Rb	37	0.8
Sr	38	1.0
Y	39	1.2
Zr	40	1.4
Nb	41	
Mo	42	2.2
Tc	43	
Ru	44	
Rh	45	2.3
Pd	46	2.2
Ag	47	2.0
Cd	48	1.7
In	49	1.8
Sn	50	2.0
Sb	51	2.1
Te	52	2.1
I	53	2.7
Xe	54	3.0
Cs	55	0.8
Ba	56	0.9
La	57	
Ce	58	
Pr	59	
Nd	60	
Pm	61	
Sm	62	
Eu	63	
Gd	64	
Tb	65	
Dy	66	
Ho	67	
Er	68	
Tm	69	
Yb	70	
Lu	71	
Hf	72	
Ta	73	
W	74	2.4

Atom	Atomic No.	Electronegativity
Re	75	
Os	76	
Ir	77	2.2
Pt	78	2.3
Au	79	2.6
Hg	80	2.0
Tl	81	2.1
Pb	82	2.4
Bi	83	2.0
Po	84	2.0
At	85	2.2
Rn	86	

Allred, A. L. J. Inorg. Nucl. Chem. 1961, 17, 215.

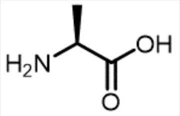
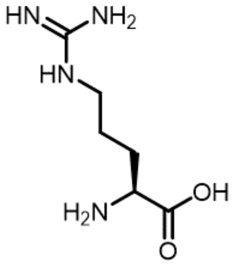
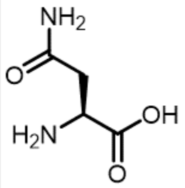
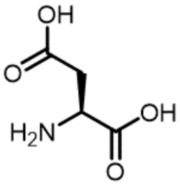
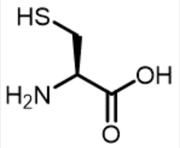
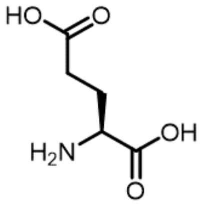
6.10: Amino Acids

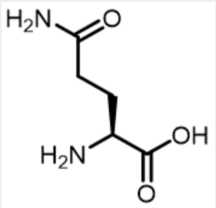
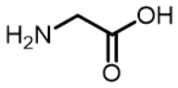
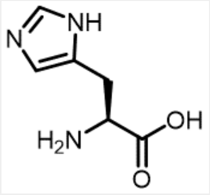
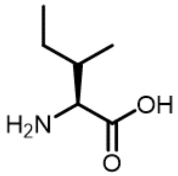
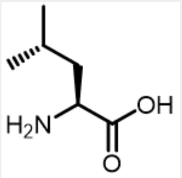
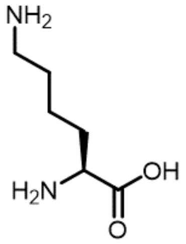
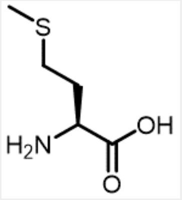
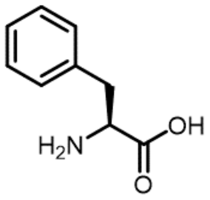
40

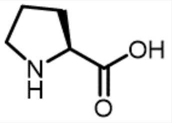
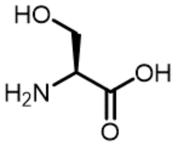
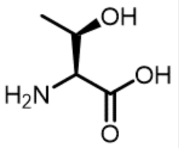
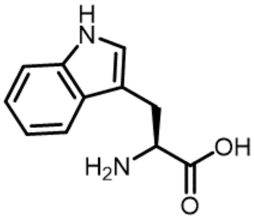
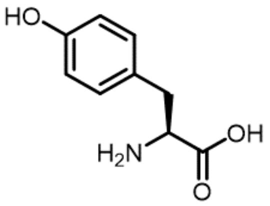
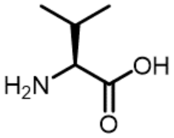
Amino Acids

John Moore, Jia Zhou, and Etienne Garand

Amino Acids

Name	Abbreviation (3 letter)	Abbreviation (1 letter)	Structure
Alanine	Ala	A	
Arginine	Arg	R	
Asparagine	Asn	N	
Aspartic Acid	Asp	D	
Cysteine	Cys	C	
Glutamic Acid	Glu	E	

Glutamine	Gln	Q	
Glycine	Gly	G	
Histidine	His	H	
Isoleucine	Ile	I	
Leucine	Leu	L	
Lysine	Lys	K	
Methionine	Met	M	
Phenylalanine	Phe	F	

Proline	Pro	P	
Serine	Ser	S	
Threonine	Thr	T	
Tryptophan	Trp	W	
Tyrosine	Tyr	Y	
Valine	Val	V	

6.11: Solubility Product Constant

Solubility Product Constant

John Moore, Jia Zhou, and Etienne Garand

Solubility Product Constants for Select Compounds

K_{sp} determined at 25 °C.

Substance	**K_{sp}**
Aluminum Compounds	
$AlAsO_4$	1.6×10^{-16}
$Al(OH)_3$ amorphous	1.3×10^{-33}
$AlPO_4$	6.3×10^{-19}
Barium Compounds	
$Ba_3(AsO_4)_2$	8.0×10^{-15}
$BaCO_3$	5.1×10^{-9}
BaC_2O_4	1.6×10^{-7}
$BaCrO_4$	1.2×10^{-10}
BaF_2	1.0×10^{-6}
$Ba(OH)_2$	5×10^{-3}
$Ba_3(PO_4)_2$	3.4×10^{-23}
$BaSeO_4$	3.5×10^{-8}
$BaSO_4$	1.1×10^{-10}
$BaSO_3$	8×10^{-7}
BaS_2O_3	1.6×10^{-5}
Bismuth Compounds	
$BiAsO_4$	4.4×10^{-10}
$BiOCl$‡	1.8×10^{-31}
$BiO(OH)$	4×10^{-10}
$Bi(OH)_3$	4×10^{-31}
BiI_3	8.1×10^{-19}
$BiPO_4$	1.3×10^{-23}
Cadmium Compounds	
$Cd_3(AsO_4)_2$	2.2×10^{-33}
$CdCO_3$	5.2×10^{-12}
$Cd(CN)_2$	1.0×10^{-8}
$Cd_2[Fe(CN)_6]$	3.2×10^{-17}
$Cd(OH)_2$ fresh	2.5×10^{-14}
Calcium Compounds	
$Ca_3(AsO_4)_2$	6.8×10^{-19}
$CaCO_3$	2.8×10^{-9}
$CaCrO_4$	7.1×10^{-4}
$CaC_2O_4 \cdot H_2O$§	4×10^{-9}
CaF_2	5.3×10^{-9}
$Ca(OH)_2$	5.5×10^{-6}
$CaHPO_4$	1×10^{-7}
$Ca_3(PO_4)_2$	2.0×10^{-29}

Substance	K_{sp}
$CaSeO_4$	8.1×10^{-4}
$CaSO_4$	9.1×10^{-6}
$CaSO_3$	6.8×10^{-8}
Chromium Compounds	
$CrAsO_4$	7.7×10^{-21}
$Cr(OH)_2$	2×10^{-16}
$Cr(OH)_3$	6.3×10^{-31}
$CrPO_4{\cdot}4H_2O$ green§	2.4×10^{-23}
$CrPO_4{\cdot}4H_2O$ violet§	1.0×10^{-17}
Cobalt Compounds	
$Co_3(AsO_4)_2$	7.6×10^{-29}
$CoCO_3$	1.4×10^{-13}
$Co(OH)_2$ fresh	1.6×10^{-15}
$Co(OH)_3$	1.6×10^{-44}
$CoHPO_4$	2×10^{-7}
$Co_3(PO_4)_2$	2×10^{-35}
Copper Compounds	
$CuBr$	5.3×10^{-9}
$CuCl$	1.2×10^{-6}
$CuCN$	3.2×10^{-20}
CuI	1.1×10^{-12}
$CuOH$	1×10^{-14}
$CuSCN$	4.8×10^{-15}
$Cu_3(AsO_4)_2$	7.6×10^{-36}
$CuCO_3$	1.4×10^{-10}
$Cu_2[Fe(CN)_6]$	1.3×10^{-16}
$Cu(OH)_2$	2.2×10^{-20}
$Cu_3(PO_4)_2$	1.3×10^{-37}
Gold Compounds	
$AuCl$	2.0×10^{-13}
AuI	1.6×10^{-23}
$AuCl_3$	3.2×10^{-25}
$Au(OH)_3$	5.5×10^{-46}
AuI_3	1×10^{-46}
Iron Compounds	
$FeCO_3$	3.2×10^{-11}
$Fe(OH)_2$	8.0×10^{-16}
$FeC_2O_4{\cdot}2H_2O$§	3.2×10^{-7}
$FeAsO_4$	5.7×10^{-21}
$Fe_4[Fe(CN)_6]_3$	3.3×10^{-41}
$Fe(OH)_3$	4×10^{-38}
$FePO_4$	1.3×10^{-22}
Lead Compounds	
$Pb_3(AsO_4)_2$	4.0×10^{-36}

Substance	K_{sp}
$PbBr_2$	4.0×10^{-5}
$PbCO_3$	7.4×10^{-14}
$PbCl_2$	1.6×10^{-5}
$PbCrO_4$	2.8×10^{-13}
PbF_2	2.7×10^{-8}
$Pb(OH)_2$	1.2×10^{-15}
PbI_2	7.1×10^{-9}
PbC_2O_4	4.8×10^{-10}
$PbHPO_4$	1.3×10^{-10}
$Pb_3(PO_4)_2$	8.0×10^{-43}
$PbSeO_4$	1.4×10^{-7}
$PbSO_4$	1.6×10^{-8}
$Pb(SCN)_2$	2.0×10^{-5}
Magnesium Compounds	
$Mg_3(AsO_4)_2$	2.1×10^{-20}
$MgCO_3$	3.5×10^{-8}
$MgCO_3 \cdot 3H_2O$§	2.1×10^{-5}
$MgC_2O_4 \cdot 2H_2O$§	1×10^{-8}

From Patnaik, P., Dean's Analytical Chemistry Handbook, 2nd ed. New York: McGraw-Hill, 2004, Table 4.2.
No metal sulfides are listed in this table because sulfide ion is such a strong base that the usual solubility product equilibrium equation does not apply. See Myers, R. J. Journal of Chemical Education, Vol. 63, 1986, pp. 687-690.
‡From Meites, L. Ed. Handbook of Analytical Chemistry, 1st ed. New York: McGraw-Hill, 1963.
§Because $[H_2O]$ does not appear in equilibrium constants for equilibria in aqueous solution in general, it does not appear in the K_{sp} expressions for hydrated solids.

6.12: Acid-Base Ionization Constant

Acid-Base Ionization Constant

John Moore, Jia Zhou, and Etienne Garand

Ionization Constants for Select Acids (a table for bases is below)

K_a determined at 25 °C.

Acid	Formula and Ionization Equation	K_a	pK_a
Acetic	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	1.8×10^{-5}	4.74
Arsenic	$H_3AsO_4 + H_2O \rightleftharpoons H_3O^+ + H_2AsO_4^-$	$K_1 = 6.17 \times 10^{-3}$	2.210
	$H_2AsO_4^- + H_2O \rightleftharpoons H_3O^+ + HAsO_4^{2-}$	$K_2 = 1.17 \times 10^{-7}$	6.932
	$HAsO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + AsO_4^{3-}$	$K_3 = 3.09 \times 10^{-12}$	11.523
Benzoic	$C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$	1.2×10^{-4}	3.92
Boric	$B(OH)_3(H_2O) + H_2O \rightleftharpoons H_3O^+ + B(OH)_4^-$	5.8×10^{-10}	9.24
Butyric	$CH_3CH_2CH_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_3CH_2CH_2COO^-$	1.5×10^{-5}	4.82
Carbonic	$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$	$K_1 = 4.3 \times 10^{-7}$	6.37
	$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$	$K_2 = 4.7 \times 10^{-11}$	10.33
Citric	$H_3C_6H_5O_7 + H_2O \rightleftharpoons H_3O^+ + H_2C_6H_5O_7^-$	$K_1 = 1.4 \times 10^{-3}$	2.85
	$H_2C_6H_5O_7^- + H_2O \rightleftharpoons H_3O^+ + HC_6H_5O_7^{2-}$	$K_2 = 4.5 \times 10^{-5}$	4.35
	$HC_6H_5O_7^{2-} + H_2O \rightleftharpoons H_3O^+ + C_6H_5O_7^{3-}$	$K_3 = 1.5 \times 10^{-6}$	5.82
Chloroacetic	$CH_2ClCOOH + H_2O \rightleftharpoons H_3O^+ + CH_2ClCOO^-$	1.4×10^{-3}	2.85
4-chlorobutyric	$CH_2ClCH_2CH_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_2ClCH_2CH_2COO^-$	3.0×10^{-5}	4.53
3-chlorobutyric acid	$CH_3CHClCH_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_3CHClCH_2COO^-$	8.9×10^{-5}	4.05
2-chlorobutyric acid	$CH_3CH_2CHClCOOH + H_2O \rightleftharpoons H_3O^+ + CH_3CH_2CHClCOO^-$	1.3×10^{-3}	2.89
Chlorous	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Dichloroacetic	$CHCl_2COOH + H_2O \rightleftharpoons H_3O^+ + CHCl_2COO^-$	4.5×10^{-2}	1.35
Formic	$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$	1.8×10^{-4}	3.75
Hydrazoic	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.0×10^{-5}	5.00
Hydrochloric	$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$	1.2×10^{6}	-6.1
Hydrocyanic	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	3.3×10^{-10}	9.48
Hydrofluoric	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.8×10^{-4}	3.17
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	2.1×10^{-12}	11.68
Hydrosulfuric†	$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$	$K_1 = 1 \times 10^{-7}$	7.0
	$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$	$K_2 = 1 \times 10^{-19}$	19.0
Hypobromous	$HOBr + H_2O \rightleftharpoons H_3O^+ + OBr^-$	3×10^{-9}	8.5
Hypochlorous	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	6.8×10^{-8}	7.17
Hypoiodous	$HOI + H_2O \rightleftharpoons H_3O^+ + OI^-$	3×10^{-11}	10.5
Nitric	$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$	27	-1.43
Nitrous	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.41×10^{-4}	3.130
Oxalic	$H_2C_2O_4 + H_2O \rightleftharpoons H_3O^+ + HC_2O_4^-$	$K_1 = 5.5 \times 10^{-2}$	1.26
	$HC_2O_4^- + H_2O \rightleftharpoons H_3O^+ + C_2O_4^{2-}$	$K_2 = 1.4 \times 10^{-4}$	3.85
Phenol	$HC_6H_5O + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.7×10^{-10}	9.77
Phosphoric	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$	$K_1 = 7.2 \times 10^{-3}$	2.14

Acid	Formula and Ionization Equation	K_a	pK_a
	$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$	$K_2 = 6.3 \times 10^{-8}$	7.20
	$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$	$K_3 = 4.6 \times 10^{-13}$	12.34
Phosphorous	$H_3PO_3 + H_2O \rightleftharpoons H_3O^+ + H_2PO_3^-$	$K_1 = 2.4 \times 10^{-2}$	1.62
	$H_2PO_3^- + H_2O \rightleftharpoons H_3O^+ + HPO_3^{2-}$	$K_2 = 2.9 \times 10^{-7}$	6.54
Propanoic	$CH_3CH_2COOH + H_2O \rightleftharpoons H_3O^+ + CH_3CH_2COO^-$	1.33×10^{-5}	4.85
Selenic	$H_2SeO_4 + H_2O \rightleftharpoons H_3O^+ + HSeO_4^-$	K_1 = very large	---
	$HSeO_4^- + H_2O \rightleftharpoons H_3O^+ + SeO_4^{2-}$	$K_2 = 2.2 \times 10^{-2}$	1.66
Selenous	$H_2SeO_3 + H_2O \rightleftharpoons H_3O^+ + HSeO_3^-$	$K_1 = 2.5 \times 10^{-3}$	2.60
	$HSeO_3^- + H_2O \rightleftharpoons H_3O^+ + SeO_3^{2-}$	$K_2 = 1.6 \times 10^{-9}$	8.80
Sulfuric	$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$	$K_1 = 4.0 \times 10^{3}$	-3.6
	$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	$K_2 = 1.1 \times 10^{-2}$	1.96
Sulfurous	$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$	$K_1 = 1.7 \times 10^{-2}$	1.77
	$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$	$K_2 = 6.3 \times 10^{-8}$	7.2
Tellurous	$H_2TeO_3 + H_2O \rightleftharpoons H_3O^+ + HTeO_3^-$	$K_1 = 7.1 \times 10^{-7}$	6.15
	$HTeO_3^- + H_2O \rightleftharpoons H_3O^+ + TeO_3^{2-}$	$K_2 = 4.0 \times 10^{-9}$	8.40
Trichloroacetic	$CCl_3COOH + H_2O \rightleftharpoons H_3O^+ + CCl_3COO^-$	0.17	0.77
Trifluoroacetic	$CF_3COOH + H_2O \rightleftharpoons H_3O^+ + CF_3COO^-$	0.30	0.52

Taken from Hogfeldt, E. and Perrin, D. D., Stability Constants of Metal-Ion complexes, 1st ed. Oxford: New York: Pergamon, 1979-1982. International Union of Pure and Applied Chemistry Commission on Equilibrium Data.
Also from Serjeant, E. P. and Dempsey, B. (eds.), “Ionization Constants of Organic Acids in Aqueous Solution,” IUPAC Chemical Data Series No. 23, Pergamon Press, Oxford, 1979.
[†]From Myers, R., Journal of Chemical Education, Vol. 63, 1986, pp. 687-690.

Ionization Constants for Select Bases

K_b determined at 25 °C.

Base	Formula and Ionization Equation	K_b	pK_b
Acetylide	$C_2H^- + H_2O \rightleftharpoons OH^- + C_2H_2$	1×10^{11}	-11
Amide	$NH_2^- + H_2O \rightleftharpoons OH^- + NH_3$	1×10^{20}	-20
Ammonia‡	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.77×10^{-5}	4.752
Aniline§	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	3.9×10^{-10}	9.41
Dimethylamine§	$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.8×10^{-4}	3.24
Ethoxide	$CH_3CH_2O^- + H_2O \rightleftharpoons OH^- + CH_3CH_2OH$	1×10^{2}	-2
Ethylenediamine	$(CH_2)_2(NH_2)_2 + H_2O \rightleftharpoons (CH_2)_2(NH_2)_2H^+ + OH^-$	$K_1 = 7.8 \times 10^{-5}$	4.11
	$(CH_2)_2(NH_2)_2H^+ + H_2O \rightleftharpoons (CH_2)_2(NH_2)_2H_2^{2+} + OH^-$	$K_2 = 2.1 \times 10^{-8}$	7.68
Hydrazine	$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$	$K_1 = 1.2 \times 10^{-6}$	5.92
	$N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$	$K_2 = 1.3 \times 10^{-15}$	14.89
Hydride	$H^- + H_2O \rightleftharpoons OH^- + H_2$	1×10^{21}	-21
Hydroxylamine	$NH_2OH + H_2O \rightleftharpoons NH_3OH^+ + OH^-$	9.3×10^{-9}	8.03
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	5.0×10^{-4}	3.30
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.6×10^{-9}	8.80
Trimethylamine§	$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.2×10^{-5}	4.21

Taken from Hogfeldt, E. and Perrin, D. D., Stability Constants of Metal-Ion complexes, 1st ed. Oxford: New York: Pergamon, 1979-1982. International Union of Pure and Applied Chemistry Commission on Equilibrium Data.
Also from Serjeant, E. P. and Dempsey, B. (eds.), “Ionization Constants of Organic Acids in Aqueous Solution,” IUPAC Chemical Data Series No. 23, Pergamon Press, Oxford, 1979.
[‡] From Read, A. J., Journal of Solution Chemistry, Vol. 11, No. 9, 1982, pp. 649-664.
[§] From Meites, L., Ed. Handbook of Analytical Chemistry, 1st ed. New York: McGraw-Hill, 1963.

6.13: Thermodynamic

Thermodynamic

John Moore, Jia Zhou, and Etienne Garand

Thermodynamic Values for Select Compounds

at 298.15 K.

Species	$\Delta_f H°$ (kJ/mol)	$S°$ (J K^{-1} mol^{-1})	$\Delta_f G°$ (kJ/mol)
Aluminum			
Al(s)	0	28.275	0
Al^{3+}(aq)	−531	−321.7	−485
$AlCl_3$(s)	−704.2	110.67	−628.8
Al_2O_3(s, corundum)	−1675.7	50.92	−1582.3
Argon			
Ar(g)	0	154.843	0
Ar(aq)	−12.1	59.4	16.4
Barium			
$BaCl_2$(s)	−858.6	123.68	−810.4
BaO(s)	−553.5	70.42	−525.1
$BaSO_4$(s)	−1473.2	132.2	−1362.2
$BaCO_3$(s)	−1216.3	112.1	85.35
Beryllium			
Be(s)	0	9.5	0
$Be(OH)_2$(s)	−902.5	51.9	−815
Bromine			
Br(g)	111.884	175.022	82.396
Br_2(ℓ)	0	152.231	0
Br_2(g)	30.907	245.463	3.110
Br_2(aq)	−2.59	130.5	3.93
Br^-(aq)	−121.55	82.4	−103.96
BrCl(g)	14.64	240.10	−0.98
BrF_3(g)	−255.6	292.53	−229.43
HBr(g)	−36.40	198.695	−53.45
Calcium			
Ca(s)	0	41.42	0
Ca(g)	178.2	158.884	144.3
Ca^{2+}(g)	1925.9	—	—
Ca^{2+}(aq)	−542.83	−53.1	−553.58
CaC_2(s)	−59.8	69.96	−64.9
$CaCO_3$(s, calcite)	−1206.92	92.9	−1128.79
$CaCl_2$(s)	−795.8	104.6	−748.1
CaF_2(s)	−1219.6	68.87	−1167.3
CaH_2(s)	−186.2	42	−147.2
CaO(s)	−635.09	39.75	−604.03

Species	$\Delta_f H°$ (kJ/mol)	$S°$ (J K^{-1} mol^{-1})	$\Delta_f G°$ (kJ/mol)
CaS(s)	−482.4	56.5	−477.4
$Ca(OH)_2$(s)	−986.09	83.39	−898.49
$Ca(OH)_2$(aq)	−1002.82	−74.5	−868.07
$CaSO_4$(s)	−1434.11	106.7	−1321.79
Carbon			
C(s, graphite)	0	5.74	0
C(s, diamond)	1.895	2.377	2.9
C(g)	716.682	158.096	671.257
CCl_4(ℓ)	−135.44	216.4	−65.21
CCl_4(g)	−102.9	309.85	−60.59
$CHCl_3$(ℓ)	−134.47	201.7	−73.66
$CHCl_3$(g)	−103.14	295.71	−70.34
CH_4(g, methane)	−74.81	186.264	−50.72
C_2H_2(g, ethyne)	226.73	200.94	209.2
C_2H_4(g, ethene)	52.26	219.56	68.15
C_2H_6(g, ethane)	−84.68	229.6	−32.82
C_3H_8(g, propane)	−103.8	269.9	−23.49
C_4H_{10}(g, butane)	−126.148	310.227	−16.985
C_6H_6(ℓ, benzene)	49.03	172.8	124.5
C_6H_{14}(ℓ, hexane)	−198.782	296.018	−4.035
C_8H_{18}(g, octane)	−208.447	466.835	16.718
C_8H_{18}(ℓ, octane)	−249.952	361.205	6.707
CH_3OH(ℓ, methanol)	−238.66	126.8	−166.27
CH_3OH(g, methanol)	−200.66	239.81	−161.96
CH_3OH(aq, methanol)	−245.931	133.1	−175.31
C_2H_5OH(ℓ, ethanol)	−277.69	160.7	−174.78
C_2H_5OH(g, ethanol)	−235.1	282.7	−168.49
C_2H_5OH(aq, ethanol)	−288.3	148.5	−181.64
$C_6H_{12}O_6$(s, glucose)	−1274.4	235.9	−917.2
CH_3COO^-(aq)	−486.01	86.6	−369.31
CH_3COOH(aq)	−485.76	178.7	−396.46
CH_3COOH(ℓ)	−484.5	159.8	−389.9
CO(g)	−110.525	197.674	−137.168
CO_2(g)	−393.509	213.74	−394.359
H_2CO_3(aq)	−699.65	187.4	−623.08
HCO_3^-(aq)	−691.99	91.2	−586.77
CO_3^{2-}(aq)	−677.14	−56.9	−527.81
$HCOO^-$(aq)	−425.55	92.0	−351.0
HCOOH(aq)	−425.43	163	−372.3
HCOOH(ℓ)	−424.72	128.95	−361.35
CS_2(g)	117.36	237.84	67.12
CS_2(ℓ)	89.70	151.34	65.27

Species	$\Delta_f H°$ (kJ/mol)	$S°$ (J K^{-1} mol^{-1})	$\Delta_f G°$ (kJ/mol)
$COCl_2(g)$	−218.8	283.53	−204.6
Cesium			
Cs(s)	0	85.23	0
$Cs^+(g)$	457.964	—	—
CsCl(s)	−443.04	101.17	−414.53
Chlorine			
Cl(g)	121.679	165.198	105.68
$Cl^-(g)$	−233.13	—	—
$Cl^-(aq)$	−167.159	56.5	−131.228
$Cl_2(g)$	0	223.066	0
$Cl_2(aq)$	−23.4	121	6.94
HCl(g)	−92.307	186.908	−95.299
HCl(aq)	−167.159	56.5	−131.228
$ClO_2(g)$	102.5	256.84	120.5
$Cl_2O(g)$	80.3	266.21	97.9
$ClO^-(aq)$	−107.1	42.0	−36.8
HClO(aq)	−120.9	142	−79.9
$ClF_3(g)$	−163.2	281.61	−123.0
Chromium			
Cr(s)	0	23.77	0
$Cr_2O_3(s)$	−1139.7	81.2	−1058.1
$CrCl_3(s)$	−556.5	123	−486.1
Copper			
Cu(s)	0	33.15	0
CuO(s)	−157.3	42.63	−129.7
$CuCl_2(s)$	−220.1	108.07	−175.7
$CuSO_4(s)$	−771.36	109	−661.8
Fluorine			
$F_2(g)$	0	202.78	0
F(g)	78.99	158.754	61.91
$F^-(g)$	−255.39	—	—
$F^-(aq)$	−332.63	−13.8	−278.79
HF(g)	−271.1	173.779	−273.2
HF(aq, un-ionized)	−320.08	88.7	−296.82
HF(aq, ionized)	−332.63	−13.8	−278.79
Hydrogen†			
$H_2(g)$	0	130.684	0
$H_2(aq)$	−4.2	57.7	17.6
HD(g)	0.318	143.801	−1.464
$D_2(g)$	0	144.960	0
H(g)	217.965	114.713	203.247
$H^+(g)$	1536.202	—	—

Species	$\Delta_f H^\circ$ (kJ/mol)	S° (J K^{-1} mol^{-1})	$\Delta_f G^\circ$ (kJ/mol)
H^+(aq)	0	0	0
OH^-(aq)	−229.994	−10.75	−157.244
$H_2O(\ell)$	−285.83	69.91	−237.129
H_2O(g)	−241.818	188.825	−228.572
$H_2O_2(\ell)$	−187.78	109.6	−120.35
H_2O_2(aq)	−191.17	143.9	−134.03
HO_2^-(aq)	−160.33	23.8	−67.3
$HDO(\ell)$	−289.888	79.29	−241.857
$D_2O(\ell)$	−294.600	75.94	−243.439
Iodine			
I_2(s)	0	116.135	0
I_2(g)	62.438	260.69	19.327
I_2(aq)	22.6	137.2	16.40
I(g)	106.838	180.791	70.25
I^-(g)	−197	—	—
I^-(aq)	−55.19	111.3	−51.57
I_3^-(aq)	−51.5	239.3	−51.4
HI(g)	26.48	206.594	1.70
HI(aq, ionized)	−55.19	111.3	−51.57
IF(g)	−95.65	236.17	−118.51
ICl(g)	17.78	247.551	−5.46
$ICl(\ell)$	−23.89	135.1	−13.58
IBr(g)	40.84	258.773	3.69
ICl_3(s)	−89.5	167.4	−22.29
Iron			
Fe(s)	0	27.78	0
FeO(s, wustite)	−266.27	57.49	−245.12
Fe_2O_3(s, hematite)	−824.2	87.4	−742.2
Fe_3O_4(s, magnetite)	−1118.4	146.4	−1015.4
$FeCl_2$(s)	−341.79	117.95	−302.3
$FeCl_3$(s)	−399.49	142.3	−344
FeS_2(s, pyrite)	−178.2	52.93	−166.9
$Fe(CO)_5(\ell)$	−774	338.1	−705.3
Lead			
Pb(s)	0	64.81	0
$PbCl_2$(s)	−359.41	136	−314.1
PbO(s, yellow)	−217.32	68.7	−187.89
PbS(s)	−100.4	91.2	−98.7
$PbSO_4$(s)	−919.94	148.57	−813.14
$PbCl_4(\ell)$	−329.3	—	—
PbO_2(s)	−277.4	68.6	−217.33
Lithium			

Species	$\Delta_f H°$ (kJ/mol)	$S°$ (J K^{-1} mol^{-1})	$\Delta_f G°$ (kJ/mol)
Li(s)	0	29.12	0
Li^+(g)	685.783	—	—
LiOH(s)	−484.93	42.8	−438.95
LiOH(aq)	−508.48	2.8	−450.58
LiCl(s)	−408.701	59.33	−384.37
Magnesium			
Mg(s)	0	32.68	0
Mg^{2+}(aq)	−466.85	−138.1	−454.8
$MgCl_2$(g)	−400.4	—	—
$MgCl_2$(s)	−641.32	89.62	−591.79
$MgCl_2$(aq)	−801.15	−25.1	−717.1
MgO(s)	−601.70	26.94	−569.43
$Mg(OH)_2$(s)	−924.54	63.18	−833.51
MgS(s)	−346	50.33	−341.8
$MgSO_4$(s)	−1284.9	91.6	−1170.6
$MgCO_3$(s)	−1095.8	65.7	−1012.1
Mercury			
Hg(ℓ)	0	76.02	0
$HgCl_2$(s)	−224.3	146	−178.6
HgO(s, red)	−90.83	70.9	−58.539
HgS(s, red)	−58.2	82.4	−50.6
Nickel			
Ni(s)	0	29.87	0
NiO(s)	−239.7	37.99	−211.7
$NiCl_2$(s)	−305.332	97.65	−259.032
Nitrogen			
N_2(g)	0	191.61	0
N_2(aq)	−10.8	—	—
N(g)	472.704	153.298	455.53
NH_3(g)	−46.11	192.45	−16.45
NH_3(aq)	−80.29	111.3	−26.50
NH_4^+(aq)	−132.51	113.4	−79.31
N_2H_4(ℓ)	50.63	121.21	149.34
NH_4Cl(s)	−314.43	94.6	−202.87
NH_4Cl(aq)	−299.66	169.9	−210.52
NH_4NO_3(s)	−365.56	151.08	−183.87
NH_4NO_3(aq)	−339.87	259.8	−190.56
NO(g)	90.25	210.761	86.55
NO_2(g)	33.18	240.06	51.31
N_2O(g)	82.05	219.85	104.20
N_2O_4(g)	9.16	304.29	97.89
N_2O_4(ℓ)	−19.50	209.2	97.54

Species	$\Delta_f H°$ (kJ/mol)	$S°$ (J K^{-1} mol^{-1})	$\Delta_f G°$ (kJ/mol)
$NOCl(g)$	51.71	261.69	66.08
$HNO_3(\ell)$	−174.10	155.60	−80.71
$HNO_3(g)$	−135.06	266.38	−74.72
$HNO_3(aq)$	−207.36	146.4	−111.25
$NO_3^-(aq)$	−205.0	146.4	−108.74
$NF_3(g)$	−124.7	260.73	−83.2
Oxygen†			
$O_2(g)$	0	205.138	0
$O_2(aq)$	−11.7	110.9	16.4
$O(g)$	249.170	161.055	231.731
$O_3(g)$	142.7	238.93	163.2
$OH^-(aq)$	−229.994	−10.75	−157.244
Phosphorus			
P_4(s, white)	0	164.36	0
P_4(s, red)	−70.4	91.2	−48.4
$P(g)$	314.64	163.193	278.25
$PH_3(g)$	5.4	310.23	13.4
$PCl_3(g)$	−287.0	311.78	−267.8
$PCl_3(\ell)$	−319.7	217.1	−272.3
$PCl_5(s)$	−443.5	—	—
$P_4O_{10}(s)$	−2984.0	228.86	−2697.7
$H_3PO_4(s)$	−1279	110.5	−1119.1
Potassium			
$K(s)$	0	64.18	0
$KF(s)$	−567.27	66.57	−537.75
$KCl(s)$	−436.747	82.59	−409.14
$KCl(aq)$	−419.53	159.0	−414.49
$KBr(s)$	−393.798	95.90	−380.66
$KI(s)$	−327.900	106.32	−324.892
$KClO_3(s)$	−397.73	143.1	−296.25
$KOH(s)$	−424.764	78.9	−379.08
$KOH(aq)$	−482.37	91.6	−440.5
Silicon			
$Si(s)$	0	18.83	0
$SiBr_4(\ell)$	−457.3	277.8	−443.8
$SiC(s)$	−65.3	16.61	−62.8
$SiCl_4(g)$	−657.01	330.73	−616.98
$SiH_4(g)$	34.3	204.62	56.9
$SiF_4(g)$	−1614.94	282.49	−1572.65
SiO_2(s, quartz)	−910.94	41.84	−856.64
Silver			
$Ag(s)$	0	42.55	0

Species	$\Delta_f H°$ (kJ/mol)	$S°$ (J K^{-1} mol^{-1})	$\Delta_f G°$ (kJ/mol)
Ag^+(aq)	105.579	72.68	77.107
Ag_2O(s)	−31.05	121.3	−11.2
AgCl(s)	−127.068	96.2	−109.789
AgI(s)	−61.84	115.5	−66.19
AgN_3(s)	620.60	99.22	591.0
$AgNO_3$(s)	−124.39	140.92	−33.41
$AgNO_3$(aq)	−101.8	219.2	−34.16
Sodium			
Na(s)	0	51.21	0
Na(g)	107.32	153.712	76.761
Na^+(g)	609.358	—	—
Na^+(aq)	−240.12	59.0	−261.905
NaF(s)	−573.647	51.46	−543.494
NaF(aq)	−572.75	45.2	−540.68
NaCl(s)	−411.153	72.13	−384.138
NaCl(g)	−176.65	229.81	−196.66
NaCl(aq)	−407.27	115.5	−393.133
NaBr(s)	−361.062	86.82	−348.983
NaBr(aq)	−361.665	141.4	−365.849
NaI(s)	−287.78	98.53	−286.06
NaI(aq)	−295.31	170.3	−313.47
NaOH(s)	−425.609	64.455	−379.484
NaOH(aq)	−470.114	48.1	−419.15
$NaClO_3$(s)	−365.774	123.4	−262.259
$NaHCO_3$(s)	−950.81	101.7	−851.0
Na_2CO_3(s)	−1130.68	134.98	−1044.44
Na_2SO_4(s)	−1387.08	149.58	−1270.16
Sulfur			
S(s, monoclinic)	0.33	—	—
S(s, rhombic)	0	31.80	0
S(g)	278.805	167.821	238.250
S^{2-}(aq)	33.1	−14.6	85.8
S_2Cl_2(g)	−18.4	331.5	−31.8
SF_6(g)	−1209	291.82	−1105.3
SF_4(g)	−774.9	292.03	−731.3
H_2S(g)	−20.63	205.79	−33.56
H_2S(aq)	−39.7	121	−27.83
HS^-(aq)	−17.6	62.8	12.08
SO_2(g)	−296.830	248.22	−300.194
SO_3(g)	−395.72	256.76	−371.06
$SOCl_2$(g)	−212.5	309.77	−198.3
SO_4^{2-}(aq)	−909.27	20.1	−744.53

Species	$\Delta_f H°$ (kJ/mol)	$S°$ (J K^{-1} mol^{-1})	$\Delta_f G°$ (kJ/mol)
$H_2SO_4(\ell)$	−813.989	156.904	−690.003
$H_2SO_4(aq)$	−909.27	20.1	−744.53
$HSO_4^-(aq)$	−887.34	131.8	−755.91
Tin			
Sn(s, white)	0	51.55	0
Sn(s, gray)	−2.09	44.14	0.13
$SnCl_2(s)$	−325.1	—	—
$SnCl_4(\ell)$	−511.3	258.6	−440.1
$SnCl_4(g)$	−471.5	365.8	−432.2
$SnO_2(s)$	−580.7	52.3	−519.6
Titanium			
Ti(s)	0	30.63	0
$TiCl_4(\ell)$	−804.2	252.34	−737.2
$TiCl_4(g)$	−763.2	354.9	−726.7
$TiO_2(s)$	−939.7	49.92	−884.5
Uranium			
U(s)	0	50.21	0
$UO_2(s)$	−1084.9	77.03	−1031.7
$UO_3(s)$	−1223.8	96.11	−1145.9
$UF_4(s)$	−1914.2	151.67	−1823.3
$UF_6(g)$	−2147.4	377.9	−2063.7
$UF_6(s)$	−2197.0	227.6	−2068.5
Zinc			
Zn(s)	0	41.63	0
$ZnCl_2(s)$	−415.05	111.46	−369.398
ZnO(s)	−348.28	43.64	−318.3
ZnS(s, sphalerite)	−205.98	57.7	−201.29

From Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., and Nuttall, R., Journal of Physical and Chemical Reference Data, Vol. 11, Suppl. 2, 1982.
†Many hydrogen-containing and oxygen-containing compounds are listed only under other elements.

6.14: Standard Potential

Standard Potential

John Moore, Jia Zhou, and Etienne Garand

Standard Electrode Potentials in Acidic Aqueous Solution (a table for basic solution is below)

at 25 °C.

Acidic Solution	**Standard Electrode Potential, *E*° (volts)**
$F_2(g) + 2e^- \longrightarrow 2\ F^-(aq)$	2.87
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	1.92
$Au^+(aq) + e^- \longrightarrow Au(s)$	1.83
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \longrightarrow 2\ H_2O(\ell)$	1.763
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	1.72
$Pb^{4+}\ (aq) + 2\ e^- \longrightarrow Pb^{2+}(aq)$	1.69
$PbO_2(s) + SO_4^{2-}\ (aq) + 4\ H^+(aq) + 2\ e^- \longrightarrow PbSO_4(s) + 2\ H_2O(\ell)$	1.690
$NiO_2(s) + 4\ H^+(aq) + 2\ e^- \longrightarrow Ni^{2+}(aq) + 2\ H_2O(\ell)$	1.68
$2\ HClO(aq) + 2\ H^+(aq) + 2\ e^- \longrightarrow Cl_2(g) + 2\ H_2O(\ell)$	1.63
$Au^{3+}(aq) + 3\ e^- \longrightarrow Au(s)$	1.52
$MnO_4^-\ (aq) + 8\ H^+(aq) + 5\ e^- \longrightarrow Mn^{2+}(aq) + 4\ H_2O(\ell)$	1.51
$BrO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \longrightarrow 1/2\ Br_2(aq) + 3\ H_2O(\ell)$	1.478
$2\ ClO_3^-(aq) + 12\ H^+(aq) + 10\ e^- \longrightarrow Cl_2(g) + 6\ H_2O(\ell)$	1.47
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \longrightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(\ell)$	1.36
$Cl_2(g) + 2\ e^- \longrightarrow 2\ Cl^-(aq)$	1.358
$N_2H_5^+(aq) + 3\ H^+(aq) + 2\ e^- \longrightarrow 2\ NH^{4+}(aq)$	1.275
$MnO_2(s) + 4\ H^+(aq) + 2\ e^- \longrightarrow Mn^{2+}(aq) + 2\ H_2O(\ell)$	1.23
$O_2(g) + 4\ H^+(aq) + 4\ e^- \longrightarrow 2\ H_2O(\ell)$	1.229
$ClO_4^-(aq) + 2\ H^+(aq) + 2\ e^- \longrightarrow ClO_3^-(aq) + H_2O(\ell)$	1.201
$IO_3^-(aq) + 6\ H^+(aq) + 5\ e^- \longrightarrow 1/2\ I_2(aq) + 3\ H_2O(\ell)$	1.195
$Pt^{2+}(aq) + 2\ e^- \longrightarrow Pt(s)$	1.188
$Br_2(\ell) + 2\ e^- \longrightarrow 2\ Br^-(aq)$	1.066
$[AuCl_4]^-(aq) + 3\ e^- \longrightarrow Au(s) + 4\ Cl^-(aq)$	1.00
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \longrightarrow NO(g) + 2\ H_2O(\ell)$	0.96
$NO_3^-(aq) + 3\ H^+(aq) + 2\ e^- \longrightarrow HNO_2(aq) + H_2O(\ell)$	0.94
$Pd^{2+}(aq) + 2\ e^- \longrightarrow Pd(s)$	0.915
$2\ Hg^{2+}(aq) + 2\ e^- \longrightarrow Hg_2^{2+}(aq)$	0.9110
$Hg^{2+}(aq) + 2\ e^- \longrightarrow Hg(\ell)$	0.8535
$SbCl_6^-(aq) + 2\ e^- \longrightarrow SbCl_4^-(aq) + 2\ Cl^-(aq)$	0.84†
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.7991
$Hg_2^{2+}(aq) + 2\ e^- \longrightarrow 2\ Hg(\ell)$	0.7960
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.771
$[PtCl_4]^{2-}(aq) + 2\ e^- \longrightarrow Pt(s) + 4\ Cl^-(aq)$	0.758
$[PtCl_6]^{2-}(aq) + 2\ e^- \longrightarrow [PtCl_4]^{2-}(aq) + 2\ Cl^-(aq)$	0.726

Acidic Solution	Standard Electrode Potential, *E*° (volts)
O_2(g) + 2 H^+(aq) + 2 e^- ⟶ H_2O_2(aq)	0.695
TeO_2(s) + 4 H^+(aq) + 4 e^- ⟶ Te(s) + 2 H_2O(ℓ)	0.604
H_3AsO_4(aq) + 2 H^+(aq) + 2 e^- ⟶ $HAsO_2$(aq) + 2 H_2O(ℓ)	0.560
I_2(s) + 2 e^- ⟶ 2 I^-(aq)	0.535
Cu^+(aq) + e^- ⟶ Cu(s)	0.521
$[RhCl_6]^{3-}$(aq) + 3 e^- ⟶ Rh(s) + 6 Cl^-(aq)	0.5
Cu^{2+}(aq) + 2e^- ⟶ Cu(s)	0.340
Hg_2Cl_2(s) + 2e^- ⟶ 2 Hg(ℓ) + 2 Cl^-(aq)	0.27
AgCl(s) + e^- ⟶ Ag(s) + Cl^-(aq)	0.222
Cu^{2+}(aq) + e^- ⟶ Cu^+(aq)	0.159
SO_4^{2-}(aq) + 4 H^+(aq) + 2 e^- ⟶ H_2SO_3(aq) + H_2O(ℓ)	0.158
Sn^{4+}(aq) + 2e^- ⟶ Sn^{2+}(aq)	0.15
S(s) + 2 H^+(aq) + 2 e^- ⟶ H_2S(aq)	0.144
AgBr(s) + e^- ⟶ Ag(s) + Br^-(aq)	0.0713
2 H^+(aq) + 2 e^- ⟶ H_2(g) (reference electrode)	0
N_2O(g) + 6 H^+(aq) + H_2O(ℓ) + 4 e^- ⟶ 2 NH_3OH^+(aq)	−0.05
HgS(s, black) + 2 H^+(aq) + 2 e^- ⟶ Hg(ℓ) + H_2S(g)	−0.085
Se(s) + 2 H^+(aq) + 2 e^- ⟶ H_2Se(aq)	−0.115
Pb^{2+}(aq) + 2 e^- ⟶ Pb(s)	−0.125
Sn^{2+}(aq) + 2 e^- ⟶ Sn(s)	−0.1375
AgI(s) + e^- ⟶ Ag(s) + I^-(aq)	−0.1522
$[SnF_6]^{2-}$(aq) + 4 e^- ⟶ Sn(s) + 6 F^-(aq)	−0.200
Ni^{2+}(aq) + 2 e^- ⟶ Ni(s)	−0.25
Co^{2+}(aq) + 2 e^- ⟶ Co(s)	−0.277
Tl^+(aq) + e^- ⟶ Tl(s)	−0.3363
$PbSO_4$(s) + 2 e^- ⟶ Pb(s) + SO_4^{2-}(aq)	−0.3505
Cd^{2+}(aq) + 2 e^- ⟶ Cd(s)	−0.403
Cr^{3+}(aq) + e^- ⟶ Cr^{2+}(aq)	−0.424
Fe^{2+}(aq) + 2 e^- ⟶ Fe(s)	−0.44
2 CO_2(g) + 2 H^+(aq) + 2 e^- ⟶ $(COOH)_2$(aq)	−0.481
TiO_2(s)+ 4 H^+(aq) + 2 e^- ⟶ Ti^{2+}(aq) + 2 H_2O(ℓ)	−0.502
Ga^{3+}(aq) + 3 e^- ⟶ Ga(s)	−0.53
Cr^{3+}(aq) + 3 e^- ⟶ Cr(s)	−0.74
Zn^{2+}(aq) + 2 e^- ⟶ Zn(s)	−0.763
Cr^{2+}(aq) + 2 e^- ⟶ Cr(s)	−0.90
V^{2+}(aq) + 2 e^- ⟶ V(s)	−1.13
Mn^{2+}(aq) + 2 e^- ⟶ Mn(s)	−1.18
Zr^{4+}(aq) + 4 e^- ⟶ Zr(s)	−1.55
Al^{3+}(aq) + 3 e^- ⟶ Al(s)	−1.676
H_2(g) + 2 e^- ⟶ 2 H^-(aq)	−2.25

Acidic Solution	Standard Electrode Potential, $E°$ (volts)
$Mg^{2+}(aq) + 2\ e^{-} \longrightarrow Mg(s)$	−2.356
$Na^{+}(aq) + e^{-} \longrightarrow Na(s)$	−2.714
$Ca^{2+}(aq) + 2\ e^{-} \longrightarrow Ca(s)$	−2.84
$Sr^{2+}(aq) + 2\ e^{-} \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2\ e^{-} \longrightarrow Ba(s)$	−2.92
$Rb^{+}(aq) + e^{-} \longrightarrow Rb(s)$	−2.925
$K^{+}(aq) + e^{-} \longrightarrow K(s)$	−2.925
$Li^{+}(aq) + e^{-} \longrightarrow Li(s)$	−3.045

From Bard, A. J., Parsons, R., and Jordan, J., Standard Potentials in Aqueous Solution, New York: Marcel Dekker, 1985. International Union of Pure and Applied Chemistry, Commission on Electrochemistry and Electroanalytical Chemistry.
†From Brown, R. A., and Swift, E. H., Journal of the American Chemical Society, Vol. 71, 1949, pp. 2719-2723.

Standard Electrode Potentials in Basic Aqueous Solution

at 25 °C.

Basic Solution	Standard Electrode Potential, $E°$ (volts)
$ClO^{-}(aq) + H_2O(\ell) + 2\ e^{-} \longrightarrow Cl^{-}(aq) + 2\ OH^{-}(aq)$	0.89
$OOH^{-}(aq) + H_2O(\ell) + 2\ e^{-} \longrightarrow 3\ OH^{-}(aq)$	0.867
$2\ NH_2OH(aq) + 2\ e^{-} \longrightarrow N_2H_4(aq) + 2\ OH^{-}(aq)$	0.73
$ClO_3^{-}(aq) + 3\ H_2O(\ell) + 6\ e^{-} \longrightarrow Cl^{-}(aq) + 6\ OH^{-}(aq)$	0.622
$MnO_4^{-}(aq) + 2\ H_2O(\ell) + 3\ e^{-} \longrightarrow MnO_2(s) + 4\ OH^{-}(aq)$	0.60
$MnO_4^{-}(aq) + e^{-} \longrightarrow MnO_4^{2-}(aq)$	0.56
$NiO_2(s) + 2\ H_2O(\ell) + 2\ e^{-} \longrightarrow Ni(OH)_2(s) + 2\ OH^{-}(aq)$	0.49
$Ag_2CrO_4(s) + 2\ e^{-} \longrightarrow 2\ Ag(s) + CrO_4^{2-}(aq)$	0.4491
$O_2(g) + 2\ H_2O(\ell) + 4\ e^{-} \longrightarrow 4\ OH^{-}(aq)$	0.401
$ClO_4^{-}(aq) + H_2O(\ell) + 2\ e^{-} \longrightarrow ClO_3^{-}(aq) + 2\ OH^{-}(aq)$	0.374
$Ag_2O(s) + H_2O(\ell) + 2\ e^{-} \longrightarrow 2\ Ag(s) + 2\ OH^{-}(aq)$	0.342
$2\ NO_2^{-}(aq) + 3\ H_2O(\ell) + 4\ e^{-} \longrightarrow N_2O(g) + 6\ OH^{-}(aq)$	0.15
$N_2H_4(aq) + 2\ H_2O(\ell) + 2\ e^{-} \longrightarrow 2\ NH_3(aq) + 2\ OH^{-}(aq)$	0.10
$HgO(s) + H_2O(\ell) + 2\ e^{-} \longrightarrow Hg(\ell) + 2\ OH^{-}(aq)$	0.0977
$O_2(g) + H_2O(\ell) + 2\ e^{-} \longrightarrow OOH^{-}(aq) + OH^{-}(aq)$	0.0649
$[Co(NH_3)_6]^{3+}(aq) + e^{-} \longrightarrow [Co(NH_3)_6]^{2+}(aq)$	0.058
$NO_3^{-}(aq) + H_2O(\ell) + 2\ e^{-} \longrightarrow NO_2^{-}(aq) + 2\ OH^{-}(aq)$	0.01
$MnO_2(s) + 2\ H_2O(\ell) + 2\ e^{-} \longrightarrow Mn(OH)_2(s) + 2\ OH^{-}(aq)$	−0.05
$CrO_4^{2-}(aq) + 4\ H_2O(\ell) + 3\ e^{-} \longrightarrow Cr(OH)_3(s) + 5\ OH^{-}(aq)$	−0.11
$Cu_2O(s) + H_2O(\ell) + 2\ e^{-} \longrightarrow 2\ Cu(s) + 2\ OH^{-}(aq)$	−0.365
$FeO_2^{-}(aq) + H_2O(\ell) + e^{-} \longrightarrow HFeO_2^{-}(aq) + OH^{-}(aq)$	−0.69
$HFeO_2^{-}(aq) + H_2O(\ell) + 2\ e^{-} \longrightarrow Fe(s) + 3\ OH^{-}(aq)$	−0.8
$2\ H_2O(\ell) + 2\ e^{-} \longrightarrow H_2(g) + 2\ OH^{-}(aq)$	−0.8277
$2\ NO_3^{-}(aq) + 2\ H_2O(\ell) + 2\ e^{-} \longrightarrow N_2O_4(g) + 4\ OH^{-}(aq)$	−0.86
$SO_4^{2-}(aq) + H_2O(\ell) + 2\ e^{-} \longrightarrow SO_3^{2-}(aq) + 2\ OH^{-}(aq)$	−0.936
$N_2(g) + 4\ H_2O(\ell) + 4\ e^{-} \longrightarrow N_2H_4(aq) + 4\ OH^{-}(aq)$	−1.16

Basic Solution	**Standard Electrode Potential, *E*° (volts)**
$Zn(OH)_2(s) + 2\ e^- \longrightarrow Zn(s) + 2\ OH^-(aq)$	−1.246
$[Zn(OH)_4]^{2-}(aq) + 2\ e^- \longrightarrow Zn(s) + 4\ OH^-(aq)$	−1.285
$Cr(OH)_3(s) + 3\ e^- \longrightarrow Cr(s) + 3\ OH^-(aq)$	−1.33
$[Zn(CN)_4]^{2-}(aq) + 2\ e^- \longrightarrow Zn(s) + 4\ CN^-(aq)$	−1.34
$SiO_3^{2-}(aq) + 3\ H_2O(\ell) + 4\ e^- \longrightarrow Si(s) + 6\ OH^-(aq)$	−1.69

From Bard, A. J., Parsons, R., and Jordan, J., Standard Potentials in Aqueous Solution, New York: Marcel Dekker, 1985. International Union of Pure and Applied Chemistry, Commission on Electrochemistry and Electroanalytical Chemistry.

6.15: Basics of Organic Nomenclature

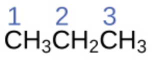
41

Basics of Organic Nomenclature

Alkanes

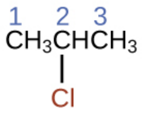
The International Union of Pure and Applied Chemistry (**IUPAC**) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10).
2. Add prefixes to the name of the longest chain to indicate the positions and names of **substituents**. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.



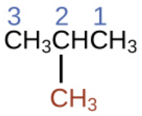
$CH_3CH_2CH_3$

propane



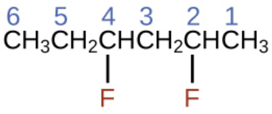
$CH_3\underset{Cl}{C}HCH_3$

2-chloropropane



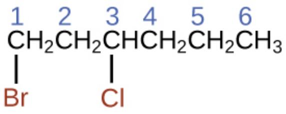
$CH_3\underset{CH_3}{C}HCH_3$

2-methylpropane



$CH_3CH_2\underset{F}{C}HCH_2\underset{F}{C}HCH_3$

2,4-difluorohexane



$\underset{Br}{C}H_2CH_2\underset{Cl}{C}HCH_2CH_2CH_3$

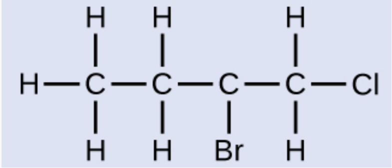
1-bromo-3-chlorohexane

When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

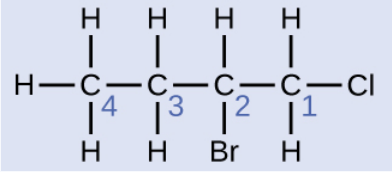
Example 1

Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



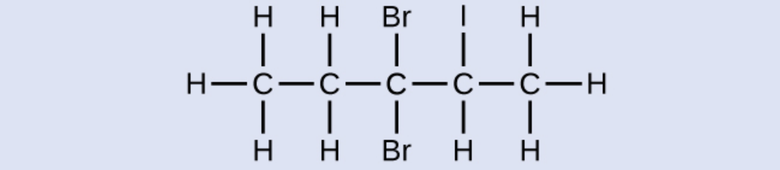
Solution



The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

Check Your Learning

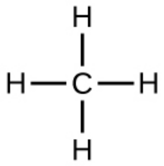
Name the following molecule:



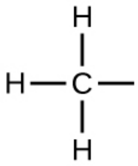
Answer:

3,3-dibromo-2-iodopentane

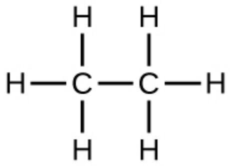
We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an **alkyl group** is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:



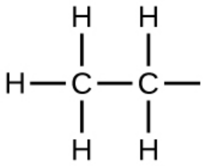
methane



methyl group



ethane



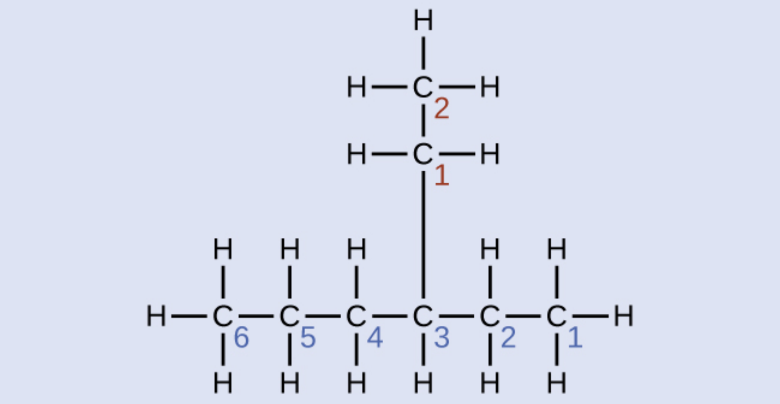
ethyl group

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

Example 2

Naming Substituted Alkanes

Name the molecule whose structure is shown here:

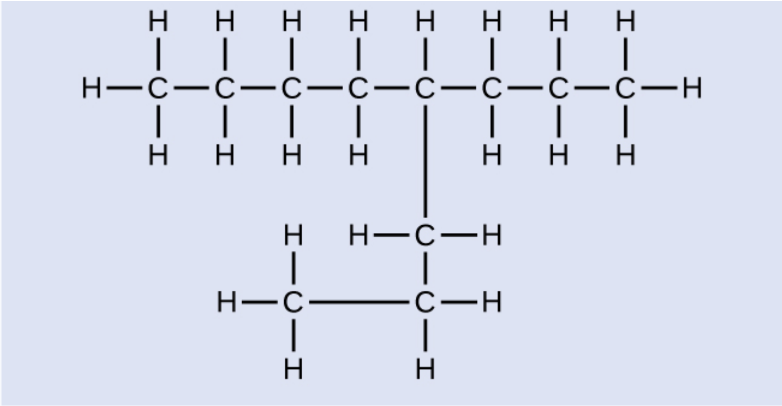


Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

Check Your Learning

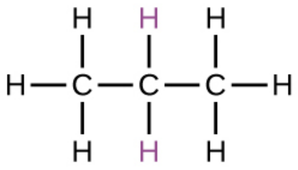
Name the following molecule:



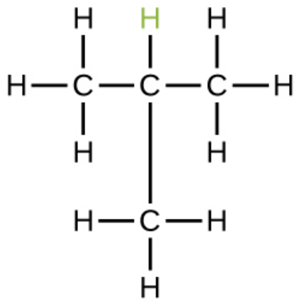
Answer:

4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2–methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:

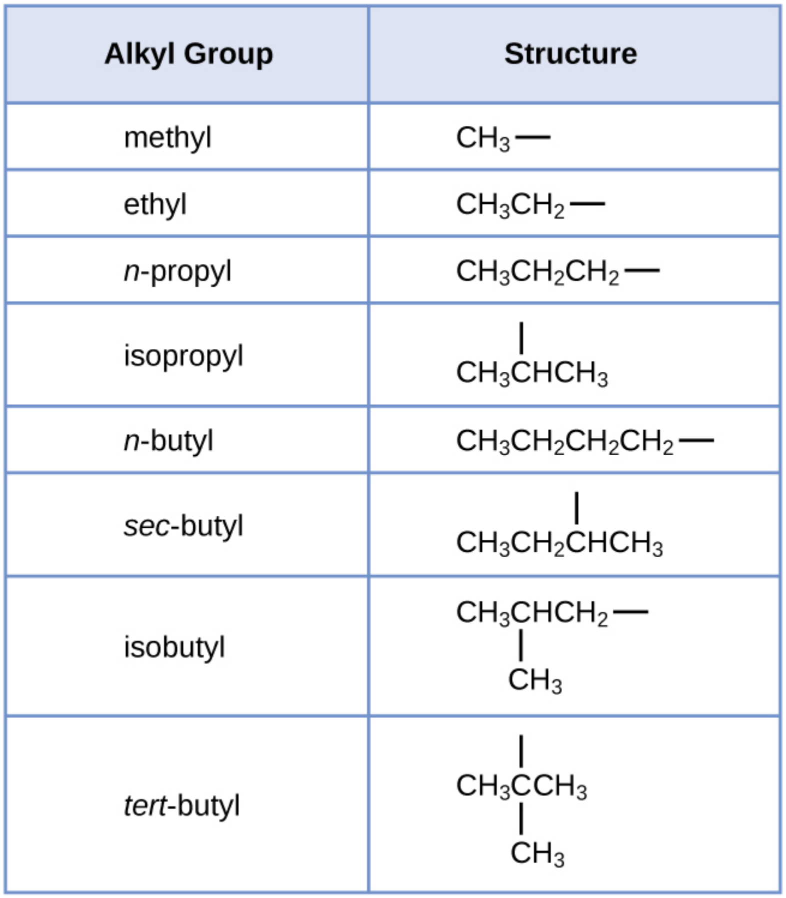


propane



2-methylpropane

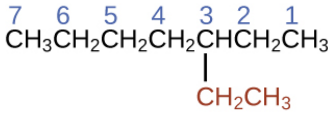
Each of the six equivalent hydrogen atoms of the first type in propane and each of the nine equivalent hydrogen atoms of that type in 2-methylpropane (all shown in black) are bonded to a carbon atom that is bonded to only one other carbon atom. The two purple hydrogen atoms in propane are of a second type. They differ from the six hydrogen atoms of the first type in that they are bonded to a carbon atom bonded to two other carbon atoms. The green hydrogen atom in 2-methylpropane differs from the other nine hydrogen atoms in that molecule and from the purple hydrogen atoms in propane. The green hydrogen atom in 2-methylpropane is bonded to a carbon atom bonded to three other carbon atoms. Two different alkyl groups can be formed from each of these molecules, depending on which hydrogen atom is removed. The names and structures of these and several other alkyl groups are listed in Figure 1.



Alkyl Group	Structure
methyl	$CH_3—$
ethyl	$CH_3CH_2—$
n-propyl	$CH_3CH_2CH_2—$
isopropyl	$CH_3\overset{\vert}{C}HCH_3$
n-butyl	$CH_3CH_2CH_2CH_2—$
sec-butyl	$CH_3CH_2\overset{\vert}{C}HCH_3$
isobutyl	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2—$
tert-butyl	$CH_3\overset{\vert}{\underset{\underset{CH_3}{\vert}}{C}}CH_3$

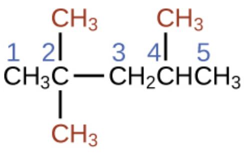
Figure 1. *This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.*

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



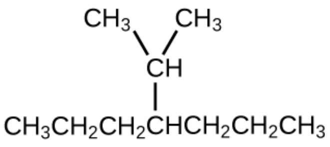
$$CH_3CH_2CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_3$$

3-ethylheptane



$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$$

2,2,4-trimethylpentane



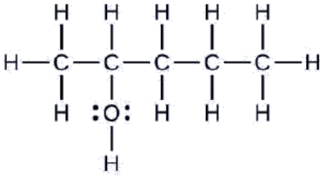
$$CH_3CH_2CH_2\overset{\overset{CH_3\ \ CH_3}{\diagdown\ \diagup}}{\overset{CH}{|}}\!\!\!\!\!\!CHCH_2CH_2CH_3$$

4-isopropylheptane

Alcohols

The name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.

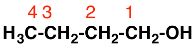
Consider the following example:



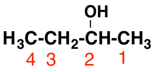
The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane.

To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

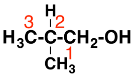
Other examples of IUPAC nomenclature are shown below, together with the common names often used for some of the simpler compounds. For the mono-functional alcohols, this common system consists of naming the alkyl group followed by the word alcohol. Alcohols may also be classified as primary, 1º, secondary, 2º, and tertiary, 3º. This terminology refers to alkyl substitution of the carbon atom bearing the hydroxyl group (colored blue in the illustration).


$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$

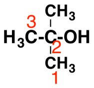
1-butanol
(butyl alcohol)
a 1° alcohol


$H_3C\text{-}CH_2\text{-}CH(OH)\text{-}CH_3$

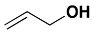
2-butanol
(sec-butyl alcohol)
a 2° alcohol


$H_3C\text{-}CH(CH_3)\text{-}CH_2\text{-}OH$

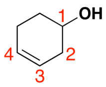
2-methyl-1-propanol
(isobutyl alcohol)
a 1° alcohol


$H_3C\text{-}C(CH_3)_2\text{-}OH$

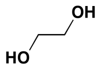
2-methyl-2-propanol
(tert-butyl alcohol)
a 3° alcohol



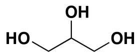
2-propen-1-ol
(allyl alcohol)



3-cyclohexen-1-ol



1,2-ethanediol
(ethylene glycol)

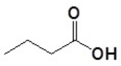


1,2,3-propanetriol
(glycerol)

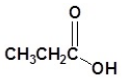
Carboxylic Acids

The **–e** ending is removed from the name of the parent carbon chain and is replaced **-anoic acid**. Since a carboxylic acid group must always lie at the end of a carbon chain, it is always is given the #1 location position in numbering and it is not necessary to include it in the name. Many carboxylic acids are called by the common names that were chosen by chemists to usually describe the origin of the compound.

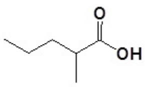
Formula	Common Name	Source	IUPAC Name
HCO_2H	formic acid	ants (L. formica)	methanoic acid
CH_3CO_2H	acetic acid	vinegar (L. acetum)	ethanoic acid
$CH_3CH_2CO_2H$	propionic acid	milk (Gk. protus prion)	propanoic acid
$CH_3(CH_2)_2CO_2H$	butyric acid	butter (L. butyrum)	butanoic acid
$CH_3(CH_2)_3CO_2H$	valeric acid	valerian root	pentanoic acid
$CH_3(CH_2)_4CO_2H$	caproic acid	goats (L. caper)	hexanoic acid
$CH_3(CH_2)_5CO_2H$	enanthic acid	vines (Gk. oenanthe)	heptanoic acid
$CH_3(CH_2)_6CO_2H$	caprylic acid	goats (L. caper)	octanoic acid
$CH_3(CH_2)_7CO_2H$	pelargonic acid	pelargonium (an herb)	nonanoic acid
$CH_3(CH_2)_8CO_2H$	capric acid	goats (L. caper)	decanoic acid



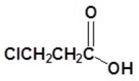
Butanoic acid
(Butyric Acid)



Propanoic acid
(Propionic Acid)

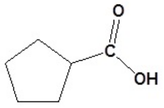


2-Methylpentanoic acid
(β-Methylvaleric acid)

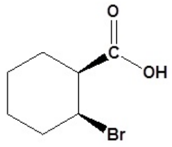


3-Chloropropanoic acid
(γ-Chloropropionic acid)

When a carboxyl group is added to a ring the suffix **-carboxylic acid** is added to the name of the cyclic compound. The ring carbon attached to the carboxyl group is given the #1 location number.

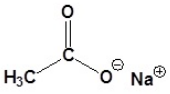


Cyclopentanecarboxylic acid



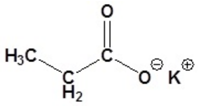
Cis-2-Bromocyclohexanecarboylic acid

Salts of carboxylic acids are named by writing the name of the cation followed by the name of the acid with the **–ic acid** ending replaced by an **–ate** ending. This is true for both the IUPAC and Common nomenclature systems.



Sodium ethanoate

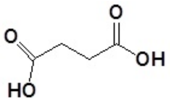
(Sodium Acetate)



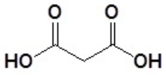
Potassium Propanoate

(Potassium propionate)

For dicarboxylic acids the location numbers for both carboxyl groups are omitted because both functional groups are expected to occupy the ends of the parent chain. The ending **–dioic acid** is added to the end of the parent chain.



Butanedioic acid

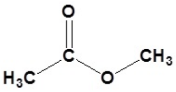


Propanedioic acid

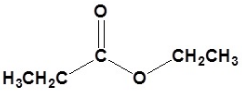
Esters

Esters are named as if the alkyl chain from the alcohol is a substituent. No number is assigned to this alkyl chain. This is followed by the name of the parent chain from the carboxylic acid part of the ester with an **–e** remove and replaced with the ending **–oate**.

For example:



Methyl ethanoate



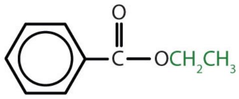
Ethyl propanoate

1. First, identify the oxygen that is part of the continuous chain and bonded to carbon on both sides. (On one side of this oxygen there will be a carbonyl present but on the other side there won’t be.)
2. Second, begin numbering the carbon chains on either side of the oxygen identified in step 1.
3. Next, use this format: [alkyl on side further from the carbonyl] (space) [alkane on the side with the carbonyl]
4. Finally, change the ending of the alkane on the same side as the carbonyl from -e to -oate.
5. When an ester group is attached to a ring, the ester is named as a substituent on the ring.

In both common and International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the *–ic* ending of the parent acid is replaced by the suffix *–ate*.

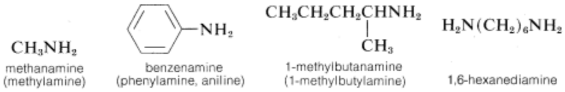
: Nomenclature of Esters

Condensed Structural Formula	Common Name	IUPAC Name
$HCOOCH_3$	methyl formate	methyl methanoate
CH_3COOCH_3	methyl acetate	methyl ethanoate
$CH_3COOCH_2CH_3$	ethyl acetate	ethyl ethanoate

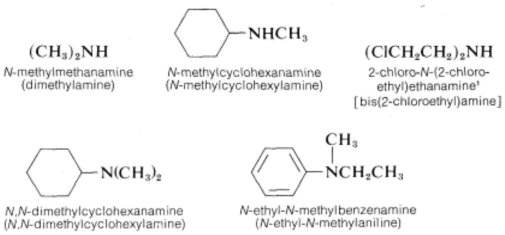
Condensed Structural Formula	Common Name	IUPAC Name
$CH_3CH_2COOCH_2CH_3$	ethyl propionate	ethyl propanoate
$CH_3CH_2CH_2COOCH(CH_3)_2$	isopropyl butyrate	isopropyl butanoate
	ethyl benzoate	ethyl benzoate

Amines

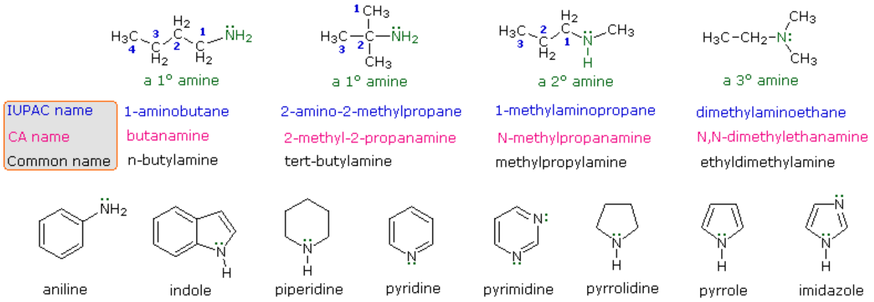
The word “amine” is derived from *ammonia*, and the class of compounds known as amines therefore are commonly named as substituted ammonias. In this system, **primary** amines (RNH_2), having only one substituent on nitrogen, are named with the substituent as a prefix. More systematic nomenclature appends -*amine* to the longest chain, as for alcohols:



Secondary (R_2NH) and **tertiary** amines (R_3N), which have two and three substituents on nitrogen, commonly are named as *N*-substituted amines. *N* is included to indicate that the substituent is on the nitrogen atom unless there is no ambiguity as to where the substituent is located. Each of the R groups is named as a separate word, except when the groups are identical, in which case the prefix *di* or *bis* may be used (*di* is used for simple groups, *bis* for substituted groups):



The nomenclature of amines is complicated by the fact that several different nomenclature systems exist. The four compounds shown in the top row of the following diagram are all $C_4H_{11}N$ isomers.

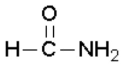


- The IUPAC names are listed first and colored blue. This system names amine functions as substituents on the largest alkyl group. The simple -NH substituent found in 1°-amines is called an **amino group**. For 2° and 3°-amines a compound prefix (e.g. dimethylamino in the fourth example) includes the names of all but the root alkyl group.
- The Chemical Abstract Service has adopted a nomenclature system in which the suffix **-amine** is attached to the root alkyl name. For 1°-amines such as butanamine (first example) this is analogous to IUPAC alcohol nomenclature (-ol suffix). The additional nitrogen substituents in 2° and 3°-amines are designated by the prefix **N-** before the group name. These CA names are colored magenta in the diagram.
- Finally, a common system for simple amines names each alkyl substituent on nitrogen in alphabetical order, followed by the suffix **-amine**. These are the names given in the last row (colored black).

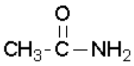
Many aromatic and heterocyclic amines are known by unique common names, the origins of which are often unknown to the chemists that use them frequently since these names are not based on a rational system.

Amides

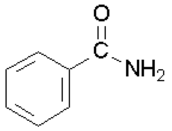
Primary amides are named by changing the name of the acid by dropping the *-oic acid* or *-ic acid* endings and adding *-amide*. The carbonyl carbon is given the #1 location number. It is not necessary to include the location number in the name because it is assumed that the functional group will be on the end of the parent chain. For example, the following three amides are called methanamide or formamide, ethanamide or acetamide, and benzamide.



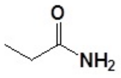
$H-\overset{\overset{O}{||}}{C}-NH_2$



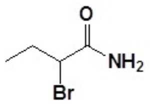
$CH_3-\overset{\overset{O}{||}}{C}-NH_2$



Further examples are shown below:

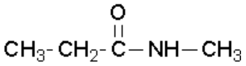


Propanamide



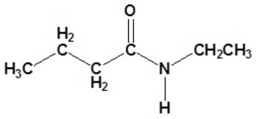
2-Bromobutanamide

Secondary amides are named by using an upper case N to designate that the alkyl group is on the nitrogen atom. Alkyl groups attached to the nitrogen are named as substituents. The letter N is used to indicate they are attached to the nitrogen. For example, the molecule below is called N-methylpropanamide:

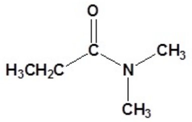


$CH_3-CH_2-\overset{\overset{O}{||}}{C}-NH-CH_3$

Tertiary amides are named in the same way as secondary amides, but with two N’s



N-Ethylbutanamide



N,N-Dimethylpropanamide

CHAPTER OVERVIEW

7: Review Section

7.1: Review- Waves

42

Review: Waves

Much of modern technology is based on electromagnetic radiation. Radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from a toaster wire, and the colors emanating from your television screen are forms of electromagnetic radiation. All exhibit behaviors that can be explained by a wave theory.

A **wave** is an oscillation or periodic movement that can transfer energy from one point to another. For example, the expansion and compression of air that accompanies a lightning strike generates sound waves (thunder) that can travel several miles and cause your ear drums (and sometimes windows) to vibrate. Kinetic energy is transferred through matter (the 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 for a few seconds before sitting down again and fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium, none of the fans actually travel with the wave—they all stay in or above their seats.

All waves are characterized by these properties: **wavelength** (λ), the distance between two consecutive peaks, troughs, or other equivalent points in a wave; **frequency** (ν), the number of wave cycles (a cycle corresponds to one complete wavelength) that pass a specified point in space in a specified time; and **amplitude** (*A*), the magnitude of the wave's displacement. See examples shown in Figure 1.

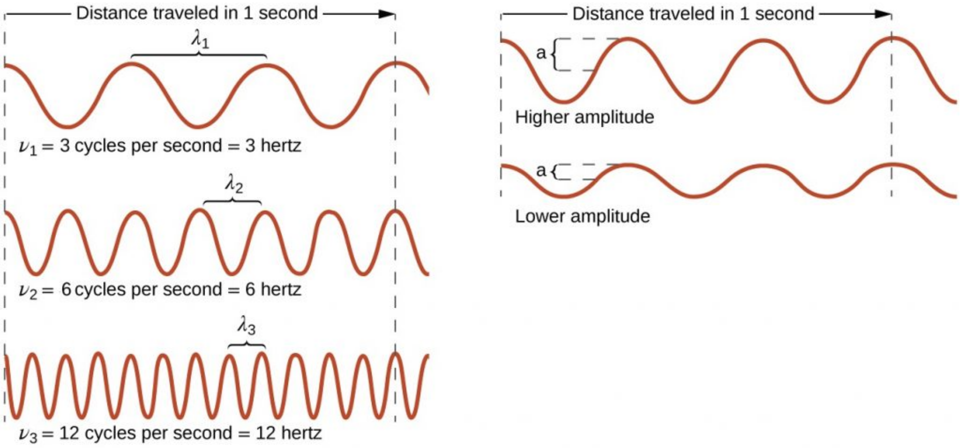


Figure 1. *Waves are characterized by wavelength (λ), frequency (ν), and amplitude (A). The product of frequency and wavelength is the distance a wave travels in a given time, i.e., the speed of propagation of the wave.*

The SI unit for λ is meter, and for ν is **hertz (Hz)**, which is the number of cycles per second.

$$[Hz = \frac{1}{s} = s^{-1}]$$

Common multiples are megahertz, (1 MHz = 1×10^6 Hz) and gigahertz (1 GHz = 1×10^9 Hz). The maximum amplitude of a wave shown in Figure 1 corresponds to one-half the height between the peaks and troughs, and is related to the intensity of the wave. For example, for sound waves, greater amplitude means louder sound.

Waves are not restricted to traveling through matter. James Clerk **Maxwell** proposed the existence of electromagnetic waves, which consist of an electric field oscillating in the x dimension in step with a magnetic field oscillating in the y dimension. The electromagnetic oscillations travel in the *z* dimension, where x, y, and z are Cartesian coordinate axes. Electromagnetic radiation travels through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (*c*).

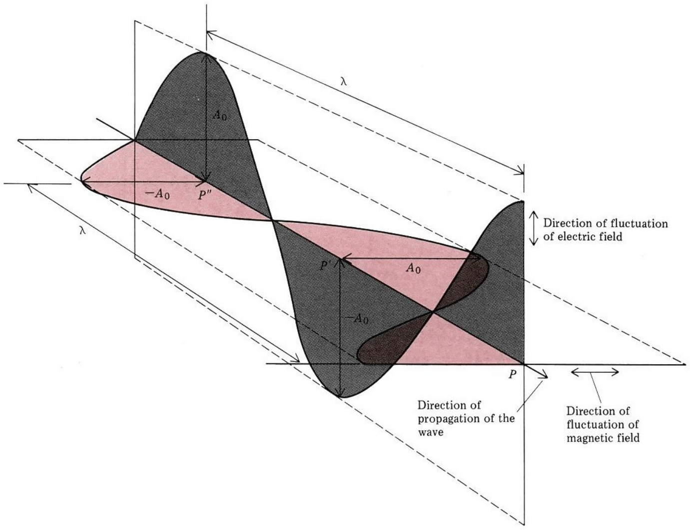


***Figure 2**. Electromagnetic radiation involves electric and magnetic fields fluctuating perpendicular to each other. A_0 is the maximum amplitude. λ is the wavelength.*

The product of a wave's wavelength and its frequency, λv, is the speed of the wave. (The wave travels distance λ per cycle and the number of cycles traveled in a given time is v.) Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8 \ \frac{\text{m}}{\text{s}} = \lambda \nu$$

Because the product λv is constant, wavelength and frequency are inversely proportional: as the wavelength increases, the frequency decreases.

Exercise 1: Photons and Laser Light

For all exercises, before doing any calculation or looking at the hint, write in your class notebook an explanation of how you plan to work out the problem. Do all the steps in the calculation in your notebook. Once you have arrived at an answer, submit your results below and click the "Check" button to see if it is correct. If one or more parts of your answer is incorrect, go over your work in your notebook carefully and check for errors. "Retry" with your new answer. Look at the hint (click on it to expand for view) only after you have made attempts at answering the question.

Additional Practice

Figure 3 shows the **electromagnetic spectrum**, the range of all types of electromagnetic radiation. It spans an enormous range—wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed, and the visible-light range makes up only a small portion of it. Given the expansive range of wavelengths, 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 or GHz), while the visible region is usually specified in wavelengths (typically in units of nm or Å).

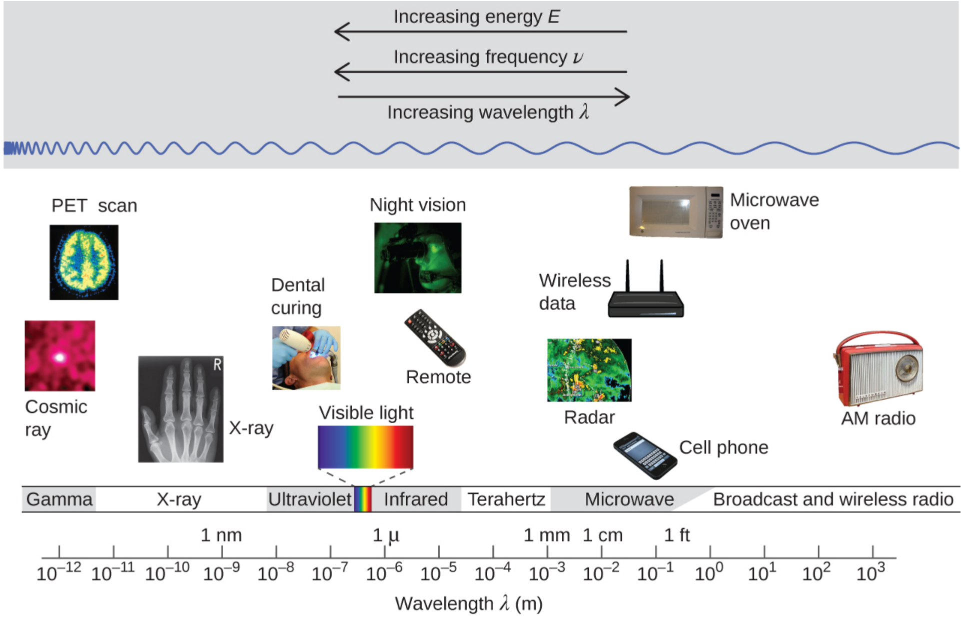
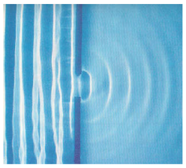


Figure 3. *Portions of the electromagnetic spectrum are shown. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit "Cosmic ray": modification of work by NASA; 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)*

D1.2 Wave Properties



When a wave passes through a pinhole or a very narrow slit, waves fan out on other side of the pinhole or slit. This is shown on the right for water waves moving from left to right through a hole about the same width as the wavelength.

When two or more waves occupy the same region, the total wave amplitude is the sum of the amplitudes of the individual waves. Figure 4 shows that this can result in a larger total amplitude if the amplitudes of the waves have the same mathematical sign (are in phase) or in a smaller total amplitude if the two waves have amplitudes with opposite sign (are out of phase).

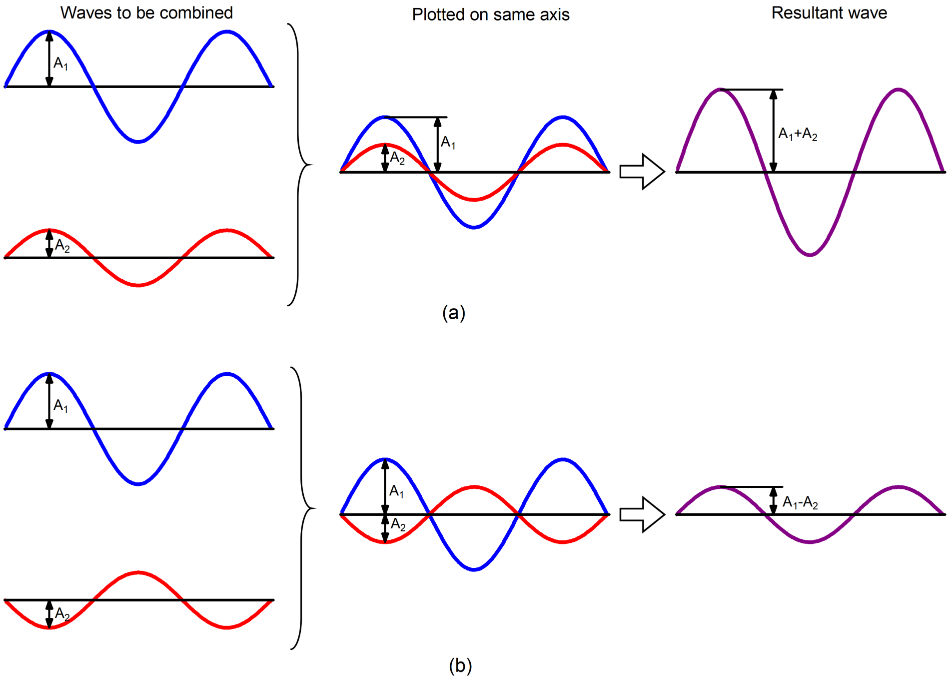


***Figure 4**. Summation of waves. When two or more waves occupy the same space the resultant amplitude is the sum of the individual amplitudes. This can result in a larger total amplitude (a) or a smaller total amplitude (b). When total amplitude is larger, we say there is constructive interference; when total amplitude is smaller there is destructive interference.*

Summation of amplitudes of waves leads to **interference** of one wave with another. Figure 5 shows the interference patterns that arise when blue or red laser light passes through a diffraction grating with many narrow, vertical slits spaced about one wavelength apart.

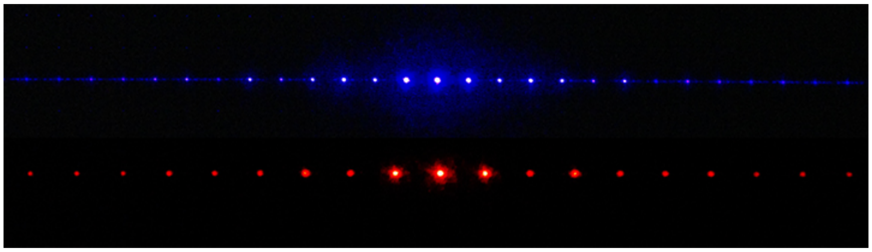


***Figure 5.** Interference patterns. Blue and red laser beams passing through the same diffraction grating produce spots that are more closely spaced for the shorter-wavelength blue light. [Photo by James Maynard]*

When laser light passes through closely spaced slits, each slit effectively acts as a new source with waves fanning out from it. This results in closely spaced waves coming into contact at the detector (the camera used to make Figure 5). The dark regions in Figure 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**, Fig. 4b), while the brightest regions correspond to regions where the peaks for the two waves (or their two troughs) happen to coincide (**constructive interference**, Fig. 4a).

Additional Practice 1

Additional Practice 2

Interference patterns are an inherent property of wave motion but they cannot be explained by particles moving according to the laws of classical mechanics. Particles would move in straight lines through a slit or pinhole and produce a single bright line or spot.

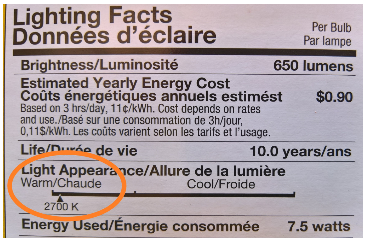
7.2: Review- Photons

43

Review: Photons

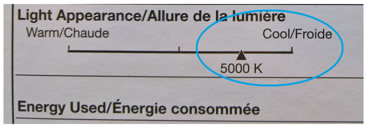
D1.3 Blackbody Radiation

Have you noticed that some LED light bulbs are a different color from others? Some are “warm” and others are “cool” (see Figure 6). Candlelight is “warmer” (yellower) than fluorescent lights: the latter have a blue cast that can make people’s faces look sickly. These observations are related to **blackbody radiation**—the continuous spectrum of light emitted by matter as the matter is heated to higher temperatures.



Lighting Facts
Données d’éclaire
Per Bulb
Par lampe

Brightness/Luminosité	650 lumens
Estimated Yearly Energy Cost Coûts énergétiques annuels estimést Based on 3 hrs/day, 11¢/kWh. Cost depends on rates and use./Basé sur une consommation de 3h/jour, 0,11$/kWh. Les coûts varient selon les tarifs et l’usage.	$0.90
Life/Durée de vie	10.0 years/ans
Light Appearance/Allure de la lumière Warm/Chaude Cool/Froide 2700 K	
Energy Used/Énergie consommée	7.5 watts



Light Appearance/Allure de la lumière
Warm/Chaude Cool/Froide
5000 K
Energy Used/Énergie consommée

Figure 6. *Labels from LED light bulb boxes. Notice that the “warm” bulb is labeled 2700 K while the “cool” bulb is labeled 5000 K.*

Figure 7 shows the **spectra**, graphs of intensity versus wavelength, for blackbody radiation emitted by matter at several different temperatures.

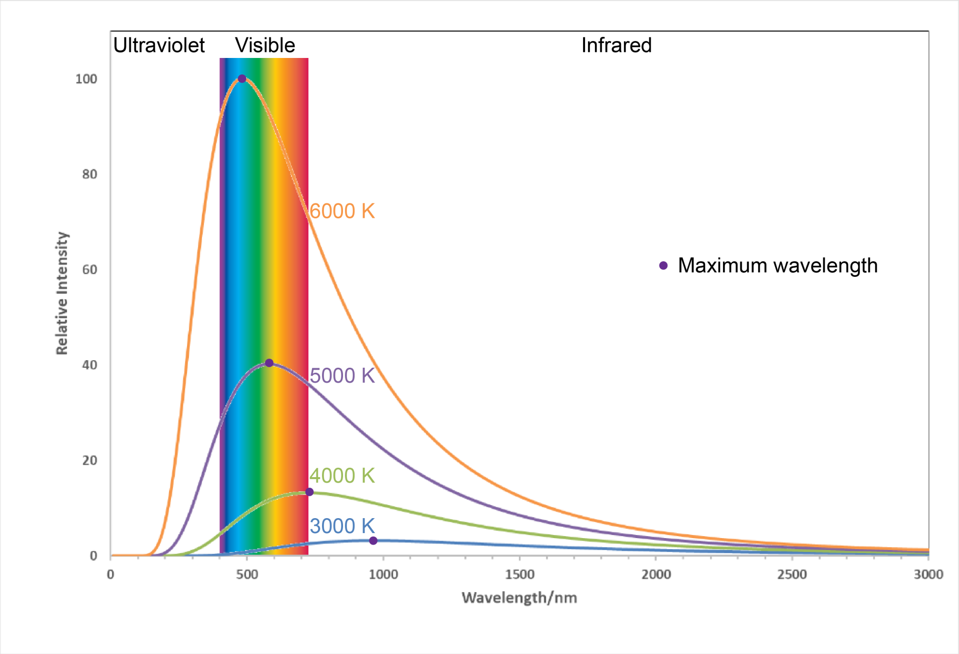


Figure 7. *Blackbody spectral distribution curves and their maxima are shown for four temperatures.*

Here, each spectrum depends only on temperature. The wavelength of the maximum in each curve,

$$\lambda_{max}$$

shifts to shorter wavelengths as the temperature increases. This corresponds to a heated metal first becoming red hot, then brighter and white hot as the temperature increases.

Additional Practice 1

Additional Practice 2

D1.4 Planck's Quantum Theory

In the late 1800s, physicists derived mathematical expressions for the blackbody curves using well-accepted concepts of mechanics and electromagnetism. They assumed that as the temperature increased the energies of atoms in a metal object would increase as the atoms vibrated more vigorously; these vibrations were assumed to create electromagnetic waves—the blackbody radiation. But no theory based on these ideas was able to predict the shapes of the curves shown in Figure 7. Even worse, the theory predicted that the intensity would become infinitely large for very short wavelengths, an absurd result.

In 1900, Max **Planck** introduced a revolutionary idea, from which he was able to derive a theoretical expression for blackbody spectra that fit the experimental observations within experimental error. Instead of assuming that the vibrating atoms could have a continuous set of energy values, Planck restricted the vibrational energies to discrete values—that is, he assumed that there must be some minimum quantity of energy that could be transferred between vibrating atoms. That quantity of energy is proportional to the frequency of vibration and is called a **quantum**.

$$\mathrm{E}_{\text{quantum}} = h\nu; \quad \text{because } c = \lambda\nu,\ \nu = \frac{c}{\lambda},\ \mathrm{E}_{\text{quantum}} = \frac{hc}{\lambda}$$

The proportionality constant "*h*" is now known as **Planck's constant**. Its value is very small, 6.626×10^{-34} J·s (joule-seconds). According to Planck's theory, electromagnetic radiation occurs in small, indivisible quantities (quanta), just as matter consists of small, chemically indivisible quantities (atoms).

Additional Practice

Although Planck had developed a theory of blackbody radiation that worked, he was not satisfied with the assumption of quantized energies for the vibrating atoms. But not for long—a few years later Albert **Einstein** used the idea of quantization of electromagnetic radiation to explain another puzzling phenomenon: the photoelectric effect, which is a topic for the next section.

D2.1 The Photoelectric Effect

Activity 1: Preparation—Photoelectric Effect

In your course notebook, make a heading for Photoelectric Effect. After the heading write down what you recall about the photoelectric effect from courses you have already taken. If you remember having a question about the photoelectric effect or if there is anything you remember being puzzled about, write that down as well. We will ask you to refer back to what you have written when you complete this section.

Planck's quantum theory was able to predict accurately the distribution of wavelengths emitted by a blackbody at various temperatures. However, Planck found it difficult to justify his assumption that vibration energies had to be multiples of a minimum energy—a quantum. When Albert **Einstein** used Planck's quantum hypothesis to explain a different phenomenon, the photoelectric effect, the validity of quantum theory became clearer.

Exercise 1: Quanta and Laser Light (Review)

Before doing any calculation or looking at the hint, write in your class notebook an explanation of how you plan to work out the problem. Do all the steps in the calculation in your notebook. Once you have arrived at an answer, then submit your results below and click the "Check" button to see if it is correct. If one or more parts of your answer is incorrect, go over your work in your notebook carefully and check for errors. "Retry" with your new answer. Look at the hint (click on it to expand for view) only after you have attempted to answer the question at least twice.

When electromagnetic radiation shines on a metal, such as sodium, electrons can be emitted and an electric current (a flow of electrons) can occur. This is called the **photoelectric effect**. The effect is complicated: for some wavelengths no electrons are emitted, but at other wavelengths electrons are emitted.

Exercise 2: Photoelectric Effect Simulation

Watch this photoelectric effect animation, where sodium is already selected, to answer the questions below. *Write down your observations as you watch the animation, and then answer the questions in your course notebook.*

1. **For which colors of visible light are electrons emitted by sodium? Determine the maximum wavelength at which electrons are emitted.**
2. **At a wavelength where electrons are emitted, describe the shape of a graph of number of electrons emitted vs. light intensity.**
3. **Determine the shape of a graph of electron energy vs. light frequency. How does this graph differ from the electrons vs. intensity graph?**
4. **Based on your observations, draw a rough graph with labeled axes to show how the number of electrons emitted varies with wavelength of light. How would the graph change if the intensity of light increased?**

If you would like to experiment with the simulation further, download and save the simulation program, go to the location where you saved it, and double-click on the file name (photoelectric_en.jar) to install and run it. You need to have Java installed for this to work.

Additional Practice

Activity 2: Summary of Photoelectric Effect Results

In your course notebook, write a brief summary of the results you obtained from experimenting with the photoelectric effect simulation. Also write a summary of how your experimental results can be interpreted based on the idea that light consists of quanta. Compare what you wrote with the summary below [also available at this link] and, if necessary, revise what you wrote.

Additional Practice

Activity 3: Wrap-up—Photoelectric Effect

Refer to what you wrote (including things that puzzled you) when you made the heading Photoelectric Effect in your class notebook. Revise what you wrote based on what you have just learned. Write a summary so that it will be a good study aid when you review for an exam. If you still have questions, ask them on Piazza.

7.3: In Depth- Atomic-scale Particles and Waves

44

In Depth: Atomic-scale Particles and Waves

D3.1 Atomic-Sized Particles Have Unusual Properties

Bohr's model predicted experimental data for the hydrogen-atom emission spectra and was widely accepted, but it also raised questions. Why did electrons have energies defined by a single quantum number $n = 1, 2, 3$, and so on, but never in between? How could the model work so well for a hydrogen atom and one-electron ions, but not accurately predict the emission spectrum for helium or any atom or ion with two or more electrons? To answer such questions, we need to explore the unusual properties of matter at the atomic scale.

It is natural to try to interpret the behavior of electrons in atoms using analogies to the behavior of things we can see and experience. By the turn of the 20th century, scientists had identified two different kinds of behavior that might serve as analogies: waves and particles. Waves, such as water waves, can bend around objects and exhibit interference. A particle, such as a pea or tennis ball, moves in a straight line unless its path is changed by a force (such as friction, gravity, or hitting something). It turns out that properties of atomic-scale matter are best explained using a combination of these analogies.

Let's think about an electron as if it were a particle and choose a very simple, but artificial, situation. Figure 1 shows an electron that is constrained to move in a single dimension, say the x direction. There are walls to the left and right of the electron that prevent it from moving beyond them; the distance between the walls is d (the electron is in a box of length d). Given an initial push, the electron will move back and forth forever (assuming no friction). The electron's kinetic energy would be given by the equation

$$E = \frac{1}{2}mv^2$$

where m is the mass and v the velocity.

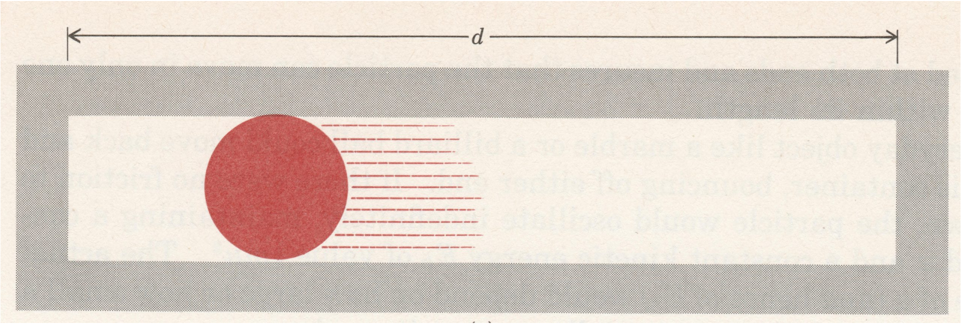


Figure 1. *Imagine an electron confined in a box of length d.*

Exercise 1: Electron in One-dimensional Box

Consider these questions regarding the electron moving in a one dimensional box:

But to explain the hydrogen-atom line spectrum, Bohr had to assume that an electron in an atom can only have certain energies. This assumption seemed very unsatisfactory based on the particle analogy—as we just saw, an electron should be able to have any energy value.

Let's explore a wave analogy instead. In 1924, Louis **de Broglie** proposed that a wave of wavelength λ is associated with every particle. The larger the mass of the particle and the faster it is moving, the smaller this wavelength becomes. The relationship is given by the formula:

$$\lambda = \frac{h}{p}$$

where p is the momentum of the electron, the product of its mass and velocity

$$p = m \times v$$

and h is Planck's constant ($h = 6.626 \times 10^{-34}$ J s).

Optional Information: Wavelike behavior of electrons was confirmed in 1927; read about it here. View this video for another description of the relevant experiments.

Suppose a wave, such as a vibrating guitar string, occupies the box. A guitar string is constrained by being fixed at each end so we assume the ends of the string are tied to the walls at the ends of the box.

Activity 2: Graphical Representation of Vibrating String

In your course notebook, make a drawing of what a vibrating string of length *d*, with its ends in fixed positions, would look like. If you are studying with someone else, each make a drawing individually and then compare.

If an electron behaves like a guitar string, then only certain wavelengths will fit within the one-dimensional box with length *d* (see the figure in Activity 2). The length of the box can thus correspond to: a single half-wavelength, two half-wavelengths, three half-wavelengths, etc., but *not* to any wave where either end of the string is moving. In other words, the length *d* must correspond to an integer number of half wavelengths:

$$d = n\frac{\lambda}{2}$$

where n = 1, 2, 3, 4,… Solving the equation for λ, we obtain:

$$\lambda = \frac{2d}{n}$$

Combining this with de Broglie's equation,

$$\lambda = \frac{h}{p}$$

we have:

$$\lambda = \frac{2d}{n} = \frac{h}{p} = \frac{h}{mv}$$

which rearranges to give:

$$v = \frac{nh}{2md} \quad n = 1, 2, 3, 4, \ldots$$

We can now calculate the kinetic energy of our wave-particle. It is given by the formula:

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{nh}{2md}\right)^2 = n^2\left(\frac{h^2}{8md^2}\right)$$

Because n is a positive whole number, this equation says that the kinetic energy of the electron can have only certain values and not others.

Exercise 2: Energy Levels for Electron in a Box

This result shows that if we think of an electron as a wave in a 100 pm box, its energy is automatically restricted to certain specific values: the electron can have an energy of 6.0 attojoules (aJ) or 24.0 aJ, but not an intermediate energy such as 7.3 aJ or 11.6 aJ. We describe this situation by saying that the energy of the electron is **quantized**. Because the energy of 6.0 aJ is the lowest possible energy, the electron is most stable at this energy, where the box contains half a wavelength. This is the ground state. If the energy has a higher value, such as 24 aJ or 54 aJ, the electron is in an excited state. Notice that for the excited states the electron waves have one or more nodes. A **node** is a point where the wave has zero amplitude; that is, where the wave is not moving up or down at all. The greater the number of nodes, the higher the energy, a generalization that is true for all kinds of waves.

This new way of approaching the behavior of electrons (and other atomic-sized particles) became known as **wave mechanics** or **quantum mechanics**. Using both wave and particle analogies to describe atomic-scale matter is referred to as **wave-particle**

duality. Wave-particle duality implies that we can no longer state that the electron is located at a specific position within the box or is moving in one direction or the other: the electron seems to be all over the box at once!

7.4: In Depth- The Heisenberg Uncertainty Principle

45

In Depth: The Heisenberg Uncertainty Principle

D3.2 The Heisenberg Uncertainty Principle

This inability to locate an electron precisely seems strange, but it is true of all atomic-scale particles. In 1927, Werner **Heisenberg** introduced the **Heisenberg uncertainty principle**: it is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle. Mathematically,

$$(\Delta x)(m\Delta v_x) = (\Delta x)(\Delta p_x) \geq \frac{h}{4\pi}$$

where Δx is the uncertainty in the position and Δp_x is the uncertainty in the momentum along the x direction. Hence, the more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa.

The result of your calculation shows that if an electron has Δx = 1 pm, the uncertainty in its velocity is at least 5×10^7 m/s. In other words, we essentially have no idea how fast it's moving.

Heisenberg's principle imposes ultimate limits on what is measurable in science. It is possible to talk about the *probability* that the electron is at a specific location, or the *probability* that it is moving at a given speed, but there will also be some probability of finding it somewhere else in the box or moving at some other speed.

Optional Information: For more details about the uncertainty principle, click here.

The uncertainty principle may seem strange, but we can say that the *probability* of finding a particle-like electron at a given location depends on the shape of the wave associated with the electron. The various wave shapes you drew in Activity 2 can be described mathematically using functions such as sines or cosines; that is, there is a mathematical **wave function** that describes each wave. The wave function is usually represented by a Greek letter

$$\psi$$

Shortly after the uncertainty principle was proposed, the German physicist Max **Born** (1882 to 1969) suggested that the square of the magnitude of the wave function,

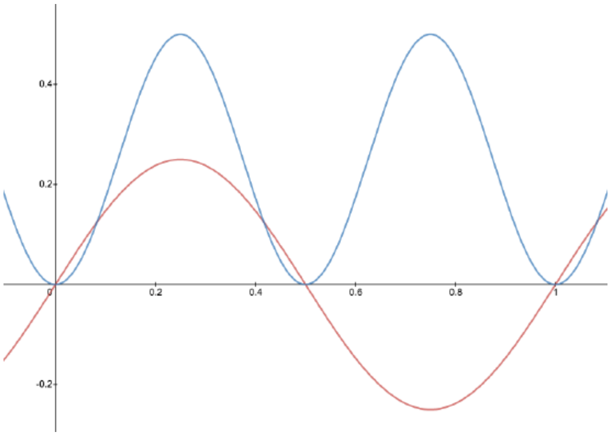
$$|\psi|^2$$

at any position is proportional to the probability of finding the electron (as a particle) at that same position. If we can determine the wave function associated with an electron, we can also determine the relative probability of the electron's being located at one point as opposed to another. Thus, each wave form you drew in Activity 2 can be represented by a different function,

$$\psi_n$$

each has a different distribution of electric charge throughout the box, and each is associated with a different, specific energy value.

A graphic way of indicating the probability of finding the electron at a particular location is by the density of shading or stippling; that is, where the probability is high we draw lots of dots or darker shading and where the probability is low we draw fewer dots. We say that where the probability is high we have a large electron probability density (or just electron density). (In the guitar-string analogy we would draw lots of dots at places where the string was vibrating quite far from its rest position. For example, consider the wave shown below in red along with its square shown in blue. Wherever there is a maximum in the square of the wave function, we would plot a lot of dots.)



Activity 3: Representing Electron Density by Density of Dots

In your course notebook, annotate each of your drawings of the vibrating string with dots such that the density of dots indicates the electron probability density.

In Bohr’s theory an electron had a well-defined orbit around the nucleus, but according to the uncertainty principle, the best we can do is indicate electron density in various regions. Consequently we use a slightly different word to refer to the wave function and its electron-density distribution: **orbital**. The electron density of orbitals of an atom or molecule is very useful because it indicates where there is negative charge (electron density) relative to positive charge (atomic nuclei). This helps us understand atomic properties, chemical bonds, and forces between molecules.

7.5: In Depth- In-Phase and Out-of-Phase

46

In Depth: In-Phase and Out-of-Phase

D6.2 Constructive and Destructive Interference

Forming a chemical bond by overlap of two atomic orbitals, which we just described, is equivalent to *constructive interference* of the electron waves for the two hydrogen atoms. It occurs when the two waves are *in-phase*.

For example, in a one-dimensional vibrating string, in-phase means when two waves are both vibrating up (or down) at the same time. In the video below, both ends of the wave device are moving up (or down) at the same time. This results in a bigger wave in the middle, where the two waves overlap.

https://mediaspace.wisc.edu/id/1_0vj...yerId=25717641

A second possibility is that the two waves are *out-of-phase*—one is moving up when the other is moving down. This results in *destructive interference* between the waves. This is shown in the video below. Note that in the destructive-interference video there is a point in the middle of the wave device that never moves up or down. This point has zero amplitude all the time and is a *node*.

https://mediaspace.wisc.edu/id/1_ycc...yerId=25717641

An atom is three dimensional, so it is difficult or impossible to visualize the waves corresponding to an electron in an atom. The principle of in-phase or out-of-phase remains the same, though. In-phase results in constructive interference and larger values of the wave function between two nuclei. Larger wave function corresponds to larger electron density, which attracts the two nuclei. Out-of-phase atomic wave functions result in a node between the nuclei, which leaves two unscreened nuclei that repel.

Index

Glossary

Sample Word 1 | Sample Definition 1

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    - 2.8: Day 16- DNA and Lipids - *CC BY-NC-SA 4.0*
  - 3: Unit Three - *CC BY-NC-SA 4.0*
    - 3.1: Day 18- Reaction Rate - *CC BY-NC-SA 4.0*
    - 3.2: Day 19- Integrated Rate Law - *CC BY-NC-SA 4.0*
    - 3.3: Day 20- Rate of Radioactive Decay - *CC BY-NC-SA 4.0*
    - 3.4: Day 21- Reaction Energy Diagram and Arrhenius Equation - *CC BY-NC-SA 4.0*
    - 3.5: Day 22- Elementary Reactions - *CC BY-NC-SA 4.0*
    - 3.6: Day 23- Reaction Mechanisms - *CC BY-NC-SA 4.0*
    - 3.7: Day 24- Enzymes and Enzyme Catalysis - *CC BY-NC-SA 4.0*
    - 3.8: Day 25- Homogeneous and Heterogeneous Catalysis - *CC BY-NC-SA 4.0*
  - 4: Unit Four - *CC BY-NC-SA 4.0*
    - 4.1: Day 27- Thermochemistry and Enthalpy - *CC BY-NC-SA 4.0*
    - 4.2: Day 28- Entropy, Gibbs Free Energy - *CC BY-NC-SA 4.0*
    - 4.3: Day 29- Gibbs Free Energy, Chemical Equilibrium - *CC BY-NC-SA 4.0*
    - 4.4: Day 30- ICE Table, Reaction Quotient, Le Châtelier’s Principle - *CC BY-NC-SA 4.0*
    - 4.5: Day 31- Le Châtelier’s Principle, Equilibrium and Gibbs Free Energy - *CC BY-NC-SA 4.0*
    - 4.6: Day 32- Gibbs Free Energy and Work, Kinetic Metastability - *CC BY-NC-SA 4.0*
    - 4.7: Day 33- Acids and Bases - *CC BY-NC-SA 4.0*
    - 4.8: Day 34- Acid-Base Reactions - *CC BY-NC-SA 4.0*
  - 5: Unit Five - *CC BY-NC-SA 4.0*
    - 5.1: Day 36- Buffer Solutions - *CC BY-NC-SA 4.0*
    - 5.2: Day 37- Acid-Base Titration - *CC BY-NC-SA 4.0*
    - 5.3: Day 38- Oxidation-Reduction Reactions, Voltaic Cells - *CC BY-NC-SA 4.0*