General Chemistry
Class Notes

Leon Hostetler

August 16, 2019
Version 0.3

Periodic Table of the Elements

Legend:
- Alkali Metal
- Alkaline Earth Metal
- Transition Metal
- Post-transition Metal
- Metalloid
- Nonmetal
- Noble Gas
- Lanthanide
- Actinide
- Unknown Properties

Key:
Z
Sym-bol
mass

Group	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** 1.0079																	2 **He** 4.0025
2	3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
3	11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.64	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.8
5	37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** 96	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.29
6	55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** 209	85 **At** 210	86 **Rn** 222
7	87 **Fr** 223	88 **Ra** 226	89 **Ac** 227	104 **Rf** 261	105 **Db** 262	106 **Sg** 266	107 **Bh** 264	108 **Hs** 277	109 **Mt** 268	110 **Ds** 281	111 **Rg** 280	112 **Cn** 285	113 **Nh** 286	114 **Fl** 289	115 **Mc** 290	116 **Lv** 293	117 **Ts** 294	118 **Og** 294

Lanthanides:

58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 145	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97

Actinides:

90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	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	103 **Lr** 262

Contents

Preface

About These Notes

These are the class notes that I took (and edited since) during three courses on general chemistry taken at the State College of Florida.

The periodic table shown on one of the first pages was derived from work done by Ivan Griffin and licensed under the LaTeX Project Public License. The original work may be viewed here.

My class notes can be found at www.leonhostetler.com/classnotes

Please bear in mind that these notes will contain errors. Any errors are certainly my own. If you find one, please email me at leonhostetler@gmail.com with the name of the class notes, the page on which the error is found, and the nature of the error.

This work is currently licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License. That means you are free to copy and distribute this document in whole for noncommercial use, but you are not allowed to distribute derivatives of this document or to copy and distribute it for commercial reasons.

Updates

Last Compiled: August 16, 2019

Version 0.3 (Aug. 15, 2019): Updated layout and modernized the periodic table

Version 0.0: (Aug. 25, 2016): Initial upload

Chapter 1

Measurement

1.1 Useful Formulas and Conversions

$$\text{cm}^3 = \text{cc} = \text{mL}$$
$$\text{density} = \frac{\text{mass}}{\text{volume}}$$
$$\text{molar mass} = \frac{\text{g}}{\text{mol}}$$

SI Standard Units:
1. Distance: meter (m)
2. Mass: kilogram (kg)
3. Time: second (s)
4. Temperature: Kelvin (K)
5. Amount of substance: mole (mol)

1.2 Significant Figures

For a reported measurement, the last digit is estimated (i.e. uncertain) and it can vary by ± 1. When adding or subtracting numbers, the result needs to have the same number of decimal places as the quantity carrying the fewest decimal places. Note, this is not the same as rounding to the same number of significant figures, which is done when multiplying or dividing numbers. When doing this with numbers that don't have decimal places, things can get weird. For example, $3200 + 48 = 3200$ because of the uncertainty in the first number.

1.3 Dimensional Analysis

Dimensional analysis—always make sure your calculations contain and properly use the proper units. When converting units, do it properly—canceling out units as appropriate. Otherwise, you could end up with 10^6 when you should get 10^{-6}.

$$\text{given unit} \times \frac{\text{desired unit}}{\text{given unit}} = \text{desired unit}$$

When doing unit conversions involving areas and volumes, the squared and cubed units may need to be handled differently. For example, when converting from cubic centimeters to cubic inches, you must use three conversion factors in a row to completely cancel out the cubic centimeters. For example:

$$5\,\text{cm}^3 \times \frac{1\,\text{in}}{2.54\,\text{cm}} \times \frac{1\,\text{in}}{2.54\,\text{cm}} \times \frac{1\,\text{in}}{2.54\,\text{cm}} = \frac{5\,\text{in}^3}{(2.54\,\text{cm})^3}$$

Chapter 2

Chemistry, Matter, and Phases

Chemistry is the science that seeks to understand the behavior of matter by studying the behavior of atoms and molecules.

Matter is anything that occupies space and has mass. Its common phases include solid, liquid, and gas.

- Solid: A phase of matter in which the atoms do not move around. A solid has a fixed volume and rigid shape. The two types of solids are crystalline and amorphous. Because the atoms are tightly packed, solids are not compressible.

    - Crystalline solids include salt.
    - Amorphous solids (e.g. glass) do not have distinct melting points. They can be thought of as being between liquids and solids.

- Liquid: A phase of matter in which the atoms are tightly packed–making liquids incompressible. They can, however, move around each other and, therefore, liquids assume the shape of their container and have fixed volume.
- Gas: A phase of matter in which the atoms are far apart and energetic, therefore, gases are compressible. It also means that gases assume the shape and volume of their containers.

When two or more elements combine chemically, they form a **molecule**. For example, O_2 and H_2O are both molecules. A **compound** is specifically a molecule with more than one kind of atom. For example, H_2O is a compound, but O_2 is not.

Pure substances or are composed of only one type of atom or molecule. Both water and helium are pure substances. Pure substances can be divided into **elements** and **pure compounds**. In chemistry, compounds are reducible, but elements are not. Pure compounds are distinguished by the fact that they have a constant composition. That is, they have a fixed ratio of elements. For example, pure water is a pure compound because any quantity of pure water will have two hydrogens for every oxygen.

Mixtures occur when substances are mixed together—their constituents are not chemically combined like the hydrogen and oxygen in water. Examples of mixtures include saltwater (which is also a solution) and the air we breathe.

Mixtures can be subdivided into **homogeneous** and **heterogeneous**. A homogeneous mixture is one that looks the same throughout. Examples of homogeneous mixtures include tea and saltwater. A heterogeneous mixture is composed of visibly different substances or substances in different phases. Examples of heterogeneous mixtures include soil, salad, and salsa. To remember whether it's a "homogeneous" or a "heterogeneous" mixture, remember that "homo" means "same" and "hetero" means "different". Homogeneous mixtures are often called **solutions**.

Mixtures can be physically separated into their constituent substances in a variety of ways depending on the mixture. A mixture of a liquid and a solid, such as dirt in water, can be separated by **filtration**. An **immiscible** liquid mixture, that is, a heterogeneous

liquid mixture, such as oil in water, can be separated by decanting—slowly pouring off the top liquid. A **miscible** liquid mixture, that is, a homogeneous liquid mixture such as alcohol and water, can be separated by **distillation**—the more volatile liquid will evaporate before the less volatile liquid. A mixture such as saltwater can also be separated by distillation.

There is not always a clear line between the different types of mixtures. A **suspension** is a mixture, generally of a solid in a liquid, in which the particles are small enough to mix well, but large enough to be seen (at least with a microscope) and to settle out of the liquid if undisturbed. Examples include tomato juice and fine sand in water. A suspension is a heterogeneous mixture since the particles are large enough to be seen. A **colloid** is similar, but the particles are too small to be seen, so they are homogeneous mixtures. Examples include milk and fog. A **solution** is a homogeneous mixture in which the particles are the size of atoms—much too small to be seen even with microscopes. For example, saltwater is a solution because the salt compounds break apart into individual atoms when in water. To tell whether a homogeneous mixture is a colloid (invisibly small particles) or a solution (extremely small atom-size particles), you can shine a light through the mixture. If you can see the light beam in the mixture, then it is a colloid and if not, it is a solution. Although the particles in a colloid are too small to be seen with the naked eye, they are large enough to reflect the light.

No chemical transformation can decompose an element into simpler substances. In other words, chemistry is not particle physics. The elements are not the simplest possible substances, for example, they can be reduced to protons, neutrons, electrons, and further to quarks. However, they can only be reduced using nuclear processes–not chemical processes.

A **physical property** is one that a substance displays without changing its chemical composition. A **chemical property** is one that a substance displays only through changing its chemical composition. Chemical changes are often evidenced by heat exchange or by color changes.

$$\text{Reactants} \xrightarrow[\text{Chemical Change}]{} \text{Products}$$

A physical change results in a different form of the same substance, while a chemical change results in a completely new substance.

Density is mass divided by volume, and in chemistry, it is calculated in grams and centimeters cubed or milliliters. The density of most substances decreases when its temperature is raised.

The temperature of a sample of matter is a measure of the average kinetic energy of the atoms and molecules that compose the sample. As such, thermometers measure energy.

When solids change state to liquid, their volume may change. Their densities can remain similar or change dramatically. Different phases of matter may have different heat capacities. Phase changes require heating or cooling, and they are physical changes as opposed to chemical changes. Phase changes include

- Boiling
- Melting
- Subliming
- Freezing
- Condensing
- Deposition
- Evaporation

An **intensive property** is a physical property that does not depend on the amount of substance (e.g. density). An **extensive property** is a physical property that does depend on the amount of substance (e.g. mass).

Chapter 3

Atoms and Elements

3.1 Atoms

According to the **law of conservation of mass**, in a chemical reaction, matter is neither created nor destroyed. In other words, the mass of reactants equals the mass of the products. According to the **law of definite proportions**, all samples of a given compound have the same proportions of their constituent elements. According to the **law of multiple proportions**, when two elements (A and B) form two different compounds, the masses of B that combine with one gram of A can be expressed as a ratio of small whole numbers. The development and acceptance of atomic theory depended on these laws.

All matter is composed of different quantities of protons, electrons, and neutrons bound together in atoms. Protons have positive elementary electric charge represented by p^+. Electrons have negative elementary charge represented e^-. Neutrons are charge neutral but they determine nuclear stability. Electric charge is a fundamental property of protons and electrons. Like charges repel and unlike charges attract. Fully understanding this fundamental behavior is key to understanding chemistry.

An element is defined by the number of protons in its nucleus. The number of **protons** in an atom is its **atomic number** designated Z. The sum of protons and neutrons in an atom is its **mass number** represented by A. Atomic mass is measured in **atomic mass units** (amu). An atomic mass unit is defined as $1/12$ of the mass of a carbon-12 atom containing 6 protons and 6 neutrons. The **atomic mass** of an element is the average mass of the element as it occurs in nature, and it accounts for the relative abundances and the mass differences of the different isotopes.

3.2 Ions

In chemical reactions, atoms often lose or gain electrons to form **ions**, that is, they become charged particles. Because ions have charge, they behave very differently than the atoms from which they are formed. A **cation** is an atom that has lost one or more electrons and thereby gains a positive charge. An **anion** is an atom that has gained one or more electrons and thereby gains a negative charge.

The charge of an ion is calculated as its sum of protons minus its sum of electrons. Main-group elements that tend to form predictable cations (i.e. the first two columns), tend to have a charge equal to the group number. Main group elements that tend to form predictable anions (i.e. the last two or three columns), tend to have a charge equal to the group number minus 8. Anions and cations always occur together in nature–matter is charge neutral. For example, Na^+Cl^- is table salt and it is charge neutral.

3.3   Isotopes

Atoms with the same number of protons but different number of neutrons are called **isotopes**. Since neutrons are charge neutral, different isotopes of an element generally exhibit the same chemical behavior. The relative amount of each isotope in a naturally occurring sample of an element is called the **natural abundance** of the isotope. For a given element, the relative amounts of each different isotope in a naturally occurring sample of that element is always the same. These percentages are referred to as the **percent natural abundance** of the isotope.

Isotopes are notated as ^A_ZX or as X-E, where A is the mass number, Z is the atomic number, and X is the chemical symbol. For example, Neon-10 can also be represented as $^{21}_{10}$Ne.

In summary, an element that gains or loses an electron in a chemical process, is considered an ion of that same element. An element that gains or loses a neutron in a nuclear process, becomes an isotope of that same element. An element that gains or loses a proton in a nuclear process, becomes an isotope of a different element.

3.4   The Periodic Table

The sequence of elements when ordered by mass has repeating sequences of properties. When arranged in the periodic table, elements are grouped into vertical columns each called a "family" or a "group". The elements in a group tend to have similar properties.

- Noble gases tend to be inert.
- Alkali metals tend to be highly reactive. They form extremely basic solutions when added to water.
- Alkaline earth metals tend to be fairly reactive.
- Halogens are very reactive nonmetals. They are diatomic, meaning the atoms tend to occur in pairs in nature (e.g. F_2).

The periodic table can also be divided in other ways. One way is to divide it into the **main-group elements** (i.e. the first two columns and the last six columns, and the **transition elements** (i.e. the middle columns). The properties of main-group elements are fairly predictable by their position in the periodic table and they tend to form ions that have the same number of valence electrons as the nearest noble gas.

The periodic table can also be divided into three general sections based on their resistance to electric charge flow.

- Metals are conductive, malleable, and ductile.
- Metalloids, or semiconductors have properties of both metals and nonmetals.
- Nonmetals are not conductive.

Chapter 4

Molecules, Compounds, and Chemical Equations

The properties of molecules are typically very different from the properties of their constituent atoms.

Chemical formulas normally list the most metallic elements first. On the periodic table, the more metallic elements are to the left and bottom. There are several different types of chemical formulas. An **empirical formula** gives the simplest whole number ratio of atoms of each element in a compound. For example, the empirical formula for ethane is CH_3. The **molecular formula** gives the actual number of atoms of each element. This is the most commonly used representation. The molecular formula for ethane is C_2H_6. The **structural formula** uses lines to show the actual chemical bonds. Ethane would be represented as:

$$\begin{array}{ccc} & H & H \\ & | & | \\ H - & C - & C - H \\ & | & | \\ & H & H \end{array}$$
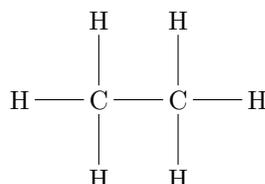
Elements can be atomic or molecular, that is, diatomic. There are seven elements that are diatomic in nature, that is, they pair up, bonding with each other. Here's a way to remember which elements are diatomic: Start at element 7 (N), now draw the character '7' (N, O, F, Cl, Br, I) plus there's H. Several elements are found in nature as polyatomic molecules. Examples include P_4 and S_8. Check out their position on the periodic table relative to the seven diatomic elements.

Compounds can be molecular or ionic. Ionic compounds occur throughout Earth's crust as minerals. **Ionic compounds** do not exist as discrete molecules, but rather as part of a larger lattice. The basic unit is a **formula unit**–the smallest electrically neutral group of ions. Ionic compounds always contain positive and negative ions. The sum of the positive (cation) charges must equal the sum of the negative (anion) charges in order for the ionic compound to be charge-neutral. Make sure the molecular formulas for the ionic compounds are reduced. If you can divide all of the subscripts by some whole number, then do so.

When you have a metal and one or more nonmetals you can assume that it's an ionic compound. Next figure out if the metal forms only one type of ion or multiple types. The alkali metals (1+), alkaline earth metals (2+), aluminum (3+), zinc (2+), and silver (3+), form only one type of ion. All the other metals can form multiple ions. Some ions are polyatomic. For example NO_3^-.

Molecular bonds are directional, but ionic bonds are not since they form a lattice with bonded ions in every direction.

The easiest way to remember how to do the stoichiometry conversions is to remember the flow chart

$$\text{grams} \leftrightarrow \text{moles} \leftrightarrow \text{number of things.}$$

This helps you to remember that a question asking you the number of atoms in x grams of something, requires that you go through the moles conversion first. The conversion factor between grams and moles is g/mol and the conversion factor between moles and number of things is Avogadro's number.

To calculate how many moles of X are in moles of XY you simply multiply the subscript of X in XY by the total moles of XY.

To calculate how many grams of X are in the compound XY is a little more involved because you have to convert the grams of XY to moles XY to moles X and then to grams X. To solve these problems, it may be easier to think in terms of **mass percent composition**.

Formula mass or **molecular mass** is simply the atomic masses of all the atoms in a molecule or formula unit. Since $1\,\text{amu} = 1\,\text{g/mol}$ then the formula mass of a molecule or formula unit is also its **molar mass**. When asked for formula mass give the unit of amu (atomic mass units), when asked for molar mass give the unit of g/mol even though the two are equal.

Mass percent composition is the percent by mass of an element in a compound. It is calculated as the mass of the element in $1\,\text{mol}$ of the compound divided by the mass of $1\,\text{mol}$ of the compound all times 100.

To calculate the empirical formula of a compound from experimental data, first make sure you're dealing with moles of material. Then use these numbers as the subscripts in your empirical formula, divide each subscript by the smallest number, and multiply everything by some factor that gives everything whole numbers. Here are the steps you might want to follow:

1. If the constituents are given by percent composition, convert these to grams
2. Convert the grams of constituent elements into moles of constituent elements
3. Build a formula with the moles as subscripts
4. Divide all subscripts by the smallest subscript
5. Multiply all subscripts by some number (if needed) such that all subscripts become whole numbers

When you're creating empirical formulas from experimental evidence, you can round up or down to get whole number values that are off by 0.1. For example, if you get 4.935, round it to 5. If you get 4.183, round it to 4. If the molar mass of the compound is given, you can convert the empirical formula to the molecular formula by multiplying the empirical formula by some small whole number such that the molar mass of the resulting compound matches the given molar mass. The molecular formula for a compound is always a whole number multiple of the empirical formula. Remember that the molar mass of diatomic elements is twice the atomic mass in grams.

For ionic compounds with transition metals of varying charge, always look up the common charges of these cations since they won't just form any charges–there are often only two different charges that these varying cations will have. Copper, for example, usually has a charge of +1 or +2 but not a charge of +3.

Chapter 5

Nomenclature

When it comes to nomenclature, there are 6 types of compounds: Type I ionic compounds, Type II ionic compounds, molecules, binary acids, oxyacids ending in "ic", and oxyacids ending in "ous".

5.1 Molecular Compounds

Molecular compounds: [prefix][name of first element] + [prefix][base name of second element][ide]. For example, N_2O is called "dinitrogen monoxide". The more metallic element is named first. Generally, write the name of the element with the smallest group number (leftmost element) first. If they're in the same group, write the element with the greatest row number (bottommost) first.

Prefixes:
1. hemi = 1/2
2. mono = 1
3. di = 2
4. tri = 3
5. tetra = 4
6. penta = 5
7. hexa = 6
8. hepta = 7
9. octa = 8
10. nona = 9
11. deca = 10

"Mono" is usually omitted from a first element. When a prefix ends in 'a' or 'o' and the second element begins with a vowel, the last letter of the prefix is dropped to avoid having two vowels appear beside each other. For example, [mono][ox][ide] becomes "monoxide".

5.2 Ionic Compounds

Type I ions: [name of cation] + [base name of nonmetal anion] + "ide".

Type II ions: [name of cation] + [cation charge in Roman numerals] + [base name of nonmetal ion] + "ide".

Some ionic compounds contain a **polyatomic ion** (a charged group of atoms that acts like an ion).

Halogen ions are called "halides".

When naming ions don't forget to include the charge when dealing with ions of variable charge. Scandium always forms a +3 ion, and rarely, silver has a charge other than its usual charge of +1.

Naming binary ionic compounds: (name of cation) + (charge if applicable) + (base name of anion + "ide")

Naming ionic compounds containing **polyatomic ions**: This is the same as naming binary ionic compounds except that you use the name of the polyatomic ions. Example: NaNO2 is sodium nitrite. Common polyatomic ions need to be memorized. Most polyatomic ions are **oxyanions**, which contain oxygen and another element. If a series of them contains different numbers of oxygen atoms, they are named according to a specific scheme. The one with fewer oxygen atoms ends in "ite", the one with more oxygen atoms ends in "ate". If there are more than two, then prefixes **hypo** (less than) and **per** (more than) are used as well. Example:

1. hypochlorite (ClO)
2. chlorite (ClO2)
3. chlorate (ClO3)
4. perchlorate (ClO4)

Some ionic compounds are called **hydrates** because they contain a specific number of water molecules per each formula unit. The formula for Epsom salts, for example is MgSO4 * 7H2O and it is called magnesium sulfate heptahydrate. Hydrates are named like regular ionic compounds with the added name of (prefix)+("hydrate"). Waters of hydration can usually be removed by heating a compound to turn a hydrate into an **anhydrous** compound.

5.3 Acids

Acids are molecular compounds that release H+ ions when dissolved in water. They include hydrogen which is usually written first in the formula. They are followed by (aq) meaning "aqueous" or "dissolved in water".

Binary acids are acids containing hydrogen and a nonmetal. They are named as: [hydro] + [base name of nonmetal] + "ic acid"

Oxyacids contain hydrogen and a polyatomic oxyanion. They are named as: [base name of nonmetal] + ["ic" for oxyanions ending in "ate" or "ous" for oxyanions ending in "ite"] + "acid".

You may want to use the mnemonic **IC I ATE an acid**.

5.4 Hydrocarbons

The hydrocarbon prefixes are

1. meth-
2. eth-
3. prop-
4. but-
5. pent-
6. hex-
7. hept-
8. oct-
9. non-
10. dec-

Use the following steps to name hydrocarbons:

1. Alkanes: The number of carbons in the longest continuous chain of carbon atoms determines the prefix (see above list) of the base name, and the ending of the base name is "ane". If this is a single chain, then that's it. However if smaller hydrocarbon groups (substituents) branch off then those are included at the beginning of the name. To name a substituent, you first determine the number of carbon atom where it's attached to the base chain, then count the number of C in the substituent

(using the above prefixes), then end with "yl". Precede the substituent name with the number of the C atom that it is affixed to on the base chain. If a base chain contains multiple of the same kind of constituents, then prefix the constituent name with "di, tri, tetra. . .". If there are multiple substituents, put them in alphabetical order.

2. Alkenes: Same as for alkanes except you prefix the base name with the number of the carbon atom where the double bond occurs, and you end the base name with "ene". Be sure to number the base chain so the double bond has the smallest possible number.

3. Alkynes: Same as for alkanes except you prefix the base name with the number of the carbon atom where the triple bond occurs, and you end the base name with "yne". Be sure to number the base chain so the triple bond has the smallest possible number.

Chapter 6

The Quantum-Mechanical Atom

Electromagnetic radiation can be described as a wave composed of oscillating, mutually perpendicular electric and magnetic fields propagating through space.

A wave can be characterized by its amplitude and wavelength. **Amplitude** is the vertical height of a crest. For light, amplitude determines the light's intensity or brightness. **Wavelength** is the distance between adjacent troughs. For visible light, wavelength determines the color. The most energetic waves have large amplitudes and short wavelengths. However, amplitude and wavelength can vary independently of each other. Wavelength is symbolized with λ the Greek letter called "lambda". Wavelength influences how much energy each photon has. The number of photons tells you how intense the light is.

Frequency is the number of cycles (or wave crests) that pass through a stationary point in a given period of time. The units are cycles per second or simply s^{-1}. An equivalent unit of frequency is the hertz (Hz) defined as

$$1\,\text{Hz} = 1\,\text{cycle/s.}$$

Frequency is symbolized by ν. The frequency of a wavelength is directly proportional to the speed at which the wave is traveling—the faster the wave, the more crests will pass a fixed location per unit time. Frequency is also inversely proportional to the wavelength—the farther apart the crests, the fewer will pass a fixed location per unit time. For light, therefore:

$$v = \frac{c}{\lambda} \qquad \text{or} \qquad \text{frequency} = \frac{\text{speed of light}}{\text{wavelength}}$$

Wavelength and frequency represent different ways of specifying the same information. Short-wavelength light inherently has greater energy than long-wavelength light.

If two waves of equal amplitude are in phase when they interact, the result is **constructive interference** or a wave with double the amplitude. When not in phase, the result is **destructive interference**—the wave disappears. Waves also exhibit **diffraction**. When a wave goes through an opening (slit) that is comparable in size to its wavelength, the wave diffracts or bends around it. This can be thought of as the wave simply spreading out after it goes through a slit. The result is that a slit becomes an apparent new source of the wave.

The **photoelectric effect** is the observation that many metals emit electrons when a light is shown on them. Experimental results, however, did not fit the explanation for this until Einstein proposed that light energy must travel in packets (i.e. photons). Einstein proposed that the energy in a light packet depends on its frequency according to following equation

$$E = h\nu$$

energy = Planck's constant $\cdot$ frequency

The energy of a photon can also be expressed in terms of wavelength as

$$E = \frac{hc}{\lambda}$$
$$\text{Energy} = \frac{\text{Planck's constant} \times \text{speed of light}}{\text{wavelength}}$$

For an electron bound to the metal with **binding energy** ϕ, the threshold frequency is reached when the energy of the photon is equal to ϕ. The **threshold frequency condition** is:

$$h\nu = \phi,$$

or in words, the energy of the photon $h\nu$ is equal to the binding energy. As the frequency of light is increased past the threshold frequency, the excess energy of the photon is transferred to the electron in the form of kinetic energy:

$$E_K = h\nu - \phi,$$

or in words, the kinetic energy is equal to the energy of the photon minus the binding energy.

The light emitted from a lamp containing an elemental gas consists of wavelengths specific to that element. When separated by a prism, these wavelengths create an **emission spectrum** that is specific to that element. Generally, the more electrons an atom has, the more lines its emission spectrum will have. Electrons are typically excited by heat or electricity. The spectrum of white light is continuous meaning there are no sudden interruptions in the intensity of light of the light as a function of wavelength. A spectrum plotted as a two-dimensional graph, then, is a plot of the amplitude as a function of the wavelength.

Absorption spectrum is the reverse of emission spectrum. It consists of the wavelengths of light that an element absorbs.

Louis de Broglie proposed that electrons, which have mass, also display wave-particle duality. This was confirmed by experiments in 1927. The wavelength of an electron is related to its kinetic energy (energy of motion). The faster the electron is moving, the higher its kinetic energy and the shorter its wavelength. The wavelength of an electron of mass m moving at velocity v is given by the **de Broglie relation**

$$\lambda = \frac{h}{mv}$$

When dealing with joules (J) remember that it can also be expressed as $1\,\text{J} = 1\,\text{kg} \cdot \text{m}^2/\text{s}^2$.

The wave and particle nature of electrons are **complementary properties**, which means we can't observe both at once. The more we know about one, the less we know about the other. This means we cannot simultaneously measure a particle's position and its velocity. This is formalized by Heisenberg's **uncertainty principle**

$$\Delta x \times m\Delta v \geq \frac{h}{4p}$$

where Δx is the uncertainty in the particle's position, m is the mass of the particle, Δv is the uncertainty of the particle's velocity, and h is Planck's constant. Since the right side of the equation is a finite number, the smaller the uncertainty of position or velocity, the greater the uncertainty must be of the other. All of this means that we cannot know the exact trajectory (position + velocity) of an electron. Instead, the trajectory becomes a quantum-mechanical probability distribution map.

Since velocity is directly related to energy ($E_{kin} = mv^2/2$), position and energy are also complementary properties. For each of the electron's energy eigenstates we can

specify the electron's energy precisely, but not its location at any given instant. Instead, the electron's position is described in terms of an **orbital**—a probability distribution map.

The mathematical derivation of energies and orbitals for electrons in atoms comes from solving the Schrodinger equation for the atom of interest. The general form of the Schrodinger equation is

$$\mathcal{H}\psi = E\psi$$

The $\mathcal{H}$ stands for the Hamiltonian operator (a set of mathematical operations that represent the total kinetic and potential energy of the electron within the atom). The E stands for the actual energy of the electron. The ψ (pronounced "sigh") is the wave function (a mathematical function that describes the wavelike nature of the electron. A plot of the wave function squared (ψ^2) represents an electron orbital.

The Schrodinger equation for multi-electron atoms is so complicated that it can't be solved exactly. All we have are the approximate solutions. When the Schrodinger equation is solved, it yields many solutions–many possible wave functions. Each electron orbital is specified by several interrelated quantum numbers: the principal quantum number, n, the angular momentum quantum number, l, and the magnetic quantum number, m_l.

The **principal quantum number** is an integer that determines the overall size and energy of an orbital. Its possible values are $n = 1, 2, 3 \ldots$ In introductory chemistry, these are called "shells". For the hydrogen atom, the energy in an orbital with quantum number n is given by $E_n = -2.18 \times 10^{-18}$ J $\times (1/n^2)$. The energy is negative because the electron's energy is lowered (made more negative) by its interaction with the nucleus (as described by Coulomb's law). The constant -2.18×10^{-18} J is the Rydberg constant for hydrogen. Notice that orbitals with higher values of n have greater energies (i.e. they're less negative) and that as n increases, the spacing between the energy levels becomes smaller.

Note: An electron's charge is completely distinct from its energy. The electron's charge is always $-1e$, but its energy, which is the sum of kinetic energy (velocity) and potential energy (position) varies.

The **angular momentum number** is an integer that determines the shape of the orbital. The possible values are $l = 0, 1, 2, \ldots, (n-1)$. In order to prevent confusion between n and l these numbers are often assigned letters as follows: $0 = s, 0 = p, 0 = d, 0 = f$. In introductory chemistry, these are called "subshells".

The **magnetic quantum number**, m_l, is an integer that specifies the orientation of the orbital. In introductory chemistry, these are called "orbitals". The possible values of m_l are the integer values (including zero) ranging from $-l$ to l.

Each combination of n, l, and m_l specifies one atomic orbital. For example the orbital with $n = 1$, $l = 0$, and $m_l = 0$ is known as the 1s orbital. The orbital with $n = 4$, $l = 3$, and $m_l = 2$ is known as the 4f2 orbital. The number of sublevels in any level is equal to n. The number of orbitals in any sublevel is equal to $2l + 1$. The number of orbitals in a level is n^2.

Each wavelength in the emission spectrum of an atom corresponds to an electron transition between quantum-mechanical orbitals. When an atom absorbs energy, an electron in a lower energy level is excited to a higher energy level. This makes for an unstable atom so the electron quickly relaxes to a lower energy orbital releasing a photon of light containing an amount of energy precisely equal to the energy difference between the two energy levels.

The energy of an orbital with principal quantum number n is given by

$$E_n = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n^2} \right).$$

The energy difference, therefore, is given by

$$\Delta E = E_{final} - E_{initial}.$$

Substituting the first into the second, we get

$$\Delta E = -2.18 \times 10^{-18} \, \text{J} \left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2} \right).$$

If you calculate the energy difference that occurs when an excited atom relaxes, you'll end up with a negative number for delta E. This is because the energy is emitted (lost) by the atom. The energy emitted by the atom is exactly the energy carried away by the photon

$$\Delta E_{atom} = -E_{photon}.$$

The negative sign is required because frequency and wavelength, which can be calculated from the E of the photon, must be positive. The wavelength can be calculated by

$$\lambda = \frac{hc}{E}.$$

Remember to convert visible light wavelengths to nanometers (10^{-9} m). Frequency ν has units of s^{-1} which are frequently expressed as hertz (Hz).

Chapter 7

Quantum Numbers and Periodic Properties

7.1   Quantum Numbers

See chapter 6 for more on quantum numbers.

Electron **spin** is a fundamental property of all electrons (just like electric charge). All electrons have the same amount of spin, but the orientation of the spin is quantized– with only two possibilities. The spin of an electron is specified by a fourth quantum number–the **spin quantum number** (m_s). There are two possibilities for this number, $+1/2$ (up spin) and $-1/2$ (down spin). The up spin in an electron configuration diagram is represented by an up half arrow and the down spin is represented by a down half arrow.

According to the **Pauli exclusion principle**, an orbital can have a maximum of two electrons and they must have opposite spin. This principle actually states that no two electrons in the same atom can have the same four quantum numbers.

In general, the lower the value of l within a principal level, the lower the energy of the corresponding orbital. That is the energy level of the s orbital is lower than the energy level of the p orbital which is less than the energy level of the d orbital which is less than the energy level of the f orbital.

Summary of Quantum Numbers

n	shell	$1, 2, 3, \ldots$
l	subshell	$0, 1, 2, \ldots (n-1)$
m_l	orbital	$-l$ to l
m_s	spin	$-\frac{1}{2}$ or $\frac{1}{2}$

7.2   Electron Configurations

The potential energy of a pair of charged particles is described by **Coulomb's Law**. For like charges, the potential energy is positive (repulsion) and decreases as the particles get farther apart. For opposite charges, the potential energy is negative (attraction) and becomes more negative as the particles get closer together. The magnitude of the interaction between particles increases as the charges of the particles increase. In other

words, an electron is attracted more strongly to a nucleus with three protons (3+) than to a nucleus with one proton (1+).

In a multi-electron atom, an electron experiences both the positive charge of the nucleus and the negative charges of the other electrons. An outer electron experiences less attraction to the nucleus because it is **shielded** from the full charge of the nucleus by the charges of the inner electrons. The **effective nuclear charge** that the outer electron experiences is (nuclear charge + the negative charges of the inner electrons). For example, an electron on the outskirts of an atom with three protons (3+) and two inner electrons (2−) experiences an effective nuclear charge of only 1+ because of the shielding by the inner electrons.

According to **Hund's Rule**, electrons fill orbitals singly with parallel spins before going back and completely filling the orbitals. This is because electrons seek the lowest energy state and electrons in different orbitals of the same energy are further away from each other and experience less repulsion from each other. Furthermore, electrons with parallel spins have correlated motion that minimizes their mutual repulsion.

Electrons fill orbitals starting with the general pattern

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2...$$

An atom's **valence electrons** are the electrons important to chemical bonding. For main-group elements, the valence electrons are those in the outermost principal energy level. For transition elements, we also count the outermost d electrons among the valence electrons. The valence electrons are distinguished from the **core electrons**.

The exceptions to the common way of building an electron configuration using the periodic table are Cr, Mo, Cu, Ag, and Au. Look at where these are positioned on the periodic table. Cr, for example, has an electron configuration of $[\text{Ar}]4s^1 3d^5$ instead of $[\text{Ar}]4s^2 3d^4$. This is because a half-filled d shell is more stable. Mo has a similar configuration–it's just one row further. Cu, on the other hand, has an electron configuration of $[\text{Ar}]4s^1 3d^{10}$ instead of $[\text{Ar}]4s^2 3d^9$ as predicted. This is because a fully filled d shell makes for a more stable atom than an almost-filled shell.

7.3   Periodic Properties

The **van der Waals radius** or **nonbonding atomic radius** is half the distance between the centers of two atoms that are touching. It gives the radius of the atoms. The **covalent radius** or **bonding atomic radius** is half the distance between the centers of two bonded atoms.

When it comes to the periodic table, atomic radius increases as you approach the bottom left corner. The atomic radius is largely determined by the valence electrons. As you move down a row on the periodic table, the atoms gain a principal shell–making their radius larger. As you move right across a row, however, the size shrinks slightly because the effective nuclear charge experienced by the electrons in the outermost principal energy level increases resulting in a stronger attraction between the outermost electrons and the nucleus.

Compare Li and Be for example. Li has 1 outer electron, 2 inner electrons and 3 protons. The outer electron is shielded from the 3+ charge of the nucleus by the 2- charge of the inner electrons. The outer electron, therefore, experiences an effective nuclear attraction of 1+. Be, on the other hand, has 2 outer electrons, 2 inner electrons and 4 protons. Each of the outer electrons are shielded from the nuclear charge by the same 2 inner electrons, therefore, they experience an effective nuclear charge of 2+. Since the outer electrons of Be experience a stronger attraction to the nucleus than the one outer electron in Li, Be ends up being a smaller atom. This pattern holds for all main-group electrons.

The radii of the transition elements, on the other hand, stay pretty much constant as you move right across the periodic table. This is because you're filling the d shell which is actually inside of the outermost shell. For example, the $4s$ orbital fills before the $3d$ orbital starts filling.

For anions, the additional electrons are simply added to the electron configuration. For cations, some electrons are removed. For main-group elements, the electrons are removed from cations in the reverse order that the electrons in the neutral atom is added. This isn't necessarily true for transition elements. The $4s$ orbital fills before the $3d$ orbital, but for transition metal cations, the $4s$ ones are the first to be removed.

An unpaired electron generates a magnetic field due to its spin. An atom with unpaired electrons is slightly attracted to an external magnetic field (i.e. it is **paramagnetic**). An atom with no unpaired electrons is slightly repelled from an external magnetic field (i.e. it is **diamagnetic**). Something that is diamagnetic is very slightly repelled. It is referred to as being non-magnetic.

Cations tend to be much smaller than their neutral counterparts. Anions tend to be much larger than their neutral counterparts. If in doubt, compare their electron configurations and think of effective nuclear charge and shielding. The way to remember this is that almost all of an atom's size comes from the electron "field"–more electrons (anions) means a larger atom, and less electrons (cations) means a smaller atom.

The **ionization energy** of an atom or ion is the energy required to remove an electron from the atom or ion in the gaseous state. Ionization energy tends to increase as we approach the top right of the periodic table. Relative ionization energy can often be predicted by comparing electron configurations and deducing from known behavior. We can also talk about second ionization energy and third ionization energy when referring to the energy required to remove the second and third electrons from an atom.

Electron affinity is a measure of how easily an atom will accept an additional electron. Electron affinity cannot be as easily predicted by looking at a table although it will tend to increase as we move to the right across a row. Obviously, chlorine will have a greater acceptance of an electron than sodium, for example.

The **metallic character** of the elements increases as we approach the bottom left of the periodic table.

Chapter 8

Basic Reactions and Balancing Chemical Equations

A chemical **reaction** occurs when multiple elements or compounds interact to form new compounds. The simplest kinds of reactions are synthesis, when two elements or compounds join together to form a new compound, and decomposition reactions when a compound separates into multiple compounds or elements.

A **synthesis reaction** otherwise called a **combination reaction** has the form

$$A + B \longrightarrow AB.$$

A **decomposition reaction** has the form

$$AB \longrightarrow A + B.$$
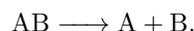
Other simple reactions include the **single displacement reaction**, which has the form

$$A + BC \longrightarrow AC + B,$$

and the **double displacement reaction**, which has the form

$$AB + CD \longrightarrow AD + CB.$$

The amount of thermal energy (heat) given off or absorbed by a chemical reaction under conditions of constant pressure can be quantified with a function called **enthalpy**. A quantity called the **enthalpy of reaction** (ΔH_{rxn}) is the amount of heat that flows when a reaction occurs under constant pressure. The enthalpy is specified in units of kJ and is negative for exothermic reactions and positive for endothermic reactions. When an equation and a measure of enthalpy are given, the said measure is for amounts of reactants where coefficients equals moles.

The **limiting reactant** is the reactant that limits the amount of product that a chemical reaction yields. The limiting reactant is the reactant that makes the *least* amount of product. The **theoretical yield** is the amount of product yielded by a 100% effective reaction. **Actual yield** is the amount of product that was actually yielded in the practice of the reaction. The **percent yield** is the portion of theoretical yield that was actually obtained. **Reactant in excess** is the reactant that is left over.

When doing stoichiometric calculations, note that molar mass, which is usually taken to be g/mol, can also be taken to be kg/kmol. In other words, it's not necessary to convert kg to g before continuing.

8.1 Balancing Chemical Equations

Chemical reactions are represented by **chemical equations**. For example, the reaction between hydrogen and oxygen gases to form water is represented by the chemical equation

$$2\,H + O \longrightarrow H_2O.$$
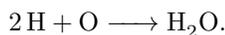
The substances on the left side of the arrow are called the **reactants** because they are the substances before the chemical reaction. The substance(s) on the right side are called the **products** since they are the results of the reaction. The arrow itself shows the direction of the reaction. In this case, the chemical equation shows that two hydrogen atoms combine with an oxygen atom to form a single molecule of water.

A key fact about chemical reactions is that they cannot create, destroy, or change elements. Therefore, in a chemical reaction, the total number of atoms of any kind of element before the reaction is exactly equal to the total number of atoms of each element after the reaction. You can see this in the chemical equation above. The total number of atoms is three—two hydrogens and one oxygen both before and after the reaction. A key part of writing chemical equations is ensuring that they are **balanced**, meaning that both sides of the arrow have the same number of each kind of element.

Example 8.1.1

Balance the chemical equation

$$HCl + Na \longrightarrow NaCl + H_2.$$
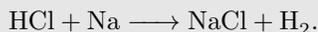
This chemical equation is clearly not balanced since there is one hydrogen atom on the left and two on the right. The first step is to list the elements and their quantity on each side. You can do this by making a table.
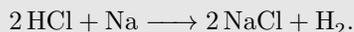
Na	1	1
Cl	1	1
H	1	2

In order for the number of hydrogens to be the same on both sides, add a coefficient of '2' in front of the HCl

$$2\,HCl + Na \longrightarrow NaCl + H_2.$$

Now, we update the table.

Na	1	1
Cl	2	1
H	2	2

Now the number of chlorine atoms don't match, so we add a coefficient of '2' on the NaCl on the right side to get

$$2\,HCl + Na \longrightarrow 2\,NaCl + H_2.$$

Now we update our table again.

Na	1	2
Cl	2	2
H	2	2

Now the number of sodium atoms no longer match, so we add a coefficient of '2' on the Na to get

$$2\,\text{HCl} + 2\,\text{Na} \longrightarrow 2\,\text{NaCl} + \text{H}_2.$$

Updating our table again, we see that each row finally matches, so the equation is balanced.

Na	2	2
Cl	2	2
H	2	2

Here are some general rules that should make it easier to balance chemical equations.

1. Only the coefficients need to be adjusted. Don't change the subscripts.
2. Leave H and O until the end
3. If an element occurs in one compound only on both sides, balance that first
4. Do metals before nonmetals
5. Do any free elements (such as diatomic gases) last
6. If any coefficients are fractional, multiply the entire equation by a factor such that all coefficients become whole numbers
7. Balance polyatomic ions as single units

Example 8.1.2

Balance the chemical equation

$$\text{CaCl}_2 + \text{AgNO}_3 \longrightarrow \text{Ca(NO}_3)_2 + \text{AgCl}.$$
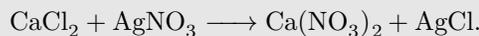
Creating a table, we get

Ca	1	1
Ag	1	1
Cl	2	1
NO_3	1	2

We see that the polyatomic ion NO_3 is not balanced, so we add a coefficient of '2' to the silver nitrate

$$\text{CaCl}_2 + 2\,\text{AgNO}_3 \longrightarrow \text{Ca(NO}_3)_2 + \text{AgCl}.$$

Next, we update our table.

Ca	1	1
Ag	2	1
Cl	2	1
NO$_3$	2	2

Now the number of chlorine and silver atoms don't match, so we also add a coefficient of '2' on the silver chloride

$$CaCl_2 + 2\,AgNO_3 \longrightarrow Ca(NO_3)_2 + 2\,AgCl.$$
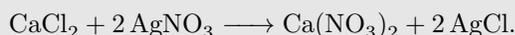
Updating our table, we see that the results match, so the equation is balanced.

Ca	1	1
Ag	2	2
Cl	2	2
NO$_3$	2	2

A **chemical equation** or **molecular equation** is a chemical equation showing the complete, neutral formulas for every chemical in the reaction. The **complete ionic equation** shows the individual ions that exist within the solution. The complete ionic equation shows the reactants and products as they actually exist in the solution. That is, as dissociated ions and undissociated molecules. The left side will show nothing but dissociated ions.

The **net ionic equation** shows only the ones that actually participate in the reaction, that is, the ones that change during the reaction. The rest of them are called **spectator ions**. When writing ionic equations, any "aq" items need to be broken into ions. Nothing else gets broken up. Remember that polyatomic ions stay intact.

Write phase designations in subscript. Use a script 'L' to designate liquid phase so it's not mistaken for a '1'.

8.2   Solutions

Homogeneous mixtures are called **solutions**. You cannot have heterogeneous solutions. **Aqueous solutions** are solutions where the solvent is water. They're important because many of the reactions pertaining to life occur in aqueous solutions (for example in our cells). The majority component is the **solvent** and the minority component is the **solute**.

A common way to express solution concentration is **molarity** which is moles solute over liters of solution. The unit for molarity is M which stands for mol/L. To make a solution of a certain molarity, add the solute to a container then add solvent until the proper volume is reached. Molarity can be used as a conversion factor between moles of solute and liters of solution.

The **solution dilution equation** is

$$M_1V_1 = M_2V_2.$$

M_1 is the molarity of the concentrated solution, and V_1 is the volume of the concentrated solution that is needed. When preparing a dilute solution, input the needed molarity and volume and the molarity of the concentrated solution and solve for V_1 which gives the volume of the concentrated solution that is needed.

Substances that dissolve in water to form solutions that conduct electricity are **electrolytes**. Those that don't are **nonelectrolytes**. Dissolved ions act as charge carriers which is why many ionic solids are electrolytes. Sugar and other molecules (with the exception of acids) dissolve whole in water rather than dissociating into ions, so they're nonelectrolytes.

When acids dissolve in water, they (despite being molecular), dissolve into ions (i.e. they ionize). Therefore, acids are electrolytes. Strong acids that completely ionize form strong electrolyte solutions and such an ionization equation is represented as

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq).$$
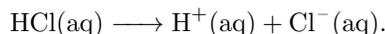
Weak acids that barely ionize and form weak electrolyte solutions are represented with double arrows

$$HC_2H_3O_2(aq) \longleftrightarrow H^+(aq) + C_2H_3O_2{}^-(aq).$$
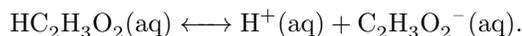
Not all ionic compounds dissolve in water. There's no easy way to tell which will and which won't. Consult solubility rules. Solubility is a continuum.

8.3   Precipitation Reactions

Precipitation reactions occur when one or more of the possible products of a reaction are insoluble.

In reality, solubility is deduced by observation. When doing these problems, check a solubility chart to see if any of the products are insoluble and will result in a precipitate. Only insoluble compounds form precipitates. If an insoluble compound can potentially form by mixing two solutions together then a precipitation reaction *will* occur.
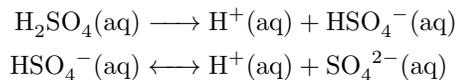
8.4   Acid-base Reactions

An **acid-base reaction** otherwise called a **neutralization reaction** can also occur in solutions. Remember that *Acid + Base = Water + Salt*. Acids form H^+ ions in solution and bases form OH^- ions in solutions.

Acids produce H^+ ions in aqueous solution and bases produce OH^- ions in aqueous solution. These definitions of acids and bases are called the **Arrhenius definitions**. In an **acid-base reaction**, these two combine to form H_2O.

An H^+ ion is a bare proton that actually combines with a water molecule to form H_3O^+ called a **hydronium ion**. Chemists use H^+ and H_3O^+ interchangeably, but it's the H^+ part of H_3O^+ that reacts with other stuff. The ionization of HCl(aq), therefore, can be represented two different ways:

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$
$$HCl(aq) + H_2O \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
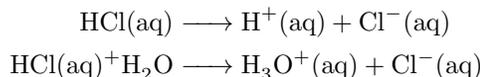
Polyprotic acids contain more than one ionizable proton and they release them sequentially. Sulfuric acid, for example, is a diprotic acid. It is a strong acid in its first ionizable proton, but weak in its second one:

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4{}^-(aq)$$
$$HSO_4{}^-(aq) \longleftrightarrow H^+(aq) + SO_4{}^{2-}(aq)$$

In analogy to diprotic acids, some bases produce 2 moles of OH^- per mole of the base.

Acid-base reactions often form water and a salt (i.e. any ionic compound). When writing the equations of acid-base reactions consider the H_2O product as being in the liquid rather than the aqueous phase.

In **titration**, a substance in a solution of known concentration is reacted with another substance in a solution of unknown concentration. **Acid-base titration** is used to measure the concentration of the substance of unknown concentration. An indicator, such as phenolphthalein, turns the end solution bright pink when the **equivalence point** is reached–that is, when the moles of H^+ ions equals the moles of OH^- ions. The concentration of one solution needs to be precisely known, and the volume carefully measured to deduce the concentration of the second substance once the equivalence point is reached.

The H_2O produced in an acid-base reaction is always considered to be in liquid phase (l).

8.5 Gas-evolution Reaction

In a **gas-evolution** reaction, two aqueous solutions mix to form a gaseous product that bubbles out of solution. Many gas-evolution reactions are also acid-base reactions. Sometimes, the gas forms right away, and sometimes an unstable intermediate product is formed first which then breaks down into gas and another substance.

Some aqueous reactions are gas evolution reactions. Many gas evolution reactions are also acid-base reactions. Some reactions produce gas directly and others form in intermediate product that quickly decomposes to form another. To show reactions for gas evolution reactions with **intermediate products**, you must simply be able to recognize the intermediate products.

When doing gas evolution reaction equations remember that some double displacement products are called **intermediate products** because they're unstable and decompose further. The two most common intermediate products are H_2SO_3 and H_2CO_3.

8.6 Combustion reactions

A combustion reaction occurs when a substance reacts with oxygen, emitting heat, and forming one or more oxygen containing compounds. It is a subcategory of oxidation-reduction reactions which includes rust.

Combustion reactions are redox reactions characterized by the reaction of a substance with gaseous oxygen to form one or more oxygen-containing compounds often including water. Compounds containing CH or CHO always form CO_2 and H_2O upon complete combustion.

Test questions may ask you to give the chemical equation of the combustion of something like CH_3NH_2. You know that by definition of it being a combustion reaction, O_2 will appear on the reactant side. All products of the combustion reaction will be gaseous. On the product side there will be CO_2 (for the C), NO_2 (for the N), and H_2O for the H. If the main reactant contains S, then one of the products will be SO_2. If the reactant contains a metal (e.g. Mg) the product will contain the metal oxide (e.g. MgO).

In **combustion analysis**, an unknown compound is burned in the presence of pure oxygen. Any H in the compound results in H_2O, and any C in the compound results in CO_2. These two substances are isolated as they are produced and are weighed. From this data, empirical formulas can be obtained from substances containing C and H.

A hydrocarbon sample with mass x is burned in a combustion analysis experiment to produce y grams of CO_2 and z grams of H_2O. Then $y + z$ will be more than x since additional O was introduced to facilitate combustion. Figure out the amount in grams

of C in the given CO_2 and the amount in grams of H in the given H_2O. Ignore the O in both since a lot of this is the O that was pumped in to facilitate combustion rather than being inherent in the sample. Now calculate the O that was originally in the sample as $x - y - z$. From here you convert the grams of CHO into moles of CHO and from there it's easy to figure out the empirical formula for the original sample.

8.7   Redox Reactions

Oxidation-reduction or **redox** reactions are reactions in which electrons transfer from one reactant to the other. Many redox reactions involve the reaction of a substance with oxygen although oxygen is not required.

Redox reactions can be identified by any of the following:
1. The reaction involves elemental oxygen.
2. A metal reacts with a nonmetal.
3. There is any transfer of electrons.

Use the mnemonic "OIL RIG", which stands for, "Oxidation Is Loss of electrons, Reduction Is Gain of electrons."

A reaction forming an ionic product involves the complete transfer of electrons. However, a transfer doesn't have to be complete in order for it to be considered a redox reaction. When a reaction forms a molecular product the covalent bond may be the partial transfer of electrons.

Identifying a redox reaction between a metal and a nonmetal is straightforward because of ion formation. It's not so straightforward for reactions between nonmetals. To figure it out, chemists use a scheme to keep track of electrons before and after reactions. A number, called an **oxidation state** is given to each atom based on the electron assignments. The oxidation state of an atom in a compound is the "charge" it would have if all shared electrons were assigned to the atom with the greatest attraction for those electrons. The electronegativity of the different elements needs to be taken into account.

Consider HCl. The covalent bond consists of 2 shared electrons. Because Cl is more electronegative than H, the shared electrons are more attracted to Cl. Now, H, which has lost its electron has an oxidation state of $+1$ and Cl has an oxidation state of -1. Do not confuse oxidation state with ionic charge. Oxidation state is merely a useful theoretical construct.

The rules for assigning oxidation states are hierarchical. If any two rules conflict, follow the rule that is higher on the list:
1. The oxidation state of an atom in a free element (e.g. Cu) is 0
2. The oxidation state of a monoatomic ion (e.g. Cl^-) is equal to its charge (e.g. -1)
3. The sum of the oxidation states of all atoms in
    a) a neutral molecule or formula is 0
    b) an ion is equal to the charge of the ion
4. In their compounds, metals have a positive oxidation state and for group 1A and 2A, the metals have oxidation states $+1$ and $+2$ respectively.
5. In their compounds, nonmetals are assigned oxidation states according to the following table ordered from most significant to least significant:
    a) $F = -1$
    b) $H = +1$
    c) $O = -2$
    d) Group 7A $= -1$
    e) Group 6A $= -2$
    f) Group 5A $= -3$

Keep in mind that the oxidation state of any given element generally depends on what other elements are present in the compound. To calculate the oxidation state of

the least significant element, use rule 3. Usually, oxidation states are positive or negative integers, but the states for an atom within a compound can be fractional. Remember that oxidation states are merely a useful construct.

Oxidation states can be used to identify redox reactions even between nonmetals. In the reaction $C + 2S \longrightarrow CS_2$, carbon goes from an oxidation state of 0 to 4 meaning it gets oxidized (electrons are added). If none of the atoms undergoes a change in oxidation state, then the reaction is not a redox reaction.

When figuring out oxidation states for each species in a reaction equation, keep in mind the difference between oxidation and reduction. Oxidation occurs when an atom loses an electron (OIL RIG) but gains in oxidation "charge". Reduction is when an atom gains an electron (OIL RIG) but is reduced in oxidation "charge".

Oxidation and reduction must occur together. A substance that causes the oxidation of another is called an **oxidizing agent**. Oxygen is a strong oxidizing agent. In a redox reaction, the oxidizing agent is always reduced.

Balancing Redox Reactions

Note that balancing redox reactions is different from balancing other reactions because there's not only a shuffling of mass, but also a shuffling of charge. When balancing redox reactions, both the mass and the charge must be balanced. When a redox reaction occurs in aqueous solution, the reaction may also involve water molecules or ions of H^+ or OH^-. The method for balancing these reactions depends on whether the solution is acidic or basic. Recall that an acidic solution will have free H^+ ions and a basic solution will have free OH^- ions.

To work through an example, we'll balance the following redox reaction: $I^-(aq) + MnO_4^-(aq) \longrightarrow I_2(aq) + MnO_2(s)$

Step 1

Assign oxidation states to each element. Follow the rules on assigning oxidation states. In our case we have $(-1) + (+7)(-2) \longrightarrow (0) + (4)(-2)$.

Step 2

Separate the reaction into two half-reactions–one for oxidation and the other for reduction. Remember that oxidation means the oxidation state has increased and reduction means that oxidation state is reduced. In our case, our oxidation half-reaction is $I^-(aq) \longrightarrow I_2(aq)$ and our reduction half-reaction is $MnO_4^-(aq) \longrightarrow MnO_2(s)$.

Step 3

Balance each half reaction with respect to mass, that is, make sure that both sides have the same number of atoms of each kind.
1. Balance all elements other than H and O
2. Balance O by adding H_2O molecules
3. Balance H by adding H^+
4. Neutralize H^+ by adding enough OH^- to neutralize each H^+. Add the same number of OH^- to each side. Note: This last step is only when the reaction is happening in a basic solution. Skip this step if the reaction is in acidic solution.
5. For acidic solutions only: Convert H^+ to H_3O^+ by adding water molecules to each side of the equation.
6. Simplify the equations by removing the same number of H_2O molecules from each side if possible.

Note that complete H_2O molecules are in liquid phase. All ions are in aqueous phase.
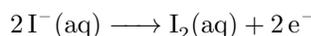
In our case, we get

$$2\,I^-(aq) \longrightarrow I_2(aq)$$

and

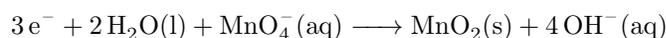$$2\,H_2O(l) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 4\,OH^-(aq)$$

Step 4

Balance each half reaction with respect to charge by adding electrons as necessary. Never try to balance by removing electrons.
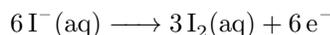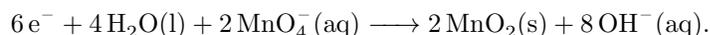
In our case we get

$$2\,I^-(aq) \longrightarrow I_2(aq) + 2\,e^-$$

and

$$3\,e^- + 2\,H_2O(l) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 4\,OH^-(aq)$$

Step 5

Make the number of electrons in both half reactions the same by multiplying the whole half reactions by smaller integers. In our case we multiply the first equation by 3 and the second equation by 2 so we have 6 electrons in both

$$6\,I^-(aq) \longrightarrow 3\,I_2(aq) + 6\,e^-$$

and

$$6\,e^- + 4\,H_2O(l) + 2\,MnO_4^-(aq) \longrightarrow 2\,MnO_2(s) + 8\,OH^-(aq).$$

Step 6

Recombine the two half reactions. Notice that the electrons should cancel out. Double check to make sure that both the mass and the charge is balanced. Remember that charges also take into account the coefficients in front of the ions. In our case, for the completed equation, we get

$$6\,I^-(aq) + 4\,H_2O(l) + 2\,MnO_4^-(aq) \longrightarrow 3\,I_2(aq) + 2\,MnO_2(s) + 8\,OH^-(aq).$$

Pay careful attention to detail while balancing–you can easily balance it wrong several times in a row just by not paying enough attention to little details. Check yourself often by counting up the number of each kind of atom and also the charges to make sure you're keeping stuff balanced as you work through it.

Chapter 9

Chemical Bonding

9.1 Lewis Theory

Without chemical bonding there would be just 91 different substances—the naturally occurring elements. Chemical bonds form because they lower the potential energy between the charged particles that compose atoms.

When two atoms are near each other, the following interactions result:

- The electrons of one atom is attracted to the nucleus of the other atom and vice versa.
- The electrons of one atom repels the electrons of the other atom.
- The nucleus of one atom repels the nucleus of the other atom.

If these interactions result in an overall net reduction of energies between the charged particles, a chemical bond forms. There are three types of chemical bonds:

- Ionic bond: This is when a metal and a nonmetal bond. We think of the electrons as having been transferred from one atom to the other.
- Covalent bonds occur between two nonmetals. We think of the electrons as being shared between the atoms.
- Metallic Bonds occur between two metals. We think of the electrons as existing in a shared sea around the atoms.

The **Lewis dot structure** for an atom is the symbol for the atom surrounded by a dot for each valence electron. Distribute the dots singly before pairing them except for helium which is represented by a single pair of electrons.

To represent an ionic compound in a Lewis dot structure write the chemical symbol for the cation with no dots (since its electrons are transferred to the anion). Show the charge of the cation. Immediately to the right, show the anion with 8 dots (because it now has a full valence shell) inside of brackets. Again, show the charge of the ion. When dealing with something like Na_2S, instead of showing the 2 in a subscript, lead with it like $2Na^+[...]^-$.

When an ionic compound forms from its constituents, the process is quite exothermic. **Lattice energy** is the energy associated with forming a crystalline (ionic) lattice of the compound from the gaseous ions. The **Born-Haber cycle** is a hypothetical series of steps that represent the formation of an ionic compound from its constituent elements. It is used to calculate lattice energies.

Coulomb's law states that potential energy of oppositely charged particles becomes less negative (more positive) as the distance between the ions increases. It also states that magnitude of the potential energy depends also on the product of the charges. For this reason, lattice energies become less exothermic (less negative) as you go down a column in the periodic table. This is because as you go down a column, the atomic radius is

increasing which means the centers of the two atoms cannot get as close to each other. Also, lattice energies become more exothermic (more negative) with increasing magnitude of ionic charge. For example, the lattice energy of CaO (+2 and -2) is much greater than the lattice energy of NaF (+1 and −1).

When doing Lewis dot structures of covalently bonded molecules, remember that a dash is used to represent a pair of bonding electrons. You can also use double and triple bonds to make sure each atom gets an octet. **Double bonds** are shorter and stronger than single bonds. **Triple bonds** are shorter and stronger yet, making triple-bonded molecules like N_2 fairly unreactive.

Ionic bonds are nondirectional and hold together an entire array of ions. In contrast, covalent bonds are directional–linking specific atoms in a single unit.

Covalent bonds are much stronger than the intermolecular forces. This is why a molecular compound tends to have a low boiling point compared to an ionic compound.

The **electronegativity** of an element is how strongly it attracts electrons. Electronegativity increases to the top right on the periodic table. When it comes to chemical bonds between atoms of different electronegativities, the shared electrons are more likely to be found closer to the more electronegative element. This creates a partial separation of charge which is depicted with $\delta+$ by the least electronegative element and $\delta-$ by the most electronegative element.

When the electrons are shared unequally like this, the bond is said to be polar. Pure covalent and ionic bonds are two extremes of a continuum with polar covalent between them. If the electronegativity difference between two elements is between 0 and 0.4, the bond is said to be a **pure covalent bond**. If the difference is between 0.4 and 2.0, the bond is said to be a **polar covalent bond**. If the difference is greater than 2.0, the bond is said to be an **ionic bond**.

The polarity of a bond can be quantified by the size of its **dipole moment**, μ. A dipole moment occurs wherever there is a separation of positive and negative charge. The dipole moment created by separating two particles of equal but opposite charges of magnitude q by a distance r is given by $\mu = qr$. The dipole moment is given in units of debye (D) where $1\,D = 2.1 \times 10^{-29}\,Cm$. The **percent ionic character** of a substance is the *measured dipole moment of the bond* divided by the *dipole moment if the electron were completely transferred* times *100*. No ionic bonds reach 100% ionic character, but a bond with greater than 50% ionic character is generally referred to as an ionic bond.

Follow these steps when writing the Lewis structures for molecular compounds:

1. Write the basic skeleton:

   - H is always terminal
   - C is usually central
   - The more electronegative are usually terminal
   - The less electronegative are usually central

2. Calculate the total electrons by summing the valence electrons of each atom in each molecule. If you're dealing with an ion, the ion charge must be accounted for. The Lewis structure for an ion is usually written within brackets with the ion's charge at the upper-right corner.
3. Distribute the electrons among the atoms, giving octets (duet for H) to as many atoms as possible. Complete octets from the outside in.
4. If any atoms lack octets, form double or triple bonds as necessary.

Note that the number of bonded electrons and free electrons of an atom can be predicted by its group:

- F = 1 bonded pair + 3 free pairs
- O = 2 bonded pairs + 2 free pairs
- N = 3 bonded pairs + 1 free pair
- C = 4 bonded pairs
- B = 3 bonded pairs

Apparently, this typical pattern is repeated down the group.

When two or more valid Lewis structures exist, this is known as **resonance**. A **resonance structure** is a Lewis structure of all valid forms equated by double-headed arrows. In nature, such molecules exist as averaged hybrids.

Sometimes, when multiple resonance structures exist, nature tends to favor one over the others. Although, in nature, the actual molecule will still be a hybrid, it will exist more like the favored one than the others. **Formal charge** is a fictitious charge assigned to each atom in a Lewis structure to help identify the favored Lewis structure. The formal charge of each atom is calculated as the number of valence electrons for the atom minus, the number of electrons it actually owns (i.e. nonbonding electrons $+\frac{1}{2}$ of the bonding electrons). When dealing with formal charge, the following rules apply:

1. The sum of all formal charges must equal the charge of the overall molecule/ion.
2. Small or zero charges are better than large ones. Minimize charge by expanding the octets of 3rd row or greater central elements.
3. When formal charge cannot be avoided, negative formal charge should reside on the most electronegative atom (should be a terminal atom).

The octet rule has several exceptions including

- **Odd-electron species** are molecules/ions with an odd number of electrons around an atom. These are called **free radicals**. Example is NO. Relatively few free radicals exist and they tend to be unstable and reactive.
- **Incomplete octets** are molecules/ions with less than 8 electrons around an atom. Boron is the most important example of this–it is fine with 6 electrons. Use formal charge to figure out the favored structure. Be is another example–it frequently forms 2 bonds with no lone pairs.
- **Expanded octets** are molecules/ions with more than 8 electrons around an atom. Elements in the third row and beyond can have expanded octets. Use formal charge to determine whether nature will favor an expanded octet. Never expand the octets of second row elements because these lack energetically-accessible d orbitals.

The **bond energy** of a chemical bond is the energy required to break 1 mole of the bond in the gas phase. In general, compounds with stronger bonds tend to be more stable and less reactive. The bond energy of say a bond between C and N varies depending on the other atoms and bonds of the molecule. The **average bond energy** would be an average C–N bond energy is calculated in a large number of different compounds.

We can use average bond energies to estimate the **enthalpy** (energy) change of a reaction the following way: *Enthalpy = the sum of the average bond energies of the bonds broken (positive) + the sum of the average bond energies for bonds formed (negative)*. Remember that the energy associated with bonds broken is positive (endothermic: requires energy input) and the energy associated with bonds formed is negative (exothermic: outputs energy).

From the above we can deduce that a reaction is exothermic when weak bonds break and strong bonds form, and it is endothermic when strong bonds break and weak bonds form. The breaking of chemical bonds does not ever release energy–it is the formation of strong bonds after weak bonds have been broken that releases energy.

In a piece of metal, each metal atom donates one or more electrons to a sea of shared electrons. The movement or flow of these electrons in response to an electric potential (voltage) is an electric current.

9.2 VSEPR Theory

Lewis theory along with the idea that electron groups repel one another (**VSEPR theory**) allows us to predict the general shape of a molecule from its Lewis structure. VSEPR stands for **valence shell electron repulsion**, and the basic idea is that the shape of a

molecule is determined by the fact that the electron groups (bonding pair, double bonding pair, triple bonding pair, free pairs, and single electrons in some cases) repel each other to the highest degree possible.

When visualizing the shape of molecules imagine each electron group being represented by balloons of equal size that are as close to each other as possible. The point where the balloons all come together is the point where the central atom is located. Therefore, for a molecule with one central atom containing 4 electron groups, the "balloons" will be arranged in a tetrahedron. Note that the terminal atoms will be on the ends of the balloons (opposite the central atom).

Note that a double bond has slightly higher electron density than a single bond or a lone pair. As such, a double bond will repel single bonds a little more strongly than single bonds will repel each other. With our analogy, for double bonds we can imagine that balloon being slightly larger than the others. However, if the terminal atoms are all the same, then the bond angles stay the same even if there's a double and two singles. This is because the double bond can resonate around the central atom.

Here are the number of electron groups of central atoms along with the shape of the molecule:

- 2 = linear
- 3 = trigonal planar
- 4 = tetrahedral
- 5 = trigonal bipyramidal (two tetrahedrons joined at the base) (3 terminal atoms in one plane and the other two on an axis. The angle between equatorial atoms is 120 degrees whilst the angle between axial and equatorial atoms is 90 degrees)
- 6 = octahedral (4 terminal atoms in one plane and the other 2 on an axis. The angles between all atoms are the same.)

Note that lone pairs are also included in the electron groups that repel and are repelled even though they don't contribute directly to the shape of a molecule by way of an attached atom. Lone pairs have slightly greater repelling power because they're more spread out around the atom whilst bonded pairs are more restricted in space by their attraction to two different atoms. Note also that the more lone pairs, the more that the angles between bonded pairs are compressed.

Returning to our analogy, think of lone pairs as slightly larger but invisible (or transparent) balloons.

When judging where lone pairs will occur around atoms with 5 or 6 electron groups, keep in mind that since the lone pairs repel more (are bigger), they will tend to occupy the places where they can be furthest from other electron groups–especially other lone pairs.

5 electron groups: A single lone pair will be one of the equatorial groups in order to minimize the number of 90 degree interactions with other groups. The resulting molecular shape is called a **seesaw**. Two lone pairs will both occupy equatorial positions to minimize interactions with other groups–especially each other. The resulting molecule is **T-shaped**. Three lone pairs will all occupy equatorial positions. The resulting shape is **linear**.

6 electron groups: Since all angles are the same, a single pair can take any position. The resulting molecular shape is **square pyramidal**. Two lone pairs occupy opposite positions to minimize interactions with each other. The resulting shape is **square planar**.

To represent 3D molecule shapes on paper, use the following convention:

- Plane of the paper = bond is a solid line
- Below the paper = bond is a hatched wedge pointed away from center
- Above the paper = bond is a solid wedge pointed toward center

To predict the shape of larger molecules, the rules of VSEPR theory must be applied to every central atom.

Molecules can be polar just as bonds can be. Use the following steps to determine the **polarity** of molecules:

1. If a molecule contains no polar bonds (no atoms bonded to each other have a large electronegativity difference, then the molecule is not polar. Otherwise, the molecule may be polar.
2. If the molecular shape and the strength of the polarities of the bonds cancel each other, the molecule is nonpolar. Otherwise, it is polar.

Calculating polarity, then, is simply a matter of deduction and visualizing the geometry. To do it mathematically, do it by adding vectors. Each bond has a specific direction (dependent on the molecular geometry) and a specific magnitude (the dipole moment or electronegativity difference). If adding the vectors results in a net dipole vector of zero, the molecule is nonpolar. Otherwise, it is polar. Note that polyatomic ions are automatically considered polar.

9.3   Valence Bond Theory

Valence bond theory is a more advanced theory that can tell us the shape of molecules. This theory is more complex and more accurate in predicting shapes. This is a more quantum-mechanical treatment of the subject.

Previously, we developed the general idea that two atoms will bond and share electrons in order to reach the stability afforded by a noble gas configuration. In valence bond theory, the general idea is that two atoms will bond if the result has lower potential energy, and that this tendency to bond is driven by half-filled electron orbitals becoming completely filled.

When two atoms with half-filled orbitals approach each other, the half-filled orbitals overlap and the electrons occupying them align with opposite spins resulting in a net energy stabilization that constitutes a covalent bond. Sometimes, a completely filled orbital of one atom will overlap with an empty orbital from another atom in a similar manner–creating a coordinate covalent bond. The shape of the molecule, then, is determined by the geometry of the overlapping orbitals.

We know the shapes of orbitals for lone atoms–the s orbital is spherical, the p orbitals are dumb bells, the d orbitals are even more funky. However, when atoms bond, their orbitals don't necessarily maintain their original shapes. In many cases (especially for interior atoms), the orbitals will **hybridize** and join together in a way that makes room for more bonds. Hybrid orbitals are still localized on individual atoms, but they have different shapes and energies from those of standard atomic orbitals. Hybrid orbitals minimize the energy of the molecule by maximizing the orbital overlap in a bond.

Here are some general things about hybridization:

- The number of standard atomic orbitals added together always equals the number of hybrid orbitals that are formed—the number of orbitals is conserved.
- The particular combinations of standard atomic orbitals added together determines the shapes and energies of the hybrid orbitals formed.
- The particular type of hybridization that occurs is the one that yields the lowest overall energy for the molecule.

Note that we're only concerned with the valence orbitals.

When doing hybridization schemes for carbon, think of it this way:

1. Carbon starts off with 2s2, 2p2. Two of the p-orbitals are half-filled, but it needs more half-filled orbitals in order to make more bonds.
2. The first thing that happens is that one of the electrons in the s orbital is excited and promoted to a p orbital. Now, C has 4 half-filled orbitals, but they're not the same energy.

3. Next the orbitals hybridize to become sp orbitals with 0 or more leftover unhybridized p orbitals that'll make pi bonds. Whenever your Lewis structure contains a double or triple bond, reserve one or more of the half-filled p-orbitals before hybridizing the rest into sp2 orbitals.

4. Note 3rd row elements have empty d-shells and any paired electrons in the s and p orbitals can be excited so that one of each goes into a d orbital to make room for more bonds.

5. Whenever there's a formal charge on the central atom that you're working with, you need to take that into account. If the atom has a formal charge of −1, then bring in 1 more electron. This is crucial because it may mean that a lower electron doesn't have to be excited.

Pi and Sigma Bonds:

There are two types of bonds. The sigma bond occurs when two orbitals overlap end to end. All single bonds are sigma bonds. Two atoms can be joined with no more than one sigma bond. The pi bond occurs when two orbitals overlap side-by-side. The result is a funky-looking looking double-horseshoe orbital. A double bond is one sigma bond and one pi bond. A triple bond is 1 sigma bond and 2 pi bonds. A single bond allows two bonded atoms to rotate relative to one another. A double or triple bond doesn't. An **isomer** is a different construction of the same molecule due to the rotations that are possible about single bonds. The pi bond comes from a pair of half-filled unhybridized p orbitals on adjacent atoms.

Remember that H cannot hybridize because it contains only a single orbital.

Use the following procedure to figure out hybridization schemes for specific a atom in a molecule:

1. Draw the Lewis structure making sure to minimize charge by thinking in terms of formal charge and expanded octets.

2. Write out the valence electron diagram for the atom. If the atom has a formal charge, you must take that into consideration. For example, if the atom has a formal charge of −1, then 1 additional electron is brought in when writing the valence electron diagram.

3. Checking the Lewis structure, determine the number of bonds that are needed. Remember that every bond needs a half-filled orbital. To create the right number of half-filled orbitals, electrons from the *s* valence shell need to be *excited* to higher shells. If you already have the right number of half-filled orbitals, then there's no need to excite. Any unneeded completely filled orbitals will appear on the Lewis structure as lone pairs of electrons.

4. Once you have the right number of half-filled orbitals, look again at the Lewis structure and determine the number of pi bonds. Remember that sigma bonds form between hybridized orbitals and pi bonds form between unhybridized p-orbitals. Note that the second bond in a double bond and the second and third bonds in a triple bond are all pi bonds. Reserve (set aside) a half-filled p-orbital for every pi bond. Now you should be left with a number of half-filled orbitals that equals the number of sigma bonds. Note that lone pairs are still hybridized in our scheme–they just happen to be completely filled orbitals when we're all done. If the atom has more than 8 electrons around it (i.e. it has an expanded octet) then electrons from the s and/or p orbitals must be excited into the d-orbital to make enough half-filled orbitals for all the bonds.

5. Before the bonds can form, the orbitals must be of equal energy–they must be hybridized. Combine all the non-reserved orbitals into hybrid orbitals. Note how many of each type of orbital were hybridized so you can write the hybridization scheme.

6. Show the valence bond theory diagram as an electron diagram. Don't forget to

show any p-orbitals (for pi bonds) at a slightly higher energy. Also prepend the row
number to both the p and hybridized orbitals.
As a double check on the hybridization scheme... the number of bonds

9.4   Molecular Orbital Theory

VSEPR theory treats electron orbitals as being unchanged and belonging to the original
atom. Valence bond theory treats orbitals as belonging to the original atoms but adjusting
their shapes and charges when bonding to other atoms. **Molecular orbital theory
(MO)** treats orbitals as being part of the whole molecule–rather than localized on the
original atoms. In MO, electrons are **delocalized** over the entire molecule.

In MO, the molecular orbitals are the result of trying various estimations in the
Schrodinger equation. The simplest trial functions turn out to be **linear combinations
of atomic orbitals**. An LCAO is analogous to a weighted average of the valence orbitals
of the atoms in the molecule.

MO can be used to predict which atoms will bond—which molecules are possible.

When two atoms are put together, their atomic orbitals are combined and restruc-
tured into **molecular orbitals**. When 2 atomic orbitals are combined, they form 2
molecular orbitals. One of the molecular orbitals is lower in energy than either of the
two atomic orbitals. The electrons from the atomic orbitals will "want" to go into this
lower energy orbital, and so a chemical bond is created. This molecular orbital is called a
bonding orbital. The other orbital that is formed is of a higher energy than the original
atomic orbital, and so it is called an **antibonding orbital**. The reason that the two are
so different is because the first is created from **constructive interference** and the other
is created from **destructive interference**. This is because atomic orbitals are actually
wave functions.

Electrons in bonding molecular orbitals are stabilizing. Electrons in antibonding
molecular orbitals are destabilizing. Fortunately for chemistry, the bonding orbitals are
lower in energy and so they're the first to be filled.

A molecular orbital diagram can be used to determine if two atoms will bond or not.
As long as the two atoms can lower their net energy by having their electrons go into
lower energy molecular orbitals, the two atoms will bond.

For our purpose, we will use only one diagram–in reality there are multiple ones
depending on which elements we are considering. Following is the procedure for doing
molecular orbital diagrams:

1. Write the molecular orbital diagram worrying only about the valence s and p or-
   bitals. Be sure to show the incoming valence electrons and account for any additional
   or missing electrons due to ionization of the molecule being considered. It really
   doesn't matter from which side the electron is added or removed. Be sure to add
   asterisks to show which orbitals are antibonding. The diagram we use for the p
   orbitals gives molecular orbitals ordered from bottom to top as 1, 2, 2, 1.
2. Fill the molecular orbitals with the available electrons. Start filling at the bottom
   of the diagram and fill the orbitals in a row singly first and then pair them up.
3. Determine if there is a bond.
4. Determine the **bond order**. This is *the number of bonding electrons minus the
   number of antibonding electrons, all over 2* (the 2 is because of the fact that there
   are 2 electrons in a bond). The higher the bond order, the shorter and stronger the
   bond is. There may be fractions.
5. Determine the type of bond:

   - 0 = no bond
   - 1 = single-type bond
   - 2 = double-type bond
   - 3 = triple-type bond

6. Determine if the molecule will be **paramagnetic** or not. It will be paramagnetic if there are unpaired electrons in the molecular orbitals.

Much like survival is the driver of biological evolution, stability is the driver of chemical evolution. Particles seek to achieve the lowest energy states given their individual characteristics.

Chapter 10

Gases

Pressure is the force exerted per unit area by gas molecules as they strike a surface.

$$P = \frac{F}{A}$$

Here are some units of pressure and conversions:

$$1\,\text{Pa} = 1\,\text{N/m}^2$$
$$1\,\text{atm} = 101.325\,\text{Pa} = 760\,\text{mmHg} = 760\,\text{torr} = 29.92\,\text{in Hg} = 14.7\,\text{psi}$$

The Pascal (Pa) is the SI unit. One atmosphere is the average atmospheric pressure at sea level.

The pressure of a gas sample in a laboratory can be measured by a **manometer**. This is a U-shaped tube containing mercury. The one end of the tube is open (atmospheric pressure is exerted on it), and the other end is connected to the sample of gas. The difference in the height of the mercury (before and after the gas being measured is connected) gives the pressure of the gas relative to atmospheric pressure. As such, to calculate the absolute pressure of the sample, you also need a barometer to measure the atmospheric pressure.

Boyle's law states that the volume of a gas and its pressure are inversely proportional

$$V \propto \frac{1}{P} \implies P_1V_1 = P_2V_2.$$

In other words, if the volume of a gas is increased, and the other factors are held steady, then the pressure of the gas will drop.

If pressure and amount of a gas is held constant, **Charles' law** states that the volume of a gas and its Kelvin temperature are directly proportional

$$V \propto T \implies \frac{V_1}{T_1} = \frac{V_2}{T_2}.$$

In other words, if the temperature of a gas is increased, its volume will also increase. Note that temperature must be measured in Kelvin.

The **combined gas law** combines the laws of Boyle and Charles to give us

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}.$$

Use this law, when possible, as it's a lot faster than applying the ideal gas law twice.

Avogadro's law states that the volume of a gas and the amount of gas in moles (n) are directly proportional

$$V \propto n \implies \frac{V_1}{n_1} = \frac{V_2}{n_2}.$$

Ideal gas law combines everything but must include a proportionality constant (R).

$$PV = nRT,$$

where $R = 0.082\,06\,\text{L} * \text{atm/mol} * \text{K}$ is the **ideal gas constant**—a constant of proportionality. In order to use the ideal gas law the units must be atm, L, mol, and K. The ideal gas law works only for ideal gases—not for high pressure or low temperature situations.

Standard temperature and pressure (STP) are at $0\,\text{C}°$ ($273.15\,\text{K}$) and $1.00\,\text{atm}$. The volume occupied by 1 mol of a substance is its **molar volume**. The molar volume of any ideal gas at STP is $22.4\,\text{L}$. This can easily be calculated from the ideal gas law by solving for volume.

The density of a gas at STP is given by

$$\text{density} = \frac{\text{molar mass}}{\text{molar volume}} = \frac{\text{molar mass}}{22.4\,\text{L}}.$$

Density for gases is given in g/L instead of the standard g/mL because of their low density. The density of a gas is directly proportional to its molar mass. The greater the molar mass, the more dense the gas. A gas with a molar mass less than air will rise in air. The average molar mass of air is 28.8 g/mol. The density of a gas in any condition is given by

$$d = \frac{PM}{RT},$$

where M is the molar mass in g/mol. Gases always become homogeneous–not heterogeneous.

The pressure due to any individual component in a gas mixture is called the **partial pressure** of that component. Partial pressure equals the fractional contribution of the component times the total pressure. **Dalton's law of partial pressures** states that the sum of partial pressures equals the total pressure. The moles of a component divided by the moles of the total mixture is called the **mole fraction**. The partial pressure of a component can be calculated as follows:

$$P_a = X_a P_{total}$$

In words, the partial pressure of the component equals its mole fraction times the total pressure of the mixture.

If a combination chemical reaction between gases occurs, the total number of gaseous particles decreases (because they have combined). This means a reduction in pressure/volume.

When the desired product of a chemical reaction is a gas, the gas is often collected by the displacement of water. However, gas collected this way is not pure–it's a mixture of the gas and of gaseous water. The partial pressure of the water in the mixture is called its **vapor pressure**, which is a function of temperature (the higher the temperature, the more that water evaporates, and the higher its partial (or vapor) pressure. The partial pressure of the desired gas in the mixture is the total pressure minus the vapor pressure of water at that temperature.

The simplest model for the behavior of gases is **kinetic molecular theory**. This model implies the ideal gas law. Its basic assumptions are as follows:

1. The size of a particle is negligibly small.
2. The average kinetic energy (*not velocity: that is dependent on the mass of the particle*) of a particle is proportional to the temperature in Kelvins.
3. The collision of particles is completely elastic (like billiard balls).

According to **kinetic molecular theory**, gas particles are far apart which allows for compressibility.

In a gas at a given temperature, lighter particles travel faster (on average) than heavier ones. The **root mean square velocity** of a collection of particles is not identical

to the average velocity, but it's close enough that we can use it. The RMS velocity depends on temperature and the mass of the particles. The root mean square velocity is calculated as:

$$u_{rms} = \sqrt{\frac{3RT}{MM}} \qquad R = 8.314 \frac{J}{mol \cdot K}$$

In the case above, MM is the molar mass in **kg/mol** of the particle and R is related to the gas constant, but it's not the same.

The average distance a particle travels between collisions is its **mean free path**. The process by which gas molecules spread out in response to a concentration gradient is called **diffusion**. RMS affects the rate of diffusion. The heavier the molecules, the slower the diffusion. **Effusion** is the process by which gas escapes from a container into a vacuum by way of a small hole. Effusion rate is inversely proportional to the square root of the molar mass of the gas and the ratio of effusion of two different gases is given by **Graham's law of effusion**

$$\frac{rate_A}{rate_B} = \sqrt{\frac{M_B}{M_A}}.$$

Keep in mind that rate is distance/time so if you're just given the times of effusion instead of the rates, then you have to flip the left side of the equation. Effusion can be used to separate gases provided that their molar masses differ enough. Multiple effusions can be used to separate gases with similar masses.

Real gases under nonstandard conditions don't always act exactly like ideal gases:

1. At high pressures the physical sizes of the particles contribute more to the overall volume than they do at low pressures. At high pressures then, the overall volume is slightly greater than that of an ideal gas.
2. At high pressures and low temperatures (particles are closer or moving slower), the miniscule effect of intermolecular forces becomes amplified, and collisions become less elastic resulting in a lower pressure than for an ideal gas.

The **Van der Waals equation** is an equation that describes the behavior of gas under non-ideal conditions. It's like the ideal gas law for non-ideal conditions

$$\left[P + a\left(\frac{n}{V}\right)^2\right] \cdot [V - nb] = nRT$$

In the equation, the first part contains a correction for intermolecular forces and the second part of the left side contains a correction for particle volume. The a and b are constants that depend on the particular gas.

Instead of approaching some of these problems in a procedural manner (remembering and applying the proper equations), learn how to deduce them from the ideal gas law. You can build an equation relating initial conditions to final conditions by identifying and removing the pieces that remain constant. For example, if your volume and moles are changing, but everything else is constant, you can build an equation starting with the ideal gas law:

The first step is to isolate the constants on one side of the equation. The right side of the last equation below will remain constant as the two variables on the left side of the last equation change relative to each other.

$$PV = nRT \implies \frac{V}{n} = \left(\frac{RT}{P}\right)$$

$$\frac{V}{n} = k$$

Because we've specified that the right side is constant from the initial to the final state of the system, we can use the following:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}.$$

Chapter 11

Energy and Thermochemistry

Energy is the capacity to do **work**, which is the result of a force acting over a distance. Energy is something that an object or set of objects possesses, and heat and work are ways that objects or sets of objects exchange energy. The **law of conservation of energy** states that energy is neither created nor destroyed. **Kinetic energy** is the energy associated with matter's motion. **Potential energy** is the energy associated with matter's position or composition. **Electrical energy** is associated with the flow of electrical charge. **Thermal energy** is associated with the random motions of atoms and molecules. **Chemical energy** is a form of potential energy associated with the positions of the particles that compose the chemical system.

Energy is exchanged between a system and its surroundings (i.e everything else in the universe) via heat and work. Because of the conservation of energy the energy lost by a system exactly equals the energy gained by its surroundings and vice versa. The **internal energy** of a system is the sum of the kinetic and potential energies of all the particles that compose the system. Internal energy is a state function which means it depends only on the state of the system, not on how the system achieved that state. The internal energy change ($\triangle E$) is the difference between the final and initial states:

$$\triangle E = E_{final} - E_{initial}$$

Notice that in a chemical system, the reactants are the initial state and the products are the final state.

Kinetic energy is given as

$$K_E = \frac{1}{2}mv^2.$$

From this equation, the units of energy can be derived. Since the SI unit for mass is kg, and the SI unit for velocity is m/s, then the unit for energy is $\text{kg} \cdot \text{m}^2/\text{s}^2$ or joule.

The SI unit for energy is the joule (J). A calorie (cal) is the energy required to heat 1 gram of water by $1\,\text{C}°$. A Calorie (Cal) is the nutritional measure and it is equal to 1000 calories. Notice that the latter is given in uppercase.

$$1\,\text{cal} = 4.184\,\text{J}$$
$$1\,\text{Cal} = 1000\,\text{cal} = 1\,\text{kcal}$$
$$1\,\text{kWh} = 3.60 \times 10^{66}\,\text{J}$$
$$1\,\text{W} = 1\,\text{J/s}$$

In an **exothermic reaction**, energy is released in the form of heat. In an **endothermic reaction**, energy is absorbed in the form of heat. The reverse of an exothermic reaction must be endothermic.

When a system transfers energy to its surroundings by performing work on its surroundings or by heating up its surroundings, the energy change of the system is negative–

the change was exothermic. When the surroundings transfer energy to the system by performing work on the system or by heating up the system, the energy change is positive–the change was endothermic.

Since a system can exchange energy with its surroundings through heat and work, the change in internal energy is given by

$$\Delta E = q + w,$$

where q is the heat transferred and w is the work done. Remember that energy entering the system carries a positive sign and energy leaving the system carries a negative sign.

While internal energy is a state function, heat and work are not. For example, the very same system that achieves the very same change in internal energy could have two different sets of values for q and w depending on the nature of the surroundings.

When asked to determine the sign of energy, figure out whether the energy is being done on the surroundings by the system (negative) or being done on the system by the surroundings (positive).

Heat is the exchange of thermal energy between a system and its surroundings caused by a temperature difference. **Temperature** is a *measure* of thermal energy and heat is the *transfer* of thermal energy. In our universe thermal energy always flows from matter at higher energies to matter at lower energies. To convert between the Celsius and Fahrenheit temperature scales, use

$$^\circ C = \frac{^\circ F - 32}{1.8}.$$

The degree symbol is not used with the Kelvin scale.

The heat absorbed by a system and its corresponding temperature change are directly proportional. The constant of proportionality is the system's **heat capacity**, C, which is a measure of the system's ability to absorb thermal energy without undergoing a large change in temperature.

$$q = C\Delta T$$

The smaller the heat capacity, the greater the change in temperature for a given amount of heat. The heat capacity of a system is defined as the quantity of heat required to change its temperature by $1\,^\circ$C. The units of heat capacity are J/$^\circ$C. Heat capacity is an extensive property–it depends on the amount of matter being heated and the matter's resistance to temperature change.

Specific heat capacity brings the amount of matter into the equation, so it's purely a measure of the matter's resistance to temperature change rather than also the amount of matter. It is the amount of heat required to raise 1 gram of a substance by $1\,^\circ$C. The units of specific heat capacity are J/g$^\circ$C. The specific heat capacity can be used to quantify the relationship between heat and temperature change

$$q = mC_s\triangle T.$$

Molar heat capacity is the amount of heat required to raise 1 mole of a substance by $1\,^\circ$C. Its units are J/mol$^\circ$C.

When two substances are combined, thermal energy flows from the hotter substance to the cooler substance until thermal equilibrium is achieved. The energy lost by one exactly equals the energy gained by the other. The exact temperature change that occurs depends on the masses and specific heat capacities of the substances. Solve the equation

$$m_1 C_{s1}[T_f - T_{i,1}] = -(m_2 C_{s2}[T_f - T_{i,2}]),$$

for the final temperature.

A chemical reaction can do several types of work, but we'll consider only the work related to volume expansion. This is **pressure-volume work**. For example, any chemical

reaction that produces gases will produce pressure-volume work because the evolved gases will exert a pressure on the reaction's surroundings. The energy for this work comes from the potential energy of the reactants. The amount of work produced is the negative of the pressure that the volume expands against times the change in volume that occurs during the expansion

$$w = -P\Delta V.$$

To convert between L*atm and J, use the conversion factor $101.3\,\text{J} = 1\,\text{L} \times \text{atm}$.

The change in internal energy is the sum of all the energy (heat and work) that is exchanged with the surroundings. With our equations for q and w, we can calculate the total internal energy change for a chemical reaction. However, an easier way is to force all of the energy to manifest as heat (by forcing the volume to stay constant) and then just measure the temperature change. This is the purpose of the bomb calorimeter. In a bomb calorimeter, the energy put out by the reaction is exactly equal (but opposite in sign) to the energy taken in by the entire calorimeter assembly, which is measured by the specific heat of the calorimeter assembly and the temperature change of the calorimeter assembly. Note that the heat capacity of the calorimeter takes into account all of the heat absorbed by all of the components within the calorimeter including the water. When calculating the ΔE for a reaction taking place in a bomb calorimeter, use the equation

$$q_{calorimeter} = C_{cal}\Delta T = -\Delta E_{reaction}.$$

If the substance amount is given in grams, be sure to convert it to moles at the end.

The **enthalpy**, H, of a system is the sum of its internal energy and the product of its pressure and volume. The change in enthalpy for any process occurring under constant pressure is given by

$$\Delta H = \Delta E + P\Delta V = q_p,$$

where q_p is the heat at constant pressure.

ΔH and ΔE are similar both conceptually and numerically. ΔE is the change in total energy and ΔH is the change in heat at constant pressure. For chemical reactions that do not exchange much work, that is, they don't cause a large change in reaction volume as they occur, the two are close to each other. However, for reactions that produce or consume large amounts of gas, there is a difference.

The **enthalpy of reaction** or **heat of reaction**, ΔH_{rxn}, is the heat emitted or absorbed by a chemical reaction. The enthalpy of reaction is specific to a reaction. That is, if you're given an enthalpy of reaction you should also be given the associated chemical reaction equation. For example, given the equation and enthalpy of reaction

$$X + Y = XY \qquad \Delta H_{rxn} = 10\,\text{kJ},$$

we can see that 10 kJ of heat is absorbed in the reaction of 1 mole of X with 1 mole of Y. The magnitude of the enthalpy of reaction depends on the quantity of material. Knowing this relationship between ΔH_{rxn} and moles allows us to calculate the heat emitted/absorbed for the same reaction with different quantities of reactants. Note that "rxn" stands for "reaction".

A **coffee cup calorimeter** can be used to measure the ΔH_{rxn} of many aqueous reactions. If we know the specific heat capacity of a solution, normally assumed to be that of water, we can calculate the heat lost or absorbed by the solution using

$$q_{soln} = m_{soln} * C_{s,soln}\Delta T.$$

Since the insulated calorimeter keeps heat from escaping we can assume that the heat gained by the solution equals the heat lost by the reaction

$$q_{soln} = -q_{rxn}.$$

Since the reaction happens under constant pressure, we have that

$$q_{rxn} = q_p = \triangle H_{rxn}.$$

Putting it all together, to calculate the ΔH for a reaction occurring at a constant pressure (i.e. coffee cup calorimeter) use

$$\Delta H_{rxn} = q_{constant\,pressure}$$
$$= -q_{soln}$$
$$= -m_{soln}C_{s,soln}\Delta T.$$

The $C_{s,soln}$ if occurring in water is usually assumed to be that of water, which is $4.184\,\mathrm{kJ/gC}$. The mass of solution is the mass of water (remember the density of water is 1 g/mL) plus the mass of the solute. You might have to convert from kJ for entire reaction to kJ/mol in the end.

The change in enthalpy for a reaction is always associated with a particular reaction. If we change the reaction in well-defined ways then ΔH_{rxn} also changes in well-defined ways:

1. If a chemical equation is multiplied by some factor, then ΔH_{rxn} is also multiplied by the same factor.
2. If a chemical equation is reversed, then ΔH_{rxn} changes sign.
3. If a chemical equation can be expressed as the sum of a series of steps, then ΔH_{rxn} for the overall equation is the sum of the heats of reactions for each step. This is known as **Hess's law**.

Hess's law allows us to determine ΔH_{rxn} for a reaction without directly measuring it provided that we can find related reactions that sum to the reaction of interest. To cancel terms they must be equal and on opposite sides of the reaction arrow. Also, keep in mind that the liquid form of a substance won't directly cancel the gaseous form of the substance.

Calorimetry allows us to experimentally measure ΔH_{rxn}. Hess's law allows us to infer ΔH_{rxn}. A third way is to use a table of **standard enthalpies of formation**. The standard enthalpy of formation corresponds to the formation of a compound from its constituent elements in their standard states. Standard enthalpy of reaction comes from three concepts:

1. Standard State

   - Gases: Pure gas at 1 atm
   - Liquids and Solids: Pure substance in its most stable form at 1 atm and at the temperature of interest (usually 25 C).
   - Substance in Solution: Concentration of exactly 1 M.

2. Standard Enthalpy of Change

   - The change in enthalpy for a process when all reactants and products are in their standard states.

3. Standard Enthalpy of Formation

   - For a pure compound this is the change in enthalpy when 1 mole of the compound is formed from its constituent elements
   - For a pure element in its standard state, the standard enthalpy of formation is taken to be 0

The negative of the standard enthalpy of formation corresponds to the decomposition of the compound.

Calculating Standard Enthalpy Change of Reaction To calculate the standard enthalpy change of reaction

1. Decompose the reactants into their constituent elements in their standard states.

2. Form the products from the constituent elements in their standard states.

3. Use Hess's law to calculate the standard enthalpy of change for the overall reaction.

To calculate the enthalpy of reaction when given the enthalpy of formation for each product and reactant, simply replace each term with its enthalpy of formation, and sum each side. Then cancel the equivalent from each side so the reactant side is left with nothing. What's on the product side will be the enthalpy for the reaction.

When writing **formation reactions** you must provide the standard states for the reactants, and some must be specific. For example, the standard state of carbon is not just *solid* but solid and *graphite*. Also, formation reaction equations must give a1 mole of product even if that means having fractional coefficients on the other stuff.

Essentially there are four ways to figure out the ΔH for a reaction:

- Constant pressure calorimetry
- Hess's law
- Standard enthalpies of formation
- Bond energies

The last one we haven't looked at yet. Recall that **bond energy** is the energy required to break the bonds of 1 mole of a compound. The ΔH of a reaction can be calculated by comparing the cost of breaking old bonds to the profit from making new bonds. Use a of average bond energies. Remember that bond breaking is endothermic—it has a positive ΔH and bond making is exothermic–it has a negative ΔH. This method is not as accurate as the other methods, but it gives us a good idea. First, we need to make Lewis structures to enumerate the bonds and then check a table for those bond energies before plugging it all into the equation

$$\Delta H_{rxn} = \sum \Delta H_{bonds\,broken} - \sum \Delta H_{bonds\,formed}.$$

Chapter 12

Liquids, Solids, and Intermolecular Forces

Solids and liquids are known as *condensed states* of matter. In gases, intermolecular forces are negligible. Not so in liquids and solids. The strength of **intermolecular forces** determines the phase of a sample of matter at a given temperature. The densities of solids are usually just slightly greater than those of the corresponding liquids. Water and ice are a rare exception. Ice is less dense than water which is why ice floats.

Kinetic molecular theory has been extended from gases to include liquids and solids.

Atoms and molecules have three degrees of freedom:

1. Translational (gases, liquids to a limited extent)
2. Rotational (gases, liquids to a limited extent)
3. Vibrational: (gases, liquids, solids)

The more kinetic energy (i.e. the higher the temperature), the more motion.

12.1   Intermolecular Forces

Intermolecular forces are attractive forces between *molecules*. For example, water is a highly polar molecule, and so the positively charged end of one water molecule is attracted to the negative end of another. This is called **hydrogen bonding**. It is an intermolecular force, as opposed to an interatomic force, since the attraction is between molecules instead of atoms. Intermolecular forces are much weaker than covalent bonds. In the image below, the hydrogen bond between the two water molecules is much weaker than the covalent bonds between the two hydrogens and the oxygen in a water molecule.
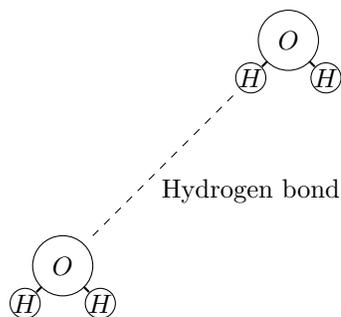
Without intermolecular forces all matter would be gaseous. They are generally much weaker than the bonding forces of atoms. They are significant only at close distances–as in liquids and solids, but not in gases. Most solids are slightly more dense than their liquid phases. Water is an exception. To change the state of a sample of matter we can apply or remove heat. The transition between liquid and gas can also be done by

decreasing the pressure (liquid turns to gas) or by increasing the pressure (gas turns to liquid).

The strength of intermolecular forces determines the state (solid, liquid, or gas) of a substance at room temperature. At room temperature, moderate to strong intermolecular forces tend to result in solids and liquids (high melting and boiling points) and weak intermolecular forces tend to result in gases (low melting and boiling points). Intermolecular forces include the following:

1. London dispersion force
2. Dipole-dipole force
3. Hydrogen bonding
4. Ion-dipole force

The **London dispersion force** occurs in all atoms and molecules. This is the weakest intermolecular force and is the result of "random" fluctuations in the distribution of electrons around atoms and molecules. These temporary charge separations are called **instantaneous/temporary dipole moments**. Such a dipole moment attracts/repels electrons in neighboring atoms inducing dipoles on those. This process is propagated throughout a sample of matter.

The strength of the London dispersion forces for a substance depends on several things:

1. Volume of electron cloud: the larger the volume, the more polarizable the electrons are
2. Molar mass: The more molar mass, the more electrons, the stronger the dispersion force
3. Shape: The more surface-to-surface contact, the stronger the dispersion forces.

Remember that the higher the normal boiling point of a substance, the stronger the intermolecular forces.

If asked to order a group of molecules by boiling point, for the nonpolar molecules, the greater the molar mass, the higher the boiling point. A polar molecule of similar mass to a nonpolar molecule, will have a much higher boiling point due to the dipole-dipole force. This polarity also helps determine the miscibility of two liquids. In general, two polar liquids will mix, but a polar liquid will not mix with a nonpolar liquid. When ordering polar molecules, do a Lewis structure to determine if there are hydrogen bonds.

The **dipole-dipole force** occurs in all polar molecules. Polar molecules have permanent dipoles. The positive end of one dipole attracts the negative end of a neighboring dipole. Polar molecules, therefore, have higher melting and boiling points compared to nonpolar molecules of similar molar mass.

Hydrogen bonding is also an intermolecular force. It is the strongest intermolecular force that occurs in pure substances but still only 2-5% the strength of a covalent chemical bond. Hydrogen bonds occur in any molecule where hydrogen is bonded directly to small electronegative atoms like F, O, or N. It is a super dipole-dipole force because the large electronegativity creates a strong charge separation and the small size of the H atom allows it to come very close to neighboring molecules. Because of hydrogen bonding, molecules with H bonded to F, O, or N, have much higher boiling points than would be suggested by their molar mass.

The **ion-dipole force** occurs when an ionic compound is mixed with a polar compound. This is especially important in aqueous solutions involving ionic compounds (saltwater, for example). In such a mixture, you have the positive and negative ends of the polar molecules and the positive and negative ions. These all interact in obvious ways. The ion-dipole force is the strongest intermolecular force and is responsible for the ability of ionic substances to form solutions with water.

Intermolecular forces cause **surface tension** in liquids. Surface tension is the tendency of liquids to minimize their surface areas because of their attraction to each other. This is because molecules on the surface can interact only with molecules beside and below them causing a net inward force. Surface tension explains why water droplets tend

to be spherical and why some items (e.g. paper clips) can float despite being denser than water. Surface tension is measured as the energy required to increase the surface area by a unit amount. For example, at room temperature, water has a surface tension of $72.8 \, \text{mJ/m}^2$. Surface tension decreases as intermolecular force decreases. Note that if you raise the temperature of a liquid, you reduce its surface tension because the increase in temperature reduces the intermolecular forces.

Viscosity is another example of intermolecular forces. Liquids with stronger intermolecular forces tend to be more viscous. Viscosity is also influenced by the shapes of molecules. Liquids composed of long-chained molecules (such as oil) tend to be more viscous because the molecules become entangled with each other. Viscosity is measured in units called the Poise (P) defined as 1 g/cm*s. Viscosity also depends on temperature since thermal energy partially overcomes intermolecular forces.

Capillary action is the ability of a fluid to flow up a narrow tube against gravity. It's caused by a combination of forces–cohesive forces (i.e. the attraction between molecules in a liquid) and adhesive forces (i.e. the attraction of the molecules to the surface of the tube). The adhesive forces cause the fluid to spread out over the surface of the tube and cohesive forces pull along the molecules that are not in direct contact with the surface of the tube. If the adhesive forces are smaller than the cohesive force, capillary action will NOT occur. Note that you can actually judge whether a surface is polar or nonpolar based on whether or not water beads up on it. Water will tend to bead up on nonpolar surfaces because the cohesive forces are stronger than the adhesive forces.

12.2   Vaporization and Condensation

In most liquids, at any given moment, some molecules are moving faster than the average (i.e. they have higher energy). Sometimes, these molecules are moving fast enough to break free from the surface. **Vaporization** is when molecules at the surface break free into gaseous form. Vaporization increases with increasing surface area, increasing temperature, and decreasing intermolecular forces. Liquids that vaporize easily are **volatile** and those that don't are **nonvolatile**. Vaporization is endothermic because energy is required to break molecules away from the rest of a liquid. As water evaporates it cools because only the fast-moving molecules break away–leaving behind the slow-moving ones. When sweating, our bodies are cooled by the endothermic process of evaporation. Condensation, on the other hand, is exothermic.

Condensation is the opposite. It occurs when a substance converts from its gaseous state to its liquid state. It is the opposite of evaporation.

The amount of heat required to vaporize 1 mole of a liquid to gas is its **heat of vaporization**, ΔH_{vap}. The heat of vaporization of water at its normal boiling point is $40.7 \, \text{kJ/mol}$. In other words,

$$\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(g)}; \quad \Delta H_{vap} = \frac{40.7 \, \text{kJ}}{\text{mol}} \text{ at } 100 \, ^\circ\text{C}.$$

ΔH is positive because heat must be added to cause vaporization.

The heat of vaporization is somewhat temperature dependent. When the substance condenses, the same amount of heat is involved, but it has opposite sign (negative because exothermic). Heat of vaporization is used to calculate heat transfer at the phase change from liquid to gas with no temperature change.

The heat of vaporization of a liquid can be used to calculate the amount of heat energy required to vaporize a given amount of that liquid by using heat of vaporization as a conversion factor.

The rate of evaporation of a liquid in a sealed container at a constant temperature is constant. As the pressure of the gas at the top builds up, the rate of condensation increases. At some point the system will reach **dynamic equilibrium**—when the rate of

evaporation equals the rate of condensation. The pressure of the gas in such an equalized system is the liquid's **vapor pressure**. Vapor pressure increases with temperature and decreases with increasing intermolecular forces. For water at 25 °C, the vapor pressure is 23.8 mmHg.

When a system in dynamic equilibrium is disturbed, the system responds so as to minimize the disturbance and return to a state of equilibrium. For example, a container of liquid in dynamic equilibrium with its vapor pressure, if you reduce its volume, the pressure of the gas will briefly increase but then return to dynamic equilibrium as more of the gas condenses to liquid. This principle called **Le Chatelier's principle** is applicable to any chemical system in equilibrium.

The **boiling point** of a liquid is the temperature at which its vapor pressure equals the external pressure. The **normal boiling point** of a liquid is the temperature at which its vapor pressure equals 1 atm. For water, this is 100 °C. At the boiling point of a liquid, the thermal energy is enough for molecules in the interior of the liquid (not just at the surface) to break free into gaseous state. The bubbles formed thereby, rise to the surface where they release the molecules of steam. Once the boiling point is reached, additional heating doesn't raise the temperature–it just boils it faster (as long as it's a pure liquid).

When bubbles form in a liquid at a temperature lower than the boiling point of the liquid, the bubbles are dissolved air–not gaseous water–leaving the liquid. This is because the solubility of a gas in a liquid decreases with increasing temperature.

The relationship between temperature and vapor pressure, P_{vap}, is exponential. The **Clausius-Clapeyron equation** turns this relationship into a linear relationship of logs. That equation is

$$\ln P_{vap} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + \ln\beta,$$

where β is a constant that depends on the gas and R is the gas constant $8.314\,\text{J/mol}\cdot\text{K}$. This equation allows us to easily determine the heat of vaporization ΔH_{vap} given the vapor pressure and temperature. If we plot the natural log of the vapor pressure of a liquid as a function of the inverse of the temperature, then $-\Delta H_{vap}/R$ is the slope of the linear line.

There's also a two-point form of the Clausius-Clapeyron equation that allows us to predict the vapor pressure of a liquid at any temperature given the enthalpy of vaporization and the normal boiling point (or the vapor pressure at some other temperature). It also allows us to determine the heat of vaporization given only two measurements of vapor pressure and temperature.

$$\ln\frac{P_2}{P_1} = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

When a liquid is heated in a sealed container, the density of the liquid decreases and the density of the gas above it increases (because the vapor pressure is increasing). At some point, the density of the liquid equals the density of the gas and the substance is neither liquid nor gas. It is a **supercritical fluid** which is intermediate between a liquid and a gas. The temperature at which this occurs is the **critical temperature** for the liquid and the pressure at which this occurs is the **critical pressure** of the liquid. Supercritical fluids have unique properties. Note that a substance cannot exist as a liquid above its critical temperature regardless of the pressure. Look at the phase diagram for water and you can see that to the right of the critical point (higher temperature), the liquid state is no longer possible–it's either a gas or a supercritical fluid.

12.3   Sublimation, Deposition, and Melting

Sublimation occurs when molecules at the surface of a solid substance have the thermal energy to escape from the surface (i.e. the solid turns directly into gas without going through the melting phase). **Deposition** occurs when the intermolecular forces of the solid recaptures such a gaseous molecule. As with liquids, the pressure of a gas in dynamic equilibrium with its solid is its vapor pressure.

$$\Delta H_{sublimation} \approx \Delta H_{fusion} + \Delta H_{vaporization}.$$

As a solid is heated, thermal energy causes the molecules and atoms composing the solid to vibrate faster. At the **melting point**, the molecules have enough energy to overcome the intermolecular forces that hold them together as solids, and the solid turns into a liquid. Once the melting point of a solid is reached additional heating will only cause more rapid melting–the temperature of the substance cannot rise until all of it is melted. In other words, a mixture of water and ice will always have a temperature of $0\,°C$ at 1 atm. The process of melting is also called **fusion**.

The amount of heat required to melt 1 mol of a solid is its **heat of fusion**, ΔH_{fus}. The temperature of a substance will stay constant at the melting point as long as both solid and liquid states coexist. The heat of fusion for water is $6.02\,kJ/mol$. The same amount of heat is involved when one mole of water freezes but the sign of the heat of fusion is negative instead of positive.

In general, the heat of fusion is significantly less than the heat of vaporization. In other words, it takes a lot more heat energy to turn a liquid into gas than it takes to turn a solid into liquid. This is because melting only partially overcomes intermolecular forces whereas vaporization completely overcomes them.

Heat of fusion is used to calculate heat transfer at the phase change from solid to liquid with no temperature change.

12.4   Summary of Phase Transitions

As heat is added to a substance (at a constant pressure) and it goes through its phase transitions, it can be broken into 5 segments that can be visualized on a chart called a **heating curve**:

1. Warming solid: The temperature increases linearly and the relationship between heat and temperature is given by $q = mC_{s,\,ice}\Delta T$.
2. Melting solid: The temperature stays constant and the amount of heat required to complete the transition can be found with $q = n\Delta H_{fus}$.
3. Warming liquid: The temperature increases linearly and the relationship between heat and temperature is given by $q = mC_{s,\,liquid}\Delta T$.
4. Vaporizing liquid: The temperature stays constant and the amount of heat required to complete the transition can be found with $q = n\Delta H_{vap}$.
5. Warming gas: The temperature increases linearly and the relationship between heat and temperature is given by $q = mC_{s,\,gas}\Delta T$.

Notice that specific heat capacity is used to calculate heat transfer when there is temperature change but no phase change.

We can combine temperature dependence and pressure dependence of the state of a substance in a graph called a **phase diagram**. The **triple point** is the unique point on such a graph where the substance will be equally stable and in equilibrium as a solid, liquid, and a gas.

Here are the regions of a phase diagram that you should be able to identify:

- Solid
- Liquid
- Gas

- Triple point
- Critical point
- Sublimation curve
- Fusion curve
- Vapor pressure curve

12.5   Crystal Structure

X-ray diffraction is a laboratory technique used to determine the arrangements of atoms in a larger structure.

There are 3 basic crystalline structures. The number of atoms that every atom is in direct contact with is the **coordination number**. The **packing efficiency** is the volume that is occupied by atoms.

- Simple cubic: Visualize an atom at every corner of a cube. The coordination number is 6 and the packing efficiency is 52%.
- Body-centered cubic: Visualize an atom at every corner of a cube, plus one in the very center. The coordination number is 8 and the packing efficiency is 68%.
- Face-centered cubic: Visualize an atom at every corner of a cube plus one centered in each face of the cube. The coordination number is 12 and the packing efficiency is 74%.

Solids can be amorphous or crystalline. Crystalline solids can be molecular, ionic, or atomic. Here we look at the three types of crystalline solids:

- Molecular solids: Repeating crystalline structure is formed by entire molecules instead of single atoms. They are held together by all kinds of intermolecular forces including dispersion forces, dipole-dipole forces, and hydrogen bonding. Example: Water ice.
- Ionic solids: Are held together by coulombic interactions, the interaction between cations and anions. Table salt, NaCl, is an example of an ionic solid.
- Atomic solids: There are three kinds of these.
    - Nonbonding: Held together only by dispersion forces. Only examples are solid forms of noble gases.
    - Metallic: Held together by metallic bonds (i.e. sea of electrons). Example: gold.
    - Network covalent: A crystalline structure of a single kind of atom bonded covalently to other atoms of the same element. Example: diamonds.

A more sophisticated (than sea of electrons) model for metallic and covalent atomic solids bonding is **band theory**. It grows out of molecular orbital theory. In band theory, electrons are delocalized over the entire crystal.

Chapter 13

Solutions

Solutions, are by definition, homogeneous mixtures of two or more substances. They cannot be heterogeneous. Substances put together tend to mix into homogeneous solutions unless it is highly unfavorable energetically. Solutions can be of various types:

1. Gaseous solution: Gas added to gas
2. Liquid solutions: Gas added to liquid (e.g. carbonated beverage), liquid added to liquid (e.g. vodka), and solid added to liquid (e.g. saline)
3. Solid solutions: Solid added to solid (e.g. metal alloys)

Whenever a solution contains significant water, it is called an **aqueous solution**. In a solution, the majority component is called the **solvent** and the minority component is called the **solute**. The exception is aqueous solutions in which case water is considered the solvent regardless of relative proportions. In general, polar solvents (e.g. water) dissolve polar and ionic solutes, and nonpolar solvents dissolve nonpolar solutes. In general, we can use the rule of thumb that *like dissolves like*.

Solubility is the amount of substance that will dissolve in a given amount of solvent at a given temperature. Solubility depends on nature's tendency toward mixing and on the strength of intermolecular forces.

The formation of a solution does not necessarily lower the potential energy of its constituent particles. The tendency to mix into a solution is related to entropy. **Entropy** is a measure of energy randomization or energy dispersal in a system. The pervasive tendency for energy to spread out, or disperse, whenever it is not restrained from doing so is why two ideal gases mix. Entropy can also be thought of as the disorder of a system. The entropy of the universe can only increase. The transfer of thermal energy from a hot body to a cold body is another example of entropy.

In the absence of intermolecular forces, two substances (e.g. gases) will spontaneously mix. The presence of intermolecular forces may increase or decrease the tendency to form solutions:

1. If solvent-solute interactions > solvent-solvent and solute-solute interactions, then a solution will form.
2. If solvent-solute interactions = solvent-solvent and solute-solute interactions, then a solution will form.
3. If solvent-solute interactions < solvent-solvent and solute-solute interactions, then a solution may or may not form depending on the relative disparity of the interaction strengths.

We've studied enthalpy of reactions–the fact that chemical reactions cause a change of energy, but there are also energy changes associated with solution formation. This process is called **enthalpy of solution formation**. This energy change can be broken into three steps:

1. Solute separates into constituent particles (endothermic)

2. Solvent separates to make room for solute (endothermic)
3. Solute particles mix with solvent particles (exothermic)

$$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$$

Whether the overall solution formation is exothermic or endothermic depends on the relative strengths of the intermolecular forces.

When ions dissolve in water, they become **hydrated**. **Heat of hydration** is the enthalpy change that occurs when 1 mol of the gaseous solute ions are dissolved in water. The energy change when the ion solute separates into its constituent particles is the negative of that ion's **lattice energy**. When dealing with ions in aqueous solutions, then, the above equation can be shortened to

$$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{hydration}.$$

As a solute dissolves in a solvent there is also some **recrystallization**. As the concentration of solute increases, the rate of recrystallization also increases. When the rate of dissolution and rate of recrystallization are equal, the solution has reached **dynamic equilibrium** and is called a **saturated** solution. A **supersaturated** solution has more than the equilibrium amount of dissolved solute and is very unstable. Solid solute will tend to **precipitate** out of such a solution. An **unsaturated** solution has less. Supersaturated solutions and recrystallization can be utilized to purify a solid, which crystallizes as decreasing solution temperature causes the solution to become supersaturated.

The solubility of gases in gases is infinite. Gases tend to be nonpolar simply because polar substances tend not to be gases–polarity tends to pull particles into solid or liquid phases. The solubility of most solids in water increases with increasing temperature. For example, salt dissolves more readily in hot water.

The solubility of gases in water decreases with increasing temperature. For example, the carbonation will escape quickly from warm soda. Most liquids exposed to air will contain dissolved gases. Liquids can be degassed by heating them. Gases will begin bubbling out of water before it reaches its boiling point. For example, you don't want to put boiled water in a fish tank because it won't contain any oxygen for the fish to breathe.

The solubility of of a gas in a liquid increases with increasing pressure (i.e. pressure of the gas above the liquid). The deeper a scuba diver goes, the more soluble becomes the gas that he is breathing. The relationship between gas solubility and pressure is given by **Henry's Law**

$$S = k_H P,$$

where S is the solubility of the gas, which is usually given in units of molarity, k_H is **Henry's law constant** (units of M/atm), which depends on the specific solute and solvent and is determined experimentally, and P is the partial pressure of the gas (usually in atm) above the liquid.

The measures of concentration we may use are:
1. Molarity (M) = mol solute / L solution
2. Molality (m) = mol solute / kg solvent
3. Mole fraction (χ) = mol solute / mol solution
4. Mole percent (mol %) = (mol solute / mol solution) * 100
5. Percent by mass (%) = (kg solute / kg solution) * 100
6. Parts per million by mass (ppm) = (kg solute / kg solution) * 1,000,000
7. Parts per billion by mass (ppb) = (kg solute / kg solution) * 1,000,000,000
8. Percent by volume (%) = (L solute / L solution) * 100
9. Parts per million by volume (ppm) = (L solute / L solution) * 1,000,000
10. Parts per billion by volume (ppb) = (L solute / L solution) * 1,000,000,000

The molarity of a solution can be used as a conversion factor between moles of solute and liters of solution. Molarity varies with temperature because volume does. Molality

does not. If asked for mole fraction when the substance isn't specified, either do it for the solute or do it for both the solute and the solvent.

A solution containing a solute that dissolves into ions is called an **electrolyte solution** and it can conduct electricity. In general, soluble ionic solids form electrolyte solutions while soluble molecular solids form **nonelectrolyte solutions**.

A **colligative property** is a property that depends on the number of particles dissolved on solution–not the type of particles. When counting the number of particles dissolved in solutions remember that electrolyte solutes (solutes such as ions that dissolve into charged particles) must be treated differently. For example, 1 mol of NaCl dissolves into 2 moles of particles.

Recall that vapor pressure is the pressure of a gas above a liquid when the two are in equilibrium (i.e. the rate of evaporation equals the rate of condensation). When a nonvolatile nonelectrolyte solute is added to a solvent, the resulting solution tends to have a lower vapor pressure than the pure solvent. The simple explanation is that solute particles displace some of the solvent particles at the surface of the solution resulting in a solution that is slightly less volatile (i.e. slightly less likely to evaporate) than the pure solvent. This relationship between solvent, solution, and vapor pressure is called **Raoult's Law**

$$P_{solution} = \chi_{solvent} P^{\circ}_{solvent},$$

where $P_{solution}$ is the vapor pressure of the solution, $\chi_{solvent}$ is the mole fraction of the solvent, and $P^{\circ}_{solvent}$ is the vapor pressure of the pure solvent at the same temperature. Because $\chi_{solvent} = 1 - \chi_{solute}$ for a two component solution, we can show the vapor pressure lowering by

$$\Delta P = \chi_{solute} P^{\circ}_{solvent}.$$

When asked to calculate the vapor pressure of a solvent in a solution and the vapor pressure of the pure solvent is not given, use the Clausius-Clapeyron equation to solve for pressure.

When a volatile solute is added to a volatile solvent then both substances contribute to the vapor pressure above the solution. Such a solution may be an **ideal solution**, in which case it follows Raoult's law for both substances, or it may be a nonideal solution in which case it doesn't follow Raoult's law. In an ideal solution all the interactions are of the same magnitude so the solute simply dilutes the solvent. If we represent one liquid as A and the other liquid as B, then the following 3 equations describe the vapor pressures:

$$P_{total} = P_A + P_B$$
$$P_A = X_A P^{\circ}_A$$
$$P_B = X_B P^{\circ}_B$$

Because the vapor pressure is lowered at all temperatures when a nonvolatile solute is added, the result is **freezing point depression** and **boiling point elevation**. You can visualize this on a phase change diagram of the solvent and the solution. The phase diagram of the solution is shifted downward from that of the solvent. The two arms of the solution will be start lower and spread wider (as a result) compared to the solvent alone.

The amount that the freezing point is lowered is given by

$$\Delta T_f = m K_f,$$

where m is the molality of the solution in moles solute / kg solvent, and K_f is the freezing point depression constant for the solvent. The temperature change must be given in $^{\circ}C$. Note that this change in freezing temperature must be subtracted from

the substance's normal freezing point. Different solvents have different freezing point depression constants. For water,

$$K_f = 1.86 \frac{^\circ C \cdot \text{kg solvent}}{\text{mol solute}}.$$

The amount that the boiling point is elevated is given by

$$\Delta T_b = mK_b,$$

where m is molality of the solution in moles solute / kg solvent, and K_b is the boiling point elevation constant for the solvent. The temperature change must be given in $^\circ C$. Note that this change in boiling temperature must be added to the substance's normal boiling point. Different solvents have different boiling point elevation constants. For water,

$$K_b = 0.512 \frac{^\circ C \cdot \text{kg solvent}}{\text{mol solute}}.$$

Osmosis is the flow of solvent from a solution of lower concentration to a solution of higher concentration. Concentrated solutions draw solvent from more dilute solutions because of nature's tendency to mix. In an osmosis cell, a semi-permeable membrane allows water to flow through but not solute particles. If a solution is on one side of the membrane then water will flow from the pure side. The pressure required to stop this flow of water is **osmotic pressure**, and is given by

$$\Pi = MRT,$$

where M is molarity of the solution, T is temperature in Kelvins, and R is the ideal gas constant $0.082\,06\,\text{L} * \text{atm}/\text{mol} * \text{K}$.

Since electrolytes dissociate into charged ions (e.g. NaCl), these colligative properties must be considered differently. The ratio of moles of particles in solution to moles of formula units dissolved is called the **van't Hoff factor**, i. The actual van't Hoff factor for an electrolyte is close to the expected value but not exact. This is because ions in solution may not be completely dissociated. At any one time, some cations will be paired with anions–reducing the number of particles in solution. Therefore, the van't Hoff factor is actually experimentally determined rather than a straight forward calculation from the chemical equation of the electrolyte. To calculate freezing point depression, boiling point elevation, and osmotic pressure for ionic solutions we must include the van't Hoff factor,

$$\Delta T_f = imK_f$$
$$\Delta T_b = imK_b$$
$$\Pi = iMRT$$

These three colligative properties are affected more dramatically by electrolyte solutes due to the increased number of particles. This must be taken into account when calculating the vapor pressure reduction of a solvent when an electrolyte solute is added. When calculating the vapor pressure of the solution you must multiply the moles of solute by the number of particles each formula unit will dissociate into.

A **colloid** is a mixture in which a dispersed substance is finely divided in a dispersing medium. The difference between a colloid and a solution is that in a colloid, the particles are relatively large, but in a solution, the particles are much smaller–individual atoms or molecules. A colloid can be identified by shining a light through the mixture (i.e. the **Tyndall effect**). If the beam of light can be seen going through the mixture, that is, the particles are large enough to scatter light, then the mixture is a colloid. Examples of colloids are fog, smoke, milk, and fine dust in the air. Colloidal particles exhibit **Brownian motion**–moving in a jerky, haphazard manner.

Chapter 14

Chemical Kinetics

Chemical kinetics is the study of how the molecular world changes with time. Reaction rates are important. A rocket burn that is too fast results in an explosion. A burn that is too slow results in the rocket not achieving enough thrust to leave the ground. Thermodynamics tells you whether a reaction will happen. Kinetics tells you how long it will take.

Reaction rate is a measure of how fast a chemical reaction occurs. It can be measured as the negative of the change in the concentration of one of the reactants divided by the time (negative because the reactant is decreasing as the reaction progresses. This makes the overall rate positive.) or as the positive of the change in the concentration of one of the products divided by the change in time. Keep stoichiometric coefficients in mind. You may have to multiply your formula by a factor so that you get the same reaction rate no matter which reactant or product you base it on.

Diamonds go spontaneously into graphite (according to thermodynamics), however, kinetics tells us that it'll take over a million years. This is simply because the reaction rate is extremely low.

Reaction rate depends on several factors including

- The nature of the reactants
- Temperature
- Catalyst
- Concentration

If you have the generic reaction

$$\mathrm{aA + bB \longrightarrow cC + dD.}$$

Then you could calculate the reaction rate using any of the following (change in concentration is often given as change in molarity):

$$\text{Reaction Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Generally, as a reaction progresses it slows down. This is because the reaction rate depends on the concentration of the reactants. As the reaction progresses the concentration of the reactants drops which results in a drop in the reaction rate as well.

Reaction rates are determined experimentally, often using spectroscopy to measure color change with respect to time. For gaseous reactions in which the moles of particles changes, which results in an increase or decrease of pressure, the rate of reaction can be calculated from the changing pressure exerted by the reaction. For slow reactions, small amounts can be drawn off periodically and tested (e.g. by titration) to determine the concentrations.

14.1   Concentration and Reaction Rate

The rate of reaction may depend on the concentration of one or more of the reactants.

When a single reactant decomposes into products, and the reverse reaction is negligible, the **rate law** for relationship between concentration and reaction rate is

$$\text{Rate} = k[A]^n,$$

where k is a proportionality constant called the **rate constant**, and n is the **reaction order**. The value of n determines how the rate depends on the concentration of the reactant.

- If $n = 0$, the reaction is zero order and the rate is independent of the concentration of A. In this case, the concentration of the reactant decreases linearly with time. This kind of reaction occurs when the reactant available for reaction is unaffected by a decrease in the overall quantity of the reactant. An example is sublimation since this reaction only occurs at the surface of the solid reactant.
- If $n = 1$, the reaction is first order and the rate is directly proportional to the concentration of A. In this case, the rate of reaction slows as the concentration of reactant decreases.
- If $n = 2$, the reaction is second order and the rate is proportional to the square of the concentration of A. In this case, the rate of reaction is even more affected by a decrease in concentration.

Other orders are possible, but the ones listed above are the most common.

The order of a reaction can be determined only by experimentation, and it is usually done by the *method of initial rates*. This method involves measuring the initial reaction rate (a short period at the beginning) for several different initial concentrations. For a given reaction, then, a small table is created that contains initial concentrations and initial rates. Compare the relationships between the two sets to determine the reaction rate. For example, if the rate doubles when the concentration is doubled, the initial rate is proportional to the initial concentration, and the reaction is first order. If the rate is constant regardless of the concentration, then the reaction is zero order. If the reaction quadruples when the concentration is doubled, then the reaction is second order.

If the order is unclear, you can substitute any two initial concentrations and the corresponding rates into a ratio. Then k will cancel and you can solve for n

$$\frac{\text{rate } 2}{\text{rate } 1} = \frac{k[A]_2^n}{k[A]_1^n}.$$

Once the order has been determined, you can substitute it for n in the rate law and solve for k to get the rate constant.

The rate constants of different order reactions have different units:

- $n = 0$ has units of Ms^{-1}
- $n = 1$ has units of s^{-1}
- $n = 2$ has units of $\text{M}^{-1}\text{s}^{-1}$

To remember these, remember that all of them contain s^{-1} and that M starts at M^1 and decreases. Also remember that the rate should always have units of M/s. In other words, the units of the right side of every rate law equation should reduce to M/s when the left side is simply "Rate".

When dealing with reactions with multiple reactants such as in aA+bB $\longrightarrow$ cC+dD, as long as the reverse reaction is negligible, the rate law is

$$\text{Rate} = k[A]^m[B]^n.$$

In this case, m is the reaction order with respect to reactant A and n is the reaction order with respect to reactant B. The overall order of the reaction is the sum of the exponents $(m + n)$.

The above rate laws look at the relationship between rate of reaction and concentration of a reactant. To look at the relationship between concentration of a reactant and time, we must use integration. Let's consider a simple reaction consisting of 1 reactant decomposing into products. Following are the integrated rate laws for the three different orders. Zeroth Order Integrated Rate Law:

$$[A_t] = -kt + [A_0]$$

First Order Integrated Rate Law:

$$\ln[A_t] = -kt + \ln[A_0]$$

Second Order Integrated Rate Law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

When asked to determine the concentration of a reactant after a given amount of time has passed, and you're given the initial concentration, rate constant, and order, you can simply substitute those into the appropriate equation and solve for $[A_t]$.

Notice that the integrated rate laws are all linear equations with slope and y-intercepts. This makes it easy to graphically analyze them. Here is how to graphically analyze the integrated rate laws, say, if you have a table of concentrations and times:

- Zeroth Order: A plot of the reactant concentration as a function of time (x-axis) yields a straight line with a slope of $-k$ and a y-intercept of $[A_0]$.
- First Order: A plot of the natural log of the reactant concentration as a function of time (x-axis) yields a straight line with a slope of $-k$ and a y-intercept of $\ln[A_0]$.
- Second Order: A plot of the inverse (i.e. $1/x$) of the reactant concentration as a function of time (x-axis) yields a straight line with a slope of k and a y-intercept of $1/[A_0]$.

If you don't know what order the reaction is, plot the relationship between reactant concentration and time using all three of the methods above. Whichever one yields a straight line will tell you the order of the reaction. To obtain the rate constant graphically, determine the slope of the best fitting line, keep in mind that the units of the rate depends on which order it is.

When it's unclear which graph produces the straightest line use the R^2 feature in Excel. The closest one to the value of 1 is the one that should be considered the best linear fit.

The **reaction half-life**, $t_{1/2}$, is the time required for the concentration of a reactant to fall to one-half of its initial value. The half-life can be solved for by using the relevant integrated rate law and the knowledge that $[A_t] = \frac{1}{2}[A_0]$. Here are the half-life equations for the different orders. Zeroth Order:

$$t_{1/2} = \frac{[A_0]}{2k}$$

First Order: (notice that half-life is independent of initial concentration)

$$t_{1/2} = \frac{0.693}{k}$$

Second Order:

$$t_{1/2} = \frac{1}{k[A_0]}$$

When working with half-lives, it may be helpful to know that

$$A_f = A_i \left(\frac{1}{2} \right)^s,$$

where A_f is the final amount, A_i is the initial amount, and s is the elapsed time measured in half-lives.

An easier, faster, and better way to deal with half-lives, initial amounts, final amounts, and elapsed time, is to use the appropriate half-life equation to calculate k, and then plug everything into the appropriate integrated rate law to calculate the missing information. Much better than using the equation above.

Reaction rates are usually expressed in M/s but note that that is the same as mol/Ls.

14.2 Temperature and Reaction Rate

The rates of chemical reactions tend to be highly sensitive to temperature. At around room temperature, a $10\,^{\circ}$C increase in temperature increases the rate of a typical reaction by 2 or 3 times. An increase in temperature, generally results in an increase in k, which is what results in an increased reaction rate.

The **Arrhenius equation** shows the relationship between the rate constant, k, and the temperature in Kelvins

$$k = Ae^{\frac{-E_a}{RT}},$$

where R is the gas constant $8.314\,\text{J/mol K}$, A is a constant called the **frequency factor**, and E_a is the **activation energy** or activation barrier. The $e^{\frac{-E_a}{RT}}$ term is called the **exponential factor**.

The activation energy is an energy hump that must be surmounted for the reactants to transform into products. This is despite the fact that the reaction is energetically favored. To get from reactant to product, a molecule must first go through a high-energy intermediate state called the **activated complex** or **transition state**. Think of activation energy as the energy required to break the bonds so that new compounds can be formed from the reactants.

The frequency factor can be thought of as the number of times that the reactants approach the activation barrier per unit time. If your units are seconds, you can think of it as the number of times per second that the reactant tries to surmount the activation barrier.

The exponential factor is a number between 0 and 1 that represents the fraction of reactant molecules that have enough energy to make it over the activation barrier on a given approach. This fraction increases with increasing temperature and decreases with increasing activation energy.

The Arrhenius equation can be manipulated to produce a linear equation that is used to create an **Arrhenius plot**

$$\ln k \ = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A \ .$$

A plot of the natural log of the rate constant ($\ln k$) versus the inverse of the temperature in Kelvins ($1/T$) (x-axis) yields a straight line with a slope of $-\frac{E_a}{R}$ and a y-intercept of $\ln A$. This allows us to easily determine the frequency factor and activation energy when given a set of rate constants and temperatures.

If data or plotting capabilities are limited, we can determine the activation energy with the two-point form of the Arrhenius equation. This form is very helpful in determining the activation energy when given two rate constants at two different temperatures.

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

In the collision model, a chemical reaction occurs after a sufficiently energetic collision between two reactant molecules. However, in reality, the frequency factors of most gas-phase reactions are smaller than the number of collisions per second (which can be calculated from pressure and temperature). This is because not all energetic collisions will result in a reaction because the colliding reactants may not be oriented properly. The Arrhenius equation can be rewritten in light of this as

$$k = Ae^{\frac{-E_a}{RT}} = pze^{\frac{-E_a}{RT}}.$$

Here, p is the **orientation factor** (i.e. the fraction of sufficiently energetic collisions that actually results in a reaction) and z is the **collision frequency**. For atoms the orientation factor is around 1 since atoms are spherical. For most molecules, the orientation factor is far less than 1 (i.e. most sufficiently energetic collisions do not result in a reaction because the molecules have to be oriented in very specific ways for a reaction to occur). A small minority of reactions have orientation factors greater than one which means they don't even have to collide to react.

The bigger the molecules, the more that orientation affects the rate. In other words, bigger molecules tend to react slower because there are more ways in which they can be oriented the wrong way.

Exothermic reactions produce heat which helps get the remaining reactants over the energy hump. The resulting shift in the temperature graph can result in a runaway reaction, that is, an explosion.

14.3 Reaction Mechanisms

Most reactions occur in several steps even though our overall equations for them show just the reactants and final products. Our overall equation doesn't show the intermediate steps that a reaction may take. A **reaction mechanism** is the actual series of chemical steps by which an overall reaction occurs. Each step in the reaction mechanism is an **elementary step**. An atom or molecule that appears in the reaction mechanism but not in the overall equation is a **reaction intermediate**, which forms in one intermediate step and is consumed in another. A reaction mechanism is a complete, detailed description of a reaction at the molecular level.

Elementary steps are characterized by their **molecularity** which is the number of reactant particles involved in the step. If only one reactant is involved (i.e. it decomposes), the step is unimolecular. If two particles are involved (i.e. A + A or A + B), the step is bimolecular. If three particles are involved, the step is termolecular. Termolecular steps are rare because the probability of 3 particles colliding at once is very low.

The rate law for an overall reaction cannot be deduced from the overall equation but the rate law for an elementary step can be deduced from the equation for the elementary step. This is because the rate law is proportional to the product of the concentrations of those particles. The molecularity of the elementary step is equal to the overall order of the step.

- (A = products): Rate = $k[A]$
- (A + A = products): Rate = $k[A]^2$
- (A + B = products: Rate = $k[A][B]$
- (A + A + A = products): Rate = $k[A]^3$
- (A + A + B = products): Rate = $k[A]^2[B]$
- (A + B + C = products): Rate = $k[A][B][C]$

In most chemical reactions, one of the elementary steps, called the **rate-determining step**, is much slower than the other steps. This step limits the overall rate of the reaction mechanism and therefore determines the rate law for the overall reaction.

Reaction mechanisms can be valid but not proven since multiple reaction mechanisms may actually do the job. To be valid, a reaction mechanism must fulfill the following requirements:

1. The elementary steps must sum to the overall reaction (i.e. with intermediates canceling out).
2. The rate law predicted by the mechanism must be consistent with the experimentally determined rate law.

In a multistep reaction when the first step is fast, the products of the first step build up until the reverse reaction of the first step engages and equilibrium of the reactants and products of the first step are achieved. In such a case, the rate law predicted by the slowest elementary step in the reaction mechanism, may contain intermediates. Since the experimentally observed rate does not contain intermediates, to check if the predicted rate equals the experimentally observed rate we must express the concentration of the intermediate in terms of reactants of the overall equation.

Given an overall reaction aA $\longrightarrow$ bB and an experimentally observed Rate = $k[A]^2[B]^{-1}$ suppose our proposed reaction mechanism is

$$A \longleftrightarrow B + C \qquad \text{Fast}$$
$$A + C \longrightarrow 2\,B \qquad \text{Slow}$$
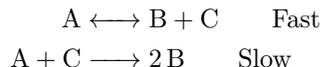
The second step is the rate-limiting step since it is the slowest and step one has double arrows because since it is fast, its reactants and products reach equilibrium in a relatively short time. From the proposed reaction mechanism, our predicted rate law is

$$\text{Rate} = k\,[A]\,[C].$$

Our predicted rate law includes an intermediate (C) which is not in the actual rate law. Therefore, we must replace the C component with something else. Noticing that the first reaction reached equilibrium, which means the rate of the left side equals the rate of the right side, we can express

$$k_1\,[A] = k_{-1}\,[B]\,[C].$$

Solving for C, we get

$$\frac{k_1\,[A]}{k_{-1}\,[B]} = [C].$$

Simplifying, we get

$$\frac{k_1}{k_{-1}}\,[A]\,[B]^{-1} = [C].$$

Now replacing the C in our predicted rate law with the left side of the above equation, we get:

$$\text{Rate} = \ k\,[A]\,\frac{k_1}{k_{-1}}\,[A]\,[B]^{-1} = k\frac{k_1}{k_{-1}}[A]^2[B]^{-1}.$$

Finally, realizing that a constant times a ratio of a constant is a constant, we can simplify to get our experimentally-observed rate law. Therefore, the proposed reaction mechanism is valid:

$$\text{Rate} = \ k[A]^2[B]^{-1}.$$

When a chemist is trying to figure out the reaction mechanism of a reaction, he may come up with a whole bunch of proposed mechanisms. Then he'll test and deduce to see if there's any evidence for any of the mechanisms. For example, if his proposed mechanism contains an intermediate that has a specific color, then he should see a hint of that color as the reaction is occurring if the proposed mechanism is the real one. The experimentally determined rate law tells him something about the slowest step in the reaction.

14.4 Catalysis

Reaction rates can be increased with a **catalyst**, which is a substance added to increase the speed of reaction but which is not actually consumed by the reaction. A catalyst provides an alternative mechanism of reaction which has a lower activation energy than the reaction without the catalyst. In other words, a catalyst increases reaction rate by lowering the activation energy of the reaction.

An example is the rusting of iron. Iron reacts with oxygen to form rust, but the reaction is very slow unless water is included. Water greatly increases the rate at which iron rusts, so water is a catalyst in this example.

A **homogeneous catalyst** exists in the same phase as the reactants–for example, the chlorine catalyst in ozone destruction. A **heterogeneous catalyst** exists in a different phase–for example, the metal catalysts in vehicular catalytic converters.

Enzymes are biological catalysts. They have **active sites** where the **substrate** (reactant molecule) binds).

Catalysts can increase the rate of a reaction by as much as millions. There are also negative catalysts which slow reactions down.

Chapter 15

Radioactivity and Nuclear Chemistry

Chemical reactions involve electrons and nuclear reactions involve protons and neutrons. Radioactivity is the emission of subatomic particles or high-energy electromagnetic radiation by the nuclei of certain atoms. Radioactivity was discovered by Becquerel.

Remember the symbolization for isotopes

$$^{A}_{Z}X,$$

where A is the mass number (protons + neutrons), Z is the atomic number (protons), and X is the element symbol. Most elements have multiple isotopes, usually referred to as **nuclides** when talking about nuclear properties.

The elementary particles can be represented with the notation

- Proton: $^{1}_{1}$p
- Neutron: $^{1}_{0}$n
- Electron: $^{0}_{-1}$e

Alpha (α) **decay** occurs when an unstable nucleus emits a particle composed of 2 protons and 2 neutrons. Since this is He-4, the symbol for alpha radiation is the isotopic symbol of helium-4. Here's an example **nuclear equation** showing the alpha decay of uranium

$$^{238}_{92}U \longrightarrow ^{234}_{90}Th + ^{4}_{2}He.$$
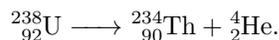
Notice that the sum of mass numbers on the reactant side matches the sum of mass numbers on the product side. Same with the sum of atomic numbers. When asked to give the alpha decay equation for an element, on the product side you simply subtract an He-4 from the original element. The new element is 2 elements below on the periodic table. Just remember that during alpha decay, the mass number reduces by 4 and the atomic number by 2.

Beta (β) **decay** occurs when an unstable nucleus emits an electron. It does this when a neutron changes into a proton and emits an electron in the process

$$^{1}_{0}n \longrightarrow ^{1}_{1}p + ^{0}_{-1}e.$$
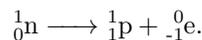
When an atom emits a beta particle, its atomic number increases by one. Here's an example

$$^{228}_{88}Ra \longrightarrow ^{228}_{89}Ac + ^{0}_{-1}e.$$
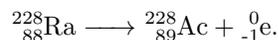
Gamma (γ) **ray emission** is different from the others because it is a form of electromagnetic energy. Gamma rays are high energy, massless, chargeless, photons. The symbol for a gamma ray is $^{0}_{0}\gamma$. Gamma radiation doesn't change the mass or atomic number, however, they're usually seen in conjunction with other forms of radiation. Example

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He} + {}^{0}_{0}\gamma.$$
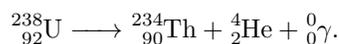
Radiation Comparison:

Type	Size of	Charge	Penetration	Energy	Exposure Danger	Ingestion Danger	Blocked By
Alpha	He nucleus	$+2$	low	high	low	high	paper
Beta	electron	-1	med	med	med	med	sheet of metal
Gamma	photon	0	high	low	high	low	inches of lead

Positron emission occurs when an unstable nucleus emits a positron (i.e. anti-electron). This occurs when a proton decays into a neutron and positron

$$^{1}_{1}\text{p} \longrightarrow {}^{1}_{0}\text{n} + {}^{0}_{+1}\text{e}.$$
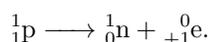
When this happens, the atomic number decreases by one.

Electron capture is when a nucleus captures one of the inner electrons, combining it with a proton to create a neutron.

$$^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \longrightarrow {}^{1}_{0}\text{n}.$$
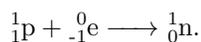
The result is that the atomic number by 1.

When neutrons (y-axis) are plotted against protons (x-axis), the stable nuclides fall on a curve that is higher than a 1 to 1 ratio of them. This curve is the **valley of stability**. In a nucleus, the protons repel each other because of their charge due to the Coulomb force. However, protons and neutrons are attracted to each other via the **strong nuclear force**. When they are extremely close to each other the attraction of the strong force is greater than the repulsion of the Coulomb force. The neutrons play an important role because they offer attractive force (strong force) but no repulsive force (Coulomb force).

An important number in determining stability is the ratio of neutrons to protons. For lighter elements, the N/Z ratio is about 1, but for heavier elements, this ratio is greater than one. Nuclides that lie above the valley of stability (N/Z is too high) have too many neutrons and tend to convert neutrons to protons via beta decay. Nuclides that lie below the valley of stability (N/Z too low) have too many protons and tend to convert protons to neutrons via positron emission or electron capture.

When asked to predict for a specific isotope whether it's more likely to decay via beta decay or positron emission, here's how you can figure it out:

1. Compare the atomic mass of the given isotope with the listed atomic mass on the periodic table.
2. If the number on the periodic table is lower, then the isotope you're considering must have too many neutrons. To convert a neutron to a proton, an electron is emitted–beta decay.
3. If the number on the periodic table is higher, then the isotope you're considering must have too few neutrons. To convert a proton to a neutron, a positron is emitted–positron emission.

Atoms with atomic numbers higher than 83 (i.e. higher than Bismuth) are radioactive and decay in one or more steps involving primarily alpha and beta decay (with some gamma radiation to carry away excess energy). Some isotopes with atomic numbers less than 83 are also radioactive. The multi-step process a radioactive nuclide may take to decay into a stable element is a **radioactive decay series**.

Radioactivity is detected via film-badge dosimeters (passive) due to the fact that radioactivity slowly but surely exposes film, **Geiger-Muller counters** (real-time), and scintillation counters (real-time). In a Geiger counter tube, radiation ionizes a string of radon gas which allows the temporary conduction of current which is transduced into a "click." In a scintillation counter, radiation passes through a material that emits light when it happens, which is detected.

All radioactive nuclei decay via first-order kinetics, so the rate of decay is directly proportional to the number of nuclei present

$$\text{Rate} = kN.$$

where k is the rate constant. Different radioactive nuclides decay with different rate constants. The time it takes for half of the parent nuclides to decay, is the half-life of the isotope given by

$$t_{1/2} = \frac{0.693}{k}.$$

Because of the proportional relationship between rate and rate constant, a large rate constant equates to a fast rate of decay–or a short half-life.

The first-order integrated rate law is useful here to think of the number of nuclei as a function of time. Instead of concentration, we use the number of nuclei

$$\ln \frac{N_t}{N_0} = -kt.$$

To solve for remaining amount of radioactive substance after a period of time when given the initial amount and the half-life, use the half-life equation to calculate k and then use the integrated rate law to solve for N_t.

To predict how the rate of decay of a radioactive sample will change with time, or how much time has passed based on how the rate has changed we can use the derived equation

$$\ln \frac{\text{Rate}_t}{\text{Rate}_0} = -kt.$$

Carbon-14 has a half-life of 5730 years. To find the age of an organic object given a current decay rate and an initial decay rate, use the half-life equation to determine k and then plug the values into the equation above and solve for t. Radio carbon dating is accurate (to around 5%) to about 50,000 years. Remember that radiocarbon dating only works to date things that were once alive (because they sequestered carbon up until they died).

U-238 decays into Pb-206 with a half-life of around 4.5×10^9 years. When given the current ratio of Pb-206 to U-238 in a sample, to calculate the age of the sample, start by calculating k using the half-life equation. Next, to calculate the initial amount of U-238, we assume that the number of particles of Pb-206 were all U-238 particles back then. When we do this calculation we have to do a molar mass conversion for each item, but we don't use the mass number from the periodic table because we are given the actual isotope mass (i.e. 238 g/mol and 206 g/mol).

Uranium bombarded with neutrons splits into Ba, Kr, several free neutrons, and produces energy. This nuclear **fission** reaction can be used in atomic bombs and in nuclear energy. In this reaction a small amount of the mass on the reactant side does not appear on the product side. This missing mass was converted to energy via $E = mc^2$.

As seen above, mass is not conserved in nuclear reactions as it is in chemical reactions. However, mass-energy is conserved. Also, a fission reaction produces over a million times more energy per mole than even a highly exothermic chemical reaction. If we calculate the expected mass of something, say C-16 with a known mass, we determine the number of protons, neutrons, and electrons in a neutral version of the isotope and (checking the back of the book) add up the masses of all of them. However, this number is slightly less than

the measured amount. This is known as the **mass defect**. This missing mass is actually manifested as the **nuclear binding energy** that holds the nucleus together. To calculate the nuclear binding energy, determine the mass defect and use the conversion factor 1 amu = 931.5 MeV (calculated from $E = mc^2$ and the conversion 1 MeV = 1.602×10^{-13} J). The MeV is an energy unit commonly used by nuclear physicists. When asked for binding energy per nucleon, divide it by the sum of protons and neutrons in the item.

When two elements are combined to form a heavier element, this is **fusion**. There are many nuclear reactions beyond just fission and fusion. The process of transforming one element into another via a nuclear reaction is known as **transmutation**.

The difference between a radioactive nucleus and a stable nucleus is due to the neutron to proton ratio. All radioactive decays obey first-order kinetics.

Radon is the only noble gas (very chemically stable) that is also radioactive. It accounts for more than 55% of natural radioactivity on Earth. 10% of lung cancer deaths is caused by radon.

Note, when working with radioactive half-lives always convert them to seconds since the k has units of inverse seconds.

Chapter 16

Chemical Equilibrium

During a chemical reaction a point is often reached where the forward reaction equals the reverse reaction. The **equilibrium constant**, K, is an experimentally-measured number that allows us to quantify the extent of a reaction. For a reaction with a large equilibrium constant, almost all of the reactants will react to form products. For a reaction with a small equilibrium constant, almost none of the reactants will react to form products.

Nearly all chemical reactions are reversible, but for some, the reversibility is so small that it can be ignored. **Dynamic equilibrium** happens when the reaction has lowered the concentration of reactants and increased the concentration of products such that the rate of reverse reaction equals the rate of forward reaction. Once equilibrium is reached, the concentrations of reactants and products no longer changes, but that doesn't mean they're equal to each other. It depends on the reaction. The relative concentrations of reactants and products becomes constant.

Consider the generic reaction aA + bB $\longleftrightarrow$ cC + dD. The equilibrium constant, according to the **law of mass action**, is the ratio (at equilibrium) of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients ([A] is the molar concentration of A)

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}.$$

The equilibrium concentration is experimentally determined, but once we have it we can determine the ratios of product concentrations to reactant concentrations at equilibrium. A value of $K > 1$ indicates that the concentration of products is greater than the concentration of reactants at equilibrium. A value of $K < 1$ indicates that the reverse reaction is favored over the forward reaction.

Relationships between the equilibrium constant and the chemical equation include

- If you reverse the equation, you must invert the K.
- If you multiply the coefficients of the equation by a factor, you must raise K to that factor.
- If you add two or more chemical equations to obtain an overall equation, you must multiply the corresponding K's together to obtain the overall K.

Since the partial pressure of a gas is proportional to its concentration, for gaseous reactions, we can express the equilibrium constant in terms of pressure. This works out to

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}.$$

We can also convert between the two different measures using

$$K_p = K_c (RT)^{\Delta n},$$

where K_p is the equilibrium constant in terms of pressure (atm), K_c is the equilibrium constant in terms of concentration (molarity), and Δn is the sum of the coefficients of the products minus the sum of the coefficients of the reactants $\Delta n = (c + d) - (a + b)$. The constant to use is $R = 0.082\,06\,\text{L} \cdot \text{atm/mol} \cdot \text{K}$. Notice that if the moles of reactants equals the moles of products then $\Delta n = 0$ and $K_p = K_c$. Also note that K does not have units since they cancel out.

Chemical reactions may include solids and liquids (check their states in the equation), but K does not depend on them because the concentration of a pure liquid or solid does not change during a reaction. Simply exclude the solids and liquids from the equilibrium expression.

The most direct way to get an experimental value for K of a reaction is to measure the concentrations of the reactants and products in a reaction mixture at equilibrium. Once these are known, simply plug them into the K-expression to find its value, which won't change for the reaction unless the temperature is changed. The K is the same for a reaction regardless of the initial concentrations of reactants and products.

We don't actually need the concentrations of all items at equilibrium. If we have all the initial concentrations and the equilibrium concentration of just one of them, then we can deduce the equilibrium concentrations of the other items by using the stoichiometric coefficients of the reaction equation (since the change in concentration of one item is related to the change of the other items, depending on the coefficients). We do this by making an ICE table (initial, change, and equilibrium). We put the reactants and products along the top, their initial concentrations, the change of concentration in the second row (note that the change of reactants are usually negative), and the equilibrium row simply sums the two values above it. Then plug the values from the equilibrium row into the K-expression to calculate K.

A reaction that is not yet at equilibrium will either proceed to the right (more reactants turn into products) or to the left (more products turns into reactants) in order to achieve equilibrium. We can figure out which direction the reaction will proceed by measuring the concentrations of all reactions and products if we already know the value of K. We do this by defining a **reaction quotient**, Q, which is the exact same thing as an equilibrium constant except that it can be calculated at any time and not just at equilibrium

$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$Q_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}.$$

By comparing the reaction quotient with the known equilibrium constant, we can tell which side of equilibrium our system is:

- If $Q < K$, the reaction will proceed to the right toward equilibrium (i.e. more products will be created).
- If $Q > K$, the reaction will proceed to the left toward equilibrium (i.e. more reactants will be created).
- If $Q = K$, the reaction is at equilibrium.

To find the concentration of a single reactant or product when given the equilibrium concentrations for all other items in addition to the equilibrium constant, simply plug all the knowns into the K-expression for the reaction and solve for the single unknown.

To find the concentrations of reactants and products when given the equilibrium constant and the initial concentrations for all items, set up an ICE table, use x to represent the unknowns and insert the unknowns (containing x) into the K-expression and solve for x. Remember to bring the coefficients from the chemical equation in front of the x's. To

determine whether it's the variable under reactants or under products that gets negated, determine which direction the reaction will run by solving for the reaction quotient and comparing to the equilibrium constant. If the reaction is going to run to the right then the change of a reactant will be negative. If the reaction is going to run in the reverse then the change of the products is going to be negative. You'll often have to use the quadratic equation to solve for x. Plug the (positive) value of x back into the ICE table to find the equilibrium concentrations for everything.

Sometimes, it's helpful to remove an x from our K-expression to make it easier to solve. This can be very helpful when we'd otherwise end up with a third degree equation of x. If the initial concentration of a reactant or product is large and the equilibrium constant is very small then the equilibrium constant subtracted from the concentration will be approximately equal to simply the concentration. In other words: $[A] - x \approx [A]$. If you can ignore an x in this manner to transform a third degree equation into a quadratic equation, do it.

To verify that your result for x is accurate enough using this approximation, compare your result for x with the number it was subtracted from. If $x/[A] < 0.05$, then you're fine to use this value for x. If the approximation is judged as not being close enough then do successive approximations. Take the value of x calculated by removing one of the x's from the equation and substitute it for the very x that was taken out (not any of the other x's) and solve for x again. This result should be closer. Keep repeating this process until successive solutions are the same within significant figures.

16.1   Le Chatelier's Principle

Because of **Le Chateliers Principle**, when a chemical system at equilibrium is disturbed, the system shifts in the direction that minimizes the disturbance and brings it back into equilibrium.

Concentration Change

If reactant is added or product is removed from a system at equilibrium, the reaction will shift to the right, producing more product and bringing the system back into equilibrium.

If product is added or reactant is removed from a system at equilibrium, the reaction will shift to the left, producing more reactant and bringing the system back into equilibrium.

Think of a teeter-totter with reactants on the left and products on the right. If the balance is disturbed (e.g. by adding reactants) the side of the teeter-totter that goes up (the right side) is the side that the reaction shifts to to bring it all back into balance.

This is not true if the thing being added is solid or liquid since adding or removing solids and liquids does not affect equilibrium because their concentrations are constant.

Volume or Pressure Change

A volume or pressure change only affects gaseous reactions. Remember the inverse relation between pressure and volume.

If the volume is increased (or the pressure decreased) then the reaction has more room for gas molecules and so the reaction will shift toward the side that has the most gas molecules (sum the gas coefficients for each side and compare).

If the volume is decreased (or the pressure increased) then the reaction will shift to the side that has fewer gas molecules.

When considering only the effect of a volume/pressure change, we assume that the temperature stays constant.

Temperature Change

If the temperature of a system is changed (volume/pressure is assumed constant) then the system will shift in the direction that counters that change.

The easiest way to think of it is to add a heat term into the chemical equation

$$A + B \longleftrightarrow C + \text{heat}.$$
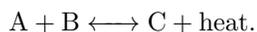
For an exothermic reaction ($\Delta H < 0$), the heat term goes on the right side. For an endothermic reaction, the heat term goes on the left side.

For an exothermic reaction, adding heat is like adding more product, which causes the reaction to shift to the left. Lowering the heat is like removing product, which causes the reaction to shift to the right. For an endothermic reaction, adding heat is like adding a reactant, which causes the reaction to shift to the right. Removing heat is like removing reactant, which causes the reaction to shift to the left.

1. If temp is increased, the reaction shifts in the endo direction.
2. If temp is decreased, the reaction shifts in the exo direction.

You can even use the teeter-totter analogy with temperature changes. If heat is added then the side containing heat gets heavier pushing the other side higher.

Several things to remember:

1. Adding an inert gas to a gaseous reaction does not affect the equilibrium because the partial pressures of the active gases are still the same, relatively speaking.
2. Adding a catalyst has no effect on equilibrium because all that a catalyst does is increase the speed at which a reaction reaches equilibrium.
3. You can also plug concentration changes into the K expression to see how they affect K. If K goes up, the reaction goes left.

The equilibrium constant is actually related to the rate constants (from the rate laws) for the forward and reverse reactions. Specifically,

$$K_c = \frac{k_f}{k_r}.$$

Chapter 17

Acids and Bases

There are three definitions of acid-base.

17.1   Arrhenius Definition

- Acids are substances that produce H^+ ions in aqueous solutions.
- Bases are substances that produce OH^- ions in aqueous solutions.

The problem with this definition is that it only applies to aqueous (water) solutions.

17.2   Bronsted-Lowry Definition

- Acids are proton (i.e. H^+ ion) donors.
- Bases are proton (i.e. H^+ ion) acceptors.

This is the most commonly used definition and is the one that we'll primarily be using. Under this definition, acids and bases always occur together. In the acid base reaction, the acid donates an H^+ ion to the base, converting what had been an acid to a base (on the other side of the reaction arrow) and converting what had been a base to an acid.

Some substances are **amphoteric** which means they can act as acids or bases. Examples include H_2O, and HSO_4^-.

A **conjugate acid-base** pair consists of 2 substances related to each other by the transfer of a proton. To go from acid to conjugate base, subtract H^+. To go from base to conjugate acid, add H^+.

A **strong acid** completely ionizes in solution and the reaction is represented with a right-pointed arrow since the reverse reaction is negligible. A **weak acid** only partially ionizes in solution. Since the reverse reaction is strong, such a reaction is represented with a double arrow.

The higher the oxidation number of the central atom, the stronger the oxyacid. Remember that O has an oxidation state of -2 and H has an oxidation state of $+1$. Generally, the more O atoms in the acid, the stronger the acid is. A positively charged (cation) acid is stronger than a neutral acid which is stronger than a negatively charged acid (anion). The trend for bases is the opposite–a negatively charged base is stronger than a neutral base which is stronger than a positively charged base.

The strong acids that you should memorize are the following. Note, you can also check a table. If their K_a values are listed as strong or are unlisted, then it's a strong acid.

- HBr
- HCl

- HI
- H_2SO_4
- HNO_3

If the attraction between the anion (i.e. the conjugate base) and cation portions of an acid molecule are weak, then they are easily separated and easily dissolved in solution, making it a strong acid. If the attraction is strong, then they are not easily separated and thus make a weak acid. In general, the stronger the acid, the weaker the base, which means the forward reaction is strong and the reverse reaction is weak.

A **monoprotic acid** has one ionizable proton and a **diprotic acid** has two ionizable protons (i.e. H^+'s). A **polyprotic acid** has multiple ionizable protons.

The relative strengths of weak acids are measured with the **acid ionization constant**, K_a, which is the equilibrium constant for the ionization of a weak acid. Consider the following generic acid-base reaction with water as the base

$$HA(aq) + H_2O(l) \longleftrightarrow H_3O^+(aq) + A^-(aq).$$
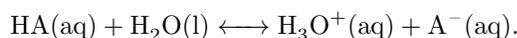
The acid ionization constant is calculated just like the regular K, by dividing the concentrations of products by concentrations of reactants, ignoring solids and liquids

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}.$$

Because water is amphoteric, it can act both as an acid and a base. Both of these happen in pure water and the phenomenon is called **autoionization**

$$H_2O(l) + H_2O(l) \longleftrightarrow H_3O^+(aq) + OH^-(aq).$$
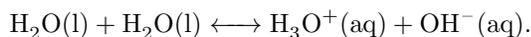
This can be quantified with the equilibrium constant for the autoionization reaction at $25\,°C$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}.$$

K_w is the **ion product constant** for water. In pure water the concentration of H_3O^+ or H^+ equals the concentration of OH^-. Since they're equal, their concentration is $\sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$ M. An **acidic solution** contains more H_3O^+ than pure water does. A basic solution contains more OH^- than pure water does. However, in both cases, the product of their concentrations remain the same: 1.0×10^{-14}. Because this is an equilibrium situation, increasing the H_3O^+ concentration by adding an acid, will shift the reaction so that the concentration of OH^- decreases such that the product of the two concentrations is still the ion product concentration. Given the concentration of one or the other we can easily calculate the concentration of the other by using the ion product constant for water.

pH is defined as

$$pH = -\log[H_3O^+].$$

The pH scale goes from 0 to 14 with

- pH < 7 = acidic
- pH = 7 = neutral
- pH > 7 = basic

Note, when taking the logarithm of a number the significant figures you should use are the sum of the sig figs of the original number plus the power that the factor of ten is raised to. In other words, the logarithm you get should have the same number of decimal places as the number of significant figures in your input.

The pOH scale is the same thing except that it's defined with respect to the concentration of OH^-

$$pOH = -\log[OH^-].$$

Note that
$$pH + pOH = 14.$$

The pK_a of an acid is also a way to quantify its strength. The larger the K_a, the stronger the acid. The smaller the pK_a, the stronger the acid.

$$pK_a = -\log(K_a)$$

When calculating the pH of a solution it depends on whether you're dealing with a strong acid or a weak acid. A strong acid, because it ionizes completely, and because the contribution of H_3O^+ from autoionization is negligible, we can assume that the concentration of H_3O^+ is simply equal to the concentration of the strong acid that was added.

Because weak acids only partially ionize, it's not so straightforward to calculate the concentration of H_3O^+. To calculate the pH we have to solve an equilibrium system and we do this by setting up an ICE table after first building an acid-base equation for the given acid. Since we have the initial concentration of the acid, and we assume the initial concentrations of H_3O^+ and OH^- to be 0, we find equilibrium concentrations involving x. We then solve for x by looking up the K_a of the acid in the back of the book, setting up an equilibrium expression, and solving for x. Often we can use the *x is small* approximation, which makes it a lot easier to solve for x. In fact, whenever the K_a of the acid is 1.0×10^{-5} or less, we can use this approximation. After we find x we still have to calculate the concentration of H_3O^+ and pH.

The **percent ionization** of a strong acid is 100%. The percent ionization of a weak acid is the concentration of H_3O^+ at equilibrium over the initial concentration of the acid all times 100. The equilibrium concentration of H_3O^+ of a weak acid increases with increasing initial concentration of the acid, but the percent ionization of a weak acid decreases with increasing concentration of the acid.

When you have a strong and a weak acid together in solution, the strong acid will be 100% converted into H_3O^+. Le Chatelier's principle tells us that H_3O^+ generated by the weak acid and autoionization of water will be suppressed to negligible levels. Therefore, with a strong and a weak acid, to find the pH we simply use the initial concentration of the strong acid.

When you have two weak acids together in a solution, we compare the K_a of the weak acids by checking a table of those values. Then we assume that the strongest of those will overpower and suppress all the others and solve as we would with a single weak acid–by using an ICE table and equilibrium expression.

Strong bases are analogous to strong acids in that they dissociate completely in solution. The group 1A and 2A metal hydroxides are all strong bases, but the group 2A ones are only slightly soluble.

Unlike diprotic acids, such as H_2SO_4, which dissolve in a 2-step process, bases with two hydroxide ions, such as $Mg(OH)_2$, will dissociate completely in a single step. Therefore, such a base will produce two moles of OH^- for every mole of base added.

Weak bases, are analogous to weak acids. Strong bases, such as NaOH, typically contain one or more OH^- ions. Weak bases typically don't–they ionize water to produce the OH^-. The ionization of a weak base is quantified by the **base ionization constant**, K_b. The smaller the K_b, the weaker the base.

$$B(aq) + H_2O(l) \longleftrightarrow BH^+(aq) + OH^-(aq)$$
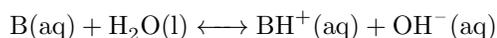
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Finding the pH of basic solutions involves the same procedures as with acidic solutions except that you use K_b instead of K_a, you look at OH^- instead of H_3O^+, and you look at pOH instead of pH, only in the end, converting the pOH to pH.

Some anions act as weak bases. Any anion can be thought of as the conjugate base of an acid. Cl-, for example, is the conjugate base of HCl, and F^- is the conjugate base of HF. Therefore, every anion can potentially act as a base. However, an anion that is a conjugate base of a strong acid such as Cl^- (HCl is a strong acid), is not basic–it is neutral. You can understand this by considering the reaction of HCL and water. Since HCl is a strong acid, the reaction goes far to the right because Cl^- does not have a significant affinity for H^+, meaning, it doesn't pull H^+ out of the solution making it less acidic. On the other hand, an anion that is the conjugate base of a weak acid is itself a weak base.

To find the pH of a solution containing an anion acting as a weak base, we need the K_b for the anion. This can be calculated from the K_a of the corresponding acid, by using the relationship

$$K_b K_a = K_w = 1.0 \times 10^{-14}.$$

The relationship may also be useful

$$pK_b + pK_a = 14,$$

may also be useful.

Some cations can act as weak acids:

- The counter ions of strong bases (Na is for example the counter ion in the strong base NaOH) are pH-neutral.
- Cations that are the conjugate acids of weak bases (for example the cation NH_4^+ is the conjugate acid of the weak base NH_3) are themselves weak acids.
- Cations that are small highly charged metals (such as Al^{+3}) are weakly acidic in solution.

To determine whether a salt, which contains both a cation and an anion, will form an acid or base when put in solution, we must consider the cations and anions individually.

- Neutral cation + neutral anion = neutral
- Acidic cation + neutral anion = acidic
- Neutral cation + basic anion = basic
- Acidic cation + basic anion = use K values from table to compare relative strengths and determine which will overpower the other.

A polyprotic acid is relieved of its H's in a step-wise fashion rather than all at once. Since the second K_a is typically much smaller than the first K_a, the H_3O^+ ions contributed by the second step are negligible and to calculate the pH, we use the same process and do it only for the first step. The only exception, for us, is with a dilute solution of sulfuric acid. In this special case, we have to find the contribution of H_3O^+ for both steps. Since the acid is strong in the first step, the concentration of H_3O^+ that results from the first step is equal to the concentration of acid that was added. For the second step we use an ICE table and an equilibrium expression to calculate the H_3O^+ contributed by the second step. Note, the initial concentration of H_3O^+ for the second step is the concentration of H_3O^+ contributed by the first step.

For a molecule to be acidic it must be able to give up an H^+ ion when in water. First of all, it must contain an H. For binary molecules containing H and another element, the bond polarity and bond strength both affect the molecule's acidity. If the bond is polar and the positive charge is on the H part of the molecule, then it's easier for the molecule to give off an H^+. If the minus charge is on the H, then the molecule may give off an H^- which, by definition, would have nothing to do with acidity. Bond strength is also a factor. For a molecule to be acidic it must be able to give an H^+ ion, so the weaker the bond, the more likely it is to give that up, and the more acidic.

An oxyacid has the H bonded to an O which is bonded to a Y. The more electronegative that Y is, the more that it pulls the electron density away from H–O making the

bond weaker and the molecule more acidic. Also, the more O's that are attached directly to Y, the more they pull the electron density away from H–O weakening the bond, and making the molecule more acidic.

17.3   Lewis Acids

In the Lewis model of acids and bases, the focus is on the electron pair (that accepts the H^+) rather than on the H^+.

- Acids are electron pair acceptors (i.e. electrophiles).
- Bases are electron pair donors (i.e. nucleophiles).

In Lewis acid-base theory, instead of acids, we have an electrophile–something that is attracted to the lone electron pair of the nucleophile (Lewis base). To complete a Lewis acid-base reaction, first make Lewis structures for each element, denoting electrons, charges, and bonds.

The substance with free electrons (the nucleophile) "attacks" the substance with an open (electron-free: incomplete octet) position on the core atom of the electrophile. Some molecules, that may not initially contain empty electron orbitals (i.e. open position) can rearrange their electrons in order to act as Lewis acids.

Since highly charged metal cations have lost electrons and have empty orbitals, they can act as Lewis acids. Under Lewis model, a substance that doesn't even contain H can be an "acid".

Chapter 18

Aqueous Ionic Equilibrium

A **buffer** contains significant amounts of both a weak acid and its conjugate base (or a weak base and its conjugate acid) and it resists pH change by neutralizing added acid or base. Both a weak acid and its conjugate base (or vice versa) must be added since weak acids don't ionize enough to create enough conjugate base to create buffers.

If a weak acid and its conjugate base are both added to a solution, the ionization of the weak acid is suppressed (because of Le Chatelier's principle) relative to what it would be if the conjugate base had not been added. This is known as the **common ion effect** since the solution contains two substances, the weak acid and its conjugate base, that share a common ion.

To calculate the pH of a buffer solution you must account for the fact that instead of just adding an acid (i.e. initial row of the ICE table contains only an amount under the left side of the arrow), you are also adding its conjugate base (i.e. the initial row of the ICE table contains an entry on both sides of the reaction arrow). When doing the ICE table, ignore the cation of the conjugate base and write only the conjugate base (anion) just like you would if you were adding only the weak acid. However, now instead of an initial amount of zero for the conjugate base, you're adding some amount.

If we set up an equilibrium expression and assume that x is small, we can solve for $[H_3O^+]$ which gives us the **Henderson-Hasselbalch equation**

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}.$$

The simple method above should only be used when the *x is small approximation* is valid. In general, this means the initial concentrations of the weak acid and conjugate base should be at least 10^2 to 10^3 times greater than the equilibrium concentration of the acid.

Although a buffer solution resists a pH change, it will still change slightly when an acid or base is added. To calculate the change in pH we have to break the problem into two parts:

1. A stoichiometric calculation: Adding a small amount of a strong acid causes the stoichiometric equivalent of conjugate base in the buffer to be converted to the conjugate acid (subtract from conjugate base and add to acid). Adding a small amount of base causes the stoichiometric equivalent of the acid to convert to the conjugate base (subtract from acid and add to conjugate base). Set up a table (not an ICE table) that tracks the these changes by having a row for before changes, amount added, and after addition. It's best to track these changes in moles rather than molarity or anything else. When adding a small amount of a strong base to a buffer, a stoichiometric equivalent of the weak acid is converted to the conjugate base.

2. An equilibrium calculation: Since adding a small amount of acid to a buffer is equivalent to changing the initial concentrations of the acid and conjugate base

present in the buffer, we can calculate the pH of the changed system using the same methods (ICE table or Henderson-Hasselbalch equation) as we do for a regular buffer solution. Consider the initial amount of H_3O^+ or OH^- to still be zero.

When using the Henderson-Hasselbalch equation to calculate the pH of a base/conjugate acid buffer solution, we must convert pK_b to pK_a in order to use the equation. The conversion is

$$pK_a = 14 - pK_b.$$

If you want a buffer with pH > 7, make a buffer using a base and its conjugate acid rather than an acid and its conjugate base.

Remember that buffers generally work within a range of 1 pH unit from their pKa.

In an **acid-base titration**, an acidic (or basic) solution of unknown concentration is reacted with a basic (or acidic) solution of known concentration. The known solution is slowly added to the unknown one while the pH is monitored. As the acid and base combine, they neutralize each other. At the **equivalence point**—when the moles of acid equal the moles of base–the titration is complete. A plot of the pH during titration gives us a **titration curve** or **pH curve**. The point of inflection in the middle of the curve is the equivalence point.

Titrating a strong acid/base with a strong base/acid

1. The initial pH (acid only) is calculated simply from the acid concentration.
2. To calculate the pH after adding a little base, you must not only recalculate the remaining moles of H_3O^+ but you must recalculate the volume of the solution.
3. At the equivalence point, the pH is 7.00 (at $25\,°C$). This is the case for the all strong acid-strong base titrations.
4. To calculate the pH after adding still more base (base in excess turns the solution basic), you have to realize that all of the H_3O^+ has been neutralized and now there is some OH^- left over. First you have to calculate the pOH based on the OH^- and then convert that to pH.

The titration of a strong base with a strong acid is essentially the same except the curve starts high (initially basic) and drops down to the right (becomes more acidic as acid is slowly added.

Titrating a weak acid/base with a strong base/acid

1. The initial pH involves only the weak acid and so an ICE table is used.
2. After adding a little bit of base, the pH is calculated by realizing that the moles of OH- (from moles of base) added to the solution equals the moles of weak acid that has been converted to the conjugate base. So, you have to calculate the change in acid and the change in conjugate base and then calculate the pH using an ICE table or the Henderson-Hasselbalch equation (since the solution is now a buffer. Remember, not only has your weak acid decreased by the stoichiometric equivalent of the strong base you added, but that weak acid didn't just disappear—it was converted into the conjugate base. Your ICE table's initial row should contain two entries (one for the weak acid and the other for the conjugate base on the other side of the arrow).
3. At the half-equivalence point, enough base has been added to convert half of the weak acid to its conjugate base. Since there are now equal moles of acid and equal moles of conjugate base, the pH now equals the pKa. Since $pH = pK_a$ halfway to the equivalence point, titrations can be used to measure the pK_a of weak acids.
4. At the equivalence point, the moles of OH^- (from the base) added now equals the original moles of weak acid, and so all of the weak acid has been converted to conjugate base and it is no longer a buffer. Since it now contains an ion acting as a weak base (the conjugate base) the solution is moderately basic at its equivalence

point (the pH curve still looks essentially the same—it's just translated upward). To calculate the pH at the equivalence point we have to solve an equilibrium problem involving the ionization of water by the conjugate base. When calculating the initial concentration of the conjugate base, remember to take into account that the solution now has a larger volume than it originally had. Also when solving the equilibrium expression, after creating an ICE table, you find the K_b of the base and convert to K_a.

5. If more base is added, the solution contains both a strong base and a weak base. The strong base completely overwhelms the weak base making it easier to calculate the new pH. Calculate the OH^- concentration by dividing the amount of OH^- remaining by the total volume.

A simple way of calculating the pH's at different titration points when titrating a weak acid (or weak base) with a strong base (or strong acid):

1. Before any titrant is added: Calculate it as a weak acid (or weak base) solution
2. After small amount of titrant is added: Calculate it as a buffer solution (with Henderson Hasselbalch equation).
3. At the half titration point: $pH = pK_a$
4. At the equivalence point: Calculate it as a weak base (or weak acid) because all the original has been converted to its conjugate.
5. Calculate it as a strong base (or strong acid) since the strong stuff overwhelms the conjugate of the original acid or base.

The titration of a weak acid by a strong base will always have a basic equivalence point. Similarly, the titration of a weak base by a strong acid will always have an acidic equivalence point.

The difference between titrating a strong acid and a weak acid are that when a strong acid is neutralized its conjugate base does nothing (because it's completely overwhelmed), but when a weak acid is neutralized its conjugate base is relevant. Just remember that the process of calculating the pH of the solution depends on where along the titration curve you are.

When a diprotic acid is titrated and the Ka's are sufficiently different, then the pH curve will have 2 equivalence points.

Solubility comes in degrees. The equilibrium expression for a chemical equation representing the dissolution of an ionic compound is the **solubility product constant**, K_{sp}.

The K_{sp} for a substance is constant for the given temperature in any solvent. The molar solubility, however, can vary depending on things like the kind of solvent being used.

Because the K_{sp} is an equilibrium expression relating the solubility constant (K_{sp}) and molarity, you can solve for the molar solubility (moles of solid that dissolves per liter) using an ICE table. The x in this case, represents the molar solubility. Using the same process, you can solve for the K_{sp} given the molar solubility.

K_{sp} values for two different compounds can be compared to gauge relative solubility only if the stoichiometry is the same for both. For example, if AY has a smaller K_{sp} than BZ, then AY also has lower solubility than BZ. However, if AY_2 has a smaller K_{sp} than BZ, then AY_2 will not necessarily be less soluble than BZ given that AY_2 dissolves to form 3 particles per formula unit.

A common ion in a solvent, will change the molar solubility of an ionic compound. For example, if you dissolve NaCl in a solvent that already contains Cl^- ions, less of the NaCl will dissolve than it would in pure solvent. Le Chatelier's principle indicates that the common ion shifts the reaction more toward the reactant (insoluble) side. The exact solubility can still be worked out. When doing the ICE table for the dissolution reaction simply account for the pre-existing ion present in the "initial" row of the ICE table.

In general, the solubility of an ionic compound with a basic anion increases with increasing acidity (decreasing pH). For example, NaOH dissolves less than normal in a

basic solution because of the pre-existing OH^- in the solution. However, it dissolves a lot more than normal in an acidic solution because the presence of H_3O^+ to neutralize the dissolving OH- drives the dissolution reaction far to the right.

To convert between molar solubility and K_{sp} for the generic dissolution equation $M_nX_m(s) \longleftrightarrow nM^{m+}(aq) + mX^{n-}(aq)$, use the formula

$$\text{molar solubility} = \sqrt[(n+m)]{\frac{K_{sp}}{n^n m^m}}.$$

The idea of equilibrium allows us to take a second look at equilibrium reactions. If $Q < K_sp$ (remember that Q is simply equilibrium expression applied to anywhere– not necessarily at equilibrium), then the solution is unsaturated and more solid can be dissolved. If $Q = K_sp$, then the solution is saturated will not dissolve in the solution. If $Q > K_sp$, the solution is supersaturated and the solid will typically precipitate out as the reverse reaction engages.

To check if a combination of solutions will result in a precipitation, you need to know the substances and their concentrations in the combined solution. Then list all the possible products. For example, a solution of AB and CD could precipitate AD and BC. Check the solubility table to find the solubility constants for the potential products. If they're not listed, then they're probably considered "soluble" in the classic sense and won't easily form precipitates. If one of the potential products is listed, write out the dissolution reaction for that product and build a Q-expression. Figure out the molarities of the ions (depends on the stoichiometry) and plug them into the Q-expression. If $Q > K_sp$ for the compound, then some of it will precipitate out of solution when the two are combined.

We now have the tools to make a far more accurate prediction of the theoretical yield of a precipitation reaction.

Selective precipitation is when a specific ion in a solution is isolated from the other ions by causing it or everything else to precipitate out of solution. For example, if you have 2 ions, A and B in a solution, and AZ has a much smaller K_{sp} than BZ, then AZ will precipitate out of solution at a much lower concentration. Therefore, you can add something like CZ that is soluble (C being something like Na or K that is completely soluble), and the Z will cause the AZ concentration to become supersaturated and precipitate before the same happens with BZ. With this knowledge, you can calculate the minimum CZ that must be added to trigger precipitation of AZ.

You can also calculate the concentrations of ions left over after selectively precipitating some or all of the one ion. Since the CZ you're adding will cause A to precipitate out of solution, it's not as simple a calculation to determine how much CZ you must add to trigger the precipitation of BZ. First find the the concentration of Z at which BZ will begin to precipitate. Then plug this value for [Z] into the Q-expression for the dissolution of AZ to see how much AZ will still be in the solution when [Z] reaches that point.

Qualitative analysis is the step-by-step process of selective precipitation to figure out the metal ions that exist in a solution.

Transition metal ions tend to be good electron acceptors (Lewis acids). In aqueous solutions, water molecules act as electron donors (Lewis bases) to hydrate transition metal ions. For example, silver ions Ag^+ are hydrated in water to form $Ag(H_2O)_2^+(aq)$. Species such as this are known as **complex ions**, which contain a central metal ion bound to one or more **ligands**—neutral molecules or ions that act as a Lewis base with the central metal ion. If a stronger Lewis base (than water) such as NH_3 is put in the same solution, the NH_3 displaces the H_2O in the complex ion as shown in the reaction equation $Ag(H_2O)_2^+(aq) + 2 NH_3(aq) \longleftrightarrow Ag(NH_3)_2^+(aq) + 2 H_2O(l)$.

When asked to show the equation for a complex ion formation, we're not expected to know how many ligands will bond with the ion. What we do is check the table in the back of the book to see how many there are.

The equilibrium constant associated with the reaction for the formation of a complex ion such as the one above is called the **formation constant**, K_f. Generally, the formation constant is large—meaning that solubility of the complex ion is highly favored. This means an essentially insoluble substance, such as AgCl, can sometimes easily by dissolved by adding a base stronger than water—turning the substance into a complex ion.

Chapter 19

Free Energy and Thermodynamics

Chemical kinetics tells us how fast chemical reactions will occur. Equilibrium constants tell us how for they will go. Now, thermodynamics will tell us why these reactions occur in the first place.

The driving force behind chemical and physical change in the universe is **entropy**, which is related to the dispersion of energy. Nature tends toward that state which in which energy is spread out to the greatest extent possible. Although it may not seem obvious at first glance, every change increases entropy in the universe. Nature takes a cut, a "heat tax", on every exchange of energy. Not only can we not create more energy in a chemical reaction (due to the conservation of energy), but we can't even break even on a chemical reaction.

A fundamental goal of thermodynamics is to predict spontaneity. A **spontaneous reaction** is one that occurs without ongoing outside intervention (e.g. iron in an oxygen atmosphere will spontaneously rust, but water will not spontaneously decompose into H and O). A nonspontaneous reaction is not impossible, but it can be made spontaneous by coupling it with another process that is spontaneous—such as an external energy source.

Much like mechanical potential energy tells us which direction an object will "fall" all on its own, the goal of thermodynamics is to develop a system of chemical potential energy that tells us which direction a reaction will proceed if left to itself. Most spontaneous reactions are exothermic, but not all of them (e.g. ice melting above $0\,°C$). Keep in mind that there's a difference between the two concepts.

The criteria for spontaneity in chemical systems is entropy, S. Entropy is a thermodynamic function that increases with the number of energetically equivalent ways to arrange the components of a system to achieve a particular state. Entropy can be calculated as

$$S = k \ln W,$$

where k is Boltzmann's constant, and W is the number of microstates–the number of energetically equivalent ways to arrange the components of the system. Boltzmann's constant is $1.3807 \times 10^{-23}\,\text{J/K}$, which is the gas constant divided by Avogadro's number.

For example, when considering a gas with a given set of conditions; pressure, volume, and temperature, then we know the energy of the system (i.e. the macrostate). However, we don't know exactly how that energy is distributed. We don't know exactly which atoms have how much energy. Each possible configuration of the system (that still yields the same macrostate) is a microstate. The number of possible microstates a given macrostate has is the W in the entropy equation for that system. This implies that an element in gaseous form has higher entropy than it in liquid form which has higher entropy than it in solid form.

The **first law of thermodynamics** is that energy is conserved.

The **second law of thermodynamics** states that for any spontaneous process, the entropy of the universe increases. The criterion for spontaneity in this case is the entropy of the universe. Processes that increase the entropy of the universe, occur spontaneously.

Entropy is a state function, so

$$\Delta S = S_{final} - S_{initial}.$$

If ΔS is positive, then the process is spontaneous.

A chemical system proceeds in a direction that increases the entropy of the universe. For example, if you have two beakers connected to each other with a tube, and you add a gas to the one beaker, the gas will spread into the other beaker too. This is because there are more microstates in a spread out system than in a system in which the gas is all in one beaker. So by spreading out, the gas is increasing its entropy.

When water freezes, the entropy of the system decreases, however, the entropy of the universe must somehow increase or otherwise water wouldn't spontaneously freeze.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}.$$

The entropy of a system can therefore decrease as long as the entropy of the surroundings increases enough to more than offset that decrease. Because water freezing is exothermic, heat is given off to the surroundings, increasing the entropy of the surroundings.

An exothermic process increases the entropy of the surroundings and an endothermic process decreases the entropy of the surroundings. Although enthalpy cannot by itself determine spontaneity, most exothermic reactions are spontaneous because they increase the entropy of their surroundings (via heat). Spontaneity is dependent on temperature (water spontaneously freezes only under $0\,^{\circ}\text{C}$) because entropy is a measure of energy dispersal (joules) per unit temperature (Kelvins).

For any chemical or physical process occurring at constant temperature and pressure, the entropy change of the surroundings is equal to the energy dispersed into the surrounds divided by the temperature of the surroundings in kelvins

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}.$$

Remember that S has units of J/K so the ΔH must be in Joules rather than kilojoules.

When asked for the sign of the ΔS of the system and you're given a chemical equation, deduce it from the states of the items. For example, if something is changing from liquid to a gas, then entropy is increasing and ΔS is positive. If everything is gaseous but the right side has more gas molecules then the left (meaning something decomposed), then the entropy of the system is positive.

Gibbs free energy is a thermodynamic function that represents the chemical potential of a chemical system. The change in Gibbs free energy at constant temperature (measured in kelvins) is given by

$$\Delta G = \Delta H - T\Delta S.$$

If ΔG is positive, then the reaction is not spontaneous. If ΔG is negative, then the reaction is spontaneous. With this equation we can determine whether a reaction is spontaneous or not by looking at the change in enthalpy, the change in entropy, and the temperature:

- If the reaction is exothermic, $\Delta H < 0$, and the change in entropy for the reaction is positive, then the reaction will be spontaneous no matter what the temperature because $\Delta G < 0$.
- If the reaction is endothermic, $\Delta H > 0$, and the change in entropy for the reaction is negative, then the reaction will not be spontaneous no matter what the temperature because $\Delta G > 0$.

- If the reaction is exothermic, $\Delta H < 0$, and the change in entropy for the reaction is negative, then the spontaneity of the reaction depends on how large the temperature is.
- If the reaction is endothermic, $\Delta H > 0$, and the change in entropy for the reaction is positive, then the spontaneity of the reaction depends on how large the temperature is.

The **standard entropy change for a reaction**, ΔS°_{rxn}, is the change in entropy for a process in which all reactants and products are in their **standard states**. The standard states for the different phases of matter are:

- Gas: Pure gas at 1 atm
- Liquid or Solid: Pure substance in its most stable format 1 atm and at the temperature of interest
- Substance in solution: Concentration of 1M

$$\Delta S^{\circ}_{rxn} = \Delta S^{\circ}_{products} - \Delta S^{\circ}_{reactants}$$

To calculate ΔS°_{rxn} we use **standard molar entropies** (units of J/mol*K), which can be found in tables.

The **third law of thermodynamics** states that the entropy of a perfect crystal at $0\,\mathrm{K}$ is 0.

At $25\,^{\circ}\mathrm{C}$, the standard entropy of any substance is the energy dispersed into one mole of the substance.There are a number of factors that affect the amount of entropy a substance might have:

- State: A gas has higher entropy than liquid which has higher entropy than the solid form.
- Molar mass: The higher the molar mass the higher the entropy.
- Molecular complexity: The more complicated the molecule, the more entropy it has.
- Allotropes: Diamond and graphite are two allotropes of solid carbon, and in this case, graphite has more entropy.
- Dissolution: Dissolving a crystalline solid results in an increase in entropy.

To calculate ΔS°_{rxn} for a reaction, use a table to find the standard molar entropy for each reactant and product. Then we subtract the standard entropies of the reactants multiplied by their stoichiometric coefficients from the standard entropies of the products multiplied by their stoichiometric coefficients

$$\Delta S^{\circ}_{rxn} = \sum n_p S^{\circ}(\text{products}) - \sum n_r S^{\circ}(\text{reactants}).$$

The criterion for spontaneity in a chemical reaction is whether or not the standard change in free energy (ΔG°_{rxn}) is negative or positive. There are three ways, depending on circumstances, in which we can calculate the ΔG°_{rxn} for a reaction:

- The **free energy of formation** ΔG°_{f} is the change in energy when 1 mole of a compound forms from its constituent elements in their standard states. To calculate for a reaction, use

$$\Delta G^{\circ}_{rxn} = \sum n_p G^{\circ}_{f}(\text{products}) - \sum n_r G^{\circ}_{f}(\text{reactants}).$$

  Note, that the free energy of formation for a pure element in standard state is zero. If the resulting ΔG°_{rxn} is negative, then the reaction is spontaneous.
- The drawback of using the above method is that it's only valid at $25\,^{\circ}\mathrm{C}$–the standard temperature for these free energies of formation. If the reaction is taking place at another temperature, then you must do the above process not with ΔG°_{rxn} but with ΔH°_{rxn} and ΔS°_{rxn}. Then you calculate ΔG°_{rxn} by using the equation $\Delta G = \Delta H - T\Delta S$. Be careful that you're using the proper units.

- If you can "construct" your reaction from other reactions with known ΔG°_{rxn} then you can deduce the ΔG°_{rxn} for your reaction of interest. Here are the rules for doing that:

  - If a chemical equation is multiplied by a factor, then ΔG°_{rxn} is multiplied by the same factor.
  - If a chemical equation is reversed, then ΔG°_{rxn} changes sign.
  - If a chemical equation can be expressed as the sum of a series of steps, then ΔG°_{rxn} is the sum of the ΔG°_{rxn} for each of the steps.

Note that ΔH gives the heat given off by an exothermic reaction, but not all of that heat can be used to power something. ΔS for the reaction quantifies the amount of heat that must escape to the surroundings in order to increase the overall entropy of the universe. ΔG, then, is the amount of energy "free" to do work. This is the theoretical limit of the energy that can be harvested from a reaction. In reality, no mechanisms are 100% efficient.

The above calculations give ΔG°_{rxn} in standard conditions, but what about nonstandard conditions which we typically find in life? Then it's calculated using

$$\Delta G_{rxn} = \Delta G^{\circ}_{rxn} + RT \ln Q,$$

where R is the gas constant $8.314 \, \text{J/mol} \cdot \text{K}$ and Q is the reaction quotient.

The free energy change of a reaction is related to the reaction's equilibrium constant by

$$\Delta G^{\circ}_{rxn} = -RT \ln K,$$

where K is the equilibrium constant.

Chapter 20

Electrochemistry

Fuel cells exploit oxidation-reduction reactions.

Electrical current is the flow of electric charge. Electrons flowing through a wire or ions flowing through a solution are both examples of electrical current. Since redox reactions involve the transfer of electrons, they have the potential to generate electrical current.

A **voltaic (or galvanic) cell** is an electrochemical cell that produces electrical current from a spontaneous chemical reaction. An **electrolytic cell** is one that consumes electrical current in order to drive a nonspontaneous reaction.

An **electrode** is a conductive surface through which electrons can enter or leave the half-cells of an electrochemical cell.

Electrical current is measured in units of Amperes, A, each amp which represents the flow of 1 coulomb of charge per second

$$A = \frac{C}{s}.$$

The force that drives electrical current, that is, the force that makes electrons move, is called **potential difference**. It's the measure of the difference in potential energy per unit of charge. The unit for potential difference is the volt, V

$$V = \frac{J}{C}.$$

A large potential difference corresponds to a large difference in charge between the two electrodes and therefore a strong tendency for electron flow. In a voltaic cell, the potential difference between the two electrodes is the **cell potential**, E_{cell}. The cell potential depends on the relative tendencies of the reactants to undergo oxidation and reduction.

In general, cell potential also depends on concentrations of reactants and the temperature. Under standard conditions, the cell potential is called the **standard cell potential**, E°_{cell}, and these values can be looked up in tables.

To understand voltaic (or galvanic cells) such as batteries, consider the chemical reaction $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$ where $E^{\circ}_{cell} = +1.10\,\text{V}$. Zinc metal is giving off electrons to copper ions. How do we harness this movement of electrons (i.e. current)? The first thing we need to do is separate the half-reactions from each other so we can force the electrons to flow through a wire instead of the solution. So we set up a jar containing zinc metal in a zinc ion solution and a second jar containing copper metal in a copper ion solution. Since zinc in this setup "wants" to give electrons to copper, we allow this by now connecting a wire between the two metals. Now, electrons can flow from the zinc to the copper. However, this quickly creates a charge imbalance which stops the reaction unless we add a **salt bridge** which neutralizes the charge buildup by adding charged ions to both solutions.

Electrochemistry   **83**

Cell potential is a measure of the overall tendency of the redox reaction to occur spontaneously–the lower the cell potential, the lower the tendency to occur. A negative cell potential indicates that the reaction is not spontaneous.

The electrode where oxidation occurs (zinc in our case above) is the **anode**. The electrode (copper) where reduction takes place is the **cathode**. Electrons flow from the anode to the cathode.

Line notation is a compact way to describe electrochemical cells. Here's how we write it: Oxidation half-reaction on the left and reduction on the right. A vertical bar separates the different states and a double vertical bar (indicating the salt bridge) separates the half reactions. Our example above would be written as

$$\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}.$$

If we compare an electrode to a **standard hydrogen electrode (SHE)** we can come up with E values specific to each electrode. Then the overall cell potential is the difference in voltage between the cathode (final state) and the anode (initial state)

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}.$$

Remember that:

1. $E^{\circ}_{cell} > 0$ means the reaction is spontaneous
2. The electrode potentials listed in tables are for reduction

To calculate the cell potential for a reaction, first separate it into half-reactions. The oxidation half reaction is the anode and the reduction half reaction is the cathode. Then look up the standard electrode potentials for both half reactions and calculate the overall cell potential using the equation above. Note, do not negate the value for the reversed reaction.

An alternative way of calculating the standard cell potential for a reaction is to write the reduction potential for the item getting reduced and write the oxidation potential (by negating the value in the table) for the one being oxidized. Then simply sum the two numbers to get the overall cell potential. This seems easier because you can just write the numbers right above the equation.

To determine the direction a reaction will spontaneously go, do the above process and if the cell potential is positive, the reaction goes spontaneously to the right. Otherwise, it goes spontaneously to the left.

The relationship between change in Gibbs free energy and standard cell potential is given by

$$\Delta G^{\circ} = -nFE^{\circ}_{cell},$$

Where n is the number of moles of electrons transferred, and F is Faraday's constant, $96\,485\,\text{C/mol}\,\text{e}^-$.

The relationship between the standard cell potential and the equilibrium constant for a redox reaction is

$$E^{\circ}_{cell} = \frac{0.0592\,\text{V}}{n} \log K,$$

Where n is the number of moles of electrons transferred, and K is the equilibrium constant at $25\,°\text{C}$ for the reaction.

The formulas given above calculate cell potential at standard concentrations of $1\,\text{M}$. What if the concentrations are changed? Then we use the **Nernst equation**, which is a variation of the above equation where we use the reaction quotient, Q, instead of the equilibrium constant K

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592\,\text{V}}{n} \log Q.$$

An **electrolytic cell** is the opposite of a galvanic cell. Instead of producing electricity by reacting spontaneously, it consumes electricity in order to cause a nonspontaneous

reaction. Most metals are found in earth's crust as oxides, and they have to be reduced via electrolysis in order to be extracted in pure form.

Electrolysis can also be used to plate a metal onto another metal. For example, if you push a current through an electrolytic cell containing a silver anode, a solution of silver ions, and a cheap metal cathode, the current will oxidize the silver metal anode, causing some of the silver to go into solution (to replenish it). An silver ions from solution will be reduced (converted from aqueous ions to solid metal) at the cheap metal cathode.

The charge labels (i.e. $+$ and $-$) are at opposite places for a voltaic cell and an electrolytic cell. Just remember that the anode is the one that is oxidized, and electrons flow from the anode to the cathode. To be able to figure out the labels, you just have to figure out where the oxidation is occurring and know that electrons are going to move away from there.

To predict the products of electrolysis

1. For a single molten salt, this is easy. The anion (negative ion) will be oxidized (increased) and the cation will be reduced.

2. In a mixture of molten salts there are multiple possibilities for what could be oxidized and what could be reduced. To figure it out, look up the electrode potentials and the pair that has the smallest absolute value (i.e. the pair that is most easily oxidized and reduced) is the pair that matters. This method of using the smallest absolute value is often, but not always correct–there's a better way of interpreting the graph.

3. In aqueous solutions, water can be reduced or oxidized, so you must consider water's potential to be oxidized or reduced and then proceed as in #2.

In electroplating, the amount of metal plated in a given time at a given current, depends on the half-reaction equation for the reaction. For example, in $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$, we see that two moles of electrons are transferred for every mole of solid copper that is plated. We can use Faraday's constant as a conversion factor between charge, C, and moles of electrons. Given a current and a length of time, we can set up a dimensional analysis problem to figure out how many grams of metal are plated for a given time at a given current. For example, if we are electroplating copper for 25 minutes at 5.5 Amp, then 2.7 grams will have been plated:

$$25\,\text{min} \cdot \frac{60\,\text{s}}{\text{min}} \cdot \frac{5.5\,\text{C}}{\text{s}} \cdot \frac{\text{mol}\,e^-}{96\,485\,\text{C}} \cdot \frac{1\,\text{mol}\,\text{Cu(s)}}{2\,\text{mol}\,e^-} \cdot \frac{63.55\,\text{g}}{\text{mol}\,\text{Cu}} = 2.7\,\text{g}\,\text{Cu}$$

Chapter 21

Organic Chemistry

Organic chemistry is the study of carbon-containing compounds. Carbon is a unique element in the diversity of compounds it can form. For example, $C_{10}H_{22}$ can form 75 distinct compounds. Carbon can form chain, branched, and ring structure and it often acts as the backbone of millions of different chemical compounds.

Carbon compounds are diverse for three reasons:
1. Carbon has a tendency to form 4 covalent bonds
2. Carbon has the ability to form double and triple bonds
3. Carbon has a tendency to concatenate (form chains with itself)

21.1   Isomers

Structural isomers are molecules with the same molecular formulas but different structures. There are two types of isomerism.
1. **Geometric isomerisms**: This results from the fact that items connected by a single bond can easily rotate whereas a double bond does not allow rotation. So some double-bonded molecules may have the same molecular formula but a different structure only because of that inability to rotate. **Cis-isomer** is one in which the two items are on the same side of the carbon double bond and a **trans-isomer** is one in which they're opposite each other.
2. **Optical isomers** or **enantiomers** are mirror image molecules. They have the same molecular formula, but a mirrored shape (think left and right hands). A molecule that exhibits this is called **chiral**. Most biological molecules are chiral.

The **carbon skeleton formula** or **line formula** is a way of showing the structure of organic molecules. Each end or bend in the line represents a carbon atom.

21.2   Hydrocarbons and their Naming

Hydrocarbons are compounds that contain only H and C (e.g. gasoline, propane, etc.). Some types of hydrocarbons include
1. Alkanes: Hydrocarbons with all single bonds.
2. Alkenes: Hydrocarbons with one or more double bonds.
3. Alkynes: Hydrocarbons with one or more triple bonds.
4. Aromatic hydrocarbons: Hydrocarbons in a ring formation.

For hydrocarbon naming conventions, refer to chapter 5.

Functionalized hydrocarbons are hydrocarbons with an added **functional group**. For example, methanol (CH_3OH) is the hydrocarbon CH_3 with a functional OH group. It is depicted as R–OH. Different compounds with the same functional group forms a family. Families have some similar characteristics. For example, alcohols are the R–OH

family. The different families are: alcohols, ethers, aldehydes, ketones, carboxylic acids, esters, and amines.

21.3 Organic Reactions

There are several ways in which hydrocarbons react. One way is **combustion** where a hydrocarbon and gaseous oxygen react to form a smaller hydrocarbon and water. The other type of reaction is **substitution**. This is when one or more of the H atoms is replaced by another atom or a string of atoms. This happens frequently with a halogen such as Cl. The result of a substitution reaction of a halogen with an alkane is a **haloalkane**. Hydrocarbons with a double or triple bond (alkenes and alkynes) can also undergo the **addition** reaction. When this occurs, the double or triple bond is broken in order to make room for one or more additional atoms or strings of atoms.

Hydrocarbons can also form a ring of 6 carbon atoms with alternating double and single bonds and an H atom attached to each C atom. This basic ring is called **benzene**. Because molecules containing benzene rings are often aromatic, these compounds are sometimes called **aromatic compounds**. Aromatic compounds are relatively stable, so they don't tend to undergo addition reactions. They will, however, undergo substitution reactions.

Alkanes react with halogens in a substitution reaction called halogenation resulting in a haloalkane. It's a substitution reaction because one of the H atoms on the alkane is replaced with a halogen atom such as Cl or Br. A halogenation reaction consists of 3 steps:

1. Initiation: In this stage, a diatomic halogen gas molecule is cleaved by heat or light. The result is a pair of **neutral radicals**.
2. Propagation: In this step, an H atom on the alkane is replaced by a halogen atom, and another halogen radical is produced to continue the reaction. This stage consists of two steps:
   a) A halogen radical attacks an H on the alkane (it's going to go for an H attached to the C atom with the most non-H bonds, or it's going for the C with the most lines attached). The free radical pulls the H off of the alkane and bonds with it resulting in an acid molecule. The alkane is now a free radical.
   b) Another diatomic halogen molecule is cleaved and one of the free radicals bonds to the alkane. The left over halogen free radical is used to repeat this whole process until the system either runs out of alkane or runs out of halogen.
3. Termination: In this stage, the alkane or the halogen is almost gone and only enough remains for the final step—termination of the reaction. Find two different free radicals from the propagation stage (probably an alkane and a halogen), and combine them in this final step.

Substitution reactions are common in organic chemistry. It occurs when an H atom is replaced with one or more other atoms. An example is halogenation.

Addition reactions are common in alkenes and alkynes. It occurs when one of a double bond pair breaks allowing two more items to be added. For example, the double bond in C_2H_4 can break and add two more hydrogen atoms turning the C_2H_4 alkene into a C_2H_6 alkane.

1. Remember, the double bond can swing either way when it is broken to allow two more atoms to be added
2. Markovnikov addition is when the incoming halogen bonds to the C with the fewest H
3. AntiMarkovnikov addition occurs when the incoming halogen bonds to another C

An **elimination reaction** is like the reverse of an addition reaction. This is the conceptually complicated reaction. Typically, two things, an H atom and another item are eliminated from the molecule. In short, two bonds are broken and a double bond is

formed. This reaction is how an alkane is turned into an alkene.

1. The H being removed is opposite from the leaving group
2. Keep in mind that every C requires 4 bonds. If the bond is not shown, assume an H attachment.
3. According to Zaitsev's Rule, the double bond formed will be the most highly substituted, i.e. the double bond will form where it will have the fewest H atoms directly attached. Zaitsev Rule identifies the major product.

To go from an alkane to an alkene, you take the alkane and add a halogen via a substitution reaction creating a haloalkane. Then you discard the halogen and form a double bond using an elimination reaction. So ALKANE > HALOALKANE > ALKENE.

Chapter 22

Practical Lab Notes

20 drops ≈ 1 mL

Simple tests can verify whether or not a metal is gold or platinum if you know the density of the elements. Simply divide the mass (use a scale to find mass) by the volume (displace it in water).

Laboratory glassware is calibrated to show the correct volume at the bottom of the meniscus.

22.1 Preparing solutions of Specified Concentration

You should be given a solution volume and molarity and your job is to make that amount of solution at that molarity. First figure out the grams of solute you need knowing that molarity is moles of solute over liters of solution. Solve for moles of solute and convert to grams. Add the solute to a beaker with less than the required amount of DI water and stir until the solute is completely dissolved. Dump beaker contents into a volumetric flask and carefully fill the flask with DI water to the specified volume.

To create a solution of specific molarity, first add the required moles of solute to a flask then add solvent until the 1 liter mark is reached.

22.2 Measuring Mass

Make sure the balance is tared before weighing. Place the object to be weighed on a sheet of weighing paper.

22.3 Measuring Density

Symmetric Solids:

1. Measure three sides or height plus radius and calculate volume
2. Weigh it
3. Density = g/cm^3

Amorphous Solids

1. Weigh it
2. Measure the volume of sufficient water in a graduated cylinder
3. Submerge the solid in the graduated cylinder and measure the new volume
4. Density = g/mL

The mL of the measured solid is the difference of measures 2 and 3.

Liquids

1. Weigh empty graduated cylinder
2. Add liquid and measure volume
3. Weigh cylinder plus liquid
4. Density = g/mL

22.4 Measuring Boiling Point

1. Heat a half full 400mL beaker of water over a Bunsen burner as a bath [1]
2. Attach a thermometer to a test tube (containing the liquid to be tested) with a rubber band and hold within the heating water using a ring stand.
3. Add a boiling stone and capillary tube (opening down) to the test tube
4. As soon as there's a continuous stream of bubbles coming from the capillary tube, remove the *whole* apparatus from heat.
5. As soon as the bubbles stop coming from the capillary tube, record the temperature, which is the boiling point temperature.
6. What about the correction factor?

22.5 Using LabQuest

LabQuest is an electronic device to which various scientific probes can be attached to record data. There's a green button at the bottom left corner that stops and starts the recording of data. You can switch between viewing modes of graph and spreadsheet by using the tabs along the top. Export data by going into "File" at the top. Remember how to adjust the mode (e.g. time-based) and the data sampling rate. Note that some TI calculators can also process LabQuest data provided that you get the special connector that allows you to connect LabQuest probes to your calculator.

22.6 Measuring the Absorbance of a Liquid

1. Go to Sensors > Calibrate > USB Spectrometer and calibrate.
2. Put empty cuvette in the holder AFTER the 60s warmup.
3. To measure absorbance, make sure spectrometer is set to FULL SPECTRUM, and press START.
4. STOP as soon as curve appears.
5. Make sure LabQuest has selected the peak. If not, select it by tapping.

22.7 Freezing Point Depression:

Solutions that contain nonvolatile solutes have a higher boiling point and lower freezing point than the pure solvent. The exact temperature elevation and depression are given by the equations:

$$\triangle t_f = m * K_f$$

$$\triangle t_b = m * K_b$$

Just remember that for freezing point, the change is downward and for the boiling point, the change is upward. Also note that the m is molality not molarity.

By measuring the freezing point depression of a substance and knowing it's freezing point depression constant, we can calculate the molality of the solution. Knowing the

---

[1] An explanation can be found on the last two pages of http://www.chem.ucalgary.ca/courses/351/laboratory/boilingpoint.pdf

molality of the solution and the mass of solute combined with mass of solvent, with some algebraic manipulation, we can calculate the molar mass of the solute:

$$\text{molar mass} = \frac{\text{g solute}}{\text{mol solute}} = \frac{\text{g solute}}{m \times \text{kg solvent}}$$

Know how to estimate the freezing point from the graph of temperature vs. time.

22.8   Measuring the rate of a chemical reaction

The order of a reaction can be determined only by experimentation, and it is usually done by the **method of initial rates**. This method involves measuring the initial reaction rate (a short period at the beginning) for several different initial concentrations. For a given reaction, then, a small table is created that contains initial concentrations and initial rates. Compare the relationships between the two sets to determine the reaction rate. For example, if the rate doubles when the concentration is doubled, the initial rate is proportional to the initial concentration, and the reaction is first order. If the rate is constant regardless of the concentration, then the reaction is zero order. If the reaction quadruples when the concentration is doubled, then the reaction is second order.

If the order is unclear, you can substitute any 2 initial concentrations and the corresponding rates into a ratio. k will cancel and you can solve for n:

$$\frac{\text{rate2}}{\text{rate1}} = \frac{k[A]_2^n}{k[A]_1^n}$$

Once the order has been determined, you can substitute it for n in the rate law and solve for k to get the rate constant.

The rate constants of different order reactions have different units:
1. n = 0 has units of $M * s^{-1}$
2. n = 1 has units of s^{-1}
3. n = 2 has units of $M^{-1} * s^{-1}$
   Graphs:
1. Zeroth Order: A plot of the reactant concentration as a function of time (x-axis) yields a straight line with a slope of $-k$ and a y-intercept of $[A_0]$.
2. First Order: A plot of the <u>natural log</u> of the reactant concentration as a function of time (x-axis) yields a straight line with a slope of $-k$ and a y-intercept of $\ln[A_0]$.
3. Second Order: A plot of the <u>inverse (1/x)</u> of the reactant concentration as a function of time (x-axis) yields a straight line with a slope of k and a y-intercept of $1/[A_0]$.

An easier, faster, and better way to deal with half-lives, initial amounts, final amounts, and elapsed time, is to use the appropriate half-life equation to calculate k, and then plug everything into the appropriate integrated rate law to calculate the missing information.

The rates of chemical reactions tend to be highly sensitive to temperature. At around room temperature, a 10 degree C increase in temperature increases the rate of a typical reaction by 2 or 3 times. An increase in temperature, generally results in an increase in k, which is what results in an increased reaction rate.

The **Arrhenius equation** shows the relationship between the rate constant (k) and the temperature in Kelvins:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A.$$

A plot of the natural log of the rate constant ($\ln k$) versus the inverse of the temperature in Kelvins (1/T) (x-axis) yields a straight line with a slope of $-E_a/R$ and a y-intercept of $\ln A$. This allows us to easily determine the frequency factor and activation energy when given a set of rate constants and temperatures.

22.9   Determining Kc from Absorption Info

On a Beer's law plot (absorbance [y-axis] vs. concentration [x-axis]), the slope of the linear line is e, the extinction coefficient.

22.10   Determining Ka of a Weak Acid

Know how to write the chemical equation for an acid dissociating in water. Also know how to write the Ka-expression, which is product concentrations over reactant concentrations with the coefficients becoming exponents. Remember that solids and liquids are not included in the K-expression.

   To calculate the Ka from the experimental determination of pH of a solution created by combining a known volume and molarity of weak acid and NaOH:

1. Calculate the initial moles of weak acid and OH^- from the given molarities and volumes.
2. Calculate the equilibrium moles of weak acid and conjugate base knowing that the NaOH neutralized an equilibrium amount of weak acid and created that same amount of weak base.
3. Then given the above and the new volume of the solution, you can calculate the equilibrium concentrations of the weak acid, the conjugate base, and the H_3O^+ can be calculated from the pH measurement.
4. Then with the above 3, the Ka can be calculated from the equilibrium expression.

22.11   Monitoring Acid/Base Titrations

Remember that at the equivalence point (i.e. inflection point), the moles of acid = the moles of base. The molarity of an unknown acid can be calculated if the volume of unknown acid and the molarity and volume of the strong base at the equivalence point are known:

$$M_{acid} = \frac{M_{base}V_{base}}{V_{acid}}.$$

This equation is derived from the fact that moles acid = moles base at equilibrium and moles = M*V, so $M_{acid}V_{acid} = M_{base}V_{base}$.

   When diluting acids, always add the concentrated acid to the water rather than the water to the concentrated acid. Doing it the other way may generate heat that can cause the acid to splatter.

Chapter 23

Element Data

Atomic Number	Symbol	Element	Atomic Mass	First Ionization Energy (eV)	Ground Shells
1	H	Hydrogen	1.008	13.598	$1s$
2	He	Helium	4.0026	24.587	$1s^2$
3	Li	Lithium	6.94	5.3917	$1s^2 2s$
4	Be	Beryllium	9.0122	9.3227	$1s^2 2s^2$
5	B	Boron	10.81	8.2980	$1s^2 2s^2 2p$
6	C	Carbon	12.011	11.260	$1s^2 2s^2 2p^2$
7	N	Nitrogen	14.007	14.534	$1s^2 2s^2 2p^3$
8	O	Oxygen	15.999	13.618	$1s^2 2s^2 2p^4$
9	F	Fluorine	18.998	17.423	$1s^2 2s^2 2p^5$
10	Ne	Neon	20.180	21.565	$1s^2 2s^2 2p^6$
11	Na	Sodium	22.990	5.1391	[Ne]$3s$
12	Mg	Magnesium	24.305	7.6462	[Ne]$3s^2$
13	Al	Aluminium	26.982	5.9858	[Ne]$3s^2 3p$
14	Si	Silicon	28.085	8.1517	[Ne]$3s^2 3p^2$
15	P	Phosphorus	30.974	10.487	[Ne]$3s^2 3p^3$
16	S	Sulfur	32.06	10.360	[Ne]$3s^2 3p^4$
17	Cl	Chlorine	35.45	12.968	[Ne]$3s^2 3p^5$

18	Ar	Argon	39.948	15.760	$[\text{Ne}]3s^2 3p^6$
19	K	Potassium	39.098	4.3407	$[\text{Ar}]4s$
20	Ca	Calcium	40.078	6.1132	$[\text{Ar}]4s^2$
21	Sc	Scandium	44.956	6.5615	$[\text{Ar}]3d4s^2$
22	Ti	Titanium	47.867	6.8281	$[\text{Ar}]3d^2 4s^2$
23	V	Vanadium	50.942	6.7462	$[\text{Ar}]3d^3 4s^2$
24	Cr	Chromium	51.996	6.7665	$[\text{Ar}]3d^5 4s$
25	Mn	Manganese	54.938	7.4340	$[\text{Ar}]3d^5 4s^2$
26	Fe	Iron	55.845	7.9025	$[\text{Ar}]3d^6 4s^2$
27	Co	Cobalt	58.933	7.8810	$[\text{Ar}]3d^7 4s^2$
28	Ni	Nickel	58.693	7.6399	$[\text{Ar}]3d^8 4s^2$
29	Cu	Copper	63.546	7.7264	$[\text{Ar}]3d^{10} 4s$
30	Zn	Zinc	65.38	9.3942	$[\text{Ar}]3d^{10} 4s^2$
31	Ga	Gallium	69.723	5.9993	$[\text{Ar}]3d^{10} 4s^2 4p$
32	Ge	Germanium	72.630	7.8994	$[\text{Ar}]3d^{10} 4s^2 4p^2$
33	As	Arsenic	74.922	9.7886	$[\text{Ar}]3d^{10} 4s^2 4p^3$
34	Se	Selenium	78.971	9.7524	$[\text{Ar}]3d^{10} 4s^2 4p^4$
35	Br	Bromine	79.904	11.814	$[\text{Ar}]3d^{10} 4s^2 4p^5$
36	Kr	Krypton	83.798	14.000	$[\text{Ar}]3d^{10} 4s^2 4p^6$
37	Rb	Rubidium	85.468	4.1771	$[\text{Kr}]5s$
38	Sr	Strontium	87.62	5.6949	$[\text{Kr}]5s^2$
39	Y	Yttrium	88.906	6.2173	$[\text{Kr}]4d5s^2$
40	Zr	Zirconium	91.224	6.6339	$[\text{Kr}]4d^2 5s^2$
41	Nb	Niobium	92.906	6.7588	$[\text{Kr}]4d^4 5s$
42	Mo	Molybdenum	95.95	7.0924	$[\text{Kr}]4d^5 5s$
43	Tc	Technetium	[97]	7.1194	$[\text{Kr}]4d^5 5s^2$

44	Ru	Ruthenium	101.07	7.3605	$[\text{Kr}]4d^75s$
45	Rh	Rhodium	102.906	7.4589	$[\text{Kr}]4d^85s$
46	Pd	Palladium	106.42	8.3369	$[\text{Kr}]4d^{10}$
47	Ag	Silver	107.868	7.5762	$[\text{Kr}]4d^{10}5s$
48	Cd	Cadmium	112.41	8.9938	$[\text{Kr}]4d^{10}5s^2$
49	In	Indium	114.82	5.7864	$[\text{Kr}]4d^{10}5s^25p$
50	Sn	Tin	118.71	7.3439	$[\text{Kr}]4d^{10}5s^25p^2$
51	Sb	Antimony	121.76	8.6084	$[\text{Kr}]4d^{10}5s^25p^3$
52	Te	Tellurium	127.60	9.0097	$[\text{Kr}]4d^{10}5s^25p^4$
53	I	Iodine	126.90	10.451	$[\text{Kr}]4d^{10}5s^25p^5$
54	Xe	Xenon	131.29	12.130	$[\text{Kr}]4d^{10}5s^25p^6$
55	Cs	Caesium	132.91	3.8939	$[\text{Xe}]6s$
56	Ba	Barium	137.33	5.2117	$[\text{Xe}]6s^2$
57	La	Lanthanum	138.91	5.577	$[\text{Xe}]5d6s^2$
58	Ce	Cerium	140.12	5.5386	$[\text{Xe}]4f5d6s^2$
59	Pr	Praseodymium	140.91	[5.473]	$[\text{Xe}]4f^36s^2$
60	Nd	Neodymium	144.24	5.525	$[\text{Xe}]4f^46s^2$
61	Pm	Promethium	[145]	[5.582]	$[\text{Xe}]4f^56s^2$
62	Sm	Samarium	150.36	5.6437	$[\text{Xe}]4f^66s^2$
63	Eu	Europium	151.96	5.6704	$[\text{Xe}]4f^76s^2$
64	Gd	Gadolinium	157.25	6.1498	$[\text{Xe}]4f^75d6s^2$
65	Tb	Terbium	158.93	5.8639	$[\text{Xe}]4f^96s^2$
66	Dy	Dysprosium	162.50	5.9391	$[\text{Xe}]4f^{10}6s^2$
67	Ho	Holmium	164.93	6.0216	$[\text{Xe}]4f^{11}6s^2$
68	Er	Erbium	167.26	6.1077	$[\text{Xe}]4f^{12}6s^2$
69	Tm	Thulium	168.93	6.1843	$[\text{Xe}]4f^{13}6s^2$

70	Yb	Ytterbium	173.05	6.2542	$[\text{Xe}]4f^{14}6s^2$
71	Lu	Lutetium	174.97	5.4259	$[\text{Xe}]4f^{14}5d6s^2$
72	Hf	Hafnium	178.49	6.8251	$[\text{Xe}]4f^{14}5d^26s^2$
73	Ta	Tantalum	180.95	7.5496	$[\text{Xe}]4f^{14}5d^36s^2$
74	W	Tungsten	183.84	7.864	$[\text{Xe}]4f^{14}5d^46s^2$
75	Re	Rhenium	186.21	7.8335	$[\text{Xe}]4f^{14}5d^56s^2$
76	Os	Osmium	190.23	8.4382	$[\text{Xe}]4f^{14}5d^66s^2$
77	Ir	Iridium	192.22	8.967	$[\text{Xe}]4f^{14}5d^76s^2$
78	Pt	Platinum	195.08	8.9588	$[\text{Xe}]4f^{14}5d^96s$
79	Au	Gold	196.97	9.2256	$[\text{Xe}]4f^{14}5d^{10}6s$
80	Hg	Mercury	200.59	10.438	$[\text{Xe}]4f^{14}5d^{10}6s^2$
81	Tl	Thallium	204.38	6.1083	$[\text{Xe}]4f^{14}5d^{10}6s^26p$
82	Pb	Lead	207.2	7.4167	$[\text{Xe}]4f^{14}5d^{10}6s^26p^2$
83	Bi	Bismuth	208.98	7.2855	$[\text{Xe}]4f^{14}5d^{10}6s^26p^3$
84	Po	Polonium	[209]	8.414(4)	$[\text{Xe}]4f^{14}5d^{10}6s^26p^4$
85	At	Astatine	[210]	9.3175	$[\text{Xe}]4f^{14}5d^{10}6s^26p^5$
86	Rn	Radon	[222]	10.749	$[\text{Xe}]4f^{14}5d^{10}6s^26p^6$
87	Fr	Francium	[223]	4.0727	$[\text{Rn}]7s$
88	Ra	Radium	[226]	5.2784	$[\text{Rn}]7s^2$
89	Ac	Actinium	[227]	5.3802	$[\text{Rn}]6d7s^2$
90	Th	Thorium	232.04	6.3067	$[\text{Rn}]6d^27s^2$
91	Pa	Protactinium	231.04	[5.89(12)]	$[\text{Rn}]5f^26d7s^2$
92	U	Uranium	238.03	6.1941	$[\text{Rn}]5f^36d7s^2$
93	Np	Neptunium	[237]	6.2655	$[\text{Rn}]5f^46d7s^2$
94	Pu	Plutonium	[244]	6.0258	$[\text{Rn}]5f^67s^2$
95	Am	Americium	[243]	5.9738	$[\text{Rn}]5f^77s^2$

96	Cm	Curium	[247]	5.9914	$[Rn]5f^76d7s^2$
97	Bk	Berkelium	[247]	6.1978	$[Rn]5f^97s^2$
98	Cf	Californium	[251]	6.2817	$[Rn]5f^{10}7s^2$
99	Es	Einsteinium	[252]	6.3676	$[Rn]5f^{11}7s^2$
100	Fm	Fermium	[257]	[6.50(7)]	$[Rn]5f^{12}7s^2$
101	Md	Mendelevium	[258]	[6.58(7)]	$[Rn]5f^{13}7s^2$
102	No	Nobelium	[259]	[6.65(7)]	$[Rn]5f^{14}7s^2$
103	Lr	Lawrencium	[262]	(4.90(15))	$[Rn]5f^{14}7s^27p$
104	Rf	Rutherfordium	[267]	(6.01(10))	$[Rn]5f^{14}6d^27s^2$
105	Db	Dubnium	[270]	(6.8(5))	$[Rn]5f^{14}6d^37s^2$
106	Sg	Seaborgium	[271]	[7.8(5)]	$[Rn]5f^{14}6d^47s^2$
107	Bh	Bohrium	[270]	[7.7(5)]	$[Rn]5f^{14}6d^57s^2$
108	Hs	Hassium	[277]	[7.6(5)]	$[Rn]5f^{14}6d^67s^2$
109	Mt	Meitnerium	[276]		
110	Ds	Darmstadtium	[281]		
111	Rg	Roentgenium	[282]		
112	Cn	Copernicium	[285]		
113	Uut	Ununtrium	[285]		
114	Fl	Flerovium	[289]		
115	Uup	Ununpentium	[289]		
116	Lv	Livermorium	[293]		
117	Uus	Ununseptium	[294]		
118	Uuo	Ununoctium	[294]		

gov/asd [2015, May 21]. National Institute of Standards and Technology, Gaithersburg, MD.

Index