AP Exam Review Guide
AP Chemistry

Contents

AP Exam Basics

Logistics

- Monday, May 1
- Starts at 7:30 AM
- Periods Missing: 1, 2, 3 (Both A and B)
- Periods Attending: 4

Format

Total (2 Parts, 195 Minutes, Equation Sheet and Constants Chart Provided)

1. Multiple Choice (60 Questions, 90 Minutes, 50% of Exam Score)
   - Each question is weighted the same
   - Calculator not allowed
2. Free Response (7 Questions, 105 Minutes, 50% of Exam Score)
   - First three questions are "long" free response questions ($\approx$ 23 minutes, 4-6 parts each)
   - Last four questions are "short" free response questions ($\approx$ 9 minutes, 2-3 parts each)
   - Calculator allowed

Resources

Khan Academy Page for AP Chemistry

CollegeBoard Course and Exam Description for AP Chemistry

Past FRQs (1999-2005)

Past FRQs (2006-2013)

Past FRQs (2014-2016)

Workbook of Multiple Choice Questions (Slightly Outdated)

1994 Full Test

1999 Full Test

Past Chemistry Olympiad Tests

1 Chemical Foundations

One of the main goals of chemistry is to relate the macroscopic world (which operates at the scale which we live at) to the microscopic world (which operates at the scale of molecules, atoms, and subatomic particles).

If atoms are the syllables or the letters of the universe, molecules are the words, and just like words they can be rearranged and do completely different things.

The scientific method is composed of the following three steps:

1. Making observations

2. Formulating hypotheses

3. Performing experiments (which produce new observations, and the cycle begins anew)

Hypotheses are assembled into theories. *Theories* (often called models) are a set of hypotheses which give an overall explanation of a natural phenomenon. Theories are interpretations which attempt to explain natural behaviors.

Natural laws are statements which follow from many, many observations and always hold true. For example, the law of conservation of mass (which states that mass of a system is not affected by a chemical change in the system) is a natural law that has never been violated.

A quantitative observation, or measurement, consists of a number and a *unit*, which is essentially a quantifier of which dimension the number describes (mass, length, time, temperature, etc). As scientists we use the SI system, which is the collective of metric units and units derived from metric units. Tables of SI units and prefixes are below.

Fundamental SI Units		
Physical Quantity	Name of Unit	Abbreviation
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Amount of substance	mole	mol
Luminous intensity	candela	cd

Common SI Prefixes			
Prefix	Symbol	Meaning	Exponential Notation
mega	M	1,000,000	10^6
kilo	k	1,000	10^3
hecto	h	100	10^2
deka	da	10	10^1
-	-	1	10^0
deci	d	0.1	10^{-1}
centi	c	0.01	10^{-2}
milli	m	0.001	10^{-3}
micro	μ	0.000001	10^{-6}
nano	n	0.000000001	10^{-9}

A measurement has some degree of uncertainty. The amount to which a measuring device marks, for example, provides a few *certain digits*. After that, an observation as to the location of the measurement between such measuring marks is just that - an observation. It requires estimation and so is an *uncertain digit*.

The *significant figures* of a measurement are all the certain digits of the measurement and the first uncertain digit.

Accuracy refers to the agreement of a particular calculated or measured value with the true value. *Precision* refers to the degree of agreement between several measurements or calculations, showing the degree of reproducibility of a measurement. High precision among several measurements is an indication of accuracy only if systematic errors are absent.

The rules for counting significant figures can be summarized:

1. *Nonzero integers.* Nonzero integers always count as significant figures.

2. *Zeros.* There are three classes of zeros:

   a. *Leading zeros* never count as significant figures.

   b. *Zeros between nonzero digits* always count as significant figures.

   c. *Trailing zeros* are only significant if the number contains a decimal point.

3. *Exact numbers.* Numbers that are counted or defined have infinite significant figures.

For *multiplication and division*, the rule for significant figures is that the result should have the same number of significant figures as the least precise measurement used in the calculation.

For *addition and subtraction*, the rule of significant figures is that the result should have the same number of decimal places as the least precise measurement used in the calculation.

In calculations which involve significant figures, carry the extra digits through to the final result, taking note of how many significant figures are involved in each step, then round until the number

of significant figures involved in the step with the least significant figures is present in the solution to the problem.

Dimensional analysis is the process of applying unit conversions to a measurement or calculation to calculate the value in a different unit or set of units. Through this method long strings of unit conversions can be chained in order to express a measurement or calculation in different units, which can hint at a possible solution.

The two units of temperature commonly seen are *Celsius* (°C) and *Kelvin* (K). Kelvin is a measure of absolute temperature, which in itself is a measure of average kinetic energy of a system. The degree is the same for Celsius and Kelvin; to get Celsius from Kelvin, subtract 273.15 (which has five, not infinite, significant figures); to get Kelvin from Celsius, add 273.15. Kelvin should be used in any and all problems which require temperature as it measures absolute temperature and isn't shifted.

Density is one example of an "identity tag" for substances. Density is defined as

$$\text{density} = \rho = \frac{\text{mass}}{\text{volume}}$$

Matter, defined as anything occupying space and having mass, takes up three elementary states: solids, liquids, and gases. *Mixtures* of solids have variable composition and can be *homogeneous* (having visibly indistinguishable parts) or *heterogeneous* (having visibly distinguishable parts). *Solutions* are homogeneous mixtures and heterogeneous mixtures can usually be split into homogeneous mixtures. All mixtures can be separated into *pure substances* with constant composition by physical methods. These methods include elementary ones like boiling or freezing, where the state of matter changes but the composition of the substance from its molecules does not change.

Some more advanced physical methods are listed below.

- *Distillation*, which depends on volatility and difference in boiling points to create two or more mixtures with differences in those two properties

- *Filtration*, which uses difference in particle or grain size to separate solids from each other, as well as from liquids and gases

- *Chromatography*, which is a series of methods that uses two phases (a solid, or stationary phase and a liquid or gas, or mobile phase) to separate out the analyte due to the analyte's affinities (polarity) for the two phases.
    - *Paper chromatography* is a special type of chromatography which uses a type of porus paper for the stationary phase.
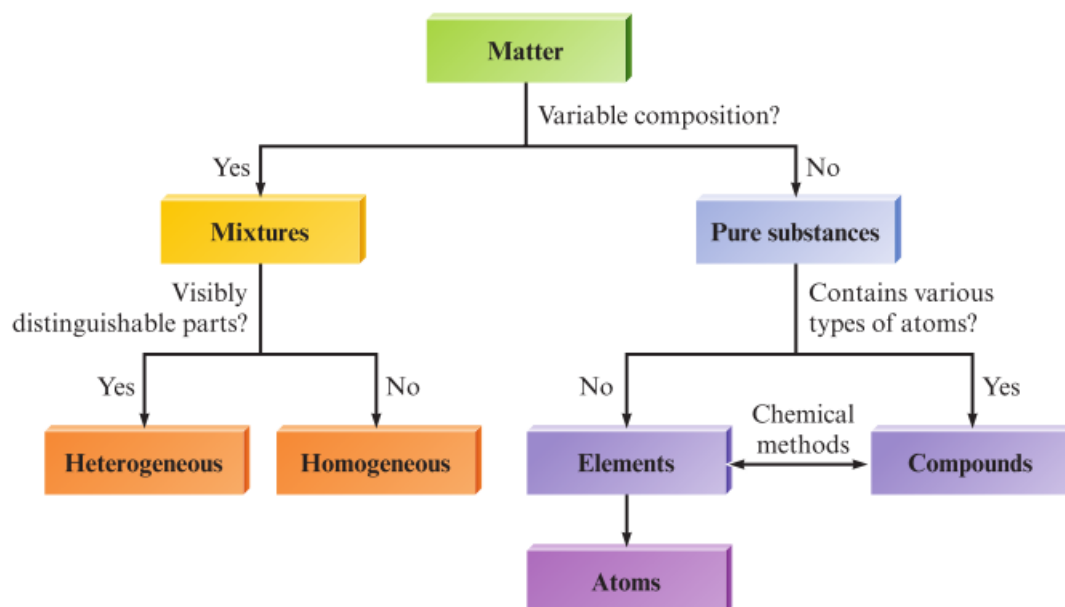
Pure substances are either compounds (combinations of elements) or free elements.

A *compound* is a substance with constant composition that can be broken down into elements by chemical processes.

A *chemical change* is one in which a given substance becomes a new substance or substances with different properties and different composition.

Elements are substances that cannot be decomposed into simpler substances by physical or chemical means.

A chart for the organization of matter is below. All pictures, unless otherwise stated, are from my own drawings or the textbook's diagrams.

Matter

Variable composition?

Yes

Mixtures

Visibly distinguishable parts?

Yes

No

Heterogeneous

Homogeneous

No

Pure substances

Contains various types of atoms?

No

Elements

Chemical methods

Yes

Compounds

Atoms

2 Atoms, Molecules, and Ions

The *law of conservation of mass* states that mass is neither created nor destroyed in a chemical reaction. The *law of definite proportion* states that a given compound always contains exactly the same proportion of elements by mass. The *law of multiple proportions* states that when two elements form a series of compounds, the ratios of the masses of the second element that combine with the same mass of the first element can always be reduced to small whole numbers.

John Dalton's theory of *atoms* is summarized below:

1. Each element is made up of tiny particles called atoms.

2. The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways.

3. Chemical compounds are formed when atoms of different elements combine with each other. A given compound always has the same relative numbers and types of atoms.

4. Chemical reactions involve reorganization of the atoms - changes in the way they are bound together. The atoms themselves are not changed in a chemical reaction.
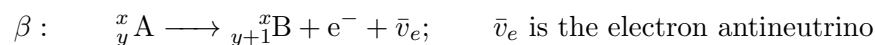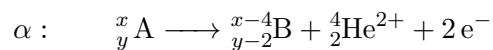
Dalton prepared the first table of *atomic masses* (sometimes called *atomic weights*).

Avogadro proposed that at the same temperature and pressure, equal volumes of different gases contain the same number of particles. This is called *Avogadro's Hypothesis* and holds if the distance between particles in a gas are so great so as to make the size of the actual particles negligible.

J.J. Thompson later posited that atoms had electrons, which he deduced were negatively charged, and that they contained some form of positive charge to balance out. He created the *plum-pudding model* of the atom and calculated the charge-to-mass ratio of an electron as $-1.76\,\frac{\text{C}}{\text{g}}$.

Robert Millikan used oil drops and the charge-to-mass ratio to calculate the mass of the electron as $9.11 \times 10^{-31}\,\text{kg}$.

Henri Becquerel defined *radioactivity* as the emission of radiation by certain elements like uranium. There are three types of radioactive emission: gamma (γ) rays, beta (β) particles, and alpha (α) particles. A γ ray is high-energy "light", a β particle is essentially a high-speed electron, and an α particle has a 2+ charge, which is twice and opposite the charge of the electron. Reactions which demonstrate each type of radioactive decay are below.

$$\alpha: \qquad {}^{x}_{y}\text{A} \longrightarrow {}^{x-4}_{y-2}\text{B} + {}^{4}_{2}\text{He}^{2+} + 2\,\text{e}^{-}$$

$$\beta: \qquad {}^{x}_{y}\text{A} \longrightarrow {}_{y+1}^{x}\text{B} + \text{e}^{-} + \bar{v}_e; \qquad \bar{v}_e \text{ is the electron antineutrino}$$

γ decay results from an unstable nucleus emitting energy as it goes to its ground state; the instability can come from α and β decay; this decay has no reaction (besides putting volts on one side).

Ernest Rutherford used the gold foil experiment to prove that atoms had a *nucleus*, a dense center

with positive charge, surrounded by electrons, with negative charge, a relatively large distance away.

Chemists now know that the nucleus contains *protons*, which have a positive charge equal in magnitude to the electron's negative charge, and *neutrons*, which have about the same mass as a proton but no charge at all. The density of the nucleus with the protons and neutrons compose is extremely high; a pea-sized amount of nuclear material would weigh 250 million tons.

The properties of each element depend on chiefly the number of electrons the element has in its standard state. These electrons comprise the vast majority of the atomic volume and are the reacting components of each atom.

Atoms with the same number of protons but different numbers of neutrons are called *isotopes*.

For a particular atom configured like so:
$$^{A}_{Z}E^{C}_{N}$$

the atomic number Z is the number of protons in the element, the mass number A is the total number of protons and neutrons, the charge C is the total charge or sum of all charges in the element, and the number of atoms N is the number of atoms in the standard state of the element - in diatomic elements, for example, $N = 2$.

The forces that hold atoms together in compounds are called *chemical bonds*. One way a bond is formed is through the sharing of electrons, which forms *covalent bonds*. The resulting collection of atoms is called a *molecule*.

Molecules can be represented through a *chemical formula* where the symbols for the elements indicate the types of atoms present and subscripts indicate the relative numbers of atoms.

Molecules can also be represented by a *structural formula*, in which the individual bonds are shown. Individual bonds are shown, but shapes are not communicated. For example, water can be

$$\text{H} \text{---} \text{O} \text{---} \text{H} \qquad \text{or} \qquad \overset{\displaystyle \text{O}}{\diagup \diagdown} \quad \text{H} \qquad \text{H}$$
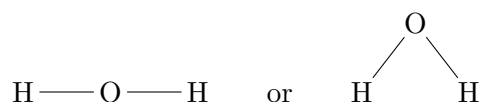
The second model shows the shape of water.

The *space-filling model* of a molecule shows the relative sizes of the involved atoms as well as their relative orientation. *Ball and stick* models do the same except they show linear bonds as well (the 'stick' portion).

An *ion* is an atom or group of atoms that has a net positive or negative charge. A *positive ion* is an ion with less electrons than protons. It is also called a *cation*. Negative ions have more electrons than protons and are called *anions*. Their opposite charges attract and form *ionic bonds* through a force known as *Coulombic attraction*.

A solid consisting of oppositely charged ions is an *ionic solid*. They consist of simple *monoatomic* ions, which have one atom per ion, or in some cases *polyatomic* ions, which have multiple atoms per ion.

The *periodic table* shows all the known elements and gives a lot of information about each element.

Most elements in the periodic table are *metals*, which have characteristic physical properties such as good conductivity of heat and electricity, malleability, ductility, and shininess. Metals tend to lose electrons to form cations, or positive ions.

The relatively few *non-metals* on the periodic table lack the physical properties that characterize the metals. They gain electrons in reactions with metals to form negative ions, or anions.

The periodic table is arranged so elements in the same vertical columns (*groups* or *families*) have similar chemical properties. The first group, the *alkali metals*, are all reactive metals that form ions with a 1+ charge when interacting with non-metals. The second group, the *alkaline earth metals*, form ions with a 2+ charge when reacting with non-metals. The second to last group, the *halogens*, all react with metals to form *salts* (ionic compounds) with a 1- charge. The last group, the *noble gases*, exist under standard conditions as monatomic gases and have little chemical reactivity.

A flowchart for naming chemical compounds is presented here in text form. If the point at the flowchart is a question, let the first option directly below it be "yes" to the question, and the second option directly below it be "no" to the question.

Is the compound an acid?

- Yes; it is an acid; does the anion contain oxygen?
    - Yes; it is an acid where the anion contains oxygen; is the ending of the anion "-ite" or "-ate"?
        * The ending is "-ite"; it is an acid where the anion contains oxygen and ends with "-ite"; the name scheme of such compounds is "(anion root)*ous* acid."
        * The ending is "-ate"; it is an acid where the anion contains oxygen and ends with "-ate"; the name scheme of such compounds is "(anion root)*ic* acid."
    - No; it is an acid where the anion does not contain oxygen; the name scheme of such compounds is "*hydro*(anion root)*ic* acid."

- No; it is not an acid; is the compound a binary compound?
    - Yes; it is not an acid, but is a binary compound; is there a metal present?
        * Yes; it is not an acid, but a binary compound with a metal; does the metal form more than one cation?
            · Yes; it is not an acid, but a binary compound with a metal that forms more than one cation; the compound is a Type II Binary Covalent compound - determine the charge of the cation and use a Roman numeral after the element name for the cation.
            · No; it is not an acid, but a binary compound with a metal which does not form more than one cation; the compound is a Type I Binary Covalent compound - use the element name for the cation.
        * No; it is not an acid, but is a binary compound without a metal; the compound is a Type III Binary Covalent compound - use the Latin prefixes on both the anion (in all cases) and cation (if the subscript is not 1).

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– No; it is not an acid and not a binary compound; are there polyatomic ions present?

  * Yes; it is not an acid or binary compound, but it does have polyatomic ions; name the compound using procedures similar to those for naming binary ionic compounds.
  * No; it is not an acid or binary compound and does not have polyatomic ions; naming procedures have not yet been considered for the compound.

The aforementioned Latin prefixes correspond to the subscript of atoms in a Type III Binary Covalent compound. For example, X_2Y_3, where X and Y are both non-metals, would be "di(root of X) tri(root of Y)", but NM_4, where N and M are a different pair of non-metals, would be "(root of N) tetra(root of Y)." A full list of the prefixes is below for subscripts 1 to 10 is below.

Latin Prefixes for Number in Chemical Names	
Prefix	Number Indicated
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Some parts of molecules, especially *organic molecules* (molecules containing carbon or using a carbon backbone), are common structures that contribute disproportionately to the function of the molecule. These structures are called *organic functional groups*.

Transition metal ions characteristically form *coordination compounds*, which are usually colored and often paramagnetic. A coordination compound typically consists of a *complex ion*, a transition metal with its attached *ligands*, and *counterions*, anions or cations used to produce a compound with no net charge. A *ligand* is simply a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond. A ligand is necessarily a *Lewis base*. The number of ligands is twice the charge of the transition metal.

A *zwitterion* is an ion or molecule that has fully positive charge at one part in the molecule and negative charge at another

3   Stoichiometry

The central enabler of analytical chemistry is that atoms behave like they are identical, because there are so many of them, so any differences are corrected by sheer sample size. Therefore we can treat each atom and molecule as if they were identical and use the average mass of the atoms involved in calculations.

The most accurate method currently viable for comparing the masses of atoms uses a *mass spectrometer* and comparing masses of atoms to the mass of carbon-12, which we have defined to be exactly 12 amu, or $12 \frac{g}{mol}$ ^{12}C. When doing calculations with carbon, we use the *average atomic mass* of the element, which is slightly more than $12 \frac{g}{mol}$ C.

The primary unit of counting atoms and particles is the *mole*, which is the number equal to the number of carbon atoms in exactly $12 \, g$ of pure ^{12}C. The mole is 6.022×10^{23} things. A mole of some substance is 6.022×10^{23} units of that substance. The constant 6.022×10^{23} is called *Avogadro's number*. An alternate definition of a mole is that a sample of a natural element with a mass equal to the element's atomic mass expressed in grams contains 1 mole of atoms.

The *molar mass* of a substance is the mass in grams of one mole of the substance. This is also known as molecular weight.

The equivalent of the term "molecule" for ionic compounds is the term "*formula unit*", that is, the chemical formula that represents an ionic compound.

To obtain the molar mass of a compound, simply sum the molar masses of the atoms involved in the compound.

There are two common ways of describing the composition of a compound: in terms of the numbers of its constituent atoms and in terms of the percentages (by mass) of its elements. We can obtain the mass percents of the elements from the formula of the compound by comparing the mass of each element present in 1 mole of the compound to the total mass of 1 mole of the compound.

The formula of a compound is determined by taking a weighted sample of the compound and decomposing or combusting it into elements or compounds with those elements in them, then collecting and weighing the products.

The *empirical formula* of a compound is the formula where the greatest common denominator of the numbers of all elements within the compound is 1 i.e. all subscripts are relatively prime. The molecular formula of the compound is the empirical formula of the compound where all the subscripts are multiplied by some integer. To find the molecular formula, the molar mass must be known (so that we can find the integer multiple and thus the number of each element in the atom).

Determining the empirical formula from given data is mostly simple. Since mass percentage gives the number of grams of a particular element per $100 \, g$ of compound, base the calculation on $100 \, g$ of compound. Each percent will then represent the mass in grams of that element. Determine the number of moles of each element present in $100 \, g$ of compound using the atomic masses of the elements present. Divide each value of the number of the moles by the smallest of the values. If the resulting numbers are all whole numbers, the molecular formula is known. If not, multiply all

of the results by the same integer so that they are all whole numbers. The results of that is the empirical formula.

Determining the molecular formula from the empirical formula is also simple but requires the molar mass. First, obtain the empirical formula and compute the mass corresponding to the empirical formula. Calculate the ratio of the molar mass to the empirical formula mass. Multiply the subscripts by this ratio, getting the molecular formula.

Determining the molecular formula from the mass percent and molar mass is done by the following steps. Using the mass percentages and the molar mass, determine the mass of each element present in 1 mole of compound. Determine the number of moles of each element present in 1 mole of compound. The integers from the previous step represent the subscripts in the molecular formula.

A chemical change involves a reorganization of the atoms in one or more substances. These changes can be represented by a *chemical reaction* with the *reactants* on the left side of an arrow and the *products* on the right side like so:

$$2\,XY\,(g) \longrightarrow X_2\,(g) + Y_2\,(g)$$
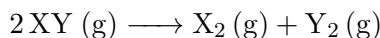
Note that states of matter are included. While not mandatory on the AP Exam, listing these is instructive towards understanding the reaction as a whole. The four states of matter are solid (s), liquid (l), gas (g), and dissolved (aq). This dissolved state is called aqueous and is the state of the vast majority of ions. Compounds use water as a medium to react and form these kinds of ions.

In a chemical reaction, bonds are broken and new bonds are formed. However, atoms are neither created nor destroyed. All atoms present in the reactants must be accounted for in the products. Altering coefficients to maintain that rule is called *balancing a chemical equation.*

When balancing equations, one must always alter coefficients, and cannot change the subscripts, as that would be changing the identities of the products or reactants. The formulas of compounds should never be changed by balancing.

Calculating masses of reactants and products in chemical reactions is a central concept in stoichiometry. The steps are listed here.

1. Balance the equation for the reaction.

2. Convert the known mass of the reactant or product to moles of that substance.

3. Use the balanced equation to set up the appropriate mole ratios.

4. Use the appropriate mole ratios to calculate the number of moles of the desired reactant or product.

5. Convert from moles back to grams if required by the problem.

A *stoichiometric mixture* is a mixture that contains the relative amounts of reactants that match the numbers in the balanced equation, where all reactants end up reacting and forming product. In cases where there is no stoichiometric mixture, there is a *limiting reactant*, which is the reactant

that runs out first and limits the amount of products that can form. Solving for the limiting reactant involves seeing how many moles of product can be made assuming excess of the other reactants. The limiting reactant is the reactant that produces the least moles. Alternatively, after converting using mole-to-mole ratios, the limiting reactant is the reactant that can react the least before running out.

The *theoretical yield* of a reaction is the amount of product formed by a reaction when the limiting reactant is completely consumed. In real life, complications with side reactions and such often render a full theoretical yield to be practically unachievable. The *actual yield* is often given as a percent of the theoretical yield, which is called the *percent yield*.

4 Types of Chemical Reactions and Solution Stoichiometry

Water (pure H_2O), one of the most important substances on Earth, has many different properties that allow it to serve a variety of purposes. One of these properties is its ability to dissolve many different substances.

In water, due to unequal levels of electron attraction of the three atoms, the two hydrogen atoms, which have less attraction on the electrons, have charges of δ^+. These charges are known as *partial charges* because their magnitude is less than a charge that exists in an ion. The oxygen of water has a partial charge of $2\delta^-$ due to attracting two electrons, one from each hydrogen. Water is a *polar molecule* because of its unequal charge distribution. As the total magnitude of the partial charges grows, the molecule becomes more polar.

Dissolution of solids is carried out by a process called *hydration*. The partial positive ends of the water molecules attract the negatively charged anion of the solid. The partial negative ends are attached to the positively charged cations. The hydration of ions causes a salt to fall apart in the water and dissolve.

When dissolution of a salt (any ionic solid) occurs, the salt breaks up in the individual cation and anion. Consider the following reaction which describes the dissolution of the ionic salt XY:

$$XY \text{ (s) } \xrightarrow{H_2O \text{ (l)}} X^+ \text{ (aq)} + Y^- \text{ (aq)}$$
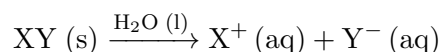
where (aq) designates that the ions are hydrated by unspecified numbers of water molecules. The H_2O (l) on top of the reaction arrow indicates that the reaction needs liquid water to proceed.

The solubility of ionic substances in water is different for each substance. However, no matter how insoluble a solid is, if any of it dissolves it is hydrated just the same way.

A *solute* is a dissolved substance. A *solvent* is the substance that something is dissolved in. In a solution, a solute is usually in less quantity than a solvent.

The rule *"like dissolves like"*, meaning that polar solvents dissolve polar molecules and nonpolar solvents dissolve nonpolar molecules, is a good rule of thumb to discuss solubility of substances in different solvents.

Electrical conductivity, or capability to conduct an electric current, of a solution is determined by the concentration and strength of electrolytes in the substance. If a solution has weak electrical conductivity, it contains *weak electrolytes*. If a solution has strong electrical conductivity, it contains *strong electrolytes*. If a solution has no electrical conductivity, it contains *nonelectrolytes*.

Strong electrolytes are substances that are completely ionized when they are dissolved in water. Strong electrolytes can be soluble salts, strong acids, or strong bases.

According to Svante Arrhenius, an *acid* is a substance that produces H^+ ions when dissolved in water. Acids are sour. The ionization of an acid can be represented by the following reaction:

$$HA \text{ (aq)} + H_2O \text{ (l)} \longrightarrow H_3O^+ \text{ (aq)} + A^- \text{ (aq)}$$
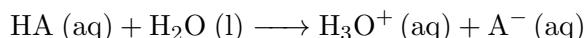
Strong acids are acids that completely ionize in water and an example of a strong electrolyte. There are only seven strong acids: $HCl\,(aq)$, $HBr\,(aq)$, $HI\,(aq)$, $HNO_3\,(aq)$, $HClO_3\,(aq)$, $HClO_4\,(aq)$, and $H_2SO_4\,(aq)$. Note the aqueous descriptor because all strong acids are aqueous as they ionize completely in water. Sulfuric acid ($H_2SO_4\,(aq)$) is a notable exception because it is a strong *polyprotic* acid, which means that it has multiple protons, as opposed to the other strong acids which are *monoprotic*. The ionization reaction for sulfuric acid only removes one proton, like so:

$$H_2SO_4\,(aq) + H_2O\,(l) \longrightarrow HSO_4^-\,(aq) + H_3O^+\,(aq)$$
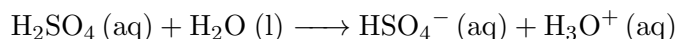
Strong bases are another class of strong electrolyte. Strong bases are soluble ionic compounds that contain the hydroxide ion (OH^-). In water, the hydroxide ions and cations dissociate completely. Bases are bitter. Examples of strong bases are KOH, $NaOH$, and $Mg(OH)_2$. These bases can come in solid form as well as in solution. The dissolution reaction for a base is

$$BOH\,(s, aq) \xrightarrow{H_2O\,(l)} B^+\,(aq) + OH^-\,(aq)$$
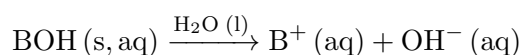
Weak electrolytes are substances that exhibit a small degree of ionization in water - not all of the molecules placed in water produce ions. Examples of weak electrolytes include *weak acids* and *weak bases*. Weak acids are acids that only ionize to a slight extent in water, and include all acids that are not strong acids. For a common weak acid, acetic acid, the ionization reaction is as follows, where the double arrow indicates that the reaction is at equilibrium and can proceed in either direction:

$$HC_2H_3O_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)$$
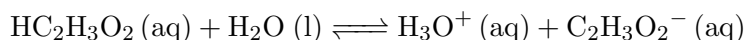
Weak bases are bases that only form few hydroxide ions in water. Weak bases more often than not involve nitrogenous structures. For the most common weak base, ammonia, the ionization reaction is as follows.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$
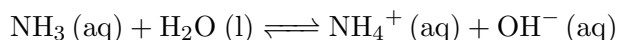
Nonelectrolytes are substances that dissolve in water but do not produce any ions. Examples of nonelectrolytes are ethanol (C_2H_5OH) and glucose ($C_{12}H_{22}O_{11}$).

To perform stoichiometry on the mixing of two solutions, two things must be known: the nature of the reaction, which bases itself on the forms chemicals take when dissolved, and the amount of each chemical in the solution.

The concentration of a solution can be described in many different ways, but the most common one is *molarity*, which is defined as moles of solute per unit volume of solution in liters:

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

A *standard solution* is a solution in which the concentration of a component is accurately known or derived through experimentation.

Dilution is when concentrated solutions of a substance (called *stock solutions*) have water added to

lower the concentration of the substance in a new solution. Since the moles of solute stays constant through the dilution, the dilution equation can be set up as:

$$M_1 V_1 = M_2 V_2$$

where M_1 and M_2 are the molarities of the substance in the solution before and after the dilution, respectively, and V_1 and V_2 are the volumes of solution before and after the dilution, respectively.

Two devices that are commonly used in dilution are *pipets* and *volumetric flasks*. A pipet is a device that accurately measures and transfers a given volume of solution. Two common types of pipets are *volumetric (or transfer) pipets* and *measuring pipets*. Volumetric pipets come in specific volumes while measuring pipets can take all kinds of volumes but not to the same efficacy.

There are three main types of solution reactions: *precipitation reactions, acid-base reactions,* and *oxidation-reduction reactions.*

A precipitation reaction is a reaction that forms an insoluble substance that is most often solid. That formation is called a *precipitate.* Precipitates must have a zero net charge, and must contain both anions and cations. Most precipitates contain only two types of ions: one type of cation and one type of anion. The precipitate must also be insoluble. The simple rules for the solubility of salts in water is below:

- Most nitrate (NO_3^-) salts are soluble.

- Most salts containing the alkali metal ions (Li^+, Na, K^+, Cs^+, Rb^+) and the ammonium ion (NH_4^+) are soluble.

- Most chloride, bromide, and iodide salts are soluble, with the exception of salts containing Ag^+, Pb^{2+}, and Hg_2^{2+}

- Most sulfate salts are soluble with the exception of $BaSO_4$, $PbSO_4$, Hg_2SO_4, and $caSO_4$.

- Most hydroxides are only slightly soluble. The important soluble hydroxides are NaOH and KOH. The compounds $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are marginally soluble.

- Most sulfide (S^{2-}), carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), and phosphate (PO_4^{3-}) salts are only slightly soluble, except for those containing the cations Li^+, Na, K^+, Cs^+, Rb^+, and (NH_4^+)

The phrase *slightly soluble* is interchangeable with *insoluble* since the amount dissolved in the prior case is too small to see.

An *overall equation,* or *formula equation* is the equation that represents a reaction where all species are represented in elemental form or compound form. It gives the overall reaction stoichiometry but not necessarily the actual forms of the reactants and products in solution. For example, the following is a overall equation:

$$AB \text{ (aq)} + 2\,CD \text{ (aq)} \longrightarrow AD_2 \text{ (s)} + B_2C \text{ (aq)}$$
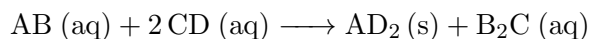
The *complete ionic equation* represents the forms of the reactants and products in a solution. Species that are strong electrolytes are represented as ions. For example, the following is a complete ionic equation:

$$A^{2+} (aq) + B^{2-} (aq) + 2\,C^+ (aq) + 2\,D^- (aq) \longrightarrow AD_2 (s) + B^{2-} (aq) + 2\,C^+ (aq)$$
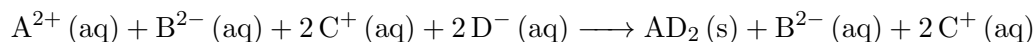
The *net ionic equation* removes all of the species that do not participate in the reaction i.e. the ions which remain in the same form in both the products and reactants. For example, the following is a net ionic equation:

$$A^{2+} (aq) + 2\,D^- (aq) \longrightarrow AD_2 (s)$$
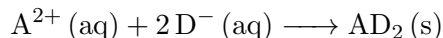
There is a series of steps to solve stoichiometry problems for reactions in solution.

1. Identify the species present in the combined solution, and determine what reaction occurs.

2. Write the balanced net ionic equation for the reaction.

3. Calculate the moles of reactants.

4. Determine which reactant is limiting.

5. Calculate the moles of product or products, as required.

6. Convert to grams or other units, as required.

The underlying concept is the same as stoichiometry of other mediums, but it is sometimes hard to identify the reaction taking place. The second step helps in this way.

A more general definition of acids and bases was provided by Johannes Bronsted and Thomas Lowry. A *Bronsted-Lowry acid* is a species that generally donates protons, while a *Bronsted-Lowry base* is a species that generally accepts protons.

The net ionic equation of the reaction between a strong acid and a strong base produces water:

$$H^+ (aq) + OH^- (aq) \longrightarrow H_2O (l)$$
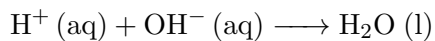
If a strong acid is present in solution, its H^+ ions will react with all the OH^- ions in the solution, even if they are attached to a base. Likewise, the OH^- ions from a strong base seek out and react with any H^+ ions, even if they are attached to a weak acid. In short, a strong acid or base reacts with all of the hydroxide or hydronium/hydride (H_3O^+/H^+) ions in a solution.

There is a set of steps to do calculations for acid-base reactions.

1. List the species present in the combined solution before any reaction occurs, and decide what reaction will occur.

2. Write the balanced net ionic equation for this reaction.

3. Calculate the moles of reactants. For reactions in solution, use the volumes of the original solutions and their molarities.

4. Determine the limiting reactant when appropriate.

5. Calculate the moles of the required reactant or product.

6. Convert to grams or volume (of solution), as required.

An acid-base reaction is often called a *neutralization reaction*. When enough base or acid is added to react exactly with the acid or base in a solution, we say the acid or base has been *neutralized*.

Volumetric analysis is a technique for determining the amount of a certain substance by doing a titration. A *titration* involves delivery from a buret of a measured volume of a solution of known concentration (the *titrant*) into a solution containing the substance being analyzed (the *analyte*). The titrant and the analyte are known to react. The point in the titration where enough titrant has been dispensed to react exactly with the analyte is called the *equivalence point* or *stoichiometric point*. This point is marked by an *indicator*, which is a substance added to the solution that changes color at or near the equivalence point. The *endpoint* of the titration is the point where the indicator changes color. The goal is to get the endpoint and equivalence point as close as possible by choice of indicator.

Standardization of solution is a method to determine the concentration of a solution through experimentation and titration.

Reactions in which one or more electrons are transferred between species are *oxidation-reduction* or *redox* reactions. *Combustion reactions* are a special type of redox reaction where oxygen is added to compounds and heated to form water, carbon dioxide, and oxides of any other nonreacted elements in the product.

Oxidation states or *oxidation numbers* in a covalent compound are the imaginary charges the atoms would have if the shared electrons were divided equally between identical atoms bounded to each other or, for different atoms, were all assigned to the atom in each bond that has the greater attraction for electrons. There are a set of rules for assigning oxidation states:

1. The oxidation state of an atom its elemental form is 0.

2. The oxidation state of a monatomic ion is the same as its charge.

3. The oxidation state of fluorine is -1 in its compounds.

4. The oxidation state of oxygen is usually -2 in its compounds (except for peroxides, in which oxygen is -1).

5. The oxidation state of hydrogen is +1 in its covalent compounds.

6. The sum of the oxidation states must be zero for an electrically neutral compound. Likewise, the sum of the oxidation states must be the charge of the ion.

Oxidation-reduction reactions are characterized by a transfer of electrons. When forming ionic compounds, the transfer is literal. In some cases, when forming covalent compounds, the transfer is less literal, and the transfer of electrons is shown by changes in oxidation state.

Oxidation is an increase in oxidation state (a loss in electrons). *Reduction* is a decrease in oxidation state (a gain in electrons). An *oxidizing agent* is a species that accepts electrons, and a *reducing gent* is a species that donates electrons.

There is a strategy for balancing redox reactions by oxidation states:

1. Write the unbalanced equation.

2. Determine the oxidation states of all atoms in the reactants and products.

3. Show electrons gained and lost in each species.

4. Use coefficients to equalize the electrons gained and lost.

5. Balance the rest of the equation by inspection.

6. Add appropriate states.

5 Gases

A gas uniformly fills any container, is easily compressed, and mixes completely with any other gas. A gas exerts *pressure* on its surroundings.

Pressure is a force per unit area. Atmospheric and gaseous pressure results from the weight of the gas being pulled down from gravity. Atmospheric pressure can be measured from the *barometer* and gaseous pressure can be measured from the *manometer*. The SI unit for pressure is the *Pascal* (Pa), which is defined as 1 newton per square meter ($\frac{\text{N}}{\text{m}^2}$). The most common unit of pressure is the *standard atmosphere* (atm), which is $101\,325\,\text{Pa}$. Another unit of pressure is the *millimeter of mercury* (mmHg), whose name comes from the barometer's methodology. This unit is also called the *torr* (torr) in honor of the scientist Evangelista Torricelli. One standard atmosphere is $760\,\text{mmHg}$ (three significant figures).

Boyle's law states that there is an inverse relationship between pressure and volume of a gas sample, that is

$$PV = k$$

where k is an arbitrary constant that is dependent on the conditions that the gas is in, and to a lesser degree the composition of the gas.

Charles's law states that there is a direct relationship between volume and temperature of a gas sample, that is

$$V = bT$$

where b is a proportionality constant that depends on the conditions that the gas is in and to a lesser degree the composition of the gas, and T is in Kelvin.

Absolute zero is the state of $0\,\text{K}$, and has never been reached in laboratory settings. It is theorized that it is impossible to reach.

Avogadro's law states that there is a direct relationship between volume and number of moles of the gas, that is

$$V = an$$

where a is a proportionality constant that depends on the conditions that the gas is in and to a lesser degree the composition of the gas, and n is the number of moles of the gas.

By combining the three laws, we get the *ideal gas law*, or

$$PV = nRT$$

where R is the combined proportionality constant called the *ideal gas constant*. R has the value $0.0821\,\frac{\text{L atm}}{\text{K mol}}$ or $62.4\,\frac{\text{L mmHg}}{\text{K mol}}$.

The ideal gas law is an *equation of state* for a gas, where the state of the gas is its condition at a given time. A particular *state* of a gas is described by its pressure, volume, temperature, and number of moles.

A gas that obeys this equation is said to behave ideally. At high temperature and low pressure,

a gas approaches the behavior set by this law; however, even at different conditions, the inherent error is minimal. No gas is truly ideal; it's more like a spectrum.

From the ideal gas law we can derive the *combined gas law*, which relates the same gas sample under different conditions. Assume moles of gas stay constant.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Standard temperature and pressure (STP) is the conditions $273.15\,\text{K}$ or $0\,°\text{C}$ and $1.00\,\text{atm}$. The *molar volume* of a gas, the volume that one mole of a gas takes up, at STP is $22.4\,\text{L}$.

A slight modification to the ideal gas law can find a relationship between the density of a gas and the molar mass.

$$\text{Molar mass} = M = \frac{\rho R T}{P}$$

Dalton's Law of Partial Pressures states that the total pressure of a system is the sum of all the partial pressures of all the gas samples in the system.

$$P_{tot} = \sum P_{partial} = P_1 + P_2 + P_3...$$

It can be derived from this equation that it is the total number of moles of particles that is important for a mixture of ideal gases, not the identity or composition of the involved gas particles. Moreover, the partial pressure of a gas divided by the total pressure of the gas mixture is the *mole fraction*, or moles of substance over total moles, of the gas in the mixture.

The *Kinetic Molecular Theory of Gases* is a simple model that attempts to explain the properties of an ideal gas.

1. The particles of an ideal gas are so small compared to the distances between them that the volume of the individual particles is negligible and can be assumed to be zero.

2. The particles of an ideal gas are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.

3. The particles are assumed to exert no forces on each other; they are assumed neither to attract nor to repel each other.

4. The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temperature of the gas.

An *ideal gas* is a gas that fulfills all these criterion. In a real gas, the criteria are almost fulfilled, but real limitations impose some deviations from Kinetic Molecular Theory conditions.

Diffusion is the term used to describe the mixing of gases. *Effusion* is the term used to describe the passage of gases through tiny holes into evacuated chambers.

Assuming two gases with same temperature and pressure, deriving the relative rate of effusion or diffusion (basically, speed) the first gas to the second can be derived through the kinetic energy

formula. It is

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \sqrt{\frac{M_2}{M_1}}$$

where M_1 is the molar mass of the first gas and M_2 is the molar mass of the second. This equation is called *Graham's law of effusion*.

The *van der Waals equation* is the ideal gas law when corrected for real factors.

$$[P_{observed} + a(\frac{n^2}{V})] \times (V - nb) = nRT$$

where a and b are experimentally derived correction factors.

6   Thermochemistry

Energy is the capacity to do work or to produce heat. The *law of conservation of energy* states that energy can be converted from one form to another but can neither be created nor destroyed. Energy can be in either kinetic or potential form. *Potential energy* is energy due to position or composition. Kinetic energy of an object is energy due to the motion of the object.

Temperature is a property that reflects the random motion of the particles in a substance (fun fact: this is called Brownian motion.) *Heat* is a property that involves the transfer of energy between two objects due to a temperature difference. Heat is not contained by an object, but rather is a transfer of energy. *Work* is a force acting on a distance, and the energy required to exert the force is the work done. The way the energy transfer is divided between work and heat depends on the specific conditions, or the *pathway*, of the process.

A *state function*, *state property*, or *state variable* is a property of a system that depends only on its present state. In practical terms, the pathway does not matter. Energy transferred is a state function, but work and heat are not state functions.

The *system* of a chemical reaction is the part of the universe in which the reaction takes place. The *surroundings* is everything else in the universe.

A reaction is said to be *exothermic* if energy flows out of the system. A reaction is said to be *endothermic* if the system takes in energy from the surroundings. The energy gained by the surroundings must be equal to the energy lost by the system. The vice versa also holds true.

The study of energy and its interconversions is called *thermodynamics*. The *first law of thermodynamics* is essentially equivalent to the law of conservation of energy and is stated as follows: the energy of the universe is constant.

The *internal energy* E of a system can be defined as the sum of the kinetic and potential energies of all the particles in the system. The internal energy of a system can be changed by a flow of work, heat, or both, that is

$$\Delta E = q + w$$

where ΔE is the change in the system's internal energy, q represents heat, and w represents work.

The sign of a thermodynamic quantity describes the direction of the flow of energy. The sign describes the transfer from the point of view of the system. The positive sign indicates that the system's energy is increasing and the negative sign indicates that the system's energy is decreasing.

The work done on a system is the pressure of the system multiplied by the change in volume of the system, where W is the work:

$$W = -P\Delta V$$

The gas is pressing on its surroundings and doing work on them, so the negative is required.

The *enthalpy* H of a system is defined as

$$H = E + PV$$

Since internal energy, pressure, and volume are all state functions, enthalpy is a state function. The change in enthalpy of a system is equivalent to the heat taken in by the process causing the change in enthalpy.

$$\Delta H = q$$

For a chemical reaction,

$$\Delta H_{rxn} = \frac{q}{\text{mol rxn}}$$

The change in enthalpy can also be defined by

$$\Delta H_{rxn} = H_{products} - H_{reactants}$$

A *calorimeter* is a device used experimentally to determine the heat associated with a chemical reaction.

The *heat capacity* C of a substance is defined as

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

If the heat capacity is given per gram of substance, it is called the *specific heat capacity* (units $\frac{J}{g\,°C}$), and if it is given per mole of substance, it is called the *molar heat capacity* (units $\frac{J}{mol\,°C}$). In both cases, Kelvin can be substituted for degrees Celsius, since the degree of both is the same.

Styrofoam coffee cups work as calorimeters because they are strong insulators and their material does not take in much heat. The heat absorbed by a system during a temperature change can be calculated by the following equation:

$$q_{sys} = mC_p\Delta T$$

where m is the mass of the system, C_p is the specific heat capacity of the system, and ΔT is the change in temperature. Swapping m with moles n and C_p with the molar heat capacity C_m works as well. Going back to the first law of thermodynamics, we find that the following relation holds:

$$q_{sys} = -q_{surr}$$

showing that heat is transferred but universally preserved.

Heat of a reaction is *extensive*, in that it varies directly with much substance is reacted. The alternative would be for it to be *intensive*, where quantity does not matter.

Hess' law states that in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. This is derived from the definition of a state function - the pathway between reactants and products is irrelevant. In this way we can add and subtract reactions and corresponding changes in enthalpy to get a new reaction and change in enthalpy that may be useful and solve a problem.

The characteristics of ΔH for a reaction are necessary to compute enthalpy changes for a reaction:

- If a reaction is reversed, the sign of ΔH is also reversed.

- The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH multiplied by the same integer.

Calculations involving Hess' law typically require that several reactions be manipulated and combined to finally give the reaction of interest. In doing this procedure you should work backward from the required reaction, using the reactants and products to decide how to manipulate the other give reactions at your disposal. Then, reverse any reactions as needed to give the required reactants and products. Lastly, multiply reactions to give the correct number of reactants and products.

The *standard enthalpy of formation* (ΔH_f°) of a compound is defined as the change in enthalpy that accompanies the formation of 1 mole of a compound from its elements with all substances in their standard states. A degree symbol on a thermodynamic function indicates that the corresponding process has been carried out under *standard conditions*, which are 1 atm and 25 °C unless otherwise stated. For a substance in a solution, the standard concentration is 1 M.

The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products:

$$\Delta H_{rxn}^\circ = \Delta H_{f\ products}^\circ - \Delta H_{f\ reactants}$$

Also, the heat of formation for an element in its standard state is zero.

7   Atomic Structure and Periodicity

Energy travels through space by *electromagnetic radiation*. All types of this radiation are wavelike. Waves have three primary characteristics: wavelength, frequency, and speed.

Wavelength (λ) is the distance between two consecutive peaks or troughs in a wave (unit: m). Frequency (ν) is defined as the number of waves per unit time that pass a given point in space (unit: $\frac{1}{s}$).

Wavelength and frequency are inversely proportional, so we get the following relationship:

$$\lambda \nu = c$$

where c is the speed of light ($3.00 \times 10^8 \frac{m}{s}$).

Max Planck found that energy was quantized and can only be gained or lost in whole number multiples of the quantity $h\nu$, where h is a constant called *Planck's constant* and is equal to 6.626×10^{-34} J s. The energy of a radiation particle, or *photon*, is

$$E_{photon} = h\nu = h\frac{c}{\lambda}$$

Similarly, the minimum energy required to remove an electron is

$$E_0 = h\nu_0$$

Because a photon with energy less than E_0 cannot remove an electron, light with a frequency less than the threshold frequency produces new electrons. If the photon has more energy, then the remainder is given to the electron as kinetic energy.

Using the equation $E = mc^2$ and substituting into other equations yields a variety of useful functional forms.

Diffraction is the process of scattering light from a source into an array of points or lines. A *diffraction pattern* is the array of points or lines.

When a molecule absorbs energy, some bonds are broken and excess energy remains. The resulting atoms are *excited*, and contain excess energy, which they release by emitting light of various wavelengths to produce what is called the *emission spectrum*.

A *continuous spectrum* is an emission spectrum which contains all wavelengths of visible light. In contrast, the vast majority of elements only emit select discrete wavelengths of visible light, forming a *line spectrum*. Due to the line spectrum, we know only certain energies are allowed for the electron in any atom, that is, the energy of the electron in an atom is quantized.

Niels Bohr proposed that the electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits. He worked out that the energy available for an electron in the hydrogen atom is as follows, where n is a whole number corresponding to an energy level and Z is the nuclear

charge:

$$E = -2.178 \times 10^{-18} \, \text{J} \left(\frac{Z^2}{n^2} \right)$$

For an electron, the lowest possible energy state is its *ground state*, or the state where n is the lowest. For a hydrogen atom, the above equation can be used to calculate ΔE for an electron being excited and rising up energy levels, or an electron being grounded and falling down energy levels.

Bohr's model was eventually proved incorrect since it only worked for hydrogen, but it paved the way for more complex theories.

Erwin Schrödinger believed that electrons were better modeled as waves, not particles, and in particular *standing waves*. The form of Schrödinger's equation is

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

where ψ is the wavefunction where the input is the coordinates and the output is the square root of the probability that the electron is at those coordinates. $\hat{H}$ is an operator which produces the total energy of the atom when applied to the wavefunction. Each solution consists of a wave function ψ characterized by a particular value of E. A specific wavefunction is an *orbital*.

The *Heisenberg uncertainty principle* states that there is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time.

The square of the wave function is most conveniently represented as a probability distribution, also called an *electron density map*. A *radial probability distribution* is a graph of a specific electron's or a specific orbital's probability of being at a specific distance away from the nucleus, with probability on the y-axis and distance on the x-axis.

The size of an orbital is the radius of the shape that encloses 90 % of the total electron probability, that is, 90 % of the time the electron is inside the shape.

Quantum numbers are a series of numbers which describe various properties of a given orbital.

The *principal quantum number* (n) has integer values. The principal quantum number is related to the size and energy of the orbital. As n increases, the orbital becomes larger and the electron spends more time farther from the nucleus. An increase in n also means higher energy, because the electron is less tightly bound to the nucleus, and the energy is less negative.

The *angular momentum quantum number* (l) has integer values from 0 to $n - 1$ for each value of n. This quantum number is related to the shape of atomic orbitals. The value of l for a particular orbital is commonly assigned a letter: $l = 0$ is called s, $l = 1$ is called p, $l = 2$ is called d, $l = 3$ is called f, and $l = 4$ is called g.

The *magnetic quantum number* (m_l) has integer values between l and $-l$, including 0. The value of m_l is related to the orientation of the orbital in space relative to the other orbitals in the atom.

Lastly, the *spin quantum number* (m_s) has $+\frac{1}{2}$ and $-\frac{1}{2}$ as values and denotes the spin of an electron in an orbital.

For an energy level n there are n possible l values and n^2 possible m_l values.

Areas in an atom between orbitals, that is areas with zero probability, are called *nodes* and increase as n increases. For s orbitals the number of nodes is given by $n - 1$.

The general shape of s orbitals are spheres.

The general shape of p orbitals are elongated propeller-shaped structures. Each one of the particular structures which jut out from the nucleus are called *lobes* and have a node at the nucleus. Each lobe goes along a particular axis, so there are p_x, p_y, and p_z orbitals.

The general shape of d orbitals are fatter lobes aligned between axes. The d_{xz} orbital is aligned on the x-z axis, but offset so that the lobes are halfway between the x-z axis; the d_{yz} orbital is aligned on the y-z axis, but offset so that the lobes are halfway between the y-z axis; the d_{xy} orbital is aligned on the x-y axis, but offset so that the lobes are between the x-y axis; the $d_{x^2-y^2}$ orbital is aligned on the x-y axis; the d_{z^2} orbital has two lobes aligned on the z-axis and a hoop surrounding them around the nucleus.

The general shape of f orbitals are elongated lobes emerging from the nucleus, along with some pacifier shapes. Their structures get complex and are not covered.

Orbitals with the same value of n and l have the same energy, since they are in the same energy level - they are *degenerate*. Greater values of n are higher energy orbitals. For l, the classification goes as follows:

$$E_s < E_p < E_d < E_f$$

The *Pauli exclusion principle* states that no two electrons can have the same set of four quantum numbers, that is, there can only be two electrons in an orbital, and they have to have opposite spins.

The *aufbau principle* states that as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to the lowest energy orbitals, and the lowest energy orbitals need to be filled up before the higher energy orbitals are occupied.

Hund's rule states that the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli exclusion principle in a particular set of degenerate orbitals.

Orbital diagrams represent electron configurations. *Electron configurations* denote the locations of the electrons in an atom or ion. Some sample electron configurations that follow the rules are below:

$$H = 1s^1$$

$$He = 1s^2$$

$$O = 1s^2 2s^2 2p_x^2 p_y^1 p_z^1 = [He]2s^2 2p_x^2 p_y^1 p_z^1$$

$$Ti = [Ar]4s^2 3d^2$$

Valence electrons are the electrons in the outermost principal quantum level of an atom. The inner electrons are *core electrons*.

The elements in the same group have the same valence electron configuration. Elements in the chromium group have only one electron in their s sublevel and five in their d sublevel. Elements in the copper group have one electron in their s sublevel and ten in their d sublevel.

When forming ions, electrons are removed from the highest energy level (p before s before d before f).

Periodic trends can mostly be summarized by two factors: the effective nuclear charge (number of protons minus number of core electrons, or Z_{eff}) and principal energy level. While higher Z_{eff} causes a pull towards the nucleus, causing the bond between the nucleus and electrons to have more energy and thus be harder to break, higher principal energy level makes the electrons farther away, causing the electrons to be easier to lose and more likely to react due to their high energy. Periodic trends can be expressed in terms of those two factors.

Ionization energy is the energy required to remove an electron from a gaseous atom or ion. The first ionization energy I_1 is the energy required to remove the highest-energy electron of an atom. The second ionization energy I_2 is the energy required to remove the second-highest-energy electron of an atom, and so on. As we go across a period (row) of the periodic table from left to right, the first ionization energy increases. First ionization energy goes decreases during a group. The boron group and the oxygen group break this pattern and are lower than their neighbors. This is because their electron being pulled off makes for a more stable electron configuration with either one electron per p orbital (in the case of the oxygen group) or no electrons in the p orbitals (in the case of the boron group). Ionization energy is positive as it reflects the energy input required.

Electron affinity is the energy change associated with the addition of an electron to a gaseous atom. Since the electron affinity is a change in energy, values are expressed as negatives. The ionization energy of an atom is the electron affinity of that element without one electron. So:

$$\text{x} \longrightarrow \text{X}^+ + \text{e}^-$$

$$\text{X}^+ + \text{e}^- \longrightarrow \text{X}$$
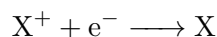
For the two reactions the change in energy is equal and opposite. Since it is the opposite sign of ionization energy, the same trends are obeyed (e.g. the magnitude increases left to right and top to bottom).

Electronegativity is the measure of an atom to attract a bonding pair of electrons. It follows the opposite trend as electron affinity and ionization energy in that the magnitude generally decreases left to right and top to bottom. The most electronegative element is fluorine, with an electronegativity of 4.0.

Atomic radii, or *covalent atomic radii*, is the distance between two atoms in chemical compounds. The radii for metal atoms are called *metallic radii* and are obtained from half the distance between metal atoms in solid metal crystals. The atomic radii decrease left to right but increase top to bottom.

8   Bonding: General Concepts

We can measure the strength of a bonding interaction by measuring the *bond energy*, which is the energy required to break a bond.

Ionic bonding is bonding in which electrons are completely transferred in order to result in a system which has the lowest possible energy out of all configurations. The strong mutual attractions from both ions and the anion's strong desire for electrons in an ionic bond cause the electrons to be transferred. An *ionic compound* results when a metal reacts with a nonmetal. The energy of interaction between a pair of ions can be calculated using Coulomb's law in the form

$$E = (2.31 \times 10^{-19}\,\mathrm{J\,m})(\frac{Q_1 Q_2}{r})$$

where E has units of joules, r is the distance between the ion centers in meters, and Q_1 and Q_2 are the numerical ion charges.

The *bond length* is the distance between two atoms where the energy of their bond is minimal. Compounds will optimize for the least energy in their bonds.

Covalent bonding is bonding in which electrons are shared by nuclei. *Polar covalent bonds* are bonds that have unequal sharing of electrons, but attractive forces are not so unbalanced as to necessitate an electron transfer. This is what gives individual atoms in a bond partial charges. The electron attraction from each atom is based on the electronegativity of each atom. The "location" that the electrons take up in the bond is based on the electronegativty difference between the two atoms. Bonds with an electronegativity difference of 0 to 0.4 are nonpolar covalent bonds, 0.5 to 1.6 are polar covalent bonds, and 1.7 and up are traditionally ionic bonds.

A molecule that has a center of positive charge and a center of negative charge is said to be *dipolar*, or to have a *dipole moment*. The dipolar character of a molecule is often represented by an arrow pointing to the negative charge center with the tail of the arrow indicating the positive center of charge.

Some molecules have polar bonds but no resulting dipole moment. For example, linear molecules with two identical bonds like CO_2, planar molecules with three identical bonds 120 degrees apart like SO_3, and tetrahedral molecules with four identical bonds 109.5 degrees apart like CCl_4 do not have dipole moments.

When two nonmetals react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. That is, both nonmetals attain noble gas electron configurations. When a nonmetal and a metal from the first two or last six groups react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom and the valence orbitals of the metals are emptied. In this way both ions achieve noble gas configurations.

Isoelectronic ions are ions that contain the same number of electrons. For isoelectronic ions, due to the nuclear attraction to the electrons, the smallest ions are the ones with the most protons (highest atomic number).

Removing electrons from an atom results in a smaller ion than the parent atom. Adding electrons to an atom results in a larger ion than the parent atom, especially if the electron starts a new energy level. Otherwise, ions have the same trends as their parent atoms.

The strength of the attraction between ions in the solid state is indicated by the *lattice energy*, which is the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid:

$$X^+ (g) + Y^- (g) \longrightarrow XY (s)$$
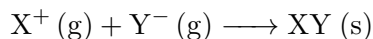
The lattice energies of multiple ionic compounds can be compared by first looking at the relative charges of each ion - the stronger the charges are, the stronger the lattice energy. If the charges of two ionic solids are the same, the solid with the shorter bond distance (sum of both principal energy levels) has the stronger lattice energy.

Bond energies are an average, and not necessarily an exact measurement. However, we treat them as being exact, because the variance in strength statistically cancels out.

A bond where one pair of electrons is shared is a *single bond*. A bond where two pairs of electrons are shared is a *double bond*. A bond where two pairs of electrons are shared is a *triple bond*.

Bond energy values can be used to calculate approximate energies for reactions. For bonds to be broken, energy must be added to the system, an endothermic process, and so the sign of that process is positive. The formation of a bond releases energy, an exothermic process, and so the sign of that process is negative. For reactions,

$$\Delta H_{rxn} = \Delta H_{bonds\ reactants} - \Delta H_{bonds\ products}$$

The reason this is reversed from the typical products minus reactants framework is because the signs of the heats are reversed from traditional frameworks.

The *localized electron model* assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms. Those pairs of electrons localized on an atom are called *lone pairs*, and those found in the space between the atoms are called *bonding pairs*.

The *Lewis structure* of a molecule shows how the valence electrons are arranged among the atoms in the molecule. The most important requirement for the formation of a stable compound is that the atoms achieve noble gas electron configurations. In writing Lewis structures, the rule is that only the valence electrons are included.

Hydrogen forms stable molecules where it shares two electrons. That is, it follows a duet rule. Helium does not form bonds because its valence electron is already filled; it is a noble gas. The second row nonmetals carbon through fluorine form stable molecules when they are surrounded by enough electrons to fill the valence orbitals. Since eight electrons are required to fill these orbitals, these elements typically obey the octet rule; they are surrounded by eight electrons. The third and up energy levels are exempt because they can draw on unfilled d, f, and g sublevels.

There is a series of steps to write Lewis structures:

1. Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the total number of electrons that is important.

2. Use a pair of electrons to form a bond between each pair of bound atoms.

3. Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.

There are some exceptions to the octet rule. Boron only requires three valence electrons in its shell to be satisfied. Beryllium can have two valence electrons in its shell to be satisfied.

Sometimes more than one valid Lewis structure is possible for a given molecule. In those cases, the bonds that are different between those two molecules have properties that are in between the two types of bonds in the structure. They are no longer only single, double, or triple bonds - their strength and length are between them. *Resonance* is invoked when more than one valid Lewis structure can be written for a particular molecule. The resulting electron structure of the molecule is given by the average of these *resonance structures*.

For molecules with odd numbers of valence electrons, the odd electron goes to the atom with the greater electronegativity (in the localized electron model).

The *formal charge* of an atom in a molecule is the difference between the number of valence electrons that the atom normally has and the sum of the number of bonds the atom has with the number of valence electrons attributed to it on the localized electron model. Atoms in molecules try to achieve formal charges as close to zero as possible. Any negative formal charges are expected to reside on the most electronegative atoms. The method of formal charges can be used to evaluate the correctness of Lewis structures - the structure with the formal charge closer to the overall charge of the species is more correct and should be used.

Molecular structure is the three dimensional arrangement of the atoms in a molecule. The model that predicts molecular structure is the *valence shell electron-pair repulsion (VSEPR) model*. This model's main principle is that the structure around a given atom is determined mostly by minimizing electron-pair repulsions.

There are a series of steps to apply the VSEPR Model:

1. Draw the Lewis structure for the molecule.

2. Count the electron pairs and arrange them in the way that minimizes repulsion (that is, put the pairs as far apart as possible).

3. Determine the positions of the atoms from the way the electron pairs are shared.

4. Determine the name of the molecular structure from the positions of the atoms.

A chart showing electronic and molecular structures is below. For the VSEPR model, multiple models count as one effective electron pair. When a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model.

Bonded Pairs	Lone Pairs	Electron Geometry	Molecular Geometry	Hybridization	Bond Angle
2	0	Linear	Linear	sp	180°
3	0	Trigonal Planar	Trigonal Planar	sp^2	120°
2	1	Trigonal Planar	Bent	sp^2	120°
4	0	Tetrahedral	Tetrahedral	sp^3	109.5°
3	1	Tetrahedral	Trigonal Pyramidal	sp^3	107.5°
2	2	Tetrahedral	Bent	sp^3	104.5°
5	0	Trigonal Bipyramidal	Trigonal Bipyramidal	sp^3d	90°, 180°
4	1	Trigonal Bipyramidal	Seesaw	sp^3d	90°, 120°
3	2	Trigonal Bipyramidal	T-Shaped	sp^3d	90°
2	3	Trigonal Bipyramidal	Linear	sp^3d	180°
6	0	Octahedral	Octahedral	sp^3d^2	90°
5	1	Octahedral	Square Pyramidal	sp^3d^2	90°
4	2	Octahedral	Square Planar	sp^3d^2	90°

For molecules with no central atom, each atom which is connected to more than one other atom has its own structure that can be explained through VSEPR theory.

9 Covalent Bonding: Orbitals

The overlap of orbitals during covalent bonding to form new bonding orbitals is *hybridization*. The type and shape of hybridization is dictated by the number and type of orbitals that overlap, and is determined by the total electron domains on the atom. Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of sp^3 orbitals; the atom becomes sp^3 hybridized. The other hybridizations are computed using the trigonal planar, trigonal bipyramidal, and octahedral electron domains. The new bonding orbitals are called *hybrid orbitals*.
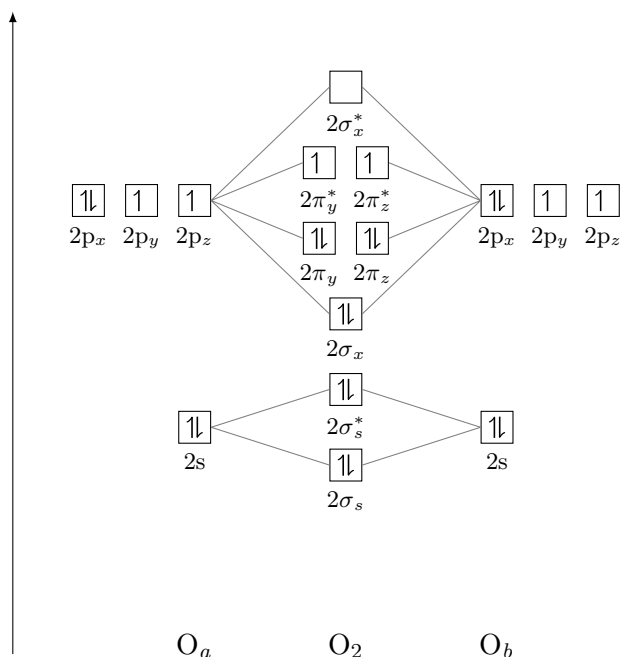
A covalent bond that is the result of the intersection of two s orbitals is called a σ *bond*. Each covalent bond in a Lewis structure contains a σ bond. A covalent bond that is the result of the intersection of two p, d, or f orbitals is called a π *bond*. These bonds are more difficult to form, but when they form they are stronger. They also shorten the bond. You will notice that strength and length of a bond are inversely proportional. A double bond is composed of one σ bond and one π bond.

The problem solving strategy for describing molecules using the localized electron model is listed.

1. Draw the Lewis structure(s).

2. Determine the arrangement of electron pairs using the VSEPR model.

3. Specify the hybrid orbitals needed to accommodate the electron pairs.

Another model used to describe bonding is the *molecular orbital model*. It answers the question of magnetism, among other considerations.

Molecular orbitals, a key construction of molecular orbital theory, are useful solutions to the quantum molecular theory of molecules. A sample molecular model is below.

The diagram shows the molecular orbital energy level diagram for O_2, with atomic orbitals of O_a on the left and O_b on the right, and molecular orbitals of O_2 in the center.

Left atom (O_a): $2p_x$ (↑↓), $2p_y$ (↑), $2p_z$ (↑); $2s$ (↑↓)

Molecular orbitals (from top): $2\sigma_x^*$ (empty); $2\pi_y^*$ (↑), $2\pi_z^*$ (↑); $2\pi_y$ (↑↓), $2\pi_z$ (↑↓); $2\sigma_x$ (↑↓); $2\sigma_s^*$ (↑↓); $2\sigma_s$ (↑↓)

Right atom (O_b): $2p_x$ (↑↓), $2p_y$ (↑), $2p_z$ (↑); $2s$ (↑↓)

- The electron probability of both molecular orbitals is centered along the line passing through the two nuclei. For a bonding s orbital the greatest electron probability is between the nuclei, and for an antibonding s orbital it is on either side of the nuclei. This type of electron distribution is described as sigma (σ), as in the localized electron models. Accordingly, we refer to s orbitals as *sigma (σ) molecular orbitals*. The other molecular orbitals are composed of more combinations of orbitals that have nodes at the nucleus and are as such π *molecular orbitals*.

- In the molecule only the molecular orbitals are available for occupation by electrons. The atomic orbitals no longer exist, because the new molecule has its own set of new molecules.

- The bonding orbitals of the molecule of a diatomic element are lower energy than the orbitals of free atoms, while the antibonding orbitals of the molecule are higher energy than the orbitals of free atoms. This holds true for every diatomic element because it makes the bond favorable to form i.e. probonding. The situation would be antibonding if the two electrons had to reside in the antibonding orbital.

- The labels on molecular orbitals indicate their symmetry (shape), the parent atomic orbitals, and whether they are bonding or antibonding.

- Molecular electron configurations can be written in much the same way as atomic (electron) configurations.

- Each molecular orbital can hold two electrons, but the spins must be opposite.

- Orbitals are conserved. The number of molecular orbitals will always be the same as the number of atomic orbitals used to construct them.

The *bond order* is the difference between the number of bonding electrons and the number of anti-bonding electrons divided by 2. A larger bond order means greater bond strength and stability and

a shorter length. A bond order of zero indicates that no bond will occur under regular conditions.

A *paramagnetic molecule* is attracted by an inducing magnet field. A *diamagnetic molecule* is repelled by an inducing magnetic field. Paramagnetism is associated with unpaired electrons and diamagnetism is associated with paired electrons. Any substance that has both paired and unpaired electrons will exhibit a net paramagnetism, since the effect of paramagnetism is much stronger than that of diamagnetism.

When the molecule is *homonuclear* (two of the same type of atom, or diatomic), the two atoms are equal in their elevation in the molecular orbital diagram since they exhibit the same energy characteristics. When the molecule is *heteronuclear* (two different types of atoms), one atom is much lower or higher than the other on the energy scale. The atom that is lower is the one with the higher electronegativity because it holds onto its electrons very tightly, and in some cases the orbital of the very electronegative atom can be lower in energy than the orbital of the other atom, even if the second orbital is of a lower energy level.

σ bonds are constant across all resonance structures. π bonds vary with resonance and are called *delocalized* because the bond is never fully present in one bonding domain at once.

Photoelectron spectroscopy is a technique that can determine relative energies of electrons in individual atoms as well as molecules. PES spectrums show peaks at the energy required to remove the electrons from each sublevel (since orbitals within a sublevel are degenerate). The height of the peak is the number of electrons in the sublevel. The highest energy electrons take the least to remove, so they are on the extreme (pay attention to the axes), and from there moving in the other direction the sublevels get progressively closer to the nucleus.

10   Liquids and Solids

Bonding is an *intramolecular* force, that is, it occurs within molecules. Condensed states of matter are formed by condensations or aggregations of molecules, which may occur through covalent or ionic bonding, or weaker interactions called *intermolecular forces* (because they occur between molecules).

Changes in state (solid to liquid, liquid to gas, etc) keep the molecules intact. They are due to changes in the forces among the molecules. From solid to liquid, intermolecular forces are weakened; from liquid to gas, intermolecular forces are broken. This is why the energy (in the form of heat energy) required for a change of state in solid to liquid is much less than the energy required for a state change from liquid to gas or solid to gas and lesser still than the energy required to break the bonds of the molecules themselves.

Dipole-dipole attraction is an intermolecular force where the dipole moments of molecules line up due to the fact that opposites attract. Positive ends attract negative ends. This intermolecular force is a force that all polar covalent molecules exhibit. The strength of dipole-dipole attractions increases as the polarity of the molecule increases.

Hydrogen bonding is a special type of dipole-dipole attraction where hydrogen is covalently bonded to a nitrogen, oxygen, or fluorine atom. Since the polarity of the bond is so high and the dipoles can be close, the intermolecular force of hydrogen bonding is extremely high. The strength of hydrogen bonding increases as the polarity of the molecule increases.

London dispersion forces, also known as *van der Waals forces*, are intermolecular forces that all molecules (with electrons) exhibit. They are formed by the temporary formation of a dipole moment through a temporary asymmetrical electron distribution. This is called an *instantaneous dipole*. These can induce instantaneous dipoles in neighboring atoms. The London dispersion forces are generally the weakest type of intermolecular forces, but since they scale with the number of electrons in an atom or molecule, they can become stronger than dipole-dipole interactions for massive molecules.The term *polarizability* means the ease with which the electron cloud of an atom can be distorted to give a dipolar charge distribution. Large atoms have higher polarizability, higher chance to form instantaneous dipoles, and so have stronger London dispersion forces.

Ion-dipole forces are intermolecular forces that occur between a charged ion and the partial charge of a covalent molecule of the opposite charge. They are strong, but not as strong as hydrogen bonding.

The *surface tension* of a liquid is resistance to an increase in its surface area. Liquids with relatively high intermolecular forces, particularly polar molecules, have relatively high surface tensions.

Polar liquids typically exhibit *capillary action*, which is the rising of a liquid in a narrow tube. This happens because of the liquid's *cohesive forces*, the intermolecular forces among the molecules of the liquid, and *adhesive forces*, the forces between liquid molecules and their container. Adhesive forces occur when some molecules in the container have partial charges that are attracted to the opposite partial charges in the polar covalent liquid.

Viscosity is a measure of a liquid's resistance to flow. Liquids with high intermolecular forces tend

to be highly viscous.

The use of *spectroscopy*, the study of the manner in which substances interact with electromagnetic radiation, make it possible to follow the changes that happen in liquids. A unified model of liquids is still being developed, and the structures of liquids is highly dynamic.

A type of spectroscopy that is used to analyze solutions is called Ultraviolet-Visible spectroscopy. *Spectrophotometers* are used to carry out spectroscopy. This spectroscopy analyzes the content of a solution by using samples of a species in higher concentrations in a solution to develop a calibration curve, then analyzing a solution by applying Beer's Law:

$$A = abc$$

where A is the absorbance of light at a set wavelength, a is the molar absorptivity constant of the substance at a set wavelength, b is the path length (the shortest path the light takes from one end of the container, or *cuvette*, to the other), and c is the concentration of the substance. Absorbance of light is also the negative logarithm of the transmittance of light, and is unitless:

$$A = -\log_{10}(T) = -\log_{10}(\frac{\text{light coming out}}{\text{light put in}})$$

UV-Vis spectroscopy analyzes electronic transitions. Other types of spectroscopy include microwave spectroscopy, which analyzes molecular rotation to find which molecules are in the substance being analyzed, and infrared spectroscopy, which analyzes molecular vibration to find the composition of the molecules analyzed.

The broadest categories of solids are *crystalline solids*, which have highly regular arrangement of their components, and *amorphous solids*, those with considerable disorder in their structures. The positions of the components in a crystalline solid are usually represented by a *lattice*, a three-dimensional system of points designating the positions of the components (atoms, ions, or molecules) that make up the substance. The smallest repeating unit of the lattice is called the *unit cell*. A particular lattice can be generated by repeating the unit cell in all three dimensions to form the extended structure. An example of an amorphous solid is glass. The structures of crystalline solids are most commonly determined by *X-ray diffraction*.

Types of crystalline solids are *ionic solids*, which are solids that are composed of ions, *molecular solids* (also called *molecular covalent solids* due to their bonding), which are solids that are composed of covalent molecules, and *atomic solids*, which are solids composed entirely of atoms and have several subcategories. Atomic solids can either be *metallic solids*, which are metal ions in a sea of delocalized electrons, *network solids* (also called *network covalent solids* due to their bonding), which are composed of nonmetal or metalloid atoms bonded in all directions to create massive structures, and *group 8A solids*, which are solids made from noble gases that are held together by London dispersion forces at extremely low temperatures. A chart of characteristics for each solid is below.

	Metallic	Group 8A	Network	Molecular	Ionic
Conductivity	Yes	No	Very little	No	Yes
Plyability	Yes	No	No	Yes	No
Hardness	Hard	Very soft	Very hard	Soft	Hard

An *alloy* is a substance that contains a mixture of elements and has metallic properties. In a *substitutional alloy* some of the host metal atoms are replaced by other metal atoms of similar size. In an *interstitial alloy* some of the holes in the metal structure are occupied by small atoms.

When molecules escape the liquid's surface and form a gas, the process is called *vaporization*. Vaporization is endothermic because energy is required to overcome the strong intermolecular forces in the liquid. The energy required to vaporize one mole of a liquid at a pressure of one atmosphere is called the heat of vaporization, or the enthalpy of vaporization, and is usually symbolized as ΔH_{vap}. Evaporation is a form of vaporization that happens stochastically; some molecules have greater than average kinetic energy and can vaporize by themselves. The process by which vapor molecules reform a liquid is called *condensation*. Eventually, evaporation and condensation reach an equilibrium in a closed system, which is why the level of a liquid first decreases then becomes constant. The pressure of the vapor present at equilibrium is called the *equilibrium vapor pressure* or simply the *vapor pressure* of the liquid. It can be calculated by a barometer by the following equation:

$$P_{vapor} = P_{atmosphere} - P_{barometer}$$

Liquids with high vapor pressure are said to be *volatile*, as in they evaporate rapidly. The vapor pressure of a liquid is determined mostly from the strength of the liquid's intermolecular forces - if the liquid's intermolecular forces are strong, the liquid is *nonvolatile*, as in it does not evaporate easily, and so it has low vapor pressure. Vapor pressure increases significantly with temperature since the process is endothermic equilibrium.

A *heating curve* is a plot of temperature versus time for a process where energy is added at a constant rate. The *melting point* is when the molecules in a substance become so energetic that they break from their lattice positions, and is also when the liquid and the solid have identical vapor pressures. The enthalpy change that occurs at the melting point is called the *enthalpy of fusion* ΔH_{fus}. The *boiling point* is when the molecules in a substance become so energetic that they break free from their intermolecular forces, and also when the vapor pressure of the liquid is exactly one atmosphere. The enthalpy change that occurs at the melting point is called the *enthalpy of vaporization* ΔH_{vap}. The equation for calculating the heat of fusion and heat of vaporization are below.

$$q_{fus} = n\Delta H_{fus} = m\Delta H_{fus} \quad \text{(if } \Delta H_{fus} \text{ is given in per gram, not per mole)}$$

$$q_{vap} = n\Delta H_{vap} = m\Delta H_{vap} \quad \text{(if } \Delta H_{vap} \text{ is given in per gram, not per mole)}$$

A *phase diagram* is a way to represent the phases of a substance in a closed systems a function of temperature and pressure.

At the *triple point*, all three states of a substance are present. The *critical temperature* is defined as the temperature above which the vapor cannot be liquefied no matter what. The *critical pressure* is the pressure required to produce liquefaction at the critical temperature. Together they define the *critical point*. For water, specifically, on a phase diagram, the solid-liquid line has a negative slope. For all other substances the solid-liquid line is positive.

The Maxwell-Boltzmann diagram of a substance at a set of conditions shows the distribution of molecules with a certain kinetic energy along with a threshold beyond which a phase change occurs or a reaction happens. With higher temperature, the curve is flatter, and more molecules pass the

threshold to react or change phase. At lower temperatures, most of the curve occurs to the left of the threshold.

11 Properties of Solutions

Along with molarity, there are other ways to describe solution composition. The qualitative terms *dilute* (relatively little solute present) and *concentrated* (relatively large amount of solute) are used to describe solution content. The *mass percent* (sometimes called *weight percent*) is the percent by mass of the solute in the solution:

$$\text{Mass percent} = (\frac{\text{mass of solute}}{\text{mass of solution}}) \times 100\%$$

Another way of describing solution composition is the mole fraction (symbolized by the lowercase Greek letter chi, χ), the ratio of the number of moles of a given compound to the total moles of solution. For a two-component solution, where n_A and n_B represent the number of moles of the two components:

$$\text{Mole fraction of component A} = \chi_A == \frac{n_A}{n_A + n_B}$$

Another way of describing solution composition is molality (symbolized by m), the number of moles of solute per kilogram of solvent:

$$\text{Molarity} = m = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

Another concentration measure sometimes encountered is *normality* (symbolized by N). Normality is defined as the number of *equivalents* per liter of solution. For an acid-base reaction, the equivalent is the mass of acid or base that can furnish or accept exactly 1 mole of protons (H^+ ions). For an oxidation-reduction reaction, the equivalent is defined as the mass of oxidizing or reducing agent that can accept or furnish 1 mole of electrons.

The last concentration measure that is covered is the *parts-per-million*, or *ppm*, which is a unit gram of solute out of one million grams of solvent.

$$\text{ppm} = \frac{\text{grams of solute}}{1 \times 10^6 \text{ gram of solution}}$$

The cardinal rule of solubility is *like dissolves like*, with regards to polarity. The formation of a liquid solution takes place in three distinct steps:

1. Separating the solute into its individual components (expanding the solute)

2. Overcoming intermolecular forces in the solvent to make room for the solvent (expanding the solvent)

3. Allowing the solute and solvent to interact to form the solution.

The enthalpy of solution (ΔH_{soln}) is the sum of the ΔH values for the steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

where ΔH_{soln} may be positive (energy absorbed) or a negative sign (energy released).

In water, ΔH_2 is large and positive, ΔH_1 is small and positive, and ΔH_3 is varying magnitude and negative. The *enthalpy of hydration* (ΔH_{hyd}) combines ΔH_2 and ΔH_3 and represents the enthalpy change associated with the dispersal of a gaseous solute in water (since gases have negligible intermolecular forces, so ΔH_1 is negligible).

One factor that favors a process is an increase in probability (see entropy, Chapter 17). Processes that require large amounts of energy tend not to occur (see Gibbs Free Energy, Chapter 17).

Structural effects cause molecules to be polar or nonpolar. Polar molecules are water-soluble (hydrophilic) and nonpolar molecules are fat-soluble (hydrophobic).

Henry's law states that the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution, that is

$$C = kP$$

Dissolution of a solid occurs more rapidly with higher temperature, but the amount of solid able to be dissolved can increase or decrease with increased temperature. Dissolution and solubility of a gas generally increases with temperature.

The presence of a nonvolatile solute lowers the vapor pressure of a solvent.

Raoult's law states that

$$P_{soln} = \chi_{solvent} P^0_{solvent}$$

where P_{soln} is the observed vapor pressure of the solution, $\chi_{solvent}$ is the mole fraction of solvent, and $P^0_{solvent}$ is the vapor pressure of the pure solvent. A solution that obeys this law is called an *ideal solution*. Deviations from this law are due to intermolecular forces.

For a solution with multiple volatile solvents, the total pressure is the sum of the different partial pressures:

$$P_{soln} = \chi_{solvent\ 1} P^0_{solvent\ 1} + \chi_{solvent\ 2} P^0_{solvent\ 2} + ...$$

Colligative properties like freezing-point depression, boiling-point elevation, and osmotic pressure depend only on the number, and not the identity, of the solute particles in an ideal solution.

A nonvolatile solute elevates the boiling point of the solvent. The change in boiling point can be represented by the equation

$$\Delta T_{boiling} = iK_b m_{solute}$$

where i is the van't Hoff factor which is the ratio between the moles of particles in solution and moles of solute dissolved, or in other words the number of ions a particle splits up into while dissolved, $\Delta T_{boiling}$ is the boiling point elevation, or the difference between the boiling point of the solution and that of the pure solvent, K_b is a constant that is characteristic of the solvent and is called the *molal boiling-point elevation constant*, and m_{solute} is the molality of the solute in the solution.

A nonvolatile solute also lowers the freezing point of the solvent. The change in freezing point can

be represented by the equation

$$\Delta T_{freezing} = iK_f m_{solute}$$

Where $\Delta T_{freezing}$ is the freezing point depression, or the difference between the freezing point of the solution and that of the pure solvent, and K_f is a constant that is characteristic of a particular solvent and is called the *molal freezing-point depression constant*.

The *Tyndall effect* is the scattering of light by particles and is often used to distinguish between a suspension and a true solution. A suspension of tiny particles in some medium is called a *colloidal dispersion* or a *colloid*. The particles in a colloid stay suspended instead of aggregating and precipitating because of electrostatic repulsion.

The destruction of a colloid, called *coagulation*, can be accomplished generally by heating or adding an electrolyte.

12   Chemical Kinetics

The *reaction rate* of a chemical reaction is the change in concentration of a reactant or product per unit time:

$$\text{Rate} = \frac{\text{concentration of A at time } t_2 \text{ - concentration of A at time } t_1}{t_2 - t_1} = \frac{\Delta[A]}{\Delta T}$$

Rates are not constant; they can decrease or increase with time. The above formula calculates *average rates*. The *instantaneous rate* is the rate at a particular time.

Rates of consumption and production at a particular time or over a particular time interval can be manipulated stoichiometrically to get the rates of consumption and production for other species in the reaction at the time or interval.

Chemical reactions are reversible. If the reverse reaction can be neglected, the reaction rate depends only on the concentration of the reactants:

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

Such an expression, which shows how the rate depends on the concentrations of reactants, is called a *rate law*. The proportionality constant k is called the *rate constant* and the exponent n is called the *order* of the reactant. Both of the values are determined by experiment. In the above rate law, the concentrations of the products do not appear because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.

A rate law that expresses how the rate depends on concentration is called the *differential rate law*, but more commonly just the *rate law*. Another form of the rate law, the *integrated rate law*, expresses how the concentrations depend on time. Each generalized differential rate law corresponds to a generalized integrated rate law. Experimental convenience chooses the rate law.

Determining the form of the differential rate law requires seeing how initial concentrations affect initial rates. If doubling the initial concentration doubles the initial rate, then the reaction is first order in the reactant. If doubling the initial concentration quadruples the initial rate, then the reaction is second order in the reactant, and so on.

The *overall reaction order* is the sum of all the exponents in the differential rate law.

For a differential rate law that is first order in A, the integrated first-order rate law is

$$\ln[A] = -kt + \ln[A]_0$$

Note that the integrated rate law is only in one reactant. You cannot tell the overall reaction order from an integrated rate law; you can say that the rate is "pseudo-nth order" or "nth order in A".

The time required for a reactant to reach half its original concentration is called the *half-life of a reactant* and is designated by the symbol $t_{\frac{1}{2}}$. For a first order decay, the half life can be expressed

as follows:
$$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$$

For a differential rate law that is second order in A, the integrated second-order rate law is

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

The half-life equation for a second-order reaction is

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

Most reactions involving a single reactant show either first-order or second-order kinetics. However, sometimes such a reaction can be a *zero-order reaction*. The rate law for a zero-order reaction is

$$\text{Rate} = k$$

The integrated rate law for a zero-order reaction is

$$[A] = -kt + [A]_0$$

The half-life equation for a zero-order reaction is

$$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$

Most chemical reactions occur by a series of steps called *reaction mechanisms*. In terms of reaction mechanisms, *intermediates* are species that are neither reactants nor products but that are formed then consumed during the reaction sequence, and *catalysts* are species that are neither reactants nor products but that are consumed then formed during the reaction sequence.

Each step in a reaction mechanism is an *elementary step*, a reaction whose rate law can be written from its molecularity. *Molecularity* is defined as the number of species that must collide to produce the reaction indicated by that step. A reaction involving one molecule is called a *unimolecular step*, two molecules are called *bimolecular*, and three molecules are called *termolecular*.

A reaction mechanism, more precisely, is a series of elementary steps that fulfill the following two requirements:

- The sum of the elementary steps must give the overall balanced equation for the reaction.

- The mechanism must agree with the experimentally determined rate law.

The *rate-determining step* of a reaction mechanism is the elementary step whose activation energy is the highest and therefore the step is the slowest. The rate law is calculated using the molecularity of the rate-determining step, substituting in for intermediates and catalysts as necessary (using algebraic manipulations of the rate laws of other steps), since neither an intermediate nor catalyst

can be in the final rate law.

The model that governs chemical kinetics is the *collision model*, which states that molecules need to collide to react. However, only a small fraction of collisions result in a reaction. The answer to this conundrum comes in the fact of activation energy, which is not reached by the majority of collisions. Svante Arrhenius proposed this theory. The arrangement of atoms found at the top of the activation energy barrier is called the *activation complex*, or *transition state*. Molecular orientation similarly reduces the rate law from the expected collisions with a certain activation energy.

The Arrhenius equation shows how the rate law shifts with temperature, where A is the frequency factor for the reaction and R is the gas constant in joules:

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

Catalysts are substances that reduce the activation energy requirement of a reaction by shifting the rate determining step to require less energy. *Enzymes* are examples of biological catalysts. A *homogeneous catalyst* is one that is present in the same phase as the reacting molecules. A *heterogeneous catalyst* exists in a different phase, usually a solid.

Heterogeneous catalysis often involves gaseous reactants being adsorbed onto the surface of a solid catalyst. *Adsorption* refers to the collection of one substance on the surface of another substance; absorption refers to the penetration of one substance onto another.

13 Chemical Equilibrium

Chemical equilibrium is the state of a system where the concentration of all reactants and products remain constant with time. For some reactions the equilibrium so favors the products that the reaction appears to have gone to completion. The equilibrium position for such reactions lies to the *right* or to the *direction of the products*. A reaction that appears to not happen but is thermodynamically favorable (see Gibbs Free Energy, Chapter 17) has an equilibrium position that lies to the *left* or to the *direction of the reactants*. Equilibrium is highly *dynamic*, that is, the reaction happens in both directions at a molecular level and balances out. Equilibrium is reached when all of the concentration levels as a function of time plateau out. Another way to view this is to say that equilibrium is reached when the reaction rates equal each other for the forward and reverse reactions.

The *law of mass action* is a general description of the equilibrium condition. For the following type of reaction:

$$aA + bB \rightleftharpoons cC + dD$$
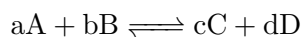
where the capital letters are species and the lower case letters are their coefficients, the equilibrium expression is as follows:

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

where the square brackets indicate the concentrations of the chemical species at equilibrium, and K is a constant called the equilibrium constant (which is unitless). The value of the equilibrium constant at a given temperature can be calculated if we know the equilibrium concentrations of the reaction components. For a given reaction, the equilibrium expression only involves gaseous and aqueous species. Solids and liquids are assumed to be in excess and the extra amount added will not matter.

The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse. When the balanced equation for a reaction is multiplied by a factor n, the equilibrium expression for the new reaction is the original expression raised to the nth power. Thus $K_{new} = (K_{original})^n$.

An equilibrium constant has the same value regardless of the amounts of the gases that are mixed together initially. The equilibrium concentrations, however, will not always be the same. However, their ratio will remain the same as it determines the constant. Subscript zeros indicate initial concentrations.

Each set of equilibrium concentrations is called an *equilibrium position*. While there is only one equilibrium constant for a particular system at a particular temperature, there are an infinite number of equilibrium positions.

For gases, since concentration is proportional to partial pressure, there is another equilibrium constant K_p such that

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

The relationship between K_c (or sometimes simply K) and K_p is

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

where Δn is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.

Homogeneous equilibria are equilibria where all species present and taking place in the reaction are of the same phase. *Heterogeneous equilibria* are equilibria that involve more than one phase.

For a K_c that is much larger than 1, the corresponding reaction consists of mostly products, that is, the equilibrium lies to the right (products side). For a K_c that is much smaller than 1, the corresponding reaction consists of mostly reactants, that is, the equilibrium lies to the left (reactants side). A K_c that is close to or equal to 1 represents an equilibrium where the concentration of all species is dictated by their coefficients in the reaction. To solve equilibrium problems, an ICE (initial-change-equilibrium) table is used. A generalizeable form of an ICE table is below, for the reaction aA (aq) + bB (s) $\rightleftharpoons$ cC (aq) + dD (g).

	A	B	C	D
I	i_A	-	i_C	i_D
C	$-ax$	-	$+cx$	$+dx$
E	$i_A - ax$	-	$i_C + cx$	$i_D + dx$

Then, the equilibrium constant can be used in the following manner:

$$K_{eq} = \frac{(i_C + cx)^c(i_D + dx)^d}{(i_A - ax)^a}$$

From there, the desired variable can be solved for. The units of x are generally $\frac{\text{mol}}{\text{L}}$, or M.

The *reaction quotient* Q is used to identify which direction a reaction will shift in given initial concentrations. To find Q, an equilibrium expression is constructed, except inside the brackets initial concentration, not equilibrium concentration, is used. If Q is equal to K, the system is at equilibrium, and no shift will occur. If Q is greater than K, the ratio of initial concentrations of products to initial concentrations of reactants is too large. To reach equilibrium, a net change of products to reactants must occur. The system *shifts to the left*, consuming products and forming reactants, until equilibrium is achieved. If Q is less than K, the reverse happens, and the system *shifts to the right* to attain equilibrium.

There is a strategy to solve equilibrium problems:

1. Write the balanced equation for the reaction.

2. Write the equilibrium expression (using the law of *mass action* and taking out solids and liquids)

3. List the initial concentrations.

4. Calculate Q, and determine the direction of the shift to equilibrium.

5. Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.

6. Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.

7. Check your calculated equilibrium concentrations by making sure they give the correct value of K.

Le Chatelier's principle is a way to qualitatively predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium which states that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

If a component (reactant or product) is added to a reaction system at equilibrium (at constant temperature and either pressure or volume), the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs.

There are three ways to change the pressure of a reaction system involving gaseous components:

- Add or remove a gaseous reactant or product.

- Add an inert gas (one not involved in the reaction).

- Change the volume of the container.

The addition of an inert gas increases the total pressure but has no effect on the concentration or partial pressures of the reactants or products, and so has no effect on the equilibrium position.

When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system. In other words, if a reaction has more gaseous species on one side, increasing pressure shifts the reaction to the side with the fewer gaseous species. Increasing the volume of the container has the opposite effect on the system.

While changes in pressure and volume may change the equilibrium position, they do not alter the equilibrium constant. The effect of temperature on equilibrium is different because the value of K_c changes with temperature. A reaction that has energy added in the form of heat shifts the equilibrium position away from the kilojoules involved in the reaction, that is, if the reaction is endothermic the equilibrium position shifts to the right. If the reaction is exothermic, the equilibrium position shifts to the left. Decreasing temperature produces the opposite effect.

14 Acids and Bases

Acids were first recognized as a class of substances that taste sour. Bases, sometimes called *alkalis*, are characterized by their bitter taste and slippery feel.

Svante Arrhenius postulated that acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions. This is called the *Arrhenius concept of acids and bases*. It was the first attempt at formalizing acid-base chemistry, but only allows for one kind of base and only aqueous species. Johannes Bronsted and Thomas Lowry proposed the *Bronsted-Lowry model of acids and bases*. In this model, an acid is a proton or hydride (H^+) donor, and a base is a proton or hydride acceptor. H_3O^+, one of the products of acid ionization, is called the *hydronium ion*. The equation for acid ionization is

$$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$$
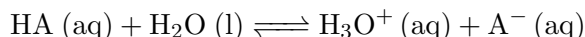
where HA is the acid, H_2O is the (Bronsted-Lowry) base, H_3O^+ is the *conjugate acid*, and A^- is the *conjugate base*.

The conjugate base is everything that remains of the acid molecule after a proton is lost. The conjugate acid is formed when the proton is transferred to the base. A *conjugate acid-base pair* consists of two substances related to each other by the donating and accepting of a single proton. In a standard acid ionization reaction there are two conjugate acid-base pairs.

The equilibrium expression for the acid-base ionization is

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

where K_a is a special type of equilibrium constant called the acid dissociation constant.

H_3O^+ (aq) and H^+ (aq) are often used interchangeably - in an aqueous solution, H^+ is hydrated. The corresponding acid ionization equation becomes a lot simpler as a result of this:

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$$
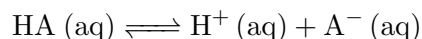
and all species can be used in the equilibrium reaction. The downside to this form is that there is only one conjugate acid-base pair (conjugate pair for short) since there are only three species.

A *strong acid* has an acidic ionization equilibrium position that is far to the right. Almost all the original acid is ionized at equilibrium (in calculations, we usually treat that small amount that is not ionized as negligible). A strong acid yields a relatively weak conjugate base, whose alkalic quality is weaker than water. Thus, their conjugate bases do not affect the acidity of the solution, since the water takes up the free protons. There are only seven strong acids:

1. Hydrochloric acid, HCl (aq)

2. Hydrobromic acid, HBr (aq)

3. Hydroiodic acid, HI (aq)

4. Nitric acid, HNO_3 (aq)

5. Chloric acid, $HClO_3$ (aq)

6. Perchloric acid, $HClO_4$ (aq)

7. Sulfuric acid, H_2SO_4 (aq)

Sulfuric acid is a *diprotic acid*, which has two acidic protons. Each of them has their own ionization reaction and thus a K_a. The K_as for a *polyprotic acid* (acid with multiple protons) are described in the order they leave, so they are K_{a1}, K_{a2}, K_{a3}, etc. Usually their magnitude, and thus acid strength, goes down as the protons fall off the acid. (Fun fact: the strongest acid, fluoroantimonic acid, chemical formula H_2FSbF_6, has a theoretical Hammett acidity, which is an extension of pH for extremely strong acids and bases, of -31.3 at its most concentrated form. The reason it is measured theoretically is because it destroys any pH indicator that is used to measure it.)

A *weak acid* has an acidic ionization equilibrium position that is far to the left. Most of the acid originally placed in the solution is still present as HA at equilibrium. A weak acid only dissociates only to a very small extent in aqueous solution. Weak acids are every other acid except for the strong acid. A weak acid has a conjugate base that is stronger than water and so affects the pH. The weaker the acid, the stronger its conjugate base. However, the conjugate acids are, in the vast majority of cases, much weaker than the acid themselves.

Most acids are *oxyacids*, in which the acidic proton is attached to an oxygen atom. *Organic acids* have a carbon atom backbone and contain the *carboxyl group*, an organic functional group. Acids of this type are weak acids. The hydrogens that are not in the carboxyl group in an organic acid are not acidic, and do not dissociate in water.

A substance is said to be *amphoteric* if it can behave either as an acid or as a base. Water is the most common *amphoteric substance*. The *autoionization of water* involves the trasnfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion:

$$2\,H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$

or equivalently:

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$
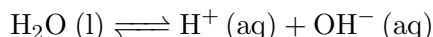
This reaction leads to the equilibrium expression

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

where K_w, called the *ion-product constant* or the *dissociation constant* for water, always refers to the autoionization of water. At 25 ° °C, in pure water:

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\,M$$

which means that at 25 °C:

$$K_w = [H^+][OH^-] = (1.0 \times 10^{-7})^2 = 1.0 \times 10^{-14}$$

A *neutral solution* is where $[H^+] = [OH^-]$. An *acidic solution* is where $[H^+] > [OH^-]$. A *basic*

solution is where $[\text{H}^+] < [\text{OH}^-]$. In each case (at 25 °C):

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

The *pH scale* provides a convenient way to represent solution acidity. The pH of a solution is governed by the following equation:

$$\text{pH} = -\log_{10}([\text{H}^+])$$

Thus, for a solution where

$$[\text{H}^+] = 1.0 \times 10^{-7}\,\text{M}$$
$$\text{pH} = -(-7.00) = 7.00$$

Significant figures for logarithms are different than multiplication. The number of decimal places in the logarithm is equal to the number of significant figures in the original number. Conversely, the number of significant figures in the antilogarithm is equal to the number of decimal places in the original number.

The pH changes by 1 for every power of 10 change in $[\text{H}^+]$. The pH decreases as $[\text{H}^+]$ increases. A pH meter shows the pH of the solution it is placed in. Generally, the prefix p is used as an operator which takes the negative logarithm of a quantity, stripping it of its units. In this way:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$
$$\text{p}K_a = -\log_{10}(K_a)$$
$$\text{p}K_w = -\log_{10}(K_w)$$

At 25 °C, $\text{p}K_w = -\log_{10}(1.0 \times 10^{-14}) = 14.00$. Also, due to properties of logarithms, pH + pOH $= \text{p}K_w = 14.00$.

In dealing with acid-base equilibria, we must focus on the solution components and their chemistry (e.g. whether they ionize in water or not). The next step in dealing with aqueous solutions is to determine which components are significant and which can be ignored. We need to focus on the *major species*, those solution components present in relatively large amounts. In all cases except when dealing with extraordinarily weak acids or bases, the products from the autoionization of water can be ignored - they, among others, are *minor species*. If the acid is a strong acid, concentration of H^+ can be determined stoichiometrically. If it is a weak acid, equilibrium and ICE tables should be used to determine concentration. For polyprotic acids, unless the K_a are similar in magnitude, only the first should be used to determine concentration, as the other K_a are so small that he corresponding production of hydrogen ion is negligible. When solving an ICE table quadratic, x can be ignored in any binomial term that involves it if the following condition is met:

$$\frac{x}{[\text{HA}]_0} \times 100\,\% < 5\,\%$$

because the values for K_a are typically known to an accuracy of $\pm 5\,\%$. From the table and con-

centration of H^+ every other quantity is known.

The process is analogous for strong and weak bases, using K_b of the base instead of K_a of the acid. By finding concentration of OH^-, every other quantity can be derived.

For mixtures of acids, the strongest acid is assumed to be the primary producer of H^+, and the concentration of H^+ it produces is used as the initial value for the other acids' ICE tables.

The percent ionization of a weak acid is as follows:

$$\text{Percent ionization} = \frac{\text{amount ionized of } H^+ \ (\frac{\text{mol}}{\text{L}})}{\text{initial concentration of HA} \ (\frac{\text{mol}}{\text{L}})} \times 100\,\%$$

For solutions of any weak acid, $[H^+]$ decreases as $[HA]_0$ decreases, but the percent ionization increases as $[HA]_0$ decreases. There is a massive set of steps for solving acid-base problems:

1. List the major species in solution.

2. Look for reactions that can be assumed to go to completion - for example, a strong acid dissociating or H^+ reacting with OH^-.

3. For a reaction that can be assumed to go to completion:

   (a) Determine the concentration of the products.

   (b) Write down the major species in solution after the reaction.

4. Look at each major component of the solution and decide if it is an acid or a base.

5. Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.

   (a) Write the equation for the reaction and the equilibrium expression.

   (b) Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, and so on).

   (c) Define x.

   (d) Substitute the concentrations into the equilibrium expression, and solve for x.

   (e) Check the validity of the approximation.

   (f) Calculate the pH and other concentrations as required.

Strong bases are bases which contain hydroxide ion. Strong bases with one hydroxide ion are called *monohydroxic* (the obvious analogue to monoprotic), two hydroxide ions are called *dihydroxic*, and so on, and the general identifier for a base with multiple hydroxide ions is the term *polyhydroxic*. *Weak bases* can be constructed from a lot of substances, but their defining characteristic is one or more lone pairs of electrons. Many of these bases are formed from a central nitrogen with three bonds and one lone pair. The general reaction between a base B and water is given by

$$B(aq) + H_2O(l) <=> BH^+(aq) + OH^-(aq)$$
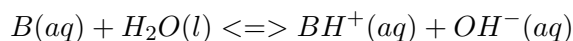
where B is the base, H_2O is the acid, BH^+ is the conjugate acid, and OH^- is the conjugate base. The equilibrium constant for this general reaction is

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

where K_b always refers to the reaction of a base with water to form the conjugate acid and the hydroxide ion. The K_b for a weak base tends to be small, as they have to compete with OH^-, an extremely strong base, for the H^+ ion.

A *salt* is another name for an ionic compound. Salts that consist of the cations of strong bases and the anions of strong acids have no effect on $[H^+]$ when dissolved in water. For any salt whose cation has neutral properties (such as Na^+ or K^+) and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic. The K_b value for the anion can be obtained from the relationship $K_b = \frac{K_w}{K_a}$. In general, salts in which the anion is not a base and the cation is the conjugate acid of a weak base produce acidic solutions. The K_a value for the cation can be obtained from the relationship $K_a = \frac{K_w}{K_b}$.

There are two main factors that determine whether a molecule containing an $X - H$ bond will behave as a Bronsted-Lowry acid: the strength of the bond and the polarity of the bond. The weaker the bond, the stronger the acid characteristic of the molecule is; the more polar the bond is, the stronger the acid characteristic of the molecule is. In oxyacids, the strength of the acid characteristic is proportional to the number of oxygens in the molecule. This is because the oxygens' partial charges pulls the electron away and functionally makes the $O - H$ bond more polar. Lastly, resonance stabilization makes it harder for the bond between hydrogen and the rest of the molecule to destabilize and the hydrogen to be lost.

When a covalent (nonmetal) oxide dissolves in water, an acidic solution forms. When an ionic oxide dissolves in water, a basic solution forms.

A Lewis acid is an electron-pair acceptor, that is, an acid has an empty atomic orbital that it can use to accept an electron pair. A Lewis base is an electron-pair donor, that is, it has a lone pair of electrons that it can donate.

15   Acid-Base Equilibria

When multiple compounds are in a solution, they may have a *common ion*. Their common ion is the ion that they all produce. The shift in equilibrium position that occurs because of an ion already involved in the equilibrium reaction is called the *common ion effect*. Usually, this manifests itself in different initial concentrations of the common ions.

A *buffered solution* is one that resists a change in its pH when either hydroxide ions or protons are added. A buffered solution may contain a weak acid and its salt or a weak base and its salt. By choosing the appropriate components, a solution can be buffered at virtually any pH.

Buffers work by replacing the OH^- and H^+ ions produced by base and acid ionization by the conjugate base or acid ions produced by the compounds already in the buffer. When H^+ is added to a buffered solution, it reacts essentially to completion with the weak base present:

$$H^+ + A^- \longrightarrow HA \qquad \text{or} \qquad H^+ + B \longrightarrow BH^+$$
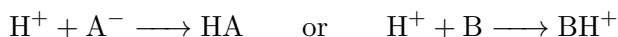
When OH^- is added to a buffered solution, it reacts essentially to completion with the weak acid present:

$$OH^- + HA \longrightarrow A^- + H_2O \qquad \text{or} \qquad OH^- + BH^+ \longrightarrow B + H_2O$$
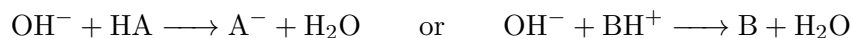
An expression to dictate the pH of a buffer is given by the *Henderson-Hasselbalch equation*:

$$pH = pK_a + \log_{10}(\frac{[A^-]}{[HA]})$$

where pK_a is the pK_a of the acid used to make the base. There is an analogous form to find the pOH of a buffer with a weak base and a conjugate acid:

$$pOH = pK_b + \log_{10}(\frac{[BH^+]}{[B]})$$

Since pH = 14.00 - pOH, the pH can be derived in a similar way from the second form:

$$pH = 14.00 - (pK_b + \log_{10}(\frac{[BH^+]}{[B]}))$$

For a particular buffering system (conjugate acid-base pair), all solutions that have the same ratio of acid to conjugate base or base to conjugate acid will have the same pH. Keep in mind that you can only use the Henderson-Hasselbalch equation to compute the pH of a buffer if and only if the percent dissociation is under 5% and the solution actually forms a buffer with a conjugate pair.

The *buffering capacity* of a buffered solution represents the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH. A buffer with a large capacity contains large concentrations of buffering components and so can absorb a relatively large amount of protons or hydroxide ions and show little pH change.

To create a buffer with some pH, the pK_a of the weak acid to be used in the buffer should be as close as possible to the desired pH.

The progress of an acid-base titration is often monitored by plotting the pH of the solution being analyzed as a function of the amount of titrant added. Such a plot is called a *pH curve* or *titration curve*. Calculating the points on a pH curve for a weak acid-strong base titration takes place in two steps: the reaction of hydroxide ion with the weak acid is assumed to run to completion and the concentrations of the acid remaining and the conjugate base formed are determined, and the position of the weak acid is determined and the pH is calculated. Titration curves are distinctly different depending on which types of acids or bases are titrated. The *equivalence point* or *stoichiometric point* of a titration is when enough base or acid has been added to react completely with the initial amount of acid or base. The *endpoint* of a titration is when the *indicator* changes color. The *buffer region* of a titration graph is when the conjugate base or acid and the original acid or base forms a buffer, so the pH does not go up linearly with the input of water. The middle of the buffer region is called the *half-equivalence point*. At that point the pH is equal to the pK_a of the acid or base.

An indicator is a complex molecule that is usually a weak acid. They exhibit one color when the proton is attached to the molecule and a different color when the proton is absent. The color change usually starts at pH = (pK_a - 1) and ends at pH = (pK_a + 1). This can be proven from Henderson-Hasselbalch and the observation that indicators tend to start color change when ten percent of their molecules lose their protons and stop their color change when ninety percent of their molecules lose their protons.

16 Solubility and Complex Ion Equilibria

Solids dissolving in water is actually an equilibrium process. Consider the following dissolution process:

$$A_2B_3\,(\text{s}) \xrightarrow{\text{H}_2\text{O}} 2\,A^{3+}\,(\text{aq}) + 3\,B^{2-}\,(\text{aq})$$
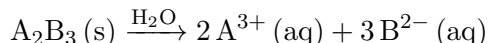
This can be written in a different way, because precipitation happens as well, and so the process reaches dynamic equilibrium:

$$A_2B_3\,(\text{s}) \rightleftharpoons 2\,A^{3+}\,(\text{aq}) + 3\,B^{2-}\,(\text{aq})$$
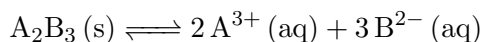
This process can be represented by the following equilibrium expression:

$$K_{sp} = [A^{3+}]^2[B^{2-}]^3$$

which can be solved in the usual way. The constant K_{sp} is called the *solubility product constant* or simply the *solubility product.* Neither the amount of excess solid nor the size of the particles present will shift the position of the solubilty equilibrium. It is important to note that the *solubility* of a product is different (it is the value of "x", in moles per liter, that is calculated from the ICE table for the equilibrium given). The solubility of the reactant is not well-defined.

Substances can be compared in their solubilities if they split up into equal numbers of ions. In that case, the substance with the greater K_{sp} has the greater solubility. If the substances being compared do not break up into the same number of ions, then it is much harder to compare solubilities. In that case the ICE table needs to be computed.

The common ion effect is a factor in the solubilities of substances and is taken care of with the ICE table. The pH of a solution can affect a salt's solubility if the salt contains hydroxide. If it does, calculating the H^+ concentration from the pH and then calculating the OH^- concentration from the H^+ concentration, then plugging that in as the initial value on the ICE table should produce an instance of the common ion effect. From there calculation in the usual manner is sufficient.

Precipitation is handled in the same way as determining equilibrium position. The *ion product Q* of a solubility reaction is defined just like the expression for K_{sp} for a given solid except that initial concentrations are used instead of equilibrium concentrations. For a solid A_2B_3, the expression for the ion product Q is written

$$Q = [A^{3+}]_0^2[B^{2-}]_0^3$$

If Q is greater than K_{sp}, precipitation occurs and will continue until the concentrations are reduced to the point that they satisfy K_{sp}. If Q is less than K_{sp}, no precipitation occurs. If, when two solutions are mixed, a reaction occurs that goes virtually to completion, it is essential to do the stoichiometry calculations before considering the equilibrium calculations. Therefore, in this case we let the system go completely in the direction towards which it tends. Then we will let it adjust back to equilibrium.

Mixtures of metal ions in aqueous solution are often separated by *selective precipitation*, that is, by using a reagent whose anion forms a precipitate with only one or a few of the metal ions in the mixture.

A *complex ion* is a charged species consisting of a metal ion surrounded by ligands. A ligand is simply a Lewis base - a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond. The number of ligands attached to a metal ion is called the coordination number. Metal ions add ligands one at a time in steps characterized by equilibrium constants caleld formation constants or stability constants. Metal ions in water after dissolving often form complex ions with water as the ligand.

17   Spontaneity, Entropy, and Free Energy

A process is said to be spontaneous, or *thermodynamically favorable*, if it occurs without outside information. Thermodynamically favorable processes may be fast or slow - the rate of reaction depends on activation energy and reaction path length, while thermodynamics deals with state function pathless variables.

The characteristic common to all spontaneous processes is an increase in a property called *entropy*, denoted by the symbol S. The driving force for a spontaneous process is an increase in the entropy of the universe. Entropy can be viewed as a measure of molecular randomness or disorder. The natural progression of things is from order to disorder. More precisely, it describes the number of arrangements (positions and/or energy levels) that are available to a system existing in a given state. Nature spontaneously proceeds toward the states that have the highest probabilities of existing. Each arrangement of particles is a *microstate*. The probability of each microstate existing is called *conditional probability*. The entropy of a solid is generally smaller than that of a liquid, and the entropy of a liquid is much, much smaller than the entropy of a gas (aqueous compounds have varying levels of entropy but are generally around the same entropy as liquids). Thus, the side of a reaction with more gaseous particles has greater entropy.

The *second law of thermodynamics* states that in any spontaneous process there is always an increase in the entropy of the universe. The entropy of the universe is continually increasing. The only exception to this is a system at equilibrium, where the change in entropy of the universe is zero. The change in the entropy of the universe can be defined as

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

for an arbitrary system and surroundings (which is everything else not in the system). For our purposes it is extremely convenient to assign the system to be the solution in which the given reaction takes place (or else, problems would be impossible).

To predict whether a given process will be spontaneous, we must know the sign of ΔS_{univ}. If ΔS_{univ} is positive, the entropy of the universe increases, and the process is spontaneous in the direction written. If ΔS_{univ} is negative, the process is spontaneous in the opposite direction. If ΔS_{univ} is at zero, the process has no tendency to occur.

The sign of ΔS_{surr} depends on the direction of the heat flow - an exothermic process increases entropy of surroundings, while an endothermic process decreases entropy of surroundings. The magnitude of ΔS_{surr} depends on the temperature - at low temperature, entropy of surroundings changes much more rapidly. The quantitative way to write ΔS_{surr} is:

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

where ΔH is taken with respect to the system, not the surroundings.

Another function which determines spontaneity is called the *Gibbs free energy* or *free energy* of a process. It is symbolized by G and defined by the relationship

$$G = H - TS$$

where H is the enthalpy, T is the Kelvin temperature, and S is the entropy. For a process that occurs at constant temperature, the change in free energy (ΔG) is given by the equation

$$\Delta G = \Delta H - T\Delta S$$

By a series of mathematical manipulations, we can show that at constant temperature and pressure,

$$\Delta S_{universe} = -\frac{\Delta G}{T}$$

This reveals that a process (at constant temperature and pressure) is spontaneous in the direction in which the free energy decreases.

For phase changes, ΔG is zero, and so the system is at equilibrium. At equilibrium, $\Delta H = T\Delta S$. This is shown through simplification.

Fewer molecules mean fewer possible configurations. The number of molecules, however, does not necessarily dictate the sign of ΔS - this is usually the case when gaseous molecules are involved. In general, however, when a reaction involves gaseous molecules, the change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products.

The *third law of thermodynamics* states that the entropy of a perfect crystal at $0\,\mathrm{K}$ is zero.

Entropy is a state function of a system, the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of products and those of the reactants:

$$\Delta S_{rxn} = S_{prod} - S_{react}$$

The heats of formation method can be formulated as entropies of formation:

$$\Delta S_{rxn} = \Delta S_{f\ prod} - \Delta S_{f\ react}$$

The more complex the molecule, the higher the standard entropy value.

The *standard free energy of formation* (ΔG_f°) of a substance is defined as the change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states. The standard free energy of formation of an element in its standard state, just like the standard enthalpy of formation of an element in its standard state, is zero.

The equilibrium position represents the lowest free energy values available to a particular reaction system.

At a given temperature for 1 mole of ideal gas, $S_{large\ volume} > S_{small\ volume}$, or since pressure and volume are inversely related, $S_{low\ pressure} > S_{high\ pressure}$. This is the qualitative argument for changes in entropy, which extends to free energy. Quantitatively, we have the formal equation:

$$G = G^\circ + RT\ln(P)$$

For changes in the free energy, we have the equation

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

where Q is the reaction quotient for the equation. Writing this in the combined form, we get

An equation to find the change in free energy of a reaction with equilibrium constant K at standard conditions is

$$\Delta G^\circ = -RT \ln(K)$$

Writing this in a combined form, we get

$$\Delta G = RT \ln(Q) - RT \ln(K) = RT(\ln(Q) - \ln(K))$$

This intuitively makes sense because the change in free energy is related logarithmically to the amount the system has to move to get to the equilibrium position.

The maximum work done by a process is equivalent to the change in free energy:

$$w_{max} = \Delta G$$

This is because the change in free energy is carried along an ideal path since it is a state function, while work is path-dependent. Ideally work takes the same path. However, in reality, some energy is lost to the path. If an ideal path was taken, then the process would be reversible. However, in reality, since nonideal paths are taken, then they are irreversible.

18 Electrochemistry

Electrochemistry is the study of the interchange of chemical and electrical energy. It is primarily concerned with two processes that involve oxidation reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process of the use of a current to produce chemical change.

There is a special technique for balancing the equations of redox reactions that occur in acidic solution called the *half-reaction method*.

1. Write separate equations for the oxidation and reduction half-reactions.

2. For each half reaction,

   (a) balance all the elements except hydrogen and oxygen.

   (b) balance oxygen using H_2O.

   (c) balance hydrogen using H^+.

   (d) balance the charge using electrons.

3. If necessary, multiply one or both balanced half-reactions by an integer to equalize the number of electrons transferred in the two half-reactions.

4. Add the half-reactions, and cancel identical species.

5. Check that the elements and charges are balanced.

In basic solution, the technique is a little different.

1. Use the half-reaction method as specified for acidic solutions to obtain the final balanced equation as if H^+ ions were present.

2. To both sides of the equation obtained above, add a number of OH^- ions that is equal to the number of H^+ ions. (We want to eliminate H^+ by forming H_2O.)

3. Form H_2O on the side containing both H^+ and OH^- ions, and eliminate the number of H_2O molecules that appear on both sides of the equation.

4. Check that elements and charges are balanced.

A *galvanic cell* is a system which utilizes a thermodynamically favorable chemical reaction to generate electric current, that is, where chemical energy is changed to electrical energy. It does this by separating two solutions and two metal electrodes (if the solution is of metal, the electrode is usually the same metal) into two *half-cells*. A half-cell houses an oxidation or reduction reaction. The metal electrodes are connected by a conductive wire, where electrons flow. A *salt bridge* or *porus disk* connects the two solutions which allow ions to flow and prevent charge buildup. Electrons flow through the wire from reducing agent to oxidizing agent and ions flow from one compartment to another to keep the net charge zero. The half-cell where reduction is carried out is called the

cathode; the half-cell where oxidation is carried out is called the *anode*; this is easily rememberable by the mnemonic *AnOx RedCat*.

The "pull", or driving force, on the electrons is called the *cell potential* (E_{cell}), or the electromotive force (emf) of the cell. The unit of electrical potential is the volt (abbreviated V) which is defined as 1 joule of work per coulomb of charge transferred. We can measure the cell potential through a voltmeter or potentiometer.

Combining two half-reactions to obtain a balanced oxidation-reduction reaction often requires two manipulations:

1. one of the reduction half-reactions must be reversed. The half-reaction with the largest positive potential will run as written (as a reduction), and the other half-reaction will be forced to run in reverse (as an oxidation). The net potential o the cell will be the difference of the two. Since the reduction process occurs at the cathode and the oxidation process occurs at the anode, we can write
$$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ$$
Because subtraction means "change the sign and add," it is also valid to change the sign of the oxidation (anode) reaction and reverse it before adding it to the reduction (cathode) reaction.

2. Since the number of electrons lost must equal the number gained, the half-reactions must be multiplied by integers as necessary to achieve the balanced equation. However, the value of E° is not changed when a half-reaction is multiplied by an integer. Since a standard reduction potential is an *intensive property* (it does not depend on how many times the reaction occurs), the potential is not multiplied by the integer required to balance the cell reaction.

Electrochemical cells can be described by *line notation*. In this notation the anode components are listed on the left and the cathode components are listed on the right, separated by double vertical lines (indicating the salt bridge or porus disk). A phase difference is indicated by a single vertical line. Multiple species of the same phase are separated by commas. If all components in the oxidation-reduction reaction are ions (meaning that they cannot act as electrodes, since every other state of matter can act as an electrode), then an inert or nonreactive metal is chosen as the electrode so it can conduct electrons and not react. A typical choice is platinum. An example showcasing these rules is below.

$$\text{Pt (s)} \,|\, \text{X}^{2+}\,\text{(aq)}, \text{Y}^{3+}\,\text{(aq)} \,||\, \text{X}^{2+}\,\text{(aq)}, \text{Z}^{4+}\,\text{(aq)} \,|\, \text{Pt (s)}$$

Given two options, a cell will always run spontaneously in the direction that produces a positive cell potential. This helps with choosing the anode and cathode when constructing a cell, since you know that if the total cell potential can be positive, it will be positive.

An important electrochemical constant is the faraday (abbreviated F). It is the charge of one mole of electrons. The constant is
$$F = \frac{96\,485\,\text{C}}{\text{mol e}^-}$$

For an ideal electrochemical process,

$$\Delta G = -nFE_{cell}$$

where n is the number of moles of electrons exchanged in the process. Consequently (note the standard signs):

$$\Delta G^{\circ} = -nFE_{cell}^{\circ}$$

Through this line of thinking, we can see that if E_{cell} is zero, ΔG is zero, and K is 1 (each one of the three implies the other two). If E_{cell} is greater than zero, ΔG is negative, and K is greater than 1. If E_{cell} is less than zero, ΔG is positive, and K is less than 1.

Cell potential varies with concentration of the solutions in the half-cells. After writing out the full equation for the electrochemical process, Le Chatelier's principle dictates the way the equilibrium shifts with concentration. A way to describe this shift qualitatively is called the *Nernst equation* (note that indicating that a set of conditions is standard means that all solutions in the system are concentrated at 1 M):

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF}\ln(Q)$$

Another, simpler way of writing this which is valid at 25 °C is

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n}\log_{10}(Q)$$

Measured potentials can be used to determine the concentration of an ion. Common pH meters contain an electrode that is sensitive to the pH of the solution. Electrodes that are sensitive to the concentration of a particular ion are called *ion-selective electrodes*, which are sensitive to the ion in place of H^{+}.

Many types of batteries and fuel cells are galvanic cells. Corrosion is an electrochemical process that conducts itself in a similar way to a galvanic cell.

An *electrolytic cell* uses electrical energy to produce a chemical change, which is the opposite of a galvanic cell. The process of *electrolysis* involves forcing a current through a cell to produce a chemical change for which the cell potential is negative; that is, electrical work causes an otherwise nonspontaneous chemical reaction to occur. Electrolytic cell problems are basically long stoichiometric problems using the fact that an ampere (A), which is a unit of current, is one joule per coulomb, and Faraday's constant to arrive at the answer.