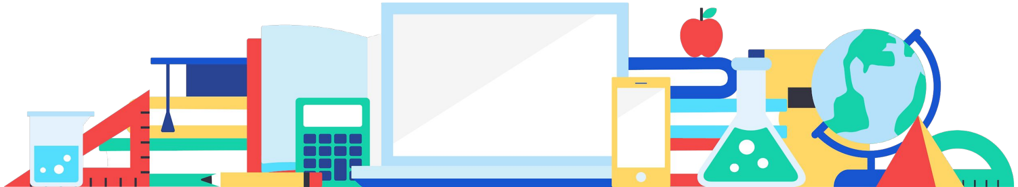
AP Chemistry Concepts & Vocab

Updated January 2021



Topics to Discuss

1. Atoms, Compounds, and Ions
2. Chemical Reactions
3. Stoichiometry
4. Electronic Structure of Atoms
5. Periodic Table
6. Chemical Bonds
7. Gas Laws
8. States of Matter and Intermolecular Forces
9. Chemical Equilibrium
10. Acids and Bases
11. Buffers, Titrations, and Solubility Equilibria
12. Thermodynamics
13. Redox Reactions and Electrochemistry
14. Kinetics
15. Nuclear chemistry

1. Atoms, Compounds, and Ions

- Introduction to the Atom
- Ions and compounds
- Names and Formulas of Ionic Compounds

Atoms, Compounds, and Ions

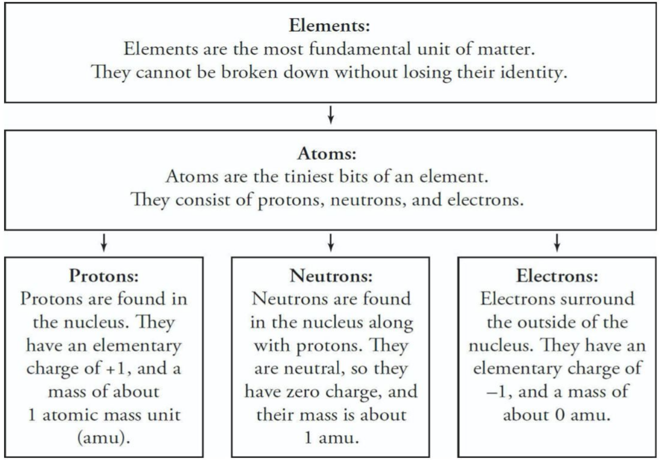
An **element** cannot be broken down into simpler substances, and an **atom** is the smallest particle of an element that still maintains the properties of an element. Atoms are made up of **protons**, **electrons**, and **neutrons**.

When atoms combine with one another, they form **chemical compounds**. A given chemical compound always has the same relative numbers and types of atoms.

An **ion** is an atom that does not have neutral charge. **Cations** have positive charges, while **anions** have negative charge. Be familiar with the rules and examples: positive ion first, negative ion second; -ate and -ite suffix; per- and hypo- prefix; roman numerals for oxidation states. Also, practice going from the ionic name to the formula as worked out in this video.

By examining the electron configurations that are most stable for an ion, **the charge of the ion can be predicted**. This will be covered more in-depth in section #5 on the periodic table.

Molecular compounds and **acids** also have their specific naming conventions (see next slide).



Elements:
Elements are the most fundamental unit of matter.
They cannot be broken down without losing their identity.

Atoms:
Atoms are the tiniest bits of an element.
They consist of protons, neutrons, and electrons.

Protons:
Protons are found in the nucleus. They have an elementary charge of +1, and a mass of about 1 atomic mass unit (amu).

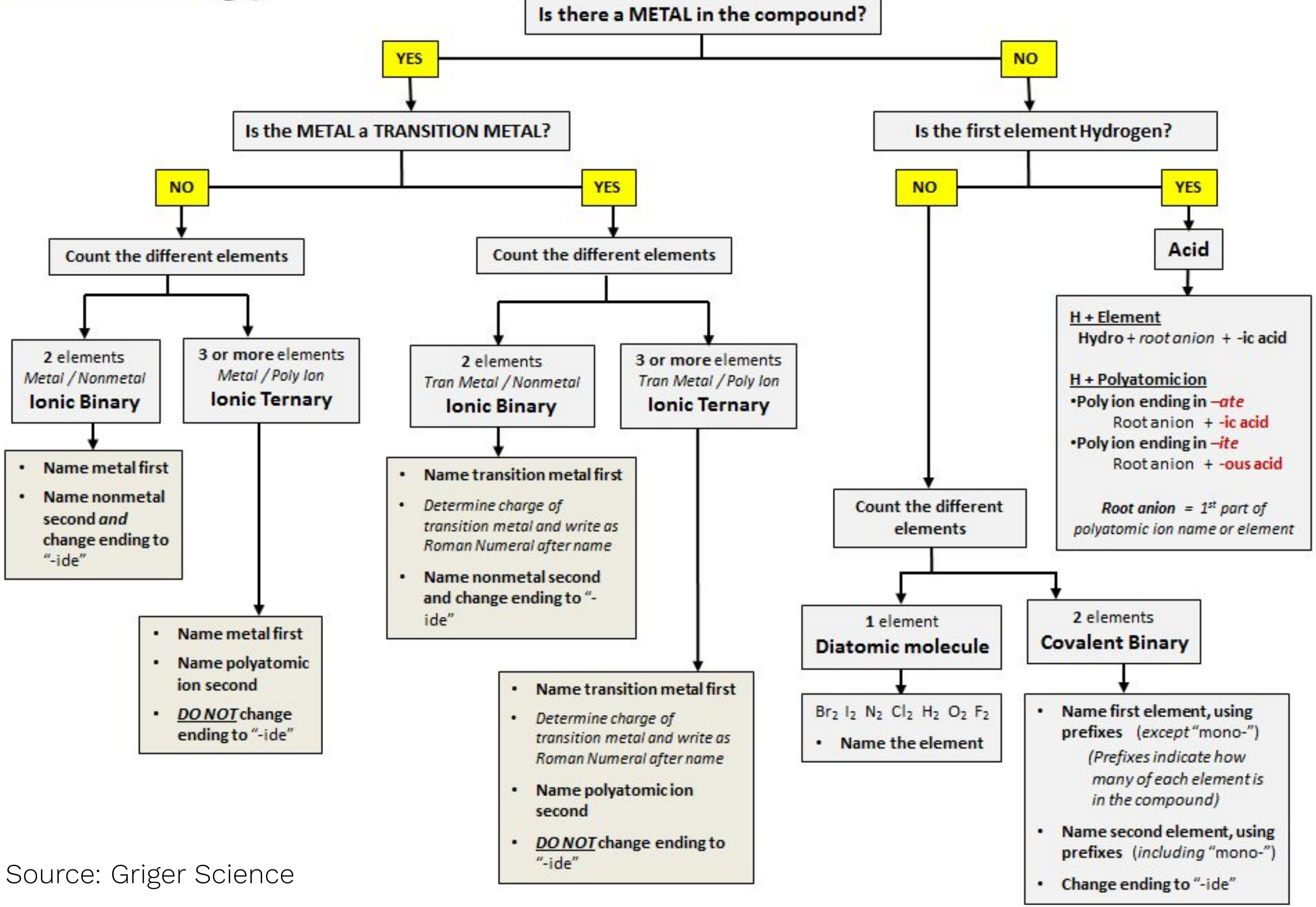
Neutrons:
Neutrons are found in the nucleus along with protons. They are neutral, so they have zero charge, and their mass is about 1 amu.

Electrons:
Electrons surround the outside of the nucleus. They have an elementary charge of −1, and a mass of about 0 amu.

Source: Princeton Review

LOOK ON BACK FOR EXAMPLES OF EACH!

Naming Compounds Flowchart



Is there a METAL in the compound?

YES

Is the METAL a TRANSITION METAL?

NO

Count the different elements

2 elements
Metal / Nonmetal
Ionic Binary

- **Name metal first**
- **Name nonmetal second *and* change ending to** "-ide"

3 or more elements
Metal / Poly Ion
Ionic Ternary

- **Name metal first**
- **Name polyatomic ion second**
- ***DO NOT* change ending to** "-ide"

YES

Count the different elements

2 elements
Tran Metal / Nonmetal
Ionic Binary

- **Name transition metal first**
- *Determine charge of transition metal and write as Roman Numeral after name*
- **Name nonmetal second and change ending to** "-ide"

3 or more elements
Tran Metal / Poly Ion
Ionic Ternary

- **Name transition metal first**
- *Determine charge of transition metal and write as Roman Numeral after name*
- **Name polyatomic ion second**
- ***DO NOT* change ending to** "-ide"

NO

Is the first element Hydrogen?

NO

Count the different elements

1 element
Diatomic molecule

Br_2 I_2 N_2 Cl_2 H_2 O_2 F_2

- **Name the element**

2 elements
Covalent Binary

- **Name first element, using prefixes** (*except* "mono-")
  (Prefixes indicate how many of each element is in the compound)
- **Name second element, using prefixes** (*including* "mono-")
- **Change ending to** "-ide"

YES

Acid

H + Element
Hydro + *root anion* + **-ic acid**

H + Polyatomic ion
•**Poly ion ending in** ***–ate***
Root anion + **-ic acid**
•**Poly ion ending in** ***–ite***
Root anion + **-ous acid**

Root anion = *1st part of polyatomic ion name or element*

Source: Griger Science

2. Chemical Reactions

- Types of Reactions
- Balancing Chemical Equations

Types of Chemical Reactions

The basic **solubility rules** that should be known are:
1. If a compound has an alkali metal cation (Na^+, Li^+, K^+, etc.) or an ammonium cation (NH_4^+), then it is soluble.
2. Compounds with a nitrate (NO_3^-) anion are always soluble. (Alkali metals are explained in section 4 on the periodic table.)

- **Synthesis Reactions**: When elements or compounds combine to form a single, more complex compound.
  - Example: $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
- **Decomposition**: When a single compound splits into two or more elements or compounds.
  - Example: $HgO(s) + \text{Heat} \rightarrow Hg(s) + \frac{1}{2}O_2(g)$
- **Acid-Base Reaction**: When an acid reacts with a base to form water and a salt.
  - Example: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
- **Oxidation-Reduction Reaction**: When the oxidation states change for the elements or compounds involved.
  - Example: $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$.
- **Combustion**: When a covalent substance containing carbon, hydrogen, and sometimes oxygen is ignited and reacts with atmospheric oxygen, producing CO_2 and H_2O.
  - Example: $2C_4H_{10}(l) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$
- **Single Displacement**: When a metal is placed in an aqueous solution and causes one of the cations precipitates out of solution.
  - Example: $2AgNO_3(aq) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$
- **Double Displacement**: When two aqueous solutions mix, a new cation/anion pairing may form, producing an insoluble salt.
  - Example: $K_2CO_3(aq) + Mg(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + MgCO_3(s)$
  - The **net ionic equation** for the above reaction is: $CO_3^{2-} + Mg^{2+} \rightarrow MgCO_3(s)$. This is because the potassium and nitrate ions are **spectator ions**.

Balancing Chemical Reactions

A **skeleton equation** is a chemical equation without coefficients and provides information on what are the reactants and products. For example: $Mg + O_2 \rightarrow MgO$. However, the number of atoms of each type must be the same on both the reactant and product sides.

Never change the subscripts in a chemical equation, **only the coefficients** can be changed. Also be on the lookout for groups of atoms that can be grouped together to simplify balancing (e.g, SO_4 in $Al_2(SO_4)_3$). Guess-and-check may work for balancing more simple equations, but the guidelines for balancing more complex equations are as follows:

1. Balance the element with the greatest number of atoms in any reactant or product, other than oxygen or hydrogen.
2. Balance other elements, other than hydrogen or oxygen.
3. Balance oxygen or hydrogen, whichever one is present in the combined state. Leave whichever one is present in the uncombined state for the very end.
4. Check that the equation is balanced by counting the number of atoms of each element on each side of the equation.
5. The coefficients should be in whole numbers and in their lowest terms (get rid of fractions by multiplying by the denominator).

Source: notes, linked in the additional resources to the left

Please consult online articles or videos for more practice problems and examples! Be familiar with **chemical reaction calculations** -- given a balanced equation and the number of grams of one reactant, find the number of grams of the products generated. Also, be comfortable with **combustion analysis** -- given the number of grams of the products of a combustion reaction, find the empirical formula for the combustion compound.

Combustion Analysis

Sample Problem: *A combustion analysis was performed on 1.621 g of a substance composed only of carbon, hydrogen, and oxygen. This produced 1.902 g of H_2O and 3.095 g of CO_2. Determine the empirical formula of the unknown compound.*

We can first calculate the mass of carbon and hydrogen in the unknown compound since all of the carbon in the unknown compound is found in CO_2 and all of the carbon in the unknown compound is found in H_2O.

$$\begin{aligned} n_{\mathrm{C}} &= 3.095\,\mathrm{g\ CO_2}\left(\frac{1\,\mathrm{mol\ CO_2}}{44.01\,\mathrm{g\ CO_2}}\right)\left(\frac{1\,\mathrm{mol\ C}}{1\,\mathrm{mol\ CO_2}}\right) \\ &= 0.0703\,\mathrm{mol\ C} \end{aligned} \longrightarrow \begin{aligned} m_{\mathrm{C}} &= 0.0703\,\mathrm{mol\ C}\left(\frac{12.01\,\mathrm{g\ C}}{1\,\mathrm{mol\ C}}\right) \\ &= 0.8446\,\mathrm{g\ C} \end{aligned}$$

$$\begin{aligned} n_{\mathrm{H}} &= 1.902\,\mathrm{g\ H_2O}\left(\frac{1\,\mathrm{mol\ H_2O}}{18.02\,\mathrm{g\ H_2O}}\right)\left(\frac{2\,\mathrm{mol\ H}}{1\,\mathrm{mol\ H_2O}}\right) \\ &= 0.2111\,\mathrm{mol\ H} \end{aligned} \longrightarrow \begin{aligned} m_{\mathrm{H}} &= 0.2111\,\mathrm{mol\ H}\left(\frac{1.008\,\mathrm{g\ H}}{1\,\mathrm{mol\ H}}\right) \\ &= 0.2128\,\mathrm{g\ H} \end{aligned}$$

We can now subtract the mass of carbon and hydrogen from the total mass of the unknown compound to calculate the mass of oxygen in the compound.

$$\begin{aligned} m_{\mathrm{O}} &= 1.621\,\mathrm{g} - 0.8446\,\mathrm{g} - 0.2128\,\mathrm{g} \\ &= 0.564\,\mathrm{g\ O} \end{aligned} \longrightarrow \begin{aligned} n_{\mathrm{O}} &= 0.564\,\mathrm{g\ O}\left(\frac{1\,\mathrm{mol\ O}}{16.00\,\mathrm{g\ H_2O}}\right) \\ &= 0.0352\,\mathrm{mol\ O} \end{aligned}$$

We can use n_C, n_H, n_O to determine the empirical formula of the unknown compound (see section 4). Doing these calculations, we arrive at the formula C_2H_6O.

3.
Stoichiometry

- Moles
- Molecular Composition
- Limiting Reagent Stoichiometry

Moles and Molecular Composition

The coefficients in chemical equations relays the quantity of each product/reactant in terms of **moles**. The number of atoms in a single mole is 6.02 x 10^{23}. One mole of an atom is equal to its atomic mass in grams. For example, one mole of a carbon, with an atomic mass of 12 amu is 12 grams. The ideal gas equation (in section 7) can be used to find the number of moles in a gas. **Molarity**, denoted by *M*, expresses the concentration of a solute in terms of volume. Molarity can be calculated as

$$\text{Molarity} = \frac{\text{Moles Solute}}{\text{Liters of Solution}}$$

Percent composition is the percent that an element takes up, by mass, in a compound. Convert the number of moles per a compound into grams to calculate it.

The **empirical formula** gives the simplest ratio, of a compound, for each element to the others, while the **molecular formula** gives the actual formula of the compound. For example, $C_6H_{12}O_6$ is the molecular formula of glucose, while CH_2O is the empirical formula. Be able to determine the empirical and molecular formulas of a compound given the mass percents or masses.

Sample Problem: *Compute the percent composition of oxygen in* $CaCO_3$.
From the periodic table, we see that the atomic masses of Ca, C, and O are 40.08 amu, 12.01 amu, and 16.00 amu, respectively. We can solve this problem by considering the relevant masses in one mole of $CaCO_3$.

$$\begin{aligned} \mathrm{O}\% &= \frac{\text{Mass of oxygen atoms}}{\text{Mass of CaCO}_3} \\ &= \frac{(3\,\mathrm{mol})\,(16.00\,\mathrm{g/mol})}{(1\,\mathrm{mol})\,(40.08\,\mathrm{g/mol}) + (1\,\mathrm{mol})\,(12.01\,\mathrm{g/mol}) + (3\,\mathrm{mol})\,(16.00\,\mathrm{g/mol})} \times 100\% \\ &= 47.96\% \end{aligned}$$

Sample Problem: *Determine the empirical formula for a compound with following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O.*
We assume that we have 100 g of the sample and calculate the number of moles of each atom. We can then use mole ratios with respect to the element with the smallest number of moles in order to calculate the subscripts in the empirical formula.

$$n_{\mathrm{Mg}} = \frac{28.03\,\mathrm{g}}{24.31\,\mathrm{g/mol}} = 1.15\,\mathrm{mol} \quad n_{\mathrm{H}} = \frac{1.16\,\mathrm{g}}{1.01\,\mathrm{g/mol}} = 1.15\,\mathrm{mol} \quad n_{\mathrm{Si}} = \frac{21.60\,\mathrm{g}}{28.09\,\mathrm{g/mol}} = 0.76\,\mathrm{mol} \quad n_{\mathrm{O}} = \frac{49.21\,\mathrm{g}}{16.00\,\mathrm{g/mol}} = 3.08\,\mathrm{mol}$$

$$\frac{n_{\mathrm{Mg}}}{n_{\mathrm{Si}}} = 1.51 \approx \frac{3}{2} \qquad \frac{n_{\mathrm{H}}}{n_{\mathrm{Si}}} = 1.51 \approx \frac{3}{2} \qquad \frac{n_{\mathrm{Si}}}{n_{\mathrm{Si}}} = 1.00 \approx 1 \qquad \frac{n_{\mathrm{O}}}{n_{\mathrm{Si}}} = 4.05 \approx 4$$

$$\mathrm{Mg}_{3/2}\mathrm{Si}_1\mathrm{H}_{3/2}\mathrm{O}_4 \rightarrow \mathrm{Mg}_3\mathrm{Si}_2\mathrm{H}_3\mathrm{O}_8$$

Limiting Reagent Stoichiometry

The **limiting reagent** is the reactant that determines the total amount (in mass) of the product. The maximum amount of the product that can be produced is called the **theoretical yield**. **Percent yield** is the actual yield divided by theoretical yield (times 100%), where actual yield is the amount of the product produced in the real world, in experiment.

To find the limiting reagent, use the following steps:

1. Balance the given chemical reaction
2. Convert the amount (mass) of each compound, given in the question, to moles
3. Find the stoichiometric and actual ratios.
    a. "Stoichiometric ratio" is the ratio between compounds of the balanced chemical equation
    b. "Actual ratio" is the ratio between the compounds given in the question

An extension to finding the limiting reagent would be to find the theoretical and then percent yield.

Sample Problem: *100 g of H_2O reacts with 100 g of CaC_2 via the following reaction*: $\mathrm{CaC_2(s) + 2\,H_2O\,(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g)}$ *Identify the limiting reagent and calculate the theoretical yield of C_2H_2.*

We can calculate the number of "reaction moles" of each reactant using their molar masses and stoichiometric coefficients to find the limiting reagent.

$$n_{\mathrm{CaC_2,rxn}} = 100\,\mathrm{g\ CaC_2}\left(\frac{1\,\mathrm{mol\ CaC_2}}{64.10\,\mathrm{g\ CaC_2}}\right)\left(\frac{1\,\mathrm{mol\ rxn}}{1\,\mathrm{mol\ CaC_2}}\right) = 1.56\,\mathrm{mol\ rxn}$$

$$n_{\mathrm{H_2O,rxn}} = 100\,\mathrm{g\ H_2O}\left(\frac{1\,\mathrm{mol\ H_2O}}{18.02\,\mathrm{g\ H_2O}}\right)\left(\frac{1\,\mathrm{mol\ rxn}}{2\,\mathrm{mol\ H_2O}}\right) = 2.77\,\mathrm{mol\ rxn}$$

Because there are fewer reaction moles of CaC_2 than H_2O, CaC_2 is the limiting reagent.

We can use the number of reaction moles of CaC_2 to calculate the theoretical yield of C_2H_2.

$$m_{\mathrm{C_2H_2}} = 1.56\,\mathrm{mol\ rxn}\left(\frac{1\,\mathrm{mol\ C_2H_2}}{1\,\mathrm{mol\ rxn}}\right)\left(\frac{26.04\,\mathrm{g\ C_2H_2}}{1\,\mathrm{mol\ C_2H_2}}\right) = 40.6\,\mathrm{g\ C_2H_2}$$

4. Electronic Structure of Atoms

- Coulomb’s Law
- Bohr’s Model of the Hydrogen Atom
- Quantum Numbers and Orbitals
- Electron Configurations
- Predicting Ionic Charges

Coulomb’s Law and the Bohr Model

The energy of electrons is **quantized**, meaning electrons only exist at discrete energy levels and not in between. **Coulomb’s law** calculates the energy of an electron using the distance of the electron from the nucleus. The force between two charged particles with charges q_1 and q_2 that are a distance r apart is given by

$$F = \frac{kq_1q_2}{r^2}$$

where k is Coulomb’s constant ($8.988\times10^{9}\ \mathrm{N\cdot m^2\cdot C^{-2}}$). If F is positive, then the force is repulsive. If F is negative, then the force is attractive. Be comfortable with the general trends of Coulomb’s law: the greater the charge of the nucleus, the greater the energy of the electron. The energy needed to remove a 3s electron is lower than for a 1s electron.

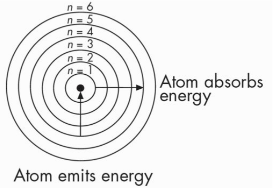
The **Bohr model** is a quantized shell model of the atom that has electrons orbiting the nucleus as planets do the sun. The closer the energy level is to the nucleus, the less energy the electrons have. When an atom absorbs energy, electrons jump to higher energy levels. The Bohr model is not the perfect model of the atom, but it helps us understand quantized energy levels.

The energy E of a photon absorbed or emitted by an electron is given by $E = h\mathbf{v}$, where h is Planck’s constant ($6.626 \times 10^{-34}\ \mathrm{J\cdot s}$) and **v** is the frequency of the photon with units of Hz.

The **Rydberg equation** can be used to predict the lines in the hydrogen emission spectrum. Let $n_1 < n_2$ be positive integers representing the principal energy levels in a hydrogen atom. Then the wavelength **λ** of the photon emitted by an electron falling from energy level n_2 to energy level n_1 is given by

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

where R_H is Rydberg’s constant ($109{,}737\ \mathrm{cm^{-1}}$).



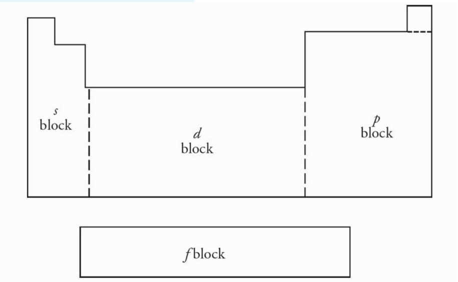
Quantum Numbers and Configuration

Name	Symbol	Allowed Values	Property
Principal	n	Positive Integers (1,2,3,...)	Orbital size and energy level
Secondary (Angular Momentum)	l	Integers from 0 to n-1	Orbital shape (sublevels/subshells)
Magnetic	m_l	Integers from -l to +l	Orbital orientation
Spin	m_s	+½ or -½	Electron spin direction

Quantum numbers categorize electrons, indicating their atomic states. Quantum numbers build off the Bohr model, which has only *one* quantum number. However, these four numbers, the principal, azimuthal (electron subshells), magnetic, and spin, allow electrons to occupy 3-dimensional space.

Subshells, denoted by the secondary quantum number, describe the shape of space in which an electron can be found. We can describe an electron by its subshell (space it takes up) and energy level (distance from nucleus). Four subshells are *s, p, d,* and *f*. Important **configuration rules** are as follows:

- **The Aufbau principle**:when building up the electron configuration of an atom, electrons are placed in orbitals and subshells in order of increasing energy.
- **The Pauli Exclusion Principle**: two electrons sharing an orbital do not have the same spin (m_s). Only one can be counter clockwise, vice versa.
- **Hund's Rule**: when an electron is added to a subshell, it occupies an empty orbital if available. Electrons always occupy orbitals singly if possible and pair up only if no empty orbitals are available.



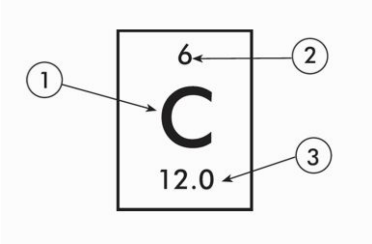
5. Periodic table

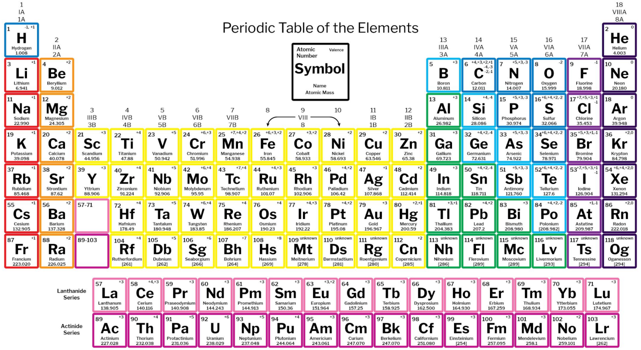
- Periodic trends

Periodic Table

The periodic table gives **symbol** for the element (1), the **atomic number** (number of protons in an element) (2), **average atomic mass** (in amu's) (3). The horizontal rows of the periodic table are called **periods**, and the vertical columns are called **groups**. It is important to know important groups and their respective properties.

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Metalloid | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide





Atoms with the same number of protons but different numbers of neutrons are called **isotopes**. For example, a carbon atom with 6 neutrons is carbon-12 (because 6 protons + 6 neutrons), while a carbon atom with 8 neutrons is carbon-14 (6 + 8).

The periodic table is structured so that the length of each area is also the length of an electron subshell (**electron configuration** was covered in section 4!).

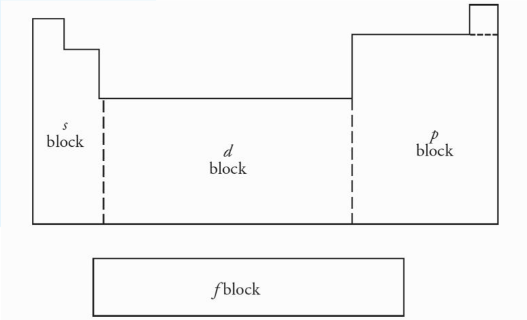


Diagram sources: Bryn Mawr College and Princeton Review

Periodic Trends

Periodic trends can be remembered using three basic rules:

1. Electrons are attracted to protons. So, electron-proton attraction is stronger when an electron is close to the nucleus and/or the nucleus has more protons.
2. Electrons repel other electrons. **Shielding** is when the electrons between the valence electrons and protons decrease the attraction that the valence electrons have
3. Completed shells are stable. Elements on the left-hand side of the periodic table, metals, will give up electrons. Nonmetals on the right hand side will gain.

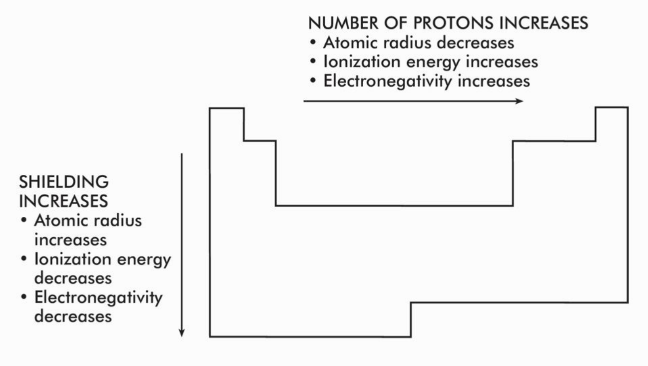
With these three basic rules, we can briefly cover the various periodic trends:

- From left to right, **atomic radius** *decreases* as protons increase and shielding electrons stay the same. From top to bottom (down a group), atomic radius *increases* as shells increase.

- **Cations** (positively charged ions) are *smaller* than atoms, while **anions** (negatively charged ions) are *larger*. This results from how electron-electron repulsion effects valence electrons.

- **Ionization energy** is the energy necessary to remove an electron from an atom. Ionization energy *increases* left to right and *decreases* top to bottom because of the attraction of valence electrons to protons.

- **Electronegativity** refers to how strongly the nucleus of an atom attracts electrons from other atoms in a bond. Electronegativity is affected by the size of the atom and the number of electrons needed to fill out the valence shell. From left to right, electronegativity *increases* (since atomic radius decreases). From top to bottom, electronegativity *decreases*.



NUMBER OF PROTONS INCREASES
- Atomic radius decreases
- Ionization energy increases
- Electronegativity increases

SHIELDING INCREASES
- Atomic radius increases
- Ionization energy decreases
- Electronegativity decreases

Source: Princeton Review

6. Chemical Bonds

- Types of Bonds
- Lewis Dot Structures
- Polarity

Types of Chemical Bonds

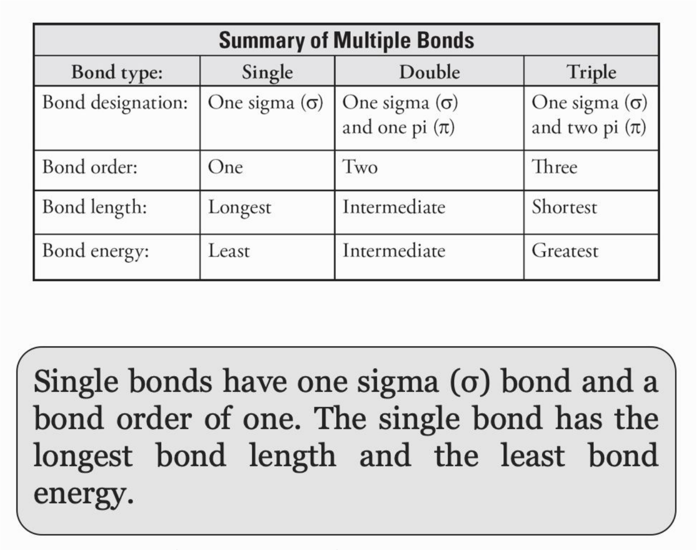
Bonding refers to the sharing or transferring of electrons so that atoms can reach a more stable, lower-energy state. This occurs when an atom has a complete set of **valence electrons**, or equivalently, when the outermost shell is full with 8 electrons.

Ionic bonds usually occur between a nonmetal and metal, involving a transferring of electrons. Ionic solids are held together by **electrostatic attraction**. **Metallic** bonds form **interstitial** and **substitutional alloys**, and can be understood through the sea of electrons model. **Covalent bonds** involve the sharing of electrons; each atom considers the shared electron as part of its valence electrons.

The **internuclear distance** between two atoms in a covalent bond must balance the the attraction and repulsion forces.

Network (covalent) bonds hold together atoms in a lattice structure, forming a **network solid**. Common examples of network solids contain carbon and silicon. They have the strongest bond, though ionic bonds are generally stronger than covalent bonds.

Network solids make poor conductors, but **doping** (adding an impurity) creates a positive or negative charge to increase conductivity.



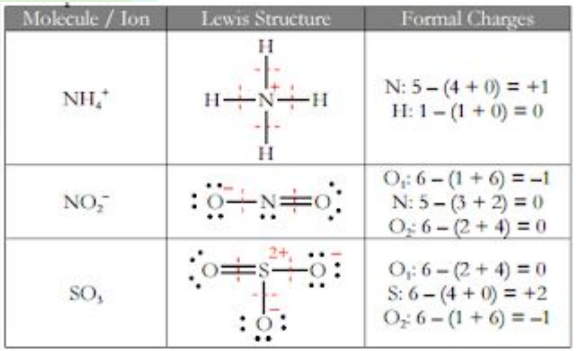
Summary of Multiple Bonds

Bond type:	Single	Double	Triple
Bond designation:	One sigma (σ)	One sigma (σ) and one pi (π)	One sigma (σ) and two pi (π)
Bond order:	One	Two	Three
Bond length:	Longest	Intermediate	Shortest
Bond energy:	Least	Intermediate	Greatest

Single bonds have one sigma (σ) bond and a bond order of one. The single bond has the longest bond length and the least bond energy.

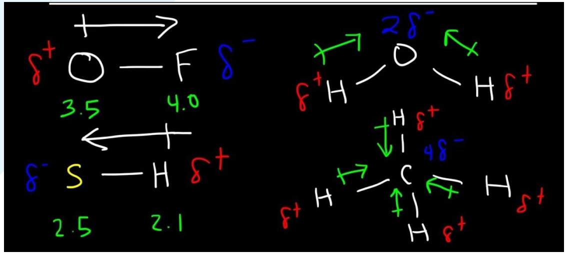
Source: Princeton Review

Lewis Dot Structures and Polarity



Molecule / Ion	Lewis Structure	Formal Charges
NH_4^+		N: 5 – (4 + 0) = +1 H: 1 – (1 + 0) = 0
NO_2^-		O_1: 6 – (1 + 6) = –1 N: 5 – (3 + 2) = 0 O_2: 6 – (2 + 4) = 0
SO_3		O_1: 6 – (2 + 4) = 0 S: 6 – (4 + 0) = +2 O_2: 6 – (1 + 6) = –1

Molecular geometry
Source: Lovejoy pre AP chemistry



A summary of the steps of drawing a **Lewis dot structure**: count the number of valence electrons for the ionic compound or molecule; add/subtract electrons based on the ionic charge; deduce the central atom based on **electronegativity** and place two electrons (representing a single bond) between each bonded atom; add electrons and rearrange until the central atom has at least a complete octet.

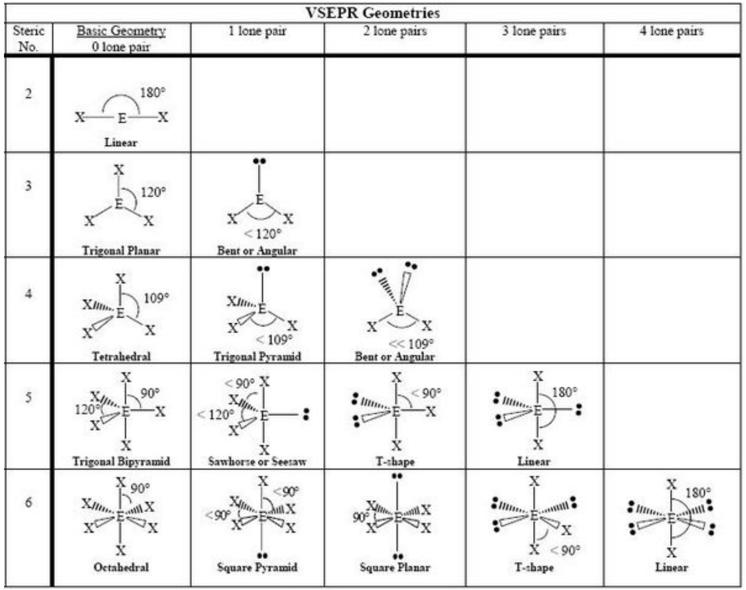
Be familiar with **resonance forms**, **incomplete octets**, **expanded octets**, **formal charge** (to determine the more likely form), and **molecular geometry**, which is connected to the **valence shell-electron pair repulsion theory**. For VSEPR theory, remember that lone electron pairs have slightly more repulsive strength than bonding pairs, and multiple bonds have more repulsive strength than single bonds.

Polarity results when electrons are shared unequally in a covalent bond, resulting from differing electronegativities.

Polarity results in **dipoles**, or areas of positive or negative charges. Dipoles are denoted by the lowercase letter delta: δ.

If a covalent bond doesn't result in the creation of dipoles, then it is a **nonpolar covalent bond**.

Left: Examples of bond polarity from The Organic Chemistry Tutor on Youtube.



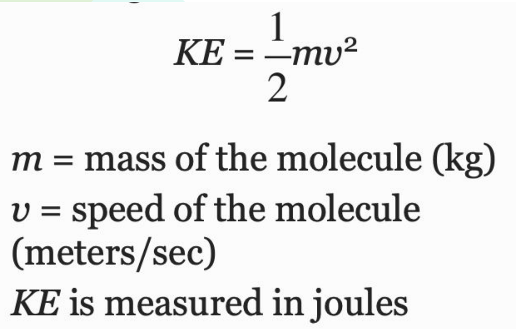
VSEPR Geometries

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal Planar	< 120° Bent or Angular			
4	109° Tetrahedral	< 109° Trigonal Pyramid	<< 109° Bent or Angular		
5	90° 120° Trigonal Bipyramid	< 90° < 120° Sawhorse or Seesaw	< 90° T-shape	180° Linear	
6	90° Octahedral	<90° <90° Square Pyramid	90° Square Planar	< 90° T-shape	180° Linear

7. Gas laws

- Kinetic Molecular Theory
- Maxwell-Boltzmann Diagram
- The Ideal Gas Equation
- Dalton’s Law
- Non-Ideal Gas Behavior

Gas Laws



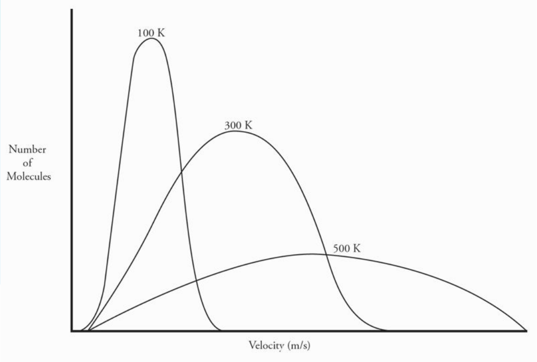
$$KE = \frac{1}{2}mv^2$$

m = mass of the molecule (kg)

v = speed of the molecule (meters/sec)

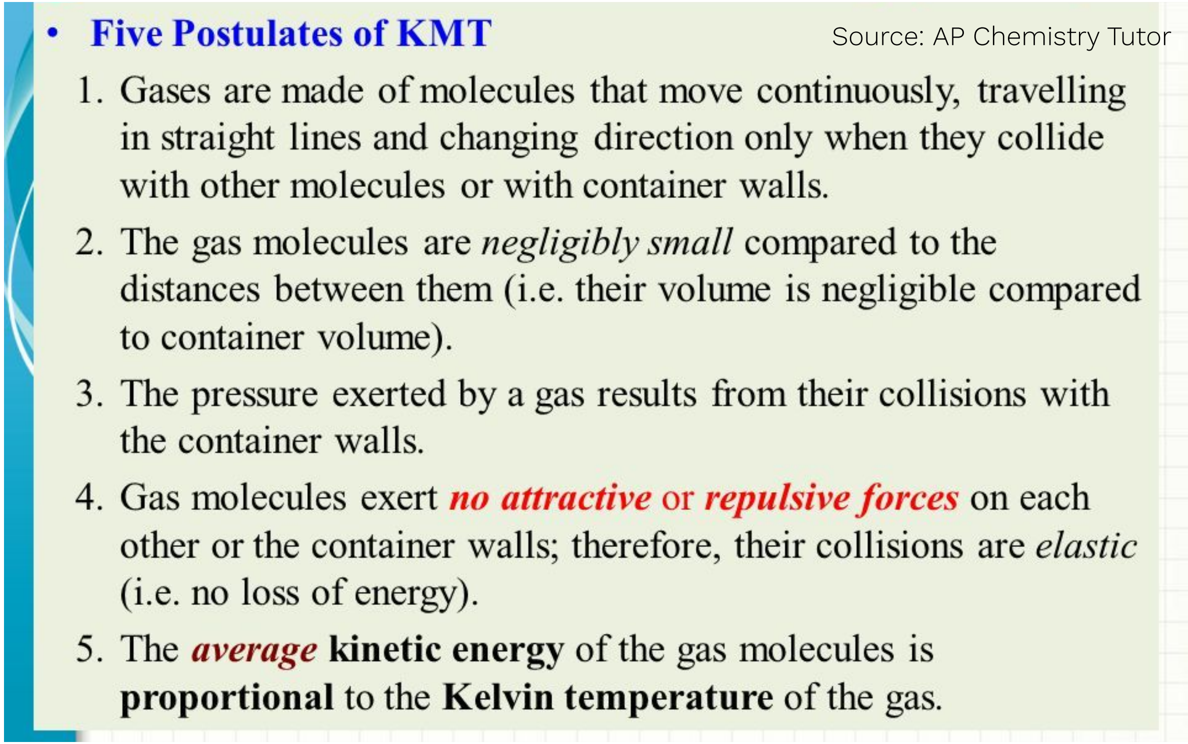
KE is measured in joules

Source: Princeton Review



Source: Princeton Review

The **kinetic molecular theory (KMT)** applies to ideal gases. The postulates are:



- **Five Postulates of KMT**

Source: AP Chemistry Tutor

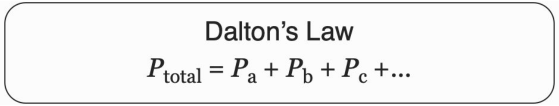
1. Gases are made of molecules that move continuously, travelling in straight lines and changing direction only when they collide with other molecules or with container walls.
2. The gas molecules are *negligibly small* compared to the distances between them (i.e. their volume is negligible compared to container volume).
3. The pressure exerted by a gas results from their collisions with the container walls.
4. Gas molecules exert ***no attractive*** or ***repulsive forces*** on each other or the container walls; therefore, their collisions are *elastic* (i.e. no loss of energy).
5. The ***average*** **kinetic energy** of the gas molecules is **proportional** to the **Kelvin temperature** of the gas.

Maxwell-Boltzmann diagrams show the range of velocities (x axis) for a given number of molecules of a gas (y axis). They can display the different velocities for 1) the same type of gas at different temperatures or 2) different types of gas at the same temperature. The left diagram displays nitrogen velocities at different temperatures.

Gas Laws

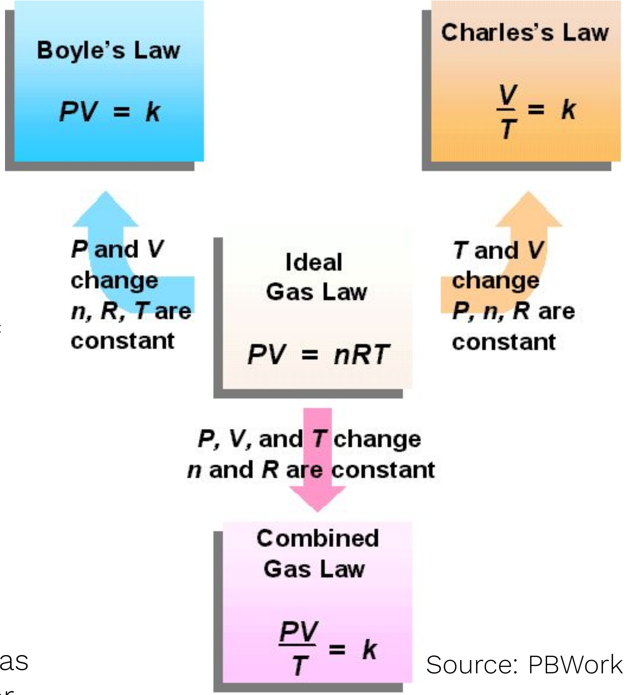
The **ideal gas equation** relates four variables: pressure, volume, moles, and absolute temperature of a gas. This equation can be used to derive the **combined gas law**, which can be used when the number of moles is constant. Be familiar with how changing one variable impacts the other three.

Dalton's law says that the total pressure of a mixture of gases is the sum of the partial pressure of each individual gas. The partial pressures of a gas is proportional to the number of moles in the mixture.



Dalton's Law

$$P_{\text{total}} = P_a + P_b + P_c + \ldots$$



Boyle's Law

$PV = k$

Charles's Law

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

P and V change
n, R, T are constant

Ideal Gas Law

$PV = nRT$

T and V change
P, n, R are constant

P, V, and T change
n and R are constant

Combined Gas Law

$\frac{PV}{T} = k$

Source: PBWorks

Non-ideal gas behavior occurs when the gas molecules are packed too tightly together, or which happens under low temperatures or extremely high pressure. These conditions violate the KMT assumption that individual gas molecules do not occupy volume.

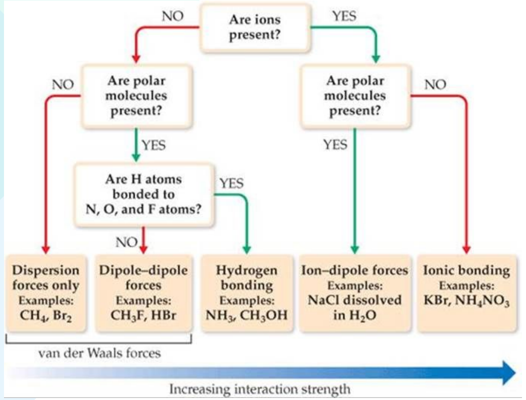
Under non-ideal conditions, gas molecules

1. stick to each other due to intermolecular forces and
2. have volume that is significant.

8. States of Matter and Intermolecular Forces

- States of Matter
- Intermolecular Forces
- Solutions

Intermolecular Forces



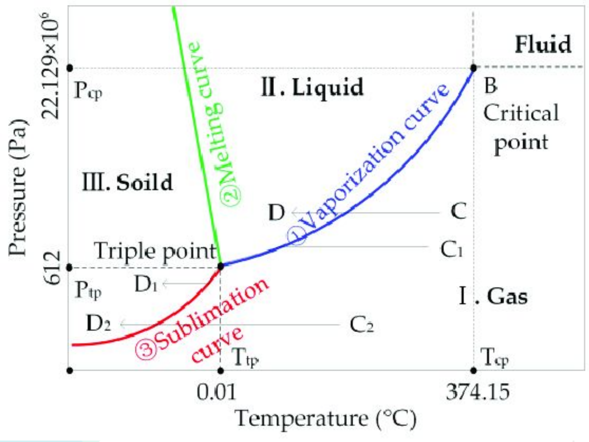
Source: HollyAsChemBlog

Charge and charge distribution plays a central role in determining the type and strength of intermolecular forces that exist within a sample. The **dipole moment** of a molecule measures the separation of partial charges. A higher dipole moment is associated with a greater degree of charge separation. **Polarizability** is the ability of a molecule's electron cloud to be distorted. A greater polarizability is associated with an electron cloud that can be distorted more, which leads to the formation of more instantaneous dipoles.

The following are important intermolecular forces to be aware of:
Ion-Ion: Coulombic interactions between ions.
Ion-Dipole: Interaction between a full charge (ion) and a partial charge (dipole). Stronger when ion's charge is larger or ionic radius is smaller. Responsible for hydration of ions in water.
Dipole-Dipole: Interaction between two dipoles. Stronger in a liquid than a gas due to more opportunities for interaction in liquid. Stronger with an increase in dipole moment.
London Dispersion: Attraction between nonpolar molecules based on the propagation of instantaneous dipoles. Stronger with an increase in polarizability
Dipole-induced-dipole: Interaction between polar and nonpolar molecule, with the permanent dipole of the polar molecule inducing a temporary dipole in the nonpolar molecule. Stronger with a high permanent dipole moment in the polar molecule and a high polarizability in the nonpolar molecule.
Hydrogen Bonding: Interaction between molecules which contain a hydrogen bonded to electronegative nitrogen, oxygen, or fluorine. Generally the strongest intermolecular interaction (excluding ion-ion).

The phase (solid/liquid/gas) of a substance is related to the strengths of its intermolecular forces. Gases tend to have London dispersion forces, while liquids like water have hydrogen bonds.

Phases and Phase Transitions



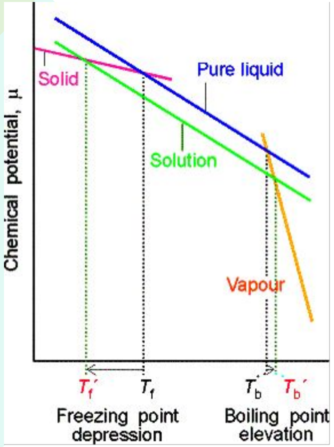
Source: Zhang et al.

In a phase transition, there is a dynamic equilibrium between the two phases involved. Taking vaporization as an example, while the formation of gas increases the entropy of the system, it comes at the cost of lowering the entropy of the surroundings because vaporization is endothermic, resulting in no net tendency toward vaporization or condensation.

In a closed container containing liquid, there is a dynamic equilibrium between the liquid and its vapor as liquid molecules at the surface are able to escape at the same rate as vapor molecules above the liquid condense back to the liquid. This equilibrium gives rise to the **vapor pressure**. Liquids with weaker intermolecular forces will have a higher vapor pressure (making them more **volatile**) because it is easier for their molecules to escape the liquid phase. An increase in temperature also increases vapor pressure as it increases the energy of the molecules. **Boiling** occurs when the vapor pressure is equal to the atmospheric pressure.

A **phase diagram** shows the dominant phase of a substance as a function of temperature and pressure. A **phase boundary** represents an equilibrium between two phases. A **triple point** represents an equilibrium between three phases. At and beyond the **critical point**, the density of the vapor equals the density of the liquid, so there cannot be a transition from the gas phase to the liquid phase.

Solutions



Source: Dr. Mary Tecklenburg, CMich

We may consider the y-axis of this graph to be the Gibbs free energy, *G=H-TS* (see section 12). The shape of the lines in this graph can be explained by noting that $H_{solid} < H_{liquid} < H_{vapor}$ and $S_{solid} < S_{liquid} < S_{vapor}$.

In a saturated solution, there is a dynamic equilibrium between the dissolved and undissolved solute. When a solute is dissolved, the solute-solute interactions must be replaced with solute-solvent interactions. Thus, a solute is more likely to be soluble in a solvent that has similar intermolecular reactions as exist already in the solute ("like-dissolves-like").

The solubility of a gas is, by **Henry's law**, directly proportional to the partial pressure of the gas. Gases tend to be less soluble at higher temperatures, though the rate of dissolving generally increases with temperature.

Raoult's law states that the vapor pressure of a liquid decreases as more solute is added. In particular the vapor pressure of a solution is given by $P = x_{solvent} P_{pure}$, where $x_{solvent}$ is the **mole fraction** of the solvent in the solution. Raoult's law generally holds for dilute solutions. The reason a decrease in vapor pressure occurs when adding a solute to a pure solvent is that the addition of solute increases the entropy of a pure solvent. This increase in entropy decreases the Gibbs free energy of the liquid phase. Because at equilibrium, the Gibbs free energy of the liquid phase equals that of the vapor phase, the Gibbs free energy of the vapor phase must also decrease because the Gibbs free energy of a gas increases with pressure. This decrease in the Gibbs free energy and vapor pressure of a solution as compared to the pure solvent is responsible for the phenomena of **boiling-point elevation** and **freezing-point depression**, as shown on the figure to the left. The change in the boiling point/freezing point of a solution as compared to the pure solvent is directly proportional to **van't Hoff factor**, which is roughly how many particles the solute dissociates into in solution, and the **molality**, which is the ratio of the number of moles of solute to the mass of solvent.

Osmosis is the flow of solvent from a dilute solution to a more concentrated solution, which is spontaneous because of the decrease in Gibbs free energy associated with adding solute to a solution. The **osmotic pressure** of a solution is the pressure that would have to be applied to a solution in order to prevent the flow of pure solvent across a semipermeable membrane. This pressure is given by $\Pi = iMRT$, where *i* is the van't Hoff factor and *M* is the molarity of the solution.

9. Chemical equilibrium

- Equilibrium Constant, K_{eq}
- Changes in the Equilibrium Constant
- Le Châtelier’s Principle (Reaction Quotient)
- Solubility

Equilibrium Constant

***K_c*:** Equilibrium constant in terms of molar concentrations. Note that for gases, K_c is not equal to K_{eq} defined in terms of activities.

***K_{sp}*:** Also known as the solubility product, this refers to the equilibrium constant associated with the dissolution of an ionic solid.

A **chemical equilibrium** occurs when the progress of a reaction has *appeared to* stop. If we think of a chemical reaction as being **reversible**, that is, consisting of both a forward and reverse reaction, then equilibrium is achieved when the rate of the forward reaction equals the rate of the reverse reaction.

For a reversible reaction of the form $a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D}$, the composition of the reaction mixture at equilibrium is dictated by the **equilibrium constant K_{eq}**, given by

$$K_{\mathrm{eq}} = \frac{(a_\mathrm{C})^c\,(a_\mathrm{D})^d}{(a_\mathrm{A})^a\,(a_\mathrm{B})^b},$$

where a_X is a unitless quantity denoting the **activity** of compound X.

Phase	Activity
Ideal gas	$a_X = P_X/P^o$, or simply P_X
Solute in a dilute solution	$a_X = [X]/c^o$, or simply $[X]$
Pure solid or liquid	$a_X = 1$

Sample problem: You have a reaction vessel filled with 3 bar $N_2(g)$ and 6 bar $O_2(g)$. Given that N_2O forms via the reaction $2\,N_2(g) + O_2(g) \rightleftharpoons 2\,N_2O(g)$, which has an equilibrium constant $K_{eq} = 3.2 \times 10^{-28}$, calculate the partial pressure of N_2O at equilibrium.

Solution:	**N_2**	**O_2**	**N_2O**
Initial	3	6	0
Change	-2x	-x	+2x
Equilibrium	3-2x	6-x	2x

$$\rightarrow \quad K_{\mathrm{eq}} = \frac{(P_{\mathrm{N_2O}})^2}{(P_{\mathrm{N_2}})^2\,(P_{\mathrm{O_2}})} = \frac{(2x)^2}{(3-2x)^2\,(6-x)}$$

Because K_{eq} is very small, we expect that only a small amount of product will be formed. Thus, we can use an approximation to replace **3-2*x*** with **3** and **6-*x*** with **6** since the subtraction of a small number will negligibly affect the original number.

$$K_{\mathrm{eq}} = 3.2 \times 10^{-28} \approx \frac{(2x)^2}{(3)^2(6)}$$

$$\Rightarrow \ x \approx 6.6 \times 10^{-14}$$

Final Answer: The partial pressure of N_2O at equilibrium is $2x$ = **1.3×10^{-13} bar**

Deviations from Equilibrium

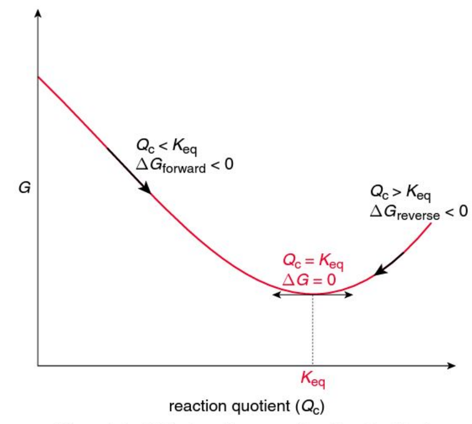


Figure 6.2. Gibbs Free Energy *vs.* Reaction Quotient

Le Châtelier's principle states that a system in dynamic equilibrium will respond to stress in such a way so as to minimize the effect of the stress.

- Adding a reactant causes the reaction to shift right, away from the reactants
- Adding a product causes the reaction to shift left, away from the products
- Removing a reactant causes the reaction to shift left, toward the reactants
- Removing a product causes the reaction to shift right, toward the products
- Compressing a reaction mixture causes the reaction to shift in the direction that forms fewer moles of gas
- Expanding a system causes the reaction to shift in the direction that forms more moles of gas
- Increasing the temperature of a reaction causes the reaction to shift in the direction that absorbs heat
- Decreasing the temperature of a reaction causes the reaction to shift in the direction that releases heat

Tip: Think of moles of gas and heat as reagents when applying Le Châtelier's principle. For example, we may annotate the exothermic combustion of sulfur dioxide as follows:

$$2\ SO_2(g) + O_2 + [\text{More moles of gas}] \rightleftharpoons 2\ SO_3\ (g) + [\text{Heat}]$$

Whereas the equilibrium constant gives information about a reaction at equilibrium, the **reaction quotient (*Q*)** is a description of the reaction's current state of progress. It is calculated the same way as K_{eq}, using the current activities of the reagents instead of their equilibrium values.

- When $Q < K_{eq}$, the forward reaction is favored.
- When $Q = K_{eq}$, the reaction is at equilibrium.
- When $Q > K_{eq}$, the reverse reaction is favored.

These statements can be explained in the language of thermodynamics via the following equation:

$$\Delta G = \Delta G^o + RT \ln Q.$$

When the reaction is at equilibrium, $Q = K_{eq}$ and $\Delta G = 0$, so we find that $\Delta G^o = -RT \ln K_{eq}$. When $Q < K_{eq}$, $\Delta G < 0$ and the forward reaction is favored. Otherwise, when $Q > K_{eq}$, $\Delta G > 0$ and the reverse reaction is favored.

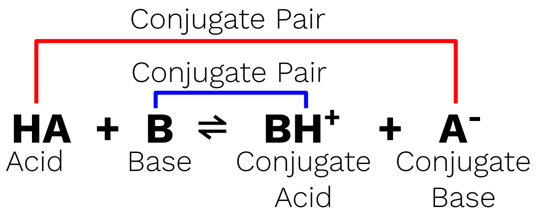
10. Acids and bases

- pH
- Acid strengths
- Acid-base equilibria

Acid/Base Concepts

Acid/Base Definitions:

	Arrhenius $\xrightarrow{\text{subset of}}$	**Brønsted-Lowry** $\xrightarrow{\text{subset of}}$	**Lewis**
Acid	Produces hydrogen ions in water	Proton donor	Electron pair acceptor
Base	Produces hydroxide ions in water	Proton acceptor	Electron pair donor
Examples	Acid: HCl Base: NaOH	Acid: CH_3COOH (in liquid NH_3) Base: NH_3	Acid: Al^{3+}, CO_2 Base: O^{2-}, NH_3



Conjugate Pair

Conjugate Pair

$$HA + B \rightleftharpoons BH^+ + A^-$$

Acid Base Conjugate Acid Conjugate Base

Strong acids/bases are fully deprotonated in solution. **Weak acids/bases** are only partially deprotonated in solution.

Key Concept: The stronger an **acid**/**base**, the weaker, or more stable, its conjugate **base**/**acid**.

Important Reactions:

Autoionization of Water:

$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $\quad K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

Acid Dissociation:

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$ $\quad K_a = [H_3O^+][A^-] / [HA]$

Base Ionization:

$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$ $\quad K_b = [HB^+][OH^-] / [B]$

Identities and Relations:

$pX = -\log X$. Therefore, $X = 10^{-pX}$.

$pH + pOH = pK_w = 14.00$

For a conjugate acid-base pair,

$pK_a + pK_b = pK_w = 14.00$

The weaker the **acid**/**base**, the smaller the value of K_a/K_b and the larger the value of pK_a/pK_b.

pH < 7 ⇒ Acidic Solution

pH = 7 ⇒ Neutral Solution

pH > 7 ⇒ Basic Solution

Acid Strength

For a binary acid HA, the more electronegative the atom A is, the stronger the acid will be.

- This trend dominates over a period of the periodic table.
  - Example: $NH_3 < H_2O < HF$ with respect to acidity
- In general, electronegative atoms are better at “carrying” negative charge, so conjugate bases with electron density distributed over electronegative atoms will be more stable.
- Electronegative atoms attached to a proton can also pull electron density away from a proton, making it easier to abstract.

For a binary acid HA, the weaker the H-A bond, the stronger the acid will be.

- This trend dominates of a group of the periodic table.
  - Example: HF < HCl < HBr < HI with respect to acidity (However, HI actually a stronger bond than HBr)
- A strong bond makes it harder to abstract a proton

For an oxoacid, the greater the number of oxygens attached to the central atom, the stronger the acid.

- This can be attributed to resonance stabilization, which causes negative charge to be distributed over the electronegative oxygen atoms.

For oxoacids with the same number of oxygens, the greater the electronegativity of the central atom, the stronger the acid

- This can be attributed to the inductive effects of electronegative atoms to spread out electron density

Key Concept: Distribution of electron density in the conjugate base and ease of abstracting a proton are important ideas to consider when evaluating the acidity of a species.

11. Buffers, titrations, and solubility

- Neutralization reactions
- Indicators

Buffers

A **buffer** is a mixed solution of a weak conjugate acid-base pair that resists changes in pH when small amounts of strong acids or bases are added. This occurs because the conjugate base can neutralize some of the added acid and the conjugate acid can neutralize some of the added base.

Sample Problem: Suppose we dissolve 0.030 mol NaOH in 500. mL of a buffer solution consisting of 0.040 M $NaCH_3CO_2$(aq) and 0.080 M CH_3COOH(aq) at 25°C. What is the pH of the solution before and after the NaOH is added?

Before Addition of Base: Because we are working with a weak conjugate acid-base pair system, CH_3COOH will form only produce small concentrations of H_3O^+, so we may assume that the equilibrium concentrations of CH_3COOH and $CH_3CO_2^-$ differ negligibly from their initial concentrations (go through the full equilibrium calculations if you are unsure of why this is the case).

$$[\mathrm{H_3O^+}]_{\mathrm{eq}} = K_{\mathrm{a}} \frac{[\mathrm{CH_3COOH}]_{\mathrm{eq}}}{[\mathrm{CH_3CO_2}^-]_{\mathrm{eq}}} \approx K_{\mathrm{a}} \frac{[\mathrm{CH_3COOH}]_{\mathrm{ini}}}{[\mathrm{CH_3CO_2}^-]_{\mathrm{ini}}} = \left(1.8 \times 10^{-5}\right) \frac{0.080}{0.040} = 3.6 \times 10^{-5} \implies \mathrm{pH} = 4.44$$

After Addition of Base: The base will be neutralized neutralized in part by the CH_3COOH, which will lead to the production of $CH_3CO_2^-$ via the reaction

$$\mathrm{CH_3COOH\,(aq) + OH^-\,(aq) \rightleftharpoons CH_3CO_2{}^-\,(aq) + H_2O\,(l)}$$

Thus, there are (0.500 L)(0.080 M) - 0.030 mol = 0.010 mol of CH_3COOH and (0.500 L)(0.040 M) + 0.030 mol = 0.050 mol $CH_3CO_2^-$. Converting these to molar concentrations, we get 0.020 M CH_3COOH and 0.10 M $CH_3CO_2^-$. Performing similar calculations as before,

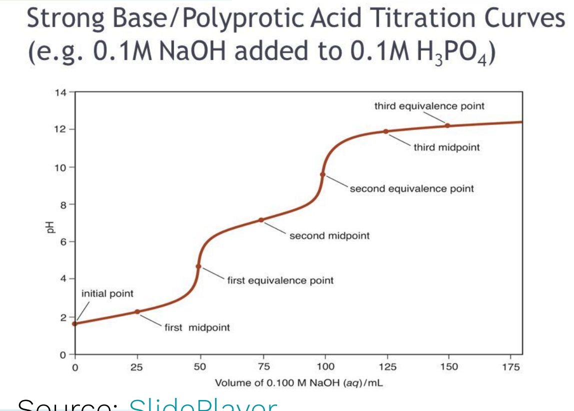
$$[\mathrm{H_3O^+}]_{\mathrm{eq}} = K_{\mathrm{a}} \frac{[\mathrm{CH_3COOH}]_{\mathrm{eq}}}{[\mathrm{CH_3CO_2}^-]_{\mathrm{eq}}} \approx K_{\mathrm{a}} \frac{[\mathrm{CH_3COOH}]_{\mathrm{ini}}}{[\mathrm{CH_3CO_2}^-]_{\mathrm{ini}}} = \left(1.8 \times 10^{-5}\right) \frac{0.020}{0.10} = 3.6 \times 10^{-5} \implies \mathrm{pH} = 5.44$$

The **Henderson-Hasselbalch** equation can be used to estimate the pH of a buffer under the assumption that the concentrations of acid and base are large compared to the concentration of hydronium ions.

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log \frac{[\mathrm{A^-}]_{\mathrm{initial}}}{[\mathrm{HA}]_{\mathrm{initial}}}$$

Titrations

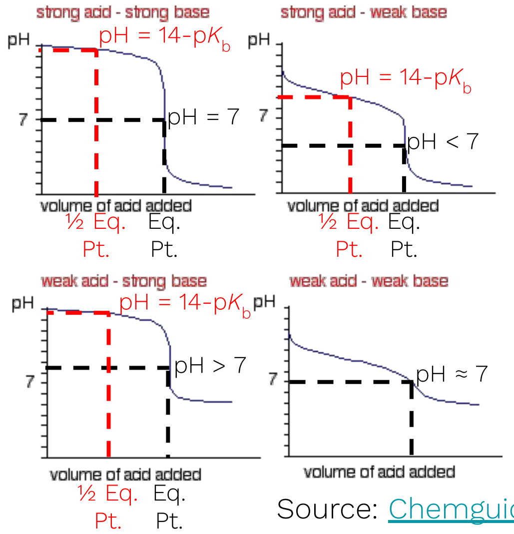
Polyprotic acid titration



Strong Base/Polyprotic Acid Titration Curves (e.g. 0.1M NaOH added to 0.1M H_3PO_4)

Source: SlidePlayer

In a **titration**, a **titrant** solution of known concentration is added to an **analyte** solution, the concentration of which can be determined by finding the **equivalence point**, which is the point at which the amount of added **H_3O^+**/**OH^-** is equal to the initial amount of **OH^-**/**H_3O^+** in the analyte. The **half-equivalence point** of the titration is the point at which [HA] = [A^-], so pH=pK_a (recall Henderson-Hasselbalch).



Source: Chemguide

At the equivalence point there is a sudden change in pH, which makes it easy to identify. However, this sudden change is generally observed when either the titrant or the analyte is a strong acid/base. This is why titrations between a weak acid and a weak base are not as useful.

At the half-equivalence point, the titrant-analyte solution acts as a buffer since it resists changes in pH. This is why the flat region of the titration curve before the equivalence point is known as the **buffer region**.

An **indicator** is a dye that changes color with the pH of a solution. Indicators are weak acids that exhibit different colors between their protonated and deprotonated states. The **end point** of the indicator is when the indicator changes colors. This occurs when [HIn] = [In^-], or equivalently, when pH=pK_{In}, where K_{In} is the acid dissociation constant of the indicator.

Solubility Equilibria

$$\mathrm{A}_m\mathrm{B}_n(\mathrm{s}) \rightleftharpoons \mathrm{mA}^{n+}(\mathrm{aq}) + \mathrm{nA}^{m-}(\mathrm{aq})$$

The **solubility product K_{sp}** is the equilibrium constant of the dissolution reaction of an ionic solid. It is generally used for calculations involving sparingly soluble salts. If the molar solubility of an ionic salt A_mB_n is s, then its K_{sp} is given by $(ms)^m(ns)^n$.

By Le Châtelier's principle, the presence of a common ion in solution (A^{n+} or B^{m-}) will reduce the solubility of the original salt. This is known as the **common-ion effect**.

Similarly, dissolution of a salt can be increased by removing one of the ions (A^{n+} or B^{m-}). Some methods to remove ions from solution include:

- Neutralization (e.g., neutralizing OH^- with acid)
- Evolution of Gas (e.g., reacting CO_3^{2-} with acid to form CO_2 gas)
- Complex ion formation (e.g., reacting Ag^+ with NH_3 to form $Ag(NH_3)_2^+$

Sample Problem: Calculate the molar solubility of AgCl in 0.10 M NH_3(aq) given the solubility product K_{sp} of AgCl and the formation constant K_f of $Ag(NH_3)_2^+$.

Solution: We combine the two relevant reactions as follows:

$$\left.\begin{aligned}\mathrm{AgCl(s)} &\rightleftharpoons \mathrm{Ag^+(aq) + Cl^-(aq)},\ K = K_{\mathrm{sp}}\\ \mathrm{Ag^+(aq) + 2\,NH_3(aq)} &\rightleftharpoons \mathrm{Ag(NH_3)_2{}^+(aq)},\ K = K_{\mathrm{f}}\end{aligned}\right\}$$

$$\mathrm{AgCl(s) + 2\,NH_3(aq)} \rightleftharpoons \mathrm{Ag(NH_3)_2{}^+(aq) + Cl^-(aq)},\ K = K_{\mathrm{sp}}K_{\mathrm{f}}$$

The problem is now a standard equilibrium problem. We can solve for the equilibrium concentration of $Ag(NH_3)_2^+$ or Cl^- since they are both equal to the concentration of AgCl that gets dissolved.

$$K_{\mathrm{sp}}K_{\mathrm{f}} = \frac{[\mathrm{Ag(NH_3)_2{}^+}][\mathrm{Cl^-}]}{[\mathrm{NH_3}]^2} = \frac{x^2}{(0.10-2x)^2} \rightarrow \boxed{x = \frac{0.10\sqrt{K_{\mathrm{sp}}K_{\mathrm{f}}}}{1+2\sqrt{K_{\mathrm{sp}}K_{\mathrm{f}}}}}$$

12. Thermo-dynamics

- Heat and temperature
- Enthalpy
  - Enthalpy of Formation, ΔHºf
  - Bond Energy
  - Hess’s Law
  - Calorimetry and heating Curves
- Entropy
  - Gibbs Free Energy
  - Free Energy Change, ΔG
  - ΔG, ΔH, and ΔS
  - Energy Diagrams

Fundamentals of Thermodynamics

Thermodynamics is the study of transformations of energy from one form to another. In thermodynamics, we analyze transfer of energy between a **system** (something we are interested in) and its **surroundings** (everything else). An **open system** exchanges matter and energy with its surroundings. A **closed system** contains matter, but only exchanges energy with its system. An **isolated system** exchanges neither matter nor energy with its surroundings.

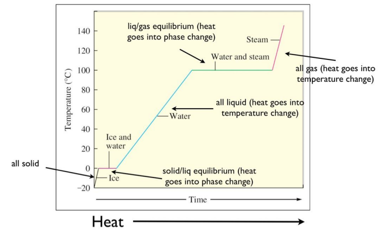
The total amount of energy (kinetic plus potential) contained in a system is its **internal energy**, denoted by U. At the molecular level, internal energy is contributed to by **translational energy**, **rotational energy**, and **vibrational energy**, and the **absolute temperature** of the system is proportional to the average kinetic energy of the molecules in the system. The change in the internal energy of a system is given by **$\Delta U=q+w$**, where **q** represents heat transferred to the system, and **w** represents work done on the system. The **first law of thermodynamics** states that the internal energy of an isolated system is constant.

Heat is energy transfer that occurs due to a temperature difference. A process that releases heat is **exothermic**, while a process that absorbs heat is **endothermic**. The **heat capacity C** of a system is the ratio of the heat supplied to the resulting temperature change **ΔT** in the system. Thus, **$q = C\Delta T$**. The **specific heat capacity** and **molar heat capacity** can be obtained by dividing the heat capacity by the mass of the sample and the number of moles in the sample, respectively. **Calorimetry** can be used to heat transfer between a system and its surroundings. A constant-pressure calorimeter (e.g., coffee cup calorimeter) is used to measure a system's change in enthalpy, and a constant-volume calorimeter (e.g., bomb calorimeter) is used to measure a system's change in internal energy.

Work is performed by moving something against an opposing force. There are two types of work: **expansion work**, which involves a change in the volume of the system, and **nonexpansion work**, which does not involve a change in the volume of the system. The work done by a system expanding against a constant external pressure **P_{ex}** is given by **$P_{ex}\Delta V$**, so **$w = -P_{ex}\Delta V$** (notice the sign convention). In the case of a vacuum, **$P_{ex} = 0$**, and this is known as **free expansion**. A **reversible process** is a process that can be reversed by an "infinitesimal" change in a variable (e.g., the movement of a piston when the pressure of the gas in the system is equal to the external pressure). The work done by a system can be maximized by using a reversible process. The work associated with the reversible, isothermal expansion of an ideal gas is given by $w = -nRT \ln \frac{V_f}{V_i}$.

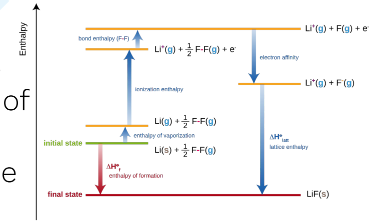
Enthalpy

A **heating curve** shows that change in temperature of a sample as heat is added at a constant rate at constant pressure. The slope of the heating curve is proportional to the inverse of the heat capacity of the sample.



Source: Chemistry301 UoT

The **Born-Haber cycle** is an application of Hess's Law to calculate lattice enthalpy.



Source: Wikimedia, Jkwuchi

Enthalpy is a state function that is useful in analysis of systems under constant pressure, which occurs often in chemistry when performing a reaction that is in exposed to the atmosphere. The enthalpy H is equal to $U+PV$. It can be shown that for reactions occurring at constant pressure that are only capable of performing expansion work, the change in enthalpy, ΔH, is equal to the heat transferred to the system, q.

Enthalpies of Physical Changes (note: H_m is molar enthalpy)

- Vaporization: $\Delta H_{vap} = H_m(\text{vapor}) - H_m(\text{liquid})$
- Fusion: $\Delta H_{fus} = H_m(\text{liquid}) - H_m(\text{solid})$
- Freezing: $\Delta H_{freeze} = H_m(\text{solid}) - H_m(\text{liquid}) = -\Delta H_{fus}$
- Sublimation: $\Delta H_{sub} = H_m(\text{vapor}) - H_m(\text{solid}) = \Delta H_{vap} + \Delta H_{fus}$.

The **standard reaction enthalpy** ΔH° of a reaction is the change in enthalpy that occurs when the reactants and products are in their standard states at a pressure of 1 bar and a temperature of 298.15 K (25°C). Two important examples of standard reaction enthalpies are the **standard enthalpy of combustion**, ΔH_c°, which is the standard reaction enthalpy per mole for the combustion of a substance. The **standard enthalpy of formation**, ΔH_f°, is the standard reaction enthalpy per mole for the formation of a substance from its elements in their most stable form. The standard reaction enthalpy can be calculated using standard enthalpies of formation as follows:

$$\boldsymbol{\Delta H^\circ = \Sigma n_i \Delta H_f^\circ(\text{products}) - \Sigma n_i \Delta H_f^\circ(\text{reactants}),}$$

where n_i represents the corresponding coefficients on the product/reactant in the reaction.

Hess's Law states that the reaction enthalpy of a reaction which can be written as a reaction sequence can be calculated as the sum of the enthalpies in the reaction sequence.

Bond enthalpy is a measure of the strength of the chemical bond, and it is defined as

$$\boldsymbol{\Delta H_B(\text{X-Y}) = H_m^\circ(\text{X,g}) + H_m^\circ(\text{Y,g}) - H_m^\circ(\text{X-Y,g}),}$$

where X and Y are the two fragments of the molecule on either side of the bond. Note that bond enthalpies are always positive. Reaction enthalpies can be estimated using bond enthalpies by analyzing which bonds are broken and formed in a reaction.

Entropy

Qualitatively, **entropy** can be thought of as a measure of disorder or energy dispersal in a system. As heat is added to a system, the **thermal disorder** of the system increases due to increased molecular motion. At a constant temperature T, the change in entropy of a system is given by $\Delta S = q_{rev}/T$, where q_{rev} is the heat transferred to the system in a *reversible* process. The change in entropy associated with changing the temperature of a system from T_1 to T_2 is $\Delta S = C \ln(T_2/T_1)$, where C is the heat capacity of the system. In a physical change, such as vaporization or fusion, the temperature and pressure of the system is constant and heat transfer is reversible, so we have that $\Delta S_{vap} = \Delta H_{vap}/T_b$ and $\Delta S_{fus} = \Delta H_{fus}/T_f$, where T_b is the boiling point and T_f is the melting point.

An equivalent definition of entropy is given by the Boltzmann formula, $S = k \ln W$, where $k = 1.381 \times 10^{-23}$ J/K, and W is the number of **microstates**, or arrangement of molecules in the sample, that have the same total energy as the original system. The **third law of thermodynamics** states that the entropy of a perfect crystal approaches zero as the absolute temperature approaches zero. This can be seen from the Boltzmann formula since a perfect crystal at 0 K will have only one microstate, and ln 1 = 0.

The **standard molar entropy** $S_m°$ of a substance at a temperature T can be defined as the change in entropy per mole associated with heating the substance from absolute 0 to T. The **standard reaction entropy** $\Delta S°$ can be calculated from standard molar entropies as follows:

$$\Delta S° = \Sigma n_i \Delta S_m°(\text{products}) - \Sigma n_i \Delta S_m°(\text{reactants})$$

where n_i represents the corresponding coefficients on the product/reactant in the reaction.

Spontaneity and Gibbs Free Energy

A **spontaneous process** is a process that can occur without external input. The **second law of thermodynamics** states that the entropy of an isolated system increases with any spontaneous change. The total change in entropy associated with a process is given by $\boldsymbol{\Delta S_{tot} = \Delta S + \Delta S_{surr}}$, where $\boldsymbol{\Delta S}$ is the change in entropy of the system and $\boldsymbol{\Delta S_{surr}}$. At constant temperature and pressure, $\boldsymbol{\Delta S_{surr} = -\Delta H/T}$. For a general process, if $\Delta S_{tot} > 0$, then the forward process is spontaneous. If $\Delta S_{tot} < 0$, then the reverse process is spontaneous. If $\Delta S_{tot} = 0$, then there is no tendency in either direction. Instead of using ΔS_{tot} for determining spontaneity of a process, we can define the **Gibbs free energy**, $\boldsymbol{G = H - TS}$. The Gibbs free energy has the property that $\boldsymbol{\Delta G = \Delta H - T\Delta S = -T\Delta S_{tot}}$ at constant temperature and pressure. We can thus say that a process is spontaneous if $\Delta G < 0$ and that equilibrium is reached if $\Delta G = 0$. The Gibbs free energy has the advantage of not needing to consider the surroundings in order to determine spontaneity.

The **Gibbs free energy of reaction** and the **standard Gibbs free energy of reaction** can be calculated similarly to the standard reaction enthalpy and standard reaction entropy.

$$\boldsymbol{\Delta G^{o} = \Sigma n_i \Delta G_m{}^{o}(\text{products}) - \Sigma n_i \Delta G_m{}^{o}(\text{reactants})}$$

A second interpretation of the Gibbs free energy is that the change in Gibbs free energy ΔG is equal to the amount of nonexpansion work the system can do at constant temperature and pressure.

13. Redox reactions and Electrochemistry

- Oxidation States
- Oxidation-Reduction Reactions
- Galvanic and Electrolytic cells
- Electrolytic Cells and Electrolysis

Redox Reactions

A **redox reaction** is one in which there is a change in the oxidation states of the atoms in the reactants. In particular, a redox reaction consists of an **oxidation**, which is a loss of electrons and an increase in oxidation number, and a **reduction**, which is a gain of electrons and a decrease in oxidation number. An **oxidizing agent** accepts electrons from a species that is being oxidized and is itself reduced. Conversely, a **reducing agent** provides electrons to a species that is being reduced and is itself oxidized. When analyzing a redox reaction, we may separate it into two independent **half-reactions**, one for the reduction reaction and one for the oxidation reaction.

Sample Problem: Balance the following net ionic equation assuming acidic conditions:

$$\mathrm{MnO_4{}^-(aq) + H_2C_2O_4(aq) \longrightarrow Mn^{2+}(aq) + CO_2(g)}$$

Reduction Half-Reaction: The Mn in MnO_4^- is reduced from a +7 oxidation state to +2.

1. Balance non-oxygens and non-hydrogens
   $\mathrm{MnO_4{}^- \longrightarrow Mn^{2+}}$
2. Add waters to balance oxygens
   $\mathrm{MnO_4{}^- \longrightarrow Mn^{2+} + 4\,H_2O}$
3. Add protons to balance hydrogens
   $\mathrm{MnO_4{}^- + 8\,H^+ \longrightarrow Mn^{2+} + 4\,H_2O}$
4. Add electrons to balance charges
   $\mathrm{MnO_4{}^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O}$

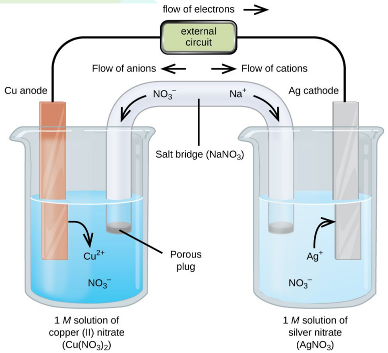
Oxidation Half-Reaction: The C in $H_2C_2O_4$ is oxidized from a +3 oxidation state to +4.

1. Balance non-oxygens and non-hydrogens
   $\mathrm{H_2C_2O_4 \longrightarrow 2\,CO_2}$
2. Add waters to balance oxygens
   $\mathrm{H_2C_2O_4 \longrightarrow 2\,CO_2}$
3. Add protons to balance hydrogens
   $\mathrm{H_2C_2O_4 \longrightarrow 2\,CO_2 + 2\,H^+}$
4. Add electrons to balance charges
   $\mathrm{H_2C_2O_4 \longrightarrow 2\,CO_2 + 2\,H^+ + 2\,e^-}$

Combining the half-reactions: We can multiply the coefficients in the reduction half-reaction by two and the coefficients in the oxidation half-reaction by five to produce a transfer of 10 electrons in the overall redox reaction. Adding these scaled reactions together and cancelling 10 electrons and 10 protons, we obtain

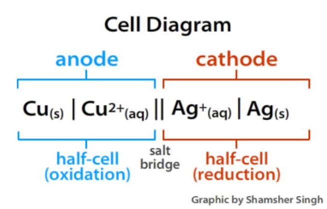
$$\mathrm{2\,MnO_4{}^- + 5\,H_2C_2O_4 + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 10\,CO_2}$$

Electrochemical Cells



Source: OpenStax

$$\mathrm{Cu(s)} + 2\,\mathrm{Ag^{+}(aq)} \longrightarrow \mathrm{Cu^{2+}(s)} + 2\,\mathrm{Ag(s)}$$



Source: LibreText

A **galvanic/voltaic cell** is an electrochemical cell that uses a spontaneous reaction to produce electric current. A **battery** is a series of galvanic cells. A galvanic cell consists of two **electrodes** and **electrolyte**, which allows for the conduction of ions. The electrode at which oxidation occurs is known as the **anode**, and the electrode at which reduction occurs is known as the **cathode**. The flow of electrons from anode to cathode is a current that can be used to do work. A **salt bridge** can be used to supply ions to the electrolyte in order to counterbalance the excess positive charge at the anode and the excess negative charge at the cathode. The salt used in the salt bridge should be inert so as to not affect the voltage of the cell. We may use a **cell diagram** a shorthand for representing electrochemical cells. For example, the cell on the right would be represented as $Cu(s)|Cu^{2+}(aq)||Ag^{+}(aq)|Ag(s)$, where the single vertical lines represent a phase interface, and the double vertical lines represent the salt bridge.

An **electrolytic cell** is an electrochemical cell that uses electric current to perform a nonspontaneous reaction. In order to drive the nonspontaneous reaction in an electrolytic cell, an external voltage source must be used. For example, if a nonspontaneous reaction has an associated cell potential of -1.2 V, then the external voltage source must exceed 1.2 V in order for the reaction to occur. In practical applications, an **overpotential** may need to be supplied in order for the reaction to occur at an appreciable rate, depending on the type of electrode. If the electrolytic cell carrying out the reaction from the previous example required an overpotential of 0.6 V, then a voltage source that supplies 1.8 V would be required. The number of moles of electrons ***n*** supplied by a current is given by ***n = It/F***, where ***I*** is the current in amperes, ***t*** is the time in seconds, and *F* is Faraday's constant.

Cell Potentials

The standard Gibbs free energy of a cell is given by $\boldsymbol{\Delta G^{o} = -nFE_{cell}^{o}}$, where ***n*** is the number of moles of electrons transferred in the reaction, ***F*** is Faraday's constant (96485 C/(mol e$^-$)), and $\boldsymbol{E_{cell}^{o}}$ is the **standard cell potential.** Recalling the equations $\Delta G^{o} = -RT \ln K$ and $\Delta G = \Delta G^{o} + RT\ln Q$ from section 9, we obtain

$$\ln K = \frac{nFE^{\circ}_{\text{cell}}}{RT} \quad \text{and} \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF}\ln Q$$

The latter equation is known as the **Nernst equation**. The Nernst equation has implications for **concentration cells**, where both electrodes are the same except for the concentrations of ions, so $\boldsymbol{E_{cell}^{o}}$ is zero while $\boldsymbol{E_{cell}}$ is non-zero. In general, the sign of E_{cell}^{o} indicates whether the reaction favors reactants or products, and the sign of E_{cell} indicates whether the reaction will spontaneously proceed forwards or backwards.

Each electrode has a **standard potential**, E^{o}. For a galvanic cell, the standard cell potential can be calculated from the standard potentials by

$$\boldsymbol{E_{cell}^{o} = E^{o}(\textbf{right electrode}) - E^{o}(\textbf{left electrode}),}$$

where "right" and "left" refer to the positions of the electrode in the cell diagram. The **standard hydrogen electrode** is defined to have a standard potential of zero, and all other standard potentials are calculated relative to the standard hydrogen electrode.

14. Kinetics

- Rate law with initial Concentrations
- Rate law with Concentration and Time
- Collision Theory
- Reaction Mechanisms
- Catalysts
- Arrhenius Equation and Reaction Mechanisms

Rate Laws

Chemical kinetics studies the rates of chemical reactions. The **average rate of formation** of a product P is given by Δ[P]/Δt, and the **average rate of consumption** of a reactant R is given by -Δ[R]/Δt. By stoichiometry, reaction rates of different species in a reaction are related by their coefficients in the reaction. It is useful to define the **unique average rate** of a reaction *a*A + *b*B → cC + *d*D as

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

To calculate the **instantaneous rate** of a reaction, the Δ's above may be replaced by the appropriate time derivatives.

A **rate law** for a reaction is an equation of the form **Rate =** $\boldsymbol{k[\mathrm{A}]^{a}[\mathrm{B}]^{b}}$**...**, where **Rate** is the instantaneous reaction rate, ***k*** is the **rate constant**, **A** and **B** are reactants, and ***a*** and ***b*** are the orders of the reaction in **A** and **B**, respectively. The **overall order** of the reaction is given by the sum of the orders of the reaction in each reactant. Note that orders can be positive or negative, integral or fractional. In an experiment, if the rate of a reaction increases ***K***-fold when the concentration of a reactant increases ***M***-fold, then the order of the reaction in that reactant is calculated using **log *K*/log *M***.

A **integrated rate law** is an equation that gives the concentration of a reactant or product as a function of time. These are derived from the previously discussed rate laws using integral calculus.

	Zeroth-Order	**First-Order**	**Second-Order**
Rate Law	Rate = k	Rate = $k[\mathrm{A}]$	Rate = $k[\mathrm{A}]^2$
Integrated Rate Law	$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0$	$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-kt}$	$[\mathrm{A}]_t = \frac{[\mathrm{A}]_0}{1 + [\mathrm{A}]_0 t}$
Linearized Integrated Rate Law	$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0$	$\ln{[\mathrm{A}]_t} = \ln{[\mathrm{A}]_0} - kt$	$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + kt$
Half-Life (only used for first-order)	$t_{1/2} = \frac{[\mathrm{A}]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[\mathrm{A}]_0}$

Reaction Mechanisms

A **reaction mechanism** is a sequence of simpler elementary reactions that describe how a reaction is believed to proceed. An **elementary reaction** is a simple reaction that often describes a collision of particles. The **molecularity** of an elementary reaction is the number of reactant molecules. A **reaction intermediate** is a species that is produced in one step of a reaction mechanism and is consumed in a later step of the mechanism, and a **catalyst** is a species that is consumed in one step of a reaction and is regenerated in a later step. For an elementary reaction, the exponents in the rate law are given by the coefficients on the corresponding reactant. The **rate-determining step** in a reaction mechanism is the slowest step in the mechanism and is the step that will be used as the basis for the rate law of the overall mechanism.

Sample Problem: Compute the rate law for the formation of NO_2 from NO and O_2 implied by the following reaction mechanism:

Step 1: $2\,\mathrm{NO} \rightleftharpoons \mathrm{N_2O_2}$ (fast)
Forward Reaction: $\text{Rate of Formation of } \mathrm{N_2O_2} = k_1[\mathrm{NO}]^2$
Reverse Reaction: $\text{Rate of Consumption of } \mathrm{N_2O_2} = k_{-1}[\mathrm{N_2O_2}]$

Step 2: $\mathrm{O_2} + \mathrm{N_2O_2} \longrightarrow 2\,\mathrm{NO_2}$ (slow)
Forward Reaction: $\text{Rate of Consumption of } \mathrm{N_2O_2} = k_2[\mathrm{O_2}][\mathrm{N_2O_2}]$
Reverse Reaction: Negligible

We first use the rate-determining step (step 2) to get the general form of the rate law:

$$\text{Rate of Formation of } \mathrm{NO_2} = 2k_2[\mathrm{O_2}][\mathrm{N_2O_2}]$$

Note the constant factor of 2 that is present for stoichiometric reasons because we are not dealing with the unique reaction rates (see previous slide). Now we must eliminate the presence of the intermediate from the rate law, which we can do in one of two ways.

Approach 1 (Steady-State Approximation): For the steady-state approximation, we assume that the intermediate is at a constant low concentration, so its net rate of formation is zero. For our problem, this means we may impose the following constraint:

$$\text{Net Rate of Formation of } \mathrm{N_2O_2} = k_1[\mathrm{NO}]^2 - k_{-1}[\mathrm{N_2O_2}] - k_2[\mathrm{O_2}][\mathrm{N_2O_2}] = 0$$

Solving for N_2O_2, $[\mathrm{N_2O_2}] = \dfrac{k_1[\mathrm{NO}]^2}{k_{-1} + k_2[\mathrm{O_2}]} \implies \boxed{\text{Rate of Formation of } \mathrm{NO_2} = \dfrac{2k_1k_2[\mathrm{O_2}][\mathrm{NO}]^2}{k_{-1} + k_2[\mathrm{O_2}]}}$

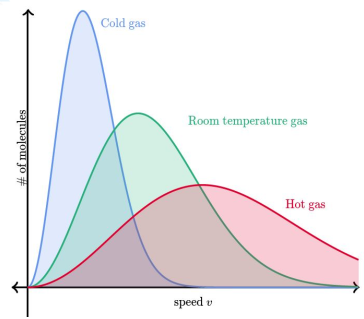
Approach 2 (Pre-Equilibrium Condition): For the pre-equilibrium condition, we assume that the rate of consumption of the intermediate in the slow step is negligible compared to its rates of formation and consumption in the fast equilibrium step. Therefore, we can use the equilibrium constant as a constraint as follows:

$$K = \frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2} \implies \boxed{\text{Rate of Formation of } \mathrm{NO_2} = 2k_2K[\mathrm{O_2}][\mathrm{NO}]^2}$$

Notice that the rate law derived using Approach 1 can be reduced to the law derived using Approach 2 by noting that $k_{-1}[N_2O_2] >> k_2[O_2][N_2O_2]$ since step 2 is slow. Therefore, $k_2[O_2]$ is negligible compared to k_{-1} and may be removed from the denominator of the rate law derived using Approach 1. Then, by equating k_1/k_{-1} with K, we arrive at the rate law derived using Approach 2.

Collision Theory

Kinetics can be related to equilibrium concepts by noting that the equilibrium constant of an elementary reaction is given by the ratio between the rate constant of the forward reaction and the rate constant of the reverse reaction. For a multistep reaction, the equilibrium constant can be found by taking the product of these ratios for each step in the mechanism.



Source: KhanAcademy

According to **collision theory**, chemical reactions between gas molecules can be modeled as occurring when there is a sufficiently energetic collision between reactant molecules. In the collision theory model, the frequency of collisions is equal to the product of:

- the collision cross section area ($\boldsymbol{\sigma}$),
- the mean relative speed ($\bar{v}_{rel}$),
- the concentration of reactants,
- the square of Avogadro's constant (N_A^2), and
- The steric factor (P).

The rate of reaction is equal to the product of the collision frequency and the fraction of collisions with a sufficient energy E_{min}. By the Boltzmann distribution, this fraction is $\exp(-E_{min}/RT)$. Thus, in an elementary bimolecular reaction between two gases **X** and **Y**, the rate of reaction is given by

$$\text{Rate} = P\sigma\bar{v}_{rel}N_A^2\exp(-E_{min}/RT)[X][Y],$$

so the rate constant of this reaction is given by

$$k = P\sigma\bar{v}_{rel}N_A^2\exp(-E_{min}/RT).$$

From this we can derive the **Arrhenius equation**, $k = A\exp(-E_a/RT)$, by equating A to $P\sigma\bar{v}_{rel}N_A^2$ and the activation energy E_a to E_{min}.

- **Note:** From this derivation, we see that A is dependent on temperature since $\bar{v}_{rel}$ has a square root dependence on temperature. However, this is outweighed by the exponential dependence on temperature in the rest of the Arrhenius equation.

A **catalyst** increases the rate of a reaction while not being consumed in the reaction, by allowing the reaction to proceed via an alternative pathway with a lower activation energy. This alternative pathway does not alter the free energy change of the reaction, so a catalyst cannot make a nonspontaneous reaction spontaneous. A **homogeneous catalyst** exists in the same phase as the reactants, while a **heterogeneous catalyst** exists in a different phase. **Enzymes** are proteins that acts as catalysts in biological systems.

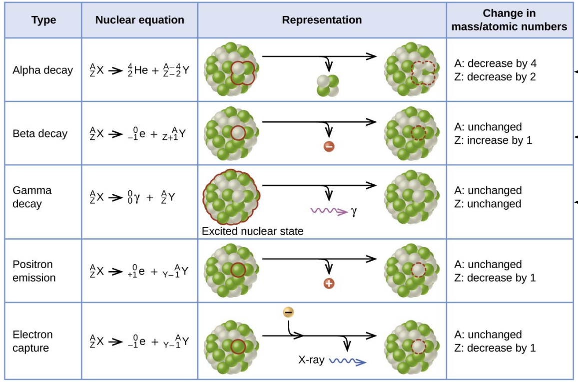
15. Nuclear chemistry

- Radioactive Decay

Radioactive Decay

Nuclear fusion: Combining of smaller nuclei to form larger nuclei
Nuclear fission: Splitting of large nuclei to form smaller nuclei
Magic Numbers: 2, 8, 20, 28, 50, 82, 126. Nuclei with these numbers of protons or neutrons tend to be stable.

Radioactive decay or **nuclear decay** is the partial decomposition of an atom's nucleus. A **nuclear reaction** is a reaction which causes a change in the composition of a nucleus.



Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$	γ Excited nuclear state	A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Y-1}Y$	X-ray	A: unchanged Z: decrease by 1

Helium-4 nucleus
Not penetrating

Electron
Moderately penetrating

Photon of gamma radiation
Very penetrating

Source: OpenStax

Radioactive decay follows a first-order rate law (recall from kinetics). Therefore, for radioactive decay with decay constant $\boldsymbol{k}$, the number of radioactive nuclei $\boldsymbol{N}$ at a time $\boldsymbol{t}$ is given by $\boldsymbol{N = N_0 \exp(-kt)}$, where $\boldsymbol{N_0}$ is the number of radioactive nuclei at time $\boldsymbol{t=0}$. The half-life $\boldsymbol{t_{1/2}}$ of a nuclear reaction with decay constant $\boldsymbol{k}$ is given by $\boldsymbol{t_{1/2} = (\ln 2) / k}$.

The **nuclear binding energy** $\boldsymbol{E_{bind}}$ of a nucleus is the energy released when all of the component nucleons combine to form that nucleus. By Einstein's mass-energy equivalence, there is a decrease in mass associated with the formation of stable nuclei. For a nuclide **X** with atomic number **Z** and mass number **A**, the mass deficit $\boldsymbol{\Delta m}$ associated with the formation of the nuclide is given by:

$$\Delta m = \Sigma\text{mass(products)} - \Sigma\text{mass(reactants)} = \text{mass(X)} - Z*\text{mass}({}^{1}\text{H}) - (A-Z)*\text{mass}({}^{1}\text{n}).$$

The nuclear binding energy can then be calculated as $\boldsymbol{E_{bind} = |\Delta m|\, c^2}$, where **c** is the speed of light, 3.00×10^{8} m/s.