

CHEM 154 Notes

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1 Atoms, Ions, and Isotopes

1.1 Subatomic Particles

Particle	Mass (g)	Mass (amu or g mol ⁻¹)	Relative Charge
Proton	1.673×10^{-24}	1.007	+1
Neutron	1.675×10^{-24}	1.009	0
Electron	9.109×10^{-28}	5.485×10^{-4}	-1

1.2 Chemical Symbols and Notation



- X: chemical symbol for the element
- A: atomic mass = number of protons + neutrons
- Z: atomic number = number of protons
- n: charge of element

2 Early Atomic Theory to Quantum Theory

2.1 Photon Equations

$$E = \frac{hc}{\lambda} = h\nu$$

- E : energy in J
- h : Planck's constant = 6.626×10^{-34} J s
- c : speed of light = 3.0×10^8 m s⁻¹
- λ : wavelength in m
- ν : frequency in s⁻¹ or Hz

2.2 Bohr Model

2.2.1 Energy of a Specific n Level

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

- n : shell number (1, 2, 3, etc)
- E : energy of a specific n level in J
- Z : atomic number

2.2.2 Energy Difference Between n Levels

$$\Delta E = (-2.178 \times 10^{-18} \text{ J})(Z^2) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- ΔE : difference in energy in J
- n_f : final energy level
- n_i : initial energy level

2.2.3 Wavelength of the Photon Absorbed or Emitted

$$\frac{1}{\lambda} = R_h \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- R_h : Rydberg's constant = $1.097 \times 10^7 \text{ m}^{-1}$

2.2.4 Hydrogen Emission Spectral Series

Hydrogen Emission Spectrum Series Name	n_f
Lyman	1
Balmer	2
Paschen	3
Brackett	4
Pfund	5

3 The Quantum Model and Orbitals

3.1 Quantum Numbers

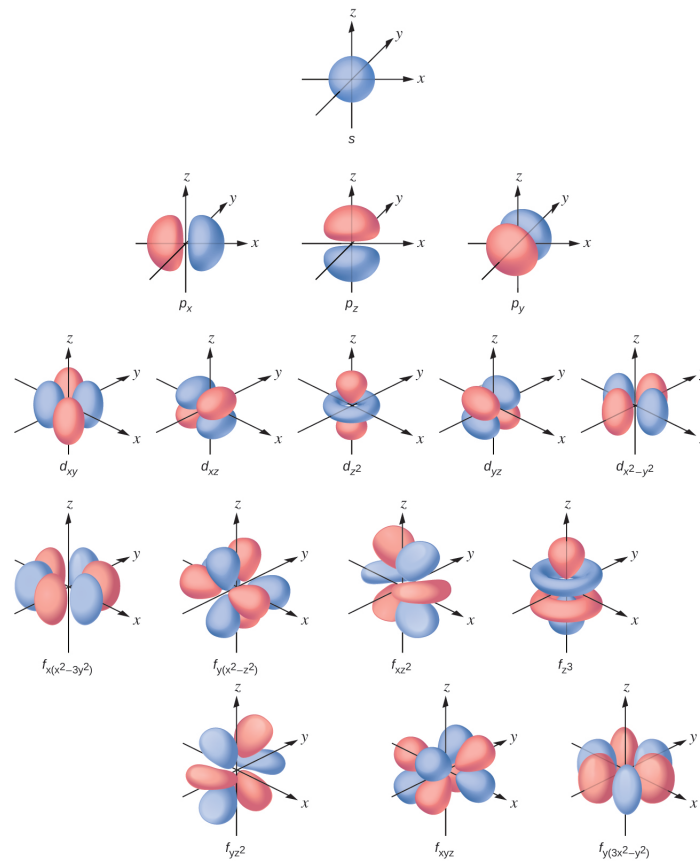
Letter	Quantum Number	Description
n	Principal	Size
l	Orbital Angular Momentum	Shape
m_l	Magnetic	Orientation
m_s	Electronic Spin	Electron Up or Down

- n : Can be any positive integer. As n increases, energy and size of the shell increases. Indicates shell.
- l : Can be any non-negative integer up to $n - 1$. Indicates sub-shell within shell.

Sub-shell	l	Number of electrons
s	0	2
p	1	6
d	2	10
f	3	14

- m_l : Can be any integer from $-l$ to $+l$. Indicates orbital within sub-shell.
- m_s : Can be $+\frac{1}{2}$ or $-\frac{1}{2}$. Indicates spin of an electron. There are always 2 electrons per orbital.

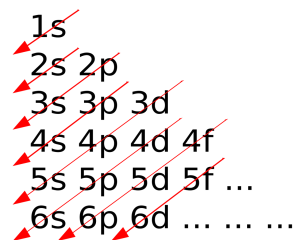
3.2 Orbital Shapes



3.3 Rules for Orbital Filling

3.3.1 Aufbau Principle

- Electrons will always occupy the lowest available energy level first.



1s																		1s
2s																		
3s																		
4s						3d								2p				
5s						4d								3p				
6s						5d								4p				
7s						6d								5p				
														6p				
														7p				
										4f								
										5f								

3.3.2 Hund's Rule

- Due to electron-electron repulsion, electrons will fill orbitals of the same energy singly before pairing up.

3.3.3 Pauli Exclusion Principle

- No two electrons in an atom will have the same set of 4 quantum numbers.

3.4 Electron Configurations

3.4.1 Electron Configurations of Elements

- Fill with Aufbau principle.
- $1s^2 2s^2 2p^6 \dots$
- Shorthand notation: write the name of the previous noble gas in square brackets, and then the rest of the electron configuration.
- Exceptions: Cr, Cu, Mo, Ag, Au (Elements in group 6 and 11). Electron configuration is a half filled s sub-shell and a half or fully filled d sub-shell.

3.4.2 Electron Configurations of Ions of Main Group Elements

- Write out the electron configuration of the neutral element.
- For anions: add electrons according to the Aufbau principle.
- For cations: remove electrons from the highest n level and highest energy sub-shell.
- Isoelectronic: same number of electrons and same electron configuration.
- Most stable ions of atoms are isoelectronic with noble gases or have filled shells.

3.4.3 Electron Configurations of Ions of Transition Elements

- Transition metals can lose both n and $n - 1$ valence electrons, but n electrons are always lost first.

3.4.4 Diamagnetic vs Paramagnetic Electron Configurations

- Diamagnetic: all electrons are paired. Will be repelled from externally produced magnetic fields.
- Paramagnetic: at least one electron is unpaired. Will be attracted to externally produced magnetic fields.

4 Periodic Table Trends

4.1 Effective Nuclear Charge

- Inner electrons shield the outer electrons from the attractive force of the nucleus.

$$Z_{eff} = Z - S$$

- Z_{eff} : effective nuclear charge
- Z : atomic number
- S : number of shielding electrons
- As we move to the right, Z_{eff} increases. Z increases and S stays the same.
- As we move down a group, Z_{eff} decreases. S increases, more shielding.

4.2 Atomic Radius

- Atomic radius: estimated radius from the nucleus to the outermost valence electrons.
- As we move to the right, Z_{eff} increases, and the atomic radius decreases.
- As we move down a group, Z_{eff} decreases, and the atomic radius increases.

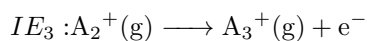
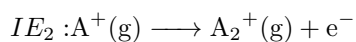
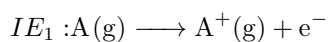
4.2.1 Ranking Sizes: Ionic Radius

- Same element different charge: anions bigger, cations smaller.
- Different element same charge: identical trends to neutral atoms.
- Different element different charge:
 - Can only be assessed for isoelectronic species.
 - More protons: smaller radius.
 - Less protons: greater radius.

4.3 Ionization Energy

- Ionization energy: the amount of energy required to remove the outermost electron in the gaseous phase.
- $E \longrightarrow E^+ + e^-$, $\Delta E = \text{Ionization Energy (IE)}$.
- As we move to the right, Z_{eff} increases, ionization energy increases.
- As we move down a group, Z_{eff} decreases, ionization energy decreases.

4.3.1 Comparing Ionization Energies



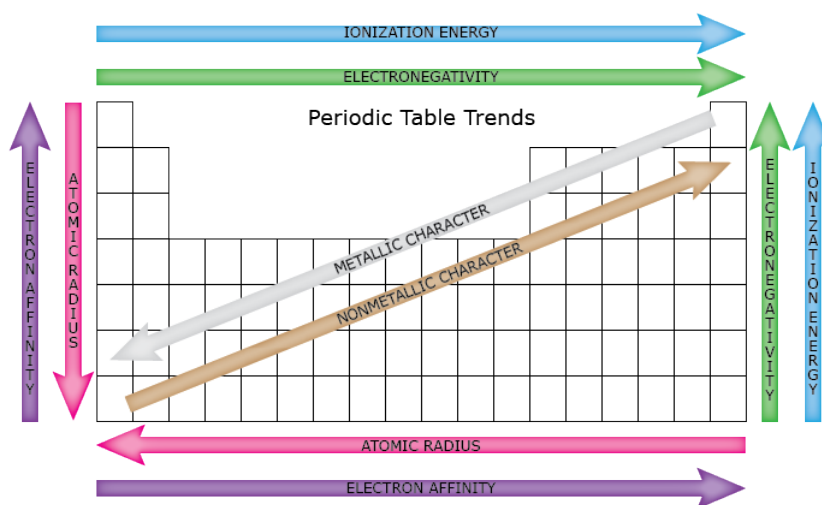
- $IE_1 < IE_2 < IE_3 < IE_4 \dots$
- To remove a core electron, ionization energy becomes much higher.

4.4 Electron Affinity

- Electron affinity: the amount of energy involved with adding an electron.
- $E + e^- \longrightarrow E^-, \Delta E = \text{Electron Affinity (EA)}$.
- EA is negative means energy is released and the atom is more stable with the electron added.
- EA is positive means energy is absorbed and the atom is less stable with the electron added.
- Unless otherwise stated, use a negative EA as a reference point (A negative EA is greater).
- As Z_{eff} increases, electron affinity increases. (This trend excludes noble gases).

4.5 Electronegativity

- Electronegativity: a measure of electron pull. More electronegative elements will be more greedy for electrons.
- Electronegativity increases going up and to the right.
- General electronegativity order: $F > O > N > Cl > Br > I > S > C \approx H$



5 Chemical Bonding

5.1 Intramolecular Bonds

- Intramolecular bond: a bond that connects two atoms within a molecule together.
- Electronegativity: the tendency of an atom to pull bonding electrons towards itself.
- Increase in electronegativity difference: Non-polar Covalent bond \rightarrow Polar Covalent Bond \rightarrow Ionic Bond.

5.2 Ionic Bonds

- Between a metal and a non-metal.
- Ionic compounds can be called salts.
- Large difference in electronegativity: $\Delta EN > 1.7$.
- The metal gives electrons to the non-metal.

5.3 Covalent Bonds

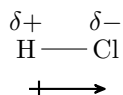
- Between two non-metals.
- Electrons are shared.

5.3.1 Non-polar Covalent Bonds

- Electrons are shared equally between 2 (often the same) non-metals.
- Small difference in electronegativity: $0 < \Delta EN < 0.4$.

5.3.2 Polar Covalent Bonds

- Electrons are shared unequally between 2 different non-metals.
- Difference in electronegativity: $0.4 < \Delta EN < 1.7$.
- There is a vector dipole moment.
 - Partial negative charge ($\delta-$) is assigned to atom with higher EN.
 - Partial positive charge ($\delta+$) is assigned to atom with lower EN.



5.3.3 Coordination Covalent Bonds

- Both electrons are donated by one of the nonmetals.
- The product can weakly conduct electricity in a solution.

5.4 Properties of Covalent Bonds

5.4.1 Bond Length

- Bond length: the distance between two nuclei that are bound together when they are at their lowest possible energy state.

5.4.2 Bond Dissociation Energy

- Bond dissociation energy: the amount of energy needed to break a bond homolytically.
- Breaking bonds will require energy, the higher the bond dissociation energy the stronger the bond.

5.4.3 Bond Order

- The number of bonds between adjacent atoms.
- H–F: single bond, bond order = 1.
- C=O: double bond, bond order = 2.
- C≡C: triple bond, bond order = 3.

5.4.4 Relationship

- For bonds between the same elements, the higher the bond order the bond length and the stronger the bond (higher bond dissociation energy)

5.5 Metallic Bond

- Metal nucleus and inner shell electrons are surrounded by a sea of electrons.
- Conduction electrons are free to move around and are delocalized.
- Gives metal their properties: ductile, malleable, conduct thermal energy, conduct electricity, lustre/shine.

6 Lewis Structures and Resonance Structures

6.1 Drawing Lewis Structures

1. Calculate the total number of valence electrons for the molecule.
2. Write out all the atoms, with the central atom (usually the least electronegative) in the middle.
3. Connect all atoms with single bonds.
4. Put lone pairs on atoms, except H, until there are no more electrons. Put extra lone pairs on the central atom.
5. Shift lone pairs to make double or triple bonds to satisfy the Octet Rule and get the best formal charges.

- Octet rule: atoms tend to bond to have 8 valence electrons.
- Formal charges: the best Lewis Structure will have the lowest possible formal charge, with 0 being best.

$$FC = V - N - \frac{B}{2}$$

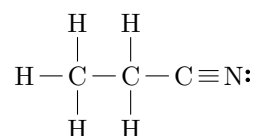
- FC : formal charge of the atom
- V : number of valence electrons
- N : number of non-bonding valence electrons
- B : total number of electrons shared in bonds
- If the formal charge is not zero, consider assigning negative formal charge to more electronegative elements, if possible.

6.1.1 Exceptions to the Octet Rule

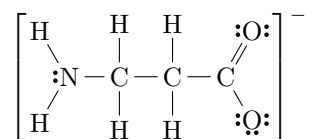
- Octet deficient elements: less than 8 electrons.
 - H and He can only have 2 electrons.
 - Be can only have 4 electrons.
 - Al and B can only have 6 electrons.
- Expanded octet elements: more than 8 electrons.
 - P can have 10 electrons.
 - S can have 12 electrons.
- Radicals: odd number of electrons, unpaired electron makes it short-lived and highly reactive.

6.1.2 Lewis Structures of Organic Compounds

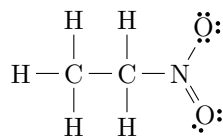
- Carbon will usually be the central atoms.
- Carbon will form four bonds.
- Add lone pairs and shift them to satisfy Octet Rule.
- Example: $\text{CH}_3\text{CH}_2\text{CN}$ would be drawn as:



- Example: $\text{NH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-$ would be drawn as:

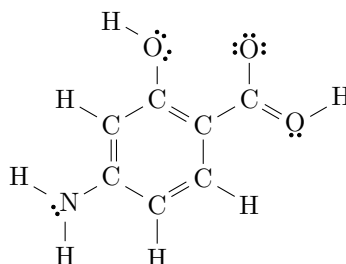


- Example: $\text{CH}_3\text{CH}_2\text{NO}_2$ would be drawn as:



6.1.3 Benzene Derivatives

- Benzene: 6 carbon ring with 3 double bonds. The double bonds are in resonance and can move around the ring.
- Example: p-aminosalicylic acid ($\text{C}_7\text{H}_7\text{NO}_3$) would be drawn as:



6.2 Resonance Structures

- Resonance structures: used to describe molecules with delocalized electrons which cannot be described by a single Lewis structure.
- Resonance structures follow the same rules as Lewis structures.
- Move lone pairs and double bonds in a Lewis structure around to spread out the charge.
- Resonance hybrid: the "average" of all of a molecule's resonance structures. Consider the average bond order.
- Equivalent resonance structures: equally stable.
- Non-equivalent resonance structures: some are better than others.
 - The major contributor (best resonance structure) will tend to have the smallest formal charges, and the negative charge resides on the more electronegative elements.

7 VSEPR Shapes and Polarity

7.1 VSEPR

- VSEPR (Valence Shell Electron Pair Repulsion theory): electron pairs in the valence shell dictates the molecular geometry.

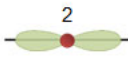




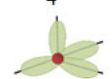








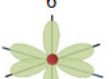





7.1.1 Electron Geometry

- Based on the central atom

$$EG = l + n$$

- EG : number of electron groups
- l : number of lone pairs
- n : number of bound atoms to the central atom

7.1.2 Molecular Geometry Table

Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2 	Linear	 Linear				
3 	Trigonal planar	 Trigonal planar	 Bent			
4 	Tetrahedral	 Tetrahedral	 Trigonal pyramidal	 Bent		
5 	Trigonal bipyramidal	 Trigonal bipyramidal	 Sawhorse	 T-shaped	 Linear	
6 	Octahedral	 Octahedral	 Square pyramidal	 Square planar	 T-shaped	 Linear

7.2 Molecular Polarity

- If there are no polar bonds, the molecule is non-polar.
- If there are polar bonds but they are symmetrical, the molecule is non-polar.
- If there are polar bonds that are not symmetrical, there is a net dipole moment and the molecule is polar.

8 Intermolecular Forces and Physical Properties

- Intramolecular forces: forces acting between atoms within a molecular. Strong forces, such as covalent and ionic bonding.
- Intermolecular forces: attractive forces acting between molecules that are relatively weak.

Intermolecular Forces

- Intermolecular forces are electrostatic in nature.
- Three main types:
 - Hydrogen bonding.
 - Dipole-Dipole bonding.
 - London Dispersion Forces/Van der Waals forces.
- Intermolecular forces are broken by physical changes.
- Intermolecular forces define physical properties of compounds (boiling points, melting points, solubility, vapour pressure, viscosities, etc.)
 - The stronger the intermolecular forces, the higher the boiling and melting points.

8.0.1 Hydrogen Bonding

- Strongest intermolecular force.
- A H from H-F, H-O, or H-N bond interacts with a lone pair of electrons from another F, O, or N atom.
 - The $\delta-$ on the electronegative atom attracts the $\delta+$ on the hydrogen atom that is bound to a highly electronegative atom (N, O, or F).
 - A hydrogen bond that involves F will be the strongest, O will be the second strongest, and N will be the third strongest.
- More hydrogen bonds implies higher boiling point.

8.0.2 Dipole-Dipole Interactions

- Second strongest intermolecular force.
- The positive end of one polar molecule interacts with the negative end of another polar molecule.

8.0.3 London Dispersion Forces/Van der Waals Forces

- Weakest intermolecular force.
- Interactions between temporary instantaneous dipoles that occur as electrons move around.
- London Dispersion Force is the interaction between two molecules with instantaneous dipoles.
- All substances can have London Dispersion Forces.

8.1 Physical Properties

8.1.1 Phases

- Solids:
 - Does not take the volume or shape of the container.
 - Are not fluids.
 - Has the strongest intermolecular forces.
- Liquids:
 - Does not fill the volume, but fills the shape, of the container.
 - Are fluids.
 - Has the weaker intermolecular forces.
- Gases:
 - Fills the volume and shape of the container.
 - Are fluids.
 - Has the weakest intermolecular forces.

8.1.2 Boiling and Melting Points

- Generally, a molecule with stronger intermolecular forces will have a higher boiling/melting point.
- When two molecules have the same type of intermolecular forces, the larger molecule based on molecular weight will have a higher boiling/melting point due to increased London Dispersion Forces.
- When two molecules have the same molecular weight, molecules with branched chains is easier to break apart and have lower boiling/melting points than molecules with linear chains.

8.1.3 Solubility

- Polar molecules are soluble in polar molecules, but are not soluble in non-polar molecules.
- Non-polar molecules are soluble in non-polar molecules, but are not soluble in polar molecules.

8.1.4 Vapor Pressure

- Vapor pressure: pressure exerted by the gaseous phase of a liquid that evaporated from the exposed surface of a liquid.
- Molecules with lower intermolecular forces have higher vapor pressures.
- Liquids with high vapor pressures are called volatile.
- As temperature increases, vapor pressure increases.

9 Solids, Polymers, Phase Transitions & Phase Diagrams

9.1 Solids

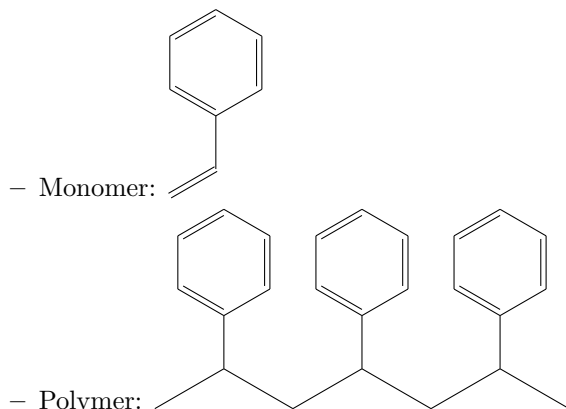
- Solids: one of the states of matter and are typically rigid.

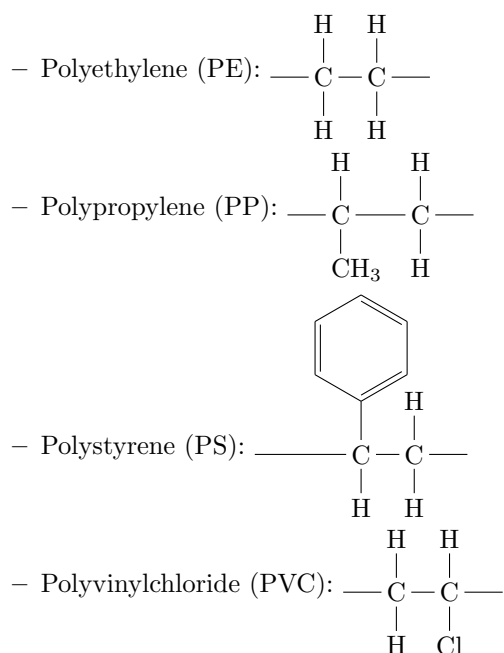
9.2 Polymers

- Polymers: a class of solids characterized by long chains of covalently linked atoms with a defined repeat unit.
- Made from a repeating monomer and usually have high molecular weight.
- Tend to form plastics or elastomers.
 - Plastic: a material that can be changed into a new shape.
 - Thermoplastic: a material that can be repeatedly reshaped.
 - Thermosets: a plastic that cannot be reshaped.
 - Elastomers: a material that exhibit elastic or rubbery behavior.
- Tacticity: the relative arrangement of adjacent groups on a polymer chain.
 - Isotactic: same side.
 - Syndiotactic: alternating sides.
 - Atactic: random.
- Tacticity can influence physical properties of the polymer.
 - Polymers with high degree of isotacticity or syndiotacticity tend to have higher melting points.

9.2.1 Polymerization Reactions

- Addition polymerization:
 - Monomer repeating unit is coupled with another monomer.
 - The monomer unit usually has a double bond that breaks apart to form a chain of single bonds.
 - Initiation, propagation, termination.
 - Double bond becomes two single bonds. Example:





- Condensation polymerization:
 - Two different monomer units are joined to form a polymer and a small molecule is eliminated.

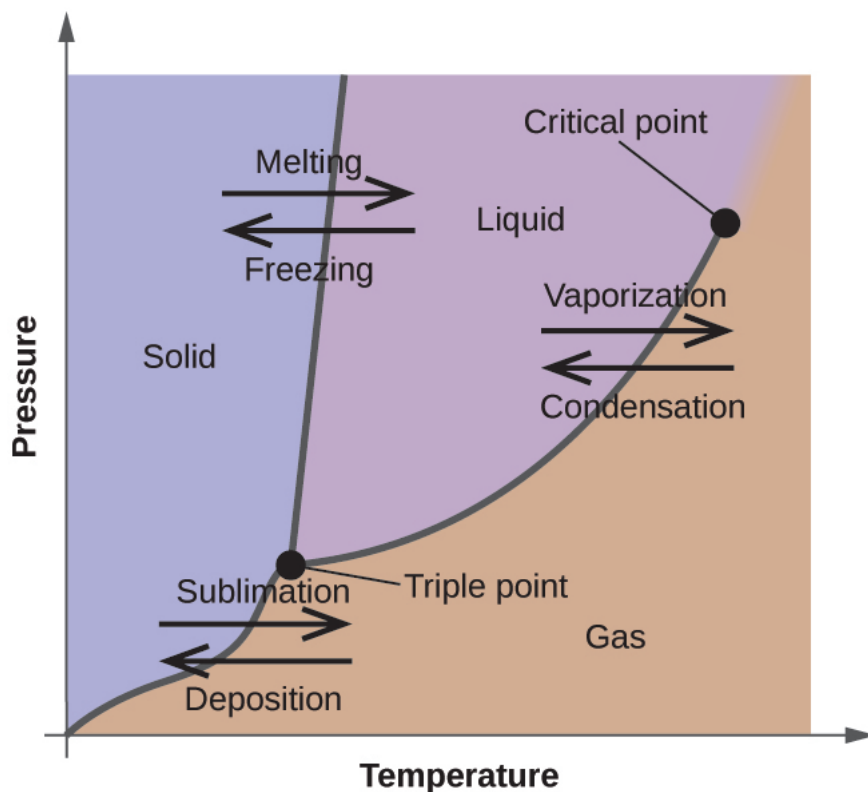
9.3 Phase Changes

- Melting: solid to liquid. Freezing: liquid to solid.
- Vaporization: liquid to gas. Condensation: gas to liquid.
- Sublimation: solid to gas. Deposition: gas to solid.
- Terminology:
 - Melting = fusion.
 - Freezing = crystallization.
 - Boiling = vaporization.
- Endothermic: $\Delta H > 0$, heat is added.
- Exothermic: $\Delta H < 0$, heat is released.

9.4 Phase Diagrams

- A plot of pressure vs temperature.
- Triple point: where solid, liquid, and gas are at equilibrium.
- Critical Point: the point at which liquid and gas are indistinguishable.
- Supercritical fluid: matter which has been pushed to temperatures and pressures beyond its critical point.

- For most compounds, the melting curve has a positive slope. Uncommonly, the melting curve for some compounds (such as water) has a negative slope. The liquid form of these compounds are more dense than their solid form.



10 Gases and Their Properties

10.1 Ideal Gas

- Ideal gases have negligible volume and no intermolecular forces.

10.1.1 Ideal Gas Law

$$PV = nRT$$

- P: pressure in Pa or kPa or bar or atm or mmHg or torr
- V: volume in L or m³
- n: amount of substance in mol
- R: ideal gas constant = $8.3145 \frac{\text{J}}{\text{mol K}} = 8.3145 \frac{\text{kPa L}}{\text{mol K}} = 0.08206 \frac{\text{atm L}}{\text{mol K}}$
- T: temperature in K

10.1.2 Gas Laws

Name	Conditions	Equation
Boyle's Law	Constant T and n	$P_1 V_1 = P_2 V_2$
Charles' Law	Constant P and n	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay Lussac's Law	Constant V and n	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Avogadro's Law	Constant P and T	$\frac{V_1}{n_1} = \frac{V_2}{n_2}$
Combined Gas law	Constant n	$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

10.1.3 Standard Molar Volume

- At STP (standard temperature and pressure) where $P = 1 \text{ atm}$ and $T = 0^\circ\text{C} = 273.15 \text{ K}$, 1 mol of any gas occupies 22.4 L.

10.2 Real Gas

- Real gases have volume and have intermolecular forces.
- Real gases act most like ideal gases when temperature is high and pressure is low.
- In a constant pressure container:
 - For real gases, volume of the container is less than that for ideal gases.
- In a constant volume container:
 - For real gases, pressure of the container is less than that for ideal gases.

10.2.1 Van der Waals Equation

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

- a : attractive force correction.
 - a increases with increasing intermolecular attraction between gas molecules.
- b : bulkiness correction.
 - b increases with molecular weight of gas molecules.
- a and b are experimentally determined.

10.2.2 Compressibility Factor

$$Z = \frac{PV}{RT}$$

- Z : compressibility factor
- V : molar volume in $\frac{\text{L}}{\text{mol}}$
- For an ideal gas, $Z = 1$.

10.3 Gas Mixtures and Partial Pressures

10.3.1 Total Pressure

$$P_{total} = P_1 + P_2 + P_3 \cdots = \sum P_i$$

$$P_{total} = \frac{n_{total}RT}{V}$$

- P_{total} : the measured pressure of the mixture
- P_i : the partial pressure of gas i
- Partial pressure: the pressure that would be exerted by one of the gases in the mixture if it occupied the same volume on its own.
- The total pressure depends only on the total moles of gas, and not the identity of the gases.

10.3.2 Partial Pressure

$$P_A = \frac{n_A}{n_{total}} P_{total} = X_A P_{total}$$

- P_A : partial pressure of gas A
- X_A : mole fraction of gas A

10.4 Kinetic Molecular Theory (KMT)

10.4.1 Assumptions of KMT

- Ideal gases are in constant, random motion and move in straight lines.
- Volume is considered to be 0.
- Collisions are completely elastic.
- There are no intermolecular forces.
- Temperature is directly proportional to the average kinetic energy.

10.4.2 Kinetic Energy, Temperature, and Speeds

- Average kinetic energy of a gas:

$$KE_{avg} = \frac{3}{2}RT$$

- R: ideal gas constant = $8.3145 \frac{\text{J}}{\text{mol K}}$
- T: temperature in K
- Speed of gas particles in one container:
 - Speed is distributed according to the Maxwell-Boltzmann distribution.
 - The higher the temperature, the broader the speed distribution
- Average speed of two different gases at the same temperature:
 - Same kinetic energy \implies heavier gases will have a slower average speed than lighter gases.
 - Lighter gases have a broader speed distribution.
- Root Mean Squared Speed:

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

- R: ideal gas constant = $8.3145 \frac{\text{J}}{\text{mol K}}$
- T: temperature in K
- M: molar mass in $\frac{\text{kg}}{\text{mol}}$

10.5 Diffusion and Effusion

10.5.1 Diffusion

- Mixing molecules of one gas with another as a result of random molecular movement.

10.5.2 Effusion

- Escape of gas molecules from their container through a tiny pinhole.
- Lighter molecules effuse faster.
- Graham's Law of Effusion:

$$\frac{r_A}{r_B} = \frac{(u_{rms})_A}{(u_{rms})_B} = \sqrt{\frac{M_B}{M_A}}$$

- r : rate of effusion
- M : molar mass

11 Thermochemistry

11.1 Introduction

Term	Definition
System	The collection of matter under consideration
Surroundings	Everything not part of the system
Open System	Can exchange matter and energy with surroundings
Closed System	Can only exchange energy with surroundings
Isolated System	Cannot exchange matter or energy with surroundings

- State variable: a variable that depends only on the current state of the system, independent of the path taken to get to that state.
- Extensive properties: depends on the amount of a substance.
- Intensive properties: does not depend on the amount of substance.

11.2 0th Law of Thermodynamics

- If two bodies are both in thermal equilibrium with a third body, then they are also in thermal equilibrium with each other.

11.3 1st Law of Thermodynamics

- The energy of an isolated system is constant.

$$\Delta E = \Delta U = Q + W$$

- $E = U$: internal energy of a closed system
 - Q : heat in J
 - W : work in J
 - Net energy transfers into the system is positive and net energy transfer from the system is negative.
 - Internal energy of a closed system is only dependent on its temperature.
- Calculating work for constant external pressure:

$$W = -P\Delta V$$

- W : work in J
- P : pressure in kPa
- V : volume in L

11.4 Calorimetry

- Enthalpy: a state function which measures the heat flow of a reaction at constant pressure.

$$H = E + PV$$

- H : enthalpy
- E : internal energy
- P : pressure
- V : volume
- $-\Delta H$ means an exothermic process.
- $+\Delta H$ means an endothermic process.

- Heat Capacity:

$$q = C\Delta T = nC_m\Delta T = mC_s\Delta T$$

- q : heat in J
- n : amount of substance in mol
- m : mass in g
- C : heat capacity in $\frac{\text{J}}{^\circ\text{C}}$
- C_m : molar heat capacity in $\frac{\text{J}}{\text{mol } ^\circ\text{C}}$
- C_s (also written as c): specific heat in $\frac{\text{J}}{\text{g } ^\circ\text{C}}$

- Calorimeters: an insulated container that usually holds water.

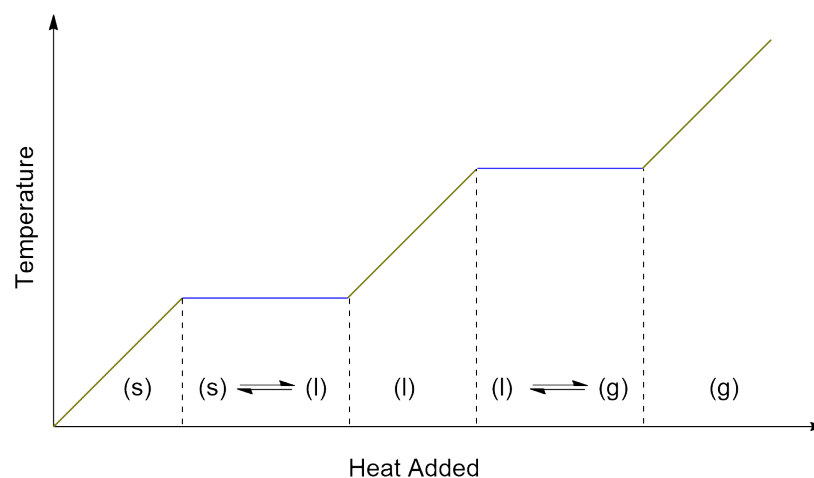
- A thermometer measures the temperature of the water.
- If the temperature of the water increases, then the reaction is exothermic. If the temperature of the water decreases, then the reaction is endothermic.
- Coffee cup calorimeter: pressure is constant.
- Bomb calorimeter: volume is constant.

- Heat during a phase change:

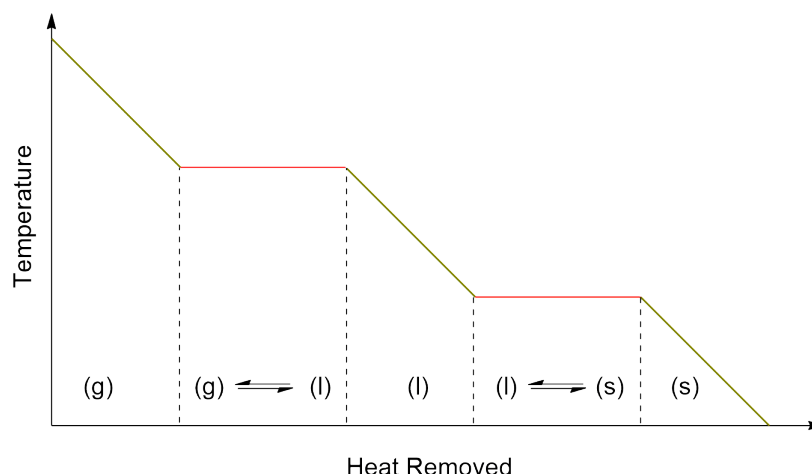
$$q = mL$$

- q : heat in J
- m : mass
- L : specific latent heat

- Heating curve:



- Cooling curve:



11.5 Heat of Formation and Reaction

11.5.1 Heat of Formation

- Formation reaction: reactants are elements in their standard state, and there is only one mole of product.
- ΔH_f° : standard heat of formation in $\frac{\text{kJ}}{\text{mol}}$.
- Standard heat of formation of any element is 0.
- ΔH° of the reaction can be calculated from the ΔH_f° of the chemicals, which can be looked up in a table.

11.5.2 Heat of Reaction

- Standard heat of a reaction: ΔH° . The heat when the number of moles of chemicals specified in the balanced chemical equation reacts at standard state. Positive ΔH° means heat is required, negative ΔH° means heat is produced.

$$\Delta H^\circ = \Sigma(\Delta H_f^\circ \times \text{coefficient})_{\text{products}} - \Sigma(\Delta H_f^\circ \times \text{coefficient})_{\text{reactants}}$$

- When the reaction is no longer in standard state, the superscript $^\circ$ is dropped.
- Hess's Law: when mathematical operations are performed on a chemical equation, the same mathematical operations are applied to the heat of reaction.
 - If the coefficients are multiplied by a constant, ΔH° is multiplied by the same constant.
 - If multiple equations are added, the ΔH° of the equations are also added to give the heat of the overall equation.
- $\Delta H_{\text{forward}}^\circ = -\Delta H_{\text{reverse}}^\circ$.

11.6 2nd and 3rd Law of Thermodynamics

- Entropy (S): the state of disorder of a system, in $\frac{\text{J}}{\text{°C}}$.
- 2nd Law of Thermodynamics: the entropy of an isolated system cannot decrease.
- 3rd Law of Thermodynamics: the entropy of a system approaches a constant value when its temperature approaches absolute zero.
- Statistical method for determining entropy: $S = k \ln w$.
 - k : Boltzmann constant = $1.380\,649 \times 10^{-23} \frac{\text{J}}{\text{K}}$
 - w : number of microstates
- Experimental method for determining entropy: $S^\circ = \frac{q_{\text{rev}}}{T}$.
 - S° : standard entropy, the entropy of one mole of a chemical at a temperature
 - q_{rev} : the heat added to raise the temperature very slowly from absolute zero up to T
 - T : temperature in K
- Change in entropy during a chemical process:

$$\Delta S^\circ = \Sigma(\Delta S_f^\circ \times \text{coefficient})_{\text{products}} - \Sigma(\Delta S_f^\circ \times \text{coefficient})_{\text{reactants}}$$

- Estimating entropy:
 - Formation of a gas increases entropy greatly.
 - Changes from solid to liquid increases entropy.
 - Increase in temperature increases entropy.

11.6.1 Predicting Spontaneity from Gibbs Free Energy

- Under constant temperature and pressure, the state function Gibbs Free Energy ΔG can predict whether a reaction is spontaneous.

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

- ΔG : Gibbs Free Energy in J
- ΔH : enthalpy in J
- T : temperature in K
- ΔS : entropy in $\frac{\text{J}}{\text{K}}$
- If $\Delta G > 0$, the reaction is non-spontaneous and the reverse reaction is spontaneous.
- If $\Delta G < 0$, the reaction is spontaneous and irreversible.

ΔH°	ΔS°	ΔG° as T increases	Spontaneity
Negative	Positive	Always negative	Always spontaneous
Positive	Negative	Always positive	Always nonspontaneous
Negative	Negative	Becomes positive	Becomes nonspontaneous
Positive	Positive	Becomes negative	Becomes spontaneous

11.6.2 Predicting Spontaneity from Entropy

ΔS_{system}	$\Delta S_{\text{surroundings}}$	Spontaneity
Positive	Positive	Spontaneous
Negative	Negative	Nonspontaneous
Negative	Positive	Depends on the magnitude
Positive	Negative	Depends on the magnitude

12 Equilibrium

- Reactions reach an equilibrium when the rate of the forward reaction and reverse reaction are equal.
- Changes still occur on the microscopic level, but on the macroscopic level, the concentrations remain constant.

12.1 The Equilibrium Constant K

- Represented by the symbol K . Subscripts indicate the type of equilibrium constant.

12.1.1 K_c

- When concentration is expressed in molarity, K_c is used.
- For a general reaction $aA + bB \rightleftharpoons cC + dD$, $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ when the reaction is at equilibrium.
 - Example: For the reaction $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$, $K_c = \frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}$.
- Liquids and solids are never included in the equilibrium expression.
- What the magnitude of K_c indicates:
 - $K_c > 1$: the reaction is thermodynamically favoured, and there are more products.
 - $K_c = 1$: there are equal amounts of products and reactants.
 - $K_c < 1$: the reaction is not thermodynamically favoured, and there are more reactants.
- Manipulating the equilibrium constant:
 - K'_c for the reverse reaction is equal to $\frac{1}{K_c}$.
 - K'_c for the reaction where coefficients are multiplied by C is equal to $(K_c)^C$.
 - K'_c for the sum of two reactions is equal to K_1K_2 .

12.1.2 K_p

- When partial pressures are involved, K_p is used.

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

- R : ideal gas constant

- T : temperature in K
- Δn : moles of gas on products - moles of gas on reactants
- When given partial pressures, K_p is calculated in the same way as K_c .

12.2 The Reaction Quotient Q

- When the reaction is not in equilibrium, $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.
 - If $Q = K_c$, the reaction is in equilibrium.
 - If $Q < K_c$, the reaction will move in the forward direction (to the right) in order to achieve equilibrium.
 - If $Q > K_c$, the reaction will move in the reverse direction (to the left) in order to achieve equilibrium.

12.2.1 K_{sp}

- When solubility is involved, K_{sp} is used.
- Calculated using the molar solubility of reagents at equilibrium.
- Solubility of Ionic Compounds at SATP

		Anions						
		Cl^- , Br^- , I^-	S_2^{2-}	OH^-	SO_4^{2-}	CO_3^{2-} , PO_4^{3-}	$\text{C}_2\text{H}_3\text{O}_2^-$	NO_3^-
Cations	High solubility $\geq 0.1 \text{ mol/L}$	most	Group 1, Group 2, NH_4^+	Group 1, NH_4^+ , Sr^{2+} , Ba^{2+} , Tl^+	most	Group 1, NH_4^+	most	all
	Low solubility $< 0.1 \text{ mol/L}$	Ag^+ , Pb^{2+} , Tl^+ , Hg_2^{2+} , Cu^+	most	most	Ag^+ , Pb^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Ra^{2+}	most	Ag^+	none

- When a combination of ions is highly soluble, no precipitate will form.
- When a combination of ions has low solubility, a precipitate might form, but we must verify that $Q > K_{sp}$.
- Factors that affect solubility:
 - Common ion effect: the solubility of a salt is reduced by the presence of another salt having a common ion.
 - Complex ion formation: reactions that use up one of the ions, to form a complex ion, will increase the solubility of a salt.
 - Acid-base neutralization: if the anion of the salt is the conjugate base of a weak acid, the solubility of the salt will increase in an acidic solution.

12.3 Le Chatelier's Principle

- Henry Le Chatelier's fundamental principle of chemical equilibrium, proposed in 1888.
- Whenever a system in dynamic equilibrium is disrupted, the system will respond to reestablish a new equilibrium state, if possible.

- Consequences of Le Chatelier's Principle:

- When the concentration of a reagent is increased, the reaction will shift towards the opposite side.
- When the pressure is increased, the reaction will shift towards the side with less moles of gas.
- When the volume is increased, the pressure decreases, the reaction will shift towards the side with more moles of gas.
- When the heat is added, it depends on whether the reaction is endothermic or exothermic. We treat heat as a reagent, and consider adding heat as increasing the concentration of a reagent.

12.4 ICE Tables

- Initial concentration, change in concentration, concentration at equilibrium.
- Example usage of ICE table: At 150 °C, K_c for the reaction $\text{I}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{IBr}(\text{g})$ is 1.20×10^2 . Starting with 4 mol each of iodine and bromine in a 2 L flask, calculate the equilibrium concentrations of all reagents.

Reaction	I_2	Br_2	IBr
I	2 M	2 M	0
C	$-x$	$-x$	$+2x$
E	$2 - x$	$2 - x$	$2x$

- $K_c = \frac{[\text{IBr}]^2}{[\text{I}_2][\text{Br}_2]} = \frac{(2x)^2}{(2-x)^2} = 1.20 \times 10^2$. Solving gives $x = 1.69$, so the concentrations of I_2 , Br_2 , and IBr are 0.309 M, 0.309 M, and 3.38 M respectively.