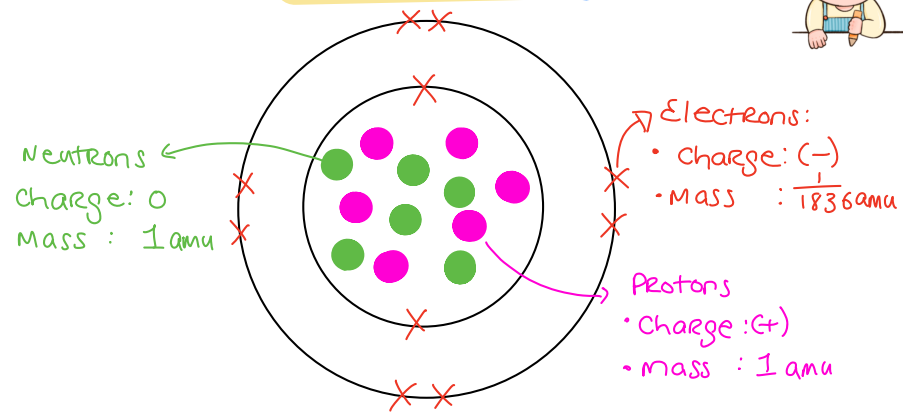


Unit 1: Atomic Structure

Atomic Structure



X^A_Z
Mass Number (A): $p^+ + n^0$
Atomic Number (Z): # p^+ / Nuclear charge
neutrons (n) = $A - Z$
electrons = # protons

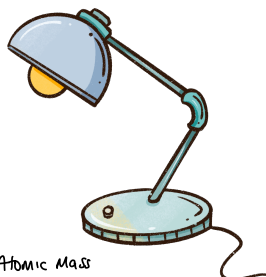
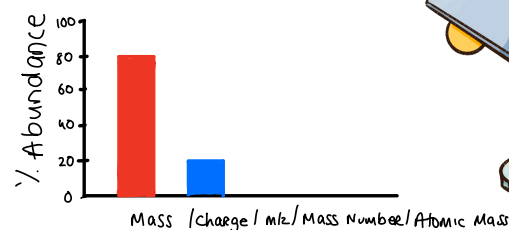
Isotopes: Atoms of the same element, same atomic number but a different mass number (n). C^{12} and C^{14}

Atomic Mass: $\sum (\text{isotopic mass}) \times (\text{abundance})$
Average mass of isotopes by abundance

Spectroscopy

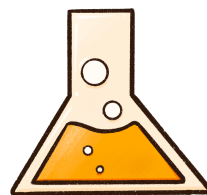
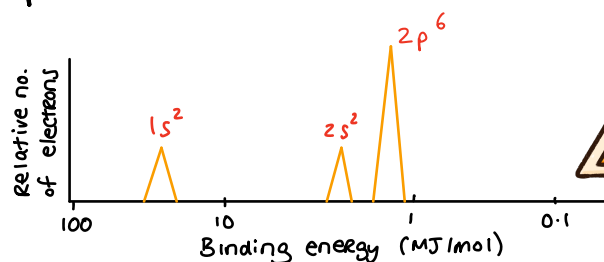
Mass Spectroscopy - identify isotopes

- Separates elements by isotopes
- Each peak represents a different isotope
- Height = relative abundance



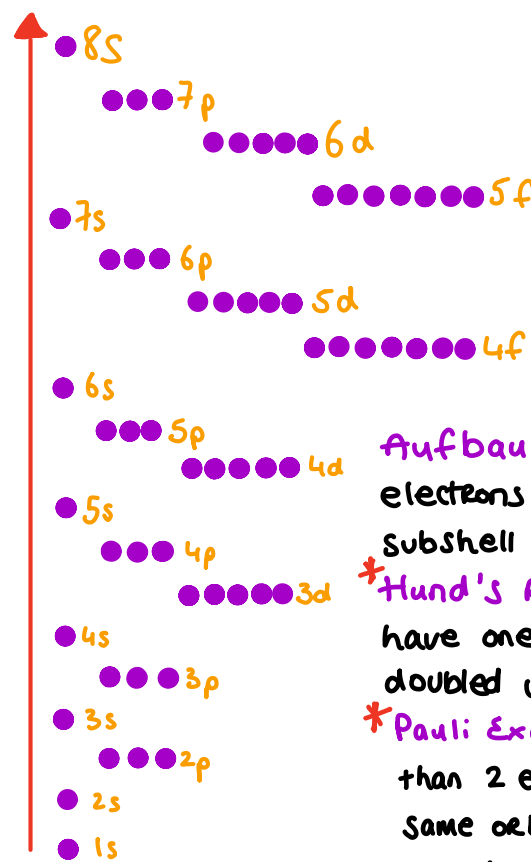
Photoelectron Spectroscopy (PES) - Energy of e^-

- uses X Rays to remove electrons
- Imagine nucleus to the left
- Each peak = subshell. Height of peak = # e^-
- Further left = $\uparrow$ Binding energy = $\downarrow$ Energy level
- For same orbital, different element: Element with more p^+ will shift peaks left.



Binding energy = energy required to remove an electron from the corresponding shell.

Electron Configuration



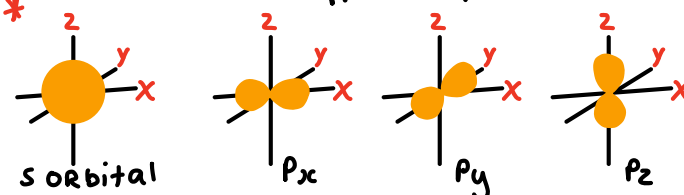
Core Electrons
= inner electrons
Valence Electrons
= outer electrons

$s = 2e^-$
 $p = 6e^-$
 $d = 10e^-$
 $f = 14e^-$

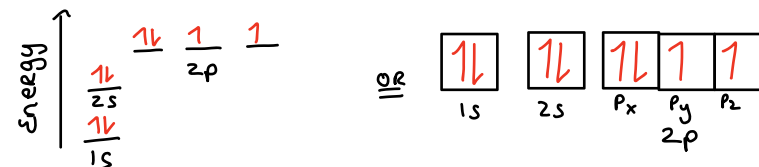
Aufbau Principle: "to build up"
electrons are added to lowest subshell first.

Hund's Rule: Each subshell should have one electron before they are doubled up

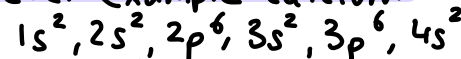
Pauli Exclusion principle: No more than 2 electrons can occupy the same orbital and they must have opposite spins.



Example: Oxygen = $8e^-$



Writing E.C. example Calcium



Shorthand: $[Ar] 4s^2$ (Noble gas preceding element)
*Not on AP exam

Moles and Molar Mass

1 mole = 6.022×10^{23} particles
Mole (n)
Molar mass: $MM = \frac{m}{n}$
Mass (m)

Use of dimensional analysis:

- Multiply known quantity by a conversion factor with the starting units in the denominator

Example: How many grams in 0.85 mol Carbon?

$$0.85 \text{ mol C} \times \frac{12.01 \text{ g}}{1 \text{ mol C}} = 10.2 \text{ g C}$$

Periodic Trends

Coulomb's Law: $F = \frac{k \cdot q_1 \cdot q_2}{r^2}$
F = Coulombic force
q = charge on particles
r = distance between particles

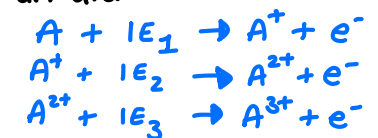
F increases when

- Charges increases
- Distance decreases

$+q_1$ $-q_2$ Attraction
 $+q_1$ $+q_2$ Repulsion

Effective nuclear charge (Z_{eff}): Approximate nuclear charge felt by the outer electron due to the shielding by core electrons. ($Z - \text{core } e^-$)

Ionization Energy (IE): Energy required to remove electrons from an atom



Electron Affinity (EA): Energy released when an electron is added to an atom. Has similar (but erratic) trend to IE.
 $A + e^- \rightarrow A^- + EA$

Electronegativity: How much an atom wants an electron from another atom. From 0-4. Similar trend as IE.

General Trends:

Down Family: $\uparrow$ Radius, $\downarrow$ IE/EA/EN
Outer e^- in higher shells ($\uparrow$ shielding), further away and less attracted to nucleus.

Across period: $\downarrow$ Radius, $\uparrow$ IE/EA/EN
More p^+ (greater Z_{eff}) outer e^- more attracted to nucleus.

Sample IE Exceptions:
Be to B ($2p > 2s$)
N to O (unpaired to paired e^-).

Radius of Cation < Element < Anion:

As # of e^- increases, there's more $e^- e^-$ repulsions

Isoelectronic species:
More p^+ (greater Z_{eff}), outer e^- more attracted to nucleus, smaller radius.

Periodic properties: Elements in the same family

Same # valence e^- , form similar ions, similar chemical props.

Describing Compounds

Empirical Formula: Mole ratio of elements in compound in simplest form

Molecular Formula: $\left(\frac{\text{Molar mass}}{\text{mass of EF}} \right) \times (EF)$

% Composition: $\frac{\text{Mass of X}}{\text{Molar mass of compound}} \times 100\%$



Unit 2 Molecular and Ionic Structure and Properties

Intramolecular Bonding

Intramolecular force: attraction within a molecule

- Strong
- Hard to break

Ionic Bonding

Transfer of electrons from a metal to a non-metal.



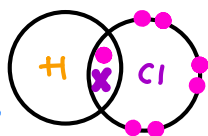
Coulomb's Law: $\uparrow$ charge, $\downarrow$ size = $\uparrow$ bond energy

Covalent Bonding

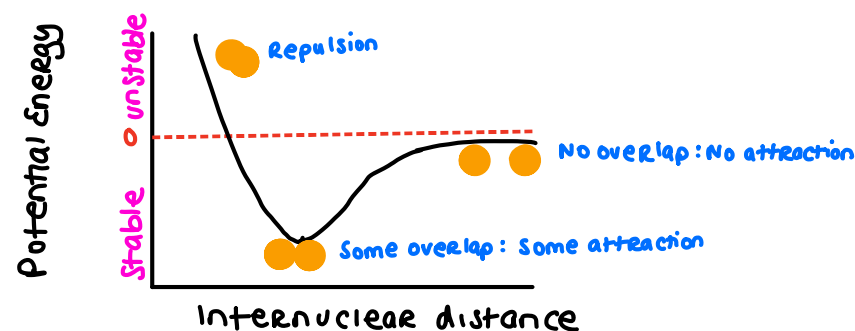
Sharing of electrons between non-metals.

Polar: Electrons not shared equally
Large $\Delta E.N.$

Non polar: Electrons shared equally.
Small $\Delta E.N.$



Balance of attraction and repulsion between atoms.



$\uparrow$ Bond order = $\uparrow$ bond energy = $\downarrow$ bond length

Bond polarity: Difference in electronegativity of two elements

δ^- partial negative charge Atoms with a high $E.N.$ difference

δ^+ partial positive charge Atoms with a low $E.N.$ difference



Dipole arrow points towards more electronegative atom

Metallic Bonding

Electrons not associated with a single atom or molecule (delocalized electrons).

$\uparrow$ delocalised e^- = $\uparrow$ bond energy

Sigma bond (σ) e^- shared between atoms
Pi bond (π) e^- shared around atoms

Single bond: σ (bond rotation)

Double bond: $\sigma + \pi$ (no rotation around bond)

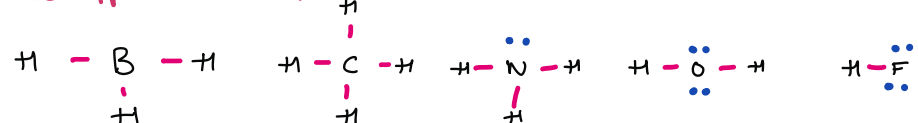
Triple bond: $\sigma + 2\pi$ (no rotation around bond)

Lewis, Resonance and Formal Charge

P.T and valence e^-

1	2		3	4	5	6	7	8
H	Be		B	C	N	O	F	He
Li	Mg	Transitions:	Al	Si	P	S	Cl	Ne
Na		Variable Valency	Ga	Ge	As	Se	Br	Ar
K	Ca		In	Sn	Sb	Te	I	Kr
Rb	Sr							Xe

Simple molecules



Diatomic molecules



Octet rule: Except for Hydrogen and Boron, all atoms end up with 8 electrons around them.

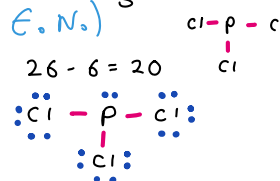
Steps to draw Lewis Structures

1. Count and sum valence electrons (adjust for ions) $PCl_3 = 5 + 7(3) = 26$

2. Determine Central atom (Written 1st/Most $E.N.$)

3. Subtract bonding electrons from total

4. Add remaining electrons as lone pairs to reach an octet around each atom

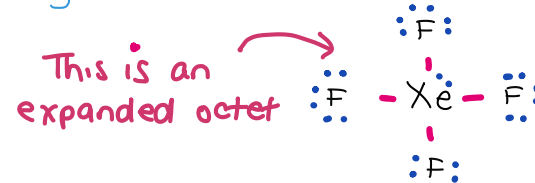


If octet has not been achieved:

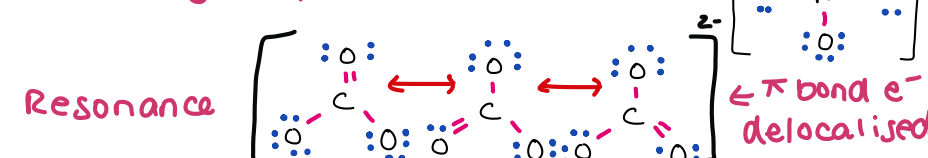
Add multiple bonds (double, triple): $O = S = O$

If all atoms have achieved an octet and not all valence electrons have been assigned:

Add remaining electrons to the central atom



Don't forget square brackets for ions!



Formal Charge: $[Valence e^-] - [lone e^- + \frac{1}{2} \text{ bond } e^-]$

Lower F.C. (0, +1, -1) are better structures

More negative F.C. on more $E.N.$ atom

Don't want F.C. with same signs on adjacent atoms

Sum of F.C. = charge on chemical species

VSEPR and Bond Hybridization

- Electrons repel due to Coulomb's forces
- Bonds and lone pairs are negative in nature so arrange themselves to minimise repulsion
- **Steric Number**: # of electron domains - influences geometry

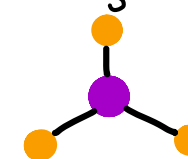
Steric 2 (sp)

Linear
 AB_2 (180°)

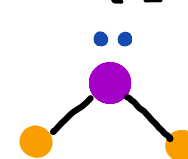


Steric 3 (sp^2)

Trigonal planar
 AB_3 (120°)

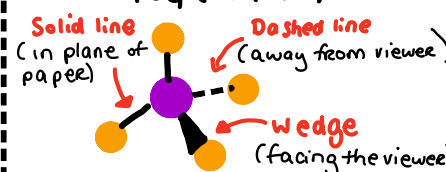


Bent
 AB_2E_1 (120°)

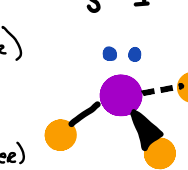


Steric 4 (sp^3)

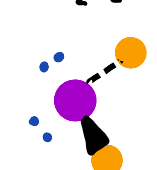
Tetrahedral
 AB_4 (109.5°)



Trigonal Pyramid
 AB_3E_1 (107°)

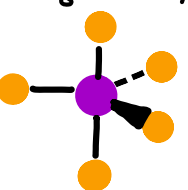


Bent
 AB_2E_2 (104.5°)

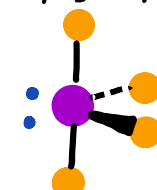


Steric 5

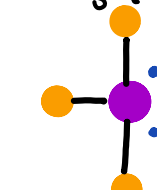
Trigonal bipyramidal
 AB_5 ($90^\circ, 120^\circ$)



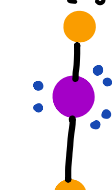
See-Saw
 AB_4E_1 ($90^\circ, 120^\circ$)



T-shaped
 AB_3E_2 (90°)

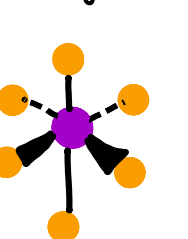


Linear
 AB_2E_3 (180°)

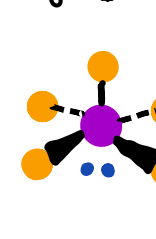


Steric 6

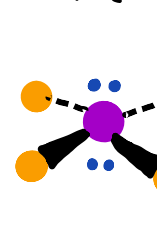
Octahedral
 AB_6 (90°)



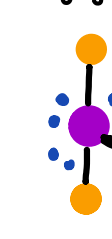
Square pyramid
 AB_5E_1 (90°)



Square planar
 AB_4E_2 (90°)



T-shaped
 AB_3E_3 (90°)



Polar compound: A compound with an uneven distribution of charges

- polar bonds don't cancel out - asymmetrical

- lone pair e^- disrupt electrical symmetry

Non polar compound: A compound with even distribution of charges - symmetrical and identical atoms.

Unit 3: ^{Ms Kelleys} Intermolecular Forces and Properties

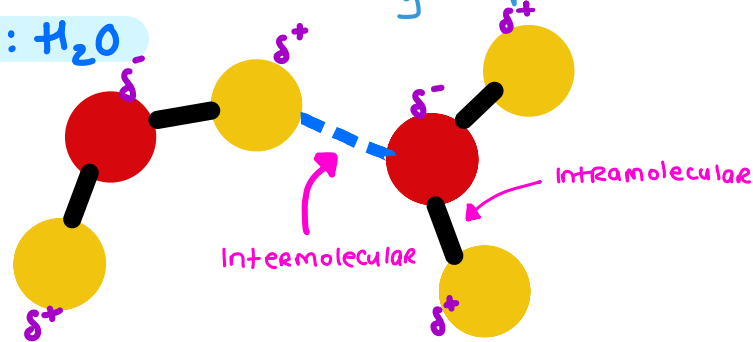
Intermolecular Forces



Intermolecular forces - attractive forces between molecules

- weak (particles/molecules relatively far apart)

Example: H_2O



Intermolecular forces

weakest to strongest →

London Dispersion (LDF)

Dipole-Dipole

Hydrogen Bonding
(Strong dipole-dipole)

All substances

Only force in non polar molecules or single non-metal atom

Ne, H_2, CO_2

Polar molecules

Asymmetrical molecules that have hydrogen with only non-metals directly bonded to

HCl, CH_2O, CH_2Cl

occurs in polar molecules

N, O or F .

HF, H_2O, CH_3OH

Metal + Non-metal

$NaCl, KBr, MgO$

Only metal atoms

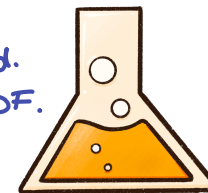
Au, Al, Zn

non-metals

- C (diamond)
- C (graphite)
- C_{60}
- SiO_2
- SiC

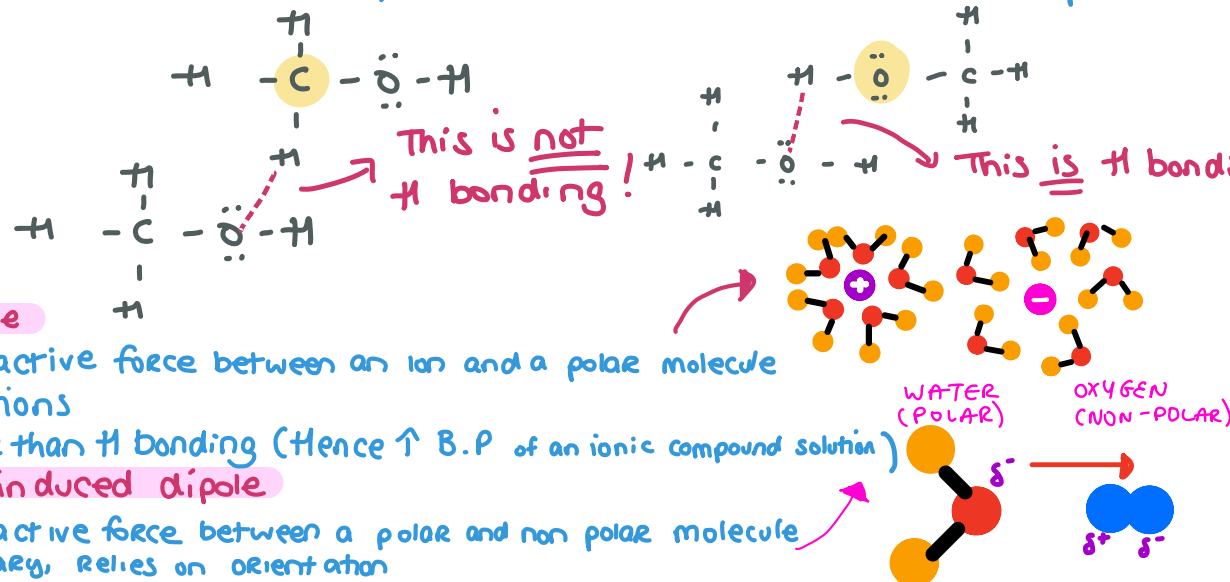
London dispersion forces

- Interactions between particles or molecules as a result of temporary or instantaneous dipoles
- occur due to the continuous motion of electrons
- Polarizability: the ease with which the charge distribution in an electron cloud can be distorted.
- Larger the atom/molecule, the larger the electron cloud, thus more polarizable and greater LDF.



Dipole-dipole

- An attraction between polar molecules in a way that the partial positive end (δ^+) of one molecule is attracted to the partial negative (δ^-) of nearby molecule.
- Hydrogen bonding: A strong dipole-dipole interaction between a hydrogen atom (bonded to an N, O or F) on one molecule and an N, O , or F on another molecule (or another part of a large macromolecule)



Ion-dipole

- An attractive force between an ion and a polar molecule
- In solutions
- Stronger than H bonding (Hence $\uparrow$ B.P of an ionic compound solution)

Dipole induced dipole

- An attractive force between a polar and non polar molecule
- Temporary, relies on orientation

Polar vs. Non polar

Non-polar

- Bond dipoles within a molecule cancel out



- Non polar molecules:

Linear, Trigonal planar, Tetrahedral, Square planar, Trigonal bipyramidal, Octahedral

Polar

- Bond dipoles do not cancel each other out



Polar molecules:

- Linear, trigonal planar, tetrahedral, If atoms around central atom are not identical

Polar geometry:

- Bent, trigonal pyramidal, see-saw, T-shaped, square pyramidal

Intramolecular forces

All strong, hard to compare

Ionic

Metallic

Covalent

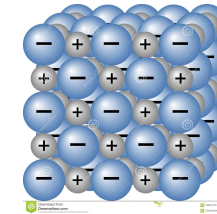
Properties as a result of increasing IMF

- $\uparrow$ Melting and Freezing Pt.
- $\uparrow$ Enthalpy of fusion/vaporization
- $\downarrow$ Vapor pressure
- $\uparrow$ viscosity
- $\uparrow$ Surface tension
- $\downarrow$ Solubility (Depends on polarity of solvent + solute)
- $\uparrow$ Lattice energy

Solids

Ionic Solids (metal + non metal)

- Electrostatic attraction between cations ($+$) and anions ($-$) held by ionic bonds e.g. $NaCl, KCl, KI, FeCl_3, CaCO_3, CaCl_2, MgSO_4, Fe_2O_3, AgNO_3$



Properties:

- High Melting point
- Conducts electricity as a liquid or aqueous solution (ions free to move)
- Hard and brittle
- often dissolves in water



Metallic Solids (metals)

- Lattice of metal cations with sea of mobile e^- (metallic bond) e.g. metals (Pb, Ag, Au, Cu, Fe, Zn) Alloys: Brass ($Cu+Zn$), Bronze ($Cu+Sn$), Steel ($Fe+C$).

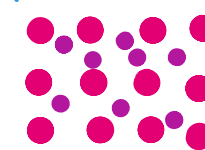
crystal lattice of positive metal cations



- "sea" of delocalized e^-
- free to move
- can conduct electricity and heat

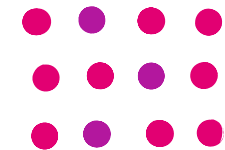
Interstitial alloy:

Small atoms fill gaps in metal lattice



Substitutional alloy:

Same sized metal replaces lattice



Properties

- High melting point
- Lustrous
- malleable and ductile
- Conducts heat + electricity



Network Covalent Solids

- Lattice of non-metal atoms with covalent bonds e.g. SiO_2 (sand, glass, quartz), SiC .

- Properties: • High Melting point
- Electrical insulator (except graphite)
- Very hard and brittle (except graphite)

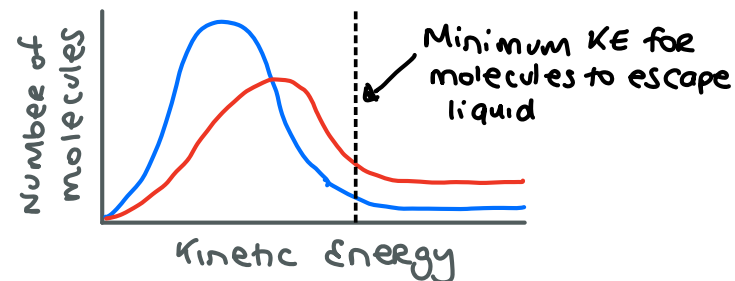
Molecular Solids (non-metals)

- Lattice of molecules with weak IMFs e.g. $He, Kr, N_2, F_2, B_2, I_2, P_4, S_8, H_2O, NH_3, CO_2, NO_2, C_6H_{12}O_6$, organic Comp.
- Properties: • Low Melting point, poor electrical conductor, brittle.

Properties of liquids

Vapor pressure

- The pressure exerted by a gas in equilibrium with its liquid phase at a given temperature



As temperature increases, a greater fraction of the molecules have the KE needed to escape the liquid and vapor pressure increases.

Solid vs Liquid vs Gas



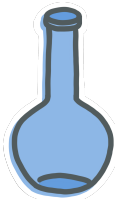
Solid

- Fixed shape
- Fixed volume
- Vibrational movement



Liquid

- Take shape of container
- Fixed volume
- Particles slide over each other
- BP/MP related to IMFs



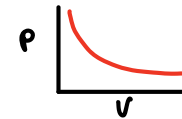
Gas



- No fixed shape
- Negligible volume

Kinetic Molecular Theory and Gas Laws

Pressure vs. Volume (Boyle's Law)



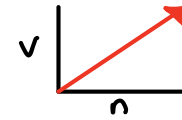
↓ V ↑ collisions
↑ pressure

Volume vs. Temperature (Charles's Law)



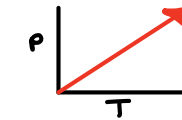
↑ temp ↑ collisions
↑ volume
— pressure

Volume vs. moles (Avogadro's Law)



↑ n ↑ collisions
↑ volume
— pressure

Pressure vs. Temperature (Gay Lussac's Law)



↑ T ↑ collisions
↑ pressure
— volume

- Gases consist of molecules in constant motion, moving in straight lines and change direction only when they collide with other molecules or walls of container
- Pressure exerted by a gas in a container results from collisions between the gas and the container walls.
- The average kinetic energy of gas molecules is proportional to the Kelvin temperature of the gas.
- The molecules composing the gas are negligibly small compared to the distance between them.
- Gas molecules exert no attractive or repulsive forces on each other; therefore, their collisions are elastic (do not involve a loss of energy).

Deviations from ideal gas law

- Gas particles DO have volume
At high pressures (low temperature and volume) the volumes of the particles is no longer negligible compared to the volume of the container
- Some gas particles DO attract or repel one another
At high pressure (low temp and volume) the attractive and repulsive forces can impact strengths of collisions.

Solutions and Mixtures

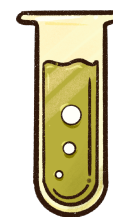
Homogenous

- Solid or Liquid
- Macroscopic properties do not vary in sample



Heterogenous

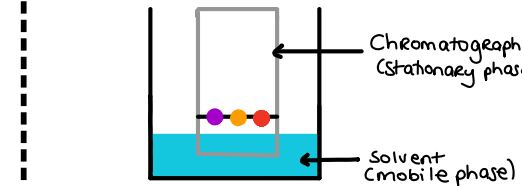
- Macroscopic properties depend on location in mixture



Molarity = $\frac{\text{moles of solute}}{\text{litres of solution}}$

Chromatography

- Paper, thin layer and column separates components of a liquid solution based on the polarity of their IMFs and their ability to bind to the stationary phase



- Larger particles move slowly
- Particles with a polarity which matches the solvent will move further.



Retention factor (R_f):
 $\frac{\text{Distance moved by sample}}{\text{Distance travelled by solvent}}$

Distillation

Separates substances based on their IMFs and their different vapor pressure / boiling points

Solubility

- Substances with similar IMFs tend to be miscible (soluble)
- Ionic compounds dissolve in polar solvents
- Molecular compounds dissolve in non polar solvents

Spectroscopy and the Electromagnetic Spectrum

← Increasing Energy / frequency (ν)
Increasing wavelength (λ)

Gamma	X-Ray	U.V	Visible	I.R.	Microwave	Radio
Core e^- (Photoelectron Spectroscopy)	e^- transitions (Spectrophotometry)	Bond vibration	Molecular Rotations	Nuclear Spins (NMR)		

Photoelectric Effect

$$c = \lambda \nu$$

c = speed of light 3.0×10^8 m/s
 λ = wavelength (m or nm)
 ν = frequency (Hz or s^{-1})

$$E = h \cdot \nu$$

E = Energy of photon (J)
 h = Planck's constant 6.626×10^{-34} J·s
 ν = Frequency (Hz or s^{-1})

Beer-Lambert Law

$A = \epsilon b c$
 A = Absorbance
 ϵ = molar absorptivity (light of a specific λ)
 b = path length
 c = concentration

In most experiments, path length and wavelength of light are held constant. Absorbance is then proportional to concentration of absorbing molecules or ions.

Gas Laws

STP:

1 atm = 760 torr = 760 mmHg = 101.325 kPa
 $0^\circ\text{C} = 273\text{ K}$ $K = ^\circ\text{C} + 273.15$

P = Pressure, atmospheres
 V = Volume, litres
 n = moles
 T = temperature, Kelvin
 $R = 0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}$

Ideal gas Law $P \cdot V = n \cdot R \cdot T$

Small, low IMF gases ideal at low P and high T

Combined gas Law $\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2}$

Dalton's Law $P_A = \left(\frac{n_A}{n_{\text{total}}} \right) (P_{\text{total}}) = \frac{n_A \cdot R \cdot T}{V}$ $P_{\text{total}} = P_A + P_B + P_C$

Graham's Law $\frac{V_A}{V_B} = \sqrt{\frac{MM_B}{MM_A}}$ At same temp, lighter gas travels faster

Unit 4: Chemical Reactions

Physical versus Chemical change

Physical change: Substances has a change in properties, but not a change in chemical composition
 Involves a change in intermolecular attractions
 Usually doesn't involve bond breaking (except dissolution)
 Phase changes (e.g. $H_2O(l) \rightarrow H_2O(g)$)
 Separating mixtures (Distillation, filtration, chromatography)

Chemical change: Substance is transformed into a new substance, with different compositions.
 Involves breaking or forming chemical bonds. Reversible
 $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
 $AgNO_3(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

Net ionic equations

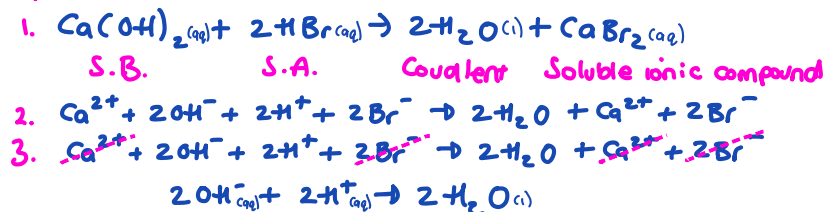
YAY

Guide lines

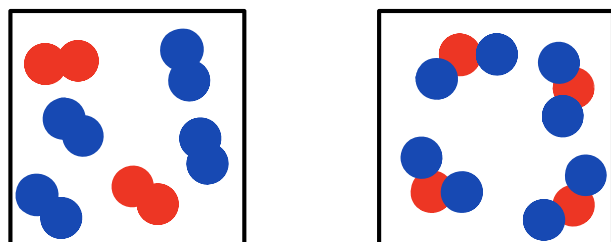
- Start with a molecular equation
- Make the transition to ionic equation or not
Tips for when to transition or not

• Break it up	Don't break it up
Strong Acid / Base	Solid substance
Ionic compound	Covalent substance
"Aqueous" substance	Weak Acid / Base
	Gas
	Pure liquid / solid
	Insoluble (slightly soluble) ionic solid
- Cross off spectator ions on both sides of the equation

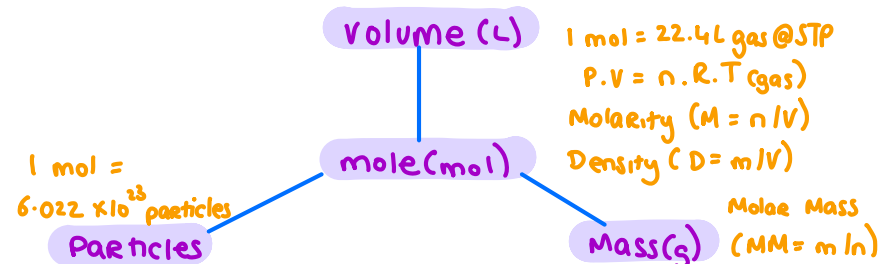
Example:



Particulate Diagrams



Stoichiometry



Example:

$Al(s) + HCl(aq) \rightarrow AlCl_3(aq) + H_2(g)$
 Balance the equation: $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$
 moles to moles - If 0.36 mol of $AlCl_3$ is produced, how much H_2 is produced?

$$AlCl_3 \times \frac{3 \text{ mol } H_2}{2 \text{ mol } AlCl_3} = 0.54 \text{ mol } H_2$$



Grams to grams How many grams of Al are required to produce 75g of H_2 . (Assume HCl is added in excess)

$$75g H_2 \times \frac{1 \text{ mol } H_2}{2.016g H_2} \times \frac{2 \text{ mol } Al}{3 \text{ mol } H_2} \times \frac{26.98g Al}{1 \text{ mol } Al} = 670g Al$$

Molarity How many mL of 5.0M HCl is needed to completely react with 4.25g of Al?

$$4.25g Al \times \frac{1 \text{ mol } Al}{26.98g Al} \times \frac{6 \text{ mol } HCl}{2 \text{ mol } Al} \times \frac{1L}{5.0 \text{ mol } HCl} \times \frac{1000 \text{ mL}}{1L} = 94.5 \text{ mL}$$

Ideal gas Law ($CPV = nRT$) 35g of Al reacts with excess HCl. What volume (in L) of H_2 is produced at 345K, 1.12 atm?

$$35g Al \times \frac{1 \text{ mol } Al}{26.98g Al} \times \frac{3 \text{ mol } H_2}{2 \text{ mol } Al} = 1.95 \text{ mol } H_2$$

$$V = \frac{nRT}{P} = \frac{(1.95 \text{ mol}) \times (0.08206 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times (345 \text{ K})}{(1.12 \text{ atm})} = 49L H_2$$

Limiting Reactant and theoretical yield

125g of Al reacts with 2.50L of 3.20M HCl
 which is the limiting reactant? What is the theoretical yield of H_2 ?

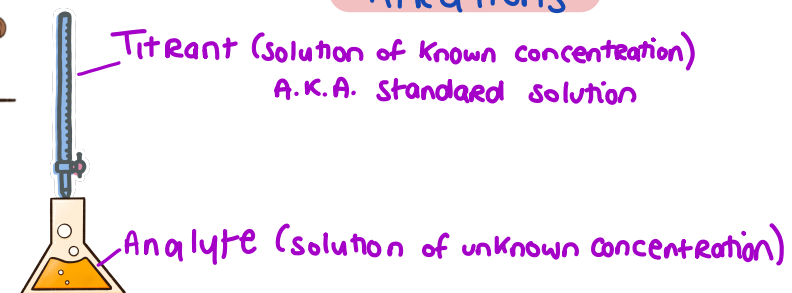
$$125g Al \times \frac{1 \text{ mol } Al}{26.98g Al} \times \frac{3 \text{ mol } H_2}{2 \text{ mol } Al} \times \frac{2.016g H_2}{1 \text{ mol } H_2} = 14.0g H_2$$

$$2.50L HCl \times \frac{3.20 \text{ mol } HCl}{1L HCl} \times \frac{3 \text{ mol } H_2}{6 \text{ mol } HCl} \times \frac{2.016g H_2}{1 \text{ mol } H_2} = 8.06g H_2$$

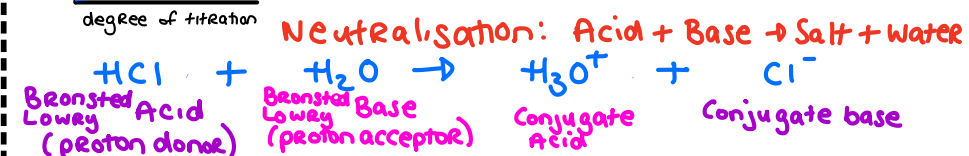
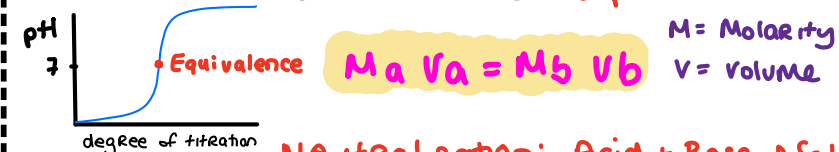
Limiting reactant is HCl and theoretical yield of H_2 is 8.06g.



Titration



Equivalence point: just enough titrant has been added to react with analyte. May be indicated by a color change. This observable event is known as the **end point**.



Types of Reactions

Sometimes REDOX

- Synthesis / Combination $A + X \rightarrow AX$
- Decomposition "Heating" $AX \rightarrow A + X$

Always REDOX

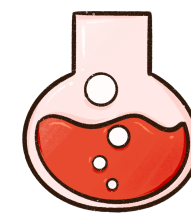
- Combustion "Burning" $CH_4 + O_2 \rightarrow CO_2 + H_2O$
- Single Replacement $A + BX \rightarrow B + AX$

NEVER REDOX

- Double Replacement $AX + BY \rightarrow AY + BX$

Product is a precipitate, gas or weak electrolyte

- Brønsted - Lowry Acid Base $HA + B \rightarrow A^- + BH^+$



Redox Reactions

Oxidation

- Loses e^-
- Ox # increases (more +)
- $A \rightarrow A^+ + e^-$
- Reducing agent
- Anode in electro cell

Reduction

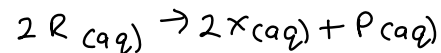
- Gain e^-
- Ox # decreases (more -)
- $A + e^- \rightarrow A^-$
- Oxidising agent
- Cathode in electro cell

Assigning Oxidation States

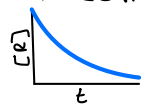
- Ox # of elements = 0 Ox # of monoatomic ions = charge
- Break up ionic compounds into ions
- In compounds F = -1; O = -2 (except peroxide = -1); H = +1 (except hydride = -1)
- Balance half reactions
 - Balance elements (not H or O)
 - Balance O with H_2O , balance H with H^+
 - Balance charges with e^-
- Balance the electrons of each half reaction
- Add up half reactions. Add OH^- in basic solution.

Unit 5 Kinetics

Reaction Rates



Rate of decomposition = $\left(\frac{\text{change in concentration of reactant}}{\text{change in time}} \right) = \left(\frac{[R]_f - [R]_i}{t_2 - t_1} \right) = \left(\frac{\Delta[R]}{\Delta t} \right)$



Rate of appearance = $\left(\frac{\text{change in concentration of product}}{\text{change in time}} \right) = \left(\frac{[P]_f - [P]_i}{t_2 - t_1} \right) = \left(\frac{\Delta[P]}{\Delta t} \right)$



Factors affecting Rates:

YOU GOT THIS

Reactant concentrations: Higher concentrations $\Rightarrow$ faster rates

Temperature: Higher temperature $\Rightarrow$ faster rates

Surface area: Greater surface area $\Rightarrow$ faster rates

Catalysts: It depends... see catalyst section!

Anything that increases collisions will increase the rate.

Rate Law

note to self:
Must be found
Experimentally!

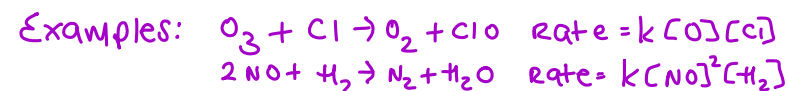


Rate Law: $\text{Rate} = k[X]^m[Y]^n$

- Reactants only
- m = order with respect to X
- n = order with respect to Y
- m + n = overall order of the reaction
- k = "Rate constant"
 - temperature dependant
 - units reflect overall order

Elementary Reactions

Reactions that occur in a single event or step.
Rate law for elementary reaction can be inferred or predicted from the stoichiometry of the molecules participating in the reaction

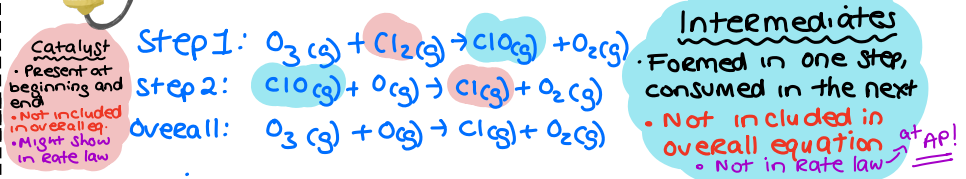


Reaction Mechanism

This is the process by which a reaction occurs, over a series of elementary steps

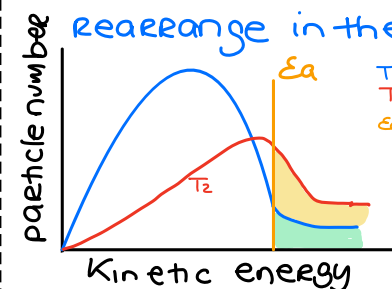


- Sum of elementary steps must lead to final, overall reaction with correct stoichiometry
- Mechanism must agree with rate law expression



Collision Model

- Successful collisions have
1. Sufficient energy to overcome activation energy (E_a)
 2. The correct orientation that allow bonds to rearrange in the correct manner

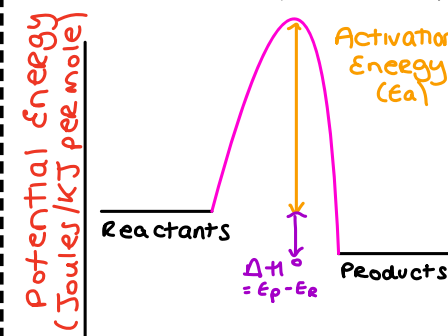


T_1 = Low temp
 T_2 = High temp
 E_a = Activation energy

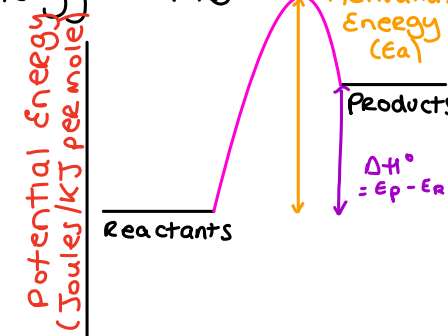
Maxwell-Boltzmann distribution curve



Reaction Energy Profiles



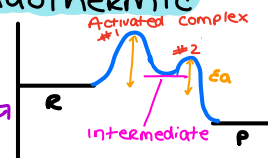
Reaction Co-ordinate
Exothermic



Reaction Co-ordinate
Endothermic

As $E_a \uparrow$ reaction rate $\downarrow$
 Step 1: Slow step (Higher E_a)
 Endothermic (P.E of intermediate higher than reactant)
 Step 2: Exothermic (P.E of product lower than reactant)

Multi-step profiles:



Arrhenius - Temperature and orientation

Factors affecting rate constant, k

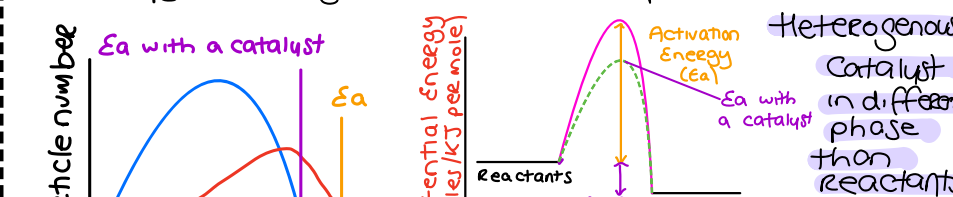
Rate = $k[X]^m[Y]^n$
 Concentration (or partial pressure)
 Everything else!

$\uparrow$ temperature $\rightarrow \uparrow$ "k" $\rightarrow \uparrow$ rate

$\downarrow$ $E_a \rightarrow \uparrow$ "k" $\rightarrow \uparrow$ rate

Improve orientation $\rightarrow \uparrow$ k $\rightarrow \uparrow$ rate

Catalysts Homogenous: Catalyst in same phase as reactants

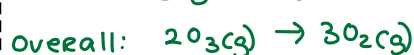
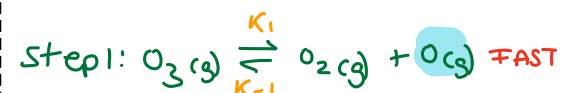


Heterogenous: Catalyst in different phase than reactants
 Maxwell Boltzmann
 When a catalyst is used, $\downarrow E_a \rightarrow$ more collisions with sufficient energy $\rightarrow \uparrow$ rate

Rate law	0 order Rate = k	1 st order Rate = k[A]	2 nd order Rate = k[A] ² / k = [A][B]	3 rd order Rate = k[A] ³ / k = [A][B] ²
units of k	$\text{mol L}^{-1} \text{s}^{-1}$ or Ms^{-1}	s^{-1}	$\text{L mol}^{-1} \text{s}^{-1}$ or $\text{M}^{-1} \text{s}^{-1}$	$\text{L}^2 \text{mol}^2 \text{s}^{-1}$ or $\text{M}^{-2} \text{s}^{-1}$
integrated rate law	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	
Straight line plot and it's relationship to k	$[A]$ vs t Y-intercept = $[A]_0$ k = -slope	$\ln[A]$ vs t Y-intercept = $\ln[A]_0$ k = -slope	$\frac{1}{[A]}$ vs t Y-intercept = $\frac{1}{[A]_0}$ k = slope	
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$ (if $t_{1/2}$ = constant e.g. n = 1 st order * Radioactive example Decay)	$t_{1/2} = \frac{1}{(k[A]_0)}$	

Reaction mechanism, Rate law and steady state approximation

- If the 1st step is slow, it determines rate
- If the 1st step is not rate limiting, use steady state approximation



At equilibrium:
Rate forward = Rate reverse

must remove intermediate

$k_1[O_3] = k_{-1}[O_2][O]$

Solve for intermediate
 $\frac{k_1[O_3]}{k_{-1}[O_2]} = [O]$

Sub into rate law
 Rate = $k_2[O_3] \frac{k_1[O_3]}{k_{-1}[O_2]}$

Combine like terms
 $\left(\frac{k_1 k_2}{k_{-1}} \right) \frac{[O_3]^2}{[O_2]} \rightarrow k = \frac{[O_3]^2}{[O_2]}$



Unit 6: Thermodynamics

Endothermic and Exothermic processes.

Exothermic: Energy is released into surroundings as heat.

- Temperature of surroundings increases.

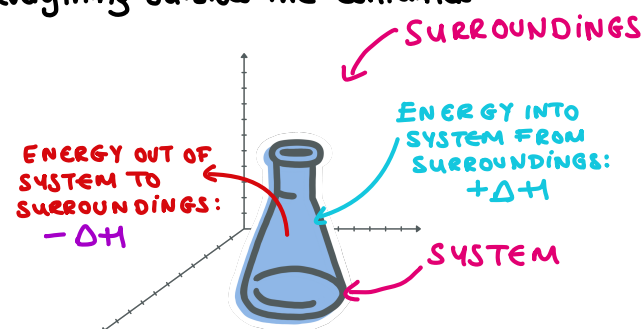
Endothermic: Energy is absorbed from surroundings.

- Temperature of surroundings decreases.

System: The part of the experiment on which we focus our attention. Normally consists of reactants and products.

Surroundings: Everything else. Normally consists of the container and everything outside the container.

When a solid is dissolved in water to form a solution, the thermometer that is used to record the temperature is considered to be part of the surroundings.



DON'T FORGET

First law of thermodynamics: Energy cannot be created or destroyed. It can change from one form to another.

Endothermic examples

Melting
Boiling
Vaporization
Sublimation
Changes involving:
Breaking
Separation

Exothermic examples

Freezing
Condensation
Deposition
Changes involving:
Combining materials

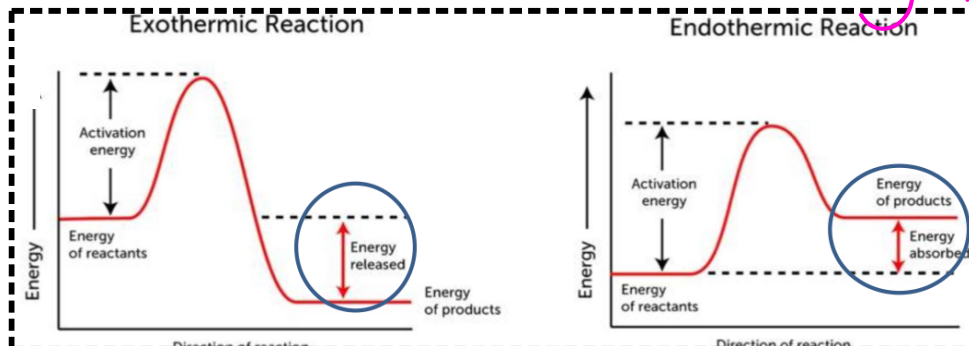
Enthalpy and Heat

Energy = capacity to do work or transfer heat
(E) $\Delta E = q + w$

Heat = the transfer of energy that takes place because of a difference in temperature, from hot to cold.
(Q) units: Joules or kilojoules

Enthalpy = used to measure changes in energy for a constant-pressure system. Units: kJ/mol, kJ/mol_{rxn}
(H)

REMINDER $\Delta H = q_p$ if $\Delta H > 0$, Endothermic, $+\Delta H$
DON'T FORGET THE SIGN!! if $\Delta H < 0$, Exothermic, $-\Delta H$



Thermal Equilibrium

When two substances at different temperatures come into contact:

The higher temperature substance will lose energy (via collision) and the lower temperature substance will gain energy (via collision)

$$q_{\text{loss}} = -q_{\text{gained}}$$

Eventually both objects will reach the same temperature and said to be at thermal equilibrium.

Heat Capacity and Calorimetry

Specific heat capacity: Amount of energy needed to raise the temperature of one gram of a substance by one degree Celsius.

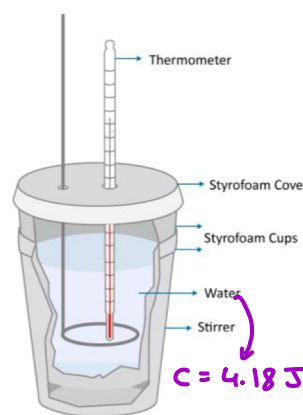
$$q = mc\Delta T$$

Heat (Joules/Calories) mass (kg) Specific heat ($J/kg^{\circ}C$) Temperature ($^{\circ}C/K$)

↳ sometimes n = moles

Calorimetry is the measure of the quantity of heat exchanged.

A calorimeter is a device used to measure the heat transfer by stopping the transfer of heat between the inside of the calorimeter and the surroundings.



To find (c) of a metal

- Heat metal to a known temperature and place into a calorimeter of water.
- Heat will transfer from metal to water to reach thermal equilibrium.

$$q(\text{metal}) = -q(\text{water})$$

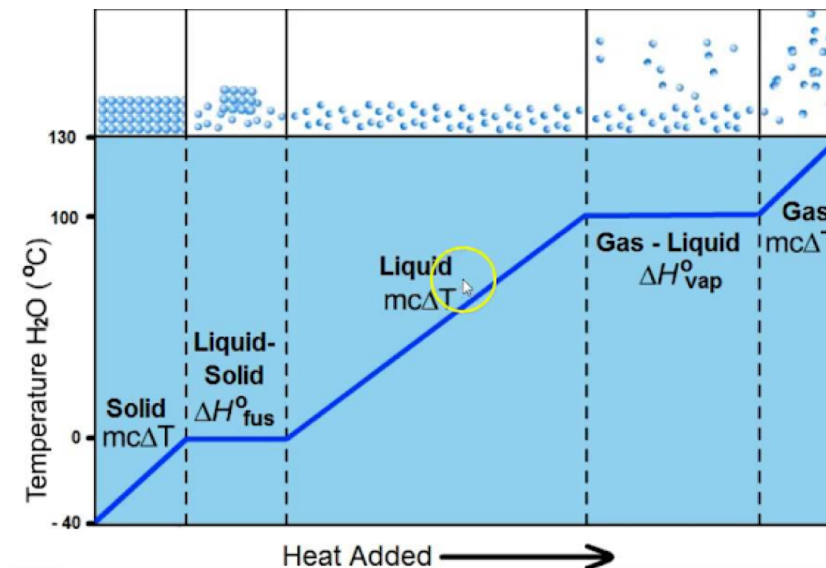
$$q = mc\Delta T$$

Sub in:

$$m_{\text{metal}} C_{\text{metal}} \Delta T_{\text{metal}} = -[m_{\text{water}} C_{\text{water}} \Delta T_{\text{water}}]$$

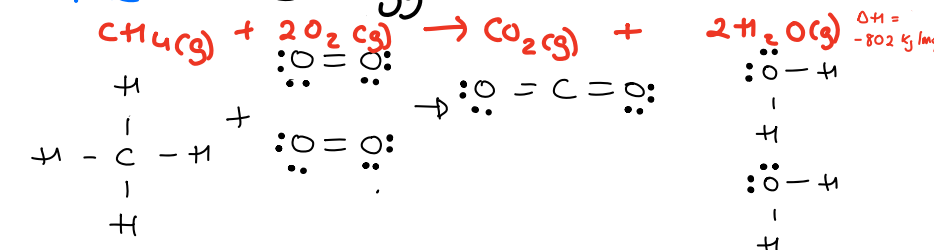
For two substances, when C is higher, ΔT is lower.

Molar heat capacity = $C \div \text{molar mass of that substance}$.



Bond Enthalpies

Endothermic Energy required to break a bond
Exothermic Energy released when a bond is made



Bonds broken - Endothermic $+\Delta H$ Bonds formed - Exothermic $-\Delta H$

$$C-H: 4 \times 413 = 1652$$

$$O=O: 2 \times 498 = 996$$

$$2648 \text{ kJ}$$

$$C=O: 2 \times 799 = 1598$$

$$O-H: 4 \times 463 = 1852$$

$$3450 \text{ kJ}$$

$$\Delta H_{\text{rxn}} = \sum \Delta H(\text{broken}) - \sum \Delta H(\text{formed})$$

$$= 2648 \text{ kJ} - 3450 \text{ kJ}$$

$$= -802 \text{ kJ/mol}_{\text{rxn}}$$

Enthalpy of formation

ΔH_f° represents the change in enthalpy associated with the formation (synthesis) of one mole of a compound from its elements under standard conditions (1 atm and $25^{\circ}C$). ΔH_f° for a pure element in its standard state = 0.

$$\Delta H^{\circ} = \sum \Delta H_f^{\circ} \text{ products} - \sum \Delta H_f^{\circ} \text{ reactants}$$

REMINDER PAY ATTENTION TO PHASES!

Hess's Law

- If equations are added together, add up total ΔH values
- If an equation is reversed, change sign of ΔH .
- If an equation is multiplied by N, multiply ΔH by N.



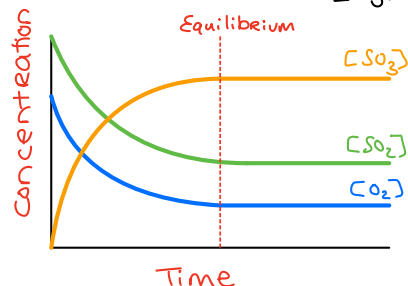
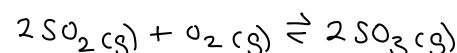
Equilibrium



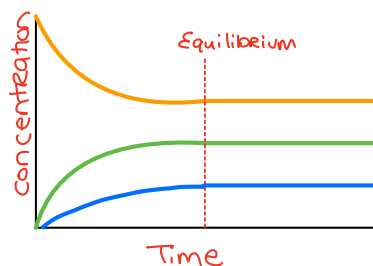
When equilibrium is reached:

- Reactants and products are simultaneously present.
- The concentrations or partial pressures of all species remain constant
- No observable changes occur in the system
- The equilibrium state is dynamic; the forward and reverse processes continue to occur at equal rates, resulting in no net observable change.

Examples:



Start with all reactants, no products and achieve equilibrium.



Start with all products, no reactants and achieve equilibrium.

Reaction Quotient and Equilibrium Constant



Q = Reaction Quotient

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

At any time in a reaction

K = Equilibrium Constant

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

$$K_p = \frac{(P_c)^c (P_d)^d}{(P_a)^a (P_b)^b}$$

At equilibrium

Tips

SOLIDS AND PURE LIQUIDS ARE NOT INCLUDED!



$$Q = \frac{[\text{CO}_2]}{[\text{CH}_4][\text{O}_2]^2}$$



Direction of Reaction

If $Q = K$, at equilibrium

If $Q < K$, too many reactants.

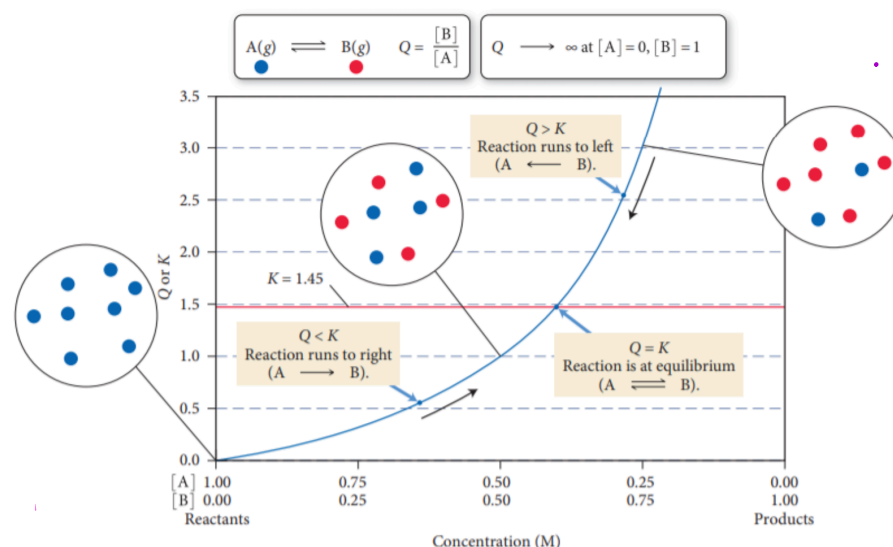
Reaction proceeds left to right until $Q = K$ $K \rightarrow Q$

If $Q > K$, too many products

Reaction proceeds right to left until $Q = K$ $K \leftarrow Q$

Unit 7: Equilibrium

Q, K and direction of Reaction



Magnitude of K.

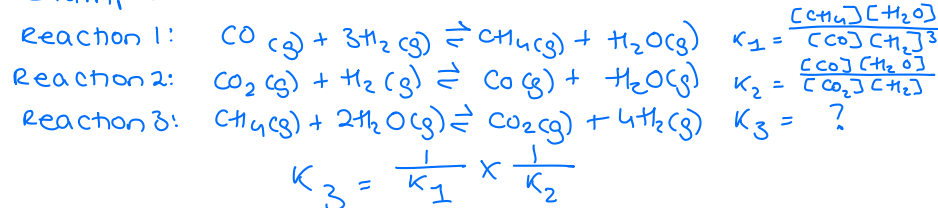
Small K values: Reactants favoured
Large K values: products favoured



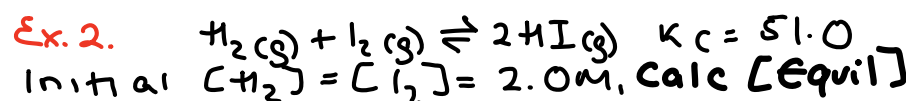
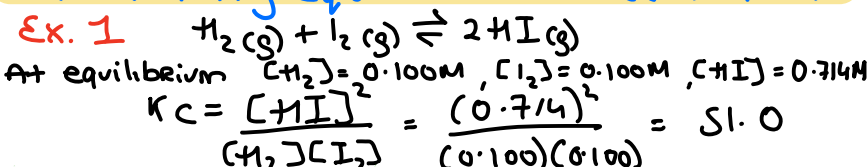
Properties of equilibrium constant

1. Reverse equation $\rightarrow$ Invert K.
2. Multiply co-efficients by a factor $\rightarrow$ Raise K to same factor
3. Add equations together $\rightarrow$ Multiply K constants

Example:



Calculating Equilibrium concentrations



	H_2	$+$	I_2	$\rightleftharpoons$	2HI
I	2.0M		2.0M		0
C	-x		-x		+2x
E	2-x		2-x		2x

$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 51.0 = \frac{(2x)^2}{(2-x)^2}$, $x = 1.56$

See more examples of ICE TABLES IN 'ICE ONE PAGER'!

Notes

Equilibrium Concentrations

- Equilibrium concentrations of reactants and products depend on initial concentrations
- K is always the same at a given temperature, regardless of initial concentrations
- There is no such thing as law of conservation of moles (moles can change, grams cannot)

Le Chatelier's principle

If a system at equilibrium experiences an external stress, the position of equilibrium will shift in the direction that relieves that stress.

Concentration

Add reactant $\downarrow Q$ $Q < K$ Shift right

Remove reactant $\uparrow Q$ $Q > K$ Shift left

Add product $\uparrow Q$ $Q > K$ Shift left

Remove product $\downarrow Q$ $Q < K$ Shift right

Adding/removing (s) or (l) inert substance/catalyst: No shift

Temperature

$\Delta H > 0$: $\uparrow$ temp $\uparrow K$ $Q < K$ Shift right

(endo): $\downarrow$ temp $\downarrow K$ $Q > K$ Shift left

$\Delta H < 0$: $\uparrow$ temp $\downarrow K$ $Q > K$ Shift left

(exo): $\downarrow$ temp $\uparrow K$ $Q < K$ Shift right

Volume / pressure

Gas: $\uparrow P / \downarrow V$ Shift to fewer moles of gas

$\downarrow P / \uparrow V$ Shift to more moles of gas

Aqueous: Add $\text{H}_2\text{O}(\text{l})$ Shift to more moles of (aq)

Remove $\text{H}_2\text{O}(\text{l})$: Shift to fewer moles of (aq)



Q = K



Solubility Equilibrium

Solubility of insoluble salts



$$K_{sp} = [A^+]^m [X^-]^n = (ms)^m (ns)^n \quad S = \text{molar solubility}$$

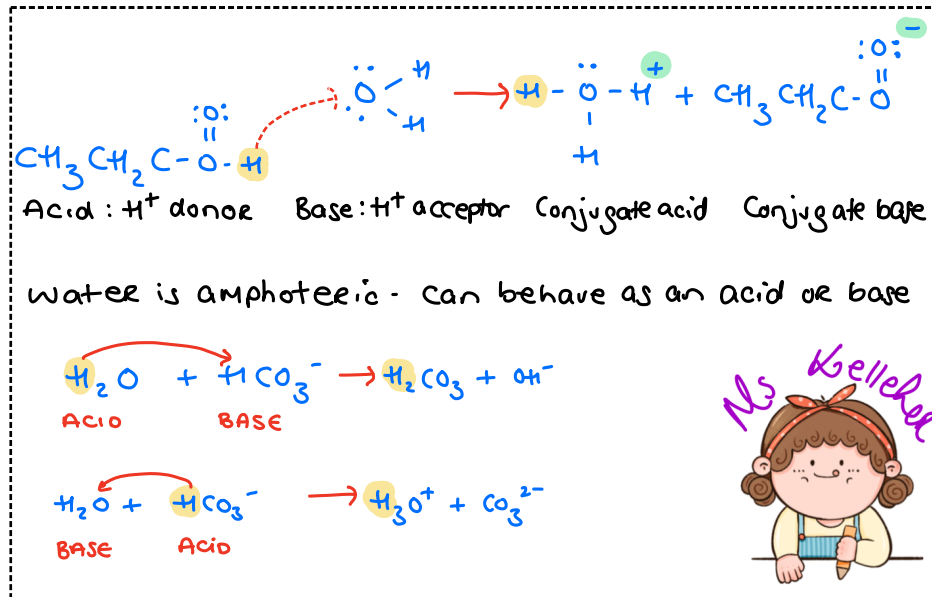
Precipitation: $Q_{sp} > K_{sp}$ Precipitate forms

$Q_{sp} < K_{sp}$ No precipitate forms

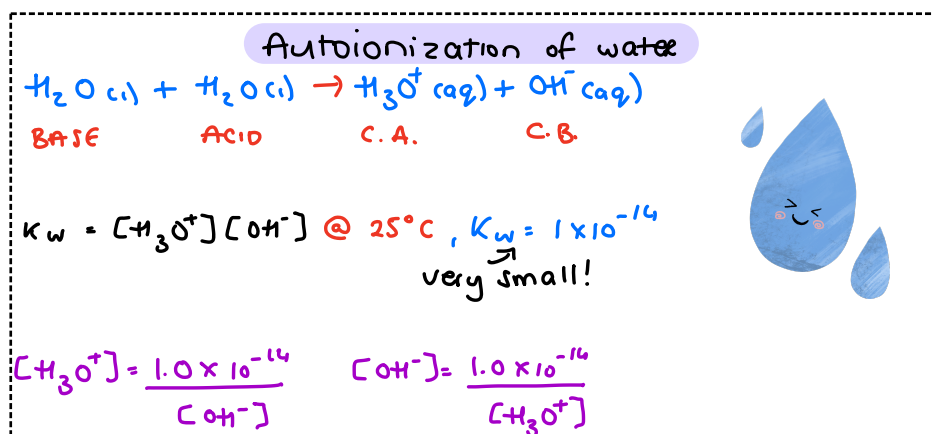
Common Ion effect:

- Solubility of a salt decreases when dissolved in a solution with an ion common with the salt.
- Solubility increases when an ion in solution reacts with an ion in the salt.

Unit 8 Acids and Bases



$\text{pH} = -\log [\text{H}_3\text{O}^+]$ $\text{pOH} = -\log [\text{OH}^-]$ Henderson-Hasselbach:
 $\text{pH} = \text{pKa} + \log \left[\frac{[\text{A}^-]}{[\text{HA}]} \right]$
 $\text{pH} = -\log [\text{H}^+]$ $10^{-\text{pH}} = [\text{H}^+]$

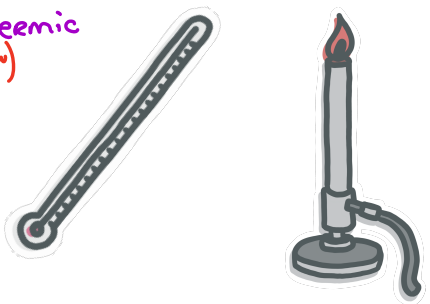
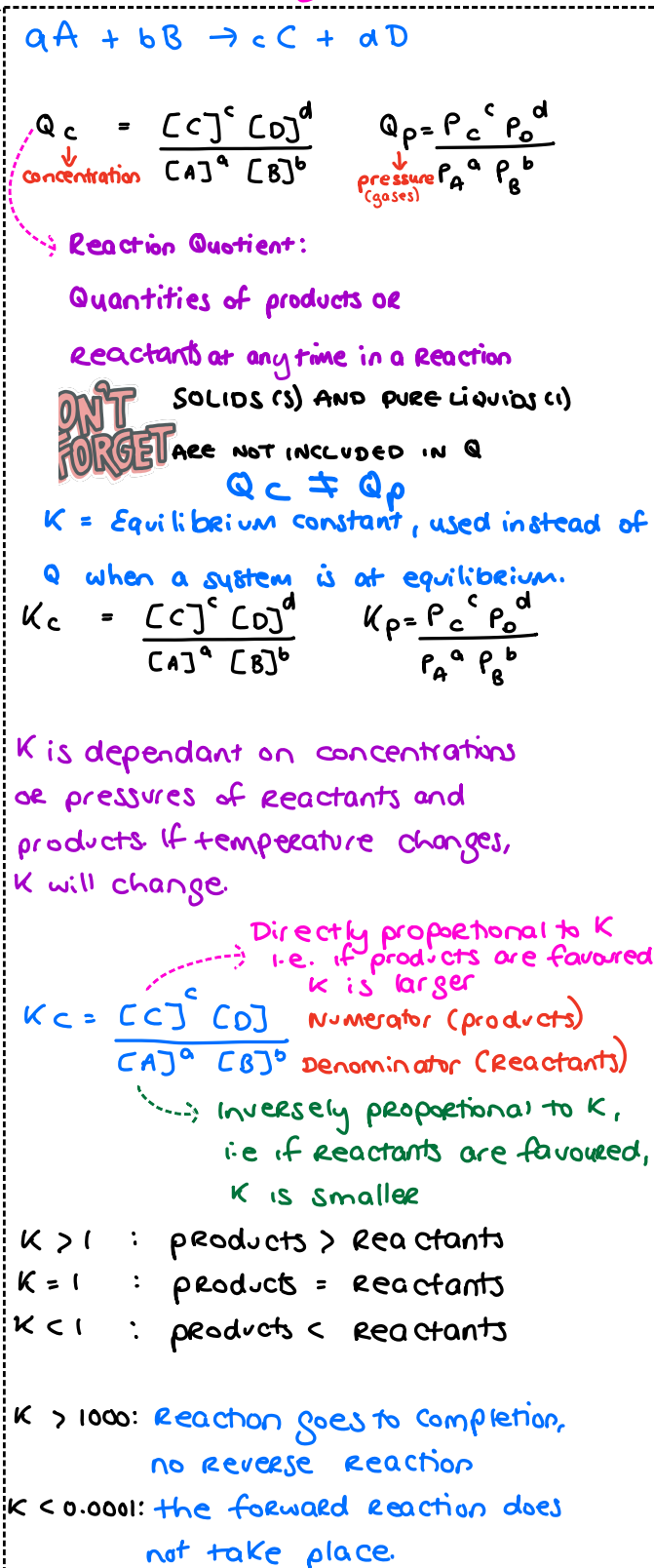


Pure water
 $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ $\text{pH} = \text{pOH} = 7$
 $\text{p}K_w = 14.0$ $\text{pH} = -\log(1.0 \times 10^{-14}) @ 25^\circ\text{C}$
 $\text{p}K_w = \text{pH} + \text{pOH}$

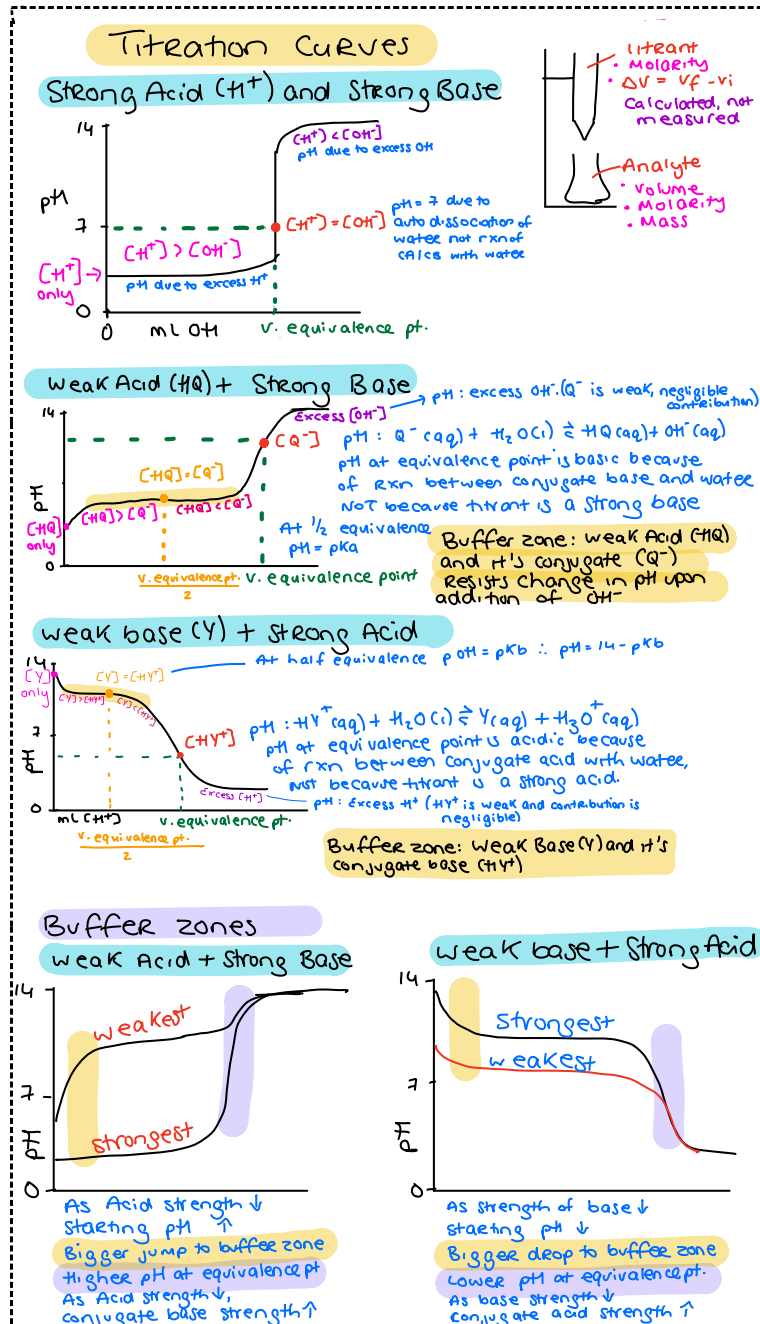
As temperature increases $\uparrow$ $\text{p}K_w$ decreases $\downarrow$
 As temperature increases $\uparrow$ K_w increases

Endothermic

Temp.	$\text{p}K_w (-\log K_w)$	$K_w (10^{-\text{p}K_w})$
10	14.5	3.2×10^{-15}
20	14.2	6.3×10^{-15}
25	14.0	1.0×10^{-14}
30	13.8	1.6×10^{-14}
40	13.5	3.2×10^{-14}

At Equilibrium $Q = K$
 If $Q > K$, the numerator must decrease to make $Q = K$. Products decrease and reverse reaction is favoured
 If $Q < K$, the numerator must increase to make $Q = K$, the products must increase and forward reaction is favoured



Strong Acids
 Fully dissociate in water to produce H_3O^+ / H^+ ions
 HCl , HBr , HI , HClO_4 , HNO_3 and H_2SO_4

Strong Bases
 Fully dissociate in water to produce OH^- ions
 LiOH , NaOH , KOH , RbOH , CsOH , $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$
 Group 1 + 2 metal hydroxides

Effect of dilution on pH
 $M_1 \times V_1 = M_2 \times V_2$

Example:
 Original $\rightarrow$ New
 100.0ml of 0.10M HCl 200.0M of 0.05M HCl 1.30 - 1.00 = 0.30
 200.0ml of 0.50M NaOH (0.50)(0.200) = (x)(0.300)
 $0.33\text{M} = x$
 300.0ml of 0.33M NaOH 13.52 - 13.70 = -0.17
 300.0ml distilled water 400.0ml distilled water pH = 7.00
 The larger the change in concentration, the larger the change in pH

Weak Acid and Base equilibria

Weak acids partially ionize in water to produce H_3O^+ ions

K_a of weak acid

- Acid dissociation constant. A measure of acid strength
- $K_a < 1$ for a weak acid.
- A solution of weak acid involves equilibrium between an un-ionized acid and it's conjugate
- $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$ $\text{p}K_a = -\log(K_a)$

when $[\text{HA}] = [\text{A}^-]$, $\text{pH} = \text{p}K_a$
 when $[\text{HA}] > [\text{A}^-]$, $\text{pH} < \text{p}K_a$
 when $[\text{HA}] < [\text{A}^-]$, $\text{pH} > \text{p}K_a$

when comparing two weak acids
 Larger K_a/K_b = stronger acid / base
 Smaller $\text{p}K_a/\text{p}K_b$ = stronger acid / base

Weak bases partially ionize in water to produce OH^- ions

K_b of weak base

- A solution of a weak base involves equilibrium between an un-ionized base and it's conjugate acid

$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$ $\text{p}K_b = -\log(K_b)$

Adding a common ion to weak acid/base decreases % ionization
 As $[\text{H}_3\text{O}^+]$ decreases, % ionization increases.
 Adding H_2O increases ionization
 Acid: $\frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_{\text{original}}} \times 100\%$ Base: $\frac{[\text{OH}^-]}{[\text{B}]_{\text{original}}} \times 100\%$

Buffers pH range = $\text{p}K_a \pm 1$

- A solution that resists change in pH when a small amount of strong acid or it's base is added to solution
- Made of a weak acid and it's C.B. (salt) or weak base and it's C.A. (salt)
 e.g. HNO_2 and NO_2^- (sourced for e.g. from sodium salt of C.A. like NaNO_2)
 $[\text{H}_3\text{O}^+] = K_a$, $\text{pH} = \text{p}K_a$ when concentrations of weak acid and conjugate base are equal.

Unit 9: Applications of Thermodynamics



Entropy

Entropy is a measure of how dispersed (spread out) the energy of a system is at a specific temperature.

Entropy increases when...

Matter / Energy spreads out

a substance changes phase

Solid $\rightarrow$ Liquid

Liquid $\rightarrow$ Gas

Solid $\rightarrow$ Gas



Particles occupy a larger volume

Gas expands to larger volume (constant temp)

Total moles of gas products > Total moles of gas reactants

Temperature of a gas increases $\rightarrow$ broader distribution of kinetic energies of gas particles
The temperature increases.

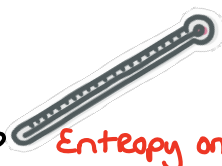
Calculating Entropy

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

Note $\Delta S^\circ = 0$ only at 0 Kelvin (-273°)
 $\Delta H^\circ_f = 0$ for a pure element, This isn't the case for ΔS°

Temperature, Entropy and Gibbs Free Energy

ΔH°	ΔS°	Symbols	$\Delta G^\circ < 0$, Reaction driven by
< 0	> 0	$< >$	all temp. Enthalpy + Entropy
> 0	< 0	$> <$	no temp.
> 0	> 0	$> >$	high temp. Entropy only
< 0	< 0	$< <$	low temp. Enthalpy only



Gibbs free energy

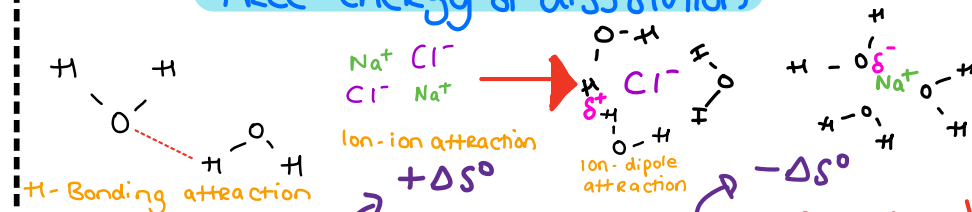
ΔG° = Energy that is "free" and available to do work.
Standard state (1.0 M, 1.0 atm, 298 K)

$$\Delta G^\circ = \sum \Delta G^\circ_f \text{ products} - \sum \Delta G^\circ_f \text{ reactants}$$

$\Delta G^\circ < 0$: Thermodynamically favored (spontaneous)

$\Delta G^\circ > 0$: Thermodynamically unfavored (non spontaneous)

Free energy of dissolution



Takes to break ($+\Delta H^\circ$) Frees to form ($-\Delta H^\circ$)

Favorable: $-\Delta H^\circ + \Delta S^\circ$ Unfavorable: $+\Delta H^\circ - \Delta S^\circ$

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

If $\Delta G^\circ > 0$: Thermodynamically unfavored - Slightly soluble / insoluble salts

If $\Delta G^\circ < 0$: Thermodynamically favored - Soluble salts **S.N.A.P.**

Kinetic Control

- ΔG° is negative, occurs extremely slowly
- Large activation energy, catalyst used to lower it

Coupled Reactions

Making a reaction with a $\Delta G^\circ > 0$ occur.

- External source of energy
 - A thermodynamically favored rxn. coupled with unfavored
- Share a common intermediate
Use Hess's Law to determine ΔG
Sum of reactions ΔG° values < 0 , $\therefore$ thermodynamically favorable

Galvanic (Voltaic) Cell

- Thermodynamically favorable.
- Anode and cathode in separate chambers (half cells).
- Salt bridge needed
- Produces electrical energy (+V)
- Oxidation at anode, Reduction at cathode
- Require ion flow in the cell for a reaction to occur
- Cations $\rightarrow$ Cathode; anions $\rightarrow$ anode

Electrolytic Cell

- Thermodynamically unfavored
- Anode and cathode often in the same chamber.
- Power source needed (e.g. battery)
- Uses electrical energy (-V).

Both cells:

Faraday's Law

$$I = \frac{Q}{t}$$

I = current, Amperes (A)
 Q = amount of charge
 t = time, seconds (s)

- Moles of e^- determined from chemical equation
- Pay attention to unit
- Use dimensional analysis
- Moles and Molar mass used: g / mole

Cell potential and Free energy

$$\mathcal{E}^\circ_{\text{cell}} = \mathcal{E}^\circ_{\text{cathode}} - \mathcal{E}^\circ_{\text{anode}}$$

- Units: Volts (V)
- Standard Reduction potentials $\mathcal{E}^\circ_{\text{red}}$ (1 M solutions, 1 atm, 25°C) used to compare reduction potentials
- For an oxidation process, the reduction half reaction equation and sign of voltage are reversed.
- Don't multiply $1/2$ rxn. potentials by coefficients in equation.

$\mathcal{E}^\circ_{\text{cell}} > 0$: thermodynamically favorable Galvanic Cells

$\mathcal{E}^\circ_{\text{cell}} < 0$: thermodynamically unfavored Electrolytic cells

$$\Delta G^\circ = -nF\mathcal{E}$$



Faraday's constant, F is the amount of charge (q) in Coulombs (C) per mole of electrons. $F = 96,485 \text{ C/mol } e^-$
 n = moles of electrons

Non standard conditions

Standard conditions (1 M solution, 1 atm gas, 25°C)
 $Q = 1$, not at equilibrium. **COMPARE Q to K**

Voltaic cell ($K > 1$)

$\uparrow Q$ $\downarrow \mathcal{E}^\circ_{\text{cell}}$ closer to equilibrium

$\downarrow Q$ $\uparrow \mathcal{E}^\circ_{\text{cell}}$ further from equilibrium

Electrolytic cell ($K < 1$)

$\uparrow Q$ $\uparrow |\mathcal{E}^\circ_{\text{cell}}|$ Absolute value because these cell potentials are negative.

$\downarrow Q$ $\downarrow |\mathcal{E}^\circ_{\text{cell}}|$

Equilibrium and Thermodynamics

At Non-standard states

$$\Delta G = \Delta G^\circ + R.T \ln Q \quad \mathcal{E} = \mathcal{E}^\circ - \frac{R.T}{n.F} \ln Q$$

At Equilibrium

$Q = K$, $\Delta G = 0$

Nernst Equation

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$K = e^{\frac{-\Delta G^\circ}{R.T}} = e^{\frac{\mathcal{E}^\circ_{\text{cell}} \cdot n \cdot F}{R.T}}$$

If $\Delta G^\circ < 0$, $\mathcal{E}^\circ > 0$, $K \gg 1$ Thermodynamically favorable

If $\Delta G^\circ > 0$, $\mathcal{E}^\circ < 0$, $K \ll 1$ Thermodynamically unfavored