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1 Mole Concept

- A **mole of substance** is the amount of substance which contains 6.02×10^{23} elementary entities of that substance.
- **Empirical formula** is the formula that shows the simplest whole number ratio of the atoms of different elements present in 1 molecule or formula unit of compound.
- **Molecular formula** is formula showing actual number of atoms of each element present in 1 molecule of compound.

2 Atomic structure

When particle passed through an electric field, angle of deflection $\propto \frac{Q}{m}$

2.1 Orbitals

- S orbital spherical shape, non-directional
- P orbital dumbbell shape, 3 orbitals, 1 on each axis
- 5D orbitals
 - 3 orbitals have 4-lobed shape and point between axes
 - 4 lobed shape aligned along x and y axes $d_{x^2-y^2}$
 - Dumbbell surrounded by small doughnut shaped at waist, aligned along z-axis d_{z^2}

2.2 Electronic Configuration

- Fill orbitals in order $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, \dots$, in order of increasing energy level
- Fill orbitals of subshell singly by electrons of parallel spins before pairing. Minimise inter-electronic repulsion.
- Chromium (24): fills up all of $3d$ to minimise inter-electronic repulsion since 3d and 4s orbitals about equal in energy. Hence $3d^5 4s^1$ more stable than $3d^4 4s^2$.
- Copper (29): fully filled $3d$ subshell unusually stable due to symmetrical charge distribution around metal centre. Hence $3d^{10} 4s^1$ more stable than $3d^9 4s^2$.

. Ground state is when electrons are in the orbitals of lowest available energy level, excited state is when one or more electrons absorb energy and are promoted to higher energy level. Excited atoms unstable and can emit energy to return to ground state

2.3 Strength of electrostatic attraction between nucleus and electrons

Energy required to remove valence electron from atom

- Number of electron shells: Number of shells increase \rightarrow principal quantum number of the valence shell increases \rightarrow distance between the nucleus and the valence electron increases \rightarrow electrostatic attraction between nucleus and valence shell decreases
- Effective Nuclear Charge (Compare Factor, mention other one remain constant)
 - Nuclear charge: Number of protons increases \rightarrow nuclear charge increases (isoelectric species, same shielding effect)
 - Shielding effect: Number of inner shell electrons increases \rightarrow shielding effect experienced by the valence electron increases (electrons added to outermost shell, shielding effect approximately constant)
- Effective nuclear charge increases \rightarrow electrostatic attraction between nucleus and valence shell increase.

2.4 Atomic radius

Atomic radius is defined as half the shortest inter-nuclear distance found in the structure of the element.

- Atomic radii decrease down a period (nuclear charge)
- Down a group, atomic radius increases (electronic shells)
- Ionic radius decreases from Na to Si (nuclear charge), sharp increase from Al^{3+} to P^{3-} due to number of electronic shells.

2.5 Ionisation Energies

First ionisation energies generally increase down a period (Nuclear Charge)

- Group 2 less than group 13 because of 2p/3p electron at a higher energy level than 2s/3s
- Group 15 less than group 16 because 3p electron removed from group 16 is a paired electron while electron removed from 15 is an unpaired electron. Inter-electronic repulsion between paired electrons, less energy required to removed paired 3p electron.

Successive ionisation energies of an element

- Once first electron removed from neutral atom, each successive electron removed from ion of increasing positive charge which attracts electrons more strongly.
- Increase with special jumps for electrons from different subshells (small jump) and different electron shells (big jump)

2.6 Electronegativity

Electronegativity of an atom in a molecule is a relative measure of its ability to attract bonding electrons.

- Increases down period (nuclear charge)
- Decreases down a group (Number of shells)

3 Chem Bonding

3.1 Giant Ionic Lattice

- Lattice energy in ionic bond $\propto \frac{Q_+ \times Q_-}{R_+ + R_-}$
- Greater charge and smaller radius, shorter inter-ionic distance, greater magnitude of lattice energy.
- Soluble in polar solvent but insoluble in non-polar solvent
 - Tend to dissolve in water: large amount of energy released from ions forming strong ion-dipole interactions with the polar water molecules greater than energy required to break hydrogen bonds in water
 - Ion-dipole interactions: bond from δ^- O atom to cation and δ^+ H atom to anions.
- Hard and brittle, slight displacement along cleavage plane brings ions of opposite charges to one another
- Ionic bonds with covalent character
 - Polarising power of cation: higher charge and smaller cation, stronger polarising power
 - Polarizability of anion: Electron clouds of large anions easier to distort
 - Greater covalent character: greater deviation (stronger bond) from theoretical strength of bond (weaker bond, lower MP and BP)

3.2 Giant molecular lattice

Graphite

- Each C atom bonded to 3 other C atoms in layered structure, weak intermolecular attraction between layers. Last electron not used in bonding, delocalised over the layer and used as mobile charge carrier.
- Graphite is the most stable allotrope of carbon

Diamond

- Diamond: Each C atom bonded to 4 other C atoms in 3-dimensional lattice by forming strong covalent bonds.

3.3 Giant Metallic lattice

Metallic bond is the electrostatic attraction between a lattice of positive ions and delocalised electrons.

- Number of electrons available / Higher charge of cation: greater number of valence electron, stronger bonds
- Smaller size of cation, stronger bonds

Delocalised electrons allow for high electrical conductivity (charge carriers flow towards positive terminal) and thermal conductivity (by moving faster and more randomly, colliding with other electrons and passing off energy).

3.4 Dot and Cross Diagram

- Central atom is less electronegative with more unpaired electrons
- Electrons are lost from the less electronegative (central) atom
- Electrons are gained by the more electronegative (side) atom
- Group III elements have vacant, low-lying 3d orbitals available for the expansion of the octet, allowing for compounds such as PCl_5 to form.

Lone electrons unstable and readily dimerise. Example of this is NO_2 and Al_2Cl_6 (2 central Cl atoms form dative covalent bonds with Al)

3.5 Bond Angles

- Lone pair exerts greater repulsion than a bond pair. Lone pair **attracted by only one nucleus and hence is closer to the central atom**, compared to bond pair electrons attracted by 2 nuclei. This results in lone pair repulsion being greater than bond pair and lone electron repulsion.
- Separate lone pairs in VSEPR diagram if possible.
- Repulsion between bond pairs increased by an increase in the electronegativity of central atom. More electronegative atom draws bond pair closer to itself \rightarrow closer to nucleus, exert more repulsion
- Opposite is true for side atom, more electronegative \rightarrow further away from central atom.

3.6 Intermolecular forces of attraction

3.6.1 Instantaneous dipole-induced dipole (id-id) interactions

- Electrons constantly moving around, causing electron density to sometimes be asymmetrical, resulting in an instantaneous dipole. This can induce a **short-lived dipole in a neighbouring particle**, causing an attraction between them.
- Present in all particles
- Strength of id-id interactions increases with number of electrons because large electron clouds are **more easily polarised** than smaller electron clouds, formation of stronger id-id interactions
- Same number of electrons: id-id interactions stronger in molecules with greater surface area (less spherical) for inter molecular interactions. Greater extent of contact between neighbouring molecules, resulting in stronger id-id forces to overcome at higher temperature.
- Solubility
 - Dissolving favourable (i.e. I_2 , C_6H_{14}), solute-solvent interaction is id-id, **similar** to solute-solute and solvent-solvent interactions.

3.6.2 Permanent dipole-permanent dipole (pd-pd) interactions

- Polar molecules have permanent dipoles in their structures. Molecules tend to align such that partially positive $\delta+$ end of 1 molecules is near the partially negative $\delta-$ end of other molecule. Electrostatic attraction between the $\delta+$ end of 1 molecule and $\delta-$ end of other molecule gives rise to permanent dipole-permanent dipole(pd-pd) interactions
- Molecules with **similar number of electrons**, those with pd-pd tend to have higher boiling points than those with only id-id

3.6.3 Hydrogen bonding

- Highly $\delta+$ H atom can form a particularly strong attraction with a lone pair of electrons on an adjacent **small, highly electronegative (F,O,N) molecule**, creating an intermolecular force known as hydrogen bond
- One lone pair of electrons on F,O,N atom in neighbouring molecule bearing a $\delta-$ which can attract $\delta+$ on H atom
- Extensiveness of hydrogen bonding: More extensive hydrogen bonding due to an average of 2 H-bonds per molecule of H_2O compared to an average of 1 H-bond per molecule of NH_3
- Formation of intramolecular hydrogen bonding \rightarrow less sites available for hydrogen bonding with other molecules \rightarrow intermolecular hydrogen bonding **less extensive**
- Strength of H-bond: Dipole moment of H-X bond is greater than for H-F than for H-N since F is more electronegative than N \rightarrow stronger hydrogen bond
- Solubility
 - Energy released in forming (id-id) interactions between solute and solvent molecules cannot compensate for breaking stronger hydrogen bonds in water.

Structure of ice: Ice is less dense than water due to highly ordered 3-dimensional structure whereby each oxygen atom is **tetrahedrally bonded** to 4 hydrogen atoms, 2 by covalent bonds and 2 by hydrogen bonds. Rigid open structure, larger volume for same mass as molecules prevented from getting too close.

3.7 Types of Covalent bonds

- σ bond is formed when 2 orbitals overlap **head-on**. Electron density of a σ bond is concentrated between the nuclei of the 2 bonding atoms, along the nuclear axis.
- π bond is formed when atomic orbitals **overlap collaterally**, ie side-to-side. It has an electron cloud above and below the nuclear axis but with zero electron density along the axis.
- π bonding takes place when atoms undergo multiple bonding. One of the bonds must be a σ bond while the rest are π bonds.
- σ bond is stronger than π bond because head-to-head orbital overlap in a σ bond has **greater degree of overlap** than side-to-side orbital overlap in a π bond
- π bonding often requires p orbitals while σ bonding will use sp hybridised orbitals

3.8 Strength of Covalent Bonds

Stronger covalent bond leads to a shorter bond length.

- Increase in number of bonds increasing number of shared electrons, thus bond strength is increased
- Smaller size \rightarrow **valence orbital used in bonding is less diffuse** \rightarrow more **effective orbital overlap**
- Greater difference in electronegativity \rightarrow **more polar covalent** bond \rightarrow increase in electrostatic attraction in bond due to **2 partial charges** \rightarrow increased bond strength

4 Hybridisation

Hybridisation is the formation of **equivalent orbitals** with equal bond lengths between s and p orbitals. Number of subshells involved in hybridisation is equal to the number of regions of electron density.

- Higher s -character of hybrid orbital, **less diffuse** hybrid orbital and more tightly shared electrons are held.
- More effective overlap with orbital of other atom.
- If lone pair exists (like in nitrogen), electrons less available as nucleophile and for acid-base electrons as **more strongly attracted by nucleus**.
- Bond strength increases and bond length decreases.

Geometry

- In NH_3 the hybrid orbital containing lone pair forms the apex of pyramid due to greater lone-pair repulsion (as compared to bond pair)
- Thus the bond angles smaller than the expected 109.5°

Orbitals

- sp orbitals required for σ bonding while p orbitals required for π bonding

5 Gaseous State

- $\rho = \frac{M}{V} = \frac{pM}{RT}$
- $pV = nRT$
- Assumption of an ideal gas: Gas particles have negligible volume and exert negligible attractive forces on one another.
- Dalton's law of partial pressures states that total pressure of mixture of non-reacting gases is equal to the sum of the partial pressures of the individual gases in the mixture.

5.1 Conditions for ideal gas

- At low pressures, gas particles are very far apart. Volume occupied by gas particles can be considered negligible as compared to the volume of the container. Intermolecular attractive forces between widely spaced gas particles are negligible.
- At high temperatures, gas particles possess sufficiently high kinetic energy to overcome the intermolecular attractive forces. Thus, intermolecular attractive forces can be considered negligible.

5.2 Graph of ideal-ness of gas

Graph of $\frac{pV}{RT}$ against p looks like a tick: lower than an ideal gas at moderately high pressures but linearly higher than ideal gas at higher pressure.

- Moderately high pressure is exerted on system \rightarrow volume of the system becomes smaller \rightarrow gas particles come closer together, intermolecular attractive forces between gas particles is significant \rightarrow gas occupies smaller volume than ideal gas $\rightarrow \frac{pV}{RT} < n$.
- Very high pressure is exerted on the system \rightarrow volume of the system is very small \rightarrow gas particles are so close together that there is repulsion between electron clouds, known as intermolecular repulsive force \rightarrow gas occupies larger volume than if it were ideal $\rightarrow \frac{pV}{RT} > n$.

5.3 Factors affecting deviation from ideal gas

- Negative deviation from ideal gas: Stronger intermolecular forces of attraction \rightarrow greater negative deviation from ideal gas.
- Positive deviation from ideal gas: Bigger electron cloud \rightarrow more significant intermolecular repulsive force \rightarrow greater positive deviation from ideal gas.

6 Energetics

6.1 Enthalpy

- Enthalpy: The **enthalpy** of a system is a measure of the energy content of the system and has the symbol H . The higher the energy content of a system, the more unstable it is.
- When bonds are broken, energy of the products is higher than that of the reactants (due to greater freedom of atoms). $H_{\text{reactants}} < H_{\text{products}}$, endothermic reaction and heat is absorbed.
- Standard enthalpy change (or energy released) of a reaction ΔH_r is the energy change when (the molar quantities of reactants stated in the chemical equation) react **under standard conditions (298K, 1bar)**
- Definitions: reaction, formation, atomisation x2, combustion, neutralisation, hydration, solution, IE, BE, BDE, EA, LE
- Heat change, $q = mc\Delta T$, where c is heat capacity of substance to which temperature change occurs, m does not include any mass added in
- Enthalpy change $\Delta H = -\frac{q}{n}$
- Assumptions
 - Density of solution = Density of water = 1.0gcm^{-3}
 - Specific heat capacity of solution, c = specific heat capacity of water = $4.18\text{Jg}^{-1}\text{K}^{-1}$
 - Heat loss to surrounding air is corrected for via extrapolation to find highest temperature reached from the graph
 - 100% efficiency in transfer of heat from reaction to solution
- **Hess Law** states that enthalpy change of a chemical reaction is the same regardless of whether the reaction took place in 1 step or several steps, provided the initial and final states of the reactants and products are the same.
- Lattice energies
 - Predominantly ionic compounds, experimental lattice energy values are in good agreement with theoretical lattice energy values \rightarrow structure of the lattice for these compounds quite close to being purely ionic
 - Partial covalent character: Discrepancy between experimental and theoretical lattice energies shows that bonding is not as close to purely ionic as they have some covalent character. Experimental energy values more negative, bonding stronger than predicted.
- Dissolving Ionic Solid
 - Step 1: Separation of ions in solid ionic lattice into isolated gaseous ions (endothermic)
 - Hydration of gaseous ions, formation of ion-dipole interactions (exothermic)
 - $\Delta H_{\text{soln}}^{\circ} = -LE + \Delta H_{\text{hyd}}^{\circ}$

6.2 Entropy

Spontaneous process is a process that once started will continue without any external assistance.

Entropy(S) of a system is a measure of the disorder of matter and energy in the system. The more ways matter in the system can be arranged, and the more ways energy in a system can be dispersed, the more disordered the system is and the larger its entropy.

6.2.1 Factors affecting entropy

- Increasing the temperature → broadening of the Boltzmann energy distribution → more ways of arranging energy quanta in the hotter system → increase in entropy
- Change in state
 - When solid melts into liquid, order in solid is destroyed → particles more randomly arranged and more disordered → increase in entropy
 - Gas is the most disordered since gas particles can move freely and are the most randomly arranged → largest increase in entropy from liquid to gas
- When number of particles in system increases, more ways to arrange the particles and more ways to distribute energy, greater disorder
- Mixing always mixes to create more disordered state. Each gas expands to occupy whole container, more ways for molecules to arrange themselves in larger volume. Liquids of similar polarities mix together to form solution with molecules that are randomly mixed.
- Ionic solid dissolving in water: Disruption of crystal increases disorder, ions previously held rigidly in solid lattice free to move about. Hydration process decreases disorder because it puts hydrating water molecules into an orderly arrangement around ions
 - When ions are more highly charged, more water molecules are ordered around ions, dissolution process results in net decrease in entropy as decrease in entropy from hydration outweighs increase in entropy due to disruption of crystal lattice.

6.2.2 Gibbs free energy change

- $G^\circ = \Delta H^\circ - T\Delta S^\circ$
- $G = H - T\Delta S$
- ΔH and ΔS generally constant with respect to temperature unless there is state change
- When $\Delta G < 0$, process exergonic, forward reaction spontaneous
- When $\Delta G > 0$, process endergonic, forward reaction not spontaneous
- Limitations: Provides thermodynamic feasibility, no information about kinetic feasibility

7 Kinetics

Rate of reaction is defined as change in concentration of a particular reactant or product per unit time

- Reaction $aA + bB \longrightarrow cC + dD$
- $rate = -\frac{dA}{adt} = \frac{dB}{bdt} = \frac{dC}{cdt} = \frac{dD}{ddt}$

7.1 Experimental Techniques

- Continuous method: measure concentration of reactant/product species over time
 - Titration and quenching: stop reaction mixture in withdraw sample by adding large volume of ice-cold water or excess of quenching agent (reacts immediately with reactant or catalyst)
 - Colour intensity (filter selects only wavelengths absorbed by solution) / Electrical Conductivity / Volume or Pressure of gas / Mass of reaction mixture
- Clock reaction: measuring time taken for stated change to occur
 - Prominent visual change: forming of precipitate or change in colour
 - Volume of water may be varied to keep total volume of reaction mixture constant. Initial concentration of each reactant must be directly proportional to volume used.
 - Initial rate of formation is approximated by average rate of formation since time interval t is small. Hence average rate $= \frac{x}{t}$, where x is volume required for observable change, thus rate $\propto \frac{1}{t}$.
 - $S_2O_3^{2-}$ present in formation of I_2 reaction: iodine slowly produced immediately react, $[I^-]$ is effectively 0 until no more thiosulfate ions.

7.2 Reaction Mechanism

Rate equation $rate = kA^mB^n$ relates rate of reaction to the concentration of each reactant raised to the appropriate power. It shows exact dependence of a reaction rate on the concentration of all the reactants.

- **Rate constant** is the constant of proportionality in the rate equation of the reaction
- **Rate determining step** is the slowest step in the reaction mechanism of a multi-step reaction and it determines the overall reaction rate. It is the step with the highest activation energy. To determine rate equation, consider slow step and all the fast steps before the slow step
- **Order of reaction** with respect to given reactant is power to which concentration of reaction is raised in rate equation. Overall order of reaction is sum of powers of the concentration terms in the rate equation (zero-/first-/second- order).
- Catalyst not included in rate equation as it participates in reaction but is regenerated and hence its concentration can be regarded as constant.
- Present by letting $rate = k[P]^m[Q]^n$ and sub values.
- **Half life $t_{\frac{1}{2}}$ of a reaction** is the time taken for the concentration of a reactant to decrease to half its initial value
 - First order reaction: $t_{\frac{1}{2}} = \frac{\ln 2}{k}$
- Pseudo-order reaction
 - Presence of large excess of reactant or catalyst, concentration of excess reactant hardly changes during reaction relative to initial concentration, effectively constant throughout reaction. Exhibits pseudo-first-order kinetics

7.3 Factors affecting rate of reactions

In order to react, reactant particles must collide in a favourable orientation with a certain minimum amount of energy.

- Arrhenius equation: $k = Ae^{-\frac{E_a}{RT}}$. Rate $\propto [A]^m$.
- Physical state of reactants
 - Reactants in solid form do not react
 - Molecules require heating to break bond (as opposed to ions)
 - Surface area: finely divided state like powder would react faster
- Concentration/Partial Pressure of reactants
 - Reactant particles must collide to react
 - Concentration/Pressure of reactant increase \rightarrow reactant particles come closer together \rightarrow frequency of collisions increase \rightarrow frequency of effective collisions increase
- Temperature: increases temperature increases rate of reaction
- Presence of catalyst

7.4 Maxwell-Boltzmann distribution

Distribution of kinetic energies of molecules at particular temperature.

- Temperature increase, curve flattens. Peak moves to higher speeds and distribution broadens out.
 - Average KE of reactant particles increase
 - Significantly more reactant particles have energy greater than or equal to the activation energy of the reaction \rightarrow increase in effective collision frequency and hence increase in the rate of reaction
- Catalyst: Leftward shift of E_a
 - Providing alternative reaction pathway of lower activation energy than the uncatalysed reaction
 - Significantly more reactant molecules have energy greater than or equal to the activation energy for the catalysed reaction \rightarrow increase in effective collision frequency \rightarrow increase in rate of reaction
 - Alternative reaction pathway of lower AE also results in larger rate constant k

7.5 Catalysts

Catalyst is a substance which increases the rate of a chemical reaction without itself undergoing a permanent chemical change

- Homogeneous catalyst: Catalyst and reactants are in same phase. Alternative pathway through intermediate reaction (2 reaction on profile diagram) with lower activation energy
 - $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \longrightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$
 - Uncatalysed reaction, direct reaction between 2 anions. Electrostatic repulsion between 2 anions of like charges causes reaction to have high activation energy. Metal cation like Fe^{3+} can serve as catalyst.
 - $\text{Fe}^{3+} + \text{I}^- \longrightarrow \text{Fe}^{2+} + \text{I}_2$, Fe^{3+} regenerated through $\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \longrightarrow 2\text{SO}_4^{2-} + \text{Fe}^{3+}$
- Heterogeneous catalyst: Different phase

- Reactant molecules readily adsorbed onto active sites of catalyst. Weak bonds are formed between surface of catalyst and reactant molecules.
- Weakens covalent bonds within reactant molecules, lowering AE and increases concentration of reactant molecules at catalyst surface, allowing reactant molecules to come into close contact with proper orientation.
- After reaction, reactant molecules can break free of the weak bonds, diffuse away (desorption)
- Catalytic converter
- Inhibitor is a substance which decreases the rate of a chemical reaction
- Autocatalysis
 - Catalytic action whereby product of reaction acts as catalyst for the reaction
 - Initially slow since no catalyst
 - As catalyst ions produced, rate of reaction increases as catalyst ions act as autocatalyst
 - Towards end of reaction, concentration of reactants has fallen to a low level so rate of reaction decreases even though there is adequate supply of catalyst
- Enzymes are globular proteins with active sites contained in a 3-dimensional structure (Heterogeneous catalysts)
 - Specific to a particular reaction or type of reaction due to 3D confirmation of active site. Operate most effectively at body temperature $37^{\circ}C$
 - Low substrate, not all active sites occupied, reaction first order with respect to substrate
 - High substrate, all active sites occupied, reaction zero order with respect to the substrate

8 Equilibrium

- A reversible reactions are reactions that proceed in both the forward and backward directions.
- Dynamic equilibrium refers to a state in a reversible system in which the rates of the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties of the reactants and products.
- Equilibrium constant at a given temperature, $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
- Equilibrium constant of a gaseous system, $K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$
- K_c and K_p expressions of heterogeneous equilibrium exclude concentration of pure solids and pure liquids because they are constant and the concentration of water when present in large amounts
- Degree of dissociation, $\alpha = \frac{\text{amount dissociated}}{\text{total initial amount}}$

8.1 Le Chatelier's principle

- LCP states that when a system at equilibrium is subjected to a change, the system will react to counteract the change imposed so as to re-establish the equilibrium.
- When extra A is added at constant V, [A] increases. By LCP, equilibrium position will shift right to partially offset the increase in [A] by removing A until a new equilibrium is reached.
- When total pressure of the equilibrium mixture is increased, by LCP, the system will try to counteract the increase in total pressure by favouring the reaction that decreases the total pressure. Hence, the forward reaction is favoured as it produces fewer gas particles. The position of equilibrium shifts to the right.
- Since the number of gaseous particles on both sides of the system is equal, the change in total pressure does not favour the forward or the backward reaction. Position of equilibrium shifts neither to the left nor the right, system remains at equilibrium with no change to the composition of equilibrium mixture.
- Increase in volume leads to decrease in pressure. Partial pressures of all gases decrease, since $p \propto \text{conc}$, conc decreases and rate of both forward and backward reactions decrease. Reaction takes longer time to reach equilibrium.
- By LCP, the system will try to counteract the increase in temperature by favouring the forward endothermic reaction in order to absorb (or release) heat. Equilibrium position shifts right favouring formation of more products.
- When temperature increased, rate constants k of both forward and backwards reactions increase. The number of particles with energy greater than or equal to activation energy E_a increases. Hence rates of forward and backward reactions both increase and dynamic equilibrium reached more quickly, t_{eqm} decreases.
- Catalyst: A catalyst lowers the activation energy of both the forward and backward reactions to the same extent. As such, adding a catalyst **has no effect on the equilibrium constant**, K , and the composition of an equilibrium mixture. Since both forward and backward rates increase, equilibrium is reached more quickly.

8.2 Haber Process

- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H^\circ(298\text{K}) = -92\text{kJmol}^{-1}$
- Maximum amount of product in the shortest time and minimum cost.

- Temperature 450°C
- Pressure 200atm
- Continual removal of ammonia, shifts position of equilibrium to the right
- Catalyst: finely divided iron catalyst with Al_2O_3 as promoter
- Molar ratio of $\text{N}_2 : \text{H}_2 = 1 : 3$, minimising excess reactants

9 Solubility Equilibrium

- The **solubility** of a solute in a solvent is the maximum amount of solute that can dissolve in a given amount of solvent at a particular temperature.
- The **solubility product K_{sp}** , for the sparingly soluble salt M_aX_b is the equilibrium constant for the equilibrium established between the undissolved salt and its constituent ions in a saturated solution. It varies only with temperature.
- Sparingly soluble salt containing conjugate base of weak acid, solubility of salt in aqueous solution increased when a strong acid is added.

9.1 Common Ion Effect

- Reduced solubility of a salt in a solution that already contains an ion common to the salt.
- $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- Added NaCl(s) dissolves in solution and dissociates momentarily, resulting in $[\text{Cl}^-]$ in solution increasing momentarily
- Causes equilibrium position of reaction to shift left in accordance with Le Chatelier's principle to counteract the increase in $[\text{Cl}^-]$.
- Solubility of AgCl decreases.

9.2 Complex Ion formation

- **Complex ion** contains a central metal ion linked to 1 or more surrounding ions or molecules called ligands by dative covalent bonds.
- $\text{NH}_3(\text{aq})$ is weak base which undergoes hydrolysis to produce OH^- ions.
- $\text{NH}_3(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
- When $\text{NH}_3(\text{aq})$ is added, $[\text{OH}^-]$ in solution increased, making ionic product of Cu(OH)_2 solution exceed K_{sp} of Cu(OH)_2 . Blue precipitate of Cu(OH)_2 is formed and equilibrium established:
- $\text{Cu(OH)}_2(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \dots (1)$
- Excess $\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Cu(NH}_3)_4]^{2+}(\text{aq}) \dots (2)$
- Formation of $[\text{Cu(NH}_3)_4]^{2+}$ decreases concentration of uncomplexed Cu^{2+} ions in the solution. To counteract the decrease in $[\text{Cu}^{2+}]$, the equilibrium position of reaction (1) shifts left, resulting in more Cu(OH)_2 dissolving, hence blue ppt dissolves.
- When sufficient $\text{NH}_3(\text{aq})$ added, ionic product $[\text{Cu}^{2+}][\text{OH}^-]^2$, will be **less than K_{sp}** and hence all the Cu(OH)_2 eventually dissolves to form dark blue solution containing $[\text{Cu(NH}_3)_4]^{2+}$ ions.

10 Acid-Base Equilibria

10.1 Definitions of Acids and Bases

- **Arrhenius theory**: An acid releases H^+ ions in aqueous solution and a base releases OH^- ions in aqueous solution.
- **Lewis acid** is an electron-pair acceptor and base is an electron-pair donor. Reaction involves forming a dative covalent bond between acid and base.
- **Bronsted-Lowry acid** is proton donor and base is a proton acceptor. Reaction involves a transfer of a proton from acid to base.

A strong acid/base undergoes complete dissociation while weak acids and bases only undergo partial dissociation.

10.2 Ionic Product of water

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

- Value of K_w increases with temperature (14 when temperature is $25^\circ C$)
- Self-ionisation of water $H_2O \rightleftharpoons H^+ + OH^-$ is an endothermic process with $\Delta H > 0$ (since products more energy)
- Temperature increases, position of equilibrium shifts right to absorb heat. K_w increases.

10.3 Acid Dissociation Constant (Weak Acid/Base)

K_a is the acid dissociation constant of acid HA, and is the measure of strength of the acid. $K_a = \frac{[H^+][A^-]}{[HA]}$.

- Larger K_a and K_b values denote stronger acids and bases.
- Successive K_a values become smaller because successive dissociations involve acidic species that are increasingly more negatively charged, making **donation of positively charged H^+ ions** increasingly difficult.
- pH of weak acid/base: $[H^+] = \sqrt{K_a[HA]_{initial}}$

10.4 Conjugate Acid-base pair

Conjugate pair: acid and base differ from each other by a H^+ proton, $HA + B \rightleftharpoons A^- + HB^+$

- Stronger acid implies weaker conjugate base as $K_w = K_a K_b = \text{constant}$

10.5 Salt Hydrolysis

- Salt undergoes hydrolysis if anion is conjugate base of weak acid or cation is conjugate base of weak base.
- Conjugate acid of weak base, NH_4^+ undergoes hydrolysis to give H^+ ions.
- Conjugate base of weak acid, CH_3COO^- undergoes hydrolysis to give OH^- ions.

10.6 Buffer solution

Buffer solution is solution that is able to resist pH changes when a small amount of an acid or base is added.

- Acidic buffer consists of weak acid and its conjugate base, alkaline buffer consists of weak base and conjugate acid.
- Weak acid/base used to ensure large reservoir of ions present ensuring nearly all added H^+ or OH^- ions are removed. This keeps pH approximately constant.
- Acidic buffer: $pH = pK_a + \lg\left(\frac{[A^-]}{[HA]}\right)$
- Basic buffer: $pOH = pK_b + \lg\left(\frac{[HB^+]}{[B]}\right)$
- Maximum Buffer capacity occurs when $pH = pK_a$ and $[A^-] = [HA]$.
- Effective buffer range is $pK_a \pm 1$

HCO_3^-/H_2CO_3 buffer in the bloodstream: Able to help convert lactic acid (H^+) into H_2CO_3 which is then converted into H_2O and CO_2 and expelled through heavy breathing

10.7 Acid-Base Titration

- Equivalence point is stage reached when amount of acid needed to react with amount of base is precisely that required by stoichiometric equation.
- Completion can be detected by distinct colour change brought about by use of suitable indicator. This is known as the end-point

Indicator	pH Range	Colour
Methyl Orange	3.2-4.4	red-orange-yellow
Screened Methyl Orange	3.2-4.4	violet-grey-green
Thymol blue	8.0-9.6	yellow-green-blue
Thymolphthalein	9.4-10.6	colourless - light blue - blue

- Suitable indicator is one where pH range coincides with region of rapid pH change on pH curve (fall on vertical portion).

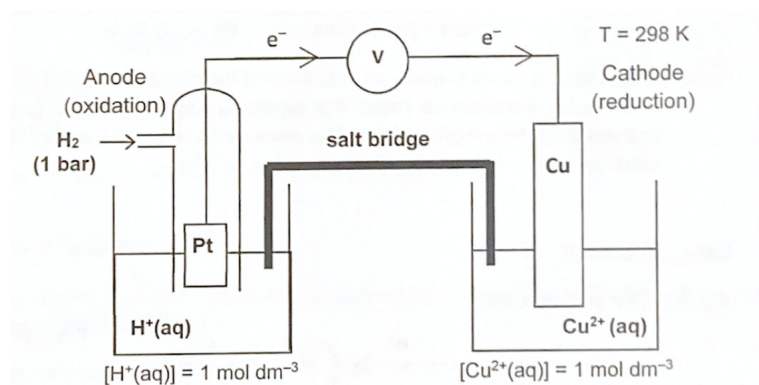
10.8 Enthalpy

Reactions that involves a strong acid are more exothermic as strong acids dissociate completely in aqueous solution and energy is not needed to bring about further dissociation of acid.

11 Electrochemistry

11.1 Electrochemical Cell

- **Standard electrode potential E^\ominus** of a half-cell is the electromotive force, measured at 298K, between the half-cell and the **standard hydrogen electrode**, in which the concentration of any reacting species in the solution is 1mol dm^{-3} and any gaseous species is at a pressure of 1 bar.
- **Standard cell potential E_{cell}^\ominus** is the potential difference between 2 half-cells under standard conditions. It gives a measure of EMF of the cell.



- Standard Hydrogen Electrode consists of platinum electrode coated with finely divided platinum.
- More positive e^\ominus value, forward reaction more favoured, more likely reduction occurs, higher tendency to gain e^- , stronger oxidising agent.
- Measuring Standard Electrode Potential
 - Metal / Metal ion solution (i.e. Cu , $\text{Cu}^{2+}(\text{aq})$)
 - Gas / ion system (i.e. $\text{F}_2(\text{g})$, $\text{F}^-(\text{aq})$)
 - Ion / Ion system (i.e. MNO_4^- , $\text{Mn}^{2+}(\text{aq})$)
 - * Need H^+ present in solution for reduction half-equation
 - Metal Cathode/anode becomes Platinum if not used in redox reaction.
 - Draw from lower redox potential (anode) to higher redox potential (cathode).
- More reactive metal: Reactivity increases and E^\ominus becomes more negative.
- Daniell Cell
 - **Anode is metal that had higher tendency to lose electrons (half cell more negative). Anode is negatively charged and ions undergo oxidation.**
 - Cathode is positive electrode as **electrons consumed** in reduction reaction. Anode is negatively charged as **electrons discharged** through oxidation process.
 - Half equations and overall equation written with \longrightarrow sign not \rightleftharpoons .
- Salt Bridge
 - To maintain **electrical neutrality** of each half cell: Zn^{2+} cell builds up positive charge as Zn^{2+} continue to be produced. Cu^{2+} deposits as metal atoms on copper electrode, solution depletes in positive charge.
 - Ions in salt bridge migrate to **neutralise the increasing charge in two-half cells**. Cations migrate to the cathode and anions migrate to the anode.
- Changing conditions

- Change in concentration, shifts equilibrium to right or left. Rightward shift in equilibrium results in $E_{cell} > E_{cell}^{\ominus}$.
- For example, $2\text{Fe}^{3+}(\text{aq}) + \text{Cu}(\text{s}) \rightleftharpoons 2\text{Fe}^{2+}(\text{aq}) + \text{Cu}^{2+}(\text{aq})$. Adding water to $\text{Cu}^{2+} / \text{Cu}$ half cell, decrease in concentration of Cu^{2+} . Equilibrium shifts right and $E_{cell} > E_{cell}^{\ominus}$.
- Ion has greater tendency to be oxidised/reduced, resulting in an E value more/less positive than E^{\ominus} .
- $E_{cell}^{\ominus} = E_{cathode}^{\ominus} - E_{anode}^{\ominus}$. Reaction is thermodynamically feasible and spontaneous if $E_{cell}^{\ominus} > 0$.
- $\Delta G^{\ominus} = -nFE^{\ominus}$. where F is the Faraday constant and n is **number of moles of electrons transferred in the redox equation**. Spontaneous if $E^{\ominus} > 0$ and $\Delta G^{\ominus} < 0$.
- Limitations of Spontaneity Predictions
 - Kinetic factor: No reaction may take place as activation energy for the reaction is high, hence kinetically not feasible.
 - Non-standard conditions: Varying conditions such as concentration, reaction may be made to proceed.
 - Side reactions may occur
 - * $\text{I}_2(\text{aq}) + 2\text{e}^{-}(\text{aq}) \rightleftharpoons 2\text{I}^{-}(\text{aq})$
 - * $\text{Cu}^{2+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Cu}^{+}(\text{aq})$
 - * But cream precipitate of $\text{CuI}(\text{s})$ is observed. Could make reaction become spontaneous as $[\text{Cu}^{+}(\text{aq})]$ becomes very low
- Fuel Cell
 - At anode: Fuel is oxidised (i.e H_2, CH_4) and electrons released to external circuit
 - At cathode: oxygen reduced by electrons received from external circuit. $\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \longrightarrow 2\text{H}_2\text{O}$ or $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \longrightarrow 4\text{OH}^{-}$
 - Advantages
 - * Minimum weight and volume
 - * High efficiency of conversion
 - * Reactants are supplied continuously and products continually removed. Spent electrolyte can be replaced by fresh electrolyte so battery does not run out of power.
 - * Non-polluting, water produced can be used for drinking and washing.
 - Disadvantages
 - * Expensive due to Pt catalyst
 - * Most fuels require high temperature to react
 - * Hydrogen potentially explosive
 - Overcharging
 - * Electrolysis of water takes place, H_2 gas and O_2 gas released.

11.2 Electrolysis

- **Electrolysis** is the process of passing electricity (from an external source) to force a non-spontaneous redox reaction to occur.
- Oxidation still occurs at anode and Reduction still occurs at cathode.
- External cell supplies e^- into cathode, resulting in negatively charged cathode and positive anode. As external cell directs electrons from anode to cathode, negative terminal connected to cathode and positive to anode. Opposite of electrochemical cell.
- Factors affecting discharge of ions
 - Physical State of Electrolyte: molten electrolyte $NaCl(l)$ only has Na^+ and Cl^- and no solvent. Aqueous electrolyte has to compare with half reaction of reaction of water.
 - A more positive E^\ominus implies a higher tendency for reduction to occur and conversely, a more negative E^\ominus implies a higher tendency for oxidation to occur. Species has greater tendency to be reduced/oxidised and thus is preferentially discharged.
 - If concentrations are non-standard, then consider effect on position of equilibrium and hence value of E . E^\ominus must be sufficiently close so the change in concentration affects E value sufficiently.
 - Reactive electrodes must be considered in addition to species present in the electrolyte (for example Cu electrode).
- Polyatomic ions such as SO_4^{2-} , PO_4^{3-} , NO_3^- will not usually be discharged during electrolysis.
- **Faraday's First Law** states that the mass of substance/volume of gas liberated during electrolysis is directly proportional to the amount of charge passed through the cell. $m \propto Q = It$.
 - 1 Faraday is the charge carried by 1 mole of reaction. $F = Le$, hence $1F = 96500Cmol^{-1}$, where L is Avogadro's Constant and e is charge on one electron.
 - Amount of electrons, $n_e = \frac{Q}{F}mol$, hence $Q = It = n_eF$.
- Anodising of Aluminium
 - Aluminium is not oxidised during electrolysis and is highly corrosion resistant.
 - Aluminium when exposed to oxygen in the air acquires a protective layer of aluminium oxide which protects the underlying metal from water and any further chemical attack.
 - H_2O is preferentially oxidised, $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$. Oxygen reacts with aluminum $4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$
 - Anodising of aluminium is of substantial commercial value as aluminium is widely used especially where lightness and corrosion resistance are important. It is hard, resistant to wear and good electrical insulator.
- Electrolytic Purification of Copper
 - Anode has impure copper and cathode is pure copper.
 - Cell potential adjusted such that Cu at anode dissolves. Anode dissolves and copper is deposited on the cathode.
 - Impurities with E^\ominus values less positive: preferentially oxidise and goes into solution as Zn^{2+} ions. Cu^{2+} is preferentially reduced at cathode, Cu deposited on pure Cu rod. Zn^{2+} ions remain in electrolyte and are not plated onto Cu .
 - Impurities with E^\ominus values more positive: Cu preferentially oxidised and fall to bottom as sludge.
- Graphite Anode may be oxidised by $O_2(g)$ to form $CO_2(g)$.

12 Periodic Table (I)

12.1 Physical Properties

Melting point: increases from Na to Si, then in order Cl_2 , P_4 , S_8 .

- Na to Al, strong metallic bonds between positive metal ions and sea of delocalised electrons. Increasing cationic charge and decreasing cationic size, increasing **cationic charge density**.
- Si giant molecular structure with strong covalent bonds between Si atoms
- $\text{Cl}_2 < \text{P}_4 < \text{S}_8$ due to strength of id-id bonding

Electrical Conductivity

- Increasing, high from Na to Al due to delocalised electrons which act as mobile charge carriers.
- Si is a metalloid, poor electrical conductivity
- P to Cl simple molecular structures, non-conductors of electricity due to absence of mobile charge carriers.

Melting Point (of oxides and chlorides)

- Increases from Na_2O to MgO then decreases.
- Did not increase for Al_2O_3 and MgCl_2 because of difference in packing in solid state and slight covalent character of Al_2O_3 due to high charge density and high polarising power of Al^{3+}
- AlCl_3 forms crystalline lattice of Al_2Cl_6 in solid phase and exists as dimers of Al_2Cl_6 . Hence higher boiling point than SiCl_4 due to stronger id-id interactions. Dissociates to give monomers at high temperatures.

12.2 Hydrolysis of Metal Chlorides

Mg and Al

- Cations with **high charge density** and hence **high polarising power** able to distort the electron cloud of water molecules, weakening the O–H bond. O–H bond undergoes **heterolytic fission** to release H^+ .

SiCl_4 and CCl_4

- Si has **empty, low-lying 3d orbitals to accept lone pair of electrons from water** as valence shell has **principal quantum number of 3**.
- Silicon atom larger in size than carbon atom, less steric hindrance around Si atom for H_2O nucleophile to attack. For carbon atom, 4 relatively large Cl atoms hinder approach of H_2O nucleophile.

13 Periodic Table (II)

13.1 Group 2

- Physical Properties (explain with electronic shells)
 - Atomic and Ionic radius increases down group 2
 - First ionisation energy decreases
 - Electronegativity decreases
 - No clear trend of melting points
- Reactivity increases down group
 - Sum of first and second ionisation energies decrease down a group, greater ease of losing 2 valence electrons.
 - Down group, E^\ominus becomes more negative. Tendency of backwards reaction occurring increases and tendency of metal losing electrons increases. More spontaneous reaction.
 - Reducing power of metal and hence reactivity of metal increases.
- Thermal Stability (Ease of Thermal Decomposition)
 - $\text{MCO}_3 \longrightarrow \text{CO}_2(\text{g}) + \text{MO}(\text{s})$
 - Feasibility
 - * $\Delta H > 0$ and $\Delta S > 0$ (as CO_2 gas produce in the reaction)
 - * At high T, negative $-T\Delta S$ outweighs positive ΔH , resulting in $\Delta G < 0$. Reaction is entropy driven.
 - Thermal Stability increases down group.
 - Down group, ionic radius increases, resulting in smaller charge density and lesser polarising power.
 - Decreasing extent of distortion of electron cloud of anion, decreasing extent of weakening of covalent bonds within anion.
 - More heat energy required to break covalent bonds and causing decomposition temperature to increase.

13.2 Group 17

- Physical Properties
 - Atomic radius increases, first ionisation energy decreases, electronegativity decreases.
 - Bond Dissociation energy decreases (orbital overlap as valence orbitals more diffuse)
 - * F–F bond not as strong as expected. Small atomic size of fluorine atom, great repulsion between lone pairs of electrons on 2 fluorine atoms.
 - Volatility decreases (due to stronger id-id forces and more easily polarisable electron cloud).
- Oxidising power
 - Decreases down group.
 - E^\ominus value become less positive, tendency of forward reaction and halogen gaining electrons decreases. Thus oxidising power of halogen decreases and reactivity decreases.
 - More reactive halogen displaces less reactive halogen from compound. In other words, halide ion can be oxidised by halogens above it in group.
 - * Test by addition organic aqueous layer like hexane or CCl_4 for formation of colours.
 - Thiosulfate $\text{S}_2\text{O}_3^{2-}$

- * Chlorine and Bromine oxidise from $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-} , average oxidation state increases from +2 to +6.
- * Iodine can only oxidise to $\text{S}_4\text{O}_6^{2-}$, average oxidation state increases from +2 to +2.5.
- Reactions with Iron
 - * Cl_2 and Br_2 can oxidise Fe to Fe^{3+} while I_2 can only oxidise to Fe^{2+}
- Thermal Stability of HX
 - $2\text{HX}(\text{g}) \longrightarrow \text{H}_2(\text{g}) + \text{X}_2(\text{g})$
 - Thermal Stability decreases down group
 - Down group, halogen gets bigger and valence orbital used for bonding more diffuse. Less effective orbital overlap between 1s orbital of hydrogen and valence p orbital of halogen.
 - Electronegativity difference between hydrogen and halogen decrease, resulting in decreased bond polarity.
 - HX bond strength decreases down group, hence bond dissociation energy decreases down group.
 - More endothermic bond dissociation energy, H–X bond stronger and more thermally stable. Thermal stability decreases down group.
- Solubility of I_2 in KI
 - $\text{I}_2(\text{s}) \rightleftharpoons \text{I}_2(\text{aq})$
 - $\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$
 - Addition of I^- , formation of soluble brown triiodide complex ion causes $[\text{I}_2(\text{aq})]$ to decrease. LCP, equilibrium 1 shift to right, iodine more soluble.

14 Periodic Table (III)

14.1 Orbitals

- Atoms: Generally occupy 4s subshell before 3d subshell, except for $_{24}\text{Cr}$ and $_{29}\text{Cu}$, which have $3d^5 4s^1$ and $3d^{10} 4s^1$ respectively.
- Ions: 4s electrons are at a higher energy level than 3d electrons are removed first.
- Transition element is a d-block element which can form one or more stable ions with a partially filled d subshell.
 - Scandium and Zinc are not transition elements as they can only form Sc^{3+} and Zn^{2+}