5.1.1 How fast?

Definitions

Term	Definition
Order	The power to which the concentration of a reactant is raised in the rate equation
Overall order	The sum of the individual orders of reactants in the rate equation
Rate constant k	The constant that links the rate of reaction with the concentrations of the reactants raised to the powers of their orders in the rate equation
Initial rate of reaction	The change in the concentration of a reactant or product per unit time at the start of the reaction ($t = 0$)
Rate-determining step (RDS)	The slowest step in the reaction mechanism of a multi-step reaction
Molecularity	The number of molecules in the slow rate determining step

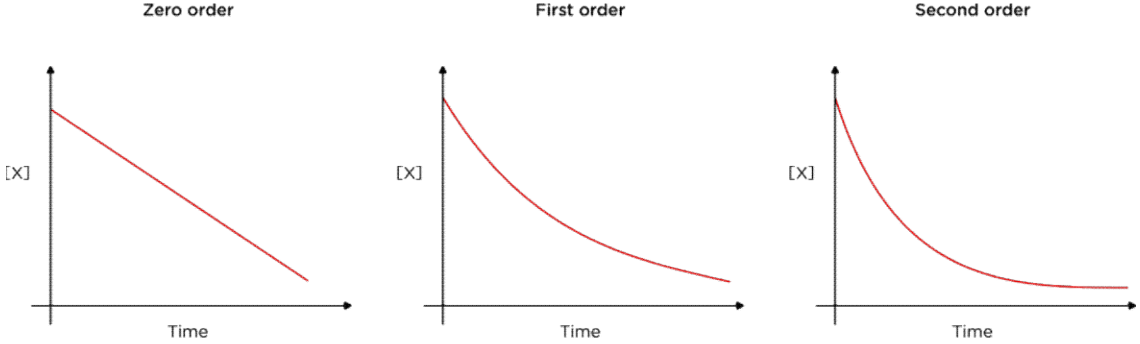
Orders, rate equations and rate constants

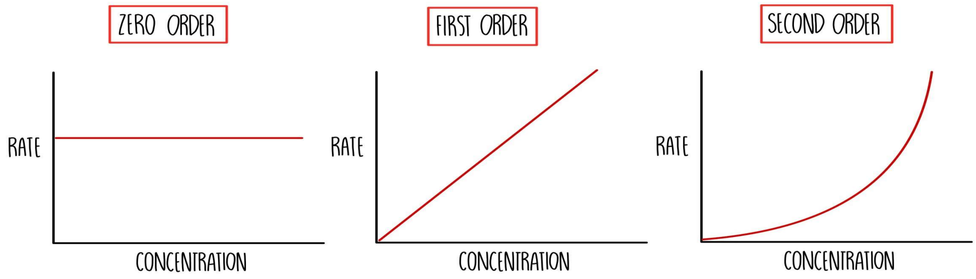
- Rate of reaction
    - $\text{rate} = \frac{\text{change in concentration}}{\text{time}}$
    - Unit = mol dm^{-3} s^{-1}
- Order of reaction
    - $\text{rate} \propto [\text{A}]^n$
    - n = order of reaction
    - Zero order: $n = 0$
    - First order: $n = 1$
    - Second order: $n = 2$
- Rate equation
    - $\text{rate} = k[\text{A}]^m[\text{B}]^n$
    - $\text{overall order} = m + n$
    - $k = \text{rate constant}$
    - Unit of k = $mol^{(1\text{-overall order})}$ $dm^{3\times(\text{overall order}-1)}$ s^{-1}
- Answer template for determining the orders of reaction
    - One change only
        - Using experiments x and y:
        - [A] changes from m to n: doubled / tripled / etc.
        - [B] constant
        - Rate doubled / quadrupled / etc.
        - Hence the order wrt A is … order
    - Multiple changes - choose 2 experiments where all the concentrations are multiplied by the same amount
        - Using experiments x and y:
        - [A] changes from w to x: multiplied by m
        - [B] changes from y to z: multiplied by m
        - Rate multiplied by n
        - $n = m^k$ hence the overall order is k
        - The order wrt B is $k - order\ of\ A$
- Monitoring concentration

Scenario	Method
Coloured compounds present	Colorimeter
Acidic / alkaline compound	Monitor pH

present	Use pH meter / titration to determine pH if reaction is slow
Gas produced	Measure volume of gas produced / mass loss if gas escapes
Aqueous reactions	Measure conductivity

Rate graphs and orders

- Concentration-time graph shape
  - Zero order
    - Rate does not change with concentration
    - Straight line with **negative gradient**
  - First order
    - Downward curve with decreasing gradient over time
    - **Constant half-life ($t_{1/2}$)**
    - $k = \frac{\ln 2}{t_{1/2}}$ (k can also be worked out by finding the gradient of the rate-concentration graph)
  - Second order
    - Rate is directly proportional to the square of concentration
    - Downward curve steeper at start + tailing off more slowly
  - 

- Rate-concentration graph shape
  - Zero order
    - Horizontal straight line
    - Rate = y-intercept = k
  - First order
    - Straight-line **through origin**
    - Gradient = k
  - Second order
    - Upward curve with increasing gradient
  - 

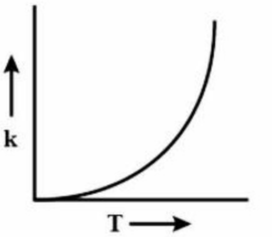
- Measuring initial rate with clock reaction
  - Several experiments with different concentrations of one reactant, all other reactant concentrations are kept constant
  - Time (t) measured from the start of reaction to when a visual change is observed (colour change / precipitate)
  - Initial rate is directly proportional to $\frac{1}{t}$
  - Iodine clocks
    - Measure time taken for iodine colour (orange-brown) to appear

  - Colour change is delayed by adding a small amount another chemical that removes iodine as it forms
  - Starch can be added to form a blue-black colour
- Plot a graph of $\frac{1}{t}$ against concentration
  - Deduce order of reaction from shape of graph (same as rate-concentration graphs)
- Shorter time = higher accuracy

Rate-determining step

- Predicting the rate-determining step (slowest step)
  - Reactants only include the species involved in the rate equation
  - Stoichiometry in the rate equation should match the stoichiometry in the overall reaction

Effect of temperature on rate constants

- Effect of temperature on rate constants
  - Increase temperature = increase k
  - Higher temperature shifts the Boltzmann distribution to the right → higher proportion of particles has a higher energy than E_a
  - Particles move faster + collide more frequently
  - 

- Arrhenius Equation
  - $k = Ae^{-\frac{E_a}{RT}}$
  - $A =$ pre-exponetial factor / frequency factor
  - $R =$ ideal gas constant (8.314 J mol^{-1} K^{-1})
  - $T =$ temperature (K)
- Logarithmic graphs
  - $\ln k = -\frac{E_a}{RT} + \ln A$
  - Graph can be plotted with $\frac{1}{T}$ on x-axis and $\ln k$ on y-axis
  - Gradient = $-\frac{E_a}{R}$
  - y-intercept = $\ln A$

5.1.2 How far?

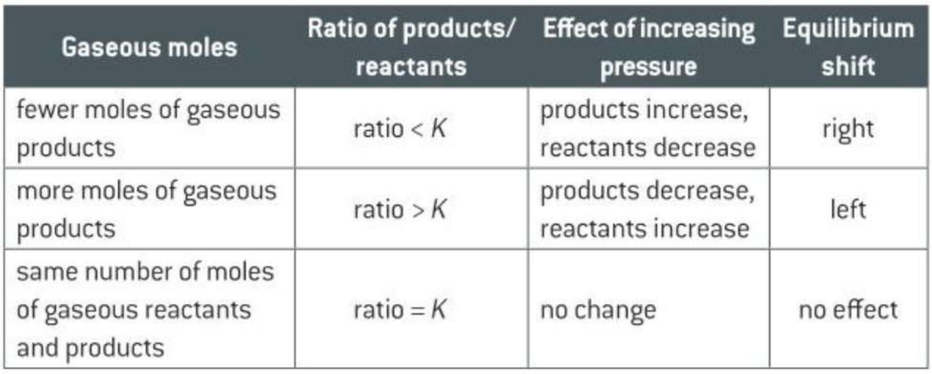
Equilibrium

- Types of equilibria
  - Homogenous equilibria
    - Contains equilibrium species that all have the same state or phase
    - K_c contains concentrations of all species
  - Heterogenous equilibria
    - Contains equilibrium species that all have different states or phases
    - K_c only contains concentrations of gaseous or aqueous species (concentration of solid and liquid is constant)

Equilibrium constant K_p

- Mole fraction
  - $\text{mole fraction } x(\text{A}) = \dfrac{\text{number of moles of A}}{\text{total number of moles in gas mixture}}$
  - (for gases mole fraction can also be calculated by volume of gas divided by total volume)
  - Sum of mole fractions = 1
- Partial pressure
  - The contribution that a gas makes to the total pressure P
  - $\text{partial pressure } p(\text{A}) = x(\text{A}) \times P$
  - Sum of partial pressures = total pressure

Changes that affect equilibrium

- Effect of temperature change
  - When the forward reaction is exothermic
    - K_c or K_p decreases as the temperature goes up
    - K_c or K_p increases as the temperature goes down
  - When the forward reaction is endothermic
    - K_c or K_p increases as the temperature goes up
    - K_c or K_p decreases as the temperature goes down
- Effect of concentration / pressure change
  - The value of K **stays constant**
  - e.g. concentration of one of the reactants increase
    - The ratio is now less than K
    - The system is no longer in equilibrium
    - Concentration of products increase + Concentration of reactants decrease
  - Total pressure changes
    - Partial pressure + ratio change
    - 

Gaseous moles	Ratio of products/ reactants	Effect of increasing pressure	Equilibrium shift
fewer moles of gaseous products	ratio < K	products increase, reactants decrease	right
more moles of gaseous products	ratio > K	products decrease, reactants increase	left
same number of moles of gaseous reactants and products	ratio = K	no change	no effect

- Effect of catalysts on K
  - Equilibrium reached quicker
  - **No change** in value of K or equilibrium position

5.1.3 Acids, bases and buffers

Definitions

Term	Definition
Monobasic acid	1 hydrogen ion can be replaced per molecule in acid-base reaction
Dibasic acid	2 hydrogen ions can be replaced per molecule in acid-base
Tribasic acid	3 hydrogen ions can be replaced per molecule in acid-base reaction
End point	Where the indicator changes colour

Brønsted–Lowry acids and bases

- Brønsted-Lowry acids and bases
  - Brønsted-Lowry acid = **a proton donor**
  - Brønsted-Lowry base = **a proton acceptor**
- Conjugate acid-base pairs
  - Two species that can be interconverted by transfer of **a proton (cannot be more than 1 protons)**
  - Conjugate acid (aq) ⇌ H^+(aq) + Conjugate base (aq)

pH and [H^+(aq)]

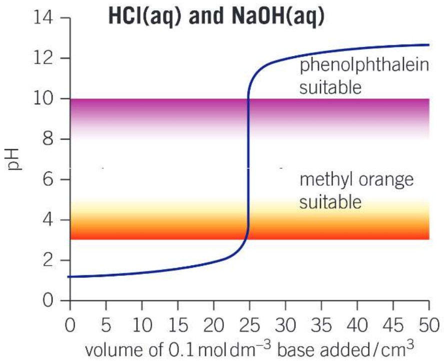
- pH formula
  - $\mathrm{pH} = -\log[\mathrm{H}^+]$
  - $[\mathrm{H}^+] = 10^{-\mathrm{pH}}$
- Acid dissociation constant K_a
  - For reaction HA(aq) ⇌ H^+(aq) + A^-(aq)
    - $K_\mathrm{a} = \dfrac{[\mathrm{H}^+(\mathrm{aq})][\mathrm{A}^-(\mathrm{aq})]}{[\mathrm{HA}(\mathrm{aq})]}$
  - Unit = mol dm^{-3}
  - Changes with temperature, recorded values normally standardised at 25°C
- pK_a values
  - $\mathrm{p}K_a = -\log K_a$
  - $K_a = 10^{-\mathrm{p}K_a}$
  - Used when K_a is small
  - Stronger acid = higher K_a + lower pK_a
- pH calculations
  - pH for strong monobasic acid
    - Assume $[\mathrm{H}^+(\mathrm{aq})] = [\mathrm{HA}(\mathrm{aq})]$ (= acid concentration)
  - pH for weak monobasic acid
    - $K_a = \dfrac{[\mathrm{H}^+(\mathrm{aq})]^2}{[\mathrm{HA}(\mathrm{aq})]}$
    - Precise formula: $K_\mathrm{a} = \frac{[\mathrm{H}^+(\mathrm{aq})]_\mathrm{eqm}[\mathrm{A}^-(\mathrm{aq})]_\mathrm{eqm}}{[\mathrm{HA}(\mathrm{aq})]_\mathrm{start}-[\mathrm{H}^+(\mathrm{aq})]_\mathrm{eqm}}$
    - Equal concentration of H^+ and A^-: $[\mathrm{H}^+(\mathrm{aq})]_\mathrm{eqm} = [\mathrm{A}^-(\mathrm{aq})]_\mathrm{eqm}$
      - Not valid for very weak acids / very dilute solutions
    - $[\mathrm{H}^+(\mathrm{aq})]_\mathrm{eqm}$ is negligible: $[\mathrm{HA}(\mathrm{aq})]_\mathrm{eqm} = [\mathrm{HA}(\mathrm{aq})]_\mathrm{start}$
      - Not valid for stronger weak acids with $K_a > 10^{-2}$ mol dm^{-3} / very dilute solutions
- Ionic product of water K_w
  - How water ionises: H_2O(l) ⇌ H^+(aq) + OH^-(aq)
  - $K_w = [\mathrm{H}^+(\mathrm{aq})][\mathrm{OH}^-(\mathrm{aq})]$
  - K_w at 298K = 1.00×10^{-14} mol^2 dm^{-6} (varies with temperature, can assume it is this value)

Buffers: action, uses and calculations

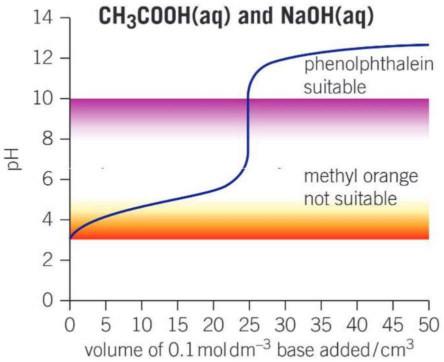
- Buffer solution
  - A system that minimises pH changes on addition of **small amounts** of acid or alkali
  - Contains a weak acid + its conjugate base in a salt
- Preparing buffer solutions
  - Mixing weak acid + one of its salts
    - e.g. CH_3COOH + CH_3COONa
    - Weak acid partially dissociates when added to water → provide the weak acid component
    - Salts of weak acids = ionic compounds → completely dissolve + dissociate into ions in water → provide the conjugate base
  - Adding a strong alkali to an excess of a weak acid
    - e.g. excess CH_3COOH + NaOH
    - Weak acid partially neutralised by the alkali → conjugate base formed
    - Some weak acid left unreacted
    - A mixture of salt of weak acid + unreacted weak acid
- How buffer solutions work
  - Equilibrium established e.g. $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
  - Acid / $H^+(aq)$ added
    - $[H^+(aq)]$ increases
    - $H^+(aq)$ ions react with the conjugate base
    - Equilibrium position shifts to the left
    - Most of the $H^+(aq)$ ions added is used up so pH change is minimised
  - Alkali / $OH^-(aq)$ added
    - $[OH^-(aq)]$ increases
    - $OH^-(aq)$ reacts with H^+ to form water so H^+ is used up
    - The equilibrium moves to RHS to replace most of the H^+ used up and minimise the pH change
    - HA dissociates → shifts the equilibrium to the right → restore most of the $H^+(aq)$ ions
    - Overall reaction: $HA(aq) + OH^-(aq) \rightarrow H_2O(l) + A^-(aq)$
- Calculating pH of a buffer solution
  - Acid + alkali: calculate how much A^- is in the solution and how much HA is left
  - Acid + salt: assume all A^- from salt
  - Assume [HA] stays constant in both cases
  - $[\mathrm{H^+(aq)}] = K_\mathrm{a} \times \dfrac{[\mathrm{HA(aq)}]}{[\mathrm{A^-(aq)}]}$
  - Quick formula: $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{salt}]}{[\mathrm{acid}]}$
- Control of blood pH
  - Blood plasma needs to have a pH between 7.35 to 7.45
  - pH below 7.35→ acidosis (fatigue, shortness breath, shock, death)
  - pH above 7.45→ alkalosis (muscle spasms, light headedness, nausea)
  - pH maintained by carbonic acid(H_2CO_3)-hydrogencarbonate(HCO_3^-) buffer system: $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

Neutralisation

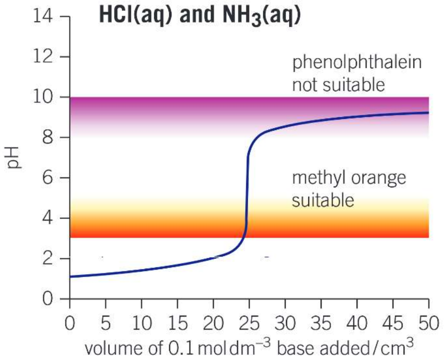
- pH titration curve
  - Weak base - steeper gradient for basic section
  - Weak acid - steeper gradient for acidic section



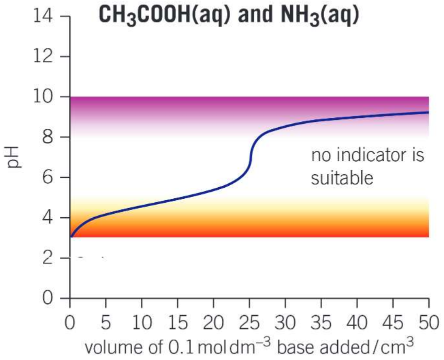
▲ **Figure 7** *Strong acid–strong base titration*



▲ **Figure 8** *Weak acid–strong base titration*



▲ **Figure 9** *Strong acid–weak base titration*

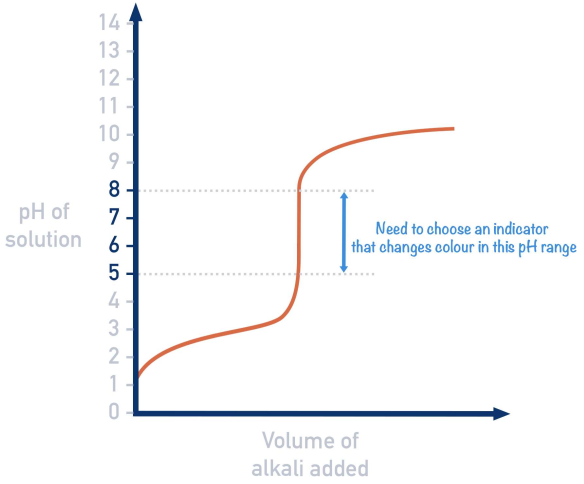


▲ **Figure 10** *Weak acid–weak base titration*

  - (Acid to base: mirror the shapes)
- Equivalence point
  - Halfway up the vertical section
  - Where the amount of acid exactly neutralises the amount of alkali
- Indicator colour change explanation
  - Indicator = **weak acid** with distinctively different colour to conjugate base
  - $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
  - Equilibrium position shifts toward LHS in acidic conditions
  - Equilibrium position shifts toward RHS in basic conditions
- Common indicators

Indicator	**pH at colour change**	**Colour in acid**	**Colour in base**
Methyl orange	3-5	**Red**	**Yellow**
Phenolphthalein	8-10	**Colourless**	**Pink**
Litmus	5-8	**Red**	**Blue**

  - (Most indicators change colour over a range of 2 pH units)
- Choice of suitable indicators for titration
  - Choose indicator with a colour change range that coincides with the vertical section of the pH titration curve
  - Ideally same end point and equivalence point
  - End point not in vertical section: range of volumes for colour change is too big



- No indicator suitable for weak acid-weak base titrations as there is no vertical section + even at steepest requires several cm^3 to pass through a range of 2 pH units

5.2.1 Lattice enthalpy

Definitions

Term	Definition
Lattice enthalpy ($\Delta_{LE}H$)	The enthalpy change when one mole of a solid ionic crystal lattice is formed from its constituent gaseous ions (A measure of the strength of ionic bonding in a giant ionic lattice)
(First) Electron affinity ($\Delta_{EA}H$)	The enthalpy change that takes place when one mole of gaseous atoms gains one mole of electrons to form one mole of gaseous 1- ions
Atomisation energy	The enthalpy change required to form 1 mole of gaseous atoms from the element in its standard state
Dissociation energy	The energy required to break one mole of a bond in the gas state
Enthalpy change of solution (dissolution) ($\Delta_{sol}H$)	The enthalpy change when one mole of an ionic solid dissolves in a solvent (to form aqueous ions)
Enthalpy change of hydration	The enthalpy change that accompanies the dissolving of one mole of gaseous ions in water to form one mole of aqueous ions

Born–Haber and related enthalpy cycles

- Born-Haber cycle calculation

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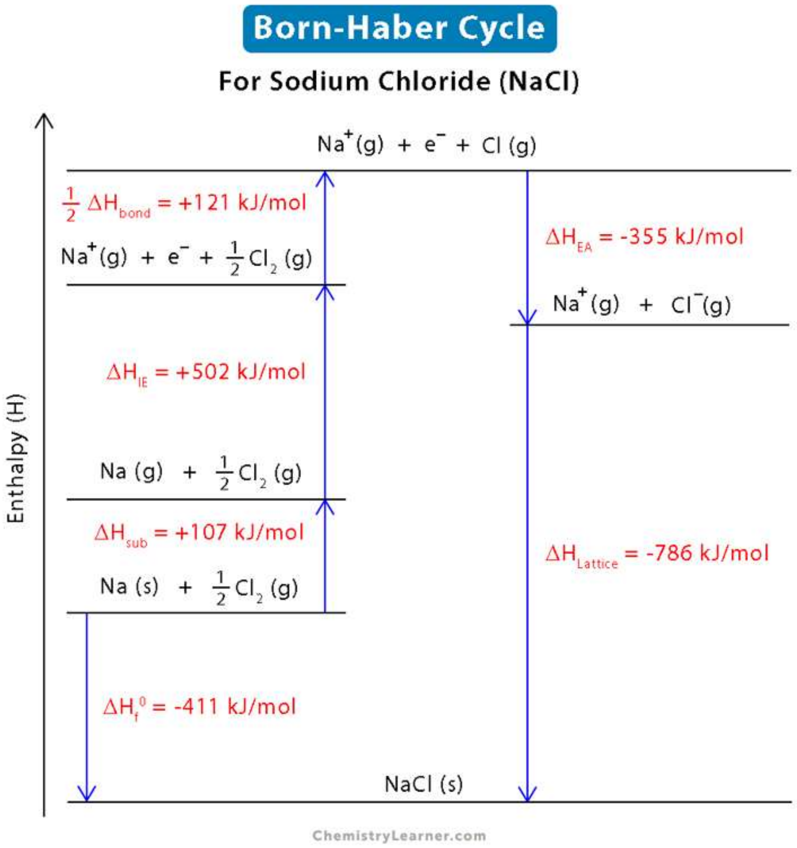
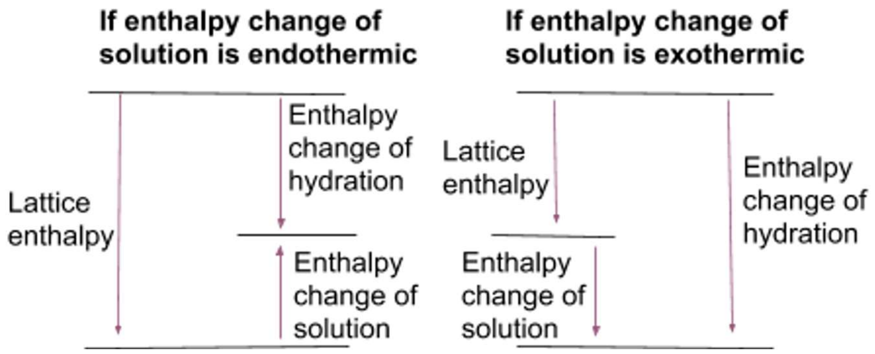


- 

- Lattice enthalpy = enthalpy change of formation - (enthalpy change of atomisation + ionisation energy + electron affinity)

- Exothermic / endothmic energy changes

Always exothermic	Always endothermic	Varies
• First electron affinity • Lattice enthalpy • Enthalpy change of hydration	• Atomisation energies • Dissociation energies • All other electron affinity • Ionisation energies	• Enthalpy change of solution

Factors affecting enthalpy changes

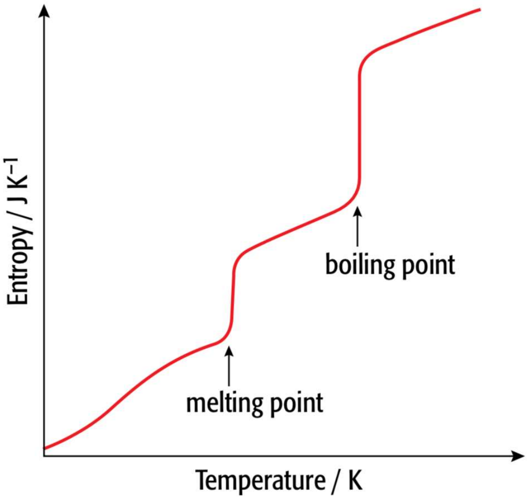
- Factors affecting lattice enthalpy
  - Ionic size
    - Ionic radius increases → charge density decreases → attraction between ions decreases
    - **Less exothermic** lattice enthalpy
    - Lower melting point
  - Ionic charge
    - Increasing charge = attraction between ions increases
    - More exothermic lattice enthalpy
    - Higher melting point
- Factors affecting enthalpy change of hydration
  - Ionic size
    - Ionic radius increases → attraction between ion and water molecules decreases
    - Hydration energy less exothermic
  - Ionic charge
    - Ionic charge increases → attraction with water increases
    - Hydration energy more exothermic
- Predicting solubility
  - To dissolve an ionic compound in water, attraction between ions in lattice must be overcome
    - Energy needed = lattice enthalpy
  - Water molecules are attracted to ions, surrounding them and releasing energy
    - Energy released = hydration enthalpy
  - If sum hydration enthalpies > magnitude lattice enthalpy the overall the reaction is exothermic so the compound should dissolve
  - Solubility also depends on other factors + entropy

5.2.2 Enthalpy and entropy

Definitions

Term	**Definition**
Standard entropy ($S°$)	The entropy of one mole of a substance under standard conditions. Unit J K^{-1} mol^{-1}
Entropy (S)	A measure of the dispersal of energy within the chemicals that make up the chemical system; the greater the entropy, the more disordered a system. Unit J K^{-1} mol^{-1}
Free energy change	The balance between enthalpy entropy and temperature for a process given by $\Delta G = \Delta H - T\Delta S$. A process is feasible when $\Delta G < 0$.
Feasibility of reaction	Whether a reaction is able to happen and is energetically feasible

Entropy

- When does entropy increase
  - Solid → liquid → gas
  - More complex substances with more atoms → simpler substances with fewer atoms
  - Increasing the number of molecules (especially gas)
  - Increasing the temperature (at 0 K there is no energy and all substances have entropy of 0)
  - 

- Calculating entropy changes
  - $\Delta S° = \Sigma S°(\text{products}) - \Sigma S°(\text{reactants})$

Free energy

- Free energy change (ΔG)
  - Overall energy change during a chemical reaction
  - Made up of enthalpy change (ΔH) and entropy change at the temperature of the reaction ($T\Delta S$)
- The Gibbs' equation
  - $\Delta G = \Delta H - T\Delta S$
  - (Convert the unit of ΔS to kJ K^{-1} mol^{-1})
- Gibbs' equation graph
  - Graph of ΔG against T
  - y-intercept = ΔH
  - x-intercept = temperature where feasibility changes
  - Gradient = $-\Delta S$
- Conditions for feasibility

  - There must be a decrease in free energy: $\Delta G < 0$
  - Depends upon enthalpy change (ΔH) and entropy change + temperature ($T\Delta S$)
- Limitations or predictions made for feasibility
  - Many reactions with $\Delta G < 0$ don't take place
  - E_a is too high
  - The rate is too slow
  - Catalysts can be used to overcome the high E_a so the reaction can take place

5.2.3 Redox and electrode potentials

Definitions

Term	**Definition**
Oxidising agent	A reagent that **accepts / takes in** electrons / oxidises another species / is reduced
Reducing agent	A reagent that **donates / gives out** electrons / reduces another species / is oxidised
Standard electrode potential $E°$	The emf of a half-cell compared to a hydrogen electrode under standard conditions
Standard half cell	The pure metal in contact with a **1 molar** solution of its ions at a temperature of **298 K**

Balancing chemical equations

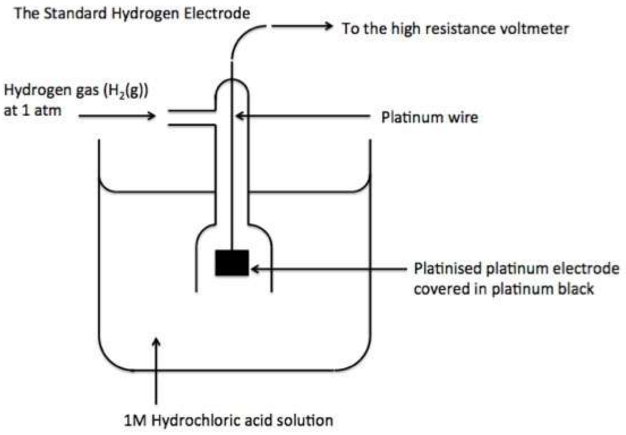
- Balancing equations with missing oxygen
    - Acidic condition
        - Add 1 H_2O on the side with less oxygen for every missing oxygen
        - Add 2 H^+ on the other side for every H_2O added
    - Alkaline condition
        - Add 2 OH^- on the side with less oxygen for every missing oxygen
        - Add 1 H_2O on the other side for every pair of OH^- added
    - Balance changes in oxidation numbers with electrons
- Balancing equations using oxidation numbers
    - Sum of oxidation numbers on LHS = sum of oxidation numbers on RHS
    - Look at the change in oxidation number of each element
    - Multiply chemicals by different amounts so total change = 0

Redox reactions and titrations

- Carrying out Maganate(VII) titrations
    - Manganete reduced from Mn^{7+} to Mn^{2+}
    - $KMnO_4$ is used as the oxidation agent and added to burette
    - The reducing agent is added to the conical flask
    - Excess dilute H_2SO_4 added to provide H^+ for reduction of MnO_4^-
    - Manganate in the burette is deep purple → reacts and become colourless when added to the flask
    - Once all reducing agent has reacted there will be nothing to decolourise the manganate
    - End point = when permanent pink colour appears in flask
    - $KMnO_4$ is self indicating so no indicator needed
- Iodine / thiosulfate redox titrations
    - $Na_2S_2O_3$ (sodium thiosulfate) reduces iodine to iodide ions and forms $Na_2S_4O_6$ (sodium tetrathionate)
        - $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
    - Standard solution of $Na_2S_2O_3$ added to burette
    - An excess of iodide is added to conical flask as iodine is almost insoluble in water but very soluble in iodide solution
    - Solution of oxidising agent being analysed is added to conical flask with excess KI
    - Oxidising agent reacts with iodide ions to produce iodine → turn solution yellow-brown
    - Iodine reduced back to I^- ions → brown colour fades gradually
    - Indicator is starch: added towards the end when most of the iodine has reacted and gives a blue-black colour
    - End point: blue black disappears when iodine is used up and reaction mixture becomes

colourless

Electrode potentials

- Intepreting electrode potential value
  - More positive value: greater tendency to **gain electrons + undergo reduction**
  - More negative value: greater tendency to **lose electrons + undergo oxidation**
- Half cell
  - Contains the species present in a redox half equation (forward reaction shows reduction)
  - Consists of a piece of pure metal in contact with a solution of its ions
  - Electron can be transferred between the metal and its ions
- Factors affecting electrode potential of a half cell
  - The metal used
  - Concentration of the solution of ions
  - Temperature
- Hydrogen half cell
  - Half cell containing $H_2(g)$ and solution of H^+
  - Inert platinum electrode to allow electrons in and out of the half cell
  - Given standard electrode potential value of 0
- Measuring standard electrode potentials
  - Standard conditions must be used
    - Metal ion solutions must have a concentration of 1 mol dm^{-3}
    - Gas half cells must be at 100kPa pressure + use inert electrode
    - Temperature must be 298K
  - Half cell measured connected by wire with a standard hydrogen half cell
  - Two solutions connected with a salt bridge to complete the electrical circuit
    - Typically contains a concentrated solution of an electrolyte that does not react with either solution
  - Connect the half-cells to voltmeter
  - Measured under standard conditions (298K, 100kPa)
  - 

- Predicting feasibility of reactions with standard cell potentials
  - **Strongest oxidising agent = most positive E°** + most likely to be reduced (will be on right of equation if written as standard form)
  - **Strongest reducing agent = most negative E°** + most likely to be oxidised
  - (… system is more negative than … system → … shifts right and … shifts right / … reduces …)
- Limitations of predictions using E° values
  - Reactions can have very high activation energies → very slow reaction rates
  - Actual conditions may not be standard
    - Value of electrode potential will be different from standard value if concentration isn’t 1 mol dm^{-3}
      - Increasing ion concentration: equilibrium shifts right, removes electrons, E° less negative
      - Reducing ion concentration: equilibrium shifts left, increases electrons in system, E° more negative

    - Standard potentials are for aqueous equilibria: many reactions aren’t aqueous
  - There may be an alternative reaction that is more favourable

Storage and fuel cells

- Storage cells
  - 3 main types
  - Primary (non-rechargeable) cells
    - Electrical energy produced by **an irreversible reaction**
    - The reactants will be used up eventually and the reaction becomes too slow to create enough voltage
    - Used for low current, long-storage devices e.g. clocks or smoke detectors
  - Secondary (rechargeable) cells
    - Electrical energy produced by **a reversible reaction**
    - The cell can be recharged by reversing cell polarities and forcing electrical energy through the cell
    - Cell reaction is reversed during recharging
- Lithium-ion/lithium-ion polymer cells
  - Can be regular shape or a flexible solid polymer
  - Charging / discharging: Li^+ ions move between electrodes, electrons move through connecting wires
  - Negative electrode: graphite coated with lithium metal, $Li \rightarrow Li^+ + e^-$
  - Positive electrode: metal oxide (typically CoO_2), $Li^+ + CoO_2 + e^- \rightarrow LiCoO_2$
- Lithium-ion/lithium-ion polymer cells limitations
  - Can become unstable at high temperatures
  - Can ignite devices
  - Hard to recycle since lithium is very reactive
- Fuel cells
  - Use energy from reaction of fuel with oxygen to create voltage
  - A **continuous supply of fuel and an oxidising agent** (usually oxygen) to the cell
  - Fuel supplied to one electrode; oxidising agent to the other electrode
  - Can operate continuously if fuel and oxygen are continuously supplied - don’t have to be recharged
- Hydrogen-oxygen fuel cells
  - Produce only water as combustion product, no CO2 produced
  - Fuel cells using hydrogen rich fuels e.g. methanol are being developed
    - Will produce carbon dioxide alongside water
    - May produce more pollution but liquid fuel is much easier to store than gaseous ones
  - Hydrogen supplied to anode
    - Oxidation in anode / negative electrode = oxidation
  - Oxgen supplied to cathode
    - Reduction in cathode / positive electrode = reduction
- Hydrogen fuel cell equations
  - Alkaline conditions
    - Negative electrode / anode: $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
    - Positive electrode / cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$
  - Acidic conditions
    - Negative electrode / anode: $2H_{2(g)} \rightarrow 4H^+_{(aq)} + 4e^-$
    - Positive electrode / cathode: $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$

5.3.1 Transition elements

Definitions

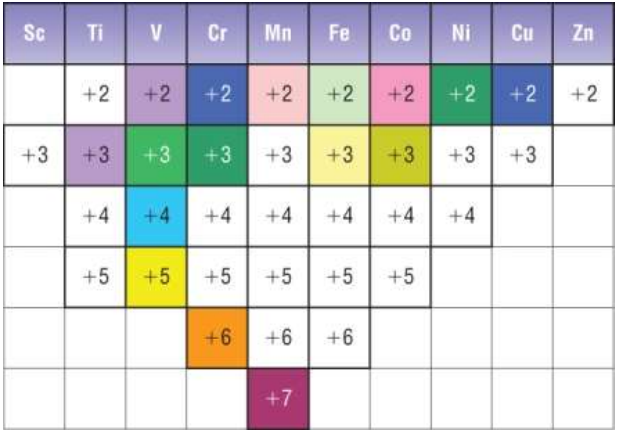
Term	Definition
Transition element	A d-block element that has an **ion** with an **incomplete** d sub-shell
Complex ion	A transition metal ion bonded to one or more ligands
Ligand	A molecule or ion that donates a pair of electrons to a central metal ion to form a coordinate bond
Coordination number	The number of dative bonds the transition metal ion has to its ligands
Monodentate ligands	Donate one pair of electrons to a central metal ion e.g. H_2O:, :Cl^-, :NH_3
Bidentate ligands	Donate two pairs of electrons to the central metal ion e.g. $NH_2CH_2CH_2NH_2$ (shortened to en), ethanedioate
Optical isomers	Non-superimposable mirror images of each other

Properties

- Electron configuration of period 4 atoms (Sc → Zn)
  - Highest energy subshell=3d, electrons are added to 3d
  -

Element	Number of electrons	Electron configuration
Scandium	21	$[Ar]3d^1 4s^2$
Titanium	22	$[Ar]3d^2 4s^2$
Vanadium	23	$[Ar]3d^3 4s^2$
Chromium	24	$[Ar]\mathbf{3d^5 4s^1}$
Manganese	25	$[Ar]3d^5 4s^2$
Iron	26	$[Ar]3d^6 4s^2$
Cobalt	27	$[Ar]3d^7 4s^2$
Nickel	28	$[Ar]3d^8 4s^2$
Copper	29	$[Ar]\mathbf{3d^{10} 4s^1}$
Zinc	30	$[Ar]3d^{10} 4s^2$

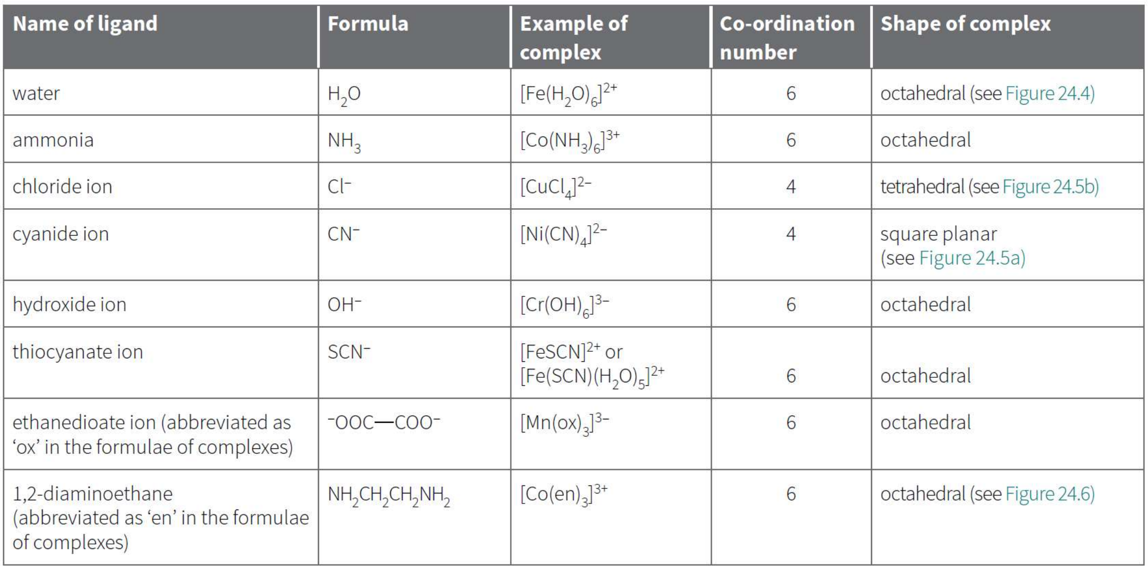
  - Chromium and copper do not follow the expected pattern
    - Half-filled / fully filled d sub-shell gives **additional stability**
- Electron configuration of period 4 ions (Sc → Zn)
  - 4s orbital is filled before 3d as it has a lower energy level when unfilled
  - The 4s orbital empties before the 3d orbitals as the 3d energy level drops below 4s after it is filled
- Exceptions in d-block
  - **Scandium and zinc are not transition elements**
  - Scandium only forms Sc^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6$ (empty d-sub-shells)
  - Zinc only forms Zn^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (full d-sub-shells)
  - Their only ions do not have an incomplete d-sub-shell
- Properties of transition metals
  - Form compounds with different oxidation states / multiple positive ions
  - Form coloured compounds (dissolve in water to form coloured solutions)
  - Elements / compounds can act as catalysts

- Oxidation states
    - They all form 2+ ions by losing the 4s electrons
    - They can then easily lose some / all of the 3d electrons
    - Species with transition element in highest oxidation state are often strong oxidising agents
    - Often form complex ions in higher oxidation states
    - 

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
	+5	+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

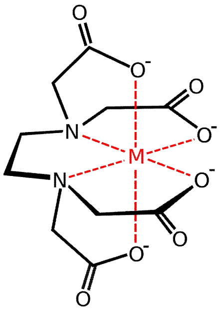
- Colour of transition elements
    - Linked to partially filled d-orbitals, can vary depending on oxidation state
    - Potassium dichromate(VI) = bright orange
    - Cobalt(II) chloride = pink/purple
    - Nickel(II) sulfate = green
    - Hydrated copper(II) sulphate = blue
- Transition elements as catalysts
    - Heterogeneous catalysts are preferred as they are in a different state to reactants so easy to separate
    - Allow reactions to carry out at lower temperature and pressure which **reduces energy usage**
    - Benefits of energy savings is often counteracted by the **toxicity of many transition metals**

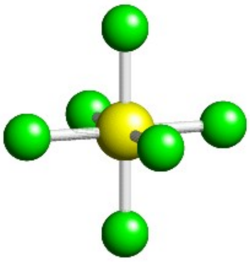
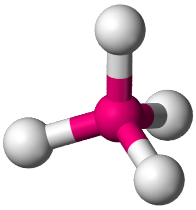
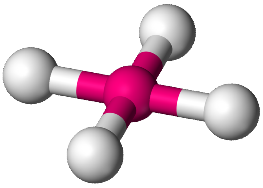
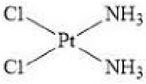
Ligands and complex ions

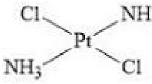
- Common ligands
    - 

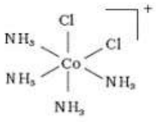
Name of ligand	Formula	Example of complex	Co-ordination number	Shape of complex
water	H_2O	$[Fe(H_2O)_6]^{2+}$	6	octahedral (see Figure 24.4)
ammonia	NH_3	$[Co(NH_3)_6]^{3+}$	6	octahedral
chloride ion	Cl^-	$[CuCl_4]^{2-}$	4	tetrahedral (see Figure 24.5b)
cyanide ion	CN^-	$[Ni(CN)_4]^{2-}$	4	square planar (see Figure 24.5a)
hydroxide ion	OH^-	$[Cr(OH)_6]^{3-}$	6	octahedral
thiocyanate ion	SCN^-	$[FeSCN]^{2+}$ or $[Fe(SCN)(H_2O)_5]^{2+}$	6	octahedral
ethanedioate ion (abbreviated as 'ox' in the formulae of complexes)	$^-OOC—COO^-$	$[Mn(ox)_3]^{3-}$	6	octahedral
1,2-diaminoethane (abbreviated as 'en' in the formulae of complexes)	$NH_2CH_2CH_2NH_2$	$[Co(en)_3]^{3+}$	6	octahedral (see Figure 24.6)

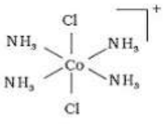
    - EDTA (ethylenediaminetetraacetic acid, a hexadentate ligand)

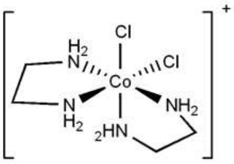


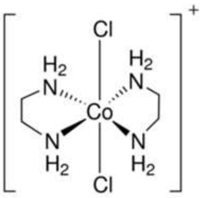
- Six-coordinate complexes shapes
  - Octahedral shape
  - Bond angle 90° around the central metal ion
  - e.g. $[Cu(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Mn(H_2O)_6]^{2+}$
  - 
- Four-coordinate complexes shapes
  - Tetrahedral shape (more common)
    - Bond angle 109.5° around the central metal ion
    - e.g. $[CuCl_4]^{2-}$, $[CoCl_4]^{2-}$
    - 
  - Square planar shape
    - Bond angle 90° around the central metal ion
    - e.g. complexes of Pt: $[Pt(NH_3)_4]^{2+}$, $[Pt(NH_3)_2Cl_2]$
    - 
- Cis-trans isomerism in square planar ions
  - **No more than 2** identical ligands of each type attached to the central metal ion
  - e.g. $[Pt(NH_3)_2Cl_2]$: Pt^{2+} ion + 2 × NH_3 + 2 × Cl^-
    - 

      (cis)
      

      (trans)
- Cis-trans isomerism in octahedral ions
  - Cis = identical groups adjacent (90°); trans = identical groups opposite (180°)
  - Monodentate ligands only
    - 4 of one type of ligand and 2 of another type
    - e.g. $[Co(NH_3)_4Cl_2]^+$: cis-isomer = violet, trans-isomer = green
    - 

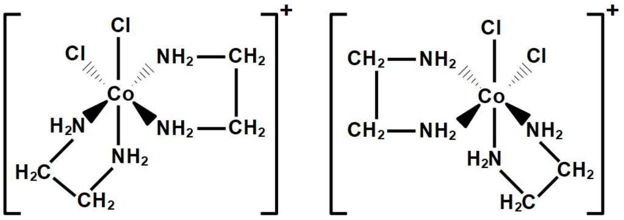
      cis
      

      trans
  - Bidentate ligands
    - 2 bidentate ligands + 2 monodentate ligands
    - e.g. $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$
    - 

      cis-isomer
      

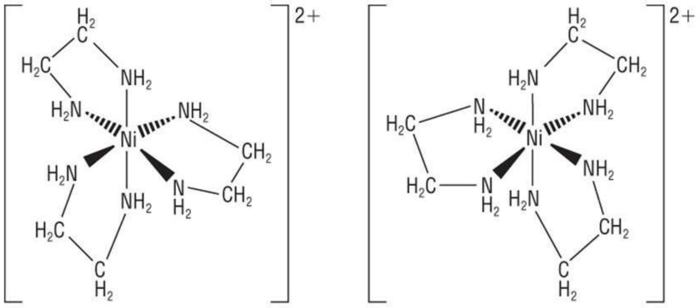
      trans-isomer

- Optical isomerism in octahedral complexes
    - 2 or more bidentate ligands
    - 2 bidentate ligands: e.g. cis-isomer of $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$



cis form

        - (Optical isomerism cannot exist for trans-isomers as the mirror image is exactly the same as the original image and can be superimposed)
    - 3 bidentate ligands: e.g. $[Ru(NH_2CH_2CH_2NH_2)_3]^{2+}$ / $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$
        -



- Use of cis-platin in medicine
    - Used as an anti-cancer drug to attack + shrink tumours
    - Bind to DNA in cancer cells → preventing cell division
    - It forms a platinum complex inside a cell
    - An example of chemotherapy
    - Drugs used in chemostherapy are always toxic which means that they also lead to side effects
- Common complexes
    -

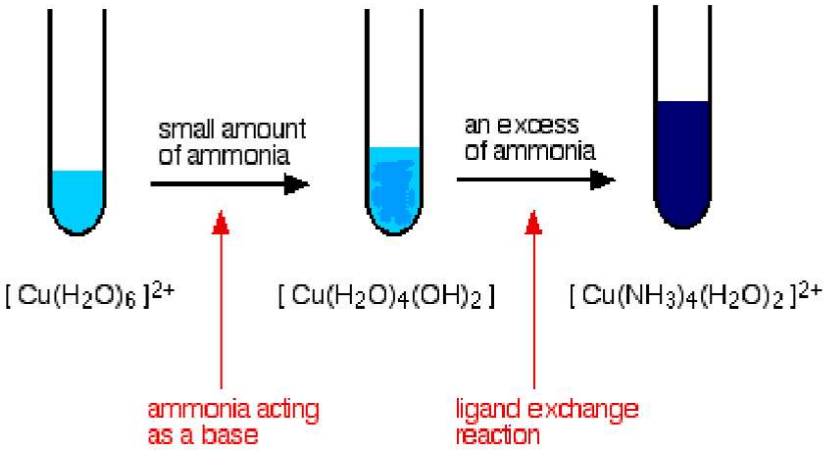
Complex	**Shape**	**Colour**
$[Cu(H_2O)_6]^{2+}$	Octahedral	(Pale) blue
$[Fe(H_2O)_6]^{3+}$	Octahedral	Brown
$[CuCl_4]^{2-}$	Tetrahedral	Yellow
$Pt(NH_3)_2Cl_2$ (platin)	**Square planar**	No colour
$[CoCl_4]^{2-}$	Tetrahedral	Blue
$[Co(H_2O)_6]^{2+}$	Octahedral	Pink
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	Octahedral	Deep blue solution
$[Cu(H_2O)_4(OH)_2]^{2+}$	Octahedral	Pale blue **precipitation**
$[Cr(NH_3)_6]^{3+}$	Octahedral	Purple
$[Cr(H_2O)_6]^{3+}$	Octahedral	Violet
$[Mn(H_2O)_4(OH)_2]^{2+}$	Octahedral	Light brown

Ligand substitution

- Ligand substitution reaction
    - A reaction in which one ligand in a complex ion is replaced by another ligand
    - The final outcome mainly depends on **which ligand is more abundant**
    - Sometimes this will result in **a change in colour**
- Common ligand substitution reactions
    - Hydroxide ions to copper

        - $[Cu(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Cu(H_2O)_4(OH)_{2(s)} + 2\ H_2O_{(l)}$

          pale blue ppt
    - Ammonia to copper
        - $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$

          pale blue solution   dark blue solution
        - Ammonia can deprotonate water molecules / substitute them
        - 2 step reaction: pale blue precipitate of $Cu(OH)_2$ formed first which then dissolves in excess ammonia
        - 

    - Chloride ions to copper
        - $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CuCl_4]^{2-}(aq) + 6H_2O(l)$

          pale blue solution   yellow solution

          octahedral   tetrahedral
    - Ammonia to chromium
        - $[Cr(H_2O)_6]^{3+}(aq) + 6NH_3(aq) \rightarrow [Cr(NH_3)_6]^{3+}(aq) + 6H_2O(l)$

          violet   purple
- Haemoglobin
    - Five of the octahedral positions are filled by lone pairs on nitrogen atoms within the protein structure
    - The final position can be filled by O_2 / CO_2 / H_2O / CO
    - **Lone pair on oxygen atom** forms a **coordinate bond** to the central Fe^{2+} ion
    - Oxygen bonds to the central Fe^{2+} ion as blood passes through the lungs due to increased oxygen pressure in capillaries → oxyhaemoglobin forms
    - The oxygen is released to body cells when required
    - CO_2 binds to haemoglobin and is carried back to the lungs and then released by exhalation
    - CO can also bind to haemoglobin to form carboxyhaemoglobin by replacing oxygen in oxyhaemoglobin
        - Carbon monoxide binds more strongly than oxygen so the bond is irreversible
        - If carboxyhaemoglobin concentration is too high, oxygen transport is prevented → death

Precipitation reactions

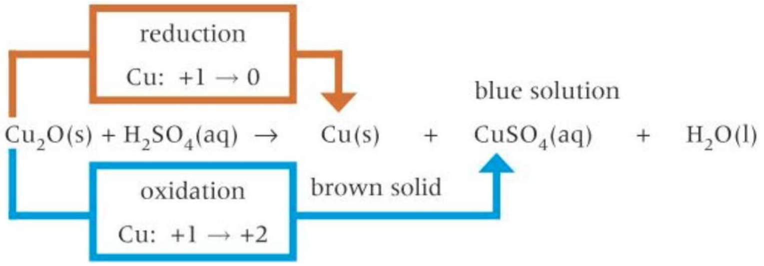
- Precipitation reactions
    - Occurs when two aqueous solutions containing ions react to form an insoluble ionic solid (precipitate)
- Precitation reactions with NaOH
    -

Ion	**Solution colour**	**Precipitate colour**	**Soluble / insoluble in excess NaOH**
Cu^{2+}	Blue	Blue	✗
Fe^{2+}	Pale green	Green Turns brown on surface in air (iron (II)→ iron (III))	✗

Fe^{3+}	Pale yellow	Orange-brown	✗
Mn^{2+}	Pale pink	Light brown Darkens on standing in air	✗
Cr^{3+}	Violet	Grey-green	✓ $Cr(OH)_3(s) + 3OH^-(aq) \rightarrow [Cr(OH)_6]^{3-}(aq)$

  - Overall equations: $M^{a+}(aq) + aOH^-(aq) \rightarrow M(OH)_a(s)$
  - Can also form complex ions e.g. $[Cu(H_2O)_6]^{2+}$
- Precipitation reactions with ammonia
  - In the first stage of ligand substitution reactions with excess ammonia precipitation reaction takes place
  - e.g. $Cu^{2+} \rightarrow Cu(OH)_2$, $Cr^{3+} \rightarrow Cr(OH)_3$, same for other ions
  - Further reactions: $Cr(OH)_3$ dissolves to form $[Cr(NH_3)_6]^{3+}$, $Cu(OH)_2$ dissolves to form $[Cu(NH_3)_4(H_2O)_2]^{2+}$, other precipitates don't react further

Redox reactions

- Oxidation of Fe^{2+} to Fe^{3+}
  - $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O^-(l)$
  - Fe^{2+} oxidised to Fe^{3+}, MnO_4^- reduced to Mn^{2+}
  - In acid conditions
  - Used as a basis for redox titration
  - Purple from MnO^{4-} → colourless Mn^{2+}
- Reduction of Fe^{3+} to Fe^{2+}
  - $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$
  - Fe^{3+} reduced to Fe^{2+}, I^- oxidised to I_2
  - Orange-brown from Fe^{3+} → pale-green from Fe^{2+}
  - Colour change obscured by I_2 (brown)
- Reduction of $Cr_2O_7^{2-}$ to Cr^{3+}
  - $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 3Zn(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Zn^{2+}(aq)$
  - Orange from $Cr_2O_7^{2-}$ → green from Cr^{3+}
  - With an excess of zinc, Cr(III) ions are reduced further because zinc is a powerful reducing agent
  - $Zn(s) + 2Cr^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Cr^{2+}(aq)$
  - Green from Cr^{3+} → pale blue from Cr^{2+}
- Oxidation of Cr^{3+} to CrO_4^{2-}
  - $3H_2O_2 + 2Cr^{3+} + 10OH^- \rightarrow 2CrO_4^{2-} + 8H_2O$
  - H_2O_2 is a powerful oxidising agent
- Reduction of Cu^{2+} to Cu^+
  - $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(s)$
  - Pale blue from Cu^{2+} → white precipitate in CuI + brown I_2
- Disproportionation of Cu^+ ions
  - Cu^+ readily disproportionates in aqueous conditions
  - 

- Ligand colours list

Cu^{2+}	$[Cu(H_2O)_6]^{2+}$ Pale blue (aq)	$Cu(H_2O)_4(OH)_2$ Pale blue (s)	N/A	$[Cu(NH_3)_4(H_2O)_2]^{2+}$ Dark blue (aq)
Fe^{2+}	$[Fe(H_2O)_6]^{2+}$ Pale green (aq)	$Fe(H_2O)_4(OH)_2$ Dark green (s)	N/A	N/A
Fe^{3+}	$[Fe(H_2O)_6]^{3+}$ Yellow (aq)	$Fe(H_2O)_3(OH)_3$ Orange-brown (s)	N/A	N/A
Mn^{2+}	$[Mn(H_2O)_6]^{2+}$ Pale pink (aq)	$Mn(H_2O)_4(OH)_2$ Pale brown (s)	N/A	N/A
Cr^{3+}	$[Cr(H_2O)_6]^{3+}$ Pale purple / green (aq)	$Cr(H_2O)_3(OH)_3$ Grey-green (s)	$[Cr(OH)_6]^{3-}$ Dark green (aq)	$[Cr(NH_3)_6]^{3+}$ Purple (aq)

Cu Brown (s)	Cu_2O Red (s)	$CuCl_4^{2-}$ Yellow (aq)	CuI White (s)	MnO_4^- Purple (aq)	$Cr_2O_7^{2-}$ Orange (aq)	CrO_4^{2-} Yellow (aq)

5.3.2 Qualitative analysis

Test for anions

- See 3.1.4

Test for cations

- Test for ammonium ion (NH_4^+)
  - See 3.1.4
- Precitation reactions with NaOH
  - See 5.3.1