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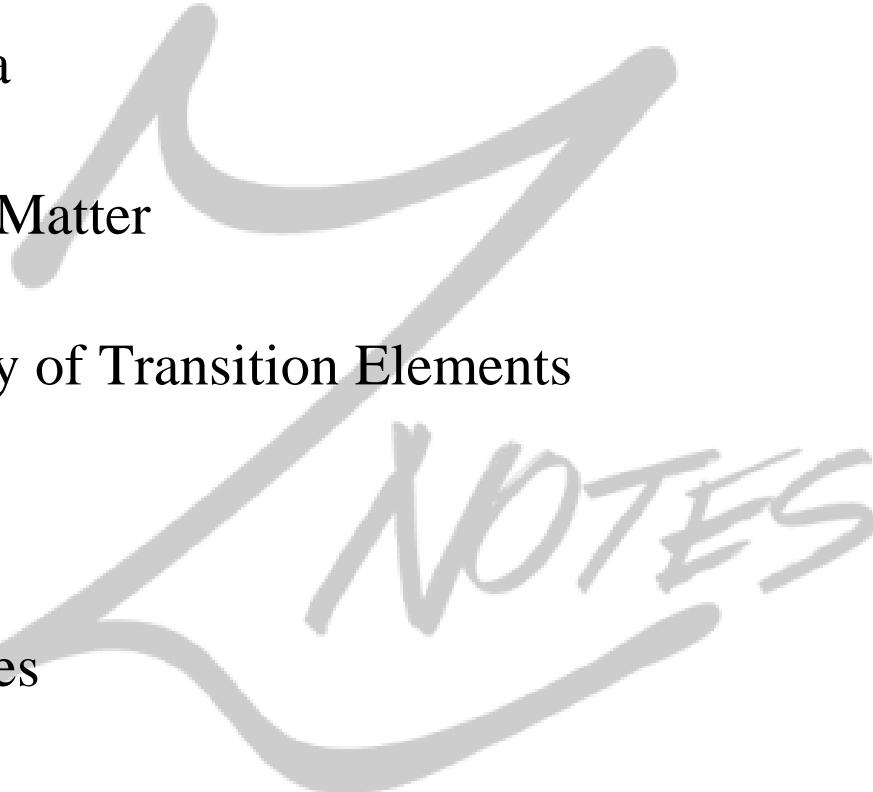
Updated to 2016-18 Syllabus

CIE A2-LEVEL CHEMISTRY 9701

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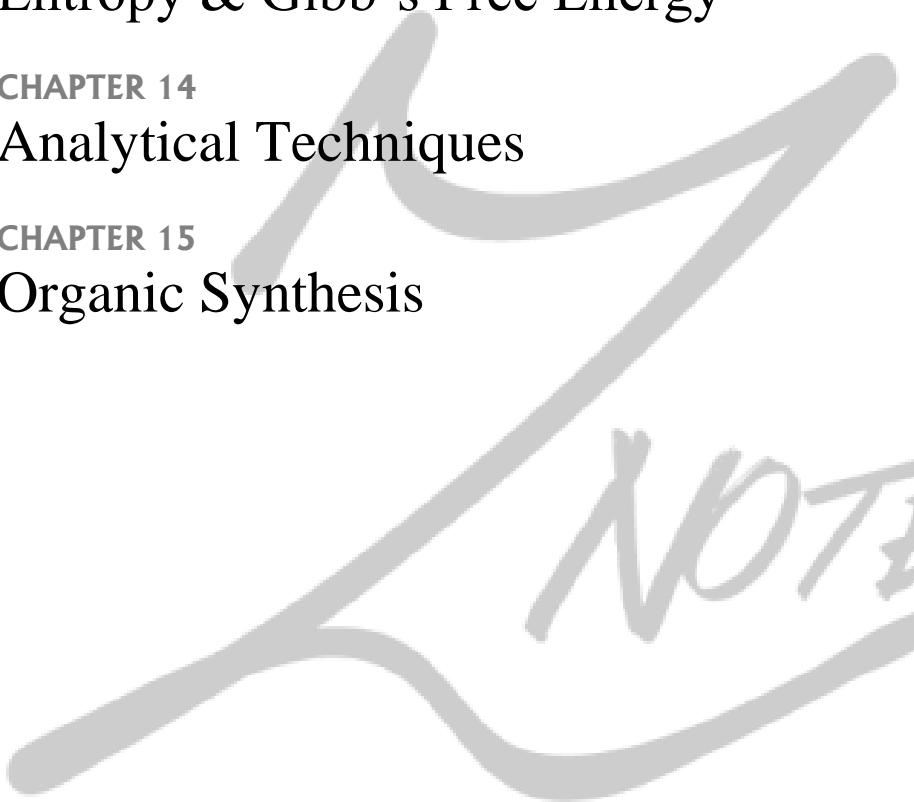
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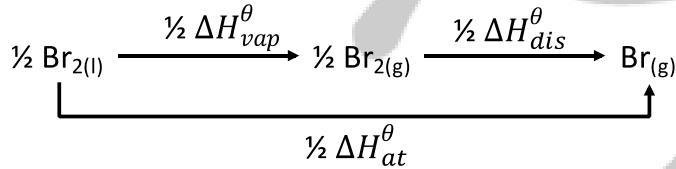
1. CHEMICAL ENERGETICS

1.1 Electron Affinity

- Electron Affinity (ΔH_{ea}^θ):** enthalpy change when a gaseous atom gains an electron to form a negative ion under standard conditions
- 1st electron affinity is exothermic
- 2nd, 3rd... electron affinities are endothermic because when electron added to -ve ion, increased repulsion present therefore requires input of energy

1.2 Atomization

- Enthalpy change of atomization (ΔH_{at}^θ):** enthalpy change when one mole of gaseous atom is formed from its elements under standard conditions
- Note:** specific value may not be given and you must use combination of enthalpies e.g.



1.3 Lattice Energy

- Lattice Energy (ΔH_{lat}^θ):** enthalpy change when one mole of an ionic compound is formed from its gaseous ions under standard conditions.
- More -ve $\Delta H_{lat}^\theta \rightarrow$ stronger ionic bonding \rightarrow more stable ionic compound
- If theoretical and experimental ΔH_{lat}^θ value similar, bonding is pure ionic, otherwise it is intermediate between ionic and covalent

1.4 Factors Affecting Lattice Energy

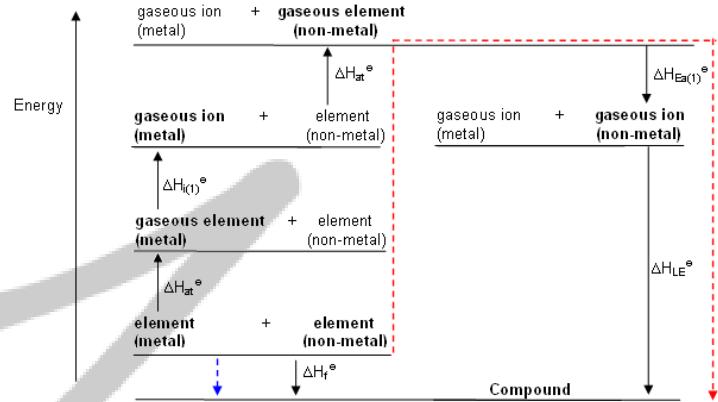
$$\Delta H_{lat}^\theta \propto \frac{\text{Charge on Ion}}{\text{Radius of Ion}}$$

Charge	Radius
• Greater the charge	• Smaller the radius
• Greater charge density	
• Greater electrostatic attraction between ions	
• ΔH_{lat}^θ more exothermic	
• Compound more stable	

1.5 Born-Haber Cycle

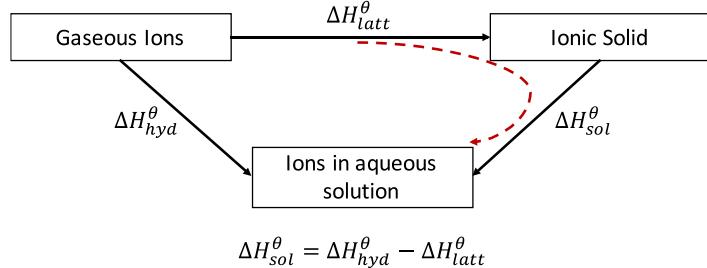
- ΔH_f^θ of an element under standard conditions = 0

Endothermic Processes	Exothermic Processes
<ul style="list-style-type: none"> ΔH_i^θ ΔH_{at}^θ ΔH_{ea}^θ 2nd and 3rd 	<ul style="list-style-type: none"> ΔH_f^θ ΔH_{ea}^θ 1st ΔH_{latt}^θ ΔH_{hyd}^θ



1.6 Dissolving Salts

- Enthalpy change of solution (ΔH_{sol}^θ):** enthalpy change when one mole of ionic solid is dissolved in sufficient water to form a very dilute solution under standard conditions (can be +ve or -ve)
- e.g. $\text{NaCl}_{(s)} + \text{aq} \rightarrow \text{NaCl}_{(aq)}$
- Enthalpy change of hydration (ΔH_{hyd}^θ):** enthalpy change when one mole of specified gaseous ions dissolves in sufficient water to form a very dilute solution under standard conditions
- e.g. $\text{Na}^+_{(g)} + \text{aq} \rightarrow \text{Na}^+_{(aq)}$
- Factors affecting ΔH_{hyd}^θ = factors affecting ΔH_{latt}^θ
- Solubility of ionic salts depend on value of ΔH_{sol}^θ : the more -ve = more soluble



1.7 Ion Polarization

- Ion polarization:** distortion of the electron cloud on an anion by a neighbouring cation

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- **Polarizing power:** ability of a cation to attract electrons and distort anion
- Polarization will be increased by:
 - Cation has a higher charge density: high positive charge and small size
 - Anion has greater polarisability: high negative charge and large size

1.8 Thermal Stability of Gp.2 CO_3 and $(\text{NO}_3)_2$

- Down the group, polarizing power decreases
- $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$
- The greater the polarization, the more distorted is the anion causing it to weaken the C – O bond
- Therefore, easier to form CO_2 and XO and compound less stable.
- **Order of stability:** $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$

1.9 Solubility of Gp.2 Hydroxides & Sulphates

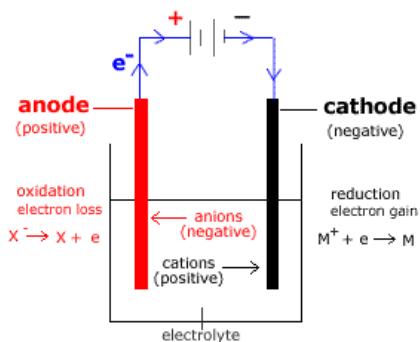
- Radius of cation increases down group ∵ charge density decreases
- Attraction of cation to water molecule decreases ∵ value of ΔH_{hyd}^θ becomes less exothermic
- ΔH_{lat}^θ also decreases but decrease is relatively smaller because of large size of anions compared to cations
- ΔH_{sol}^θ becomes less exothermic because decrease in ΔH_{hyd}^θ is greater than decrease in ΔH_{lat}^θ
- ∵ solubility decreases down the group

2. ELECTROCHEMISTRY

2.1 Electrolysis

- **Electrolysis:** decomposition of a compound into its element by an electric current

Electrolysis cell:



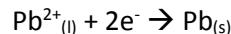
- **Electrolyte:** compound that is decomposed (molten/ionic)

- **Electrodes:** rods which allow current to enter electrolyte (inert/reactive)

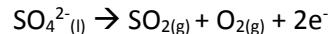
2.2 Product of Electrolysis

Molten Electrolyte:

- **At the cathode:** positive ions reduced to atoms



- **At the anode:** negative ions oxidized to atoms/molecules



Aqueous Electrolyte:

	At the cathode	At the anode
By E^θ	<ul style="list-style-type: none"> • $E^\theta > 0$ then metal less reactive than H so metal formed • $E^\theta < 0$ then metal more reactive than H so $\text{H}_{2(g)}$ formed 	<ul style="list-style-type: none"> • $E^\theta > 0.4$ then non-metal less reactive than OH so non-metal formed • $E^\theta < 0.4$ then non-metal more reactive than OH so $\text{H}_2\text{O}_{(l)}$ formed
By Conc.	Following results from above, if solution very dilute, this occurs greater:	$2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_{2(g)}$ $4\text{OH}^-_{(aq)} \rightarrow 2\text{H}_2\text{O}_{(l)} + \text{O}_{2(g)} + 2e^-$

2.3 Quantitative Electrolysis

- Calculating quantity of charge passed during electrolysis:

$$Q = It$$
 in Coulombs (C)
- Mass of a substance liberated is proportional to the quantity of electricity which passes through electrolyte
- **1 faraday (F):** quantity of electric charge carried by 1 mol of electrons = 96,500 C
- Relationship:
$$F = Le$$
 - F = Faraday's Constant
 - L = Avagadro's Constant
 - e = charge on 1 electron
- Example:
 - To liberate 1 mol of $\text{H}_{2(g)}$

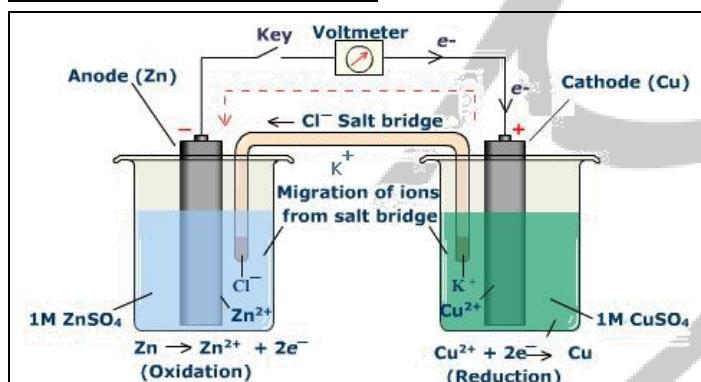
$$2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_{2(g)}$$
 - ∵ requires 2 faradays of electricity to form 1 mole

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2.4 Standard Electrode Potentials

- Standard electrode (redox) potential E^θ :** the electrode potential of a half cell measured under standard conditions using a standard hydrogen electrode as the other half cell
- Standard cell potential E_{cell}^θ :** the difference in standard electrode potential between two half cells
- Standard conditions:**
 - Temperature: 298 K
 - Pressure: 1 atm (101 kPa)
 - Concentration: 1.00 mol dm⁻³

2.5 Electrochemical Cell

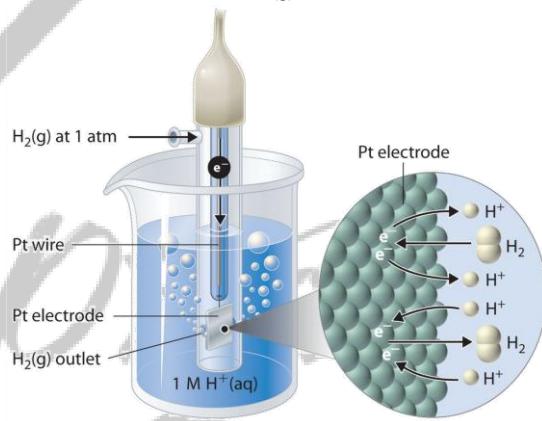
 <p>ANODE -ve electrode/half cell • E^θ of half cell is more -ve (less +ve) • Metal loses e⁻, forms +ve ions = oxidation occurs</p> <p>CATHODE +ve electrode/half cell • E^θ of half cell is more +ve (less -ve) • Metal ion gains e⁻, solid metal deposited = reduction occurs</p>	
Cell Notation $Zn(s) \mid Zn^{2+}(aq)$ $Cu^{2+}(aq) \mid Cu(s)$ <p>Salt bridge</p> <p>Anode half-cell Cathode half-cell</p> <p>$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$</p> <p>Phase boundary Electrons flow this way Phase boundary</p>	
<p>The more -ve (less +ve) the E^θ, the more easily it gets oxidized ∵ stronger reducing agent</p> $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^\theta = -0.76$ $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^\theta = +0.34$ $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$	<p>The more +ve (less -ve) the E^θ, the more easily it gets reduced ∵ stronger oxidizing agent</p>
$E_{cell}^\theta = E_{Red}^\theta - E_{Ox}^\theta$ $E_{cell}^\theta = 0.34 - -0.76 = 1.10$	

2.6 Salt Bridge

- Used to complete the electrical circuit allowing the movement of ions between two half cells so that ionic balance is maintained; electrically neutral
- A strip of filter paper soaked in $KNO_3(aq)$
- Salt used should not react with ions forming a ppt. e.g. KCl in a cell containing Ag^{2+} would form insoluble ppt.

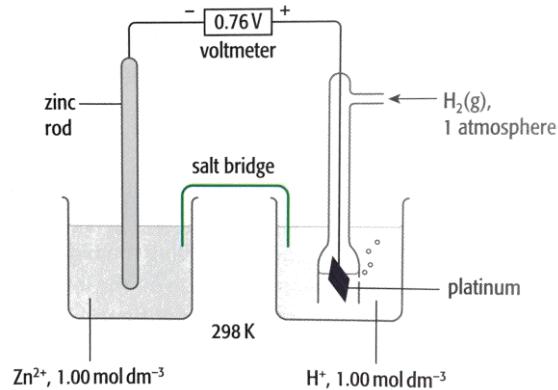
2.7 Standard Hydrogen Electrode (S.H.E.)

- It is a reference cell, used to measure E^θ of any other half cell
- Consists of $H_{2(g)}$ at 298K and 1atm bubbling around a Pt electrode in contact with an aq. solution of H^+ ions at 1.00 mol dm⁻³ conc. (e.g. $HCl_{(aq)}$ or $\frac{1}{2} H_2SO_4_{(aq)}$)
- Pt electrode is inert, allows conduction and is coated with finely divided Pt serving as a catalyst. Being porous, retains large amounts of $H_{2(g)}$



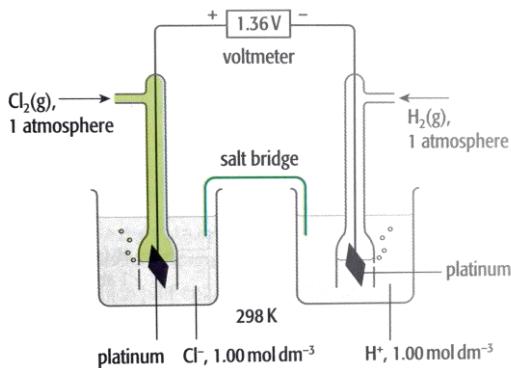
2.8 Measuring E^θ of a Half Cell using S.H.E.

Metals in contact with their aq. solution

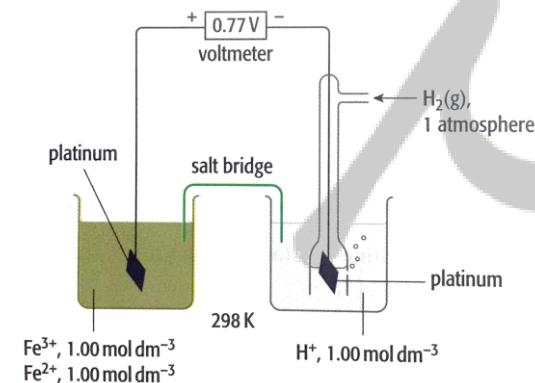


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Non-metals in contact with their aq. solution



Pairs of ions with different oxidation states



2.9 Feasibility of a Reaction

- For a spontaneous (i.e. feasible) reaction, E_{cell}^θ must be positive

Finding whether a reaction is feasible:

Will chlorine oxidize Fe^{2+} ions to Fe^{3+} ions?

Solution:

Identify which is the R.A./O.A. from question
Chlorine is the O.A therefore is reduced

Identify relevant equations from data booklet and place in correct direction. If using opposite direction, switch sign for value of E^θ



Add E^θ 's together. If positive, reaction occurs and is feasible otherwise, does not occur spontaneously.

$$1.36 - 0.77 = 0.59$$

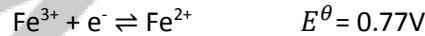
Reaction occurs spontaneously and is feasible

2.10 Oxidizing Ability of Halogens (Gp. 17)

- Electrode potential values can be used to determine ease of oxidation or reduction
- The more +ve E^θ , the easier it is to reduce therefore stronger oxidizing agent (ability).
- Relative reactivity of halogens can be determined by ordering them in descending order of E^θ , most reactive to least

Reaction	E^θ
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.07
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.54

2.11 Concentration of aq. Ions



- If $[\text{Fe}^{3+}]$ increased or $[\text{Fe}^{2+}]$ decreased, equi. favours forward reaction $\therefore E$ becomes more +ve (0.85V)
- If $[\text{Fe}^{2+}]$ increased or $[\text{Fe}^{3+}]$ decreased, equi. favours backward reaction $\therefore E$ becomes more -ve (0.70V)

- A given reaction will occur under non-standard conditions if the E^θ values of the two half reactions involved differ by more than 0.30V
- Changing conc. and non-standard conditions can also cause non-feasible standard reactions to occur as E values can change greatly

2.12 Nernst Equation

- Equation relating voltage of chemical cell to its standard potential and to concentrations of reactants & products

$$E = E^\theta + \frac{RT}{zF} \ln \frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

- z is number of electrons transferred in reaction

- F is the value of the Faraday constant 96,500 C mol⁻¹

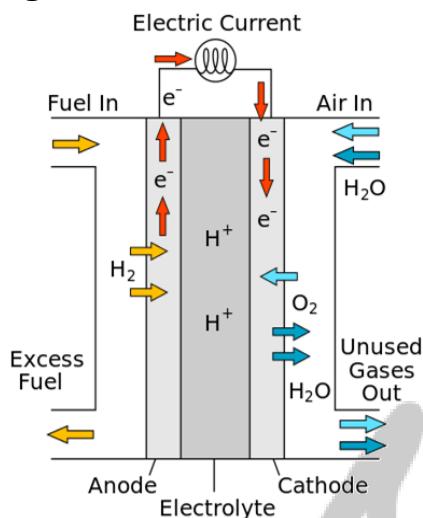
Simplified relationship by substituting standard values:

$$E = E^\theta + \frac{0.059}{z} \log \frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

- If conc. less than 1 mol dm⁻³, $\log[\text{oxidized form}]$ is -ve and E is less than E^θ
- If conc. more than 1 mol dm⁻³, $\log[\text{oxidized form}]$ is +ve and E is more than E^θ

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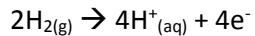
2.13 Hydrogen Fuel Cell



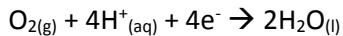
- Consists of:
 - Two platinum coated porous electrodes that allow gases to pass through
 - Electrolyte; either acidic or alkaline

Acidic electrolyte:

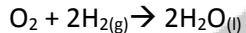
- -ve Electrode (anode):



- +ve Electrode (cathode):



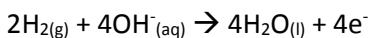
- Overall reaction:



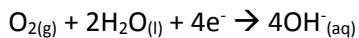
- H^+ ions removed at +ve electrode replaced by those produced at -ve electrode so conc. of electrolyte remains constant

Alkaline electrolyte:

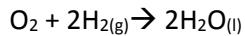
- -ve Electrode (anode):



- +ve Electrode (cathode):



- Overall reaction:



- OH^- ions removed at -ve electrode replaced by those produced at +ve electrode so conc. of electrolyte remains constant

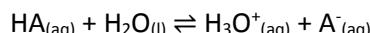
Advantages:

- No pollutants – by product is water
- More energy per gram of fuel than other fuels
- Lightweight
- Operate with high efficiency

3. EQUILIBRIA

3.1 Behaviour of Acids and Alkali

- When acids and alkalis are added to water, they dissociate/ionize and a dynamic equilibrium is set up
- General equilibrium of an acid (can be simplified to H^+)



Strong Acids	Weak Acids
$HA_{(aq)} + H_2O_{(l)} \rightarrow H^+_{(aq)} + A^-_{(aq)}$	$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$
<ul style="list-style-type: none"> • Eq. position to the right • Dissociates completely $\therefore [Acid] = [Ions]$ 	<ul style="list-style-type: none"> • Eq. position to the left • Dissociates partially $\therefore [Acid] \neq [Ions]$
$K_c = \frac{[H^+][A^-]}{[HA][H_2O]}$	

- Water dissociates very slightly; conc. remains constant \therefore can eliminate from equation

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

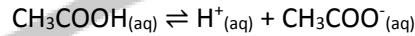
- The **acid dissociation constant**, K_a can be used to compare strengths of acids; the higher the value, the stronger the acid
- Values are extremely small so $-\log$ are used giving pK_a
 $-\log K_a = pK_a \Leftrightarrow K_a = 10^{-pK_a}$
- Smaller pK_a value, stronger the acid

Calculating pH of a weak acid from K_a :

Calculate the pH of 0.1 mol dm⁻³ ethanoic acid.

$$K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

Solution:



The conc. of ions is equal therefore

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

$$1.74 \times 10^{-5} = \frac{[H^+]^2}{0.1}$$

$$[H^+] = \sqrt{(1.74 \times 10^{-5}) \times 0.1} = 1.32 \times 10^{-3}$$

Calculate pH by logging the concentration of H^+

$$pH = -\log(1.32 \times 10^{-3}) = 2.88$$

3.2 pH Scale

- Gives strength of acid depending on $[H^+]$
- Use $-\log$ of values as they are very small giving pH
- Lower pH value, stronger the acid

$$-\log[H^+] = pH \Leftrightarrow [H^+] = 10^{-pH}$$

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Calculating pH of a strong acid:

Find the pH of 3.6×10^{-5} mol dm⁻³ HNO₃

Solution:

It is a strong acid and dissociates completely the conc. of ions is equal to conc. of the acid

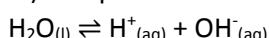
$$[H^+] = [HNO_3] = 3.6 \times 10^{-5}$$

Calculate the pH by logging the conc.

$$pH = -\log(3.6 \times 10^{-5}) = 4.44$$

3.3 Ionic Product of Water, K_w

- Water molecules can function as both acids and bases; one molecule (base) accepts H⁺ from second one (acid)



$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

- Conc. of water remains constant ∴ can eliminate from equation and find the **ionic product of water**, K_w

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

At 25°C, the K_w of water is 1.00×10^{-14} mol² dm⁻⁶

$$\begin{aligned} &- \log \text{ throughout equation}, -\log 1 \times 10^{-14} = 14 \therefore \\ &14 = pH + pOH \end{aligned}$$

- pH of an alkali can be calculated using this formula

Calculating pH of a strong base:

Calculate the pH of a solution of sodium hydroxide of concentration 0.05 mol dm⁻³

Solution:

It is a strong base and dissociates completely the conc. of ions is equal to conc. of the solution

$$[OH^-] = [NaOH] = 0.05$$

Calculate pOH by logging

$$pOH = -\log 0.05 = 1.30$$

Calculate pH by using the following

$$pH + pOH = 14$$

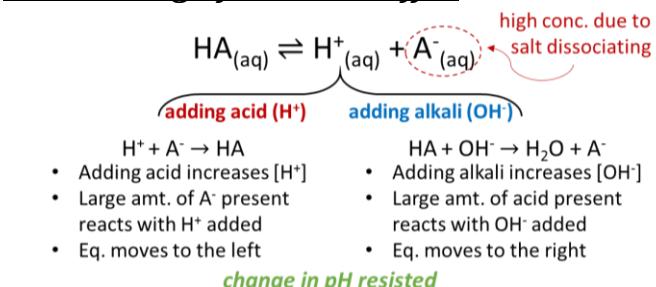
$$pH = 14 - pOH = 14 - 1.30 = 12.7$$

3.4 Buffer Solutions

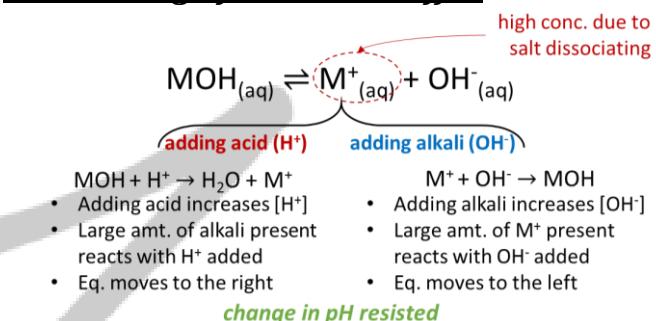
- Buffer solution:** a solution in which pH doesn't change significantly when small amounts of acids or alkali added
- A buffer solution can be:
 - Acid: Weak acid + its salt
e.g. CH₃COOH and CH₃COONa
 - Alkali: Weak alkali + its salt
e.g. NH₃ and NH₄Cl
- In both types, the salt provides more of its conjugate pair, for example



3.5 Working of an Acid Buffer

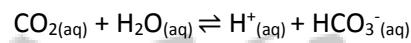


3.6 Working of an Alkali Buffer



3.7 Controlling pH of Blood

- Respiration in cells produces carbon dioxide and carbon dioxide combines with water in blood



- The enzyme carbonic anhydrase is present to supply HCO₃⁻ ions and increase its conc. similar to acidic buffers

If [H ⁺] increases:	If [H ⁺] decreases:
<ul style="list-style-type: none"> • Eq. shifts to the left • Reduces [H⁺] 	<ul style="list-style-type: none"> • Eq. shifts to the right • Increases [H⁺]
pH of blood unchanged	

3.8 Calculating pH of Buffer Solutions

$$pH = pK_a + \log\left(\frac{[Salt]}{[Acid]}\right)$$

Calculating pH of buffer solution:

A buffer solution is made by adding 3.28g of CH₃COONa to 1 dm³ of 0.01 mol dm⁻³ CH₃COOH

- What is the pH of this buffer ($K_a = 1.8 \times 10^{-5}$)
- What is the change in pH when 1 cm³ of 1 mol dm⁻³ NaOH is added to 1 dm³ of the buffer?

Solution:

Part (a):

Calculate the moles and concentration of the salt

$$\text{Moles} = \frac{\text{Mass}}{\text{Molar Mass}} = \frac{3.28}{82} = 0.04$$

$$\text{Concentration} = \frac{\text{Moles}}{\text{Volume}} = \frac{0.04}{1} = 0.04$$

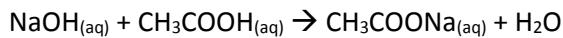
Use formula to calculate pH:

$$pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.04}{0.01}\right) = 5.35$$

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Part (b):

NaOH reacts with acid:



Calculate no. of moles of NaOH used:

$$\text{Moles} = \text{Concentration} \times \text{Volume} = 1 \times 0.001 = 0.001$$

Hence that much of acid has been reduced and the same amount has formed as salt. Calculate new concentrations of salt and acid.

$$\text{Conc. of Acid} = \frac{(0.01 \times 1) - 0.001}{1 + (1 \times 10^{-3})} = 8.99 \times 10^{-3}$$

$$\text{Conc. of Salt} = \frac{0.04 + 0.001}{1 + (1 \times 10^{-3})} = 0.0410$$

Use formula to calculate pH:

$$pH = -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.0410}{8.99 \times 10^{-3}}\right) = 5.40$$

Find the change in pH:

$$\Delta pH = 5.40 - 5.35 = 0.05$$

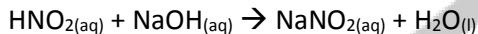
Calculating pH of buffer solution with different volumes of acid and salts:

What is the pH of the buffer solution formed when 40cm³ of 1 mol dm⁻³ of nitrous acid ($\text{pK}_a = 3.34$) is added to 20 cm³ of 1 mol dm⁻³ of sodium hydroxide

Solution:

Part (a):

Write out an equation for the reaction



Calculate the moles of each reactant

$$\text{Moles of HNO}_2 = 1 \times (40 \times 10^{-3}) = 0.04$$

$$\text{Moles of NaOH} = 1 \times (20 \times 10^{-3}) = 0.02$$

NaOH is limiting reagent therefore moles of product and reactants are:

$$\text{NaNO}_2 \text{ formed} = 0.02$$

$$\text{HNO}_2 \text{ remaining} = 0.04 - 0.02 = 0.02$$

Calculate concentration of salt and acid:

$$\text{Total Volume} (20 + 40) \times 10^{-3} = 0.06 \text{ dm}^3$$

$$\text{Conc. of HNO}_2 = \frac{0.02}{0.06} = \frac{1}{3}$$

$$\text{Conc. of NaNO}_2 = \frac{0.02}{0.06} = \frac{1}{3}$$

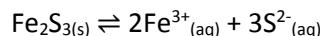
Use formula to calculate pH:

$$pH = 3.34 + \log\left(\frac{1/3}{1/3}\right) = 3.34$$

3.9 Solubility Product K_{sp}

- When a sparingly soluble salt is shaken with distilled water and left to settle, the water contains aq. ions from the salt in very small conc. and a dynamic equilibrium is set up between ions and insoluble solid

- Solubility product (K_{sp}):** product of conc. of each ion in a saturated solution of sparingly soluble salt at 298K raised to the power of moles in dissociation equation e.g.



$$K_{sp} = [2\text{Fe}^{3+}]^2[3\text{S}^{2-}]^3 \quad \text{units: mol}^5 \text{ dm}^{-15}$$

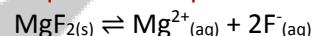
- The conc. of ions is independent of amount of solid
- K_{sp} values change only with temperature
- Concentration of ions = solubility of salt

Calculating solubility product from solubility:

A saturated solution of magnesium fluoride, MgF₂, has a solubility of 1.22×10^{-3} mol dm⁻³. Calculate the solubility product of magnesium fluoride.

Solution:

Write down the equilibrium equation



Write down the equilibrium expression

$$K_{sp} = [\text{Mg}^{2+}][\text{F}^{-}]^2$$

Solubility of salt = conc. of ions

$$\therefore [\text{Mg}^{2+}] = [\text{F}^{-}] = 1.22 \times 10^{-3}$$

Substitute into equilibrium expression

$$K_{sp} = (1.22 \times 10^{-3}) \times \{ 2 \times (1.22 \times 10^{-3}) \}^2$$

$$K_{sp} = 7.26 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$$

- To calculate solubility from solubility product, apply the same method but place x for conc. and find it

3.10 Predicting Precipitation

- Precipitation:** when two aq. solutions of ionic substance are mixed, a ppt. will form provided the K_{sp} of the insoluble solid is less than ionic product of ions present

Ionic Product > K_{sp}

Predicting if insoluble salt will precipitate:

Will a ppt. BaCO₃ ($K_{sp} = 8.1 \times 10^{-9}$) form from solution containing 0.1 mol dm⁻³ Ba²⁺_(aq) & 1.0 mol dm⁻³ CO₃²⁻_(aq)

Solution:

Calculate ionic product:

$$0.1 \times 1.0 = 1.0$$

Compare to K_{sp} value

$$1.0 > 8.1 \times 10^{-9} \therefore \text{ppt. will form}$$

3.11 Common Ion Effect

- Common ion effect:** lowering of solubility of an ionic compound by addition of a common ion to the solution

Calculating solubility with common ion:

BaSO₄ is a sparingly soluble salt ($K_{sp} = 1.0 \times 10^{-10}$ mol² dm⁻⁶). Compare the solubility at 298K of BaSO₄ in an aq. solution of 0.1 mol dm⁻³ H₂SO₄ to in pure water

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Calculate conc. of Ba^{2+} in pure water

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \text{ and both conc. are equal} \therefore$$

$$[\text{Ba}^{2+}] = \sqrt{1.0 \times 10^{-10}} = 1.0 \times 10^{-5}$$

To calculate $[\text{Ba}^{2+}]$, first find conc. of common ion, SO_4^{2-}

H_2SO_4 is a strong acid which dissociates completely

$$\therefore [\text{H}_2\text{SO}_4] = [\text{SO}_4^{2-}] = 0.1$$

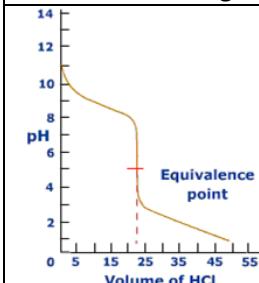
Use new conc. of SO_4^{2-} and ignore original as it is negligible to calculate new $[\text{Ba}^{2+}]$

$$[\text{Ba}^{2+}] = \frac{K_{\text{sp}}}{[\text{SO}_4^{2-}]} = \frac{1.0 \times 10^{-10}}{0.1} = 1.0 \times 10^{-9}$$

Hence, solubility has decreased by a factor of 10^{-4}

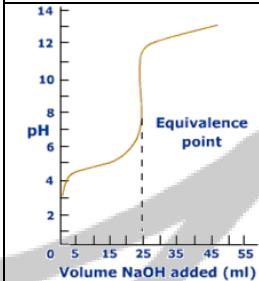
Solution:

Strong Acid added to Weak Base



- Equivalence point < 7
- Sensitive pH Range = 3.0 – 7.5
- Indicator = methyl orange

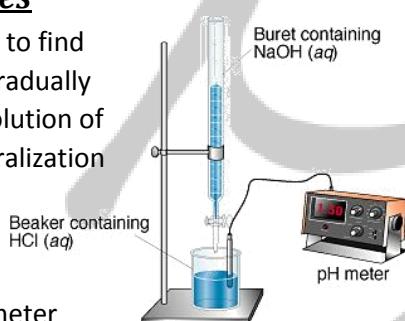
Strong Base added to Weak Acid



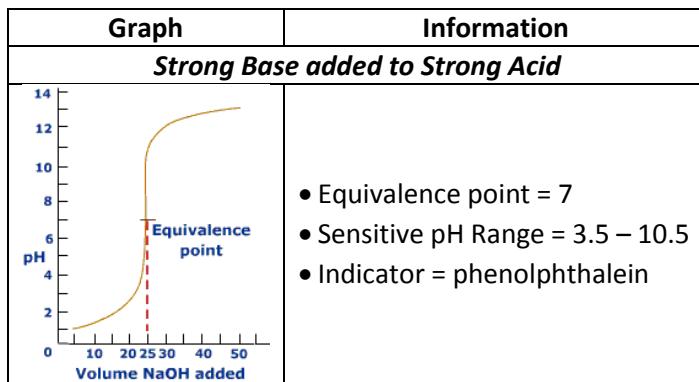
- Equivalence point > 7
- Sensitive pH Range = 6.0 – 11.0
- Indicator = phenolphthalein

3.12 Titration Curves

- **Titration:** method used to find conc. of a solution by gradually adding to it a second solution of known conc. until neutralization point is reached
- Progress of neutralization reaction monitored using a pH meter and shown on a graph
- **Equivalence point:** mid-point of near-vertical portion of the graph where no. of mols H^+ = no. of mols OH^-
- **End point:** volume of alkali/acid added when indicator just changes color
- **Choosing a suitable indicator:**
 - Sharp color change at end point
 - End point must be ± 2 pH of equivalence point
 - Indicator should give distinct colour change



Indicator	Colour at low pH	pH Range	Colour at high pH
Phenolphthalein	Colourless	8.2 – 10.0	Pink
Methyl orange	Red	3.2 – 4.4	Orange



3.13 Solvents

- **General solubility rule:** like dissolves like
 - Covalent substances dissolve/mix in other covalent substances
 - Ionic substances do not dissolve/mix in other covalent substance (exception is water)
- Solubility in water
 - Although covalent, highly polar nature makes it excellent solvent for ionic substances
 - Dissolves some covalent substances because they either react or form H-bonds with water molecules

3.14 Partition Coefficient

- **Partition law:** a solutes solubility will be different in two different liquids that are immiscible. The solute will be more soluble in one of the two.
Measured in [conc.]: g cm^{-3} or mol dm^{-3}
- When solute added to two immiscible solvents, a dynamic equilibrium is set up where particles move between the two solvents but concentration in each remains constant.
- Hence, can calculate a constant k for the equilibrium
- **Partition coefficient (K_{pc}):** equilibrium constant that relates the concentration of solute partition between two immiscible solvents at a particular temperature.

$$K_{pc} = \frac{\text{Conc. of Solute in Solvent 1}}{\text{Conc. of Solute in Solvent 2}}$$

Place concentration of the first solvent mentioned on top of the K_{pc} expression

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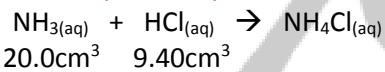
- K_{pc} can be useful to work out how much solvent needed to extract minimum amount of solute from one solvent to another
- Repeated extractions with smaller volumes of solvent more efficient than one extraction with a larger volume

Calculating K_{pc}

100cm³ of a 0.100mol dm⁻³ solution of ammonia was shaken with 50cm³ of an organic solvent and left in a separating funnel for equilibrium to establish
A 20.0cm³ portion of the aqueous layer was run off and titrated against 0.200mol dm⁻³ dilute hydrochloric acid. The end-point was found to be 9.40cm³ of acid.
What is the partition coefficient of ammonia between these two solvents?

Solution:

Calculate conc. of aqueous layer run off ($\text{NH}_3\text{(aq)}$)



Use concentration of acid used to neutralize

$$0.2 = \frac{\text{mols of NH}_3 \text{ in water}}{9.4 \times 10^{-3}}$$

$$\text{mols of NH}_3 \text{ in water} = 1.88 \times 10^{-3}$$

Use ratios to find moles of $\text{NH}_3\text{(aq)}$ in 100.0cm³

$$20.0\text{cm}^3 : 1.88 \times 10^{-3} \text{ mols}$$

$$100\text{cm}^3 : 9.40 \times 10^{-3} \text{ mols}$$

$$\therefore \text{moles of NH}_3 \text{ in water in equilibrium} = 9.40 \times 10^{-3}$$

To find moles of NH_3 in organic solvent, first find moles present originally in the ammonia solution

$$0.1 = \frac{\text{initial mols of NH}_3 \text{ in water}}{100 \times 10^{-3}}$$

$$\therefore \text{moles of NH}_3 \text{ in water initially} = 0.01 \text{ mols}$$

$$\text{Subtract initial \& final moles in water to find no. of mols in organic solvent} = 0.01 - 9.40 \times 10^{-3} = 6.0 \times 10^{-4}$$

Calculate the K_{pc} value

$$K_{pc} = \frac{\text{conc. of NH}_3\text{(org)}}{\text{conc. of NH}_3\text{(aq)}} = \frac{6.0 \times 10^{-4}}{9.4 \times 10^{-3}} / \frac{50 \times 10^{-3}}{100 \times 10^{-3}}$$

$$K_{pc} = 0.1277$$

4. REACTION KINETICS

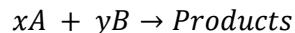
4.1 Rate of Reaction

- Rate of reaction is the change in concentration of products/reactants per unit time

$$R = \frac{[]}{t} \quad \text{Unit: mol dm}^{-3} \text{ s}^{-1}$$

4.2 Rate Equation

- **Rate equations:** states the relationship between the rate constant and the concentrations of those reactants



$$R = k[A]^m[B]^n$$

- **Rate constant (k):** proportionality constant in rate eqn.

- Larger the rate constant, faster the reaction
- Depends on temperature
- Unit depends on overall order of reaction

- **Order of reaction (m, n):** power to which conc. of the reactant is raised in experimentally determined rate eqn.

$$\text{Overall order of reaction} = m + n$$

- **Half-life, $t_{\frac{1}{2}}$:** time taken for conc. of one of the reactants to fall by half

4.3 Order of Reaction

Order	Half-life, $t_{\frac{1}{2}}$	Graph of	
		Conc./Time	Rate/Conc.
$[A]^0$	Decreases	conc. of A time	rate conc. of A
$[A]^1$	Constant	conc. of A time	rate conc. of A
$[A]^2$	Increases	conc. of A time	rate conc. of A

- For zero order, rate of reaction not dependant on conc. of that reactant but it is need for completion of reaction. Reaction continues until all of that reactant is used up.
- Recognize shapes above in graphs given to work out order of reactant and construct rate equation. Calculate k using data from graph(s).

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Constructing rate equation using conc. data:

Using following data from the experiments construct a rate equation and calculate rate constant.

Exp.	Initial [A] / mol dm ⁻³	Initial [B] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.040	0.030	4.0×10^{-4}
2	0.040	0.045	6.0×10^{-4}
3	0.060	0.045	9.0×10^{-4}

Solution:

Use data and deduce orders by looking at changes in conc. and rates (arrows added above):

Order of A = 1

Order of B = 1

Write as rate equation

$$R = k[A][B]$$

Calculate k using data given from e.g. experiment 1

$$k = \frac{R}{[A][B]} = \frac{4.0 \times 10^{-4}}{0.040 \times 0.030} = \frac{1}{3}$$

$$\therefore R = \frac{1}{3}[A][B]$$

4.4 Calculating Rate Constant from $t_{1/2}$

- Only used with first order reactions
- Use the relationship:

$$k = \frac{0.693}{t_{1/2}}$$

4.5 Relationship of Temperature and k

- Increasing the temperature, increases the value of k

$$k = \frac{R}{[A][B]}$$

- When temp. is increased, the k.e. of reacting molecules increases resulting in more successful collisions
- Reactants change faster to products therefore conc. of reactants decreases.
- Using fraction above, numerator increases and denominator gets smaller $\therefore k$ increases.

4.6 Reaction Mechanism

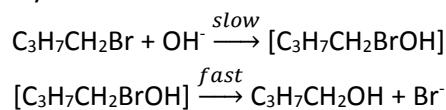
- Rate-determining step:** the slowest step in a reaction mechanism

In a multistep reaction:

- The rate of reaction is dependent on the slowest step that needs the highest activation energy.
- Rate equation includes only reactants that are present in the rate-determining step.
- The orders with respect to the reactants are the moles of the reactants in the rate determining step

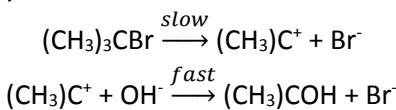
Hydrolysis of Alkyl Halide

- Primary alkyl halide mechanism:



$$\therefore R = k[\text{C}_3\text{H}_7\text{CH}_2\text{Br}][\text{OH}^-]$$

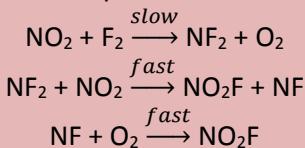
- Tertiary alkyl halide mechanism:



$$\therefore R = k[(\text{CH}_3)_3\text{CBr}]$$

Constructing rate equation for multistep reaction

The mechanism for the production of NO_2F involves



- What is the overall stoichiometric equation?
- Write a rate equation for the reaction.

Solution:

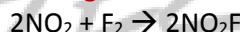
Part (a)

List all the reactants together and products together

Reactants: $\text{NO}_2 + \text{F}_2 + \text{NF}_2 + \text{NO}_2 + \text{NF} + \text{O}_2$

Products: $\text{NF}_2 + \text{O}_2 + \text{NO}_2\text{F} + \text{NF} + \text{NO}_2\text{F}$

Cancel the common things and form equation



Part (b)

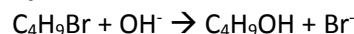
Rate equation will include only reactants of slowest step therefore:

$$R = k[\text{NO}_2][\text{F}_2]$$

4.7 Measuring Reaction Rates

Sampling: method that involves taking small sample of a reaction mixture at various times and then carrying out chemical analysis on sample.

- Chemical Analysis:**



- Sampled removed at various times and quenched – stopping/slowing down reaction (e.g. cooling in ice)
- OH^- conc. can be found using titration
- Plot graph and calculate rate of reaction

Continuous: method that involves monitoring a physical property over a period of time

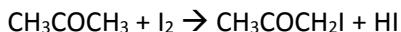
- Change in Volume of Gas Produced:**



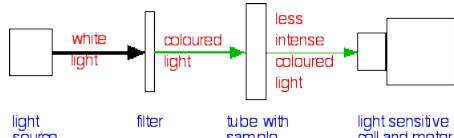
- Measure change in volume of gas using a gas syringe
- Take down readings at regular intervals
- Plot graph and calculate rate of reaction

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• Changes in Colour:



- I₂ starts brown, fades through orange to yellow to colourless as iodine used up.
- Colorimeter measures amount of light absorbed as it passes through solution; recorded as absorbance.



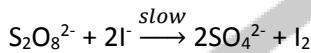
- Before experiment, create calibration curve by finding absorbance of different conc. I₂ and plot a graph of concentration against absorbance
- During experiment, measure absorbance from meter at regular intervals, and use calibration curve to convert values into concentrations

4.8 Homogeneous Catalysis

- Catalyst and reactants in same physical state
- Catalyst takes part in reaction:
 - Forms intermediate with reactant
 - Intermediate breaks down giving product
- Rate of reaction dependant on conc. of catalyst

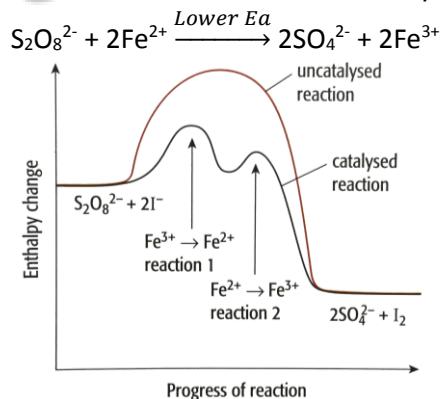
4.9 Examples of Homogenous Catalysis

Iodine-Peroxodisulfate Reaction

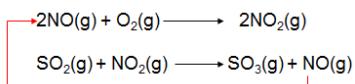


Mechanism of the catalysed reaction:

- Reaction 1: reduction of Fe³⁺ to Fe²⁺ ions by I⁻ ions
- Reaction 2: oxidation of Fe²⁺ to Fe³⁺ ions by S₂O₈²⁻ ions



Oxides of Nitrogen and Acid Rain



- SO₃ can then react with water to form H₂SO₄

4.10 Heterogeneous Catalysis

- Catalyst and reactants in different physical state
- Catalyst provides surface on which reaction occurs
 - Reactant particles adsorbed on surface on collision with catalyst
 - Molecular rearrangement occurs - bonds in reactants break and new bonds in product formed
 - Product molecules desorbed from surface
- Rate of reaction dependant on surface area of catalyst
- **Adsorption:** weak bonds formed between reactant molecules & surface of catalyst (diffusion on to surface)
- **Desorption:** releasing of product molecules from surface of catalyst (diffusion away from surface)

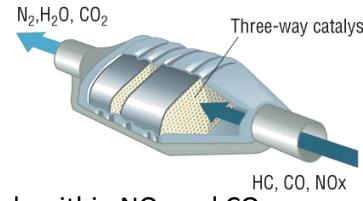
4.11 Examples of Heterogeneous Catalysis

Iron in Haber process:

$\text{N}_2 + 3\text{H}_2 \xrightarrow{\text{Fe}} 2\text{NH}_3$	
• Diffusion of N ₂ and H ₂ to the surface of iron	
• Adsorption; bonds formed between reactant and iron <ul style="list-style-type: none"> ○ Strong enough to weaken covalent bonds within N₂/H₂ ○ Weak enough to break and allow products to leave 	
• Reaction; adsorbed N and H atoms react to form NH ₃	
• Desorption; bonds break between NH ₃ and surface	
• Diffusion of NH ₃ away from surface of iron	

Transition Elements in Catalytic Converters:

- Honeycomb structure containing small beads coated with Pt, Pd and Rh
- Possible catalytic process:
 - Adsorption of NO_x and CO
 - Weakening of covalent bonds within NO_x and CO
 - Formation of new bonds between
 - Adjacent N atoms form N₂
 - CO and O atoms form CO₂
 - Desorption of N₂ and CO₂



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5. CHEMISTRY OF TRANSITION ELEMENTS

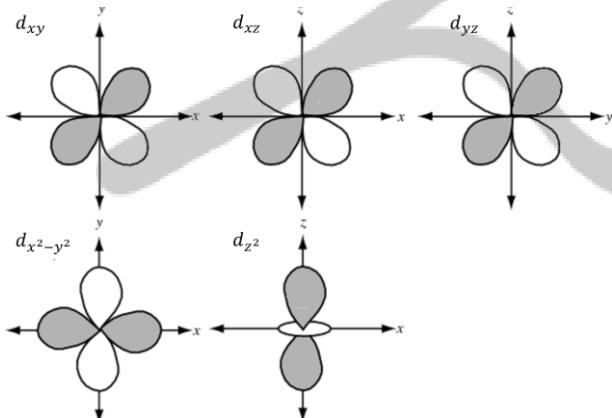
- **Transition element:** a d-block element that forms one or more stable ions with incomplete d orbitals

5.1 Electronic Configurations

Element	Electronic Config.	Oxidation States
Sc, scandium	[Ar] 3d ¹ 4s ²	+3
Ti, titanium	[Ar] 3d ² 4s ²	+3, +4
V, vanadium	[Ar] 3d ³ 4s ²	+2, +3, +4, +5
Cr, chromium	[Ar] 3d ⁵ 4s ¹	+3, +6
Mn, manganese	[Ar] 3d ⁵ 4s ²	+2, +4, +6, +7
Fe, iron	[Ar] 3d ⁶ 4s ²	+2, +3
Co, cobalt	[Ar] 3d ⁷ 4s ²	+2, +3
Ni, nickel	[Ar] 3d ⁸ 4s ²	+2
Cu, copper	[Ar] 3d ¹⁰ 4s ¹	+1, +2
Zn, Zinc	[Ar] 3d ¹⁰ 4s ²	+2

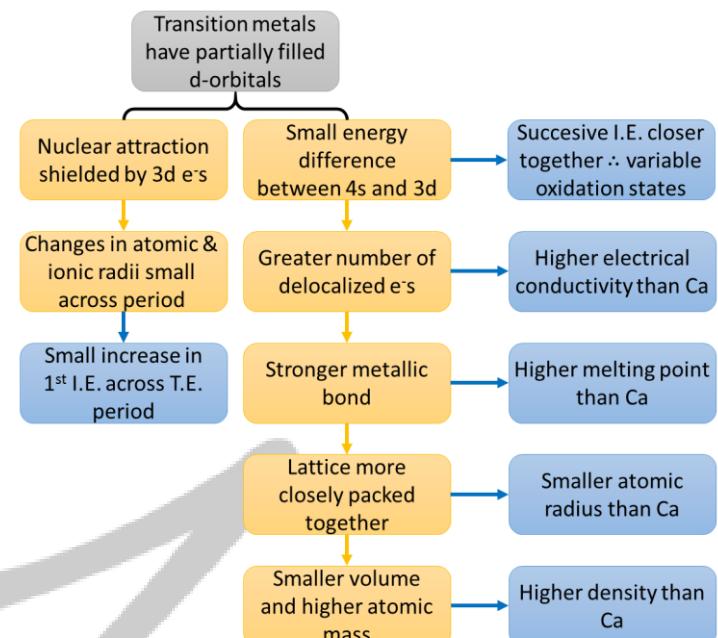
- Scandium and Zinc are not transition metals because:
 - Sc³⁺ has no e⁻s in the d-orbital
 - Zn²⁺ contains a full d-orbital
- Chromium and copper have anomalous configurations
 - Cr: 4s electron demoted to half-fill 3d shell
 - Cu: 4s electron demoted to full-full 3d shell creating a more stable configuration.
- When electrons added, fill 4s before 3d
- When electrons removed, remove from 4s before 3d

5.2 d-Orbitals



- d_{xy}, d_{xz} and d_{yz} have d-orbitals in between axis
- d_{x^2-y^2} and d_{z^2} have d-orbitals along axis
- d_{z^2} is formed by the merging of d_{x^2-z^2} and d_{y^2-z^2}

5.3 Physical Properties



5.4 Variable Oxidation States

- Small energy difference between 4s and 3d so electrons from both subshells can be removed to form a variety of oxidation states
- All transition metal exhibit two or more oxidation states
- Most common oxidation state +2 when 2e⁻s from 4s lost
- Transition elements show highest oxidation states when they combine with O or F (most electro-ve)
- When transition elements form compounds with high oxidation states above +4, they form large oxoanions and are covalent (acidic oxides) e.g. CrO₄⁻ or MnO₄⁻
- When transition elements in lower oxidation states they form ionic compounds (basic oxides)

5.5 Complexes

- **Complex:** is an ion or molecule formed by a central metal atom/ion surrounded by one or more ligands
- A complex consists of:
 - **Central transition metal ion (+ve)** that can accept e⁻s
 - **Ligand (-ve):** a species that contains a lone pair of e⁻s that forms a dative bond to a central metal atom/ion
- **Coordination no.:** number of coordinate or dative bonds to the central metal atom/ion
- Different metal ions show different coordination number with same ligands

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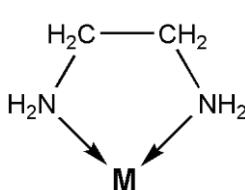
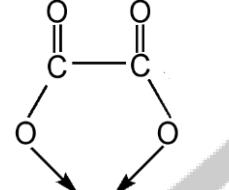
- Transition metals form complexes because
 - Ions are small in size so they have a strong electric field around them which attract e⁻-rich ligands
 - They have empty 4s and 4p orbitals that are hybridised and can accept e⁻

5.6 Ligands

- Monodentate ligands:** forms only one coordinate bond with central metal ion (donates one pair of e⁻s)

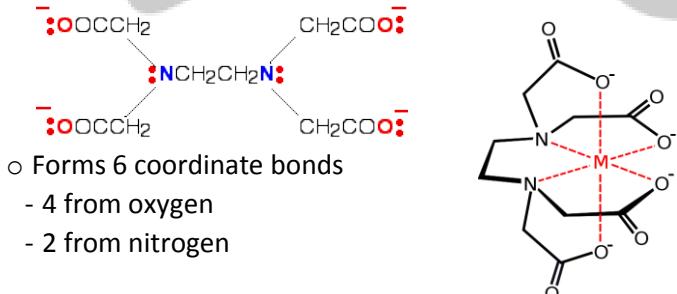
Anions	Neutral Ligands
Halide ions	F ⁻ , Cl ⁻ , Br ⁻ , I ⁻
Sulphide	S ²⁻
Nitrite	NO ₂ ²⁻
Hydroxide	OH ⁻
Cyanide	CN ⁻
Thiocyanate	SCN ⁻
Water	H ₂ O
Ammonia	NH ₃
Carbonyl	CO

- Bidentate ligands:** forms 2 coordinate bonds with central metal ion (donates 2 pairs of e⁻s per molecule)

	
H ₂ N – CH ₂ – CH ₂ – NH ₂ Ethylene diamine (en) (neutral)	O – CO – CO – O ⁻ Oxalate ion (oxalato-)

- Polydentate ligands:** forms 2 or more coordinate bonds with central metal ion

Ethylene Diamine Tetra Acetic Acid (EDTA)



5.7 Writing Names of Complexes

- To represent coordination number
 - For monodentate ligands, use prefixes mono-, di-, tri-, tetra-, hexa-
 - For bi and polydentate ligands, use prefixes mono-, bis-, tris-, tetrakis-, pentakis-

- Name the ligands

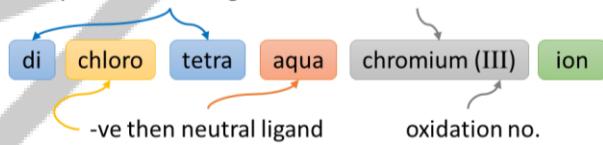
- If neutral and -ve ligands present, first name -ve ligand
- If ligands all neutral/-ve or contain more than one of each, name in alphabetical order

Anions	Neutral Ligands
• Fluoro (F ⁻), Chloro (Cl ⁻)	• Amine (NH ₃)
• Cyano (CN ⁻)	• Aqua (H ₂ O)
• Hydroxo (OH ⁻)	

- Name central metal ion

- If complex ion +ve/neutral – use normal name
- If complex ion -ve, use name ending -ate; special:
 - Iron = Ferrate
 - Lead = Plumbate
 - Copper = Cuprate

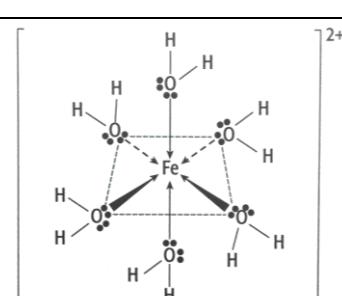
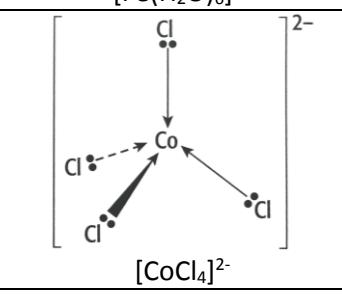
- Oxidation no. of metal ion in Roman numeral and 'ion' prefix for each ligand metal cation



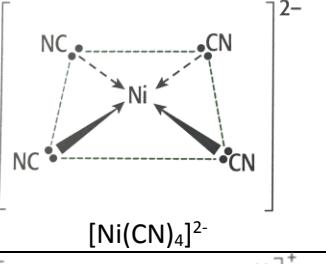
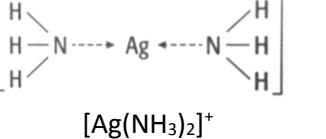
5.8 Writing Formulae of Complexes

- Metal ion written first followed by ligand
- Place charge on formula in square brackets
 - Total charge on complex = sum of charge on metal ions and charge on ligand
 - If ligands all neutral, charge on complex = charge on metal ion

5.9 Shapes of Complexes

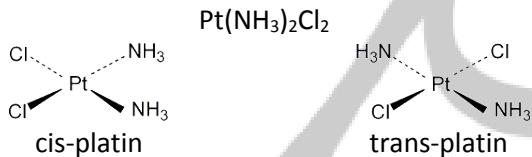
Coordination No. & Shape	Diagram
6 Octahedral	 [Fe(H ₂ O) ₆] ²⁺
4 Tetrahedral	 [CoCl ₄] ²⁻

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4 Square Planar (most Ni and Pt)	 <p>$[Ni(CN)_4]^{2-}$</p>
2 Linear	 <p>$[Ag(NH_3)_2]^+$</p>

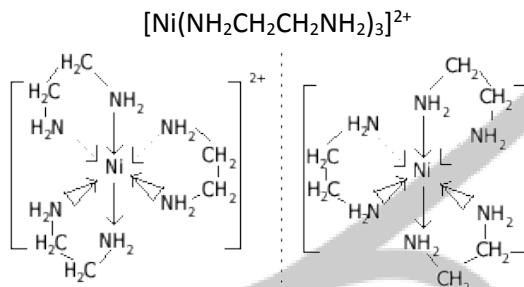
5.10 Stereoisomerism

Geometric isomerism (cis-trans)



- Cis-platin is an anticancer drug that acts by binding to DNA in cancer cells, preventing cell division

Optical isomerism

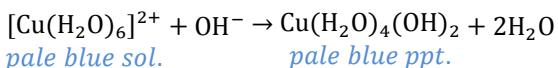


5.11 Common Complexes

Ligand	$Cu(II)$	$Co(II)$
H_2O	$[Cu(H_2O)_6]^{2+}$	$[Co(H_2O)_6]^{2+}$
NH_3 (drops)	$Cu(H_2O)_4(OH)_2$	$Co(H_2O)_4(OH)_2$
NH_3 (excess)	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	$[Co(NH_3)_6]^{2+}$
OH^-	$Cu(H_2O)_4(OH)_2$	$Co(H_2O)_4(OH)_2$
Cl^-	$[CuCl_4]^{2-}$	$[CoCl_4]^{2-}$

5.12 Copper Chemistry

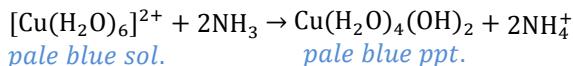
Reaction with Hydroxide Ions



- Not ligand exchange; hydroxide ions remove hydrogen ions from water ligand

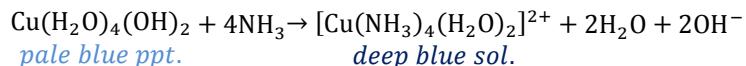
Reaction with Ammonia Solution

Small amount of ammonia



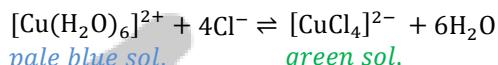
- Initially, ammonia acts as a base and hydrogen ions are pulled off the hexaaqua ion as above.

Excess ammonia



- Ammonia replaces water as a ligand
- Only 4 of the 6 water molecules replaced

Reaction with Chloride Ions

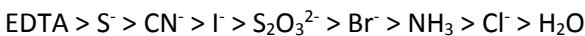


- 6 water molecules replaced by 4 chloride ions

5.13 Ligand Exchange and Stability Constant

- **Ligand exchange:** a more powerful ligand will substitute a less powerful ligand from a cation of the complex and this can produce a change in colour and shape

Strength of Different Ligands:

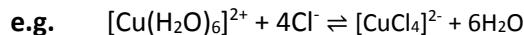


strongest → weakest

- Exchange of ligands can be explained in terms of completing equilibria of forward & backward reaction
- Equilibrium position lies towards more stable complex
- Adding excess weak ligand can shift equilibrium backward and form weaker complex

- **Stability constant, K_{stab} :** the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions or molecules

- Water not included in K_{stab} expression because concentration almost constant



$$K_{stab} = \frac{[[CuCl_4]^{2-}]}{[[Cu(H_2O)_6]^{2+}[Cl^-]^4]}$$

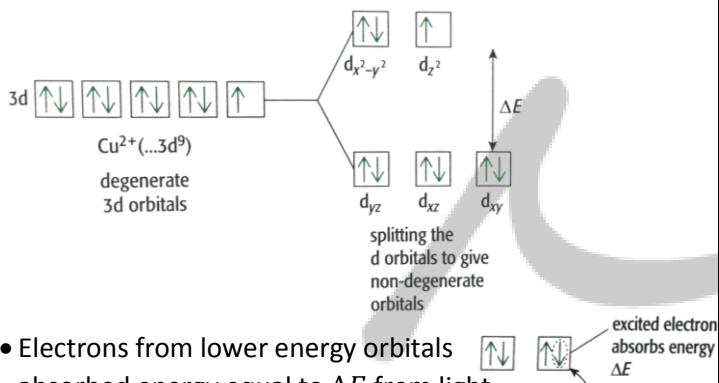
Units = mol⁻⁴ dm¹²

- Stability constants are used to compare stability of any two ligands
- The greater the K_{stab} value, the more stable the complex
- K_{stab} values may be given on log₁₀ scale as values large
- Stability constants for complexes with bi/polydentate ligands very high

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5.14 Colour of Complexes

- The five d-orbitals in isolated transition metal atoms/ions are **degenerate**; all at the same energy
- Coordinate bonding from ligands cause five d-orbitals to split into two sets of non-degenerate orbitals at ΔE
- For octahedral complexes, ligands approach along axis and increases repulsion with $d_{x^2-y^2}$ and d_{z^2} orbital causing them to be at higher energy
- e.g. an octahedral complex of Cu^{2+}



- Electrons from lower energy orbitals absorbed energy equal to ΔE from light and are excited to a higher energy level orbital
- Wavelengths of light equivalent to ΔE are absorbed and the rest are transmitted.
- Wavelengths transmitted merged together corresponds to the colour of the solution observed

Conditions for complex to be coloured:

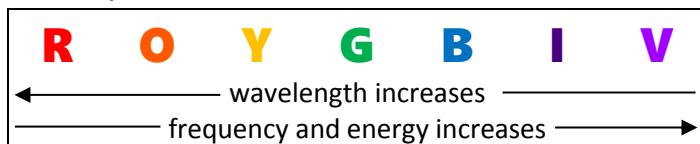
- At least one d-orbital must be occupied by an e^-
- At least one d-orbital must not be fully occupied
- Hence, some compounds of d-block metals colourless:
 - All Sc compounds colourless because $[\text{Ar}] 3d^0$
 - All Zn compound colourless because $[\text{Ar}] 3d^{10}$

Factors that determine colour of complex:

- Magnitude of ΔE
- Strength of ligands
- Oxidation state of metal ion
- Geometry of complex

affect splitting of d-orbitals

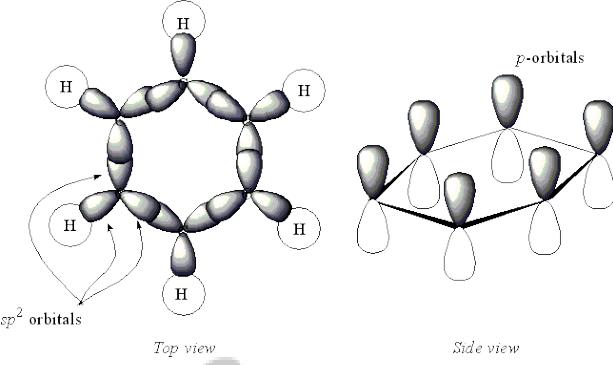
Colour Spectrum



- Large ΔE = light absorbed from blue = complex red-ish
- Small ΔE = light absorbed from red = complex blue-ish

6. ARENES

6.1 Bonding in Benzene Ring



$$\text{C} - \text{C} \text{ bond length equal} = 0.139\text{nm}$$

- Benzene is a symmetrical flat hexagonal planar molecule
- Consists of 6 C – C single bonds and remain electrons exist in delocalized system
- All C – C bonds are the same length (0.14nm) which are smaller than a single bond but greater than a double
- Each carbon forms 3 sigma bonds (sp^2 hybrid)
- o 2 between carbon and carbon (on either side)
- o 1 between carbon and hydrogen
- A p-orbital from each C atom overlaps above and below the plane of the ring forming two continuous loops; each C atom donates 1 electron into this π bond (delocalized)

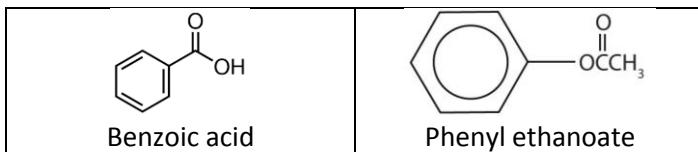
6.2 Properties of Benzene

- Clear, colourless, non-polar liquid at r.t.p
- It is volatile and has a low b.p.
- Relatively unreactive due to strong bonding
- Burns with smoky flame

6.3 Naming Aromatic Compounds

Name with Benzene	Name with Phenyl
Chlorobenzene	Phenol
Methylbenzene	Phenylethene
Nitrobenzene	Phenylamine

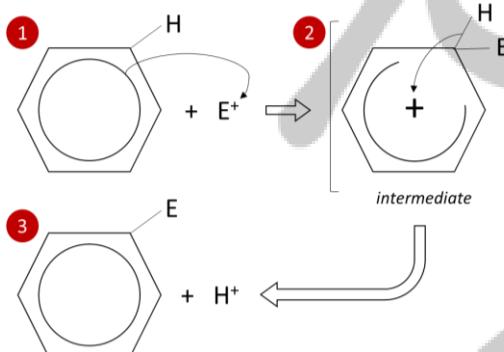
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6.4 Electrophilic Substitution Mechanism

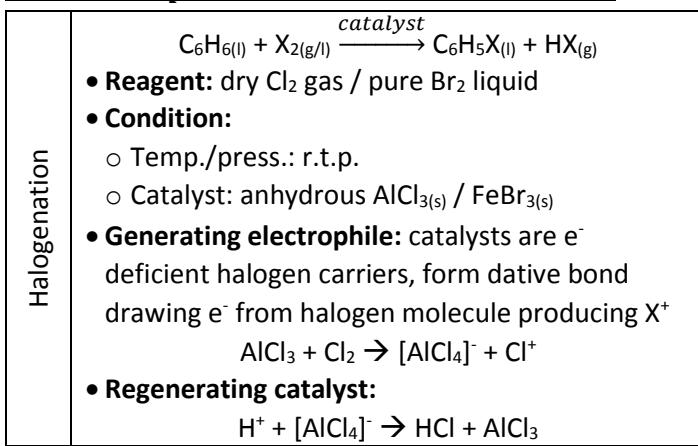
- An H-atom on the ring can be substituted by other atoms/groups
- All carbon atoms identical and benzene ring symmetrical hence any H-atom can be substituted
- An electrophile (E^+) can attack the ring of π e⁻s but benzene highly stable so E^+ must be very strong.
- A +ve ion can be generated by heterolytic fission of a covalent bond hence catalyst needed to generate E^+

Mechanism:



- E^+ attacks π e⁻ ring, accepting a pair of e⁻ from benzene
- An intermediate +ve specie is formed in which +ve charge is delocalized around the ring (more stable than a normal carbocation)
- Proton eliminated from +ve intermediate to restore stability and π system of delocalized e⁻s reformed

6.5 Electrophilic Substitution Reactions



Nitration	$C_6H_6(l) + H_2SO_4/HNO_3 \rightarrow C_6H_5NO_2(l) + H_2SO_4(g) + H_2O$ <ul style="list-style-type: none"> Reagent: nitrating mixture conc. HNO_3 / conc. H_2SO_4 Condition: <ul style="list-style-type: none"> Temp.: 45-55°C under reflux Generating electrophile: formation of nitrile ion $2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + NO_2^+ + H_3O^+$ Regenerating catalyst: $2HSO_4^- + H_3O^+ + H^+ \rightarrow 2H_2SO_4 + H_2O$
Alkylation / Acylation	$C_6H_6(l) + RCl/RCOCl \xrightarrow{AlCl_3} C_6H_5R/C_6H_5RCO + HCl(g)$ <ul style="list-style-type: none"> Reagent: alkyl halide (RCl) / acyl chloride (RCOCl) Condition: <ul style="list-style-type: none"> Temp.: heat under reflux Catalyst: anhydrous $AlCl_3$ Generating electrophile: $AlCl_3 + RCl/RCOCl \rightarrow [AlCl_4]^- + R^+/RCO^+$ Regenerating catalyst: $H^+ + [AlCl_4]^- \rightarrow HCl + AlCl_3$

6.6 Electrophilic Addition Reaction

Hydrogenation	$C_6H_6(l) + 3H_2(g) \xrightarrow{\text{nickel}} C_6H_{12}$ <ul style="list-style-type: none"> Type of reaction: electrophilic addition Reagent: hydrogen gas (H_2) Condition: <ul style="list-style-type: none"> Temp.: 150°C Catalyst: nickel
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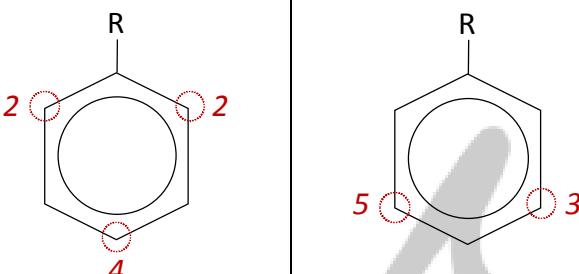
6.7 Side Chain Reactions

Chloromethyl Benzene	$C_6H_5CH_3(l) + Cl_2(g) \rightarrow C_6H_5CH_2Cl(l) + HCl$ <ul style="list-style-type: none"> Type of reaction: free radical substitution Reagent: $Cl_2(g)$ Condition: u.v. light With excess Cl_2 a mixture of di, tri chloromethyl benzene can be obtained
Benzonic Acid	$C_6H_5CH_3(l) + 3[O] \rightarrow C_6H_5COOH(l) + 2H_2O$ <ul style="list-style-type: none"> Type of reaction: oxidation Reagent: $KMnO_4(aq)$ or $K_2Cr_2O_7(aq)$ Condition: heat under reflux (2 to 3 hours) Alkyl gp. always oxidized regardless of chain length If more than one alkyl gp., each one oxidized

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6.8 Ring Activating/Deactivating Groups

Ring Activating	Ring Deactivating
Alkyls, NH ₂ , OH • Donates e ⁻ to the ring • +ve inductive effect • electro-sub faster • Increase e ⁻ density at position 2 and 4	Cl, NO ₂ , COOH • Withdraws e ⁻ from ring • -ve inductive effect • electro-sub slower • Sub. occurs at pos. 3 & 5



7. HALOARENES

7.1 Reactivity of Benzene & Chlorobenzene

Chlorobenzene is less reactive than benzene because:

- Chlorine is a ring deactivating group
- Chlorine is more electronegative than carbon, and draws electrons in the ring towards itself.
- Hence electron density around ring decreases, less attractive for electrophiles and so reaction is slower

7.2 Reactivity of Haloarenes & Haloalkenes

The halogen atom in halogenoarene is much less reactive than that in a halogenoalkane

- Lone pair of e⁻s of Cl overlap slightly with p orbitals of benzene ring giving C–Cl a double bond character
- Makes C–X bond much stronger therefore nucleophilic substitution difficult
- High density of e⁻s on benzene ring tends to repel the approaching -ve charged nucleophile.

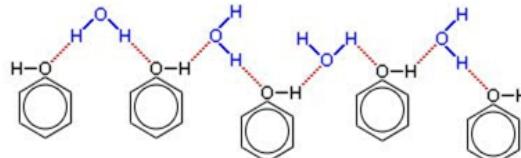
7.3 Nucleophilic Substitution Reaction

Hydrolosis $\text{C}_6\text{H}_5\text{Cl}_{(l)} + \text{NaOH}_{(aq)} \rightarrow \text{C}_6\text{H}_5\text{OH}_{(l)} + \text{NaCl}_{(aq)}$ • Type of reaction: nucleophilic substitution • Reagent: sodium hydroxide • Condition: <ul style="list-style-type: none"> ◦ Temp.: 300-330°C ◦ Press.: 150-300 atm • Rate of Hydrolosis: (slowest to fastest) 
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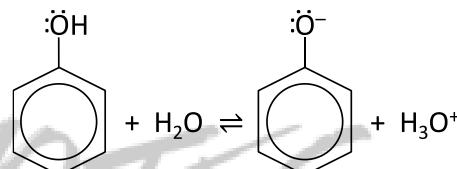
8. PHENOL

- Phenol is an aromatic alcohol; a white crystalline solid that is both corrosive and anesthetic
- OH group is ring activating so phenol more reactive than benzene and substituents attached at positions 2,4 and 6

8.1 Solubility and Acidity of Phenol



- OH group forms H-bonds with water molecules however there are weak VDW forces due to heavy nonpolar benzene ring hence phenol partially soluble in water
- Solution of phenol is slightly acidic because –OH in phenol breaks to form H⁺
- Bond breaks readily because phenoxide ion formed is stabilized by partial delocalization of -ve charge over the benzene ring



- The conjugate base (phenoxide) is stable and less likely to react with H⁺ going back to phenol

8.2 Acid-Base Reactions

Reaction with Base $\text{C}_6\text{H}_5\text{OH}_{(l)} + \text{NaOH}_{(aq)} \xrightarrow{\text{r.t.p.}} \text{C}_6\text{H}_5\text{O}^-\text{Na}^+_{(aq)} + \text{H}_2\text{O}$ • Type of reaction: neutralization • Reagent: sodium hydroxide • Condition: r.t.p. • Regenerating phenol: <ul style="list-style-type: none"> ◦ When strong acid (HCl) added to solution of sodium phenoxide, phenol regenerated $\text{C}_6\text{H}_5\text{O}^-\text{Na}^+_{(aq)} + \text{HCl}_{(aq)} \rightarrow \text{C}_6\text{H}_5\text{OH}_{(l)} + \text{NaCl}$ <ul style="list-style-type: none"> ◦ Initially dense white emulsion formed then slowly oily liquid layer of phenol separates
Reaction with Sodium $\text{C}_6\text{H}_5\text{OH}_{(l)} + \text{Na}_{(s)} \xrightarrow{\text{r.t.p.}} \text{C}_6\text{H}_5\text{O}^-\text{Na}^+_{(aq)} + \frac{1}{2}\text{H}_2\text{g}$ • Type of reaction: metal and acid • Reagent: sodium metal • Condition: r.t.p. <ul style="list-style-type: none"> • Reacts with Na liberating H₂ gas • Note: phenol does not react with metal carbonate to liberate CO₂ hence shows its fairly weaker than other carboxylic acids

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8.3 Reaction with Benzene Ring

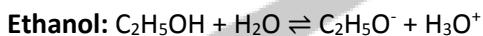
Bromination	<p> • Type of reaction: electrophilic substitution • Reagent: aq. bromine • Condition: r.t.p. (no catalyst) • Rapid reaction, forms a white ppt. • No catalyst needed since Br₂ molecule easily polarized by increase e⁻ density in ring </p>
Nitration	<p> • Type of reaction: electrophilic substitution • Reagent: dilute nitric acid • Condition: r.t.p. • If concentrated nitric acid used, then trinitrophenol produced </p>

8.4 Relative Acidity

→ increasing acidity →



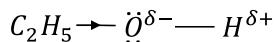
- The stronger the acid:
 - Higher the K_a value
 - More easily H⁺ is donated
 - More stable is the conjugate base



• K_a: 10⁻¹⁸ mol dm⁻³

• Ability to donate H⁺ ions:

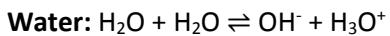
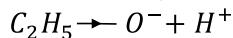
- C₂H₅ is an e⁻ donating gp. which increases charge density on O of OH



- More attraction between O-H so loss of H⁺ difficult

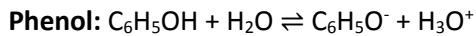
• Stability of conjugate base:

- In ethoxide ion, C₂H₅ gp. increases -ve charge
- Makes ethoxide ion more basic than OH⁻
- Ability to accept H⁺ increases, moving equi. to left



• K_a: 10⁻¹⁶ mol dm⁻³

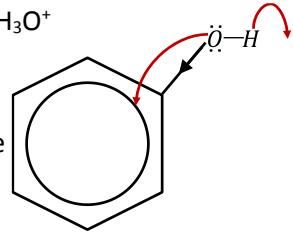
- No e⁻ donating or withdrawing gp. present hence ability to donate and accept H⁺ ion is the same



• K_a: 10⁻¹⁰ mol dm⁻³

• Ability to donate H⁺ ions:

- OH is a ring activating gp. & the lone pair of e⁻s on O becomes part of delocalized e⁻ system
- Decreases e⁻ density on O of OH and attraction between O and H decreases so H⁺ lost more easily



• Stability of conjugate base:

- In phenoxide ion, -ve charge on O delocalized around ring and reduces tendency to attract H⁺
- Conjugate base stable

8.5 Test for Phenol

Test 1:

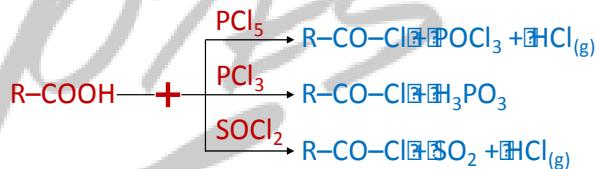
- Reagent: Iron(III) Chloride (FeCl_{3(aq)}) – yellowish brown
- Observation: violet color obtained

Test 2:

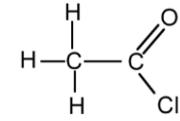
- Reagent: bromine water (Br_{2(aq)}) – orange
- Observation: white ppt. obtained

9. ACYL CHLORIDES

9.1 Preparation of Acyl Chlorides



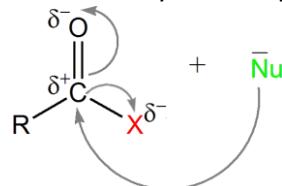
- These are derivatives of carboxylic acids; -OH gp. of acid replaced by Cl



- Named after corresponding acid using suffix -oyl followed by chloride e.g. ethanoyl chloride

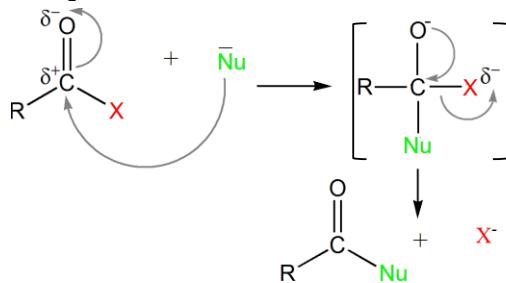
9.2 Reactivity of Acyl Chlorides

- Acid chlorides are much more reactive than the carboxylic acid from which they are derived
- Polarity of both C=O and C—Cl bond produces relatively large δ+ charge on the carbon, making it e⁻ deficient and more susceptible to attack by a nucleophile



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9.3 Nucleophilic Condensation Mechanism



- The carbonyl carbon being highly e⁻ deficient is attacked by nucleophile
- The Nu bonds to the carbon atom, the C=O bond is broken leaving O with -ve charge
- Chloride is lost and carbonyl double bond is reformed

9.4 Nucleophilic Condensation Reactions

Hydrolysis	$\text{R}-\text{CO}-\text{Cl}$ acid r.t.p alkali + H₂O → R-COOH_(aq) + HCl_(g) + NaOH → R-COO⁻ Na⁺_(aq) + H₂O_(l) + NaCl_(aq)
Forming Amides	<p>Primary amides: $\text{R}-\text{CO}-\text{Cl} + \text{NH}_3 \rightarrow \text{R}-\text{CO}-\text{NH}_2 + \text{HCl}$</p> <ul style="list-style-type: none"> Reagent: ammonia <p>Secondary amides: $\text{R}-\text{CO}-\text{Cl} + \text{R}'\text{NH}_2 \rightarrow \text{R}-\text{CO}-\text{NHR}' + \text{HCl}$</p> <ul style="list-style-type: none"> Reagent: alkylamine Note: If excess NH₃ used, the HCl formed is neutralized to NH₄Cl
Esterification	<p>$\text{R}-\text{CO}-\text{Cl} + \text{HO}-\text{R} \rightarrow \text{R}-\text{CO}-\text{OR}_{(aq)} + \text{HCl}_{(aq)}$</p> <ul style="list-style-type: none"> Reagent & Condition: <ul style="list-style-type: none"> Aliphatic alcohol at r.t.p Phenol dissolved in NaOH, warm it <p>Hydrolysis of esters:</p> <p style="text-align: center;"> under reflux acid alkali HCl_(aq) NaOH_(aq) $\text{R}-\text{COO}-\text{R}' + \text{H}_2\text{O} \rightleftharpoons \text{RCOOH} + \text{R}'\text{OH}$ RCOOH + NaOH_(aq) → RCOO⁻ Na⁺ + H₂O </p>

9.5 Relative Ease of Hydrolysis

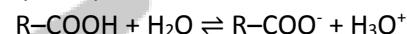
-increasing ease of hydrolysis→

Aryl Chlorides	Alkyl Chlorides	Acyl Chlorides
	R-Cl	

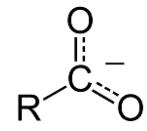
- Aryl chlorides do not undergo hydrolysis at r.t.p because the p-orbitals from chlorine overlap with delocalized p-electrons giving the C-Cl bond a double bond character
- Alkyl chlorides require a strong alkali (NaOH) under reflux to be hydrolyzed as carbon doesn't have a high δ+
- Acyl chlorides undergo hydrolysis with neutral water at r.t.p because the carbon atom is bonded to two highly electronegative atoms hence has a high δ+ therefore attack by a nucleophile is much more rapid

10. CARBOXYLIC ACIDS

- Carboxylic acids are weak acids and dissociate incompletely in aqueous solutions



- The O-H bond in carboxylic acid is weakened by the carbonyl group C=O



- The carboxylate ion is stabilized by the delocalization of e⁻s around the -COO⁻ group, spreading and reducing the density of -ve charge making it less likely to bond with H⁺

10.1 Relative Acidities of Carboxylic Acids

Acidity of carboxylic acids decreases as carbon chain length increases because:

- Alkyl groups are e⁻ donating groups which have a +ve inductive effect increasing strength of O-H bond, and making it more difficult to donate H⁺
- Alkyl groups increase -ve charge on ion formed when dissociated, making it easier to accept the H⁺ and reform the molecule

10.2 Chlorine Substituted Acids

Acidity of carboxylic acids increases when H atoms are substituted by electro-ve (withdrawing) atoms e.g Cl

- Chlorine atoms show a -ve inductive effect withdrawing -ve charge from the molecule, reducing the strength of the O-H, and hence making H⁺ be lost more easily
- Conjugate base is more stabilized due to the extended delocalization of the negative charge on the -COO⁻ and so less likely to bond with a H⁺ ion

Note:

- If an e⁻ donating gp. present → molecule less acidic
- If an e⁻ withdrawing gp. present → molecule more acidic

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10.3 Oxidation of Carboxylic Acids



Methanoic Acid	HCOOH + [O] → CO ₂ + H ₂ O
	<ul style="list-style-type: none"> With Tollens' Reagent: <ul style="list-style-type: none"> Ag⁺ gets reduced to silver – silver mirror formed With Fehling's Solution: <ul style="list-style-type: none"> Cu²⁺ gets reduced to Cu⁺ – copper(I) oxide (red) Note: can use stronger [O] agents; Mn or Cr
Ethanediolic Acid	$\text{HOOC}-\text{COOH} + [\text{O}] \rightarrow \text{CO}_2 + \text{H}_2\text{O}$ <ul style="list-style-type: none"> With warm Acidified Manganese(VII) - KMnO₄/H⁺: <ul style="list-style-type: none"> Purple/pink to colourless Note: can also use Acidified Dichromate(VI) <ul style="list-style-type: none"> Changes from orange to green

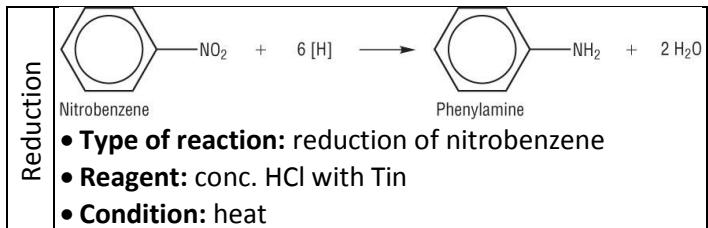
11. NITROGEN COMPOUNDS

Primary Amine	Secondary Amine	Tertiary Amine
$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N} \\ \\ \text{R}' \end{array}$	$\begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{N} \\ \\ \text{R}' \end{array}$

11.1 Formation of Alkyl Amines

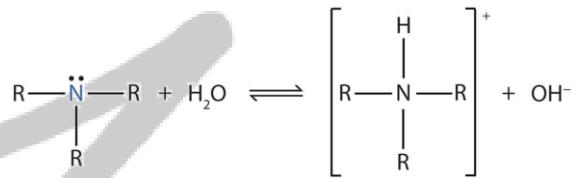
Substitution	$\text{R-X} + \text{NH}_3 \rightarrow \text{R-NH}_2 + \text{HX}_{(\text{g})}$ <ul style="list-style-type: none"> Type of reaction: nucleophilic substitution Reagent: hot conc. NH₃ in ethanol Condition: heat under reflux
Reduction	$\text{R-C}\equiv\text{N} + 4[\text{H}] \rightarrow \text{R-CH}_2\text{NH}_2$ <ul style="list-style-type: none"> Type of reaction: reduction of a nitrile Reagent: hydrogen gas Reducing Agents (catalyst): <ul style="list-style-type: none"> LiAlH₄ in dry ether Nickel Conditions: high temp. and pressure $\text{R-CO-NH}_2 + 4[\text{H}] \rightarrow \text{R-CH}_2\text{NH}_2 + \text{H}_2\text{O}$ <ul style="list-style-type: none"> Type of reaction: reduction of an amide Reagent: hydrogen gas Reducing Agent (catalyst): LiAlH₄ in dry ether Conditions: r.t.p.

11.2 Formation of Aryl Amines



11.3 Basicity of Amines

- Bases are proton acceptors (electron donors)
- N-atoms in amines have a lone pair of e⁻s
- N donates lone pair and accepts H⁺ forming dative bond

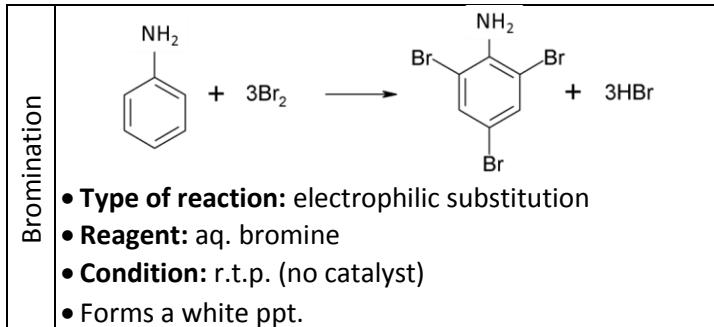


11.4 Relative Basicity

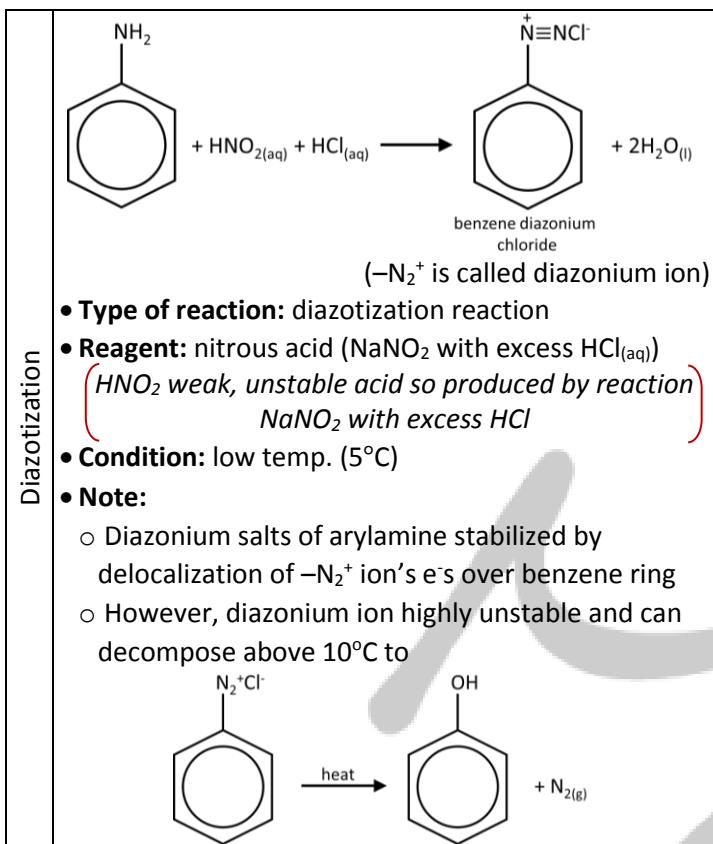
→ increasing basicity →

Phenylamine weaker than ammonia	Ammonia	Ethylamine stronger than ammonia
<ul style="list-style-type: none"> Lone pair of e⁻s on N gets partially delocalized by interaction with benzene e⁻ cloud Lone pair less available for coordination to proton 	Ammonia	$\text{CH}_3\text{CH}_2 \rightarrow \ddot{\text{N}}\text{H}_2$ <ul style="list-style-type: none"> Ethyl e⁻ donating group, increases e⁻ density on N Enhanced ability to donate lone pair of e⁻s to proton Alkyl ammonium cation formed more stable than NH₄⁺ cation from ammonia

11.5 Reactions of Phenylamine

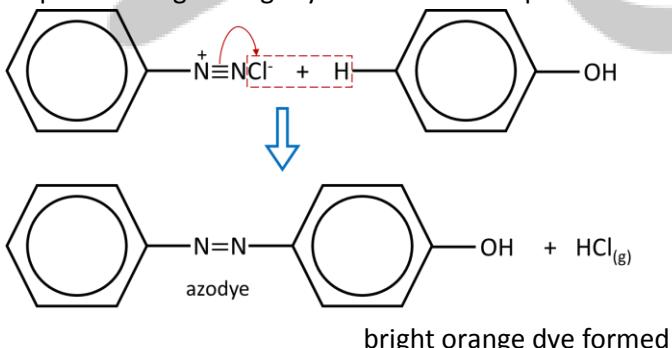


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11.6 Coupling Reactions of Diazonium Salts

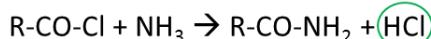
- **Type of reaction:** electrophilic substitution
- **Reagent:** aromatic amines or phenols
- Azo compounds are complex compounds involving a minimum of two aromatic rings joined by N=N coupling
- Benzene diazonium ion carries a +ve charge and readily reacts with cold alkaline solutions of aromatic amines and phenols to give brightly colored azo-compounds



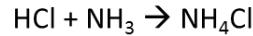
- By using alternative aryl compounds to phenol, a range of brightly colored dye can be formed.

11.7 Formation of Amides

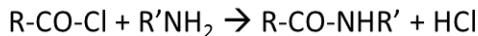
Primary Amides:



Excess NH_3

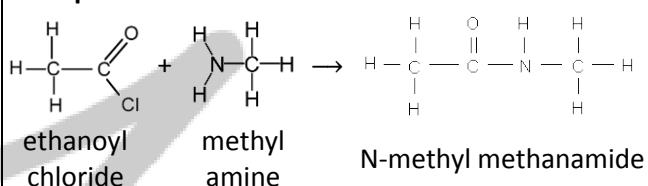


Secondary Amides:



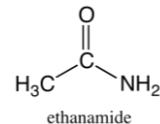
- **Type of reaction:** nucleophilic substitution
- **Reagent:** conc. $\text{NH}_3\text{(aq)}$
- **Condition:** r.t.p.

Example:

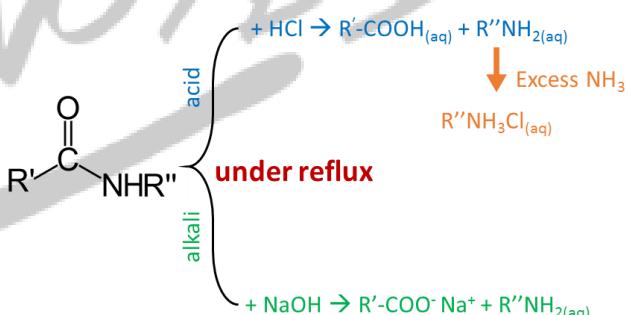


11.8 Neutrality of Amides

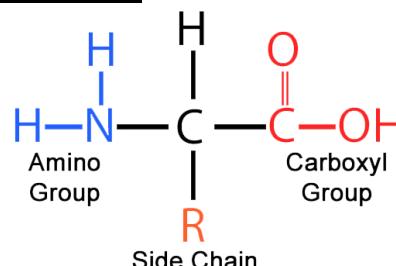
- The presence of the electron withdrawing oxygen atom means that the lone pair on the amide's nitrogen atom is not available to be donated to e.g. H^+ ions
- Hence, amides are neutral



11.9 Hydrolysis of Amides



11.10 Amino Acids

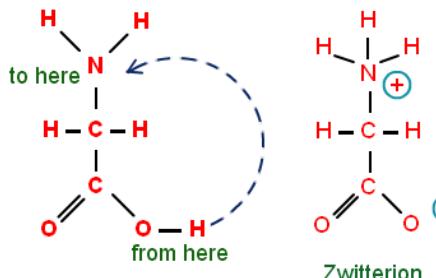


- **Optical activity:** all amino acids (except glycine) have a chiral carbon therefore they are optically active

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11.11 Acid/Base Properties of Amino Acids

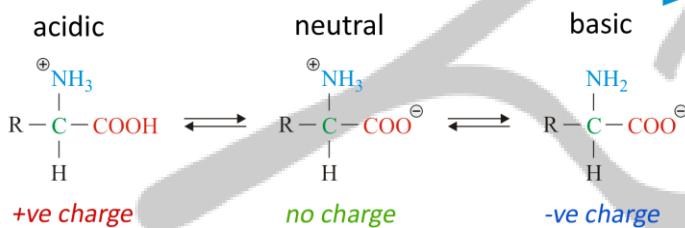
- Basic amino group and acidic carboxyl group interact:
 - Carboxyl group donates a proton to amino group
 - Amino group accepts proton and zwitterion formed



- Zwitterion:** ion that contains regions of +ve & -ve charge
- Amino acids solids at r.t.p. due to ionic bonds that exist between zwitterions
- Presence of zwitterions means that amino acids are soluble in water

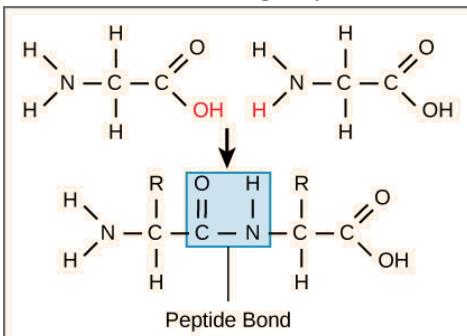
11.12 Amino Acids in Acidic/Basic Conditions

- If acid added, the COO^- part of the zwitterion accepts an H^+ ion, reforming COOH group, leaving +ve charge
- If alkali added, the NH_3^+ part of the zwitterion donates an H^+ ion to the OH^- , reforming NH_2 group and H_2O , leaving a -ve charge



11.13 Peptide Bonds

- Amide link formed by nucleophilic attack of NH_2 group of one amino acid on COOH group of another



- Reaction is a condensation reaction as H_2O eliminated

- Reaction can continue to occur as product still has NH_2 and COOH group present

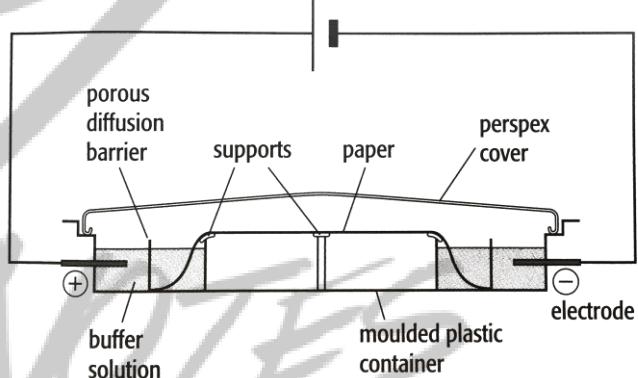
Dipeptide \rightarrow Tripeptide \rightarrow Polypeptide (protein)

- Proteins are polymers of amino acids; many polypeptide chains held together by intermolecular forces

- Hydrolysis:** involves breaking of peptide links by reaction with water catalyzed by an acid or alkali catalyst, giving back the amino acids, temp. nearly 90°C

11.14 Electrophoresis

- Electrophoresis** is used to separate, identify and purify amino acids obtained when protein hydrolyzed
- Technique based on separating ions placed in an electric field. When sample placed between two electrodes:
 - +ve charge ions move towards -ve charged electrode
 - ve charge ions move towards +ve charged electrode



- Sample placed on absorbent filter paper (or gel)
- Buffer solution carries ions along (back or forth)

Factors that Determine the Direction of Travel		Speed of Movement
• pH of buffer solution	• Charge on amino acid	• Voltage applied
• Charge on amino acid		• Temperature
		• Size (M_r) of amino acid
		• Magnitude of charge

• Larger ions with longer side chain move slower

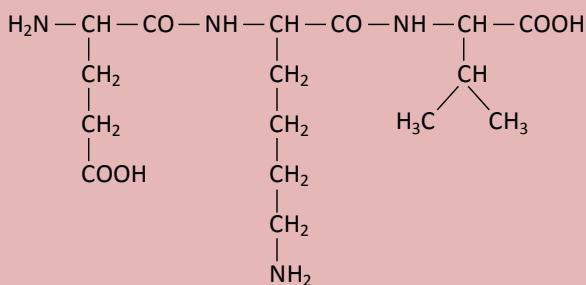
• More highly charge ions move faster

- When voltage applied, ions separate out producing a series of lines or bands on the paper or gel
- Series of bands called an **electropherogram**
- Bands made visible using chemical (ninhydrin) or sometimes ultraviolet light

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Hydrolysis and electrophoresis of a peptide

The peptide below is hydrolysed and the mixture is separated by electrophoresis.

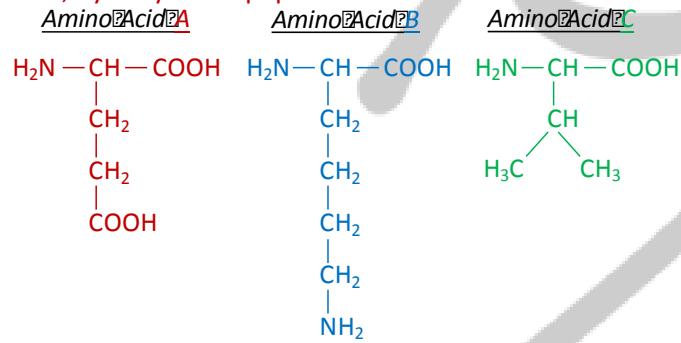


Sketch the pattern obtain when the buffer solution used is

- a. At pH 7.0
- b. At pH 12.0

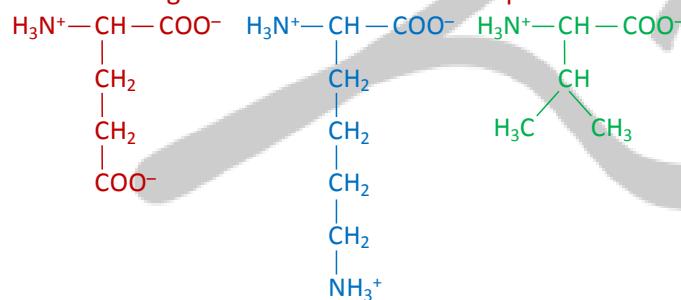
Solution:

First, hydrolyse the peptide and label each amino acid



Part (a)

Find the charge of each amino acid when pH is 7.0

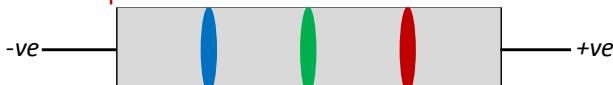


charge H_3N^+ 1 charge H_3N^+ 1 charge H_3C 0

The direction in which each amino acid will move

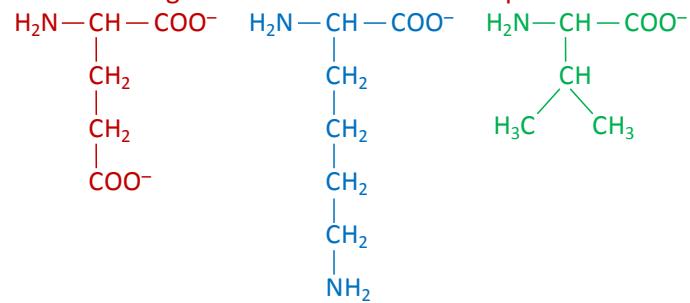
- A: moves to the +ve side as it has a -ve charge
- B: moves to the -ve side as it has a +ve charge
- C: remains in the middle as it has no charge

Sketch the pattern obtained



Part (b)

Find the charge of each amino acid when pH is 12.0



charge H_2N 2

charge H_2N 1

charge H_3C 1

The direction in which each amino acid will move

Each amino acid will move to the +ve side as they all have a negative charge but

- A: will move furthest as it has a -2 charge
- B: will not move far as it has a greater M_r than C
- C: will move further than B as it has a lower M_r

Sketch the pattern obtained



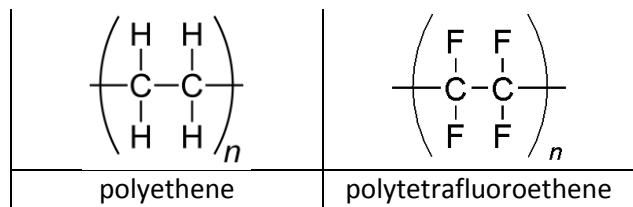
12. POLYMERISATION

12.1 Addition Polymerisation

- Monomers are alkenes; polymer formed is polyalkene
- Alkene joins to itself, no molecule lost
e.g. $nA \rightarrow -A-A-A-A-$ or $(-A-)_n$
- Molecular mass of polymer is multiple of monomer

Physical Properties of Polymers:

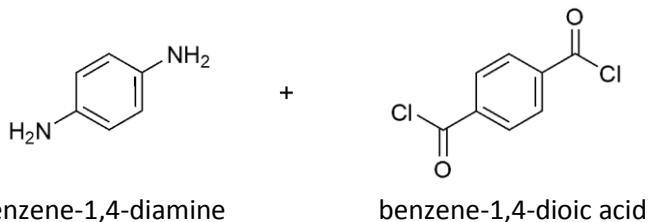
- Only C and H present = only VDW forces present
- Presence of Cl or F = dipoles = permanent dipole interaction
- Longer chains with fewer side chains have stronger VDW forces



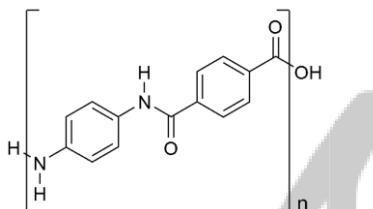
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Kevlar:

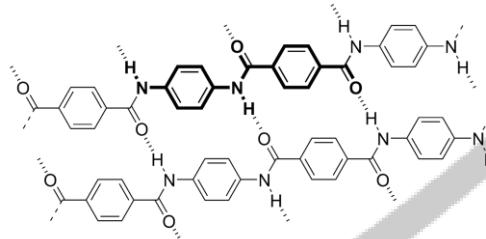
- Monomers:



- Polymer



- Extremely strong: delocalization of π electrons beyond benzene ring on to amide link, enhanced intermolecular bonding between polymer chains
- Flexible, strong, fire resistant and low density
- Hydrogen bonding between chains:



12.6 Proteins

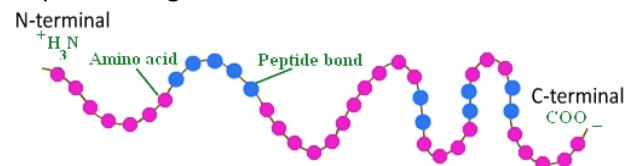
- Proteins: a natural polyamide; many polypeptide chains held together by intermolecular forces
- Amino acid residue: an amino acid unit within a polypeptide chain

Examples of Amino Acids:

Non-Polar R-Group:	Polar R-Group:
alanine	valine
Electrically Charged R-Group:	
aspartic acid	lysine

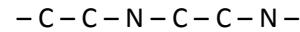
Primary structure: sequence of amino acids in the polypeptide chains

- Has an amino N-terminal and carboxylic C-terminal end
- Polypeptide chains synthesized from N-terminal hence amino acids numbered from N-terminal to C-terminal
- Primary structure stabilized by covalent bonds:
 - Bonds within amino acid residues
 - Peptide linkages between residues

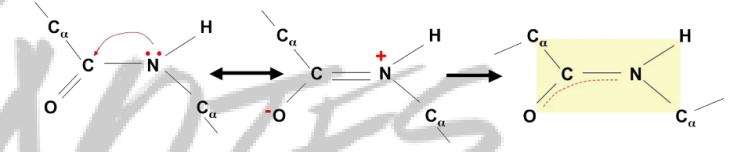


Secondary structure: a regular structural arrangement stabilized by H-bonding between NH group of one peptide bond and CO group of another peptide bond

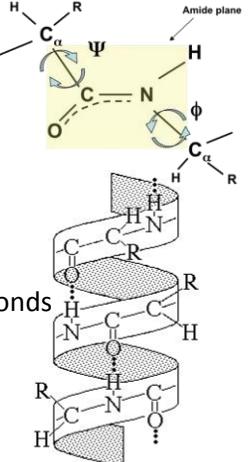
- Each polypeptide chain has a backbone of atoms that runs along the chain



- Restricted rotation about peptide links; the peptide bond has partial double bond characteristics



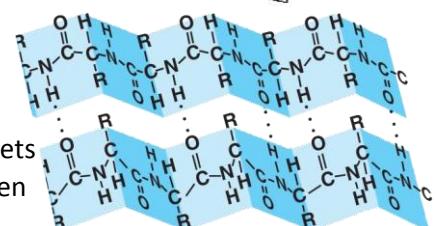
- Some points on the chain are flexible and allow free rotation around the bonds



Stable Secondary Structures:

α -helix:

- Polypeptide chain coiled in spiral
- Each peptide group involved in 2 H-bonds formed between every 4 amino acids
- H-bonds run down length of helix
- R-groups of amino acids project outwards from spiral



β -pleated sheets:

- Length of polypeptide chain lies fully stretched side by side forming sheets
- H-bonds formed between adjacent sections
- R-groups of amino acid point above and below the plane of the sheets

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Tertiary structure: the further folding of the polypeptide chain into a 3D shape.

Stabilized by attractive forces and bonding between R-groups:

Hydrogen bond

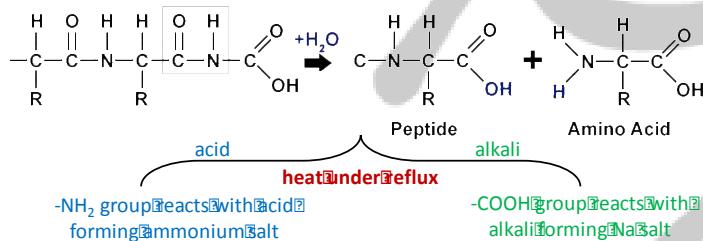
- Weak Van der Waals' forces between non-polar side chains

- Hydrogen bonding between polar R-groups

- Ionic bonds (salt bridges) between ionized R-groups

- Covalent disulfide bridges formed between cysteine

Hydrolysis of Proteins:



12.7 Structure of DNA

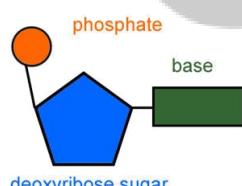
- DNA are polynucleotides; made by condensation polymerization of nucleotides.

Functions of deoxyribonucleic acid (DNA):

- Can make copies of itself so that genetic information can be passed on from generation to generation
- Contains sequence of bases that form genetic code used to synthesize proteins

Nucleotides in DNA are made up of:

- A sugar called deoxyribose
- A phosphate group
- A nitrogen-containing base

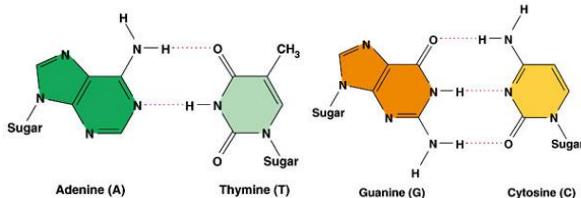


Nitrogen-containing bases:

Double Rings	Single Ring
adenine	thymine

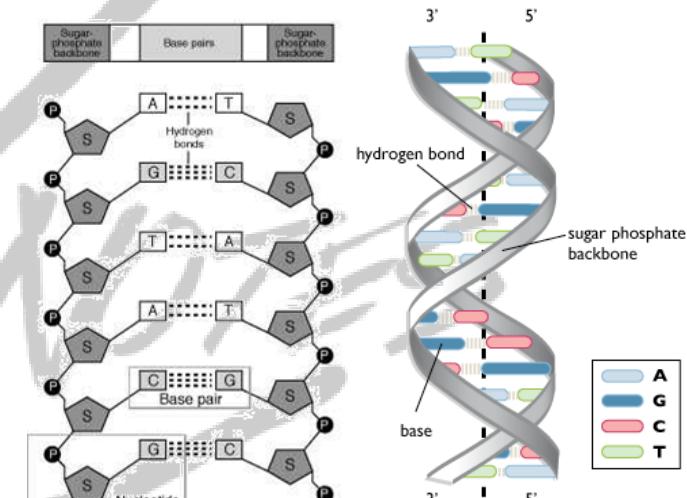
Double Rings	Single Ring
guanine	cytosine

- Complimentary base pairs:



Structure of DNA: consists of a double helix made up of two strands kept in place by H-bonds between N-bases

- Each strand has a backbone of alternating sugar and phosphate units; this is on the outside of the structure
- The 5th C of one nucleotide links with 3rd C of the next nucleotide (2 ester links with OH of sugar) forming sugar phosphate backbone; on the outside of the structure
- N-Bases are positioned between two sugar phosphate chain at right angles to the backbone on the inside, filling space between two strands so that the helix has a regular shape; stacked above each other
- Each strand has a direction: there will be a free 5th C in one end and a 3rd C on the other end
- Two strands run in opposite directions; antiparallel
- The structure of DNA is stabilized by:
 - Hydrogen bonds between base pairs
 - VDW forces between one base pair and the next



12.8 DNA Replication

- Process of copying DNA during cell division

Semi-conservative replication:

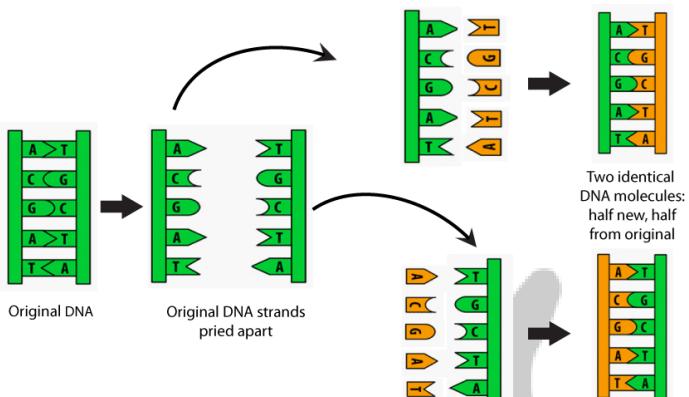
- H-bonds and VDWs between base pairs in part of a DNA are broken and this part of the double helix unwinds
- In the nucleus, there are nucleotides to which two extra phosphates have been added (nucleotide triphosphate)
- The bases of the nucleotide triphosphates pair up with complementary bases on the old strand and H-bonds & VDW forces form between original and new strands.
- Enzyme catalyzes the polymerization reaction

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- Each new strand contains a sequence of bases that is complimentary to the original strand e.g.

Original strand: –ATGCCGTTAAGT–

New strand: -TACGGCAATTCA-



- Significance of H-bonding in replication of DNA:

- When new strand strand built on template of old strand, the incoming nucleotide is selected for its ability to pair with base in the old strand
 - H-bonding plays an important role in the recognition as different number of H-bonds involved in each pair

12.9 Non-solvent based Adhesives

Silyl modified polymers (SMP):

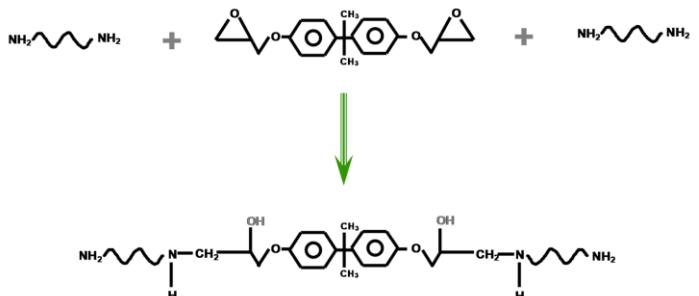
- A polymer that contains silicon bonded to oxygen
 - They set by reacting with moisture in air; water hydrolyses silicon-oxygen parts, forming cross-linkages
 - Effectively bonds polymer chains to each other with strong covalent bonds of siloxane cross-linkage

The diagram illustrates the hydrolysis of a silanol cross-linkage. On the left, a polymer chain with a silanol end group ($\text{H}_2\text{O} + \text{Si}(\text{OCH}_3)_2\text{H}_2\text{O}$) reacts with water (H_2O). An arrow labeled "hydrolysis" points to the right, where the silanol has hydrolyzed into a silanolane cross-linkage (OCH_3 $\text{Si} \text{---} \text{O} \text{---} \text{Si} \text{---} \text{OCH}_3$) and two molecules of methanol ($+2\text{CH}_3\text{OH}$).

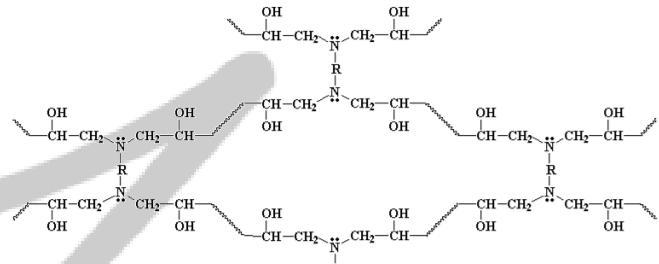
Epoxy Resins:

- Example of thermosets: polymers that form extensive networks of covalent cross-links
 - Very strong and cannot be melted and remolded
 - Formed by reacting a monomer with expoyethane (triangular molecule $\text{CH}_2\text{CH}_2\text{O}$) and a diamine are mixed

- For example:

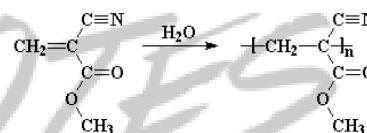


- The polymer produced forms a giant network of cross-linking with other polymers:



Superglue:

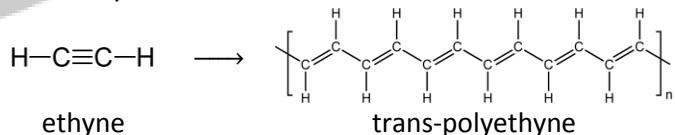
- Uses addition reaction to stick objects together
 - The monomer is $\text{CH}_2=\text{C}(\text{CN})\text{COOCH}_3$, methyl cyanoacrylate, and addition takes place across $\text{C}=\text{C}$



- Polymerisation initiated by presence of moisture

12.10 Conducting Polymers

- Polymers generally insulators but ethyne can conduct electricity



- Contains alternate single & double carbon-carbon bonds
 - Can conduct electricity because p-orbitals on neighboring carbon atoms overlap resulting in long bands of delocalized π e⁻s free to move along the chain
 - Doping: other substances, such as iodine, added to improve electrical conductivity of polymer
 - Advantages over metal conductors:
 - Do not corrode
 - Much less dense
 - Shaped more easily
 - E.g. made into thin sheets to make flat panels that light

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12.11 Degradable Polymers

• Disadvantages of plastics:

- Non-biodegradable
- On combustion, give out harmful vapors

Biodegradable Plastics:

- Can contain small amounts of starch: bacteria and fungi in moist soil can break it down into smaller compounds, increase surface area and easier to decompose
- Can be made from monomers derived from plants e.g. PLA: soil microorganism can digest it easily
- Can be hydrolyzed in acidic conditions:
 - Polyamides broken down to carboxylic acids & amines
 - Polyesters broken down to carboxylic acids & alcohols

Photodegradable Plastics:

- Carbonyl group ($-C=O$) can absorb energy from ultraviolet waves
- Causes bonds in region of carbonyl group to weaken and break
- Disadvantages:
 - Plastic usually buried under \therefore cannot get sunlight
 - If recycled, products are weaker

13. ENTROPY & GIBB'S FREE ENERGY

13.1 Entropy Change

- **Entropy:** measure of the 'disorder' of a system
- A system becomes more stable when its energy is spread out in a more disordered state
- **Spontaneous change:** a change that tends to happen naturally; once started, the change will carry on
- Spontaneous changes may not be instantaneous or happen rapidly; most are slow and need an input of energy to start

13.2 Changing Entropy

- As a substance changes state from (s) \rightarrow (l) \rightarrow (g); its entropy increases as molecules become more disordered
- When an ionic salt is dissolved in water (s) \rightarrow (aq); the entropy increases as the crystal breaks up and the ions find their way between the water molecules
- Increasing the temperature of a substance (without changing state) increases entropy e.g. when heating a gas, the number of different possibilities for arranging the energy over the molecules increases.

- If a reaction increases the number of gas molecules, the entropy increases as gases have higher entropies than solids or liquids
- Simpler substances with fewer atoms have lower entropy values than more complex substances
- For similar substances, harder substances have lower entropy values

13.3 Entropy Change in Exo/Endo Reactions

Exothermic Reactions	Endothermic Reactions
<ul style="list-style-type: none">• Energy released to surroundings• Increases ways of arranging the energy of molecules in surroundings• Entropy increases• Increased probability of chemical change occurring spontaneously	<ul style="list-style-type: none">• Energy absorbed from surroundings• Decreases ways of arranging the energy• Entropy decreases• Increased probability of chemical change occurring spontaneously

13.4 Calculating Total Entropy Change

Firstly, calculate the entropy change for a reaction

$$\Delta S_{\text{system}}^{\theta} = \Delta S_{\text{products}}^{\theta} - \Delta S_{\text{reactants}}^{\theta}$$

Next, calculate entropy change in the surroundings

$$\Delta S_{\text{surroundings}}^{\theta} = \frac{-\Delta H_{\text{reaction}}^{\theta}}{T}$$

- T in Kelvin; std. temp. = 298K
- If $\Delta H_{\text{reaction}}^{\theta}$ in kJ mol⁻¹, change to J by $\times 1000$
- Negative sign part of equation, always put it

Use values calculated to find total entropy change

$$\Delta S_{\text{total}}^{\theta} = \Delta S_{\text{system}}^{\theta} + \Delta S_{\text{surroundings}}^{\theta}$$

- If $\Delta S_{\text{total}}^{\theta}$ positive, reaction is feasible

13.5 Entropy in Equilibrium Reactions

- At position of equilibrium, the total entropy change of forward reaction equals the total entropy change of backward reaction
- Under standard reactions, the overall entropy change is zero

13.6 Gibbs Free Energy

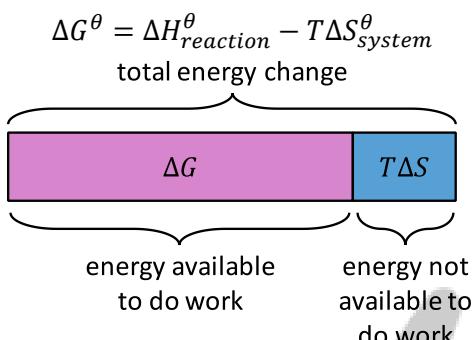
$$\Delta G = -T\Delta S_{\text{total}}$$

- **Gibbs free energy (G):** amount of energy in a system that is available to do useful work

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- Standard molar Gibbs free energy of formation (ΔG_f^θ):

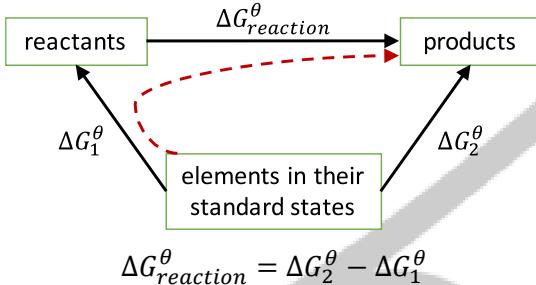
the free energy change that accompanies the formation of one mole of a compound from its elements in their standard state



Predicting spontaneity:

ΔG	State of Reaction	Stability of Compound
-ve	Spontaneous	More stable
+ve	Not Spontaneous	Less stable
0	Equilibrium	-

13.7 Gibbs Free Energy Calculations



$$\Delta G_{\text{reaction}}^\theta = \Delta G_2^\theta - \Delta G_1^\theta$$

- Form Hess's cycle and calculate Free Energy as you would enthalpies (using moles etc.)

13.8 Enthalpy and Entropy Driven

If $\Delta H > T\Delta S$	Enthalpy-driven reaction: flow of thermal energy provides most of the free energy in the reaction
If $\Delta H < T\Delta S$	Entropy-driven reaction: increased disorder provides most of the free energy in the reaction

13.9 Temperature Change & Reaction Spontaneity

- For exothermic reaction:

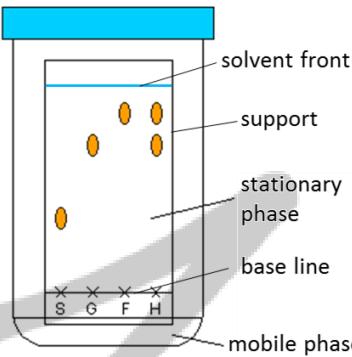
- if temperature is increased
- $T\Delta S$ value becomes more +ve
- ΔG +ve ∴ less likely to be spontaneous

- For endothermic reaction:

- if temperature is increased
- $T\Delta S$ value become more -ve
- ΔG -ve ∴ more likely to be spontaneous

14. ANALYTICAL TECHNIQUES

14.1 Paper Chromatography



- **Mobile phase:** solvent in the chromatography process, which moves through the paper or thin layer
- **Stationary phase:** immobile phase in chromatography that the mobile phase passes over or through

- As the solute rises with the solvent, they get separated by partition from mobile phase to the stationary phase
- Depending on solubility, the solutes migrate at different rates and travel up to different distances
- **Partition:** separation due to different solubilities of compound in two solvents
- The more polar a solute component is, the less it travels as there are stronger H-bonds to H_2O of st. phase
- **Identifying components:**
 - Compare position/color on filter paper with those of known pure compounds
 - Find and compare the R_f value
- **R_f value:** ratio of the distance a component has travelled compared with distance travelled by the solvent front
- When using R_f values to identify a substance, conditions in which chromatography is carried out must be identical to those quoted in R_f data table (e.g. temp, solvent)

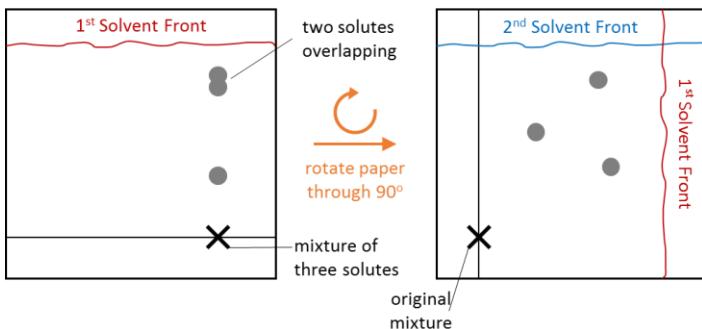
$$R_f = \frac{\text{Distance Moved by Solute Spot}}{\text{Distance Moved by Solvent Front}}$$

- Colorless chromatograms can be seen by spraying a locating agent (e.g. ninhydrin) to reveal spots

14.2 Two-way Chromatography

- When two or more components in a mixture have similar R_f values in a particular solvent, chromatography can be carried out again by rotating the chromatogram 90° and re-running in a different solvent

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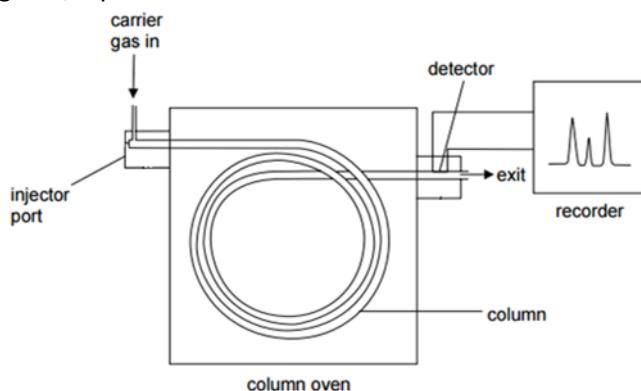


14.3 Thin Layer Chromatography

- As solute rises with solvent, they get separated from mobile phase and adsorbed to the stationary phase
- Adsorption:** separation due to different attraction between the compound and the stationary phase, relative to their solubility in the solvent
- The solid in stationary phase is either Al_2O_3 or SiO_2 ; it is spread onto a microscope slide as a slurry using water and then dried into a white coating
- Polar molecules have a greater attraction for a polar solid used as stationary phase and they are adsorbed more strongly onto its surface \therefore travel more slowly
- If dried silica or Al_2O_3 become rehydrated, water also acts as a partitioning stationary phase together with the adsorbing stationary solid phase
- TLC is quicker than paper chromatography and can be used on smaller samples
- For colorless spots:**
 - Keep plate in closed container with I_2 crystals. I_2 vapor accumulate on spots which appear dark brown
 - Place plate under UV light; the glow is reduced by solutes which appear as dark spots on the bright plate

14.4 Gas/Liquid Chromatography

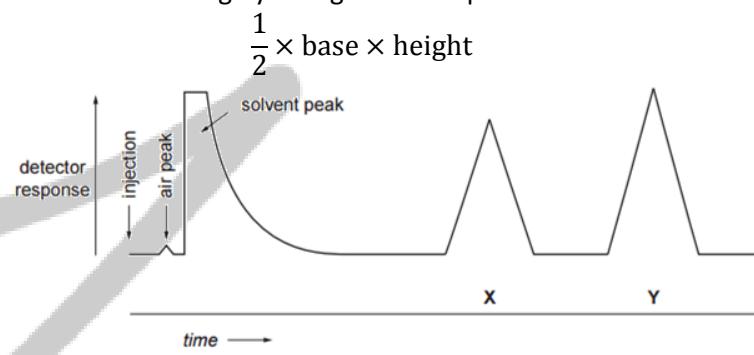
- Used to separate and identify very small samples of gases, liquid and volatile solids



- The vaporized sample is carried by an inert gas (mobile phase) over the surface of a liquid (stationary phase)

- When stationary phase is **non-polar**, rate of movement is determined principally by volatility
- When stationary phase is **polar**, it will tend to retain polar components of the mixture
- Components of a mixture leave the column after definite intervals of time and are monitored by a detector designed to record changes in composition of carrier gas
- Retention time:** time it takes components to reach the detector from time of injection
- Determination of % composition of a mixture by GLC:**

- Peaks are roughly triangular in shape so area is:

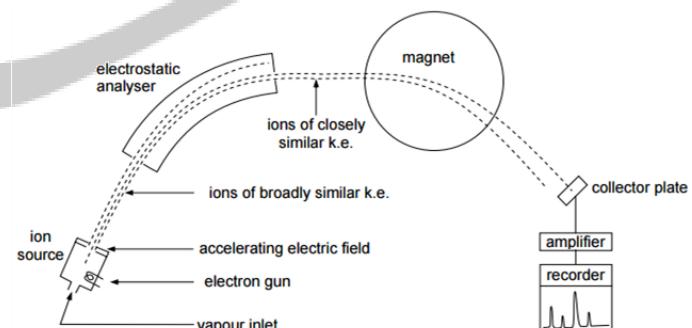


$$\text{e.g. \% of } X = \frac{\text{Peak Area of } X}{\text{Sum of Areas of } X \text{ and } Y}$$

Technique	Separation Method
Paper chromatography	Partition
Thin-layer chromatography	Adsorption
Gas/liquid chromatography	Partition

14.5 Mass Spectrometry

The mass spectrometer:



- A vaporized sample is injected through the vapor inlet
- The sample is ionized to form positive ions
- The positive ions are accelerated by an electric field
- Accelerated positive ions are deflected by magnetic field
- Positive ions of a particular mass/charge ratio are detected – recorded as a series of peaks: mass spectrum
- Molecular ion (M^+):** the peak at the highest mass to charge ratio; gives relative molecular mass of sample

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- Base peak:** peak in a mass spectrum that corresponds to the most abundant fragment
- During bombardment, some energy is transferred to the ion, weakening the bonds and breaking molecular ion into fragment +ve ions & radicals; only +ve ions detected
- Fragmentation:** the breaking up of a molecule into smaller parts by the breaking of covalent bonds

14.6 Applications of Mass Spectrometry

Finding number of carbon atoms using M and [M+1] peak

- [M+1] peak:** an ion that has a mass one unit greater than the molecular ion in a mass spectrum, due to presence of the ^{13}C isotope

$$n = \frac{100}{1.1} \times \frac{\text{abundance of } [\text{M} + 1]^+\text{ion}}{\text{abundance of } \text{M}^+\text{ ion}}$$

Identifying Cl and Br using [M+2] and [M+4] peaks

- Percentage abundance of Cl and Br isotopes

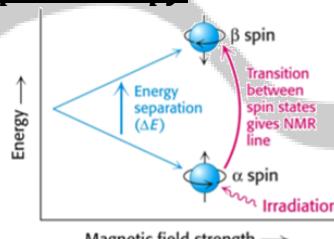
Isotope	Approx. %	Isotope	Approx. %
^{35}Cl	75%	^{79}Br	50%
^{37}Cl	25%	^{81}Br	50%

With the percentages above, the ratio of abundance is:

One Cl or Br atom		Two Cl or Br atoms	
$\text{M} : [\text{M}+2]$		$\text{M} : [\text{M}+2] : [\text{M}+4]$	
Cl	Br	Cl_2	Br_2
3 : 1	1 : 1	9 : 6 : 1	1 : 2 : 1

14.7 Proton (^1H) NMR Spectroscopy

- The hydrogen nucleus behaves as a tiny magnet.
- These "magnets" can align themselves with or against an applied magnetic field
- There is an energy gap between these two alignments, which corresponds to the energy in radio frequencies.
- The size of energy gap between the two alignments depends on the other atoms in the molecule around it – molecular environment
- TMS, $\text{Si}(\text{CH}_3)_4$ is used as standard because:
 - It is an inert volatile liquid
 - Most organic compounds are soluble in it
 - Contains 12 H atoms in the same environment which produces a single, strong peak
- NMR must be carried out in solution
- CCl_4 can be used as a solvent as it has no H & inert



- CDCl_3 (deuterated solvents) can also be used because signal produced by D does not lie in spectrum area of H

- The horizontal scale of magnetic field is measured in units called chemical shift δ (ppm)
- TMS is considered as 0 and all other compounds are compared by quoting shift away from TMS line

Low Resolution NMR:

- Shows single peaks for each non-equivalent H-atoms
- Relative peak areas proportional to no. of H-atoms
- Can use shift value to identify type of H-atom present

High Resolution NMR:

- The NMR signal is also affected by magnetic field of H-atoms on neighboring C atoms
- Causes peaks to split in particular patterns due to spin-spin splitting

14.8 (n + 1) Rule

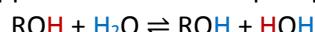
- n hydrogens on an adjacent carbon atom will split a peak into $n + 1$ smaller peaks

No. of Adjacent ^1H atoms	Splitting Pattern	Ratio of Peak Heights
0	1 peak Singlet	1
1	2 peaks Doublet	1 : 1
2	3 peaks Triplet	1 : 2 : 1
3	4 peaks Quartet	1 : 3 : 3 : 1

- The amount of splitting tells you about the no. of hydrogens attached to the carbon atom next door

14.9 Identifying -OH or -NH Signal

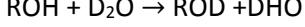
- The -OH signal always appears as a single peak because the H atom is exchanged rapidly with those in water causing it to appear unaffected to spin-spin splitting



- Deuterium is an isotope of hydrogen that behaves chemically like H but different magnetic properties to H so don't produce peaks in the area of spectrum with H

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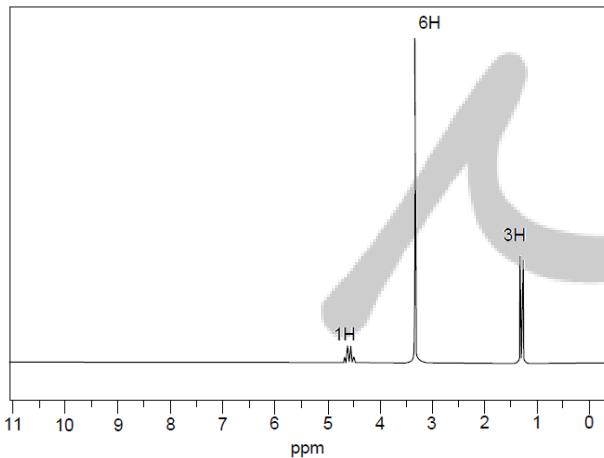
- Organic compounds are shaken with deuterium oxide (D_2O) and the H-atoms bonded to electronegative atoms ($-OH$ and $-NH$) are replaced; deuterium exchange



- When this is done, the NMR signal due to $-OH$ and $-NH$ hydrogen disappears, confirming that the peaks were caused by those groups

14.10 Describing an NMR Spectra

For example:



- To identify the protons present, set up a table as follows

No. of H	Chemical shift	Type of proton	Splitting pattern	No. of H on adj. C
3	1.30	$-CH_3$	Doublet	1
6	3.30	$-O-CH_3$	Singlet	0
1	4.60	$-O-CHR_2$	Quartet	3

- Final molecule: $(CH_3O)_2CH-CH_3$

14.11 Carbon-13 NMR Spectroscopy

- Although C-12 does not produce NMR signals as it has an even no. of protons, approximately 1.1% of an organic compound would have C-13 which produces a signal
- C-13 NMR produces a spectrum with different chemical shifts for non-equivalent carbon atoms in a molecule
- Signals produced are discrete vertical lines on the spectra (no splitting)
- The heights of the lines are **not** usually proportional to no. of ^{13}C atoms present
- The solvent used for analysis is $CDCl_3$ that produces a small signal at 80ppm which can be ignored
- Use chemical shift values as in proton spectroscopy to identify protons present & hence work out the molecule

15. ORGANIC SYNTHESIS

15.1 Chiral Drugs from Natural Sources

- Most chiral drugs extracted from natural sources often contain only a single optical isomer.
- In biological systems, molecules are synthesized and broken down by reactions involving enzymes
- These reactions work by a lock-and-key mechanism and a molecule has to be the right shape to fit the enzyme
- Different arrangements around a chiral center will force an entirely different shape on the molecule, and it may no longer fit the enzyme
- So enzyme systems will tend to produce a single optical isomer because that is the only shape they work with

15.2 Synthesis of Chiral Drug Molecules

- Each chiral center will have two possible arrangements of bonds around it and a different arrangement of bonds will mean a differently shaped molecule
- Differently shaped molecules won't necessarily fit the active site of an enzyme, and hence wouldn't function
- e.g. one enantiomer of a drug used to treat tuberculosis is effective while the other can cause blindness
- Using pure enantiomers will be beneficial as it:**
 - Reduces patient's dosage by half as pure enantiomer is more potent; better therapeutic activity
 - Minimizes risk of side effects thereby protecting patients from further problems
 - Reduces cost of production because all that is produced can be used as the drug
- Producing pure enantiomers:**
 - Optical resolution:** the drug is produced following traditional synthesis route and then a single enantiomer is separated physically by adding a substance that reacts with the other isomer
 - Optically active starting material:** drug produced from optically active starting material (e.g. carbohydrates or amino-acids) with the same orientation as desired and then synthesize drug, keeping enantiomer the same
 - Chiral catalysts:** using enzymes from living things or synthetic enzymes, the drug can be produced and only one enantiomer is formed because enzymes have specific active sites that can only produce one type
- Trying to produce just one isomer is known as asymmetric synthesis (the last 2 methods)