5. Chemical energetics

5.1. $\Delta H$ - Lattice energy - enthalpy change when 1 mole of an ionic compound is formed from its gaseous ions under standard conditions.

\[ \Delta H_{\text{latt}} = \text{negative} \]

gaseous ions $\rightarrow$ solid lattice

\[ \text{Na}^+ (g) + \text{Cl}^- (g) \rightarrow \text{Na}^+ \text{Cl}^- (s) \quad \Delta H^\circ = -787 \text{ kJ mol}^{-1} \]

- Factors affecting lattice energy
  - ion size: $\uparrow$ $\Rightarrow$ $\downarrow$ charge density $= \uparrow$ radius
  - weaker electrostatic forces of attraction in lattice $\Rightarrow \Delta H_{\text{latt}} \downarrow$ exothermic (less $-$ve)
  - charge on ions: $\uparrow$ $\Rightarrow$ $\uparrow$ charge density $\Rightarrow \Delta H_{\text{latt}} \uparrow$ exothermic (more $-$ve)

5.2. Born - Haber cycle

- determine $\Delta H_{\text{latt}} = \Delta H_f^\circ - \Delta H_{\text{at}}^\circ$

\[ \text{Li}^+(g) + \text{F}(g) + e^- \]

\[ \text{Li}^+ (g) + \frac{1}{2} \text{F}_2 (g) + e^- \uparrow \]

\[ \text{Li} (g) + \frac{1}{2} \text{F}_2 (g) \]

\[ \text{Li} (s) + \frac{1}{2} \text{F}_2 (g) \]

\[ \text{LiF} (s) \]

\[ \Delta H_{\text{latt}} \]

\[ \Delta H_f \]

\[ \text{energy} \quad (+ \Delta H) \]
1st electron affinity - $+1$ mole of $e^-$ to 1 mole gaseous atoms 
$\rightarrow$ 1 mole of gaseous 1- ions.

$\Delta H_{\text{atomisation}}$ - 1 mole gaseous atoms formed from its elements

ions in $\xrightarrow{\Delta H^*_{\text{ion}}} \text{ionic}$

gaseous state $\xrightarrow{\Delta H^*_{\text{solid}}} \text{compound}$

elements in $\xrightarrow{\Delta H^*_{f}} \text{standard states}$

5.3. Entropy change, $\Delta S^o$

$\Delta S^o$ is a measure of 'disorder' of a system.

$\uparrow$ order $\downarrow$ entropy

$\Delta S^o$ occurs:

- change in state $(s) \rightarrow (l)$; $(l) \rightarrow (g)$; $(s) \rightarrow (aq)$

- $\Delta t^o$

- in reaction: $\Delta$ of gaseous molecules

$\Delta S^o_{\text{products}} - \Delta S^o_{\text{reactants}}$

5.4. Gibbs free energy change, $\Delta G^o$

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

$\Delta G^o$:

- negative = spontaneous
- positive = not spontaneous
6. Electrochemistry

6.2. Electrolysis

Faraday's constant: \[ F = \text{L} \times e \quad \text{(C)} \]

Avogadro's constant charge on 1 mole of \( e^- \): \[ 1F = 96500 \text{C} \]

Charge \[ Q = I \times t \quad \text{current time} \]

Electrolysis of aqueous solutions:

+ cathode (-): more +ve in electrode potential series \[ \rightarrow \text{more likely to form} \]

+ anode (+): [graphite electrodes]

\[ \text{SO}_4^{2-} \quad \text{NO}_3^- \quad \text{Cl}^- \quad \text{OH}^- \quad \text{Br}^- \quad \text{I}^- \]

Not easily discharged \[ \rightarrow \text{more likely discharged} \]

b. effect of concentration on product formed

e.g. \[ \text{NaCl} \]

Concentrated Na\(^+\) Cl\(^-\) H\(^+\) OH\(^-\)

more

(-) \[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]

(+) \[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \]

d.c. power supply

variable weigh pure copper (+) and \( \Theta \) separately

resistor pass constant / current for measured t interval

- remove \( \Theta \) and (+) wash, dry, with water + propanone

- reweigh \( \Theta \) and (+)

- calculate \( L \) from \( F = Le \)
6.3. Standard electrode potentials $E^\circ$:

- standard cell potential $E_{\text{cell}}^\circ$ and Nernst equation

- standard electrode (redox) potential: the standard potential of a half cell when measured with a standard hydrogen electrode as the other half cell.

- standard cell potential $E_{\text{cell}}^\circ$: A in $E^\circ$ between 2 half cells

- standard hydrogen electrode

- $E^\circ$: 0.00V

- Pt electrode in contact with $H_2$ gas

- $H^+, 1.00 \text{ mol dm}^{-3}$ → $H_2 / H^+$ cell

Measure $E^\circ$ of non-metals ions same element, different oxidation state

- Pt electrode is inert

$Cl_2 (g) \rightarrow \leftarrow H_2 (g)$

- $Cl^-, 1.00 \text{ mol dm}^{-3}$

- $H^+, 1.00 \text{ mol dm}^{-3}$

$Fe^{3+}, 1.00 \text{ mol dm}^{-3}$

- $Fe^{2+}, 1.00 \text{ mol dm}^{-3}$

$H^+, 1.00 \text{ mol dm}^{-3}$

$Fe^{3+}, 1.00 \text{ mol dm}^{-3}$
combining half cells

\[ \frac{1}{2} \text{Cl}_2 (g) + e^- \rightarrow \text{Cl}^- (aq) \quad E^o = +1.36 \text{V} \]

more +ve → reduced

\[ \text{H}^+ (aq) + e^- \rightarrow \frac{1}{2} \text{H}_2 (g) \quad E^o = -0.00 \text{V} \]

less +ve → oxidized

\[ \text{Cl}_2 + \text{H}_2 \rightarrow 2 \text{Cl}^- + 2 \text{H}^+ \quad 1.36 - 0.00 = +1.36 \text{V} \]

Feasibility of a reaction:
- spontaneous overall \( E_{cell} > 0.3 \text{V} \)
- however
  - non-standard conditions: \( \Delta T^\circ, \Delta C, \Delta P \rightarrow \Delta E^o \)
  - activation energy, \( \Delta G \), reaction won’t occur

\( \Delta \) conc. of aqueous ions

\[ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad E^o = +0.77 \text{V} \]

\[ \text{eq to RHS} \]

\[ [\text{Fe}^{3+}] + e^- \rightarrow \text{Fe}^{2+} \quad E^o \rightarrow +0.85 \text{V} \]

Nernst equation

\[ E = E^o + \frac{0.059}{2} \log \left( \frac{\text{oxidized species}}{\text{reduced species}} \right) \]

charge
6.4. Batteries and fuel cells

- Hydrogen - oxygen \( H_2 / O_2 \) fuel cell
  - Water is only product made - no \( CO_2 \) harmful \( NO_x \)
  - Produce more energy/gram fuel burnt than petrol engines do
  - Very efficient - transmission of energy from fuel \( \rightarrow \) motor: direct
- Nickel - metal hydride battery (NiMH)
  - High energy density than NiCd
  - No toxic materials
  - Application: mobile phones, laptop computers
- Lithium ion: \((-\)) and \( MnO_2 \) or \( AgO \) at \( 0 \)
  - Lightweight + small
  - High voltage
  - Give constant voltage over time
  - Do not contain liquids or paste \( \rightarrow \) does not leak.

\[
H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \\
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- 
\]
7. Equilibria

7.2 Ionic equilibria

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)}
\]

\[
K_w = [\text{H}^+]^2 = \text{[OH}^-]\text{[H}^+\text{]} = K_c \times \text{H}_2\text{O}
\]

\( pK_w = -\log_{10} [\text{H}^+] \)

\( \text{pH} = -\log_{10} [\text{H}^+] \)

\( \text{pH} \) measures the log to base 10 of hydrogen ion concentration.

Weak acids - using the acid dissociation constant, \( K_a \)

\[
\text{HA (aq)} \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)
\]

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

\( \text{p}K_a = -\log_{10} K_a \)

\( \text{p}K_a \) weaker acid

\( \text{compare strengths of acid} \)

Acid-base indicators

\( \text{dye/mixture of dyes which changes color over a specific pH range} \)

\[
\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-
\]

unionised \( \rightarrow \) conjugate base

indicator color A \( \rightarrow \) color B

Choosing appropriate indicator:

- sharp color change, one drop of indicator gives distinct color change
- end point occurs when solution contains number \( \text{H}^+ = \text{OH}^- \)

Acid/base combination Indicator

| Strong acid/strong base | phenol/phenothalein |
| Weak acid/strong base   | phenol/phenothalein |
| Strong acid/weak base   | methyl orange       |
| Weak acid/weak base     | \( \text{N/A} \)       |
Buffer solution
- minimizes changes in pH when moderate amounts of acid/base is added
- formed from weak acid + its salt (conjugate base)
  weak base + its salt (conjugate acid)

\[\text{e.g.} \quad \text{ethanoic acid} \quad \text{ethanoate ion}\]

\[
\text{CH}_3\text{COOH (aq)} \rightleftharpoons \text{H}^+ (\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq})
\]

\[K_a \text{ relatively constant}\]

\[
\text{CH}_3\text{COONa (s) + aq} \rightleftharpoons \text{Na}^+ (\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq})
\]

sodium ethanoate

ethanoate ion
Combine → buffer solution

\[ \text{CH}_3\text{COOH (aq)} \rightleftharpoons \text{H}^+ (\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq}) \]
relatively ↑ conc
ethanoic acid relatively ↑ conc
ethanate ions
- add H⁺ - add OH⁻
- shift equil ← and CH₃COOH
- ↑ supply of CH₃COO⁻ ensures ions
- ↓ [H⁺]: shift equil →
in solution doesn't change significantly
- ↑ supply of CH₃COOH and CH₃COO⁻
→ pH doesn't change significantly
ensure ions in solution don't A sig.
→ pH doesn't change sig.

Uses of buffer solutions
- electrophotography - treatment of leather
- manufacture of dyes - check pH meters: record correct pH
- HCO₃⁻: controlling blood pH

\[ \text{CO}_2 (\text{aq}) + \text{H}_2\text{O (aq)} \rightleftharpoons \text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \]
• [H⁺]↑ = shift equil ← • [H⁺]↓ = shift equil →
• H⁺ + HCO₃⁻ → form CO₂, H₂O
• CO₂ + H₂O → H⁺ + HCO₃⁻
→ [H⁺] in blood → constant pH
• [H⁺] in blood → keep constant pH

Solubility product, Ksp

"product of the concentration of each ion in a saturated solution of a sparingly soluble salt at 298K"

\[ \text{AgCl (s)} \rightleftharpoons \text{Ag}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \]

\[ K_{sp} = [\text{Ag}^+][\text{Cl}^-] \]
number exceeds given Ksp
→ precipitate
The Common Ion Effect

The reduction in the solubility of a dissolved salt achieved by adding a solution of a compound which has an ion in common with the dissolved salt. This often results in a precipitation.

\[ [\text{Ag}^+][\text{Cl}^-] > K_{sp} \text{ of } \text{AgCl} \]

\[ \rightarrow \text{precipitate} \]

7.3. Partition coefficients \( K_{pc} \)

The ratio of the concentrations of a solute in two different immiscible solvents when an equilibrium has been established.
8. Reaction Kinetics

8.1. Simple rate equations: order of reaction; rate constants

- 0th order
  \[ \text{rate} = k \]
  \[ = k \]

- 1st order
  \[ \text{rate} = k[A] \]
  \[ = k[A] \]

- 2nd order
  \[ \text{rate} = k[A]^2 \]
  \[ = k[A]^2 \]

- Successive half-lives: constant, successive half-lives
  
  ↓ with time  half-life  ↑ with time

  \[ \text{independent of conc} \]

- Rate equation: relationship between rate constant and [reactants]
  
  that affect rate of reaction
  
  \[ A + B \rightarrow \text{products} \]

  \[ \text{orders of reaction: power to which [reactants] is raised} \]
  \[ \text{rate equation} \]

  \[ \text{rate} = k[A]^m[B]^n \]

  \[ \text{rate constant: proportionality constant} \]

  \[ \text{overall order: m + n} \]

  \[ \text{(opti-step reaction)} \]

- Half-life: time taken for the amount (or conc.) of the limiting reactant
  
  in an equation reaction to decrease to half its value.
Reaction mechanisms

- rate-determining step: slowest step in a reaction mechanism

\[
\text{rate} = k [A][B]
\]

\[
A + B \xrightarrow{\text{fast}} C \quad \text{r.d.s.}
\]

\[
C \xrightarrow{\text{slow}} D
\]

\[
\text{rate} = k [A]^2 [B]
\]

\[
A + B \xrightarrow{\text{fast}} C \quad \text{produced to be used/intermediate}
\]

\[
A + C \xrightarrow{\text{slow}} D \quad \text{r.d.s.}
\]

8.2 Effect of temperature on reaction rates and rate constants; the concept of activation energy

\[\uparrow t^\circ = \uparrow k = \uparrow \text{rate of reaction}\]

\[\uparrow \text{rate constant}\]

8.3 Homogeneous and heterogeneous catalysts including enzymes

- Homogeneous catalyst: same phase as reaction mixture

* Iodine-peroxodisulfate reaction

\[
S_2O_8^{2-}(aq) + 2I^- (aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)
\]

\[
(2Fe^{3+}(aq) + 2I^- \rightarrow 2Fe^{2+} + I_2(aq))\]

\[
(2Fe^{2+}(aq) + S_2O_8^{2-} \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq))
\]

* Catalyst usually change oxidation state
oxides of nitrogen and acid rain

\[ \text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{SO}_3 (g) \]

burn fossil fuels
contain S

\[ \text{SO}_2 (g) + \text{NO}_2 (g) \rightarrow \text{SO}_3 (g) + \text{NO} (g) \]

\[ \frac{1}{2} \text{O}_2 + \text{NO} (g) \rightarrow \text{NO}_2 (g) \]

uncatalysed reaction

\[ \Delta H \]

intermediate

catalysed reaction

heterogeneous catalyst: different phase to reaction mixture

Iron in Haber process - theory of adsorption (chemisorption)
molecules bond to atoms on surface of a solid

1. adsorption
2. diffusion
3. reaction
4. desorption
5. diffusion
6. from surface
7. new bonds forming
* **transition elements in catalytic converters**

- **catalysts**: small beads coated with:
  - platinum, palladium, rhodium

1. **adsorption of NO** and CO onto catalyst surface

2. **weakening covalent bonds**

3. **formation of new bonds**
   - adjacent N atoms \( \rightarrow \) \( N_2 \)
   - \( CO + \frac{1}{2} O_2 \rightarrow CO_2 \)

4. **desorption of \( N_2 \) and \( CO_2 \) from catalyst surface**

---

* **catalytic role of enzymes**

- **globular proteins** - biological catalyst

- **enzymes are specific**

  - **lock-and-key model**
    - enzymes → substrate → must fit

  - **active site**

  - **electrostatic complex**

  - **a.a. side chains**

---

* **adsorption**: reactant molecules chemically adsorbed onto surface of iron

  - strong enough → weakens covalent bond within reactant molecules

  - weak enough → break + allow products to leave surface

---

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10. Group 2

Thermal decomposition of nitrates + carbonates
\[ \downarrow \text{Group 2} \rightarrow \uparrow \text{thermal stability} \]

\[ \begin{align*}
\text{Mg}^{2+} & \quad \text{O} \quad \text{CO}_{3}^{2-} \\
\text{Ca}^{2+} & \quad \text{O} \quad \text{CO}_{3}^{2-}
\end{align*} \]

\[ \rightarrow \text{ion polarisation} \quad \text{cation} \quad \text{CO}_{3}^{2-} \text{ion more polarized} \quad \uparrow \text{charge} \quad \text{O} \text{- CO}_{2} \text{ bond longer} \quad \text{density} \quad \rightarrow \text{easier to break} \quad \downarrow \text{charge} \quad \text{CO}_{3}^{2-} \text{ion less polarized} \quad \text{density} \]

\[
\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g) \\
2 \text{Ca} (\text{NO}_3)_2 (s) \rightarrow 2 \text{CaO} (s) + 4 \text{NO}_2 (g) + \text{O}_2 (g)
\]

Solubility of Group 2 nitrates
\[ \downarrow \text{Group 2} \rightarrow \downarrow \text{sulfate solubility} \]

\[
\begin{align*}
\text{Ba}^{2+} (aq) + \text{SCu}^{2-} (aq) & \quad \Delta H_{\text{latt}} \\
\text{SCu}^{2-} (aq) + \text{Ba}^{2+} (aq) \quad \Delta H_{\text{sol}} \quad \Delta H_{\text{hyd}}
\end{align*}
\]

\[ \downarrow \text{Group} \leftarrow \Delta H_{\text{latt}} \text{ decrease (less } +ve) \quad \Delta H_{\text{sol}} \text{ increase} \quad \Delta H_{\text{hyd}} \text{ decrease.} \]

\[ \Delta H_{\text{sol}} : \text{energy absorbed/released when 1 mol of compound (solid) dissolves in sufficient water to form an infinitely dilute solution} \]

\[ \Delta H_{\text{hyd}} : \text{enthalpy change when 1 mol of a specific compound specified gaseous ion dissolves in sufficient water to form an infinitely dilute solution} \]
12. Transition elements

12.1. General physical properties of 1st set of transition elements:

- **Titanium (Ti)**
- **Copper (Cu)**

- Transition element: a d-block which forms one or more stable ions with an incomplete d-sub-shell.

→ **d orbitals**:

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Configuration</th>
<th>Oxidation states</th>
<th>Common Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2</td>
<td>+3, +4</td>
<td></td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>[Ar] 3d^3 4s^2</td>
<td>+2, +3, +4, +5</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>[Ar] 3d^5 4s^1</td>
<td>+3, +6</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>[Ar] 3d^5 4s^2</td>
<td>+2, +3, +4, +6, +7</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>[Ar] 3d^6 4s^2</td>
<td>+2, +3</td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>[Ar] 3d^7 4s^2</td>
<td>+2, +3</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>[Ar] 3d^8 4s^2</td>
<td>+2</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>[Ar] 3d^{10} 4s^1</td>
<td>+1, +2</td>
<td></td>
</tr>
</tbody>
</table>

- Usually lose electrons → tve charged ions
- 4s^2 electrons → o.s.: 2+
- Max o.s.: all 3d and 4s electrons
- Gain and lose 4s electrons first
Physical properties

- high melting points
- high densities
- hard and rigid → useful as construction material
- good conductors of heat and heat
- small variation in atomic radius, ionic radius

Comparing with s-block elements: Calcium (Ca)
Ca: • lower melting point • lower 1st ionisation energy
has • density
• larger atomic radius • higher ionic conductivity

12.2. General characteristic chemical properties

- metal cations interact with ligands to form complexes.
- ligand: a species that contains a lone pair of electrons that forms a dative covalent bond to a central atom/ion, including monodentate, bidentate, and polydentate ligands.
- complex: a molecule/ion formed by a central metal atom/ion surrounded by one or more ligands.

1. linear
2. octahedral
3. tetrahedral
4. square planar

\[ \text{[Ag(NH}_3\text{)}_2]^+ \]
\[ \text{[Fe(H}_2\text{O)}_6]^{2+} \]
\[ \text{[Ni(CN)}_4\text{]^3-} \]
\[ \text{[CaC}_4\text{]}^{2-} \]
coordination number: # of co-ordinative bonds formed by ligands to the central transition metal in the complex.

Ligand exchange/substitution

wholly or partially → form more stable complexes

\[
\left[ \text{Cu(H}_2\text{O)}_6 \right]^2+ \text{(aq)} + 20\text{H}^- \rightarrow \text{Cu(OH)}_2 \left( \text{H}_2\text{O}\right)_4 \text{(s)} + 2\text{H}_2\text{O} \text{(l)}
\]

blue solution pale blue ppt

\[
\text{Cu(OH)}_2 \left( \text{H}_2\text{O}\right)_4 \text{(s)} + 4\text{NH}_3 \text{(aq)} \rightarrow \left[ \text{Cu(H}_2\text{O)}_2 \left( \text{NH}_3\right)_4 \right]^2+ \text{(aq)} + 2\text{H}_2\text{O} \text{(l)}
\]
pale blue ppt deep blue solution + 20\text{H}^- \text{(aq)}

\[
\left[ \text{Cu(H}_2\text{O)}_6 \right]^2+ \text{(aq)} + 4\text{Cl}^- \text{(aq)} \rightarrow \left[ \text{CuCl}_4 \right]^2- \text{(aq)} + 6\text{H}_2\text{O} \text{(l)}
\]
blue solution yellow solution

Redox systems

\[
\text{Fe}^{3+} / \text{Fe}^{2+} \quad \text{and} \quad \text{MnO}_4^- / \text{Mn}^{2+}
\]
\[
\text{MnO}_4^- \text{(aq)} + 8\text{H}^+ \text{(aq)} + 5\text{e}^- \rightarrow \text{Mn}^{2+} \text{(aq)} + 4\text{H}_2\text{O} \text{(l)} \quad +1.52 \text{V}
\]
\[
\text{Fe}^{3+} \text{(aq)} + \text{e}^- \rightarrow \text{Fe}^{2+} \text{(aq)} \quad +0.77 \text{V}
\]

\[
\text{MnO}_4^- \text{(aq)} + 8\text{H}^+ \text{(aq)} + 5\text{Fe}^{2+} \text{(aq)} \rightarrow \text{Mn}^{2+} \text{(aq)} + 5\text{Fe}^{3+} \text{(aq)} + 4\text{H}_2\text{O} \text{(l)}
\]
very pale pink

\[
\text{Cr}_2\text{O}_7^{2-} \text{(aq)} + 14\text{H}^+ \text{(aq)} + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} \text{(aq)} + 7\text{H}_2\text{O} \text{(l)} \quad +1.33 \text{V}
\]
\[
\text{Fe}^{3+} \text{(aq)} + \text{e}^- \rightarrow \text{Fe}^{2+} \text{(aq)} \quad +0.77 \text{V}
\]

\[
\text{Cr}_2\text{C}_7^- \text{(aq)} + 14\text{H}^+ + 6\text{Fe}^{2+} \text{(aq)} \rightarrow 2\text{Cr}^{3+} \text{(aq)} + 6\text{Fe}^{3+} \text{(aq)} + 7\text{H}_2\text{O} \text{(l)}
\]
12.3. Colour of complexes

3d orbitals

- splitting of degenerate → non-degenerate d orbitals
- absorption of light energy (from visible spectrum, corresponds with ΔE) as an electron moves between 2 non-degenerate orbitals → color shown is complementary to color absorbed (ΔE)

Complexes have dif colors: dif ΔE for electron d-d transition

12.4. Stereoisomerism in transition element complexes

- Cis-trans isomerism: platin Pt(NH₃)₂Cl₂ → square planar

- Anticancer drug: bind to DNA of cancer cells, prevent cell division

- Optical isomerism: [Ni(NH₃)₆]²⁺ ↔ [Ni(en)₃]²⁺ → octahedral
12.5. Stability constants, $K_{\text{stab}}$

$K_{\text{stab}}$: the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions/molecules

$$[\text{M(H}_2\text{O)}_6]^{2+}(aq) + 6\text{X}^-(aq) \rightleftharpoons [\text{HX}_6]^{4-}(aq) + 6\text{H}_2\text{O}(l)$$

$$K_{\text{stab}} = \frac{[\text{HX}_6]^{4-}(aq)}{[\text{M(H}_2\text{O)}_6]^{2+}(aq) [\text{X}^-(aq)]^6}$$

**Ligand exchange:**

Large $K_{\text{stab}}$: formation of a stable complex ion

**Ligand exchange: cobalt**

$$[\text{Co(H}_2\text{O)}_6]^{2+} + 4\text{Cl}^- \xrightleftharpoons[\text{H}_2\text{O}]{\text{conc. HCl}} [\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O}$$

pink \quad \text{dark blue}

$$[\text{Co(H}_2\text{O)}_6]^{2+} + 6\text{NH}_3 \xrightarrow{} [\text{Co(NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$$

pink \quad \text{reddish-brown} \rightarrow \text{dark to black}

$$[\text{Co(H}_2\text{O)}_6]^{2+} + 2\text{OH}^- \rightarrow \text{Co(H}_2\text{O)}_4\text{(OH)}_2 + 2\text{H}_2\text{O}$$

pink \quad \text{blue ppt}
14. An introduction to organic chemistry

14.1. Formulae, functional groups, naming organic compounds

Arenes - contains benzene ring

Halogenoalkanes

Phenol - OH

Acyl chlorides

\[ R - C \equiv O \]

Amides

Amino acids

\[ R - C - H \]

[Diagram showing structures of various organic compounds, including halogenoalkanes, phenols, acyl chlorides, amides, and amino acids.]
15. Hydrocarbons

15. 4. Arenes

Electrophilic substitution with Cl₂ and Br₂

\[
\text{anhydrous} \quad \text{Br}_2 \quad \text{FeBr}_3 \text{ catalyst} \quad \text{Br} \quad \text{HBr}
\]

\[
\text{Br}^+ \quad \text{H} \quad \text{Br} \quad \text{FeBr}_4^- \quad \text{HBr}
\]

- Br⁺: electrophile
- catalysts: FeBr₃, AlCl₃, FeCl₂

halogen carriers

\[
\text{CH}_3 \quad + \quad 2\text{Cl}_2 \quad \text{AlCl}_3 \quad \rightarrow \quad \text{CH}_3\text{Cl} \quad + \quad \text{HCl} \quad + \quad \text{HCl}
\]

- halogens substitute at positions 2 and 4 on benzene ring

Free radical substitution

\[
\text{CH}_3 \quad + \quad \text{Cl}_2 \quad \text{boil} \quad \text{u} \quad \text{light} \quad \rightarrow \quad \text{CH}_2\text{Cl} \quad + \quad \text{HCl}
\]

- halogens substitute at side chain
- condition: UV light
Nitration (electrophilic substitution)

\[
\text{C}_6\text{H}_5 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}
\]

- \(\text{NO}_2^+\): electrophile
- reagent: conc \(\text{HNO}_3\)
  \(\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{H}_2\text{SO}_4^+ + \text{H}_2\text{O}\)
- catalyst: conc \(\text{H}_2\text{SO}_4\)
- conditions: heat under reflux; 65°C

Friedel - Crafts acylation

\[
\text{CH}_3\text{C} = \text{O} + \text{CH}_3 - \text{C} = \text{O} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{C} = \text{O} + \text{HCl}
\]

- \(\text{CH}_3\text{CO}^+\): electrophile
- catalyst: \(\text{AlCl}_3\)
- reagent: \(\text{CH}_3\text{COCl}\) (ethanoyl chloride)
- conditions: heat 60°C, 30 min

\[
\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}
\]

- with methylbenzene, sub at position 4
Friedel – Crafts alkylation

\[ \text{alkyl} \xrightarrow{\text{CH}_3\text{Cl}, \text{AlCl}_3} \text{alkylated product} + \text{HCl} \]

\[ \text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl} \]

- \( \text{CH}_3^+ \) electrophile
- reagent: \( \text{CH}_3\text{Cl} \)
- catalyst: \( \text{AlCl}_3 \)
- conditions:

Oxidation of side chains

\[ \text{benzoic acid} \]

\[ \text{CH}_3 + 3[\text{O}] \rightarrow \text{COOH} + \text{H}_2\text{O} \]

- oxidizing agent: alkaline \( \text{KMnO}_4 + \text{H}^+ + \text{heat} \)
  OR acidified \( \text{K}_2\text{Cr}_2\text{O}_7 \)

Hydrogenation: benzene ring \( \rightarrow \) cyclohexane ring

\[ \text{C}_6\text{H}_6 + 3\text{H}_2 \xrightarrow{\text{Ni}} \text{C}_6\text{H}_{12} \]

- catalyst: \( \text{Ni} \)
- conditions:
Bonding in benzene / arenes

Delocalised \( \pi \) system

- Each C atom: 3 bonds \( \sigma \)
- 1 free electron \( \pi \) bonds \( \rightarrow \) delocalised
  - Attractive for electrophile attacks
  - Undergoes electrophilic substitution

Lack of reactivity of \( \text{Cl-} \) towards e. sub

- Electron density in ring is less in \( \text{Cl-O} \) than \( \text{O-O} \)
  - Less attracted to electrophiles
  - Slower reaction

\( \text{Cl-} \) pulls \( e^- \)
17. Hydroxy compounds

17.1. Alcohols

Formation of esters, by acylation, with acyl chlorides

- formation of ethyl ethanoate

\[
\text{CH}_3\text{C} = \text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{C} = \text{O} + \text{HCl} + \text{OC}_2\text{H}_5
\]

ethanoyl chloride  ethanol  ethyl ethanoate

- formation of phenyl benzoate

\[
\text{C}_6\text{H}_5\text{C} = \text{O} + \text{Na}^+\text{O}^- \rightarrow \text{C}_6\text{H}_5\text{C} = \text{O} + \text{NaCl}
\]

benzoyl chloride  sodium  phenoxide  phenyl benzoate

17.2. Phenol

Breaking O-H bonds

- with bases

\[
\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{O}^-\text{Na}^+ + \text{H}_2\text{O}
\]

sodium phenoxide  salt: soluble in water

- with Na → vigorous reaction

\[
\text{C}_6\text{H}_5\text{OH} + 2\text{Na} \rightarrow 2\text{C}_6\text{H}_5\text{O}^-\text{Na}^+ + \text{H}_2
\]

Reaction with diazonium salts

\[
\text{N}^+\text{E} = \text{N} + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{N} = \text{N} - \text{C}_6\text{H}_5\text{O}^- + \text{H}^+
\]
azo compound  yellow-orange solution/ppt
Bromination of aromatic ring

\[
\text{C}_6\text{H}_5\text{OH} + 3\text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{Br} + 3\text{HBr}
\]

- decolourised: 2, 4, 6 - tri bromophenol
- halogens to positions 2, 4, and 6

Nitration of aromatic ring \( + \text{NO}_2^+ \)
- dilute \( \text{HNO}_3 \), room \( ^\circ \)C

\[
\text{C}_6\text{H}_5\text{OH} + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + 3\text{H}_2\text{O}
\]

- conc. \( \text{HNO}_3 \)

Product: \( \text{C}_6\text{H}_4\text{NO}_2 \)

2, 4, 6 - trinitrophenol

Relative acidity of water, phenol, and ethanol
- more acidic: phenol - water - ethanol - less acidic

Acidity of phenol: delocalisation of -ve charge on phenoxide ion into \( \pi \) bonding \( e^- \) system on benzene ring

Phenol: \( \text{C}_6\text{H}_5\text{OH} \rightarrow [\text{O}^-] + \text{H}^+ \)

\( \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \)

\( \text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}^+ + \text{C}_2\text{H}_5\text{O}^- \)

\( \text{C}_2\text{H}_5 \rightarrow \text{O}^- \) attract \( \text{H}^+ \)

\( \uparrow \) charge density on \( \text{O}^- \) compared
- with \( \text{OH}^- \) or \( \text{C}_2\text{H}_5\text{O}^- \)

\( \downarrow \) \( \text{H}^+ \) not as strongly attracted
19. Carboxylic acids & derivatives

19.1. Carboxylic acids

Formation of acyl chlorides

\[ \text{corresponding carboxylic acid} + \text{PCl}_3 / \text{PCl}_5 / \text{SOCl}_2 \]

\[ \text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl} \]

\[ 3\text{CH}_3\text{COOH} + \text{PCl}_3 \rightarrow 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_4 \]

\[ \text{CH}_3\text{COOH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{COCl} + \text{SO}_2 + \text{HCl} \]

Oxidation of carboxylic acids

i) methanoic acid

\[ \text{HCOOH} + [\text{O}] \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

with Fehling's solution

\[ \text{HCOOH} + 4\text{OH}^- + 2\text{Cu}^{2+} \rightarrow \text{CO}_2 + 3\text{H}_2\text{O} + \text{Cu}_2\text{O} \]

with Tollens' reagent

\[ \text{HCOOH} + 2\text{OH}^- + 2\text{Ag(NH}_3\text{)_2}^+ \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{Ag} + 4\text{NH}_3 \]

ii) ethanedioic acid \( \cdot \text{H}_2\text{COCO}_2\text{H} \) with warm, acidified \( \text{KMnO}_4 \)

\[ \text{COOH} \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \]

\[ 5(\text{COOH})_2 + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O} \]
Relative acidities - weak acids
weaker: alcohols < phenols < carboxylic acids

\[ \text{CH}_3-\text{C}^=\text{O} \xrightarrow{\text{e}^{-} \text{ drawn to } C=O} \text{CH}_3-\text{C}^-=\text{O}^+ + \text{H}^+ \]

\[ \text{R}-\text{C}=\text{O} \xrightarrow{\text{bond weakened}} \]

charge spread over whole group
ion stabilized
\[ \xrightarrow{\downarrow \text{ charge density} \rightarrow \text{form with } H^+} \]

by delocalised e^{-}
\[ \xrightarrow{\text{more stable ion}} \]

the more spread the charge, the more STABLE the ion

Chlorine-substituted ethanoic acids

\[ \text{H} - \text{C} \xrightarrow{1} \text{O} \]

\[ \text{H} - \text{C} \xrightarrow{2} \text{O} - \text{H} \]

\[ \text{Cl} \xrightarrow{3} \text{C} = \text{O} \]

\[ \text{Cl} \xrightarrow{4} \text{H} - \text{C} = \text{O} \]

\[ \text{Cl} \xrightarrow{5} \text{O} - \text{H} \]

weakest

\[ \text{Cl} \rightarrow \text{R}-\text{C}=\text{O} \rightarrow \text{H} \]

electron-withdrawing groups

- weaken O-H bond in undissociated acid molecule
- further delocalize -ve charge on -COO^-
- stabilize ion
- less likely bond with H^+

Cl: electron-negative atom

strongest
19.2. Aroly chlorides

**Hydrolysis** - nuc. sub.  

\[
\text{CH}_3-C=O \quad + \quad \text{O-H} \quad \rightarrow \quad \text{CH}_3-C=O \quad + \quad \text{H-O} 
\]

carboxylic acid

- @ room t° | reacts vigorously  
- C atom strongly &{ }\delta^+  
- R-C=O  
- 2 electronegative atoms

Aroly chlorides more reactive to hydrolysis than alkyl chlorides. Aryl chlorides resistant to hydrolysis

\[ \text{Acyl} \quad \text{Alkyl} \quad \text{Aryl} \]

\[ -C=O \quad R-\text{Cl} \quad \begin{array}{c}
\text{Cl} \\
\text{H}_2\text{C} \\
\text{H}_2
\end{array} \]

Reaction with alcohols + phenols  \[ \rightarrow + \text{HCl} \]

- with alcohols - acylation

\[
\text{CH}_3-C=O \quad + \quad \text{C}_2\text{H}_5\text{OH} \quad \rightarrow \quad \text{CH}_3-C=O \quad + \quad \text{HCl} 
\]

acyl chloride  

alcohol  

ester

- with phenols - acylation

\[
\text{CH}_3-C=O \quad + \quad \text{O} \quad \rightarrow \quad \text{CH}_3-C=O \quad + \quad \text{HCl} 
\]

phenol  

phenyl ester
Reactions with ammonia + primary amines

\[ \text{acyl chloride} \quad \text{primary amine} \rightarrow \text{N-substituted amide} \]

\[ \text{CH}_3 - C\text{O} + \text{CH}_2 - \text{NH}_2 \rightarrow \text{CH}_3 - C\text{O} + \text{HCl} \]

\[ \text{amide} \]

\[ \text{CH}_3 - C\text{O} + \text{NH}_3 \rightarrow \text{CH}_3 - C\text{O} + \text{HCl} \]

\[ \text{nucleophilic attack} \quad \text{elimination} \]

Hydrolysis:

\[ \text{CH}_3 - C\text{O} + \text{H}_2\text{O} \rightarrow \text{CH}_3 - C\text{OH} \]

\[ \text{reduction of nitro compound} \]

\[ \text{CH}_3 - C\text{N} + \text{H}_2\text{N} \]

\[ \text{formation of pyridine} \]

\[ \text{N}_{\text{Hz}} + \text{CH}_2\text{CH}_3 \rightarrow \text{N}_{\text{Hz}} + \text{CH}_2\text{CH}_3 \]

\[ \text{amide formation with \text{N}_{\text{Hz}}} \]

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20. Nitrogen compounds

20.1. Primary amines

Synthesis of alkyl amines - preparing ethylamine

1. Nuc. sub. with halogenaalkanes and NH₃

\[
\text{CH}_3\text{CH}_2\text{Br} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2-\text{NH}_2 + \text{HBr}
\]

- hot, excess ethanolic NH₃

2. Reduction of amides with LiAlH₄

\[
\text{R-C} = \text{O} + 4\text{[H]} \rightarrow \text{R-C} - \text{NH}_2 + \text{H}_2\text{O}
\]

- reducing agent: LiAlH₄

3. Reduction of nitriles with LiAlH₄ or H₂/Ni

\[
\text{CH}_3-\text{C}≡\text{N} + 4\text{[H]} \rightarrow \text{CH}_3\text{CH}_2-\text{NH}_2
\]

- reducing agent: LiAlH₄

\[
\text{CH}_3-\text{C}≡\text{N} + 2\text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3\text{CH}_2-\text{NH}_2
\]

4. Reduction of nitrobenzene - formation of phenylamine

\[
\text{NO}_2 + 6\text{[H]} \rightarrow \text{NH}_2 + 2\text{H}_2\text{O}
\]

- heat nitrobenzene with: \( >50°C \) (reflux)
  - Sn
  - conc. H₂O
Basicity of amines

- primary
- secondary
- tertiary

\[ R - NH_2 \]
\[ (CH_3)_2 NH \]
\[ (CH_3)_3 N \]

- base: proton / H\(^+\) acceptor
- strength of base \& availability of e\(^-\) lone pair
- N donates lone pair to H\(^+\) \(\rightarrow\) dative covalent bond

\[ RNH_2 + H^+ \rightarrow RNH_3^+ \]

\[ CH_3NH_2 + HCl \rightarrow CH_3NH_3^+Cl^- \]

Phenylamine < ammonia < ethylamine

Ethylamine \(\text{CH}_2\text{CH}_2 \rightarrow \text{NH}_2\) lone pair more readily available
Alkyl groups are electron-donating

Phenylamine

\[ \text{P} \text{ orbitals on N overlap with} \]
\[ \pi\text{-bonding system in benzene ring} \]
\[ \text{\(\downarrow\) lone pair delocalised} \]
\[ \text{\(\downarrow\) less available bond with} H^+ \]
Reactions of phenylamine

- with Br₂(aq)

\[
\text{NH}_2 + 3\text{Br}_2 \rightarrow \text{Br} \quad \text{decolourised}
\]

- with nitrous acid HNO₂

\[
\text{diazonium salt } \rightarrow \text{phenol}
\]

Step 1. diazotisation

\[
\text{NH}_2 + \text{HNO}_2 + \text{HCl} \rightarrow \text{benzenediazonium chloride}
\]

- below 10°C: diazonium salt is unstable

L → decompose to N₂

Step 2. coupling reaction -- e. sub

\[
\text{phenol}
\]

electrophile in alkaline

| azo dye

in azo dye: delocalised π-bonding system extends between \( \text{C} \) through \(-\text{N}=\text{N}\) group

→ very stable (characteristic of good dye)
20.2. Amides

**Formation of amides** \(-\text{CONH}_2\)

- \(\text{NH}_3 + R'\text{COCl}\)
  \[\text{CH}_3\text{COCl} + \text{NH}_3 \rightarrow \text{CH}_3\text{-CONH}_2 + \text{HCl}\]

- \(\text{RNH}_2 + R'\text{COCl}\)
  \[\text{C}_3\text{H}_7\text{COCl} + \text{C}_2\text{H}_5\text{-NH}_2 \rightarrow \text{C}_3\text{H}_7\text{CONH}_2\text{C}_2\text{H}_5 + \text{HCl}\]

**Amides are neutral**

**Hydrolysis of amides**

- heat with dilute acid (reflux)
  \[\text{CH}_3\text{-CONH}_2 + \text{HCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{-C}^{\circ\circ} + \text{NH}_4^+\alpha^-\]

- heated under alkaline conditions (reflux)
  \[\text{CH}_3\text{-CONH}_2 + \text{NaOH} \rightarrow \text{CH}_3\text{-C}^{\circ\circ} + \text{Na}_2\text{O}^+\]

**Reduction of amides with LiAlH}_4**

\[\text{CH}_3\text{-CONH}_2 + 4\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{-NH}_2 + \text{H}_2\text{O}\]

- \(\text{LiAlH}_4\)
- in dry ether; @ room t°
20.3 Amino acids

- R group can be:
  - acidic: $R = \text{--COOH}$
  - basic: $R = \text{NH}_2$

2-amino-carboxylic acid
- neutral: $R = \text{alkyl group}$

- contains basic $\text{--NH}_2$ and acidic $\text{--COOH}$
- each molecule can react with itself
  - crystalline solid
  - soluble in water
  - strong intermolecular forces due to attraction
  - carries 2 opposite charges

solution of a.a. contains zwitterions which have both basic and acidic properties $\rightarrow$ buffer
- resist $\Delta \text{pH}$ when small amounts of acids/alkali is added

- Amino acids (amphoteric) react with both acids and bases $\rightarrow$ form salts
Formation of peptide bonds

Condensation reaction

\[ \text{H}_2\text{N} - \text{C} - \text{C} - \text{OH} \text{ H} - \text{N} - \text{C} - \text{COOH} \rightarrow \text{H}_2\text{O} \text{ lost} \]

\[ \text{H}_2\text{N} - \text{C} - \text{C} = \text{O} \text{ dipeptide} \]

\[ \text{H}_2\text{N} - \text{C} - \text{C} - \text{N} - \text{C} - \text{COOH} \text{ peptide link} \]

dipeptide, tripeptide \(\rightarrow\) polypeptide \(\rightarrow\) protein: natural polymer

\[ \text{N} - \text{C} \text{ nucleophilic addition followed by elimination of } \text{H}_2\text{O} \]

Hydrolysis of proteins:

- refluxing with strong acid/alkali

\[ \text{C} - \text{N} - + \text{H}_2\text{O} \overset{\text{hydrolysis}}{\rightarrow} \text{C} = \text{O} + \text{N} - \]

\[ \overset{\text{A} \text{ Acid reflux: } - \text{NH}_2 \text{ react with excess acid}}{\rightarrow} \text{ammonium salts} \]

- product: 2-amino-carboxylic acids

\[ \overset{\text{A Alkali reflux: (e.g.: NaOH)}}{\rightarrow} \text{produce sodium salts of original} \]

2-amino-carboxylic acids
Reactions to form tri-iodomethane

- forms yellow ppt with methy ketone groups $\text{CH}_3\text{CO}-$

  \[
  \text{R} - \text{C} = \text{O} \\
  \text{CH}_3 \\
  \text{products}
  \]

- reagent: alkaline solution of $\text{I}_2$

- condition: warmed

\[
\text{RCOCH}_3 \xrightarrow{\text{halogenation}} \text{RCOCl}_3
\]

\[
\text{I}_2, \text{NaC}l(aq) \rightarrow \text{RCOCl}_3 \rightarrow \text{RCOONa}^+ + \text{CHI}_3
\]

- hydrolysis

- can test for $\alpha$ alcohol (oxidized $\rightarrow$ methyl ketone)

\[
\text{products}
\]

\[
\text{RCOO}^+ \rightarrow \text{CH}_3 \text{CO}^-
\]

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21. Polymerisation

21.1. Condensation polymerisation

**Polyesters**

dicarboxylic acids + diols → polyester + water

benzene - 1,4 - + ethane - → Terylene® + water
dicarboxylic acid 1,2-diol

![Polyester structure](image)

**Polyamides**

1,6-diaminohexane + hexanedioic acid → Nylon 6,6 + water

caprolactam → Nylon 6

![Polyamide structure](image)

Nylon - H², strength, elasticity → useful fibre in clothing industry,
- climbing ropes

Benzene - 1,4 - + 1,4-diamino → Kevlar® + water
dicarboxylic acid benzene

![Structure of Kevlar](image)

↑ strength to weight properties

- body armour: bulletproof vests
- sporting applications: bicycle tires, sails, racing cars
21.3. Properties of polymers

**Addition polymers**
- easily deform
  - formed from hydrocarbons → Van der Waals between chains
  - dependent on chain length
- more branched / side chains = \( \downarrow P \) = weaker
  - affects 'bulk properties'
  - polythene: LDPE: low \( P \): lots of side chains
  - non-polar \( \rightarrow \) not easily hydrolysable
  - HDPE: high \( P \): polymer strands packed closely
  - non-biodegradable

**Condensation polymers**
- strong materials: H-bonding between amide links
  - Kevlar: linear polymer chains \( \} \) high degree of alignment
  - not branched

---

**in DNA replication**

\[
\begin{align*}
A & \equiv T \\
C & \equiv G
\end{align*}
\]

- H-bonds + VdW between base pairs → broken
- double helix unwinds
  - held by H-bonds
  - nucleotides (free) brought up
  - enzymes catalyse polymerisation
  - pair up complementary base pairs

---

**in proteins**

- primary: sequence of amino acids in polypeptide chain
  - covalent bonding
• secondary: regular structural arrangements
  - stabilised by H-bonds between -NH and -CO groups
  - α-helix  β-pleated sheets
    polypeptide chain backbone (C-C-N-C-C-N-)
    → flexible, allow free rotation
  - α-helix: backbone twist → spiral, rod-like structure
    • all -NH and -CO involved in H-bond formation
    → large # H-bonds in same direction STABILISES structure
    → flat sheet-like structure

• tertiary: folding of p.p.c → 3D shape
  - disulfide bridges: covalent -S-S- bonds (SH groups)
  - weak Van der Waals'
  - relatively weak H-bonds
  - ionic bonds (salt bridges): ionised acidic/basic side chains

e) Non-solvent based adhesives
  • epoxy resin: formation of cross-linked, thermosetting polymer
    (mix contents of 2 tubes) can't alter by heat
  • superglue: polymerises during the setting process
    → triggered by H₂O/vapour/other nucleophile

Conducting polymers: acetylene (polymerised ethyne):
H-C≡C-H  →  C≡C-C≡C≡C≡C≡C≡C≡C≡C
H-C≡C-H

C = C bonds → π bonds overlap
→ delocalised system of e⁻
21.4. Degradable polymers

- polyalkenes: chemically inert → difficult to biodegrade
- some polymers degradable by light
- polyesters/polyamide degradable by hydrolysis

---

Condensation polymerisation

- a small molecule < H₂O
  - is eliminated
  - HCl
- usually needs 2 monomers
- properties of polymer
  - depends on monomer used
22. Analytical techniques

22.1. Chromatography

Thin layer chromatography (TLC) adsorption chromatography

- Stationary phase: $R_f$ value
- Mobile phase: distance travelled by component solvent
- Alumina $Al_2O_3$
- Silica $SiO_2$
- Locating agent: ninhydrin

Gas-liquid chromatography (GLC)

- Inert carrier gas (mobile phase)
- Contains stationary phase: non-volatile liquid
- Column oven
- Chromatogram
- Recorder
- Retention time: pass through column

Percentage composition

- Find area under peak for each component
- Express as $I_0$ of $\sum A_{all peaks}$

22.2. Spectroscopy

Time for a component between injection and travelling to the detector
22.3. Mass spectrometry

- molecular ion \((\text{H}^+)\)
- fragment due to fragmentation (breaking of single bonds)

\[ \text{mass-to-charge ratio (m/e)} \]

\[ \text{relative } M_r \text{ of sample} \]

\[ \text{[H + 1]} \text{ peak: molecules in which one carbon atom} \]

\[ \text{is the } ^{13}\text{C isotope} \]

\[ \text{# C atoms} \]

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

\[ [\text{H} + 2] \text{ peak: presence of Cl or Br atoms} \]

\[ \text{relative heights: } [\text{H} + 2] : [\text{H}^+] = 1:3 \text{ 1 Cl atom} \]

\[ = 1:1 \text{ 1 Br atom} \]

\[ \text{X-ray \rightarrow detectable depends on electron density of atom} \]

\[ \text{OH} + \text{D}_2\text{O} \rightarrow \text{OD} + \text{HOD} \]

\[ \text{NH-CO} + \text{D}_2\text{O} \rightarrow \text{ND-CO} + \text{HOD} \]
2.5. Proton ($^1H$) NMR spectroscopy

1 peak: singlet
2 peaks: doublet
3 peaks: triplet
4 peaks: quartet

Chemical shift: shift away from THS line

Area under peaks: relative # of equivalent $^1H$ atoms responsible for that particular shift

Splitting pattern: depends on # H atoms on adjacent C atom(s)

$n + 1 =$ # of signals a peak splits into
# H atoms on adjacent C atom

Tetramethylsilane (THS): used as standard for chemical shift measurements
- Inert, volatile liquid; mixes well with most organic compounds
- Gives 1 sharp absorption = "peak"

Identification of $O-H$ and $N-H$ protons by proton exchange using $D_2O$

$\text{OH} - \text{NH} - \xrightarrow{CH_3CH_2OH + H_2O \leftrightarrow CH_3CH_2OH + \text{HCONH}}$

Labile protons: easily displaced with traces of $H_2O$

Add $D_2O$ (deuterium oxide) → proton peaks "disappear"

D don't absorb in the same region in the electromagnetic spectrum as protons

→ Compare 2 NMR spectra
2.4. Carbon-13 NMR spectroscopy

Can tell:
- # of different types of carbons
- proximity to functional groups

Can't tell:
- # of C in each type
- # of adjacent carbons

Next to carbonyl/alkene

Carboxyl: \(-\text{C}-\text{O}\-\)

Carbonyl: \(-\text{C}=\text{O}\-\)

Alkyl: Less hydrogen @ higher ppm

- # of peaks = # of C different environments

\[ \# \text{ of peaks} < \# \text{ of C atoms} \]

\[ \Rightarrow 2 \neq 4 \text{ in some environment} \]

e.g.: SYMMETRICAL molecule
23. Organic synthesis

23.1. Synthesis of chiral drug molecules

- most chiral drugs extracted from natural sources often contain only a single optical isomer
  - in biological systems, enzymes work by lock-and-key model
    - needs only 1 arrangement (optical isomer) can fit (active site ....)

- asymmetric synthesis of drug molecules
  - better therapeutic activity
    - patient takes drugs in smaller doses as all the drug is active
  - fewer side effects
    - undesirable due to other isomers
  - cheaper in the long run
    - waste of money + materials to produce parts of drugs that have no use
20.3.e) Electrophoresis

- Separating ions placed in an electric field
  - sample placed on absorbent paper or on a gel
    - supported by solid base (e.g., glass plate)
  - buffer solution

Movement: -ve to +ve electrode

Factors affecting rate
- size of ions
- charge on ions
- pH affects charge of ions

Electropherogram
- UV light → shows bands
Enzyme break down substrate:

- Substrate binds to active site of enzyme
- Interaction with active site causes a specific bond to be weakened and broken
- Lowers activation energy
- Product released from enzyme's active site