## Oxidizing Agents

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Conditions</th>
<th>Reactions</th>
</tr>
</thead>
</table>
| KMnO₄ (aq), NaOH (aq)     | Heat       | Side chain oxidation of alkylbenzene to benzoic acid  
Oxidative cleavage of alkenes C=C to ketones or carboxylate ions or CO₃²⁻  
Oxidation of 1° alcohol to aldehyde (Heat with distill) RCH₂OH → RCHO  
Oxidation of 1° alcohol to carboxylic acid RCH₂OH → RCOO⁻  
Oxidation of 2° alcohol to ketone RCH(OH)R' → RCOR'  
Oxidation of aldehyde to carboxylic acid RCHO → RCOO⁻  
Oxidation of methanoic acid HCOOH to CO₃²⁻  
Oxidation of ethanediol acid (COOH)₂ to CO₃²⁻  
Base hydrolysis of amide to amine and carboxylic acid RCONHR' → RCOO⁻ Na⁺ + R'NH₂  
Base hydrolysis of ester to alcohol and carboxylic acid RCOOR' → RCOO⁻ Na⁺ + R'OH  
Base hydrolysis of nitrile to carboxylic acid and ammonium ions RCN → RCOO⁻ Na⁺ + NH₃  
Acid-base reaction with carboxylic acid RCOOH → RCOO⁻ Na⁺  
Acid-base reaction with phenol C₆H₅OH → C₆H₅O⁻ Na⁺  
Nucleophilic substitution of halogenoalkanes to alcohols RX → ROH |
| KMnO₄ (aq), NaOH (aq)     | Cold       | Mild oxidation of alkenes to diol C=C → C(OH)–C(OH)  
Acid-base reaction with carboxylic acid RCOOH → RCOO⁻ Na⁺  
Acid-base reaction with phenol C₆H₅OH → C₆H₅O⁻ Na⁺  |
| Tollens reagent NH₃ (aq), AgNO₃ (aq) | Heat       | Oxidation of aliphatic aldehydes and benzaldehydes to carboxylate ions RCHO → RCOO⁻  
Acid-base reaction with carboxylic acid RCOOH → RCOO⁻  
Acid-base reaction with phenol C₆H₅OH → C₆H₅O⁻  |
| Fehlings' reagent NaOH(aq), Cu²⁺ (aq) | Heat       | Oxidation of aliphatic aldehydes to carboxylate ions RCHO → RCOO⁻  
Base hydrolysis of amide to amine and carboxylic acid RCONHR' → RCOO⁻ Na⁺ + R'NH₂  
Base hydrolysis of ester to alcohol and carboxylic acid RCOOR' → RCOO⁻ Na⁺ + R'OH  
Base hydrolysis of nitrile to carboxylic acid and ammonium ions RCN → RCOO⁻ Na⁺ + NH₃  
Acid-base reaction with carboxylic acid RCOOH → RCOO⁻ Na⁺  
Acid-base reaction with phenol C₆H₅OH → C₆H₅O⁻ Na⁺  
Nucleophilic substitution of halogenoalkanes to alcohols RX → ROH |

By Stella Seah
ATOMS, MOLECULES AND STOICHIOMETRY

- Relative masses of atoms and molecules
- The mole, the Avogadro constant
- The calculation of empirical and molecular formulae
- Reacting masses and volumes (of solutions and gases)

## Learning Outcomes

Candidates should be able to:

(a) define the terms relative atomic, isotopic, molecular and formula mass, based on the $^{12}$C scale

(b) define the term mole in terms of the Avogadro constant

(c) calculate the relative atomic mass of an element given the relative abundances of its isotopes

(d) define the terms empirical and molecular formula

(e) calculate empirical and molecular formulae using combustion data or composition by mass

(f) write and/or construct balanced equations

(g) perform calculations, including use of the mole concept, involving:
   - (i) reacting masses (from formulae and equations)
   - (ii) volumes of gases (e.g. in the burning of hydrocarbons)
   - (iii) volumes and concentrations of solutions
     [when performing calculations, candidates’ answers should reflect the number of significant figures given or asked for in the question]

(h) deduce stoichiometric relationships from calculations such as those in (g)
1. Relative masses of atoms and molecules

Due to the small masses of atoms (~ $10^{-24}$ to $10^{-22}$ g), it is more practical to use relative masses rather than actual masses to describe atoms and molecules.

The $^{12}$C scale assigns an atom of $^{12}$C isotope with a mass of 12 atomic mass units. All other atomic and molecular masses are computed with comparison to $\frac{1}{12}$ the mass of one atom of $^{12}$C (i.e. 1 atomic mass unit).

1.1 Definitions

**Relative Isotopic Mass (for atoms)**

Relative isotopic mass, $A_r$, of an isotope is defined as the ratio of the mass of one atom of the isotope to $\frac{1}{12}$ the mass of one atom of $^{12}$C

Isotopes are atoms of the same element with the same proton number but different number of neutrons.

**Relative Atomic Mass (for atoms)**

Relative atomic mass, $A_r$, of an element is defined as the ratio of the average mass of one atom of the element to $\frac{1}{12}$ the mass of one atom of $^{12}$C

Note:
(1) Relative atomic mass can be obtained from the periodic table.
(2) Average mass is calculated because atoms of the same element may not have the same mass. Some elements exist as a mixture of isotopes and the average mass is a weighted average of the relative isotopic masses based on their abundance.

**Example**

Chlorine has 2 isotopes $^{35}$Cl and $^{37}$Cl of relative abundance 75% and 25% respectively. Relative atomic mass of Cl = 0.75 (35) + 0.25 (37) = 35.5

**Worked Example 1**

The relative abundances of the 4 isotopes of lead $^{204}$Pb, $^{206}$Pb, $^{207}$Pb and $^{208}$Pb are 2%, 24%, 22% and 52% respectively. Calculate the relative atomic mass of Pb.

[Ans: 207.2]
### TUTORIAL 1: ATOMS, MOLECULES AND STOICHIOMETRY

#### MCQ

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
<tr>
<td>2</td>
<td>Which of the following quantities are equal to the Avogadro constant?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 The number of ions in 41 g of CH&lt;sub&gt;3&lt;/sub&gt;COONa.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 The number of electrons in 1 g of hydrogen gas.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 The number of molecules in 24 dm&lt;sup&gt;3&lt;/sup&gt; of nitrogen at 273 K and 1 atm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Which of the following statements about a 12.0 g sample of &lt;sup&gt;12&lt;/sup&gt;C are correct?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 The number of atoms in the sample is 6.02 x 10&lt;sup&gt;23&lt;/sup&gt;.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 The number of atoms in the sample is the same as the number of atoms in 4.0 g of &lt;sup&gt;3&lt;/sup&gt;He.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 The number of atoms in the sample is the same as the number of atoms in 2.0 g of &lt;sup&gt;1&lt;/sup&gt;H&lt;sub&gt;2&lt;/sub&gt;.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Which of the following statements about one mole of a metal are correct?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 It contains the same number of atoms as 12 g of &lt;sup&gt;12&lt;/sup&gt;C.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 It contains the same number of atoms as 1 mol of hydrogen atoms.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 It contains the same number of atoms as the number of electrons in 1 g of hydrogen gas.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Which of the following statements are correct?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 6.02 x 10&lt;sup&gt;23&lt;/sup&gt; molecules of nitrogen gas weigh 28.0 g.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 24.0 dm&lt;sup&gt;3&lt;/sup&gt; of ammonia gas at r.t.p. contains 3.0 g of hydrogen.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 16.0 g of oxygen gas contains 6.02 x 10&lt;sup&gt;23&lt;/sup&gt; oxygen atoms.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Which one of the following statements about 20.3 g of Co&lt;sub&gt;2&lt;/sub&gt;(SO&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt; is correct?</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 It contains 0.10 mol of Co&lt;sup&gt;3+&lt;/sup&gt; ions.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 It contains 0.15 mol of SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt; ions.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 It contains 47.3% of oxygen by mass.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Questions

6. The greatest amount of particles is found in

A 5.0 dm<sup>3</sup> of H<sub>2</sub>S gas at r.t.p.
B 1.8 x 10<sup>23</sup> molecules of C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>
C 280 cm<sup>3</sup> of 2.5 mol dm<sup>-3</sup> HClO<sub>4</sub> (aq)
D 50 g of Fe<sub>2</sub>O<sub>3</sub>(s)
ATOMIC STRUCTURE

- The nucleus of the atom: neutrons and protons, isotopes, proton and nucleon numbers
- Electrons: electronic energy levels, ionisation energies, atomic orbitals, extranuclear structure

**Learning Outcomes**

Candidates should be able to:

(a) identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses
(b) deduce the behaviour of beams of protons, neutrons and electrons in an electric field
(c) describe the distribution of mass and charges within an atom
(d) deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (and charge)
(e) (i) describe the contribution of protons and neutrons to atomic nuclei in terms of proton number and nucleon number
   (ii) distinguish between isotopes on the basis of different numbers of neutrons present
(f) describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals
(g) describe the shapes of s and p orbitals
(h) state the electronic configuration of atoms and ions given the proton number (and charge)
(i) (i) explain the factors influencing the ionisation energies of elements (see the Data Booklet)
   (ii) explain the trends in ionisation energies across a Period and down a Group of the Periodic Table
(j) deduce the electronic configurations of elements from successive ionisation energy data
(k) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table
1. Protons, Neutrons and Electrons

Atoms are made up of three fundamental sub-atomic particles: protons, neutrons and electrons.

Protons and neutrons (collectively known as nucleons) are found in the nucleus of an atom. Electrons orbit around the nucleus.

<table>
<thead>
<tr>
<th></th>
<th>Relative mass</th>
<th>Relative charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton</td>
<td>1</td>
<td>+1</td>
</tr>
<tr>
<td>Neutron</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Electron</td>
<td>$\frac{1}{1840}$</td>
<td>-1</td>
</tr>
</tbody>
</table>

An atom contains equal number of protons and electrons and is electrically neutral.

1.1 Proton and Neutron Numbers

An atom can be represented as $X^{Z/A}$, where X is the symbol of the element.

$Z = $ number of protons = number of electrons (proton number or atomic number)

$A = $ number of protons + number of neutrons (nucleon number or mass number)

$A - Z = $ number of neutrons

Isotopes are atoms of the same element with the same proton number but different number of neutrons.

Isoelectronic species are species (atoms/ molecules/ions) with the same number of electrons

1.2 Behavior in Electric Field
Fully-filled d orbitals are more stable as the subshell has symmetric charge distribution. E.g. for Cu atom, electronic configuration should be [Ar] 3d\(^{10}\) 4s\(^1\) instead of [Ar] 3d\(^{9}\) 4s\(^2\).

Instead of

\[
\begin{array}{c}
4s \\
\end{array}
\quad \begin{array}{c}
3d \\
\end{array}
\quad \begin{array}{c}
\text{Instead of} \\
\end{array}
\begin{array}{c}
4s \\
\end{array}
\quad \begin{array}{c}
3d \\
\end{array}
\end{array}
\]

Electronic Configuration and the Periodic Table

The periodic table is arranged into s, p, d and f blocks as shown in the diagram below. It is not necessary to count the electrons to write out the configuration.

Example

The electronic configuration of Ti would contain fully filled subshells preceding the 3d subshell it is in.

\[
1s^2 2s^2 2p^6 3s^2 3p^6 4s^2
\]

Since Cr is the fourth element of the 3d orbital, the 3d orbital contains 4 electrons.

\[
1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2\]

Since 3d\(^4\) 4s\(^2\) is the exception stated above, we correct it to 3d\(^5\) 4s\(^1\).

\[
1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1
\]
CHEMICAL BONDING

• Ionic (electrovalent) bonding
• Covalent bonding and co-ordinate (dative covalent) bonding
  (i) The shapes of simple molecules
  (ii) Bond energies, bond lengths and bond polarities
• Intermolecular forces, including hydrogen bonding
• Metallic bonding
• Bonding and physical properties
• The solid state

Learning Outcomes
Candidates should be able to:
(a) describe ionic (electrovalent) bonding, as in sodium chloride and magnesium oxide, including the use of ‘dot-and-cross’ diagrams
(b) describe, including the use of ‘dot-and-cross’ diagrams,
  (i) covalent bonding, as in hydrogen; oxygen; nitrogen; chlorine; hydrogen chloride; carbon dioxide; methane; ethene
  (ii) co-ordinate (dative covalent) bonding, as in formation of the ammonium ion and in the Al2Cl6 molecule.
(c) explain the shapes of, and bond angles in, molecules such as BF3 (trigonal planar); CO2 (linear); CH4 (tetrahedral); NH3 (trigonal pyramidal); H2O (non-linear); SF6 (octahedral) by using the Valence Shell Electron Pair Repulsion theory
(d) describe covalent bonding in terms of orbital overlap, giving σ and π bonds (see also Section 10.1)
(e) predict the shapes of, and bond angles in, molecules analogous to those specified in (c)
(f) describe hydrogen bonding, using ammonia and water as examples of molecules containing -NH and -OH groups
(g) explain the terms bond energy, bond length and bond polarity and use them to compare the reactivities of covalent bonds
(h) describe intermolecular forces (van der Waals’ forces), based on permanent and induced dipoles, as in CHCl3(l); Br2(l) and the liquid noble gases
(i) describe metallic bonding in terms of a lattice of positive ions surrounded by mobile electrons
(j) describe, interpret and/or predict the effect of different types of bonding (ionic bonding; covalent bonding; hydrogen bonding; other intermolecular interactions; metallic bonding) on the physical properties of substances
(k) deduce the type of bonding present from given information
(l) show understanding of chemical reactions in terms of energy transfers associated with the breaking and making of chemical bonds
(m) describe, in simple terms, the lattice structure of a crystalline solid which is:
  (i) ionic, as in sodium chloride, magnesium oxide
  (ii) simple molecular, as in iodine
  (iii) giant molecular, as in graphite; diamond
  (iv) hydrogen-bonded, as in ice
  (v) metallic, as in copper
(n) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water
(o) suggest from quoted physical data the type of structure and bonding present in a substance
(p) recognise that materials are a finite resource and the importance of recycling processes
### Ionic Compound

<table>
<thead>
<tr>
<th>Ionic Compound</th>
<th>Cationic Radius / nm</th>
<th>Anionic Radius / nm</th>
<th>Melting Point / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.095</td>
<td>0.181</td>
<td>808</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.095</td>
<td>0.195</td>
<td>750</td>
</tr>
<tr>
<td>MgO</td>
<td>0.065</td>
<td>0.132</td>
<td>2852</td>
</tr>
<tr>
<td>CaO</td>
<td>0.099</td>
<td>0.132</td>
<td>2614</td>
</tr>
</tbody>
</table>

A larger amount of energy is required to overcome the strong electrostatic forces of attraction between smaller ions/higher charged ions.

### 1.4 Physical Properties of Ionic Compounds

1) **High Melting and Boiling Points**

A large amount of energy is needed to overcome the strong electrostatic forces of attraction between oppositely charged ions.

2) **Hard but Brittle**

Ionic bonds are **strong** and **non-directional**, making ionic crystals hard.

Stress applied on an ordered arrangement of oppositely charged ions (left) brings like charges together (right). **Repulsion between like charges** causes crystal lattice to break. Hence, ionic bonds are brittle.

3) **Generally soluble in polar solvents (e.g. water)**

When an ionic solid dissolves in water, the ionic lattice is broken up. The cations and anions interact with polar molecules. This interaction is known as **ion-dipole interactions**.

The magnitude of ion-dipole interaction increases with **charge density** (charge / radius) of the ion and the size of partial charge of the polar molecules.
• CH₄ is formed from 4 sp³ – s overlapping sigma bonds

**sp² hybridisation**

- formed from mixing of one s orbital and two p orbitals to form three sp² orbitals

```
2s
1 1 1 1
2p
```

- the three sp² orbitals form a **trigonal planar** shape in space

```
sp²
1 1 1
p
```

- the three sp² orbitals formed can form sigma bonds with other atoms while the remaining p orbital overlaps side-on to form pi bond
THE GASEOUS STATE

• Ideal gas behaviour and deviations from it
• \( pV = nRT \) and its use in determining a value for \( M_r \)

**Learning Outcomes**

Candidates should be able to:

(a) state the basic assumptions of the kinetic theory as applied to an ideal gas

(b) explain qualitatively in terms of intermolecular forces and molecular size:
   
   (i) the conditions necessary for a gas to approach ideal behavior
   
   (ii) the limitations of ideality at very high pressures and very low temperatures

(c) state and use the general gas equation \( pV = nRT \) in calculations, including the determination of \( M_r \)
1. THE KINETIC MOLECULAR THEORY OF GASES

The kinetic theory of gases is used to explain the behavior of ideal gases. The 5 basic assumptions about the behavior of the gas particles are:

1) Gas particles have negligible volume as compared to the volume in which the gas is contained.
2) Gas particles have negligible forces of attraction.
3) Gas particles are in a state of continual, random motion, moving in straight paths unless they collide with the walls of the container or with another particle.
4) Collisions between gas particles are perfectly elastic, i.e. no loss of kinetic energy.
5) The average kinetic energy of particles is directly proportional to the absolute temperature (in Kelvins).

2. THE GAS LAWS AND THE IDEAL GAS EQUATION

2.1 Ideal Gas Law

The Ideal Gas Law can be expressed in the following equation:

\[ PV = nRT \]

where:
- \( P \) is the pressure of the gas, unit: Pa
- \( V \) is the volume of the gas, unit: m³
- \( n \) is the number of moles of gas, unit: mol
- \( T \) is the temperature of the gas, unit: K
- \( R \) is the molar gas constant = 8.31 J K⁻¹ mol⁻¹

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
<th>Symbol</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>pascal</td>
<td>Pa</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>kilopascal</td>
<td>kPa</td>
<td>1 kPa = 1000 Pa</td>
</tr>
<tr>
<td></td>
<td>Atmosphere</td>
<td>atm</td>
<td>1 atm = 1.01 × 10⁵ Pa = 101 kPa</td>
</tr>
<tr>
<td>Volume</td>
<td>cubic metre</td>
<td>m³</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>cubic decimetre</td>
<td>dm³</td>
<td>1 dm³ = 10⁻³ m³ = 1000 cm³</td>
</tr>
<tr>
<td></td>
<td>cubic centimeter</td>
<td>cm³</td>
<td>1 cm³ = 10⁻⁶ dm³ = 10⁻⁴ m³</td>
</tr>
<tr>
<td>Temperature</td>
<td>Kelvin</td>
<td>K</td>
<td>T(K) = T(°C) + 273.15</td>
</tr>
<tr>
<td></td>
<td>Degree celcius</td>
<td>°C</td>
<td>T(°C) = T(K) – 273.15</td>
</tr>
</tbody>
</table>

For a fixed mole of gas,

\[ \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \]
3. NON-IDEAL BEHAVIOUR IN REAL GASES

In reality, gases do not behave ideally. Deviation from ideal behaviour occurs at HIGH PRESSURE AND LOW TEMPERATURE.

<table>
<thead>
<tr>
<th>Low Pressure</th>
<th>High Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Low Pressure Diagram" /></td>
<td><img src="image" alt="High Pressure Diagram" /></td>
</tr>
</tbody>
</table>

- Gas particles are spaced far apart.
- **Volume of gas is negligible** compared to volume of container (assumption of kinetic theory)

- Gas particles are packed close together at high pressure
- Volume occupied by gas particles is **NOT negligible** as compared to volume of container.

Actual volume of gas cannot be measured in reality. Only the volume of container can be measured.

Since volume of container > actual volume of gas,

PV/RT shows **positive deviation at high pressure**.
TUTORIAL 4: THE GASEOUS STATE

MCQ

1 Two identical bulbs at the same temperature contain ideal gases D and E separately. The density of gas D is twice that of gas E and the molecular mass of gas D is half that of gas E.

What is the ratio of the pressure of gas D to that of gas E?
A 1:2  B 1:1  C 2:1  D 4:1

2 A given mass of a diatomic gas was placed in a vessel of fixed volume V cm$^3$ at a pressure p atm and temperature T$^\circ$C.

Assuming ideal behavior, which of the following changes would cause the density of the gas to double?
A Cooling the gas to 1/2 T$^\circ$C.
B Adding a catalyst that causes the gas to dissociate into gaseous atoms at T$^\circ$C.
C Adding an equal mass of the same gas into the same vessel at T$^\circ$C.
D Connecting the vessel to an identical vessel containing the same mass of the diatomic gas at T$^\circ$C and p atm.

3 The graph below shows how pV changes with p for the three gases, J, K and L, at a fixed temperature (where p = pressure, V = volume).

Which of the following correctly identifies the gases?

<table>
<thead>
<tr>
<th></th>
<th>Gas J</th>
<th>Gas K</th>
<th>Gas L</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 mol of NH$_3$</td>
<td>1 mol of H$_2$</td>
<td>1 mol of N$_2$</td>
</tr>
<tr>
<td>B</td>
<td>2 mol of NH$_3$</td>
<td>1 mol of H$_2$</td>
<td>1 mol of NH$_3$</td>
</tr>
<tr>
<td>C</td>
<td>2 mol of N$_2$</td>
<td>1 mol of H$_2$</td>
<td>1 mol of NH$_3$</td>
</tr>
<tr>
<td>D</td>
<td>2 mol of H$_2$</td>
<td>1 mol of NH$_3$</td>
<td>1 mol of N$_2$</td>
</tr>
</tbody>
</table>
CHEMICAL ENERGETICS

- Enthalpy changes: \( \Delta H \), of formation; combustion; hydration; solution; neutralisation; atomisation; bond energy; lattice energy; electron affinity
- Hess’ Law, including Born-Haber cycles
- Entropy and Free Energy

Learning Outcomes

Candidates should be able to:

(a) explain that some chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (\( \Delta H \) negative) or endothermic (\( \Delta H \) positive)

(b) explain and use the terms:
   (i) enthalpy change of reaction and standard conditions, with particular reference to:
   formation; combustion; hydration; solution; neutralisation; atomisation
   (ii) bond energy (\( \Delta H \) positive, i.e. bond breaking)
   (iii) lattice energy (\( \Delta H \) negative, i.e. gaseous ions to solid lattice)

(c) calculate enthalpy changes from appropriate experimental results, including the use of the relationship heat change = mc\( \Delta T \)

(d) explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

(e) apply Hess’ Law to construct simple energy cycles, e.g. Born-Haber cycle, and carry out calculations involving such cycles and relevant energy terms (including ionisation energy and electron affinity), with particular reference to:
   (i) determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion
   (ii) the formation of a simple ionic solid and of its aqueous solution
   (iii) average bond energies

(f) construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy

(g) explain and use the term entropy

(h) discuss the effects on the entropy of a chemical system by the following:
   (i) change in temperature
   (ii) change in phase
   (iii) change in the number of particles (especially for gaseous systems)
   (iv) mixing of particles

(i) predict whether the entropy change for a given process or reaction is positive or negative

(j) define standard Gibbs free energy change of reaction by means of the equation
   \[ \Delta G^* = \Delta H^* - T\Delta S^* \]

(k) calculate \( \Delta G \) for a reaction using the equation \( \Delta G = \Delta H - T\Delta S \)
   [the calculation of standard entropy change, \( \Delta S \), for a reaction using standard entropies, \( S \), is not required]

(l) state whether a reaction or process will be spontaneous by using the sign of \( \Delta G \)

(m) predict the effect of temperature change on the spontaneity of a reaction, given standard enthalpy and entropy changes
1. Enthalpy $\Delta H$

Enthalpy is a term that describes the heat content of a system. We are usually interested in the enthalpy change, $\Delta H$ of a reaction, which can be measured as the amount of heat transferred to/from the system.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Exothermic Reaction

$\Delta H$ is negative. Heat is released from the reaction to the surroundings.

- Products energetically MORE stable than reactants.

Endothermic Reaction

$\Delta H$ is positive. Heat is absorbed from the surroundings.

- Products energetically LESS stable than reactants.

1.1 Standard States

Enthalpy is a state function (depends on physical states such as pressure and temperature). Certain standardized conditions are used to ensure that enthalpy changes are measured under the same conditions. This is known as the standard conditions.

The standard conditions are as follow:
- Pressure at 1 atm
- Temperature at 298 K
- Concentration of solutions at 1 mol dm$^{-3}$

The superscript $^\circ$ represents quantities measured under standard conditions.

$\Delta H^\circ$ represents enthalpy change at standard condition and is also known as the standard enthalpy change.
Bond Energy

\[
\begin{align*}
\text{H}_2 (g) + \text{Cl}_2 (g) & \rightarrow 2 \text{HCl} (g) \\
\Delta H_r & = \text{BE(H – H)} + \text{BE(Cl – Cl)} - 2 \text{BE(H – Cl)} \\
& = \Sigma \text{BE (bonds broken)} - \Sigma \text{BE (bonds formed)}
\end{align*}
\]

For the given reaction, using Hess’s Law,
\[\Delta H_r = \text{BE(H – H)} + \text{BE(Cl – Cl)} - 2 \text{BE(H – Cl)} = \Sigma \text{BE (bonds broken)} - \Sigma \text{BE (bonds formed)}\]

**Worked Example 4**

Using relevant information from the Data Booklet, find the enthalpy change of combustion of methane.

**Enthalpy Change of Combustion**

Consider the reaction \(\text{C}_2\text{H}_4 (g) + \text{H}_2 (g) \rightarrow \text{C}_2\text{H}_6 (g)\):

Introducing oxygen on both sides:

\[
\begin{align*}
\text{C}_2\text{H}_4 (g) + \text{H}_2 (g) & \rightarrow \text{C}_2\text{H}_6 (g) + 3 \frac{1}{2} \text{O}_2 (g) \\
\Delta H_c & = \Delta H_c(\text{C}_2\text{H}_4) + \Delta H_c(\text{H}_2) - \Delta H_c(\text{C}_2\text{H}_6) \\
& = \Sigma \Delta H_c \text{ (reactants)} - \Sigma \Delta H_c \text{ (products)}
\end{align*}
\]

\[\Delta H_r = \Sigma \Delta H_c \text{ (reactants)} - \Sigma \Delta H_c \text{ (products)}\]
7 Use of the Data Booklet is relevant to parts of this question.

(a) Write an equation to represent the lattice energy of calcium fluoride.
(b) Construct a Born–Haber cycle to calculate the lattice energy of calcium fluoride.

- enthalpy change of formation of calcium fluoride: $-1220 \text{ kJ mol}^{-1}$
- enthalpy change of atomisation of calcium: $+178 \text{ kJ mol}^{-1}$
- enthalpy change of atomisation of fluorine: $+79 \text{ kJ mol}^{-1}$
- first electron affinity of fluorine: $-328 \text{ kJ mol}^{-1}$

(c) How would you expect the lattice energy of calcium fluoride to compare with that of iron(II) fluoride? Explain your answer.

$[-2640 \text{ kJ mol}^{-1}]$

8 This question is about reactions involving propanone.

(a) In an experiment to determine the enthalpy change of combustion of propanone, $\Delta H_c$, the fuel was burned under a copper can containing 250 g of water. It was found that the temperature of the water rose by 23.5°C after 1.0 g of propanone had been burned. The heat transfer was known to be 80% efficient.

(i) Define enthalpy change of combustion of propanone, $\Delta H_c$.

(ii) Calculate the $\Delta H_c$ of propanone. Ignore the heat capacity of the copper can, and use 4.18 J g$^{-1}$ K$^{-1}$ for the heat capacity of water.

(b) The Wacker oxidation is an industrial process where ketones can be synthesised by the palladium-catalysed oxidation of alkene with oxygen.

Propanone can be made from propene as shown below.

$$\text{CH}_3\text{CH}=\text{CH}_2 (g) + \frac{1}{2}\text{O}_2 (g) \rightarrow \text{CH}_3\text{COCH}_3 (l)$$

(i) Using relevant bond energy data from the Data Booklet, calculate the enthalpy change for the reaction.

(ii) Given that the actual enthalpy change of this reaction is $-264 \text{ kJ mol}^{-1}$, suggest a reason for the discrepancy between your calculated $\Delta H$ value in (b)(i) and the actual $\Delta H$ value.

(iii) By considering the entropy and enthalpy change during the reaction, explain why the reaction cannot be carried out at very high temperatures.

(iv) The enthalpy change of formation of water and carbon dioxide are $-289$ and $-394 \text{ kJ mol}^{-1}$ respectively. With the aid of an energy cycle, use these values and your answer in (b)(i) to calculate the enthalpy change of formation of propene.

$[-1780 \text{ kJ mol}^{-1}, -232 \text{ kJ mol}^{-1}, -37.0 \text{ kJ mol}^{-1}]$

9 Phosphorus trichloride can be prepared by the reaction of white phosphorus with chlorine. Some related thermochemical data are shown below.

- Enthalpy change of formation of $\text{PCl}_3(l)$: $-320 \text{ kJ mol}^{-1}$
- Bond energy of $\text{P}–\text{Cl}$ bond in $\text{PCl}_3$: $+323 \text{ kJ mol}^{-1}$
- Enthalpy change of atomisation of phosphorous: $+314 \text{ kJ mol}^{-1}$

Using the above data, together with relevant data from the Data Booklet, construct an energy level diagram to determine the enthalpy change of vaporization of $\text{PCl}_3(l)$.

$[+31 \text{ kJ mol}^{-1}]$
6. REACTION KINETICS

**Learning Outcomes**

Candidates should be able to:

(a) explain and use the terms: rate of reaction; rate equation; order of reaction; rate constant; half-life of a reaction; rate-determining step; activation energy; catalysis

(b) construct and use rate equations of the form rate = k[A]^m[B]^n (limited to simple cases of single-step reactions and of multi-step processes with a rate-determining step, for which m and n are 0, 1 or 2), including:
   (i) deducing the order of a reaction by the initial rates method
   (ii) justifying, for zero- and first-order reactions, the order of reaction from concentration-time graphs
   (iii) verifying that a suggested reaction mechanism is consistent with the observed kinetics
   (iv) predicting the order that would result from a given reaction mechanism
   (v) calculating an initial rate using concentration data

(c) (i) show understanding that the half-life of a first-order reaction is independent of concentration
   (ii) use the half-life of a first-order reaction in calculations calculate enthalpy changes from appropriate experimental results, including the use of the relationship heat change = mc\Delta T

(d) calculate a rate constant using the initial rates method

(e) devise a suitable experimental technique for studying the rate of a reaction, from given information

(f) explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction

(g) show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy

(h) explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on a rate constant (and hence, on the rate) of a reaction

(i) (i) explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy, giving a larger rate constant
   (ii) interpret this catalytic effect on a rate constant in terms of the Boltzmann distribution

(j) outline the different modes of action of homogeneous and heterogeneous catalysis, including:
   (i) the Haber process
   (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines
   (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide
   (iv) catalytic role of Fe^{2+} in the I/S_{2}O_{8}^{2-} reaction

(k) describe enzymes as biological catalysts which may have specific activity

(l) explain the relationship between substrate concentration and the rate of an enzyme-catalysed reaction in biochemical systems
1.3 Zero Order Reaction

Consider the following rate equation for a single species reactant:

$$\text{Rate} = k[A]^0 = k$$

The rate of reaction is independent of $[A]$, i.e. concentration of A will not affect the rate of reaction.

Units of $k = \text{mol dm}^{-3} \text{ time}^{-1}$

Graphically, zero order reactions can be represented as:

1.4 First Order Reaction

Consider the following rate equation for a single species reactant:

$$\text{Rate} = k[A]^1 = k[A]$$

The rate of reaction is directly proportional to $[A]$, i.e. if $[A]$ increases by 2x, rate increases by 2x.

Units of $k = \text{time}^{-1}$
First order reactions can be determined from concentration-time graphs by checking if $t_{1/2}$ is a constant.

Summary of Graphs

1.7 Pseudo $n^{th}$ Order Reaction

Consider the following rate equation for two species reactant:

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

We can only find the overall order of reaction ($m+n$) but not the individual orders of reactions with respect to $A$ or $B$.

However, if $[B]$ remains constant during the reaction, the rate equation can be simplified as

$$\text{Rate} = k' [A]^m$$

Where $k' = k[B]^n$

Hence, we say that the reaction is a pseudo $m^{th}$ order reaction.

Conditions where $[B]$ is a constant:

1. $B$ is in large excess (~10x more than $[A]$) such that $[B]$ is almost constant throughout the reaction
2. $B$ is a catalyst and gets regenerated during the reaction such that $[B]$ is a constant.
4.4 Enzymes

Enzymes are biological catalysts (proteins) which catalyse reactions in living organisms.

Enzymes are **highly specific** and has an **active site** in which **only one type of substrate (reactant)** can fit.

An **enzyme-substrate complex** is formed which weakens the intramolecular bonding within the substrate, lowering the activation energy. (Similar mechanism as heterogeneous catalysts)

The products formed no longer fit in the active site and the complex breaks up, releasing the products and freeing the enzyme for further catalytic reaction.

**4.4.1 Substrate Concentration**

At low substrate concentrations, substrates **DO NOT saturate** or **fully occupy** all available active sites. As [substrate] increases, more substrate can form enzyme-substrate complex and rate of formation of products increases. Hence, rate of reaction is directly proportional to [substrate], i.e. **first order reaction**.

At high substrate concentration, **all active sites are occupied**. Even when [substrate] increases, there are no available active sites for reaction to take place, Hence, rate of reaction is independent of [substrate], i.e. **zero order reaction**.
The energy profile for a reaction, \( P \rightarrow R \) is shown below.

Which of the following statements are true?

1. The mechanism for the reaction is:
   \[ P \rightarrow Q \quad (\text{slow}) \]
   \[ Q \rightarrow R \quad (\text{fast}) \]

2. The addition of a catalyst does not affect \( \Delta H \).

3. Increasing the temperature decreases both the values of \( E_1 \) and \( E_2 \).

The reaction between iodide ions, \( I^- \), and peroxidisulfate ions, \( S_2O_8^{2-} \), is slow. The reaction can be catalysed by adding a small amount of \( Fe^{2+} \) ions.

The initial rate of the slow reaction between iodide ions and peroxidisulfate ions can be studied by using thiosulfate ions. The equations for the reactions are as follows.

\[ 2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-} \quad \text{(slow) reaction I} \]
\[ I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \quad \text{(fast) reaction II} \]

In the presence of a constant amount of thiosulfate ions, the iodine being slowly produced by reaction I will immediately react in reaction II until all the thiosulfate ions has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour if starch is present.

A series of experiments was carried out using different volumes of the five reagents. The following results were obtained.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Volume of ( S_2O_8^{2-} )/cm(^3)</th>
<th>Volume of ( I^- )/cm(^3)</th>
<th>Volume of ( S_2O_3^{2-} )/cm(^3)</th>
<th>Volume of distilled water/cm(^3)</th>
<th>Volume of Starch/cm(^3)</th>
<th>Time for the appearance of deep blue colour/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>20</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>25</td>
<td>10</td>
<td>15</td>
<td>5</td>
<td>( t_1 )</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>5</td>
<td>80</td>
</tr>
</tbody>
</table>
CHEMICAL EQUILIBRIA

- Factors affecting chemical equilibria
- Equilibrium constants
- The Haber process

**Learning Outcomes**

Candidates should be able to:

(a) explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium

(b) state Le Chatelier’s Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in concentration, pressure or temperature, on a system at equilibrium

(c) deduce whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction

(d) deduce expressions for equilibrium constants in terms of concentrations, $K_c$, and partial pressures, $K_p$ [treatment of the relationship between $K_p$ and $K_c$ is not required]

(e) calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data

(f) calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)

(g) describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry
2.4 Effect of Catalyst

Catalysts has no effect on the position of equilibrium.

It increases the rate of forward and backward reaction equally since activation energies of both forward and backward reactions decrease, allowing equilibrium to be reached more quickly.

3. Equilibrium Constants

Equilibrium constants are a measure of the position of equilibrium of a reversible reaction.

It is the ratio of equilibrium concentrations ($K_c$) or partial pressures ($K_p$) of products (raised to their stoichiometric coefficients) to that of reactants (raised to their stoichiometric coefficients).

Consider the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Equilibrium constant $K_c$ is given by:

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

Consider the reaction:

$$aA (g) + bB (g) \rightleftharpoons cC (g) + dD (g)$$

Equilibrium constant $K_p$ is given by:

$$K_p = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}$$

Note:
- **Solids** DO NOT appear in $K_c$ as concentrations of solids are constant.
- **Solids and liquids** DO NOT appear in $K_p$ since they do not exert any pressure.

<table>
<thead>
<tr>
<th>$K_c$ or $K_p$ $\gg$ 1</th>
<th>More products than reactants</th>
<th>Equilibrium lies to the right</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_c$ or $K_p$ $\ll$ 1</td>
<td>More reactants than products</td>
<td>Equilibrium lies to the left</td>
</tr>
</tbody>
</table>

Equilibrium constant can also be expressed as the ratio of rate of forward reaction to rate of backward reaction.
6 Which of the following statements about the rate constant, k, of the chemical reaction given is true?

A The rate constant is only dependent on temperature.
B The forward and backward rate constants can have different units.
C When a catalyst is added, the forward rate constant increases and the backward rate constant decreases.
D When dynamic equilibrium is established, the rate constant for the forward and backward reaction is the same.

7 X and Y were mixed in a closed vessel and the whole system was allowed to reach equilibrium, as shown in the following equation:

\[ \text{X(g)} + \text{Y(g)} \rightleftharpoons 2\text{Z(g)} \quad \Delta H < 0 \]

The concentrations of all gases were measured at one-minute intervals and the operating conditions were altered at the 4th and the 7th minute. The effects are shown in the graph below.

(i) Write an expression for the equilibrium constant, \( K_C \), and hence calculate its value at the 3rd minute.
(ii) Suggest the change that could have occurred at the:
   I 4th minute
   II 7th minute
IONIC EQUILIBRIA

- Brønsted-Lowry theory of acids and bases
- Acid dissociation constants, Ka and the use of pKa
- Base dissociation constants, Kb and the use of pKb
- The ionic product of water, Kw
- pH: choice of pH indicators
- Buffer solutions
- Solubility product; the common ion effect

Learning Outcomes

Candidates should be able to:

(a) show understanding of, and apply, the Brønsted-Lowry theory of acids and bases, including the concept of conjugate acids and conjugate bases

(b) explain qualitatively the differences in behaviour between strong and weak acids and bases in terms of the extent of dissociation

(c) explain the terms pH; K_a; pK_a; K_b; pK_b; K_w and apply them in calculations, including the relationship K_w = K_aK_b

(d) calculate [H^+(aq)] and pH values for strong acids, weak monobasic (monoprotic) acids, strong bases, and weak monoacidic bases

(e) explain the choice of suitable indicators for acid-base titrations, given appropriate data

(f) describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases

(g) (i) explain how buffer solutions control pH

   (ii) describe and explain their uses, including the role of H_2CO_3/HCO_3^- in controlling pH in blood

(h) calculate the pH of buffer solutions, given appropriate data

(i) show understanding of, and apply, the concept of solubility product, K_sp

(j) calculate K_sp from concentrations and vice versa

(k) show understanding of the common ion effect
1. Acids and Bases

1.1 Definitions

<table>
<thead>
<tr>
<th></th>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Arrhenius</strong></td>
<td>Substance that produce ( H^+ ) ions</td>
<td>Substance that produce ( OH^- ) ions</td>
</tr>
<tr>
<td>E.g. HCl → ( H^+ + Cl^- )</td>
<td>E.g. NaOH → Na(^+) + OH(^-)</td>
<td></td>
</tr>
<tr>
<td><strong>Brønsted-Lowry(^*)</strong> (‘A’ Level definition)</td>
<td>Substance that donates ( H^+ ) (proton)</td>
<td>Substance that accepts ( H^+ ) (proton)</td>
</tr>
<tr>
<td>E.g. HCl + H(_2)O → H(_3)O(^+) + Cl(^-)</td>
<td>E.g. NH(_3) + H(_2)O → NH(_4^+) + OH(^-)</td>
<td></td>
</tr>
<tr>
<td><strong>Lewis</strong></td>
<td>Substance that accepts an electron pair</td>
<td>Substance that donates an electron pair</td>
</tr>
<tr>
<td>E.g. AlCl(_3) + :Cl(^-) → AlCl(_4^-)</td>
<td>E.g. NH(_3) + H(^+) → NH(_4^+)</td>
<td></td>
</tr>
</tbody>
</table>

**Note:**
- \( H^+ \) ions are also known as proton since they only contain 1 proton.

1.2 Conjugate Acid-Base Pairs

Conjugate acid-base pairs are two substances which differ from each other by a proton (\( H^+ \)).

Consider the following reactions:

\[
HA + H_2O \rightleftharpoons H_3O^+ + A^-
\]

**Conjugate acid-base pair**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA and A^-</td>
<td>A^-</td>
</tr>
<tr>
<td>H(_2)O and H(_3)O(^+)</td>
<td>H(_3)O(^+)</td>
</tr>
</tbody>
</table>

\[
B + H_2O \rightleftharpoons BH^+ + OH^-
\]

**Conjugate acid-base pair**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>B and BH(^+)</td>
<td>B</td>
</tr>
<tr>
<td>H(_2)O and OH(^-)</td>
<td>OH(^-)</td>
</tr>
</tbody>
</table>

- An acid has **one more proton** as compared to its conjugate base.
- A **strong acid** has a **weak conjugate base**:
  \[
  HCl \rightarrow H^+ + Cl^- \quad (\text{Acid: } HCl, \text{Conjugate base: } Cl^-)
  \]
  Cl\(^-\) does not accept H\(^+\) readily to form HCl and is a weak base.

Similarly, a **weak acid** has a **strong conjugate base**.
Weak Acid – Strong Base Titration

Titration of 25.0 cm³ of 0.10 mol dm⁻³ CH₃COOH with 0.10 mol dm⁻³ NaOH
(Kₐ of CH₃COOH = 1.80 x 10⁻⁵)

Characteristics:
(1) Higher initial pH of ~3 – 4 due to presence of weak acid.
(2) Maximum buffer capacity at half-neutralisation point
(3) Equivalence point at pH > 7
(4) Sharp increase in pH with a narrower range from pH 6 to pH 11

Choice of Indicator:
(1) Phenolphthalein (Color change from colorless to light pink to pink)
(2) Any other indicators whose working range lies within the sharp increase in pH

### Region Calculation of pH

<table>
<thead>
<tr>
<th>Region</th>
<th>Calculation</th>
</tr>
</thead>
</table>
| (i) Initial Conc. | Initially, only weak acid is present. 
\[ [H^+] = \sqrt{K_a \cdot [\text{acid}]_{\text{initial}}} \]
\[ K_a = 1.80 \times 10^{-5}, [\text{acid}]_{\text{initial}} = 0.10 \]
\[ pH = -\log_{10}[H^+] = 2.87 \]
| (ii) Buffer Region | Both acid and its conjugate base is present upon addition of NaOH.
\[ [H^+] = K_a \cdot \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \]
Let volume of solution = V:
\[ [\text{CH}_3\text{COOH}] = 0.001/V, [\text{CH}_3\text{COO}^-] = 0.0015/V \]
\[ K_a = 1.80 \times 10^{-5}, [\text{acid}] = 0.001/V, [\text{base}] = 0.0015/V \]
\[ pH = -\log_{10}[H^+] = 4.92 \]

| Maximum buffer capacity | At half neutralization point, amount of base added is exactly half of what is required for neutralization, i.e. 12.5 cm³ of NaOH.
Hence, the amount of acid left = amount of conjugate base formed
\[ pH = pK_a \]

<table>
<thead>
<tr>
<th>Region</th>
<th>Calculation</th>
</tr>
</thead>
</table>
| (iia) Buffer Region | Consider the solution after 15 cm³ of NaOH is added.
\[ No. \ of \ moles \ added = 0.0025, 0.0015 \]
\[ Change \ in \ no. \ of \ moles = -0.0015 \]
\[ No. \ of \ moles \ after \ reaction = 0.001 \]
\[ pH = -\log_{10}[H^+] = 4.92 \]

| (iib) Maximum buffer capacity | At half neutralization point, amount of base added is exactly half of what is required for neutralization, i.e. 12.5 cm³ of NaOH.
Hence, the amount of acid left = amount of conjugate base formed
\[ pH = pK_a \]

\[ No. \ of \ moles \ added = 0.0025, 0.00125 \]
\[ Change \ in \ no. \ of \ moles = -0.00125 \]
\[ No. \ of \ moles \ after \ reaction = 0.00125 \]
\[ pH = pK_a = 4.74 \]
Introduction to Organic Chemistry

- Molecular, structural and empirical formulae
- Functional groups and the naming of organic compounds
- Characteristic organic reactions
- Shapes of organic molecules; σ and π bonds
- Isomerism: structural; geometrical; optical

<table>
<thead>
<tr>
<th>Learning Outcomes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candidates should be able to:</td>
</tr>
<tr>
<td>(a) interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound:</td>
</tr>
<tr>
<td>(i) alkanes, alkenes and arenes</td>
</tr>
<tr>
<td>(ii) halogenoalkanes and halogenoarenes</td>
</tr>
<tr>
<td>(iii) alcohols (including primary, secondary and tertiary) and phenols</td>
</tr>
<tr>
<td>(iv) aldehydes and ketones</td>
</tr>
<tr>
<td>(v) carboxylic acids, acyl chlorides and esters</td>
</tr>
<tr>
<td>(vi) amines, amides, amino acids and nitriles</td>
</tr>
<tr>
<td>(b) interpret, and use the following terminology associated with organic reactions:</td>
</tr>
<tr>
<td>(i) functional group</td>
</tr>
<tr>
<td>(ii) homolytic and heterolytic fission</td>
</tr>
<tr>
<td>(iii) free radical, initiation, propagation, termination</td>
</tr>
<tr>
<td>(iv) nucleophile, electrophile</td>
</tr>
<tr>
<td>(v) addition, substitution, elimination, hydrolysis</td>
</tr>
<tr>
<td>(vi) oxidation and reduction [in equations for organic redox reactions, the symbols [O] and [H] are acceptable]</td>
</tr>
<tr>
<td>(c) describe sp³ hybridisation, as in ethane molecule, sp² hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule</td>
</tr>
<tr>
<td>(d) explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to σ and π carbon-carbon bonds</td>
</tr>
<tr>
<td>(e) predict the shapes of, and bond angles in, molecules analogous to those specified in (d)</td>
</tr>
<tr>
<td>(f) describe structural isomerism</td>
</tr>
<tr>
<td>(g) describe geometrical isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds [use of E, Z nomenclature is not required]</td>
</tr>
<tr>
<td>(h) explain what is meant by a chiral centre</td>
</tr>
<tr>
<td>(i) deduce whether a given molecule is optically active based on the presence or absence of chiral centres and/or a plane of symmetry</td>
</tr>
<tr>
<td>(j) recognise that optical isomers have identical physical properties except in the direction in which they rotate plane-polarised light</td>
</tr>
<tr>
<td>(k) recognise that optical isomers have identical chemical properties except in their interactions with another chiral molecule</td>
</tr>
<tr>
<td>(l) recognise that different stereoisomers exhibit different biological properties, for example in drug action</td>
</tr>
<tr>
<td>(m) deduce the possible isomers for an organic molecule of known molecular formula</td>
</tr>
<tr>
<td>(n) identify chiral centres and/or geometrical isomerism in a molecule of given structural formula</td>
</tr>
</tbody>
</table>
1. Introduction

Organic chemistry relates solely to the chemistry (structure, reaction, properties) of carbon containing compounds. The topics that will be covered are:

1) **Hydrocarbons**: alkanes, alkenes, arenes
2) **Halogeno-compounds**: halogenoalkanes, halogenoarenes
3) **Alcohols**: primary, secondary and tertiary alcohols and phenols
4) **Carbonyl compounds**: aldehydes and ketones
5) **Carboxylic acids and derivatives**: carboxylic acids, acyl chlorides and esters
6) **Organic nitrogen compounds**: amines, amides, amino acids and nitriles

2. Classification

2.1 Arrangement of the carbon chain

A. **Aliphatic** molecules contain open (straight or branched) chains of carbon. The chains may contain single or multiple bonds.

   **Straight Chained**

   - Butane
   - Butene

   **Branched Chain**

   - 2-methylpropane

B. **Alicyclic** molecules consist of closed rings of carbon atoms. The rings may contain single or multiple bonds.

   - Cyclohexane
   - Cyclohexene

C. **Aromatic** molecules contain at least one benzene ring (ring of 6 carbon atoms where electrons in p-orbitals are delocalized to form a π electron cloud) (In Chapter 12)

   - Benzene
   - Phenol
   - Methylbenzene
4. Types of Formulae

Step 1: Naming the parent chain

1) Identify the **longest unbranched** carbon chain. This will be the parent chain.

2) The **prefix** in parent chain name denotes the number of carbon atoms in it.

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Number of Carbon</th>
<th>Prefix</th>
<th>Number of Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>meth-</td>
<td>1</td>
<td>hex-</td>
<td>6</td>
</tr>
<tr>
<td>eth-</td>
<td>2</td>
<td>hept-</td>
<td>7</td>
</tr>
<tr>
<td>prop-</td>
<td>3</td>
<td>oct-</td>
<td>8</td>
</tr>
<tr>
<td>but-</td>
<td>4</td>
<td>non-</td>
<td>9</td>
</tr>
<tr>
<td>pent-</td>
<td>5</td>
<td>dec-</td>
<td>10</td>
</tr>
</tbody>
</table>

3) The **suffix** denotes the name of the functional group. If more than one functional group is present, the compound is named after the functional group of highest precedence.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Functional Group</th>
<th>Prefix</th>
<th>Suffix</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Highest)</td>
<td>Carboxylic acid</td>
<td>carboxy-</td>
<td>-oic acid</td>
<td>Propanoic acid CH₃CH₂COOH</td>
</tr>
<tr>
<td>2</td>
<td>Ester</td>
<td>-</td>
<td>R-R’-oate</td>
<td>Methyl propanoate CH₃CH₂COOCCH₃</td>
</tr>
<tr>
<td>3</td>
<td>Acyl Halide</td>
<td>-</td>
<td>-noyl halide</td>
<td>Ethanoic chloride CH₃COCl</td>
</tr>
<tr>
<td>4</td>
<td>Amide</td>
<td>-</td>
<td>-amide</td>
<td>Ethamid CH₃CONH₂</td>
</tr>
<tr>
<td>5</td>
<td>Aldehyde</td>
<td>formyl-</td>
<td>-al</td>
<td>Propanyl CH₃CH₂CHO</td>
</tr>
<tr>
<td>6</td>
<td>Ketone</td>
<td>oxo-</td>
<td>-anone</td>
<td>Propanone CH₃COCH₃</td>
</tr>
<tr>
<td>7</td>
<td>Alcohol</td>
<td>hydroxyl-</td>
<td>-ol</td>
<td>Propanol CH₃CH₂CH₂OH</td>
</tr>
<tr>
<td>8</td>
<td>Amine</td>
<td>amino-</td>
<td>-amine</td>
<td>Propanamine CH₃CH₂CH₂NH₂</td>
</tr>
<tr>
<td>9</td>
<td>Arene</td>
<td>phenyl-</td>
<td>-benzene</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Alkene</td>
<td>(alk)enyl-</td>
<td>-ene</td>
<td>Propene CH₃CH=CH₂</td>
</tr>
<tr>
<td>11</td>
<td>Alkane</td>
<td>(alk)yl-</td>
<td>-ane</td>
<td>Propane CH₃CH₂CH₃</td>
</tr>
<tr>
<td>12 (Lowest)</td>
<td>Halogen Compounds</td>
<td>(ha)lo-</td>
<td>-</td>
<td>Chloropropane CH₃CH₂CH₂Cl</td>
</tr>
</tbody>
</table>

Table 1
**Alkanes**

- Free radical reactions

<table>
<thead>
<tr>
<th>Learning Outcomes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candidates should be able to:</td>
</tr>
<tr>
<td>(a) recognise the general unreactivity of alkanes, including towards polar reagents</td>
</tr>
<tr>
<td>(b) describe the chemistry of alkanes as exemplified by the following reactions of ethane:</td>
</tr>
<tr>
<td>(i) combustion</td>
</tr>
<tr>
<td>(ii) substitution by chlorine and by bromine</td>
</tr>
<tr>
<td>(c) describe the mechanism of free-radical substitution at methyl groups with particular reference to the initiation, propagation and termination reactions</td>
</tr>
</tbody>
</table>
To get the ratio of monosubstituted alkanes formed:

Consider the reaction of propane with Cl₂:

\[
\begin{align*}
\text{SAME REACTIVITY} & \\
\text{If all the carbon atoms have the same reactivity, there is equal probability of Cl atoms substituting any of the H atoms.} & \\
\text{Since there are 6 positions Cl can substitute to get 1-chloropropane and 2 positions Cl can substitute to get 2-chloropropane, the ratio of} & \\
1\text{-chloropropane : 2-chloropropane} & = \frac{6}{2} = 3:1
\end{align*}
\]

\[
\begin{align*}
\text{DIFFERENT REACTIVITY} & \\
\text{At low temperatures, reactivity is not the same as the stability of halogenoalkanes increases from primary < secondary < tertiary halogenoalkanes. Hence, the reactivity of carbon atoms increases from primary < secondary < tertiary carbon atoms.} & \\
\text{The reactivity of primary: secondary: tertiary = 1:4:5.} & \\
\text{Hence, for the same reaction at low temperature, we expect 2-chloropropane to be formed at 4 times the reactivity of 1-chloropropane.} & \\
\text{The probability of getting 1-chloropropane is given by the frequency of getting 1-chloropropane over the total frequency of getting 1-chloropropane and 2-chloropropane, where frequency = reactivity x number of positions} & \\
\text{probability of getting 1-chloropropane} & = \frac{1 \times 6}{(1 \times 6 + 4 \times 2)} = 43\% \\
\text{probability of getting 2-chloropropane} & = \frac{4 \times 2}{(1 \times 6 + 4 \times 2)} = 57\%
\end{align*}
\]
Carbon Monoxide
Oxidation of carbon monoxide to carbon dioxide
\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \]

Hydrocarbon
Complete combustion of hydrocarbon to carbon dioxide and water
\[ \text{C}_x\text{H}_y \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

5. Ozone Layer Depletion
The ozone layer is a region of Earth’s stratosphere that absorbs most of the Sun’s ultraviolet (UV) radiation. It arises from the use of chlorofluorocarbons (CFCs) in aerosols, air-conditioning systems, refrigerants and in packaging.
CFCs are chemically inert and remain unchanged as they diffuse through the atmosphere.
When they reach the stratosphere, in the presence of UV light, they dissociate to produce chlorine free radicals.
Step 1: Initiation

\[ \text{CF}_2\text{Cl}_2 \leftrightarrow \text{Cl}^* + \cdot\text{CF}_2\text{Cl} \]

Step 2: Propagation
The highly reactive Cl* attacks an ozone molecule to form a new radical.
\[ \text{Cl}^* + \text{O}_3 \rightarrow \cdot\text{OCl} + \text{O}_2 \]
\(\cdot\text{OCl}\) formed then reacts with oxygen atoms formed from the decomposition of \(\text{O}_3\) in the presence of UV light (\(\text{O}_3 \rightarrow \text{O}_2 + \text{O}\))
\[ \cdot\text{OCl} + \text{O} \rightarrow \text{Cl}^* + \text{O}_2 \]
Regeneration of Cl* continues to destroy other ozone molecules.

Step 3: Termination
Reaction is terminated when any two free radicals combine.
\[ \text{Cl}^* + \cdot\text{Cl} \rightarrow \text{Cl}_2 \]
\[ \text{ClO}^* + \cdot\text{NO}_2 \rightarrow \text{ClNO}_2 \]
Alkenes

- Addition and oxidation reactions

**Learning Outcomes**

Candidates should be able to:

(a) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:

(i) addition of hydrogen, steam, hydrogen halides and halogens

(ii) oxidation by cold, dilute manganate(VII) ions to form the diol

(iii) oxidation by hot, concentrated manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules

(b) describe the mechanism of electrophilic addition in alkenes, using bromine/ethene as an example
4. Physical Properties

Melting and Boiling Points

Trans isomers tend to have higher melting points than cis isomers due to more effective packing.

Cis isomers tend to have higher boiling points than trans isomers due to stronger permanent dipole-permanent dipole interactions.

Branching decreases the boiling point of alkenes since there are less contact points for dispersion forces to act on.

5. Chemical Properties

The C=C bond is composed of a strong sigma bond and a relatively weaker pi bond. The electrons in the pi bond protrude from the trigonal planar plane, creating a region of electron cloud as shown below.

![Diagram of C=C bond](image)

This region of high electron density readily attracts electrophiles.
5.1 Electrophilic Addition

The delocalized pi electrons in the C=C bond is electron rich and attracts electrophiles, which are electron seeking species. These electrophiles are electron deficient and the pi electrons are donated to form a sigma bond between the carbon in C=C and the electrophile. This causes the product to be saturated.

\[
\text{C} = \text{C} + \text{X–Y} \rightarrow \text{C} = \text{C} - \text{X} - \text{Y}
\]

**Electrophilic Addition of Halogens** \((X – Y = X – X)\)

Reagents: \(X_2\) dissolved in \(CCl_4\)
Conditions: room temperature, absence of light
Observation: reddish brown \(Br_2\) decolorises (if \(X = Br\))

Reagents: \(X_2\) (aq)
Conditions: room temperature
Observation: orange \(Br_2\) (aq) decolorises (if \(X = Br\))

*Note: To test for alkenes, it is better to use \(Br_2\) (aq) instead of \(Br_2\) in \(CCl_4\) since aqueous \(Br_2\) cannot cause free radical substitution, i.e. decolorisation of \(Br_2\) (aq) is due to the presence of C=C.

**Electrophilic Addition of HX** \((X – Y = H – X)\)

Reagents: HX (where \(X = \) halogen = F, Cl, Br, I)
Conditions: room temperature

*Note: Rate increases from \(HF < HCl < HBr < HI\) because \(H – X\) bond strength decreases down the group.

**Electrophilic Addition of \(H_2\)** \((X – Y = H – H)\)

Reagents: \(H_2\) (g)
Conditions: Pt or Ni catalyst, high pressure and temperature

**Electrophilic Addition of \(H_2O\)** \((X – Y = H – OH)\)

Reagents: \(H_2O\) (g)
Conditions: \(H_3PO_4\) catalyst, 300°C, 70 atm

OR

Reagents: conc. \(H_2SO_4, H_2O\)
Conditions: heat
Arenes

- Influence of delocalised π electrons on structure and properties
- Substitution reactions with electrophiles
- Oxidation of side-chain

Learning Outcomes

Candidates should be able to:

(a) describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene:

(i) substitution reactions with chlorine and with bromine
(ii) nitration
(iii) oxidation of the side-chain to give a carboxylic acid

(b) (i) describe the mechanism of electrophilic substitution in arenes, using the mono-nitration of benzene as an example

(ii) describe the effect of the delocalisation of electrons in arenes in such reactions

(c) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

(d) apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes
1. Introduction

Arenes are known as aromatic hydrocarbons. They contain at least one benzene ring. The simplest aromatic hydrocarbon is benzene (C₆H₆).

1.1 Structure of Benzene Ring

In the benzene molecule, each carbon atom is sp² hybridised and has a trigonal planar geometry, making benzene planar. Each carbon atom has one unhybridised p-orbital containing one remaining electron which lies perpendicular to the plane of the benzene ring.

Each p orbital overlaps equally with each of its neighbours, resulting in 6 p electrons completely delocalized in a two-lobed cloud above and below the ring of carbon atoms.

The six electrons are free to move throughout the delocalized cloud. The delocalization of the pi electrons leads to extra stability (resonance stabilized) and all the C-C bonds are identical. The circle in the structural formula of benzene indicates the delocalized cloud of electrons.

2. Nomenclature

The benzene ring is considered the parent hydrocarbon and the name of the substituent group is the prefix. In the case of monosubstituted benzenes, the position of the substituent is understood to be on carbon 1.

Example

![Chemical structures of Chlorobenzene, Methylbenzene, and Nitrobenzene]
3.1 Reaction Mechanism of Electrophilic Substitution

**Step 1: Generation of electrophile**

- $\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^- + \text{Cl}^+$
- $\text{FeBr}_3 + \text{Br}^- \rightarrow \text{FeBr}_4^- + \text{Br}^+$
- $\text{AlCl}_3 + \text{R}^- \rightarrow \text{AlCl}_4^- + \text{R}^+$

*Cl$ or Br$ or R$ is the electrophile
*AlCl$ or FeBr$ "carries" the halogen, leaving behind a positively charged electrophile

**Step 2: Formation of carbocation intermediate**

**Step 3: Restoration of stable ring structure and regenerate catalyst**

**Step 1: Generation of electrophile**

$$2\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow 2\text{HSO}_4^- + \text{NO}_2^+ + \text{H}_3\text{O}^+$$

*NO$_2^+$ is the electrophile

**Step 2: Formation of carbocation intermediate**

**Step 3: Restoration of stable ring structure and regenerate catalyst**
4 Suggest how the following compounds can be prepared giving the reagents and conditions for each step, as well as any intermediates formed.

(a) \( C_6H_6 \rightarrow C_6H_5CCl_3 \)
(b) 1,4-dimethylbenzene \( \rightarrow \) benzene-1,4-dicarboxylic acid

5 Aluminium chloride catalyses certain reactions by forming carbocations \( CH_3CH_2^+ \) with chloroethane.

(a) Write the chemical equation for the reaction of aluminium chloride and chloroethane.
(b) Explain, in terms of bonding, why aluminium chloride reacts in this way.
(c) Name and describe the mechanism that occurs with benzene when reacted with \( C_2H_5Cl \) in the presence of \( AlCl_3 \).

6 Which of the following order of synthesis from benzene will result in the highest yield of the following product?

\[ \text{COOH} \]
\[ \text{NO}_2 \]
\[ \text{Br} \]

A alklylation \( \rightarrow \) nitration \( \rightarrow \) oxidation \( \rightarrow \) bromination
B alklylation \( \rightarrow \) nitration \( \rightarrow \) bromination \( \rightarrow \) oxidation
C alklylation \( \rightarrow \) oxidation \( \rightarrow \) nitration \( \rightarrow \) bromination
D alklylation \( \rightarrow \) oxidation \( \rightarrow \) bromination \( \rightarrow \) nitration

7 In an experiment, the identity of a liquid hydrocarbon \( B \) has to be determined. \( B \) has 90.6% carbon by mass.

(a) The relative molecular mass of \( B \) is 106. Show that the molecular formula of \( B \) is \( C_8H_{10} \).

(b) \( B \) can react with \( Cl_2 \) in the absence of UV light and using a suitable catalyst to give misty fumes of \( HCl \). \( B \) can be oxidized by hot acidified \( KMnO_4 \) to form \( C \). One mole of \( C \) is exactly neutralized by one mole of \( NaOH \).

Deduce the structures of \( B \) and \( C \) and explain with equations the reactions that took place.

8 Write the structural formula for the products that are formed when the following compound reacts with the following reagents. If more than one product is formed, draw only the major products.

\[ \text{(a) Cl}_2 \text{ in CCl}_4, \text{ room temperature} \]
\[ \text{(b) HBr (g)} \]
\[ \text{(c) excess Br}_2 \text{ (l), Fe (s), room temperature} \]
\[ \text{(d) acidified KMnO}_4 \text{ (aq), heat} \]
Halogen Derivatives

- Halogenoalkanes and halogenoarenes
  (i) Nucleophilic substitution
  (ii) Elimination
- Relative strength of the C-Hal bond

Learning Outcomes

Candidates should be able to:

(a) recall the chemistry of halogenoalkanes as exemplified by
   (i) the following nucleophilic substitution reactions of bromoethane: hydrolysis; formation of nitriles; formation of primary amines by reaction with ammonia
   (ii) the elimination of hydrogen bromide from 2-bromopropane

(b) describe the mechanism of nucleophilic substitutions (by both S_N1 and S_N2 mechanisms) in halogenoalkanes

(c) interpret the different reactivities of halogenoalkanes and chlorobenzene with particular reference to hydrolysis and to the relative strengths of the C-Hal bonds

(d) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness

(e) recognise the concern about the effect of chlorofluoroalkanes (CFCs) on the ozone layer [the mechanistic details of how CFCs deplete the ozone layer are not required]
1. Introduction

Halogenoalkanes (or alkyl halides) are alkanes with one or more hydrogen atoms being replaced by halogen atoms F, Cl, Br, I, where the halogen atoms are usually represented as X.

**General formula:** $C_nH_{2n+1}X$

Halogenoarenes (or aryl halides) have one or more benzene rings in which one or more hydrogen atoms on these rings have been replaced by halogen atoms.

More generally, halogen derivatives contain $C – X$ bonds.

1.1 Classification of a Halogenoalkane

Halogenoalkanes can be classified according to the number of R groups attached to the C atom bonded to the halogen, where R = any alkyl or aryl groups.

<table>
<thead>
<tr>
<th>X</th>
<th>R – C – H</th>
<th>R – C – X</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Primary (1&lt;sup&gt;st&lt;/sup&gt;)</td>
<td>No R groups or 1 R group</td>
</tr>
<tr>
<td>R</td>
<td>Secondary (1&lt;sup&gt;st&lt;/sup&gt;)</td>
<td>2 R groups</td>
</tr>
<tr>
<td>R</td>
<td>Tertiary (1&lt;sup&gt;st&lt;/sup&gt;)</td>
<td>3 R groups</td>
</tr>
</tbody>
</table>

1.2 Physical Properties

**Boiling points**

The main intermolecular forces of interaction between halogenoalkanes are permanent dipole-permanent dipole interactions and induced dipole - induced dipole interactions.

For halogenoalkanes of the **same chain length but different halogens**, the melting and **boiling points increase from R – F < R – Cl < R – Br < R – I** as the **number of electrons increases from F to I**, leading to stronger induced dipole - induced dipole interactions.

Comparing halogenoalkanes and their corresponding alkanes, **halogenoalkanes have higher melting and boiling points** due to the polar $C – X$ bonds which result in stronger permanent dipole-permanent dipole interactions.

**Solubility**

Halogenoalkanes are generally immiscible with water as the weak permanent dipole-permanent dipole interactions and induced dipole - induced dipole interactions with water do not release enough energy to compensate the energy required to overcome the stronger hydrogen bonds between water molecules.
3.1.1 Reaction Mechanism

There are two reaction mechanisms for nucleophilic substitutions: $S_{N1}$ (unimolecular nucleophilic substitution) and $S_{N2}$ (bimolecular nucleophilic substitution).

The type of mechanism for nucleophilic substitution depends on the halogenoalkane that undergoes nucleophilic substitution.

$S_{N2}$ nucleophilic substitution

$S_{N2}$ nucleophilic substitution involves two molecules (halogenoalkane and nucleophile) in a single step mechanism. The single step reaction proceeds through a short-lived transition state.

Reaction Pathway for Negatively Charged Nucleophile

- The nucleophile approaches the $\delta^+$ carbon atom from the back directly opposite the halogen leaving group to form a transition state.
- Since this is a single step reaction that involves two species, we describe this as a $S_{N2}$ nucleophilic substitution reaction.
- The rate equation for this reaction is determined by the rate-determining step, which is the single step reaction:

$$\text{Rate} = k \ [\text{Nu}] \ [\text{halogenoalkane}]$$

- In the transition state, the nucleophile is in the process of bond-forming while the halogen is in the process of bond breaking with the carbon atom. These partial bonds are represented with dashed lines (\(-\ -\ -\))
- The final product undergoes an inversion of configuration with the nucleophile attached to the rear of the carbon instead of the front. If the halogenoalkane was chiral, the optical isomerism of the product would be reversed.
- Generally, primary halogenoalkanes undergo $S_{N2}$ mechanism, due to less steric hindrance by the R groups, which increases the ease of attack by nucleophile on the $\delta^+$ carbon atom.
When the compound \( \text{F}, \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \) reacts with hot ethanolic KOH, two products are formed: compound \( \text{G}, \text{C}_7\text{H}_8\text{O} \) and compound \( \text{H}, \text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}_3 \).

(a) Suggest an identity for compounds \( \text{G} \) and \( \text{H} \) and state the type of reaction undergone by compound \( \text{F} \), explaining how \( \text{G} \) and \( \text{H} \) are formed.

(b) Suggest how the behavior of compound \( \text{F} \) with hot ethanolic KOH differs from that of \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl} \). State the type of reaction undergone (if any) and draw the structural formula of the product.

When 1.00 g of an organic compound \( \text{R} \) was refluxed with excess aqueous KOH, it slowly dissolved in the aqueous layer.

The resultant solution was neutralized with dilute nitric acid and aqueous silver nitrate was added. The precipitate formed was filtered off and dried. The mass of the precipitate was found to be 1.37 g. The filtrate was distilled and an organic liquid \( \text{S} \) was obtained.

\( \text{S} \) has a M, of 74.0 and contains 64.9% C, 13.5 % H, 21.6% O by mass.

(a) Given that \( \text{R} \) is a tertiary monohalogenoalkane, suggest the structures of \( \text{R} \) and \( \text{S} \). Explain your reasoning with equations.

(b) Describe the mechanism of \( \text{R} \) with aqueous KOH.
HYDROXY COMPOUNDS

- Alcohols (exemplified by ethanol)
  (i) Formation of halogenoalkanes
  (ii) Reaction with sodium; oxidation; dehydration
  (iii) The tri-iodomethane test
- Phenol
  (i) Its acidity; reaction with sodium
  (ii) Nitration of, and bromination of, the aromatic ring

Learning Outcomes

Candidates should be able to:

(a) recall the chemistry of alcohols, exemplified by ethanol:
   (i) combustion
   (ii) substitution to give halogenoalkanes
   (iii) reaction with sodium
   (iv) oxidation to carbonyl compounds and carboxylic acids
   (v) dehydration to alkenes

(b) (i) classify hydroxy compounds into primary, secondary and tertiary alcohols
    (ii) suggest characteristic distinguishing reactions, e.g. mild oxidation

(c) deduce the presence of a CH3CH(OH)– group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane

(d) recall the chemistry of phenol, as exemplified by the following reactions:
    (i) with bases
    (ii) with sodium
    (iii) nitration of, and bromination of, the aromatic ring

(e) explain the relative acidities of water, phenol and ethanol
3. Reactions of Alcohols

There are 5 main reactions of alcohols:
(1) Nucleophilic substitution
(2) Elimination
(3) Acid-metal reaction
(4) Esterification
(5) Oxidation

3.1 Nucleophilic Substitution

3.1.1 Formation of Chloroalkanes

*With phosphorous pentachloride PCl\textsubscript{5} (s)*

\[ R\text{–OH} + PCl\textsubscript{5} \rightarrow R\text{–Cl} + POCl\textsubscript{3} + HCl (g) \]

Reagents: anhydrous PCl\textsubscript{5} (s)
Conditions: Room temperature
Observations: Dense white fumes of HCl evolves

Note: This is a distinguishing test for alcohol.

*With thionyl chloride SOCl\textsubscript{2} (l)*

\[ R\text{–OH} + SOCl\textsubscript{2} \rightarrow R\text{–Cl} + SO\textsubscript{2} + HCl (g) \]

Reagents: SOCl\textsubscript{2} (l)
Conditions: Room temperature
Observations: Dense white fumes of HCl evolves

Note: This is a distinguishing test for alcohol.

*With phosphorous trichloride PCl\textsubscript{3} (l)*

\[ 3 R\text{–OH} + PCl\textsubscript{3} \rightarrow 3 R\text{–Cl} + H\textsubscript{3}PO\textsubscript{4} \]

Reagents: PCl\textsubscript{3} (l)
Conditions: Room temperature

*With concentrated HCl*

\[ R\text{–OH} + HCl \rightarrow R\text{–Cl} + H\textsubscript{2}O \]

Reagents: concentrated HCl, anhydrous ZnCl\textsubscript{2}(s)
Conditions: Room temperature
5 Compound M has a molecular formula C\textsubscript{13}H\textsubscript{16}O. M decolourises aqueous bromine and produces white fumes with PCl\textsubscript{5}. No colour change is observed on heating M with acidified K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}. It reacts with hot acidified KMnO\textsubscript{4} to produce N (C\textsubscript{7}H\textsubscript{6}O\textsubscript{2}), P (C\textsubscript{4}H\textsubscript{6}O\textsubscript{5}) and Q (C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}). N gives effervescence of CO\textsubscript{2} with solid sodium carbonate. P gives effervescence of CO\textsubscript{2} with solid sodium carbonate and no color change was observed on heating it with acidified K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}. Q gives effervescence of CO\textsubscript{2} with solid sodium carbonate.

Identify M, N, P and Q and explain the reactions.

Note: -COOH groups can react with solid sodium carbonate to give CO\textsubscript{2}

6 Suggest methods by which the following compounds could be distinguished from one another by simple chemical tests. In each test, state clearly the reagents and conditions, as well as the observations obtained.
(a) CH\textsubscript{3}CH=CHCH\textsubscript{2}OH and CH\textsubscript{3}CH(OH)CH=CH\textsubscript{2}
(b) CH\textsubscript{3}OH and CH\textsubscript{3}CH\textsubscript{2}OH
(c) C\textsubscript{6}H\textsubscript{5}OH and cyclohexanol
(d) 1-chloropropane and 2-chloropropane

7 (a) State and explain how the acidities of water, phenol and ethanol compare with each other.
(b) State the reagents and conditions needed to convert phenol to 4-nitrophenol.
(c) Suggest and explain how the acidity of 4-nitrophenol might compare with that of phenol.
(d) Phenacetin can be synthesized from 4-nitrophenol by the following route:

(i) Suggest reagents and conditions for Step II.
(ii) What type of reactions are Steps II and III?
(iii) Suggest why compound J is converted to K before reaction is carried out.

8 All the isomeric alcohols with the molecular formula C\textsubscript{5}H\textsubscript{12}O are added separately to warm alkaline aqueous iodine. How many of the isomers will give a yellow precipitate? (Ignore stereoisomers)
CARBONYL COMPOUNDS

- Aldehydes (exemplified by ethanal)
  (i) Oxidation to carboxylic acid
  (ii) Reaction with hydrogen cyanide
  (iii) Characteristic tests for aldehydes

- Ketones (exemplified by propanone and phenylethanone)
  (i) Reaction with hydrogen cyanide
  (ii) Characteristic tests for ketones

<table>
<thead>
<tr>
<th>Learning Outcomes</th>
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</thead>
<tbody>
<tr>
<td>Candidates should be able to:</td>
</tr>
<tr>
<td>(a) describe the formation of aldehydes and ketones from, and their reduction to, primary and secondary alcohols respectively</td>
</tr>
<tr>
<td>(b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones</td>
</tr>
<tr>
<td>(c) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds</td>
</tr>
<tr>
<td>(d) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling’s and Tollens’ reagents; ease of oxidation)</td>
</tr>
<tr>
<td>(e) describe the reaction of CH₃CO⁻ compounds with alkaline aqueous iodine to give triiodomethane</td>
</tr>
</tbody>
</table>
1.4 Physical Properties

**Boiling points**

Aldehydes and ketones are polar molecules due to the permanent $\delta^+$ and $\delta^-$ charges on C and O atoms in the C=O bond. Hence, the intermolecular forces of attraction between aldehydes and ketones are permanent dipole-permanent dipole interactions.

For molecules with similar relative molecular mass, Aldehydes and ketones have higher boiling points than alkanes as alkanes only have weak dispersion forces but lower boiling points than alcohols as alcohols have hydrogen bonding.

**Solubility**

Short-chain aldehydes and ketones are soluble in water as they are able to form hydrogen bonds with water molecules due to lone pairs on O atom in C=O bond.

![Diagram](attachment:image)

However, as the number of carbon atoms increases, solubility decreases as the non-polar hydrocarbon chain is unable to form strong interactions with water.
Note:
• Since the carbonyl carbon is trigonal planar, CN\(^{-}\) can attack the carbon from either the top or bottom at equal probability. Hence, solution formed is **racemic and optically inactive**.

• The reaction is a **step-up** reaction as the number of carbon atoms increase.

• The nitrile group \(\text{–CN}\) can further react in the following ways:

**1. Acid hydrolysis**

\[
\text{R} - \text{CN} + 2 \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{R} - \text{COOH} + \text{NH}_4^+
\]

**Reagents:** H\(_2\)SO\(_4\) (aq)

**Conditions:** Heat under reflux

**2. Base hydrolysis**

\[
\text{R} - \text{CN} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{R} - \text{COO}^- + \text{NH}_3
\]

**Reagents:** NaOH (aq)

**Conditions:** Heat under reflux

**3. Reduction**

\[
\text{R} - \text{CN} + 4 [\text{H}] \rightarrow \text{R} - \text{CH}_2\text{NH}_2
\]

**Reagents:** LiAlH\(_4\) in dry ether

**Conditions:** Room temperature

OR

**Reagents:** H\(_2\), Pt catalyst

**Conditions:** high pressure and temperature
CARBOXYLIC ACIDS AND DERIVATIVES

• Carboxylic acids (exemplified by ethanoic acid and benzoic acid)
  (i) Formation from primary alcohols and nitriles
  (ii) Salt, ester and acyl chloride formation

• Acyl chlorides (exemplified by ethanoyl chloride)
  (i) Ease of hydrolysis compared with alkyl and aryl chlorides
  (ii) Reaction with alcohols, phenols and primary amines

• Esters (exemplified by ethyl ethanoate and phenyl benzoate)
  (i) Formation from carboxylic acids and from acyl chlorides
  (ii) Hydrolysis (under acidic and under basic conditions)

<table>
<thead>
<tr>
<th>Learning Outcomes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candidates should be able to:</td>
</tr>
<tr>
<td>(a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles</td>
</tr>
<tr>
<td>(b) describe the reactions of carboxylic acids in the formation of</td>
</tr>
<tr>
<td>(i) salts</td>
</tr>
<tr>
<td>(ii) esters on reaction with alcohols, using ethyl ethanoate as an example</td>
</tr>
<tr>
<td>(iii) acyl chlorides, using ethanoyl chloride as an example</td>
</tr>
<tr>
<td>(c) explain the acidity of carboxylic acids and of chlorine-substituted ethanoic acids in terms of their structures</td>
</tr>
<tr>
<td>(d) describe the hydrolysis of acyl chlorides</td>
</tr>
<tr>
<td>(e) describe the reactions of acyl chlorides with alcohols, phenols and primary amines</td>
</tr>
<tr>
<td>(f) explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides</td>
</tr>
<tr>
<td>(g) describe the formation of esters from acyl chlorides, using phenyl benzoate as an example</td>
</tr>
<tr>
<td>(h) describe the acid and base hydrolys of esters</td>
</tr>
</tbody>
</table>
2. Preparation of Carboxylic Acids

2.1 Oxidation of Primary Alcohols or Aldehydes

\[
\text{RCH}_2\text{OH} + 2\text{[O]} \rightarrow \text{RCOOH} + \text{H}_2\text{O}
\]

\[
\text{RCHO} + \text{[O]} \rightarrow \text{RCOOH} + \text{H}_2\text{O}
\]

**Reagents:** K\(_2\)Cr\(_2\)O\(_7\) (aq), H\(_2\)SO\(_4\) (aq)

**Conditions:** Heat

**Observations:** Orange Cr\(_2\)O\(_7^{2-}\) turns green

OR

**Reagents:** KMnO\(_4\) (aq), H\(_2\)SO\(_4\) (aq)

**Conditions:** Heat

**Observations:** Purple MnO\(_4^{-}\) decolorises

2.2 Oxidative Cleavage of Alkenes

Example:

**Reagents:** KMnO\(_4\) (aq), H\(_2\)SO\(_4\) (aq)

**Conditions:** Heat under reflux

**Observations:** Purple MnO\(_4^{-}\) decolorizes

2.3 Hydrolysis of Nitrile Groups (C≡N)

\[
\text{R-CN} + 2\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{R-COOH} + \text{NH}_4^+
\]

**Reagents:** H\(_2\)SO\(_4\) (aq)

**Conditions:** Heat under reflux

2.4 Hydrolysis of Acyl Chlorides (RCOCl)

\[
\text{RCOCI} + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{HCl}
\]

**Reagents:** H\(_2\)O

**Conditions:** Room temperature

**Observations:** White fumes of HCl evolved
1 The molecules α-Vetivone and Khusimol are isolated from the vetiver grass native to India.

α–Vetivone

Khusimol

Which of the following reactions can distinguish α–vetivone and Khusimol?

1 Acidified KMnO₄, reflux, followed by the addition of aqueous sodium carbonate.
2 Addition of 2,4-dinitrophenylhydrazine.
3 Addition of PCl₅.

For each of the following, suggest a simple chemical test to distinguish one compound from the other. State the reagents and conditions and describe the observations for each of the compound.

(a) Chloroethane and ethanoyl chloride
(b) CH₃COOH and HCOOH

For each of the following, suggest a simple chemical test to distinguish one compound from the other. State the reagents and conditions and describe the observations for each of the compound.

1. Acidified KMnO₄, reflux, followed by the addition of aqueous sodium carbonate.
2. Addition of 2,4-dinitrophenylhydrazine.
3. Addition of PCl₅.

For each of the following, suggest a simple chemical test to distinguish one compound from the other. State the reagents and conditions and describe the observations for each of the compound.

(a) Chloroethane and ethanoyl chloride
(b) CH₃COOH and HCOOH

The following table compares the pKₐ values of the two acids.

<table>
<thead>
<tr>
<th>acid</th>
<th>structure</th>
<th>pK₁</th>
<th>pK₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>maleic</td>
<td>H</td>
<td>1.90</td>
<td>6.07</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fumaric</td>
<td>H</td>
<td>3.03</td>
<td>4.44</td>
</tr>
<tr>
<td></td>
<td>COOH</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(i) Suggest a reason why the pK₁ value of fumaric acid is lower than its pK₂.
(ii) Suggest a reason why the pK₁ value of maleic acid is lower than the pK₁ of fumaric acid.
NITROGEN COMPOUNDS

• Amines (exemplified by ethylamine and phenylamine)
  (i) Their formation
  (ii) Salt formation
  (iii) Other reactions of phenylamine
• Amides (exemplified by ethanamide)
  (i) Their formation from acyl chlorides
  (ii) Their hydrolysis
• Amino acids (exemplified by aminoethanoic acid)
  (i) Their acid and base properties
  (ii) Zwitterion formation
• Proteins
  (i) Protein structure: primary; secondary; tertiary; quaternary structures
  (ii) The hydrolysis of proteins
  (iii) Denaturation of proteins

Learning Outcomes

Candidates should be able to:

(a) describe the formation of ethylamine and of phenylamine (by the reduction of nitrobenzene)
(b) explain the basicity of amines
(c) explain the relative basicities of ammonia, ethylamine and phenylamine in terms of their structures
(d) describe the reaction of phenylamine with aqueous bromine
(e) describe the formation of amides from the reaction between RNH₂ and R'COCl
(f) describe amide hydrolysis on treatment with aqueous alkali or acid
(g) describe the acid/base properties of amino acids and the formation of zwitterions
(h) describe the formation of peptide (amide) bonds between amino acids and, hence, explain protein formation
(i) list the major functions of proteins in the body
(j) describe the hydrolysis of proteins
(k) explain the term primary structure of proteins
(l) recognise that the twenty amino acids that make up all the proteins in the body are α-amino acids with the general formula RCH(NH₂)CO₂H, and be able to interpret the properties of α-amino acids in terms of the nature of the R group
(m) describe the secondary structure of proteins: α-helix and β-pleated sheet and the stabilisation of these structures by hydrogen bonding
(n) state the importance of the tertiary protein structure and explain the stabilisation of the tertiary structure with regard to the R groups in the amino acid residues (ionic linkages, disulfide bridges, hydrogen bonds and van der Waals’ forces)
(o) describe
   (i) the quaternary structure of proteins
   (ii) the protein components of haemoglobin
(p) explain denaturation of proteins by heavy metal ions, extremes of temperature and pH changes
(q) apply the knowledge of the loss and formation of secondary and tertiary structures to interpret common everyday phenomena
3. Amides

Amides can be classified as primary (1°), secondary (2°) and tertiary (3°) according to the number of R groups attached to it.

![Image of amide structures]

3.1 Physical Properties of Amides

Volatile

Primary and secondary amides have relatively high melting and boiling points due to extensive intermolecular hydrogen bonding. Most primary amides (except methanamide) exist as crystalline solids at room temperature.

Tertiary amides have lower boiling points than primary and secondary amides because there are no N – H bonds available for hydrogen bonding. As such, tertiary amides only have permanent dipole - permanent dipole interactions and it is easier to overcome this interaction, hence the lower boiling point.

Solubility

Amides are soluble in water as they form extensive hydrogen bonds with water molecules due to presence of lone pairs on N atom as well as N–H bonds. As the number of non-polar groups attached increases, solubility decreases.
Buffer Solution

Amino acids can act as a buffer to resist pH changes.

When a small amount of acid is added, NH$_2$ group can react with H$^+$:

$$RNH_2 + H^+ \rightarrow RNH_3^+$$

When a small amount of base is added, COOH group can react with OH$^-$:

$$RCOOH + OH^- \rightarrow RCOO^- + H_2O$$

4.3 Formation of Peptide Bonds

Amino acids can form peptide bonds (or amide linkage) with another amino acid through the condensation reaction between the COOH group of one amino acid and the NH$_2$ group of another amino acid, with the loss of one water molecule.

The product formed from two amino acids is a dipeptide.
The product formed from three amino acids is a tripeptide.

When many amino acids are joined by peptide bonds, they are called polypeptides.

Proteins are naturally occurring polypeptides formed from over 100 amino acids

Conventionally, we draw the amino acid from the N-terminus to the C-terminus (i.e. NH$_2$ group on the left and COOH group on the right).
3 Explain each of the following observations as fully as you can.

(a) The melting point of glycine, \( \text{H}_2\text{NCH}_2\text{COOH} \), (230 – 235 °C) is higher than that of 2-hydroxyethanamide, \( \text{HOCH}_2\text{CONH}_2 \) (102 – 104 °C).

(b) The \( pK_b \) of the following compounds:

(c) Nitration of methylbenzene, \( \text{C}_6\text{H}_5\text{CH}_3 \), produces the 1,2- and 1,4-substituted products as the major products, whereas nitration of tert-butylbenzene, \( \text{C}_6\text{H}_5\text{C(CH}_3)^3 \) gives predominantly the 1,4-substituted product.

4 Reductive amination is a common method used in the pharmaceutical industry that converts carbonyl compounds to amines.

One example of this method is the preparation of ethylamine. Ethanal can be converted to ethylamine by reductive amination with ammonia, using hydrogen gas over a nickel catalyst as the reducing agent.

The reaction is thought to proceed through the following steps.

(i) Given that ammonia acts as a nucleophile in step I, suggest a mechanism for this step. In your answer show any relevant charges, dipoles or lone pairs of electrons you consider important in this mechanism.

(ii) State the type of reaction for step II.

(iii) Suggest, in terms of the mechanism you have described in (b)(i), whether compound A has any effect on plane–polarised light.
ELECTROCHEMISTRY

- Redox processes: electron transfer and changes in oxidation number (oxidation state)
- Electrode potentials
  (i) Standard electrode (redox) potentials, \( E^\circ \); the redox series
  (ii) Standard cell potentials, \( E_{\text{cell}} \) and their uses
  (iii) Batteries and fuel cells
- Electrolysis
  (i) Factors affecting the amount of substance liberated during electrolysis
  (ii) The Faraday constant; the Avogadro constant; their relationship
  (iii) Industrial uses of electrolysis

<table>
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<tr>
<td>Candidates should be able to:</td>
</tr>
<tr>
<td>(a) describe and explain redox processes in terms of electron transfer and/or of changes in oxidation number (oxidation state)</td>
</tr>
<tr>
<td>(b) define the terms:</td>
</tr>
<tr>
<td>(i) standard electrode (redox) potential</td>
</tr>
<tr>
<td>(ii) standard cell potential</td>
</tr>
<tr>
<td>(c) describe the standard hydrogen electrode</td>
</tr>
<tr>
<td>(d) describe methods used to measure the standard electrode potentials of:</td>
</tr>
<tr>
<td>(i) metals or non-metals in contact with their ions in aqueous solution</td>
</tr>
<tr>
<td>(ii) ions of the same element in different oxidation states</td>
</tr>
<tr>
<td>(e) calculate a standard cell potential by combining two standard electrode potentials</td>
</tr>
<tr>
<td>(f) use standard cell potentials to:</td>
</tr>
<tr>
<td>(i) explain/deduce the direction of electron flow from a simple cell</td>
</tr>
<tr>
<td>(ii) predict the feasibility of a reaction</td>
</tr>
<tr>
<td>(g) understand the limitations in the use of standard cell potentials to predict the feasibility of a reaction</td>
</tr>
<tr>
<td>(h) construct redox equations using the relevant half-equations</td>
</tr>
<tr>
<td>(i) predict qualitatively how the value of an electrode potential varies with the concentration of the aqueous ion</td>
</tr>
<tr>
<td>(j) state the possible advantages of developing other types of cell, e.g. the ( \text{H}_2/\text{O}_2 ) fuel cell and improved batteries (as in electric vehicles) in terms of smaller size, lower mass and higher voltage</td>
</tr>
<tr>
<td>(k) state the relationship, ( F = Le ), between the Faraday constant, the Avogadro constant and the charge on the electron</td>
</tr>
<tr>
<td>(l) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series ( electrode potential) and concentration</td>
</tr>
<tr>
<td>(m) calculate:</td>
</tr>
<tr>
<td>(i) the quantity of charge passed during electrolysis</td>
</tr>
<tr>
<td>(ii) the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of ( \text{H}_2\text{SO}_4(\text{aq}) ); ( \text{Na}_2\text{SO}_4(\text{aq}) )</td>
</tr>
<tr>
<td>(n) explain, in terms of the electrode reactions, the industrial processes of:</td>
</tr>
<tr>
<td>(i) the anodising of aluminium</td>
</tr>
<tr>
<td>(ii) the electrolytic purification of copper</td>
</tr>
<tr>
<td>[technical details are not required]</td>
</tr>
</tbody>
</table>
2. Standard Electrode Potential

2.1 Electrode Potential

When a strip of metal M(s) is immersed in a solution of its ions, M^{n+}(aq), the following takes place:

1. **Oxidation** due to metal M ionizing to form M^{n+} ions (M ⇌ M^{n+} + n e^-)
2. **Reduction** due to M^{n+} forming metal M (M^{n+} + n e^- ⇌ M)

Hence, an equilibrium exists between the metal electrode and an aqueous solution of its ions.

\[ M^{n+} + n e^- ⇌ M \]

For reactive metals such as Mg and Zn, the equilibrium lies to the left, and electrons are produced at the electrode as M is converted to M^{n+}, making the electrode negatively charged.

For less reactive metals such as Cu, the equilibrium lies to the right, and electrons are taken from the electrode to form M metal from M^{n+} ions, making the electrode positively charged.

Hence, there exists a potential at the electrode depending on the position of the equilibrium.

If the oxidation potential of the metal (ability of M to undergo oxidation) is high, the equilibrium position lies to the left and the electrode is negatively charged.

If the reduction potential of the metal ions (ability of M^{n+} to undergo reduction) is high, the equilibrium position lies to the right and the electrode is positively charged.

The **equilibrium potential** of the electrode is known as the **electrode potential** or reduction potential.
2.4 Types of Half-Cells

**Metal/Metal Ion**

A metal electrode is in contact with its ions in aqueous solution.

![Metal/Metal Ion Diagram]

**Ion/Ion (different oxidation states)**

A platinum electrode is in contact with the ions of the same element in different oxidation states.

![Ion/Ion Diagram]

**Ion/Gas**

A platinum electrode is in contact with the ions and the gas is bubbled through the aqueous solution.

![Ion/Gas Diagram]
Worked Example 6
For a current of 1.5 A, find the time required to produce by electrolysis:

(a) 27 g of Al from Al^{3+}
(b) 100 g of Cu from Cu^{2+}
(c) 50 cm^{3} of Cl_2 from Cl^{-}
(d) 8 cm^{3} of O_2 from H_2O

Worked Example 7
The quantity of electricity that deposits 2.45 g of silver will also deposit 2.33 g of an unknown metal M in the state of M^{2+}. What is the relative atomic mass of the metal M?

Worked Example 8
0.194 g of chromium is deposited on the cathode during electrolysis when a constant current of 0.5 A is passed through a chromium containing electrolyte for 36 minutes. What is the oxidation number of chromium in the electrolyte?
3 By means of a fully labelled diagram, describe how the standard electrode potential of \( \text{Cr}^{3+} / \text{Cr}^{2+} \) system can be measured by using standard hydrogen electrode.

4 An electrochemical cell has an overall e.m.f. of +1.33 V at 25°C. The overall cell reaction is shown below.

\[
2\text{CO} (g) + \text{O}_2 (g) \rightarrow 2\text{CO}_2 (g)
\]

The cell diagram is given as:

\[
\text{Ni(s)} | \text{CO(g), CO}_2(g)|\text{CO}_3^{2-} (aq) \parallel \text{CO}_3^{2-} (aq)|\text{O}_2(g), \text{CO}_2(g)|\text{Ag(s)}
\]

The reaction occurring at the silver electrode is:

\[
2\text{CO}_2(g) + \text{O}_2 (g) + 4e^- \rightarrow 2\text{CO}_3^{2-} (aq) \quad E^\circ = +0.69V
\]

(a) Deduce the reaction occurring at the nickel electrode and calculate the standard electrode potential for the reaction involved.

(b) Draw a labelled diagram to show the laboratory experimental set-up of the electrochemical cell under standard conditions. Indicate the direction of the electron flow in your sketch.

(c) Suggest a replacement half cell, involving a gas, for \( \text{CO}_3^{2-} (aq)|\text{O}_2(g), \text{CO}_2(g)|\text{Ag(s)} \) which would reverse the direction of the electron flow in this half-cell. Your answer needs to state both the electrode and the reagents of your new half-cell.

5 Use of the Data Booklet is relevant to this question.

Hydrazine (\( \text{N}_2\text{H}_4 \)) can be used to reduce metal ions to their elemental forms in the treatment of wastewater. An important half-equation involving hydrazine is shown.

\[
\text{N}_2 + 4\text{H}_2\text{O} + 4e^- \rightleftharpoons 4\text{OH}^- + \text{N}_2\text{H}_4 \quad E^\circ = -1.17V
\]

Which of the following substances cannot be removed from a wastewater source by hydrazine?

A \( \text{Pb}^{4+} \)  B \( \text{Fe}^{3+} \)  C \( \text{Zn}^{2+} \)  D \( \text{V}^{3+} \)

6 A student set up four standard half-cells each containing one of the metals, \( \text{W}, \text{X}, \text{Y} \) and \( \text{Z} \), immersed in a solution of its metallic salts. These were then used to make different electrochemical cells. The table below shows the standard cell potential, \( E^\circ_{\text{cell}} \) and the negative terminal of each electrochemical cell.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Metals used</th>
<th>( E^\circ_{\text{cell}} / V )</th>
<th>Negative terminal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \text{W and X} )</td>
<td>+1.10</td>
<td>( \text{X} )</td>
</tr>
<tr>
<td>B</td>
<td>( \text{X and Y} )</td>
<td>+0.46</td>
<td>( \text{Y} )</td>
</tr>
<tr>
<td>C</td>
<td>( \text{X and Z} )</td>
<td>+0.47</td>
<td>( \text{X} )</td>
</tr>
</tbody>
</table>

Which one of the following statement is correct?

1  \( \text{W} \) can oxidise \( \text{X, Y} \) and \( \text{Z} \).

2  \( \text{Y} \) has a stronger reducing power than \( \text{Z} \).

3  \( \text{W and Z} \) form a cell represented as \( \text{W(s)} / \text{W}^{n+} (aq) \parallel \text{Z}^{m+} (aq) / \text{Z(s)} \).
GROUP II

- Similarities and trends in the properties of the Group II metals magnesium to barium and their compounds

Learning Outcomes

Candidates should be able to:

(a) describe the reactions of the elements with oxygen and water

(b) describe the behaviour of the oxides with water

(c) interpret and explain qualitatively the trend in the thermal stability of the nitrates in terms of the charge density of the cation and the polarisability of the large anion

(d) interpret, and make predictions from, the trends in physical and chemical properties of the elements and their compounds
1. Physical Properties of Group II Metals

1.1 Atomic Radii and Ionic Radii

<table>
<thead>
<tr>
<th></th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic radius/ nm</td>
<td>0.106</td>
<td>0.140</td>
<td>0.174</td>
<td>0.191</td>
<td>0.198</td>
</tr>
<tr>
<td>Ionic radius/ nm</td>
<td>0.030</td>
<td>0.064</td>
<td>0.094</td>
<td>0.110</td>
<td>0.134</td>
</tr>
</tbody>
</table>

Down the group, atomic radii and ionic radii **increase**.

Nuclear charge increases due to increase in protons. Shielding effect increases due to increase in number of core electrons. Effective nuclear charge remains relatively constant. Size of atom increases due to **increase in number of principal quantum shell**.

1.2 Ionisation Energy

<table>
<thead>
<tr>
<th></th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st IE (kJ mol⁻¹)</td>
<td>899</td>
<td>738</td>
<td>590</td>
<td>550</td>
<td>500</td>
</tr>
</tbody>
</table>

Down the group, first ionization energy **decreases**.

Size of atom increases due to **increase in number of principal quantum shell**, resulting in **weaker attraction between the nucleus and valence electron**. Less energy is required to remove the electron from the nucleus.

1.3 Melting and Boiling Points

<table>
<thead>
<tr>
<th></th>
<th>Be</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>1283</td>
<td>650</td>
<td>850</td>
<td>770</td>
<td>710</td>
</tr>
</tbody>
</table>

Down the group, melting and boiling points generally **decrease**.

Ionic radii of metal increases down the group but number of delocalized electrons remain the same. Weaker electrostatic attraction between the larger cations and the same sea of delocalized electrons. Hence, less energy is required to overcome the **weak metallic bonds**.
GROUP VII

- The similarities and trends in the physical and chemical properties of chlorine, bromine and iodine
  (i) Characteristic physical properties
  (ii) The relative reactivity of the elements as oxidising agents
  (iii) Some reactions of the halide ions
  (iv) The reactions of chlorine with aqueous sodium hydroxide

Learning Outcomes

Candidates should be able to:

(a) describe the trends in volatility and colour of chlorine, bromine and iodine

(b) analyse the volatility of the elements in terms of van der Waals’ forces

(c) describe and deduce from E values the relative reactivity of the elements as oxidising agents

(d) describe and explain the reactions of the elements with hydrogen

(e) (i) describe and explain the relative thermal stabilities of the hydrides, (ii) interpret these relative stabilities in terms of bond energies

(f) describe and explain the reactions of halide ions with:
   (i) aqueous silver ions followed by aqueous ammonia,
   (ii) concentrated sulfuric acid

(g) describe and analyse in terms of changes of oxidation number the reaction of chlorine with cold, and with hot, aqueous sodium hydroxide
1.6 Bond Energy

<table>
<thead>
<tr>
<th>Bond Energy of X-X (kJ mol⁻¹)</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>158</td>
<td>242</td>
<td>193</td>
<td>151</td>
</tr>
</tbody>
</table>

The bond energy decreases down the group as the atomic size of X increases and bond length increases.

Exception: F-F bond is weaker than Cl-Cl bond due to interelectronic repulsion experienced by F atoms due to their small sizes, resulting in a lesser extent of orbital overlap.

2. Chemical Properties

2.1 Oxidising Strength and Reducing Strength

Reduction potential of X₂ decreases down the group.

Consequently,

Oxidising strength of X₂ decreases down the group.
Reducing strength of X⁻ increases down the group.

2.2 Reactivity of Halogens

Reactivity of X₂ decreases down the group.

Down the group, reduction potential of X₂ decreases, hence, it is less likely for X₂ to become X⁻.

A more reactive halogen can displace a less reactive one from its ion form.
Worked Example 1
When aqueous chlorine was added to an unknown sample and the aqueous mixture was shaken with tetrachloromethane, a violet organic layer was observed. Identify the violet organic layer and explain the observations.

Worked Example 2
Aqueous potassium iodide is added to a solution of bromine in hexane in a test-tube and the mixture is shaken. Describe and explain the observations in the above experiment.

2.3 Reaction with Thiosulfate, $S_2O_3^{2-}$
$I_2$ can oxidise $S_2O_3^{2-}$ to $S_4O_6^{2-}$ as oxidation number changes from +2 to +2.5.

$$I_2 (aq) + 2S_2O_3^{2-} (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$$

Since $Br_2$ and $Cl_2$ are stronger oxidizing agents, they can oxidise $S_2O_3^{2-}$ to $SO_4^{2-}$ instead. Oxidation number changes from +2 to +6.

$$4Cl_2 (aq) + S_2O_3^{2-} (aq) + 5H_2O(l) \rightarrow 2SO_4^{2-} (aq) + 10H^+ (aq) + 8Cl^- (aq)$$
$$4Br_2 (aq) + S_2O_3^{2-} (aq) + 5H_2O(l) \rightarrow 2SO_4^{2-} (aq) + 10H^+ (aq) + 8Br^- (aq)$$
Periodicity

• Periodicity of physical properties of the elements: variation with proton number across the third Period (sodium to argon) of:
  (i) atomic radius and ionic radius
  (ii) melting point
  (iii) electrical conductivity
  (iv) ionization energy

• Periodicity of chemical properties of the elements in the third Period
  (i) Reaction of the elements with oxygen and chlorine
  (ii) Variation in oxidation number of the oxides (sodium to sulfur only) and of the chlorides (sodium to phosphorus only)
  (iii) Reactions of these oxides and chlorides with water
  (iv) Acid/base behaviour of these oxides and the corresponding hydroxides

Learning Outcomes

Candidates should be able to:

(a) describe qualitatively (and indicate the periodicity in) the variations in atomic radius, ionic radius, melting point and electrical conductivity of the elements (see the Data Booklet)
(b) explain qualitatively the variation in atomic radius and ionic radius
(c) interpret the variation in melting point and in electrical conductivity in terms of the presence of simple molecular, giant molecular or metallic bonding in the elements
(d) explain the variation in first ionisation energy
(e) describe the reactions, if any, of the elements with oxygen (to give Na₂O; MgO; Al₂O₃; P₂O₅; P₄O₁₀; SO₂; SO₃), and chlorine (to give NaCl; MgCl₂; AlCl₃; SiCl₄; PCl₃; PCl₅)
(f) state and explain the variation in oxidation number of the oxides and chlorides
(g) describe the reactions of the oxides with water [treatment of peroxides and superoxides is not required]
(h) describe and explain the acid/base behaviour of oxides and hydroxides, including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids
(i) describe and explain the reactions of the chlorides with water
(j) interpret the variations and trends in (f), (g), (h), and (i) in terms of bonding and electronegativity
(k) suggest the types of chemical bonding present in chlorides and oxides from observations of their chemical and physical properties

In addition, candidates should be able to:
(l) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity
(m) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties
1.5 Electrical Conductivity

**Na, Mg and Al**
- Na, Mg and Al are metals with metallic bonds and they have **high conductivity due to the delocalized sea of electrons**
- Electrical conductivity increases from Na to Al due to greater number of delocalized sea of electrons

**Si**
- Si exists as a **giant covalent structure** and is a semi-conductor
- It has a lower conductivity than metals but higher than non-metals

**P, S, Cl, Ar**
- P, S, Cl and Ar exist as **simple molecules** and have no mobile charged particles to conduct electricity.
2. Chemical Properties of Elements Across Period

2.1 Diagonal Relationships

A diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third periods of the periodic table due to similar charge densities.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
</tr>
</tbody>
</table>

Considering the ionic radii, charge density and electronegativity of Li, Mg, Be and Al:

<table>
<thead>
<tr>
<th></th>
<th>Be</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic Radii (nm)</td>
<td>0.031</td>
<td>0.050</td>
</tr>
<tr>
<td>Charge density (nm(^{-1}))</td>
<td>64.5</td>
<td>60</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.57</td>
<td>1.61</td>
</tr>
</tbody>
</table>

On moving across a period of the periodic table, the size of the atoms decreases, and on moving down a group the size of the atoms increases.

Similarly, on moving across the period, the elements become progressively more covalent, less basic and more electronegative, whereas on moving down the group the elements become more ionic, more basic and less electronegative.

Thus, on both descending a group and crossing the period by one element, the changes "cancel" each other out, and diagonal elements have similar chemistry.
By definition, the enthalpy change of fusion of a solid is the amount of energy, in J or kJ, needed to melt one mole of a solid at its melting point.

The enthalpy changes of fusion of four successive elements, W to Z, in the third period (sodium to argon) of the Periodic Table is given in the table.

<table>
<thead>
<tr>
<th>element</th>
<th>W</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>enthalpy change of fusion / kJ mol⁻¹</td>
<td>10.8</td>
<td>46.4</td>
<td>0.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Which sequence correctly identifies the elements W to Z?

- A
- B
- C
- D

X, Y and Z are Period 3 elements.

Element X has high thermal conductivity at room temperature. It forms a chloride that hydrolyses in water forming an acidic solution, and an oxide that reacts very slowly with aqueous acids.

Element Y and its oxide have high melting points. The chloride of Y reacts with water to form steamy fumes and an acidic solution.

Element Z has a chloride that forms an acid in water, and an oxide which reacts vigorously with water to form solutions containing strong acids.

Which of the following statements about X, Y and Z is true?

1. The chloride of X sublimes when heated.
2. A chloride of Z reacts with carboxylic acids.
3. The oxides of X and Y readily dissolve in water.

The properties of the oxides of four elements K, L, M and N in the third period in the Periodic Table are given below:

- The oxide of K is insoluble in water and in dilute acid but is soluble in hot and concentrated sodium hydroxide.
- The oxide of L is amphoteric.
- The oxide of M reacts with dilute sodium hydroxide at room temperature.
- The oxide of N dissolves in water to form a strong alkaline solution.

Which of the following is correct in order of increasing proton number?

- A: N, L, K, M
- B: K, L, M, N
- C: N, K, L, M
- D: N, M, K, L

By Stella Seah
TRANSITION METALS

- General physical and characteristic chemical properties of the first set of transition elements, titanium to copper
- Colour of complexes

**Learning Outcomes**

Candidates should be able to:

(a) explain what is meant by a transition element, in terms of d-block elements forming one or more stable ions with incomplete d orbitals

(b) state the electronic configuration of a first row transition element and of its ions

(c) state that the atomic radii, ionic radii and first ionisation energies of the transition elements are relatively invariant

(d) contrast, qualitatively, the melting point; density; atomic radius; ionic radius; first ionisation energy and conductivity of the transition elements with those of calcium as a typical s-block element

(e) describe the tendency of transition elements to have variable oxidation states

(f) predict from a given electronic configuration, the likely oxidation states of a transition element

(g) describe and explain the use of Fe$^{3+}$/Fe$^{2+}$, MnO$_4^-$/Mn$^{2+}$ and Cr$_2$O$_7^{2-}$/Cr$^{3+}$ as examples of redox systems

(h) (i) explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) ions with water and ammonia
(ii) describe the formation, and state the colour of, these complexes

(i) predict, using $E$ values, the likelihood of redox reactions

(j) explain qualitatively that ligand exchange may occur, including CO/O$_2$ in haemoglobin

(k) explain how some transition elements and/or their compounds can act as catalysts

(l) explain, in terms of d orbital splitting, why transition element complexes are usually coloured
(2) When filling a subshell, each orbital must be occupied singly before they are occupied in pairs.

![Diagram showing correct and incorrect electron configurations.]

(3) Each orbital can hold a maximum of 2 electrons with opposite spins.

**EXCEPTION:**

**Half-filled d orbitals are more stable** as electronic repulsion is minimized between singly occupied orbitals. E.g. for Cr atom, electronic configuration should be [Ar] 3d⁵ 4s¹ instead of [Ar] 3d⁵ 4s².

![Diagram showing correct and incorrect Cr electron configurations.]

**Fully-filled d orbitals are more stable** as the subshell has symmetric charge distribution. E.g. for Cu atom, electronic configuration should be [Ar] 3d¹⁰ 4s¹ instead of [Ar] 3d⁹ 4s².

![Diagram showing correct and incorrect Cu electron configurations.]

**Example**
The electronic configuration of Ti would contain fully filled subshells preceding the 3d subshell it is in.

\[
1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2
\]

Since Cr is the fourth element of the 3d orbital, the 3d orbital contains 4 electrons.

\[
1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2
\]

Since 3d⁴ 4s² is the exception stated above, we correct it to 3d⁵ 4s¹.

\[
1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1
\]
4.1.1 Stability of $M^{2+}/M^{3+}$

The reduction potential of $M^{3+}/M^{2+}$ can be used to reflect the relative stabilities of the +3 and +2 oxidation states of the transition elements in aqueous medium. The higher the $E^\Theta$, the more stable $M^{2+}$ is.

The $E^\Theta$ value generally becomes more positive, i.e. metal of +2 oxidation state is more stable across the period. This is because as nuclear charge increases, it becomes increasingly difficult for $M^{2+}$ to lose its 3rd electron.

**Anomaly: Fe$^{2+}$/Fe$^{3+}$**

The dip in $E^\Theta$ for Fe is an anomaly, i.e. Fe$^{3+}$ is more stable than expected.

Fe$^{2+}$ : [Ar] 3d$^6$
Fe$^{3+}$ : [Ar] 3d$^5$

It is easier to remove the 3rd electron from Fe$^{2+}$ because of inter-electronic repulsion in the d$^6$ configuration. Also, a half-filled d subshell is formed in Fe$^{3+}$ which is more stable.

**Anomaly: Cr$^{2+}$/Cr$^{3+}$**

The dip in $E^\Theta$ for Cr is an anomaly, i.e. Cr$^{3+}$ is more stable than expected.

Cr$^{2+}$ : [Ar] 3d$^4$
Cr$^{3+}$ : [Ar] 3d$^3$

Cr$^{3+}$ has a d$^3$ configuration which is more stable. (Not required in A-level syllabus)
4.3.6 Effect of Ligand Exchange on Color

Different ligands split the d-orbitals differently, resulting in different energy levels for d→d transition and hence, the color observed would also be different.

4.3.7 Effect of Ligand Exchange on Reduction Potential

\[
\begin{align*}
    \text{Fe}^{3+} + e^- & \rightleftharpoons \text{Fe}^{2+} & E^\theta &= +0.77 \text{ V} \\
    [\text{Fe(CN)}_6]^{3-} + e^- & \rightleftharpoons [\text{Fe(CN)}_6]^{4-} & E^\theta &= +0.36 \text{ V}
\end{align*}
\]

With the replacement of water ligands by the stronger CN⁻ ligands, the reduction potential becomes less positive, i.e. tendency for reduction is lower.

This is because reduction involves a gain of electrons and it is energetically less feasible for a negatively charged species to gain electrons. Furthermore, CN⁻ ligands stabilize the +3 oxidation state of iron, reducing its oxidizing power.

4.3.8 Effect of Ligand Exchange on Biological Functions

Haemoglobin is the iron containing protein that transports oxygen in blood. It contains iron in the +2 oxidation state.

A haemoglobin molecule (deoxyhaemoglobin) in the lungs picks up an O₂ molecule which is datively bonded to iron to form a species called oxyhaemoglobin. The bonding is reversible and enables haemoglobin to transport oxygen around the body.

![Deoxyhaemoglobin and Oxyhaemoglobin](Image)

Carbon monoxide, CO, binds irreversibly with the Fe²⁺ in haemoglobin to form a stable complex called carboxyhaemoglobin. The affinity of haemoglobin for CO is about 210 times stronger than for O₂. Hence, a relatively small quantity of CO can inactivate a substantial fraction of haemoglobin for oxygen transport. If the concentration of CO is high, the level of carboxyhaemoglobin becomes too high and oxygen transport shuts down resulting in suffocation. Treatment involves breathing pure oxygen to reverse the binding so that concentration of O₂ overrides the stability factor.

Cyanide ions, on the other hand, bind even more strongly than CO and prevent haemoglobin from taking up oxygen. Hence, cyanide is considered a poison.