Section 1.1

1. The relative number of moles of iodine and oxygen.
2. To change the relative number of moles into the ratio of moles of oxygen relative to 1 mole of iodine.
3. In order to produce a ratio involving whole numbers
4. The molar mass is needed.

7. The relative number of moles of iodine and oxygen.
8. To change the relative number of moles into the ratio of moles of oxygen relative to 1 mole of iodine.
9. In order to produce a ratio involving whole numbers
10. The molar mass is needed.

Atoms of copper are approximately twice as heavy as atoms of sulphur. Thus the same mass contains only half as many moles of copper as it does of sulphur.

Black copper(II) oxide (CuO) contains equal numbers of copper and oxygen particles (Cu²⁺ and O²⁻ ions). Red copper(I) oxide (Cu₂O) contains twice as many copper particles as oxygen particles (Cu⁺ and O²⁻ ions).

The mass of the sample is needed to be sure that iodine and oxygen are the only elements in the compound.

Section 1.2

1. All the magnesium reacts.

2. So that we know the number of moles of each substance involved in the reaction.

3. Because 2 moles of magnesium oxide are produced.

4. To find the mass of magnesium oxide produced from 1 g of magnesium.

5. 80/48 would be multiplied by 50 rather than by 6.

6. a) 2.8 g

Section 1.3

1. All the magnesium reacts.
2. So that we know the number of moles of each substance involved in the reaction.
3. Because 2 moles of magnesium oxide are produced.
4. To find the mass of magnesium oxide produced from 1 g of magnesium.
5. 80/48 would be multiplied by 50 rather than by 6.
6. a) 56 tonnes

7. a) 217 tonnes

8. a) Fe₂O₃ + 3CO → 2Fe + 3CO₂
Section 1.4

1 The particles in a gas are much further apart than in a liquid or solid. In a gas, therefore, the volume of the particles is a very small part of the total volume and does not significantly affect it. In a liquid or solid the particles are close together and their volumes must be taken into account when deciding on the total volume.

2 \(\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)\)

b Volume of oxygen is twice that of methane.

c The volume of water vapour formed is twice the volume of methane burnt.

3 \(\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)\)

b Volumes of hydrogen and chlorine are the same.

c Volume of hydrogen chloride is twice the volume of hydrogen or chlorine.

4 \(2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l)\)

b \(5\text{cm}^3\)

c \(300\text{cm}^3\)

5 \(\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l)\)

b \(500\text{cm}^3\)

c \(300\text{cm}^3\)

d \(4\)

e \(2\)

7 \(0.414\text{ dm}^3 (414\text{ cm}^3)\)

8 \(0.25\)

b \(2\)

c \(48\text{ dm}^3\)

d \(240\text{ dm}^3\)

e \(30\text{ dm}^3\)

Section 1.5

1 a i \(0.02\text{ dm}^3\)

b i \(220\text{,000 cm}^3\)

tii \(1.5\text{ dm}^3\)

2 There is 0.4 mole of sodium hydroxide dissolved in every dm\(^3\) of the solution.

3 a 0.5 b 0.4 c 1 d 0.2 e 0.05 f 0.002

4 a 2 b 2 c 5 d 0.2 e 4 f 0.2

5 a 0.25 b 0.2 c 5 d 0.4 e 0.5 f 0.125

7 a 117 g b 3.95 g c 1.4 g d 9930 g e 0.0024 g f 2.385 g g 0.0126 g h 0.1825 g

8 | Concentration/g dm\(^{-3}\) | Concentration/mol dm\(^{-3}\) |
---|---|---|
– | – | 5.15 |
– | 31.5 | 1.51 |
– | 13.4 | – |
– | – | 0.174 |
– | – | 0.065 |
– | 0.6 | – |

Section 2.1

1

| Isotope | Symbol | Atomic number | Mass number | Number of neutrons |
---|---|---|---|---|
carbon-12 | \(^{12}\text{C}\) | 6 | 12 | 6 |
carbon-13 | \(^{13}\text{C}\) | 6 | 13 | 7 |
oxygen-16 | \(^{16}\text{O}\) | 8 | 16 | 8 |
strophium-90 | \(^{90}\text{Sr}\) | 38 | 90 | 52 |
iodine-131 | \(^{131}\text{I}\) | 53 | 131 | 78 |
iodine-123 | \(^{123}\text{I}\) | 53 | 123 | 70 |

2

| Protons | Neutrons | Electrons |
---|---|---|
a | 35 | 44 | 35 |
b | 35 | 46 | 35 |
c | 17 | 18 | 17 |
d | 17 | 20 | 17 |

3 a \(A_j(\text{Br}) = 80.0\)

b \(A_j(\text{Ca}) = 40.1\)

4 a 100 – x

b 193x
c 191(100 – x)
d 193x + 191(100 – x)
e \(193x + 191(100 – x)\) + 100

f 60% iridium-193, 40% iridium-191

5 57.5% antimony-123, 62.5% antimony-121

6 23.5% rubidium-87
Section 2.2

1. a. $^{238}_{92}{}$Pu $\rightarrow ^{234}_{90}{}$U $+ ^{4}_{2}{}$He
   b. $^{235}_{92}{}$U $\rightarrow ^{231}_{90}{}$Fr $+ ^{4}_{2}{}$He
   c. $^{234}_{92}{}$Pu $\rightarrow ^{230}_{90}{}$Th $+ ^{4}_{2}{}$He

2. a. $^{90}_{38}{}$Sr $\rightarrow ^{86}_{54}{}$Kr $+ ^{0}_{-1}{}$e
   b. $^{131}_{53}{}$I $\rightarrow ^{127}_{54}{}$Xe $+ ^{0}_{-1}{}$e
   c. $^{231}_{90}{}$Th $\rightarrow ^{227}_{91}{}$Pa $+ ^{0}_{-1}{}$e

3. a. $^{7}_{3}{}$Li $+ ^{1}_{1}{}$p $\rightarrow ^{2}_{2}{}$He
   b. $^{14}_{7}{}$N $+ ^{4}_{2}{}$He $\rightarrow ^{17}_{8}{}$O $+ ^{1}_{1}{}$p
   c. $^{14}_{7}{}$N $+ ^{4}_{2}{}$He $\rightarrow ^{17}_{8}{}$O $+ ^{1}_{1}{}$p
   d. $^{17}_{7}{}$Al $+ ^{4}_{2}{}$He $\rightarrow ^{20}_{8}{}$Ca $+ ^{1}_{1}{}$p

4. a. $^{226}_{88}{}$Ra $\rightarrow ^{222}_{86}{}$Rn $\rightarrow ^{218}_{84}{}$Po
   b. $^{232}_{90}{}$Th $\rightarrow ^{232}_{90}{}$Th $\rightarrow ^{228}_{86}{}$Rn $\rightarrow ^{224}_{84}{}$Po
   c. $^{4.5}_{-1}{}$s
   d. $^{0.039}_{-1}{}$g
   e. $^{0.625}_{-1}{}$g

Section 2.3

1. No. Isotopes have the same number of protons and the same number of electrons.
2. a. X is in Group 1.
   b. Y is in Group 0.
   Group 1 elements have a single electron in their outer shell, which they lose readily. Noble gases in Group 0 have 2 or 8 electrons in their outer shell and it is difficult to remove one of these electrons.
3. a. $^{1s^{2}2s^{2}2p^{1}}$ Li
   b. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{3}}$ S
   c. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{5}}$ Cl
   d. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}}$ Ti
   e. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4d^{2}5s^{2}}$ Sn

Section 2.4

1. a. s block: metals
   b. p block: mixture of metals and non-metals
   c. d block: metals
   d. f block: metals

2. a. The electron is in the first electron shell.
   b. The electron is in an s type orbital.
   c. There are two electrons in this orbital.
3. a. s block
   b. p block
   c. p block
   d. f block
   e. d block
   f. p block
   g. f block
   h. s block

5. a. Chlorine
   b. Potassium
   c. Titanium
   d. Tin

6. a. $^{1s^{2}2s^{2}2p^{3}}$ Li
   b. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{3}}$ S
   c. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{5}}$ Cl
   d. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}}$ Ti
   e. $^{1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4d^{2}5s^{2}}$ Sn

Section 3.1

1. a. $^{2.8}_{8}{}$Li
   b. $^{2.8}_{8}{}$H
   c. $^{2.8}_{8}{}$F
   d. $^{2.8}_{8}{}$Cl
   f. $^{2.8}_{13}{}$S
   h. $^{2.8}_{17}{}$P

2. $^{+}{}$K, $^{2+}{}$Ca, $^{3+}{}$Sc, $^{2-}{}$Cl, $^{2-}{}$S, $^{3-}{}$P

3. a. $^{+}{}$Li
   b. $^{+}{}$K

4. $^{+}{}$K

5. $^{+}{}$Cl

6. $^{+}{}$F

7. $^{+}{}$S

8. $^{+}{}$P
In a normal covalent bond, each atom supplies a single electron to make up the pair of electrons involved in the bond. In a dative covalent bond one atom supplies both electrons.

Chlorine has a stronger electron pulling power. Thus in a covalent bond between carbon and chlorine, the electron pair forming the bond is more strongly attracted by the chlorine atom than by the carbon atom.

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Section 3.2

1. a. Li(g) because it has an extra electron shell.
   b. Li⁺(aq) because the ion is surrounded by water molecules.
   c. Cl⁻(g) because it has an extra electron.
   d. Cl⁻(aq) because the ion is surrounded by water molecules.

2. a. K⁺(g) because it has an extra electron shell.
   b. Br⁻(g) because it has an extra electron shell.
   c. Na⁺(g) because it has one less proton in the nucleus and therefore attracts the same number of electrons less strongly.
   d. Fe²⁺(g) because it has one more electron.

3. a. K⁺(aq)
   b. K⁺(aq)
   c. K⁺(aq)

4. a. Na⁺
   b. Na⁺Cl⁻
   c. Na⁺Cl⁻
   d. Na⁺Cl⁻

5. a. i. 11, 12, 13, 15, 16, 17
   ii. Na⁺, Mg²⁺, Al³⁺ 1s² 2s² 2p⁶
   P³⁻, S²⁻, Cl⁻ 1s² 2s² 2p⁶ 3s² 3p⁶
   b. i. Same electronic configuration.
   ii. Different number of protons in the nucleus leading to different ionic charges.
   c. Contraction of ion size as the number of protons relative to the number of electrons increases.
   d. P³⁻ is the biggest and Cl⁻ is the smallest because of the increasing attraction on the same number of electrons of an increasing number of protons in the nucleus.
   e. They each contain an extra shell of electrons.

Section 3.3

1. a. \[ \begin{array}{c}
   & \text{Si} \\
   \text{H} & \text{H} \\
   \text{Si} & \text{H} \\
   \text{H} & \text{H}
\end{array} \]
   109°

   b. \[ \begin{array}{c}
   & \text{S} \\
   \text{H} & \text{X} \\
   \text{S} & \text{X} \\
   \text{H} & \text{X}
\end{array} \]
   Approx. 109°

   c. \[ \begin{array}{c}
   & \text{P} \\
   \text{H} & \text{X} \\
   \text{P} & \text{X} \\
   \text{H} & \text{X}
\end{array} \]
   Approx. 109°

   d. \[ \begin{array}{c}
   \text{O} \\
   \text{C} & \text{X} \\
   \text{C} & \text{X} \\
   \text{O} & \text{X}
\end{array} \]
   180°

   e. \[ \begin{array}{c}
   \text{F} \\
   \text{X} & \text{X} \\
   \text{F} & \text{X} \\
   \text{X} & \text{X}
\end{array} \]
   Approx. 109°

   f. \[ \begin{array}{c}
   \text{Cl} \\
   \text{X} & \text{X} \\
   \text{Cl} & \text{X} \\
   \text{X} & \text{X}
\end{array} \]
   120°

   g. \[ \begin{array}{c}
   \text{H} \\
   \text{C} & \text{X} \\
   \text{C} & \text{X} \\
   \text{H} & \text{X}
\end{array} \]
   180°

2. a. \[ \begin{array}{c}
   & \text{H} \\
   \text{H} & \text{H} \\
   \text{C} & \text{C} & \text{H} \\
   \text{H} & \text{H} & \text{H}
\end{array} \]
   All bond angles 120°

   b. \[ \begin{array}{c}
   \text{H} \\
   \text{C} & \text{O} & \text{H} \\
   \text{H} & \text{O} & \text{H}
\end{array} \]
   All bond angles approx. 109°

   c. \[ \begin{array}{c}
   \text{H} \\
   \text{C} & \text{N} & \text{H} \\
   \text{H} & \text{N} & \text{H}
\end{array} \]
   All bond angles approx. 109°

3. \[ \begin{array}{c}
   \text{F} \\
   \text{X} & \text{N} & \text{F} \\
   \text{X} & \text{X} & \text{X}
\end{array} \]
   a. Tetrahedral
   b. Pyramidal

4. a. Tetrahedral
   b. Planar
   c. Linear

5. a. i. \[ \begin{array}{c}
   \text{H} \\
   \text{H} & \text{X} \\
   \text{C} & \text{X} \\
   \text{H} & \text{X}
\end{array} \]
   ii. Planar (trigonal)

   b. i. \[ \begin{array}{c}
   \text{H} \\
   \text{H} & \text{X} \\
   \text{C} & \text{X} \\
   \text{H} & \text{X}
\end{array} \]
   ii. Pyramidal (tetrahedral with respect to electron pairs)
Section 3.4

1. a. C₆H₁₄, C₆H₁₂, not isomers
   b. C₄H₉Cl, C₄H₉Cl, isomers
   c. C₃H₈O, C₃H₆O, not isomers
   d. C₇H₈O, C₇H₈O, isomers
   e. C₃H₉N, C₃H₉N, isomers

2. Isomers of C₅H₁₂:

3. There are 4 isomers of C₄H₉Br:

4. Isomers of C₅H₁₀ (containing a benzene ring):

5. 2-methylbutane

6. 2,2-dimethylpropane

7. pentane

8. About 109°

9. About 120°
Section 3.5

1. cis-1,2-difluoroethene
   \[ \text{ cis-1,2-difluoroethene } \]
   \[ \text{ trans-1,2-difluoroethene } \]

2. trans-pent-2-ene
   \[ \text{ trans-pent-2-ene } \]

3. cis-1,2-dichloroethene
   \[ \text{ cis-1,2-dichloroethene } \]
   \[ \text{ trans-1,2-dichloroethene } \]

4. a. \[ \text{ cis-isoform } \]
   b. No
   c. There must be the same two atoms or groups of atoms on each C atom attached to the double bond. Geometric isomers are not possible if two groups on one side of the double bond are the same.

5. a. Cis-trans isomers
   b. 2 moles of \( \text{H}_2 \)
   c. Citronellol is a partially hydrogenated form of nerol (or geraniol).
   d. Structural isomers of the cis- and trans-isomers.

6. cis-poly(ethyne)
   \[ \text{ cis-poly(ethyne) } \]
   trans-poly(ethyne)

7. a. \[ \text{ cis form } \]
   b. \[ \text{ trans form } \]

Section 3.6

1. a. A chiral centre.
   b. iii

2. a. \[ \text{ cis-form } \]
   b. \[ \text{ trans-form } \]

3. a. \[ \text{ cis-form } \]
   b. \[ \text{ trans-form } \]
   c. \[ \text{ L-cysteine } \]

4. a b. \[ \text{ cis-isomer } \]
   c. \[ \text{ trans-isomer } \]

5. \( \text{d-isoform} \)

(Use the CORN rule to name the isomers.)

6. t-Cysteine is readily available as a hydrolysis product of proteins.
   d-Cysteine has to be made synthetically. It is probably made together with t-cysteine from which it must be separated.
Section 4.1

1. **Standard enthalpy change of combustion** is the enthalpy change when 1 mole of the compound is burnt completely in oxygen, under standard conditions (i.e., the compound and the products in their most stable states at 1 atmosphere pressure and at a stated temperature, often 298 K).

2. The formation of a compound from its elements may be an exothermic reaction ($\Delta H_f$ negative) or an endothermic reaction ($\Delta H_f$ positive). However, energy is liberated whenever a substance burns, so combustion reactions are always exothermic ($\Delta H_c$ negative).

3. ![Diagram with reactions and enthalpy changes]

4. a. $2\text{C(s)} + 3\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH(l)}$
   b. $\text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(l)}$
   c. $4\text{C(s)} + 5\text{H}_2(\text{g}) \rightarrow \text{C}_4\text{H}_{10}(\text{g})$
   d. $\text{C}_4\text{H}_{10}(\text{g}) + 6\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O(l)}$

5. ![Chemical reactions with enthalpies]

6. a. Thermometer, measuring cylinder, gas meter.
   b. Volume of water used, temperature rise of water, volume of gas used.
   c. Cooling losses, impurity of the gas, etc.

7. a. $\Delta H = -667 \text{ kJ mol}^{-1}$
   b. Much heat was lost to the surroundings in the experiment whereas the accurate $\Delta H$ value in the data book would have been determined using a calorimeter in which very little heat is lost.

8. a. $M(\text{C}_7\text{H}_{16}) = 100$
   b. i. 481.7 kJ released
      ii. 481 700 kJ released
      (Assumed combustion is complete and $\text{CO}_2$ and $\text{H}_2\text{O}$ are the only products. Also, that combustion is carried out under standard conditions.)
   c. Density of heptane

9. a. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$
   b. $\Delta H_{\text{f}_{298}}(\text{H}_2\text{O}) = -286 \text{ kJ mol}^{-1}$
   c. $-143 \text{ kJ}$ (assuming combustion takes place under standard conditions)
   d. $+286 \text{ kJ mol}^{-1}$

10. a. Enthalpy change of formation of propane.
   b. Enthalpy change of combustion of 3 moles of carbon and 4 moles of hydrogen.
   c. Enthalpy change of combustion of propane.
   d. $\Delta H_f + \Delta H_c = \Delta H_i$
   e. $\Delta H_f = \Delta H_i - \Delta H_c$
   f. $3(-393) \text{ kJ mol}^{-1} + 4(-286) \text{ kJ mol}^{-1}$
   g. $-103 \text{ kJ mol}^{-1}$

11. a. $4\text{C(s)} + 5\text{H}_2(\text{g}) \rightarrow \text{C}_4\text{H}_{10}(\text{g})$
   b. $\Delta H_1 \rightarrow \Delta H_2 \rightarrow \Delta H_3 \rightarrow \Delta H_4$
   c. $\text{C}_4\text{H}_{10}(\text{g}) + 6\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O(l)}$
**Section 4.2**

1. **a** \( \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \)
   - \( \Delta H = 4(-393) + 5(-286) - (-2877) = -125 \text{ kJ mol}^{-1} \)

2. **a** \( \text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g) \)
   - \( \Delta H = 6(-393) + 8(-286) - 2(-2877) = -8542 \text{ kJ mol}^{-1} \)

3. **a** \( \text{CH}_3\text{OH}(l) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g) \)
   - \( \Delta H = 2(+464) - (+945) - 4(+391) = -581 \text{ kJ mol}^{-1} \)

4. **a** \( \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \)
   - \( \Delta H = 158 + 4(391) + (+498) + (+158) + 6(+413) + (+193) + (+413) + (+290) + (+347) = -122 \text{ kJ mol}^{-1} \)

**Section 4.3**

1. **a** Increase
   - **b** Decrease
   - **c** Increase
   - **d** Increase
   - **e** Decrease
   - **f** Decrease

2. **a** Molten wax
   - (Liquids have higher entropies than solids.)
   - **b** \( \text{Br}_2(g) \)
   - (Gases have higher entropies than liquids.)
   - **c** Brass
   - (Mixtures have higher entropies than the pure substances.)
   - **d** Octane
   - (Complex molecules have higher entropies than simpler molecules.)

3. **a** 1 in 256
   - **b** Ar molecule larger than He.
   - **c** Cl\(_2\) molecule larger than F\(_2\)

4. **a** Greater. A gas is formed as a product.
   - **b** Smaller. Number of molecules of gas in product smaller than the number of molecules of gas in reactants.
   - **c** Smaller. One reactant is a gas; product only solid.
Section 4.4

1 The entropies increase for the first four alkanes as the molecules become heavier and composed of more atoms (the number of energy levels increases with the number of atoms). Pentane is a liquid and so has a lower entropy than butane.

2 a Entropy decrease, because the number of moles of gas is reduced by half as reaction proceeds.
b Entropy increase; the number of moles of gas doubles during the reaction and a solid has much lower entropy than a gas.
c Entropy decrease; 2 moles of gaseous reactants are replaced by 1 mole of solid.
d Entropy decrease; 5 moles of gaseous oxygen are removed, the only product is a solid.
e Entropy increase; 5 moles of gaseous product are formed.

3 Students’ answers should be based on the following deductions.

<table>
<thead>
<tr>
<th>Explanation</th>
<th>ΔS_{sys}</th>
<th>ΔS_{surr}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous: total entropy change positive</td>
<td>+203</td>
<td>-44</td>
</tr>
<tr>
<td>Spontaneous: total entropy change positive</td>
<td>+63</td>
<td>+329</td>
</tr>
<tr>
<td>Not spontaneous: total entropy change negative</td>
<td>+25</td>
<td>-604</td>
</tr>
<tr>
<td>Spontaneous: total entropy change positive</td>
<td>+209</td>
<td>+416</td>
</tr>
<tr>
<td>Not spontaneous: total entropy change negative</td>
<td>-4</td>
<td>-6.7</td>
</tr>
</tbody>
</table>

4 Values for both ΔS_{sys} and ΔS_{surr} are negative. Therefore ΔS_{total} must always be negative, whatever value of T is chosen, and the process can never be spontaneous.

Section 4.5

1 a LiF; Li" has a smaller radius than Na" and attracts F' ions more strongly.
b NaO: Na" has a smaller radius than Rb" and attracts O2' more strongly.
c MgO; Mg2" is smaller and more highly charged than Na", and attracts O2' more strongly.
d KF; F' has a smaller radius than Cl' and attracts K" more strongly.

2 a SrF2; Sr2" is smaller and more highly charged than Rb" and will attract F' more strongly.
b By the same arguments as in a, BaO should have the more exothermic lattice enthalpy.
c CuCl2; Cu2" is more highly charged than Cu", so CuO should have the more exothermic lattice enthalpy.

3 a AgCl has endothermic enthalpy changes of solution and the enthalpy level diagrams will have the form shown below.

4 a Mg(OH)2 + 152 kJ mol⁻¹
   Ca(OH)2 + 7 kJ mol⁻¹
b Ca(OH)2: enthalpy change of solution much less endothermic.
c Entropy changes of the processes.

5 a The ions in the lattice attract each other less strongly as the size of the anion increases from F' to Cl'.
b ΔH_{tpd} becomes less exothermic as the anion becomes bigger and attaches water molecules less strongly.
c AgF may be soluble in water. AgCl will be insoluble.

6 a Mg(OH)2 + 152 kJ mol⁻¹
   Ca(OH)2 + 7 kJ mol⁻¹
b Ca(OH)2: enthalpy change of solution much less endothermic.
c Entropy changes of the processes.
Section 4.6

1  a  i  Li(s) + $\frac{1}{2}$Cl$_2$(g) $\rightarrow$ LiCl(s)
   ii  Li(s) $\rightarrow$ Li(g)
   iii  $\frac{1}{2}$Cl$_2$(g) $\rightarrow$ Cl(g)
   iv  Li(g) $\rightarrow$ Li$^+$ (g) + e$^-$
   v  Cl(g) + e$^-$ $\rightarrow$ Cl$^-$ (g)
   vi  Li$^+$ (g) + Cl$^-$ (g) $\rightarrow$ LiCl(s)

   b  
   \[ \Delta H_1 \]
   \[ \Delta H_2 \]
   Li(s) + Cl$_2$(g) $\rightarrow$ LiCl(s)
   Li(g) + Cl(g) $\rightarrow$ Li$^+$ (g) + Cl$^-$ (g)

   $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$
   \[ \Delta H_{LE}(LiCl) = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 \]
   \[ = (-409 \text{ kJ mol}^{-1}) - (+159 \text{ kJ mol}^{-1}) \]
   \[ + 121 \text{ kJ mol}^{-1} - (+519 \text{ kJ mol}^{-1}) \]
   \[ - 355 \text{ kJ mol}^{-1} \]
   \[ \Delta H_{LE}(LiCl) = -853 \text{ kJ mol}^{-1} \]

e  See Graph in facing column

2  a  i  Mg(s) + Cl$_2$(g) $\rightarrow$ MgCl$_2$(s)
   ii  Mg(s) $\rightarrow$ Mg(g)
   iii  $\frac{1}{2}$Cl$_2$(g) $\rightarrow$ Cl(g)
   iv  Mg(g) $\rightarrow$ Mg$^+$ (g) + e$^-$
   v  Mg$^+$ (g) $\rightarrow$ Mg$^{2+}$ (g) + e$^-$
   vi  Cl(g) + e$^-$ $\rightarrow$ Cl$^-$ (g)
   vii  Mg$^{2+}$ (g) + 2Cl$^-$ (g) $\rightarrow$ MgCl$_2$(s)

   b  
   \[ \Delta H_1 \]
   \[ \Delta H_2 \]
   Mg(s) + Cl$_2$(g) $\rightarrow$ MgCl$_2$(s)
   Mg(g) + 2Cl(g) $\rightarrow$ Mg$^{2+}$ (g) + 2Cl$^-$ (g)

   $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$
   \[ \Delta H_{LE}(MgCl_2) = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 \]
   \[ = (-641 \text{ kJ mol}^{-1}) - (+147 \text{ kJ mol}^{-1}) \]
   \[ + 2 (+121 \text{ kJ mol}^{-1}) \]
   \[ + 2 (+744 \text{ kJ mol}^{-1}) \]
   \[ + 1457 \text{ kJ mol}^{-1} + 2 (-355 \text{ kJ mol}^{-1}) \]
   \[ \Delta H_{LE}(MgCl_2) = -2521 \text{ kJ mol}^{-1} \]

As Group 1 is ascended, the enthalpy changes of formation of the chlorides become less negative and the first ionisation enthalpies of the elements become more positive.
The enthalpy change of formation of CaCl₂ is much more negative than that of CaCl. CaCl₂ has lower energy and is more stable relative to the elements Ca and Cl₂, and so it is more likely to be formed.
Section 5.1

1. \( \text{Ca}^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow \text{BaSO}_4(s) \)
2. \( \text{Mg}^{2+} (aq) + \text{SO}_4^{2-} (aq) \)
3. \( \text{K}^+ (aq) + \text{OH}^- (aq) \)
4. \( 2\text{Na}^+ (aq) + \text{SO}_4^{2-} (aq) + 10\text{H}_2\text{O}(l) \rightarrow \text{Na}_2\text{SO}_4.10\text{H}_2\text{O}(s) \)
5. \( \text{H}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) \)
6. \( \text{Zn}(s) + 2\text{H}^+ (aq) \rightarrow \text{Zn}^{2+} (aq) + \text{H}_2(g) \)
7. \( \text{CuO}(s) + 2\text{H}^+ (aq) \rightarrow \text{Cu}^{2+} (aq) + \text{H}_2\text{O}(l) \)
8. \( \text{CaCO}_3(s) + 2\text{H}^+ (aq) \rightarrow \text{Ca}^{2+} (aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \)
9. \( \text{Na}^+ (aq) + 2\text{OH}^- (aq) \)
10. \( \text{Mg}^{2+} (aq) + \text{SO}_4^{2-} (aq) \)
11. \( 2\text{Na}^+ (aq) + \text{O}_2^- (aq) \)
12. \( \text{K}^+ (aq) + \text{OH}^- (aq) \)
13. \( 2\text{Al}^{3+} (aq) + 3\text{SO}_4^{2-} (aq) \)

Section 5.2

1. The small size of the carbon atom makes it possible for carbon to form double bonds with oxygen to produce discrete covalent molecules. Silicon, on the other hand, bonds to 4 oxygen atoms to form single bonds and hence a covalent network structure. The attractive forces between the molecules of carbon dioxide (intermolecular forces) are weak so that little energy is needed to separate the individual molecules. Strong covalent bonds exist throughout the SiO\(_2\) covalent network structure so a lot of energy is needed to melt it.

2. a. Any attractive forces between the solvent and the atoms in the covalent network structure are too weak to overcome the strong covalent bonds holding the network together.
   b. At room temperature, the kinetic energy of atoms and molecules is small but it may be enough to overcome the weak attractive forces between simple molecules or isolated atoms.

Section 5.3

1. a. Kr, Xe (higher b.p.)
   b. C\(_6\)H\(_4\), C\(_6\)H\(_6\) (higher b.p.)
   c. CH\(_3\)CCl\(_3\) (higher b.p.)
   d. CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\) and CH\(_3\)CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\) (higher b.p.)
   e. CH\(_3\)CH\(_3\)CH\(_3\)
   and
   \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]
   and
   \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \] (higher b.p.)

2. In the solid or liquid state, noble gas atoms are held together by weak instantaneous dipole–induced dipole forces. It takes very little energy to break these attractions and this results in very low melting and boiling points.
4 The strength of instantaneous dipole–induced dipole forces between molecules increases as the relative molecular masses of the molecules increase. To be sure that the higher boiling point of the polar substance is due only to the increased strength of dipole–dipole attractions it will be necessary to ensure that the instantaneous dipole–induced dipole forces in both polar and non-polar substances are of similar strength. This can be done by comparing substances of similar molecular mass.

5 a A and D; C and G.
b A and G have the stronger intermolecular forces compared to D and C, respectively.

Section 5.4

1 a As the temperature rises, solids and liquids expand. The temperature increase raises the kinetic energy of the particles present. In solids, the rotational and vibrational energy increases. In liquids, rotational, vibrational and translational energy increases. The increases in vibrational and translational energy increase the volume occupied by the particles. As they occupy an increasing volume, the density of the solid or liquid decreases.
b i When ice melts, much of the open, hydrogen-bonded structure collapses. This enables the molecules to occupy less space so the density increases on melting.
ii The boiling point of water is higher than expected, as more energy is needed to break the hydrogen bonding.
iii The specific heating capacity of water is higher than expected, as more energy is absorbed by the water to break hydrogen bonds in the liquid.

2 a i H₂O instantaneous dipole–induced dipole permanent dipole–permanent dipole hydrogen bonding.
ii Intermolecular forces must be overcome when a liquid boils.

Hydrogen bonding present between molecules of H₂O—but not between those of H₂S, H₂Se or H₂Te.

6 Polarity will occur as follows:
C–F, H–Cl; H–N; C–O with charges in the order δ+ δ– in each case.

7 CHCl₃, CH₃OH, (CH₃)₂CO, cis,1,2-difluoroethene and 1,2-dichlorobenzene possess dipoles.

8 a i Eighteen
ii The attractions will be similar.
iii H₂S has a permanent dipole. It is a bent molecule with two lone pairs. SiH₄ does not have an overall permanent dipole as it is a symmetrical molecule.
b Both compounds have similar instantaneous dipole–induced dipole forces. However, H₂S also has permanent dipole–permanent dipole attractions so its boiling point is higher than that of SiH₄.

9 a Instantaneous dipole–induced dipole.
b Instantaneous dipole–induced dipole.
c Instantaneous dipole–induced dipole, permanent dipole–permanent dipole.
d Instantaneous dipole–induced dipole.
e Instantaneous dipole–induced dipole, permanent dipole–permanent dipole.
f Instantaneous dipole–induced dipole.
g Instantaneous dipole–induced dipole.
h Instantaneous dipole–induced dipole, permanent dipole–permanent dipole.

b The strength of instantaneous dipole–induced dipole and permanent dipole–permanent dipole attractions in a substance gets weaker as its relative molecular mass gets smaller. This produces a lower boiling point. The boiling point of H₂O should be lower than that of H₂S but it is in fact much higher. This suggests that, compared to H₂S, a different and much stronger type of intermolecular bonding exists in H₂O.
c ii All have instantaneous dipole–induced dipole forces.
iii The shape of the graph is nearly a straight line with positive slope. There is no hydrogen bonding between the hydride molecules of Group 4. The increase in boiling points down the group is a result of their regularly increasing molecular masses.

3 A, D, E and F

4 a Hydrogen bonding will be present in NH₃, CH₃OH, and HF.

b
Section 5.5, Part 1 (Addition polymers)

1. \( \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2 \)

2. \( \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH} \)

3. \( \text{CH}_3-\text{CH}_2-\text{CH}_3 \)

4. \( \text{H}_3\text{C} \)

5. \( \text{H}_3\text{C} \)

6. But-1-ene and propene

7. Poly(ethene), poly(propene), poly(chloroethene)

8. Poly(ethene) instantaneous dipole–induced dipole

9. Isotactic polymer is a stereoregular polymer, that is, the side-chains all have the same orientation. In an atactic polymer the side-chains are randomly orientated.

10. The regular arrangement of the side-chains in an isotactic polymer allows the polymer chains to pack together closely, which means intermolecular forces are stronger. The polymer chains do not slide past each other easily, making the polymer stronger and less flexible than the atactic form of the same polymer.
Section 5.5, Part 2 (Addition and condensation polymers)

1a  \[ \text{OCH}_2\text{CH} =\text{CH}\text{CH}_2\text{OCH}_2\text{CH} =\text{CH}\text{CH}_2\text{O} \]

bb  \[ \text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N} \]

2a  \[ \text{H}_2\text{N}-(\text{CH}_2)_3-\text{C}-\text{OH} \]

bc  \[ \text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \quad \text{and} \quad \text{HO}-\text{C}==\text{C}=\text{O} \]

c  Polarity increases from –CH₃ to –Cl to –CN so the intermolecular attractions become stronger which leads to an increase in Tᵢₘ.

4a  i Instantaneous dipole-induced dipole.
    ii Instantaneous dipole-induced dipole.

b  Permanent dipole-permanent dipole.

b (CH₂O)ₙ would have a higher Tᵢₘ because of the permanent dipole-permanent dipole interactions between the chains.

Section 5.6

1a  Ionic lattice
    b  i Ne monatomic
    ii simple molecular (covalent)
    iii simple molecular (covalent)
    iv O == C == O simple molecular (covalent)

c  i See Figure 6, page 92, Chemical Ideas.
    ii Covalent network or giant covalent.

d  The diagram should be similar to Figure 15, page 39, Chemical Ideas. There will be 2+ charges on the positive ions as the metal is magnesium. The outer electrons, two from each magnesium atom, contribute to a ‘pool’ of electrons which move randomly through the lattice of positive ions. Each positive ion is attracted to the negatively charged delocalised electrons and vice versa.

2

<table>
<thead>
<tr>
<th>Name</th>
<th>State at room temperature</th>
<th>Solubility in water</th>
<th>Electrical conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>sodium iodide</td>
<td>solid</td>
<td>soluble</td>
</tr>
<tr>
<td>b</td>
<td>carbon monoxide</td>
<td>gas</td>
<td>insoluble</td>
</tr>
<tr>
<td>c</td>
<td>diamond</td>
<td>solid</td>
<td>insoluble</td>
</tr>
<tr>
<td>d</td>
<td>tetrachloromethane</td>
<td>liquid</td>
<td>insoluble</td>
</tr>
<tr>
<td>e</td>
<td>ethanol</td>
<td>liquid</td>
<td>soluble</td>
</tr>
<tr>
<td>f</td>
<td>copper(II) chloride</td>
<td>solid</td>
<td>soluble</td>
</tr>
<tr>
<td>g</td>
<td>vanadium</td>
<td>solid</td>
<td>insoluble</td>
</tr>
<tr>
<td>h</td>
<td>poly(propene) solid</td>
<td>insoluble</td>
<td></td>
</tr>
</tbody>
</table>

3  a Isolated atoms
b Metallic; giant lattice
c Covalent network (or giant covalent); giant lattice
d Macromolecular; covalent molecular
e Ionic; giant lattice
f Simple molecular; covalent molecular

4  A Macromolecular; covalent molecular
B Metallic; giant lattice
C Ionic; giant lattice
D Metallic; giant lattice
E Simple molecular; covalent molecular
5 a In ionic substances, the charge-carriers (ions) are held in the solid lattice and are not free to move. In metals, the charge-carriers (electrons) are delocalised and are free to move throughout the lattice.

b When an ionic melt conducts electricity, the ions move to opposite electrodes where they are discharged, leading to decomposition. When a metal conducts, electrons move towards the more positive terminal and are replaced at an equal rate at the more negative terminal.

c Any attractive forces between the solvent and the atoms in the giant covalent lattice are too weak to overcome the strong covalent bonds holding the lattice together.

d At room temperature, the kinetic energy of atoms and molecules is small. It is not enough to overcome the energy of attraction between particles in giant or macromolecular structures, but it may be enough to overcome the weak intermolecular forces between simple molecules.

Section 6.1

1 a $7.22 \times 10^{-20}$ J
b $6.6 \times 10^{-17}$ J
c $9.2 \times 10^{10}$ J

2 $5.5 \times 10^{13}$ Hz

3 a The four lowest energy lines in the Balmer Series arise from transitions to level 2 from levels 3, 4, 5 and 6.

b The lines converge towards high frequency. The lines in the Balmer Series are at lower frequency than the lines in the Lyman Series.

Section 6.2

<table>
<thead>
<tr>
<th>Frequency/Hz</th>
<th>Type of radiation</th>
<th>Type of energy change in molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.8 \times 10^{-17}$</td>
<td>u.v.</td>
<td>electronic</td>
</tr>
<tr>
<td>$2.3 \times 10^{-20}$</td>
<td>l.r.</td>
<td>vibrational</td>
</tr>
<tr>
<td>$2.1 \times 10^{-13}$</td>
<td>microwave</td>
<td>rotational</td>
</tr>
<tr>
<td>$5.5 \times 10^{-19}$</td>
<td>visible</td>
<td>electronic</td>
</tr>
</tbody>
</table>

1 a $5.43 \times 10^{-20}$ J
b $8.19 \times 10^{13}$ Hz; infrared
c $3.66 \times 10^{-6}$ m

2 a $3.2 \times 10^{11}$ Hz
b $3.2 \times 10^{13}$ Hz
c $3.2 \times 10^{14}$ Hz

3 a $E = \frac{+214 \text{kJ mol}^{-1} \times 1000}{6.02 \times 10^{23} \text{mol}^{-1}} = +3.55 \times 10^{-19}$ J
b $E = \hbar \nu$

$5.5 \times 10^{-19}$ J = $6.63 \times 10^{-34} \text{J Hz}^{-1} \times \nu \text{ Hz}$

$\nu = 5.36 \times 10^{14}$ Hz
c This is in the visible region of the electromagnetic spectrum.

Section 6.3

1 F, OH, NO₂ and CH₃ are radicals.

2 a i Photodissociation
   ii Homolytic

b Reaction A initiation

Reaction B propagation

c H⁺ and HO₂⁺

d i $2 \text{O}_2 \rightarrow \text{O}_3$
   ii Catalyst

e The rates of radical reactions depend on the concentrations of the radicals involved.

f Termination

3 a Oxidation of N₂ in internal combustion engines.

b Exothermic

c i O₂ + O → O₂ + O₂
   ii Catalyst
   iii $\Delta H = -292 \text{kJ mol}^{-1}$

d It catalyses breakdown of ozone, thus removing it from the stratosphere.

4 a Initiation: reaction 1
   Propagation: reactions 2, 3 and 4
   Termination: reactions 5 and 6

b i Endothermic: reaction 1 (C=C bond broken)
   ii Exothermic: reaction 6 (C=C bond formed)
c CH₃ • methyl radical
C₂H₅ • ethyl radical
H • hydrogen radical

5 a Cl₂ + hν → Cl⁺ + Cl⁻ initiation
CH₄ + Cl⁺ → CH₃⁺ + HCl propagation
CH₃⁺ + Cl₂ → CH₃Cl + Cl⁻
Cl⁺ + Cl⁻ → Cl₂ termination
CH₃⁺ + CH₃⁻ → C₂H₆

b The chloromethane formed can also react with Cl⁻ radicals.
CH₃Cl + Cl⁻ → •CH₂Cl + HCl
•CH₂Cl + Cl⁻ → CH₂Cl₂ + Cl⁻
Similarly, CH₂Cl₂ can react with Cl⁻, and so on, until CCl₄ is produced. The chlorinated products react with Cl⁻ radicals more quickly than CH₄ does, so a mixture of products is always obtained.

**Section 6.4**

1 a 4.24 μm
b 7.08 × 10¹⁵ Hz

2

<table>
<thead>
<tr>
<th>Absorption/cm⁻¹</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>3660</td>
<td>O–H</td>
</tr>
<tr>
<td>3060</td>
<td>C–H</td>
</tr>
</tbody>
</table>

3 a \[ \text{butan-2-ol} \]
\[ \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \]

b \[ \text{butan-2-one} \]
\[ \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3 \]

4 a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption/cm⁻¹</th>
<th>Bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3660</td>
<td>O–H</td>
</tr>
<tr>
<td></td>
<td>2970</td>
<td>C–H</td>
</tr>
<tr>
<td>B</td>
<td>2990</td>
<td>C–H</td>
</tr>
<tr>
<td></td>
<td>1730</td>
<td>C=O</td>
</tr>
</tbody>
</table>

5 a

<table>
<thead>
<tr>
<th>Bond</th>
<th>Absorption/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H (phenol)</td>
<td>3600–3640</td>
</tr>
<tr>
<td>C–H (arene)</td>
<td>3000–3100</td>
</tr>
<tr>
<td>C=O (ester)</td>
<td>1735–1750</td>
</tr>
</tbody>
</table>

**Section 6.5**

1 a 78, 72, 106
b Two isotopes of chlorine leading to C₃H₇Cl₃⁵ (78) and C₃H₇Cl₃⁷ (80)

2 43, [C₃H₇]⁺
45, [CH₃CO]⁺
77, [C₄H₉]⁺

3 a, b A Ethanoic acid
B Ethanol
A 43, [CH₃CO]⁺
45, [COOH]⁺
60, [CH₃COOH]⁺
B 31, [CH₂O]⁺ or [CH₂OH]⁺
46, [CH₃OH]⁺

4 a 88, molecular ion
45, [CH₃CO]⁺

b [CH₃COOCH₂CH₃]⁺ → [CH₃CO]⁺ + OCH₂CH₃

5 a

<table>
<thead>
<tr>
<th>Mass of peak</th>
<th>Possible fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>[C₃H₇]⁺</td>
</tr>
<tr>
<td>43</td>
<td>[C₃H₇]⁺</td>
</tr>
<tr>
<td>29</td>
<td>[C₂H₅]⁺</td>
</tr>
<tr>
<td>15</td>
<td>[CH₃]⁺</td>
</tr>
</tbody>
</table>

b A carboxylic acid
D An alcohol
E An ester

6 a

\[ \text{CH}_3 - \text{CH}_2 - \text{C} = \text{O} \]
\[ \text{CH}_3 - \text{C} - \text{CH}_3 \]
c Adopting a 'Lego' approach to these fragment ions, the full structural formula of the hydrocarbon must be:

CH₃ – CH₂ – CH₂ – CH₃
CH₃ – CH – CH₂ – CH₃

Fragmentation of this by breaking C–C bonds leads to the four ions in the table. The branched isomer would not produce the C₂H₅⁺ ion by breaking C–C bonds. However, the other three ions will also appear in the spectrum of this isomer.

b 58 – 45 = 13; CH₃

b 58 – 57 = 1; H
ii 57 – 29 = 28; CO or C₂H₄

b i [CH₃CO]⁺
ii 28 [CO]⁺ or [C₂H₄]⁺
29 [CH₃CH₂]⁺
57 [CH₃CH₂CO]⁺

c C is CH₃COCH₂, D is CH₃CH₂CHO
7. Accurate atomic masses give \(\text{C}_4\text{H}_8\text{O}\) as the formula. Peaks to be identified:

<table>
<thead>
<tr>
<th>Mass of peak</th>
<th>Possible fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>([\text{CH}_3]^+)</td>
</tr>
<tr>
<td>29</td>
<td>([\text{CH}_3\text{CH}_2]^+)</td>
</tr>
<tr>
<td>43</td>
<td>([\text{CH}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>57</td>
<td>([\text{CH}_3\text{CH}_2\text{CO}]^+)</td>
</tr>
<tr>
<td>72</td>
<td>([\text{CH}_3\text{CH}_2\text{COCH}_3]^+)</td>
</tr>
</tbody>
</table>

The compound has the structure:

\[
\text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3
\]

8. The sketch should show two molecular ion peaks of equal height at 108 \([\text{C}_2\text{H}_5\text{Br}]^+\) and 110 \([\text{C}_2\text{H}_5\text{Br}]^+\). Also peaks at 93 \([\text{CH}_3\text{Br}]^+\) and 95 \([\text{CH}_3\text{Br}]^+\). (Actual data have 29 as the base peak (100%) and peaks at 108 and 110 (94%). The next largest peak is 27 (70%). Peaks at 79 and 81 are very small (3%).)

Section 6.6

1. a 3
   b 2
   c 1
   d 0

2. a 1
   b 0

3. a 0
   b 1
   c 2

4. a 0
   b 1
   c 2

5. a 0
   b 1
   c 2

6. a 0
   b 1
   c 2

7. a 0
   b 1
   c 2

8. a 0
   b 1
   c 2

It is good enough to identify two types of proton (\(\text{CH}_3\) and \(\text{C}_6\text{H}_4\)), in the ratio of 3 : 2. However, there are actually two different environments for the protons on the aryl group, one being adjacent to the ester group, and the better answer would be 3 : 1 : 1.
Section 6.7

1. a. Green 520 nm–580 nm approx.  
   b. Red 620 nm–700 nm approx.

2. Blue and blue-green; approx. 440 nm – 520 nm

3. It will appear green. The sketch should show two peaks with \( \lambda_{\text{max}} \) at about 640 nm and 410 nm.

Section 6.8

1. a. Spectrum (b)  
   b. Violet

2. a. i

   ![Graph of Intensity of absorption vs \( \lambda / \text{nm} \)]

   ii

   ![Graph of Intensity of absorption vs \( \lambda / \text{nm} \)]

3. a. Spectrum (a) \( \lambda_{\text{max}} = 440 \text{ nm (approx.)} \)  
   Spectrum (b) \( \lambda_{\text{max}} = 420 \text{ nm (approx.)} \)

   b. Spectrum (b) corresponds to haemoglobin.

4. a. Red ochre.  
   b. It absorbs violet, blue and green light \( (\lambda = 400 \text{ nm–}530 \text{ nm}) \) but reflects yellow and red light \( (\lambda = 530 \text{ nm–}700 \text{ nm}) \).

Section 6.9

1. a. A chromophore is the part of a dye molecule responsible for its colour. It contains unsaturated groups such as \( \text{C=O} \) and \( \text{N=N=} \) which are often part of an extended delocalised electron system involving arene rings.

   b. An extended delocalised system of electrons.

   c. No change

2. a. Cyanidin contains an extended delocalised (conjugated) electron system. The electrons in such systems require less energy to excite them than those in single bonds or in isolated double bonds. The excitation energy corresponds to the visible region.

   b. Molecule absorbs orange light; the diagram should show a smaller excitation energy.

Section 7.1

1. a. Rate of evaporation = rate of condensation.

   b. It is a closed system, in which there is a dynamic equilibrium between water vapour and liquid.

   c. No longer a closed system, \( \text{H}_2\text{O(g)} \) escapes.

   d. i. Towards \( \text{H}_2\text{O(l)} \)

      ii. Towards \( \text{H}_2\text{O(g)} \).

2. a. Equilibrium lies to the reactants’ side because at equilibrium there is a greater concentration of reactants than products.

   b. Equilibrium is reached at the point where the graphs become horizontal.

   c. No change

3. a. left \( \rightarrow \) right  

   b. right \( \rightarrow \) left  

   c. no change

4. a. left \( \rightarrow \) right  

   d. left \( \rightarrow \) right

5. a. The concentrated hydrochloric acid moves the position for the equilibrium to the left, the bismuth trichloride is predominantly present as BiCl\(_3\)(aq).

   b. The equilibrium would move to the right due to the large amount of water, hence a white precipitate of BiOCl(s) would be seen.

6. a. There would be no change to fizziness as the concentration of \( \text{CO}_2\text{(g)} \) is not influenced by the amount of air present since the system had already come to equilibrium.

   b. The increase in concentration of \( \text{CO}_2\text{(g)} \) would make the first equilibrium move to the right and form more \( \text{CO}_3\text{(aq)} \) which in turn would make the second equilibrium move to the right and increase the concentration of \( \text{H}^+ \text{(aq)} \).

   c. Dilute alkali would react with \( \text{H}^+ \text{(aq)} \) and the reduction in concentration of \( \text{H}^+ \text{(aq)} \) would cause the second equilibrium to move to the right. The resulting reduction in the concentration of \( \text{CO}_2\text{(aq)} \) would cause the first equilibrium to move to the right and more \( \text{CO}_2\text{(g)} \) would dissolve and so the equilibrium pressure of carbon dioxide would decrease.
**Section 7.2**

1. **a** $K = \frac{[\text{CO}_2]_\text{aq}^2}{[\text{NO}_2]_\text{aq}^2}$ $\text{mol}^{-1} \text{dm}^3$

2. **a** $K = \frac{[\text{NO}_2]_\text{aq}^2}{[\text{NO}]_\text{aq}^2}[\text{O}_2]_\text{aq}^2}$ $\text{mol}^{-1} \text{dm}^3$

2. **b** $K = \frac{[\text{H}_4]_\text{aq}^2}{[\text{C}_2]_\text{H}_4]_\text{aq}^2}$ (no units)

3. $K = \frac{[\text{H}_2]_\text{aq}^2}{[\text{H}_2]_\text{aq}}$ $\text{mol}^{-1} \text{dm}^3$

4. $K = \frac{[\text{H}_2]_\text{aq}^2}{[\text{H}_2]_\text{aq}}$ $\text{mol}^{-1} \text{dm}^3$

5. **a** $2\text{H}_2(g) + \text{O}_2(g) = 2\text{H}_2\text{O}(g)$

   **b** $K = \frac{[\text{H}_2\text{O}]_\text{aq}^2}{[\text{H}_2]_\text{aq}^2}[\text{O}_2]_\text{aq}^2}$

   **c** i Equilibrium moves towards reactants (reaction is exothermic)

   ii Equilibrium moves towards products (fewer gaseous molecules).

   **d** i Decreases

   ii No effect

6. **a** $K = \frac{[\text{PCl}_3]_\text{aq}^2}{[\text{PCl}_5]_\text{aq}^2}$ $\text{mol}^{-1} \text{dm}^3$

7. **a** $K = \frac{[\text{SO}_2]_\text{aq}^2}{[\text{SO}_3]_\text{aq}^2}[\text{O}_2]_\text{aq}^2$ $\text{mol}^{-1} \text{dm}^3$

8. **a** $K = \frac{[\text{NO}_2]_\text{aq}^2}{[\text{NO}]_\text{aq}^2}[\text{O}_2]_\text{aq}^2$ $\text{mol}^{-1} \text{dm}^3$

9. **a** $K = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]_\text{aq}}{[\text{OH}_2]_\text{aq}^2}[\text{H}_2]_\text{aq}^2$ (no units)

10. Likely to be low.

**Section 7.3**

1. **a** $K_p = \frac{p_{\text{H}_2}\text{O}_2^2}{p_{\text{H}_2}p_{\text{O}_2}^2}$ atm$^{-1}$

2. **a** $K_p = \frac{p_{\text{H}_2\text{O}_2}^3}{p_{\text{H}_2}\text{O}_2}$ (no units)

2. **b** $K_p$ unchanged

   **c** $K_p$ unchanged

   **d** No effect

   **e** $K_p$ unchanged

   **f** $K_p$ increased

2. **a** $K_p = \frac{p_{\text{PCl}_3}p_{\text{H}_2}^3}{p_{\text{PCl}_5}p_{\text{H}_2}^2}$ (no units)

2. **b** $K_p$ unchanged

   **c** A larger proportion of products (reaction is endothermic)

   **d** A larger proportion of reactants (fewer gaseous molecules)

   **e** No effect
Section 7.4

1 Experiment number

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>87.1</td>
</tr>
<tr>
<td>2</td>
<td>87.6</td>
</tr>
<tr>
<td>3</td>
<td>87.3</td>
</tr>
</tbody>
</table>

An average value of 87.3

2 a Partition coefficient = \[
\frac{[\text{butanedioic acid}]_{\text{ethoxyethane}}}{[\text{butanedioic acid}]_{\text{water}}}
\] = 0.148

Section 7.5

1 The position of equilibrium would move toward the products, i.e., Ca\(^{2+}\) ions will displace Mg\(^{2+}\) ions from the clay surface.

2 The equilibrium involved is

\[\text{R–H}^+(s) + \text{Na}^+(aq) \rightleftharpoons \text{R–Na}^+(s) + \text{H}^+(aq)\]

Washing with acid moves the equilibrium back to the left (the regenerated form). A high volume of concentrated acid is used to ensure that the equilibrium moves as far as possible to the left so that regeneration is as near complete as possible.

3 a Resin –OH\(^–\)(s) + Cl\(^–\)(aq) \rightleftharpoons resin –Cl\(^–\)(s) + OH\(^–\)(aq)

b One might expect I\(^–\)(aq) to be held more strongly by the resin than Cl\(^–\)(aq), because I\(^–\) has fewer surrounding water molecules.

c H\(^+\)(aq) reacts with OH\(^–\)(aq) to form H\(_2\)O(l)

Section 7.6

1 a \[X = 0.75; \ Y = 0.25\]

b Compared to compound X, compound Y has a greater affinity for the stationary phase and/or a lower affinity for the mobile phase.

c To maintain constant conditions in which the space around the thin layer is saturated with solvent vapour.

2 a Retention time depends on the affinity of the compound for the stationary phase compared to its affinity for the carrier gas. More volatile compounds usually have shorter retention times. Other factors include the length and packing of the column, the flow rate of the gas and the temperature.

b The extent to which a compound distributes itself between the mobile phase and the stationary phase, and hence the retention time for that compound, depends on the temperature, so this must be constant throughout the column. Most columns are kept above room temperature to give reasonably short retention times. The temperature (and other conditions) must be recorded and kept constant in order to obtain reproducible results. If the temperature varies, the rates of elution of the substances will vary and results will be inconsistent between experiments.

c Compounds with very high boiling points would have very long retention times. Compounds which decompose on heating may break down into smaller compounds in the column.

3 a Ratio of cis : trans isomers was 1 : 1.4.

b They are likely to be similar because they are isomers.

4 a Methylpropane

b The more carbon atoms in the molecule, the longer the compound takes to travel through the column. Larger molecules are less volatile, spend more time dissolved in the stationary liquid phase and less time in the gas phase.

c All the times would be longer and the peaks would be further apart.
Section 7.7

1  a  i  AgI(s) $\rightleftharpoons$ Ag$^+$ (aq) + I$^-$ (aq)
   ii  BaSO$_4$(s) $\rightleftharpoons$ Ba$^{2+}$(aq) + SO$_4^{2-}$(aq)
   iii  PbI$_2$(s) $\rightleftharpoons$ Pb$^{2+}$(aq) + 2I$^-$ (aq)
   iv  Fe(OH)$_3$(s) $\rightleftharpoons$ Fe$^{3+}$(aq) + 3OH$^-$ (aq)

 b  i  $K_{sp} = [Ag^+(aq)] [I^- (aq)]$ mol$^2$ dm$^{-6}$
   ii  $K_{sp} = [Ba^{2+}(aq)] [SO_4^{2-}(aq)]$ mol$^2$ dm$^{-6}$
   iii  $K_{sp} = [Pb^{2+}(aq)] [I^-(aq)]^2$ mol$^3$ dm$^{-9}$
   iv  $K_{sp} = [Fe^{3+}(aq)] [OH^- (aq)]^3$ mol$^4$ dm$^{-12}$

c  The reactant is a solid and so its concentration can be regarded as constant.

2  a  

<table>
<thead>
<tr>
<th>Product of ion concentrations / mol$^2$ dm$^{-6}$</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>i  4.0 x 10$^{-12}$</td>
<td>5.0 x 10$^{-13}$</td>
</tr>
<tr>
<td>ii 9.0 x 10$^{-12}$</td>
<td>1.0 x 10$^{-12}$</td>
</tr>
<tr>
<td>iii 2.0 x 10$^{-9}$</td>
<td>1.6 x 10$^{-9}$</td>
</tr>
<tr>
<td>iv 2.0 x 10$^{-6}$</td>
<td>5.0 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

b  A precipitate will form in i and iv as in these cases the product of the ion concentrations is greater than the solubility product.

3  a  $[Ag^+(aq)] = 0.005$ mol dm$^{-3}$;
   $[Cl^- (aq)] = 0.005$ mol dm$^{-3}$

 b  $[Ca^{2+}(aq)] = 0.001$ mol dm$^{-3}$

4  a  $[TI^+(aq)] = 0.5$ x $7.0$ x $10^{-3}$ mol dm$^{-3}$.
   (Remember the concentration will be halved on mixing with an equal volume of sodium chloride.)

   $K_{sp} = (0.5 \times 7.0 \times 10^{-3} \text{ mol dm}^{-3}) \times [Cl^- (aq)]$
   $[Cl^- (aq)] = 1.75 \times 10^{-4} \text{ mol dm}^{-3}$
   $= 0.5 \text{ mol dm}^{-3}$

   As with the thallium ion, the concentration of chloride ion will be halved on mixing. Hence the concentration of sodium chloride above which a precipitate will just form is 0.10 mol dm$^{-3}$.

Section 8.1

1  Acid donates hydrogen ions/protons and the base accepts hydrogen ions/protons.

2  a  HNO$_3$ + H$_2$O $\rightarrow$ H$_3$O$^+$ + NO$_3^-$
     base
   b  NH$_3$ + H$_2$O $\rightarrow$ NH$_4^+$ + OH$^-$
     acid
   c  NH$_4^+$ + OH$^-$ $\rightarrow$ NH$_3$ + H$_2$O
     base
   d  SO$_4^{2-}$ + H$_2$O $\rightarrow$ HSO$_4^-$ + H$_2$O
     base
   e  H$_2$O + H$^+$ $\rightarrow$ H$^+$ + OH$^-$
     base
   f  H$_3$O$^+$ + OH$^-$ $\rightarrow$ 2H$_2$O
     base
   g  NH$_4^+$ + HBr $\rightarrow$ NH$_4^+$ + Br$^-$
     base
   h  H$_2$SO$_4$ + HNO$_3$ $\rightarrow$ H$_2$SO$_4^-$ + H$_2$NO$_3^+$
     base
   i  CH$_3$COOH + H$_2$O $\rightarrow$ CH$_3$COO$^-$ + H$_3$O$^+$
     base

3  a  Acid–base
   b  Acid–base
   c  Redox
   d  Redox

4  Conjugate pairs: acid  base
   a  NH$_4^+$  NH$_3$
   H$_2$O$^+$  H$_2$O
   b  H$_2$SO$_4$  HSO$_4^-$
   H$_2$NO$_3^+$  HNO$_3$
   c  HClO$_4$  ClO$_4^-$
   CH$_3$COOH$^+$  CH$_3$COOH

5  a  CH$_3$COOH + OH$^-$ $\rightarrow$ CH$_3$COO$^-$ + H$_2$O

   Conjugate pairs: acid  base
   CH$_3$COOH  CH$_3$COO$^-$
   H$_2$O  OH$^-$
   b  HCO$_3^-$ + HCl $\rightarrow$ H$_2$CO$_3$ + Cl$^-$

   Conjugate pairs: acid  base
   HCl  Cl$^-$
   H$_2$CO$_3$  HCO$_3^-$
   c  H$_2$O + HSO$_4^-$ $\rightarrow$ SO$_4^{2-}$ + H$_3$O$^+$

   Conjugate pairs: acid  base
   HSO$_4^-$  SO$_4^{2-}$
   H$_3$O$^+$  H$_2$O
Section 8.2

1. a) \([H^+(aq)] = 1 \times 10^{-2} \text{ mol dm}^{-3}\); therefore pH = 2
   b) \([H^+(aq)] = 2 \times 10^{-1} \text{ mol dm}^{-3}\); therefore pH = 0.7
   c) \([H^+(aq)] = 4 \times 10^{-1} \text{ mol dm}^{-3}\); therefore pH = 0.4
   d) \([H^+(aq)] = 4 \times 10^{-1} \text{ mol dm}^{-3}\); therefore pH = 0.4

2. a) \([H^+(aq)] = 1.7 \times 10^{-5}\) mol dm\(^{-3}\); therefore pH = 4.7
   b) \([H^+(aq)] = 6.3 \times 10^{-5}\) mol dm\(^{-3}\); therefore pH = 4.6
   c) \([H^+(aq)] = 1.6 \times 10^{-4}\) mol dm\(^{-3}\); therefore pH = 4.0

Section 8.3

1. a) \(1.6 \times 10^{-4}\) mol dm\(^{-3}\) \(= [H^+(aq)] = \frac{0.1 \text{ mol dm}^{-3}}{0.1 \text{ mol dm}^{-3}}\)
   b) \(6.3 \times 10^{-5}\) mol dm\(^{-3}\) \(= [H^+(aq)] = \frac{0.03 \text{ mol dm}^{-3}}{0.01 \text{ mol dm}^{-3}}\)
   c) \(1.3 \times 10^{-3}\) mol dm\(^{-3}\) \(= [H^+(aq)] = \frac{5.0 \times 10^{-3} \text{ mol dm}^{-3}}{1 \times 10^{-3} \text{ mol dm}^{-3}}\)
   d) \(1.6 \times 10^{-4}\) mol dm\(^{-3}\) \(= [H^+(aq)] = \frac{2 \times 1.5 \times 10^{-2} \text{ mol dm}^{-3}}{2 \times 5 \times 10^{-3} \text{ mol dm}^{-3}}\)
   e) \(2 \times 10^{-4}\) mol dm\(^{-3}\) \(= [H^+(aq)] = \frac{5.3 \times 10^{-5} \text{ mol dm}^{-3}}{5.3 \times 10^{-5} \text{ mol dm}^{-3}}\)

b) The position of the equilibrium for the reaction of the strong acid with water is completely to the right:
\[\text{HCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{Cl}^-(aq) + \text{H}_3\text{O}^+(aq)\]
The amount in moles of \(H^+(aq)\) ions is equal to the amount in moles of HCl put into solution. Thus, \([H^+(aq)] = 0.01 \text{ mol dm}^{-3}\) and pH = 2.

The position of the equilibrium for the reaction of the weak acid with water is more to the left:
\[\text{HNO}_2(aq) + \text{H}_2\text{O(l)} \rightarrow \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)\]
The amount in moles of \(H^+(aq)\) ions is very much less than the amount in moles of HNO\(_2\) put into solution. To obtain a solution with pH = 2, the nitrous acid solution must be more concentrated than the hydrochloric acid solution.

5

<table>
<thead>
<tr>
<th>([\text{OH}^-\text{aq}]/\text{mol dm}^{-3})</th>
<th>([H^+(aq)]/\text{mol dm}^{-3})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 1</td>
<td>(1 \times 10^{-14})</td>
<td>14</td>
</tr>
<tr>
<td>b 0.01</td>
<td>(1 \times 10^{-12})</td>
<td>12</td>
</tr>
<tr>
<td>c 0.2</td>
<td>(5 \times 10^{-14})</td>
<td>13.3</td>
</tr>
</tbody>
</table>

6. a) In alkaline solution, the equilibrium shifts to the right as \(H^+(aq)\) is removed by reaction with \(OH^-\text{(aq)}\), so the indicator will be present as the pink \(In^-\) form.

b) \(K_a = \frac{[H^+(aq)][\text{In}^-]}{[\text{HIn}(aq)]}\)

c) \(K_a = 5.01 \times 10^{-10} \text{ mol} \text{ dm}^{-3}\) \(= \frac{[H^+(aq)][\text{In}^-]}{[\text{HIn}(aq)]}\)

At the end point \([\text{HIn}(aq)] = [\text{In}^-]\)
Hence \(5.01 \times 10^{-10} \text{ mol} \text{ dm}^{-3} = [H^+(aq)]\)

pH at end point = 9.3

7. a) i) \(K_a = 5.0 \times 10^{-10} \text{ mol dm}^{-3}\), \(pK_a = 9.3\)
   ii) \(K_a = 1.3 \times 10^{-10} \text{ mol dm}^{-3}\), \(pK_a = 9.9\)
   iii) \(K_a = 4.8 \times 10^{-4} \text{ mol dm}^{-3}\), \(pK_a = 3.3\)

b) HF, HCN, phenol

f) In 750 cm\(^3\) of solution the concentrations of acid and salt are
\([\text{acid}] = 0.1 \times 250 \text{ mol dm}^{-3}\)
\([\text{salt}] = 0.1 \times 500 \text{ mol dm}^{-3}\)
\(1.7 \times 10^{-5} \text{ mol dm}^{-3} = [H^+(aq)] = \frac{0.1 \times 500 \text{ mol dm}^{-3}}{0.1 \times 250 \text{ mol dm}^{-3}}\)
\([H^+(aq)] = 8.5 \times 10^{-6} \text{ mol dm}^{-3}\)
\[\text{pH} = 5.1\]

g) \(1.7 \times 10^{-5} \text{ mol dm}^{-3} = [H^+(aq)] = \frac{0.1 \text{ mol dm}^{-3}}{0.2 \text{ mol dm}^{-3}}\)
\([H^+(aq)] = 3.4 \times 10^{-5} \text{ mol dm}^{-3}\)
\[\text{pH} = 4.5\]

The pH of the buffer solution, on adding a higher proportion of acid, has decreased. Changing the ratio of [salt] : [acid] provides a way of fine tuning the pH of a buffer solution.
2 a Buffer solutions are made of either a weak acid and one of its salts or a weak base and one of its salts.

b i Ethanoate ions from the salt react with the extra H^+(aq) ions to form ethanoic acid and water and so prevent a fall in the pH.

ii The addition of OH^−(aq) ions removes H^+(aq) but these are replaced by further dissociation of the ethanoic acid so the pH will remain constant.

**Section 9.1**

1 a b i K → K^+ + e− oxidation

ii H₂ → 2H^+ + 2e− oxidation

iii O₂ + 2e− → O^2− reduction

iv Cu⁺ → Cu^2+ + e− oxidation

v Cr^3+ + e− → Cr^2+ reduction

2 a Ag(+1) f N(−3)

b Br(0) g Mg(+2), Cl(−1)

c P(0) h C(+4), O(−2)

d H(+1) i P(+5), Cl(−1)

e H(−1) j Al(+3), O(−2)

3 a Cl₂ → Cl^− reduced

b Fe₂⁺ → Fe^3+ oxidised

c Cl₂ → Cl^− reduced

b Cl₂ → Cl^− reduced

c Cl₂ → Cl^− reduced

d Cl₂ → Cl^− reduced

4 a i Cl₂

b i Cl₂

c i Cl₂

d i F₂

5 a Cl(+5) → Cl^− reduced

b S(−2) → S(−4) reduced

3a i 3.16 V

ii 1.10 V

iii 0.18 V

iv 0.32 V

v 1.36 V

6 a Cu₂O + 2H⁺ → Cu^2+ + Cu + H₂O

b 3Br₂ + 6OH− → BrO₃⁻ + 5Br⁻ + 3H₂O

c 4IO₃⁻ → 3IO₄⁻ + I⁻ oxidised and reduced

7 a tin(II) oxide

b tin(IV) oxide

c iron(II) chloride

d iron(III) chloride

e lead(IV) chloride

f copper(I) oxide

g manganese(II) hydroxide

h nitrate(III)

i nitrate(V)

j sulphate(IV)

k sulphate(VI)

l manganate(VII)

m chromate(VI)

n vanadate(V)

8 a KClO₂

b NaClO₃

c Fe(OH)₃

d Cu(NO₃)₂

3 a i 3.16 V

ii 1.10 V

iii 0.18 V

iv 0.32 V

v 1.36 V

b i Ag⁺(aq)/Ag(s)

ii Cu⁺(aq)/Cu(s)

iii Ni²⁺(aq)/Ni(s)

iv Fe²⁺(aq)/Fe(s)

v MnO₄⁻(aq)/Mn²⁺(aq)
Section 9.3

1. (a) $2I^-(aq) + 2e^- \rightarrow I_2(aq)$
   
   Overall: $2I^-(aq) + 2e^- \rightarrow I_2(aq)$

   (b) $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-; MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
   
   Overall: $2MnO_4^-(aq) + 16H^+(aq) + 10Br^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$

   (c) $2I^-(aq) \rightarrow 2I_2(aq) + 2e^-; Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
   
   Overall: $2I^-(aq) + Br_2(aq) \rightarrow I_2(aq) + 2Br^-(aq)$

2. (a) $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$
   
   (b) $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-; Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
   
   Overall: $Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$

3. (a) $2O_2(g), H^+(aq)/H_2O(l)$
   
   (b) $2I^-(aq) + Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
   
   (c) $2I^-(aq) + Br_2(aq) \rightarrow I_2(aq) + 2Br^-(aq)$

Section 9.4

1. (a) i. Cobalt(III) fluoride dissolves in water to form cobalt(III) ions, $[Co(H_2O)_6]^{3+}$. $E^*$ for the $[Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}$ half-cell is more positive than $E^*$ for the $O_2(g), H^+(aq)/H_2O(l)$ half-cell. Electrons are supplied to the more positive half-cell, so cobalt(III) ions are reduced to cobalt(II) ions and water is oxidised to release oxygen.
   
   ii. The overall reaction is
   
   $4[Co(H_2O)_6]^{3+}(aq) + 2H_2O(l) \rightarrow 4[Co(H_2O)_6]^{2+}(aq) + O_2(g) + 4H^+(aq)$
   
   iii. The hydrated $Co^{3+}$ ion is more stable than the hydrated $Co^{2+}$ ion.
   
   b. Oxygen in the air is unable to oxidise the pink cobalt(II) ion as the $E^*$ for the oxygen half reaction is less positive than that required for oxidising $[Co(H_2O)_6]^{2+}(aq)$.
   
   c. The $E^*$ for the oxygen half reaction is more positive than that needed to oxidise the yellow-brown $[Co(NH_3)_6]^{2+}(aq)$ to the dark brown $[Co(NH_3)_6]^{3+}(aq)$. The overall reaction is
   
   $O_2(g) + 4H^+(aq) + 4[Co(NH_3)_6]^{2+}(aq) \rightarrow 2H_2O(l) + 4[Co(NH_3)_6]^{3+}(aq)$
   
   d. $[Co(NH_3)_6]^{3+}$ is more stable than $[Co(NH_3)_6]^{2+}$.

2. (b) i. As the $E^*$ for aqueous iron(III), $[Fe(H_2O)_6]^{3+}(aq)$, is more positive than that of the iodine half-cell, the iron(II) will oxidise the aqueous iodide ion to iodine.
   
   The overall reaction is
   
   $2[Fe(H_2O)_6]^{3+}(aq) + 2I^-(aq) \rightarrow 2[Fe(H_2O)_6]^{2+}(aq) + I_2(aq)$
   
   $E_{cell} = +0.77 V – (+0.54 V) = +0.23 V$
   
   ii. As the $E^*$ for the iodine half-cell is more positive than that of the hexacyanoferrate half-cell, iodine will oxidise the hexacyanoferrate(II) to hexacyanoferrate(III).
   
   The overall reaction is
   
   $I_2(aq) + 2[Fe(CN)_6]^{3–}(aq) \rightarrow 2I^–(aq) + [Fe(CN)_6]^{2–}(aq)$
   
   $E_{cell} = +0.54 V – (+0.36 V) = +0.18 V$
   
   c. A major reason why many predicted reactions do not occur is because of high activation enthalpies, i.e. there is a kinetic barrier to the reaction despite it appearing thermodynamically feasible. Also, these calculations assume standard conditions: if conditions are not standard, the results may be different.
Section 10.1

1

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>temperature</td>
<td>rate will increase with temperature</td>
<td>rate will increase with temperature</td>
</tr>
<tr>
<td>B</td>
<td>total pressure of gas</td>
<td>rate of forward reaction not affected</td>
<td>rate increases</td>
</tr>
<tr>
<td>C</td>
<td>concentration of solution</td>
<td>increasing the concentration of acid will increase the rate</td>
<td>solutions not involved</td>
</tr>
<tr>
<td>D</td>
<td>surface area of solid</td>
<td>the more finely divided the magnesium, the faster the rate</td>
<td>the more finely divided the catalyst, the faster the rate</td>
</tr>
</tbody>
</table>

2  Both the acid and the enzyme can act as catalysts for the hydrolysis of a protein.

3  a  The greater the concentration of reactants, the greater the rate of collisions and hence the faster the reaction proceeds.
   b  A change of temperature has little effect. Most collisions result in a reaction.

Section 10.2

1  a  A  b  A  c  B  d  Mainly B, with A to a minor extent.

2  a  This reaction has a high activation enthalpy that prevents it occurring at a significant rate at room temperature, but the reaction is exothermic, and once the spark has provided the energy needed to get it started, the reaction produces enough energy to sustain itself regardless of how much is present.
   b  The platinum catalyst lowers the activation enthalpy to such an extent that it is close to the thermal energy of molecules at room temperature.

3  Above a certain temperature, enzymes are denatured and become inactive.

4  a  The surface area of the coal is much greater in the powder than in the lump. Many more collisions with oxygen molecules are possible and the speed of reaction will be much greater.
   b  Although the gas molecules are moving freely, the molecules have insufficient kinetic energy to overcome the activation enthalpy for reaction.
   c  The particles in the solids are in fixed positions in their respective lattices. The only movement will be due to low energy vibrations or rotations about these fixed positions. The number of collisions is very low indeed. There is also unlikely to be sufficient energy available to overcome the activation enthalpy for reaction.
   d  The fine flour dust allows maximum chances of collisions with oxygen molecules. A spark will cause instant ignition followed by a very rapid reaction amounting to an explosion.
   e  Catalytic converters catalyse redox reactions involving CO, NOx and oxygen from the air (see Developing Fuels for details). The catalyst lowers the activation enthalpies of these reactions, but the activation enthalpies are still high, and the reactions do not occur at a significant rate until the catalyst is hot.
   f  The added curve is above the original, with a greater slope at the start of the reaction but plateauing at the same final volume of hydrogen given off.

Section 10.3

1  a  The reaction is first order with respect to bromoethane and zero order with respect to hydroxide ion.
   b  The reaction is first order with respect to methyl methanoate, zero order with respect to water and first order with respect to H+.
   c  The reaction is first order with respect to urea, zero order with respect to water and first order with respect to urease.
   d  The reaction is a single step in the mechanism. It is first order with respect to the methyl radical and first order with respect to the chlorine molecule.
   e  The reaction is order 1 with respect to carbon monoxide and first order with respect to chlorine.
   f  The reaction is second order with respect to nitrogen dioxide.

2  a  Rate = $k[\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}] [\text{OH}^-]$
   b  Rate = $k[\text{C}_2\text{H}_5\text{O}_2\text{H}] [\text{H}^+]$
3  a  i  First order  
    ii  Second order  
  b  Rate = $k[\text{H}_2][\text{NO}]^2$  
  c  $k = 0.384 \text{mol}^{-2}\text{dm}^6\text{s}^{-1}$

4  b  All are $\approx 1150$ s (Allow within 1100–1200 s.)  
  First order.  
  c  Rate = $k[N_2\text{O}_3]$ or $-d[N_2\text{O}_3]/dt = k[N_2\text{O}_3]$  

Section 10.4

1  a  Platinum on aluminium oxide (heterogeneous catalyst).  
  b  Zeolite (heterogeneous catalyst).  
  c  Platinum on aluminium oxide (heterogeneous catalyst).

2  a  $2\text{CO}(g) + 2\text{NO}(g) \rightarrow 2\text{CO}_2(g) + \text{N}_2(g)$  
  b  These gases are hazardous to health, produce acid rain and can take part in producing photochemical smog.  
  c  i  A substance is adsorbed when it is bound to the surface of another substance.  
    ii  The mechanism should show CO and NO being adsorbed to the catalyst surface.

Section 10.5

1  a  

![Graph showing enthalpy change]

b  The rate will be faster for the enzyme catalysed reaction, as the activation enthalpy is significantly lower. This means that more pairs of colliding molecules have sufficient energy to react at room temperature.

2  a  The catalyst is in the same phase as the reactants.  
  b  i  An intermediate is formed. In this example, the intermediate is the radical, ClO.  
    ii  Use unleaded fuel.

Section 11.1

1  a  d block  
  b  p block  
  c  s block  
  d  f block

2  a  Peaks: carbon, silicon  
  b  Troughs: helium, neon, argon  
  c  Elements in the same group occur at similar positions on graph eg Group 4 at peaks, Group 0 in troughs.

3  a  They are all in Group 1.  
  b  The molar atomic volumes for each period of elements vary in similar regular patterns.

4  a  LiCl, BeCl$_2$, BCl$_3$, CCl$_4$, NCl$_3$, OCl$_2$, FCl  
  NaCl, MgCl$_2$, AlCl$_3$, SiCl$_4$, PCl$_3$, SCl$_2$, Cl$_2$  
  c  Second period: number of chlorine atoms same as group number for Groups 1–4. After Group 4, falls by one chlorine atom for each subsequent group.  
  Similar pattern for third period, rise continues to Group 5 before falling.

5  a  Li$_2$O, BeO, B$_2$O$_3$, CO$_2$, N$_2$O$_5$, F$_2$O  
  Na$_2$O, MgO, Al$_2$O$_3$, SiO$_2$, P$_2$O$_5$, SO$_3$, Cl$_2$O$_7$  
  c  Second period: number of oxygen atoms per atom of element increases by a half up to Group 5 before falling.  
  Third period, increases from Groups 1 through to 7.

  d  Same formulae except for halogens where fluorine is unable to form the higher oxides.
Section 11.2

1

<table>
<thead>
<tr>
<th>Element</th>
<th>Trend in reactivity with water</th>
<th>Trend in thermal stability of carbonate</th>
<th>Trend in pH of hydroxide with water</th>
<th>Trend in solubility of hydroxide</th>
<th>Trend in solubility of carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>increases</td>
<td>decompose at increasingly higher temperature</td>
<td>increases</td>
<td>increases</td>
<td>increases</td>
</tr>
<tr>
<td>Ca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2 Sulphate solubility decreases down group.

3 a magnesium + steam
   → magnesium hydroxide + hydrogen
   \[ \text{Mg}(s) + 2\text{H}_2\text{O}(g) \rightarrow \text{Mg(OH)}_2(s) + \text{H}_2(g) \]

b calcium oxide + hydrochloric acid
   → calcium chloride + water
   \[ \text{CaO}(s) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) \]

c beryllium carbonate
   → beryllium oxide + carbon dioxide
   \[ \text{BeCO}_3(s) \rightarrow \text{BeO}(s) + \text{CO}_2(g) \]

d barium hydroxide + sulphuric acid
   → barium sulphate + water
   \[ \text{Ba(OH)}_2(aq \text{ or s}) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + 2\text{H}_2\text{O}(l) \]

4 a Cs (or Fr)
   b Cs (or Fr)
   c +1
   d i M,O ii MOH iii M,CO_3

5 a lithium + water → lithium hydroxide + hydrogen
   \[ 2\text{Li}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{LiOH}(aq) + \text{H}_2(g) \]

b hydrochloric acid + sodium hydroxide
   → sodium chloride + water
   \[ \text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l) \]

c Little reaction even at high temperatures

d sodium oxide + sulphuric acid
   → sodium sulphate + water
   \[ \text{Na}_2\text{O}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \]

Section 11.3

1 The triple bond in N_2 is very strong (bond enthalpy = 945 kJ mol\(^{-1}\)), so a great deal of activation enthalpy must be supplied before N_2 will react. P_4, on the other hand, needs only enough energy to break one of the P–P bonds (bond enthalpy = 198 kJ mol\(^{-1}\)) to start it reacting. The reason that P does not form triple bonds like those in N_2 is related to its larger size.

2 a i +3 → +5
   ii +5 → 0
   iii −5 → −3
   iv 0 → −3
   v +2 → +4

b i A
   ii B
   iii C
   iv B
   v A

3 a +2 to +1

Section 11.4

1 a i Deep brown colour
   \[ 2\text{I}^–(aq) + \text{Cl}_2(aq) \rightarrow \text{I}_2(aq)s + 2\text{Cl}^–(aq) \]

ii No change

iii Light brown/red colour deepens in tone, becoming dark brown
   \[ 2\text{I}^–(aq) + \text{Br}_2(aq) \rightarrow \text{I}_2(aq)s + 2\text{Br}^–(aq) \]

iv Light brown/red colour
   \[ 2\text{Br}^–(aq) + \text{Cl}_2(aq) \rightarrow \text{Br}_2(aq) + 2\text{Cl}^–(aq) \]

b i Ag^+ (aq) + Cl^–(aq) → AgCl(s)
ii Ag^+ (aq) + Br^–(aq) → AgBr(s)
iii Ag^+ (aq) + I^–(aq) → AgI(s)

2 a i +1, Cl^–
   b Br^+3, F^–
   c Br^+1
   d i +5
   e i +7

3 a 2Na(s) + Br_2(g) → 2NaBr(s)

b Mg(s) + Cl_2(g) → MgCl_2(s)

c 2K(s) + I_2(s/g) → 2KI(s)

d Ca(s) + Cl_2(g) → CaCl_2(s)

4 i NO_3^–(aq) + H_2O(l) → NO_3^–(aq) + 2H^+(aq) + 2e^–
   ii NO_3^–(aq) + 6H^+(aq) + 5e^– → 3/2\text{N}_2(g) + 3\text{H}_2\text{O}(l)
   iii NH_4^+(aq) + OH^–(aq) → NH_3(g) + \text{H}_2\text{O}(l)
   iv N_2(g) + 6H^+(aq) + 6e^– → 2\text{NH}_3(g)
   v NO(g) + H_2O(l) → NO_2(g) + 2H^+(aq) + 2e^–

5 a The NO is oxidised by air as in reaction (2), to produce further NO_2 which takes part in reaction (3).

b Ammonium nitrate fertiliser.

c i 1 mole of NH_3 → 3/8 mole of HNO_3
   \[ \times \frac{1000\text{ kg}}{63/17} \times 3/8 = 2471\text{ kg} \]

ii Incomplete reaction at each of the three stages.
   Loss of intermediates.

D The reactants and intermediates include serious environmental pollutants, particularly NO_x. Escape of these, even in small quantities, would lead to acid rain and direct effects on living things. The NO_2 could be absorbed in aqueous sodium hydroxide.
3 a \( \text{Cl}_2(g) + 2\text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{NaClO(aq)} + \text{H}_2\text{O(l)} \)

b i Chlorine

ii Cl from 0 in Cl₂ to −1 in NaCl, ie reduction

Cl from 0 in Cl₂ to +1 in NaClO, ie oxidation

c i \( 2\text{NaClO(aq)} \rightarrow 2\text{NaCl(aq)} + \text{O}_2(g) \)

ii Oxygen and chlorine.

iii Oxygen from −2 in NaClO to 0 in \( \text{O}_2 \), ie oxidation

Chlorine from +1 in NaClO to −1 in NaCl, ie reduction.

4 a Isotopes and abundances

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting point/K</th>
<th>Boiling point/K</th>
<th>Solubility at 293 K/g per 100 g water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>210At</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b i The orange aqueous bromine water turns a dark brown/black and a black precipitate may form.

\( \text{Br}_2(aq) + 2\text{At}^-(aq) \rightarrow 2\text{Br}^-(aq) + \text{At}_2(s) \)

ii The orange-brown colour of iodine is replaced by a much darker colour and/or a black precipitate.

\( \text{I}_2(aq) + 2\text{At}^-(aq) \rightarrow 2\text{I}^-(aq) + \text{At}_2(s) \)

iii The two colourless solutions produce a yellow precipitate.

\( \text{Ag}^+(aq) + \text{At}^-(aq) \rightarrow \text{AgAt}(s) \)

iv The sodium burns with an orange flame and a white solid is produced.

\( 2\text{Na}(s) + \text{At}_2(g) \rightarrow 2\text{NaAt}(s) \)

---

**Section 11.5**

1

<table>
<thead>
<tr>
<th>Element</th>
<th>Electronic configuration</th>
<th>Element</th>
<th>Electronic configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>[Ar] 3d⁵ 4s²</td>
<td>Fe</td>
<td>[Ar] 3d⁶ 4s²</td>
</tr>
<tr>
<td>Ti</td>
<td>[Ar] 3d³ 4s²</td>
<td>Co</td>
<td>[Ar] 3d⁷ 4s²</td>
</tr>
<tr>
<td>V</td>
<td>[Ar] 3d³ 4s²</td>
<td>Ni</td>
<td>[Ar] 3d⁷ 4s²</td>
</tr>
<tr>
<td>Cr</td>
<td>[Ar] 3d⁵ 4s¹</td>
<td>Cu</td>
<td>[Ar] 3d⁸ 4s¹</td>
</tr>
<tr>
<td>Mn</td>
<td>[Ar] 3d⁴ 5s²</td>
<td>Zn</td>
<td>[Ar] 3d¹⁰ 4s²</td>
</tr>
</tbody>
</table>

2 a i Cu²⁺ [Ar] 3d⁷ 4s⁰

ii Cu⁺ [Ar] 3d¹⁰ 4s⁰

iii Fe³⁺ [Ar] 3d⁶ 4s⁰

iv V³⁺ [Ar] 3d⁷ 4s⁰

v Cr⁵⁺ [Ar] 3d⁷ 4s⁰

vi Ni⁶⁺ [Ar] 3d¹⁰ 4s⁰

b Cu²⁺ has a partially filled 3d sub-shell and behaves as a typical d block transition metal ion.

Cu⁺ has a filled 3d sub-shell and cannot show such properties.

3 a The three transition metals atoms (Cr, Fe, Co) are the same size as each other, but are smaller than the atoms of sodium (Na) and magnesium (Mg).

b The melting and boiling points of the transition metals are much higher than those of sodium and magnesium.

c The three transition metals are much denser than sodium and magnesium.

d Cr 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹

Fe 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁴ 4s²

Co 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁷ 4s³

Na 1s² 2s² 2p⁶ 3s¹

Mg 1s² 2s² 2p⁶ 3s²

e The properties of elements are governed by the arrangement of electrons in the outermost incomplete shells. In the first row of the d block, the inner 3d orbital is being filled and most elements have two electrons in the outer 4s shell. (Chromium is an exception, having only one electron in the 4s shell.)

Thus, transition elements have similar properties because they have essentially the same outer electronic arrangement as each other, in the same way as the elements in a vertical group. They differ only by the number of electrons in the inner incomplete 3d sub-shell.

Metals in different groups in the periodic table have different numbers of outer electrons and hence different properties.

4 a The \( \text{E}^\circ \) for the \( \text{O}_2(g), 4\text{H}^+(aq)/2\text{H}_2\text{O(l)} \) half-cell is more positive and receives electrons from the \( \text{Fe}^{3+}(aq)/\text{Fe}^{2+}(aq) \) half-cell. So overall \( \text{O}_2 \) is reduced to water and the \( \text{Fe}^{3+}(aq) \) is oxidised to \( \text{Fe}^{3+}(aq) \).

\[ \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{Fe}^{2+}(aq) \rightarrow 2\text{H}_2\text{O(l)} + 4\text{Fe}^{3+}(aq) \]

\[ \text{E}^\circ \text{cell} = +1.23 \text{V} - (+0.77 \text{V}) = +0.46 \text{V} \]

b i An acidified solution of iron(II) will be oxidised by air.

ii An acidified solution of manganese(II) will not be oxidised by air.

c The flow of electrons is to the half-cell with the most positive \( \text{E}^\circ \) value. \( \text{Cu}^+(aq) \) will be expected to be oxidised to \( \text{Cu}(s) \) and reduced to \( \text{Cu}^2+(aq) \) (disproportionation).

\[ 2\text{Cu}^+(aq) \rightarrow \text{Cu}^2+(aq) + \text{Cu}(s) \]

\[ \text{E}^\circ \text{cell} = +0.52 \text{V} - (+0.16 \text{V}) = +0.36 \text{V} \]
Section 11.6

1. a 2
   b 4
   c 6
   d 6  
2. a [Mn(H₂O)₆]²⁺  
   b [Zn(NH₃)₄]²⁺  
   c [FeF₆]³⁻  
   d [Cr(H₂O)₅OH]³⁺  
3. a +1  
   b +2  
   c +3  
   d +3  
4. a Hexaaquavanadium(III) ion  
   b Hexacyanoferrate(II) ion  
   c Tetrachlorocobaltate(II) ion  
   d Diamminesilver(I) ion  
   e Tetraaquadichlorochromium(III) ion  
5. TiO₂(s) contains titanium with a 3d⁰ electron configuration. It is white as no 3d electron transitions are possible.  
   Sc³⁺ [Ar]  
   Zn²⁺ [Ar] 3d¹⁰ no 3d electron transitions  
   Cu⁺ [Ar] 3d¹⁰ possible, hence colourless  
6. a 6  
   b +4  
   c Hexachlorotitanate(IV) ion  

Section 12.1

1. | Empirical formula | Molecular formula | Mᵣ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₇H₁₆</td>
<td>C₇H₁₆</td>
<td>44</td>
</tr>
<tr>
<td>C₈H₁₈</td>
<td>C₈H₁₈</td>
<td>58</td>
</tr>
<tr>
<td>C₁₀H₂₂</td>
<td>C₁₀H₂₂</td>
<td>72</td>
</tr>
<tr>
<td>CH₂</td>
<td>CH₂</td>
<td>12</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>18</td>
</tr>
<tr>
<td>CH₄</td>
<td>CH₄</td>
<td>20</td>
</tr>
</tbody>
</table>
2. a CH₂  
   b C₃H₄  
3. a CH  
   b C₂H₆  
4. a, b  
   Ratio by mass: 82.8 : 17.2  
   Ratio by moles: 6.9 : 17.2  
   Simplest ratio: 1 : 2.5  
   Whole number ratio: 2 : 5  
   : Empirical formula is C₂H₅  
   But Mᵣ(C₂H₅) = 29  
   So, the molecular formula is C₅H₁₁  
5. a 0.085 g C  
   b 0.0771 mol C  
   c CH₃  
   d C₅H₁₂  
   e  (or a hexene such as )  
6. a B D E  
   b A C F  
7. a C₇H₁₆  
   b C₈H₁₈  
   c C₁₀H₂₂  
8. a Monodentate  
   b Bidentate  
   c Polydentate  
   d Bidentate  
9. A complex of a metal ion with edta contains six 5-membered chelate ring systems (see Figure 32 on page 270 of Chemical Ideas). The complex is much more stable than the corresponding complexes with NH₃ or H₂O which contain no chelate rings. The extra stability is due to the large increase in entropy when edta¹⁻ displaces six ligands.  
10. a Cyclooctane  
    b Methylcyclopentane  
    c Cycloheptane  
    d Butylcyclohexane  
    e  
    f  
11. **butane**

12. a. \( \text{C}_4\text{H}_{12} + 8\text{O}_2 \rightarrow 5\text{CO}_2 + 6\text{H}_2\text{O} \)
   
   b. \( \text{C}_6\text{H}_{12} + 5\frac{1}{2}\text{O}_2 \rightarrow 5\text{CO} + 6\text{H}_2\text{O} \)

13. a. For 'cat' cracking, high temperature (500 °C) and zeolite catalyst.
   
   For steam cracking, high temperature (900 °C) with short residence time and steam as dilutent.

   b. True: (ii), (iv), (v)

   c. Three from:

   
   
   d. 

   e. 

   f. 

14. a. A
   
   B
   
   C

   D

   E

   b. D
   
   c. A
   
   d. B
   
   e. C
   
   f. C or E could have been produced by cracking D

   g. A

**Section 12.2**

1. a. 

   b. 

   c. 

   d. 

   e. 

2. a. propene
   
   b. hept-2-ene
   
   c. 2-methylbut-2-ene
   
   d. hept-1,4-diene
   
   e. 2,4-dimethylpent-2-ene
   
   f. cyclopentene

3. a. 

   b. 

   c. 

   d. 

4. \( \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \)

   \( \text{H} - \text{CH}_3 \)
The ring is not a regular hexagon, but has alternating long and short bonds.

\[ \text{CH}_3 \]  

0.154 nm  

0.134 nm  

\[ \text{CH}_3 \]

Section 12.3

1a 1,4-dimethylbenzene  
1b 1-ethy1-3-methylbenzene  
1c 1,2,4-trimethylbenzene  
1d 1,3,5-trimethylbenzene  
1e bromobenzene  
1f 1,3-dinitrobenzene  
1g 4-methylphenylamine  
1h 2,6-dimethylphenol

Shake the compound with about 1 cm depth of bromine water in a stoppered test-tube. If the compound is unsaturated, the bromine will be decolorised. The reaction occurs quickly at room temperature.

b The hydrogen bromide is polarised with the hydrogen atom being slightly positively charged. The hydrogen atom behaves as an electrophile and reacts with the double bond. One of the carbon atoms has become positively charged and so it reacts with the bromide ion to form a C–Br covalent bond.

The ring is not a regular hexagon, but has alternating long and short bonds. All the bonds in the ring are the same and so only one isomer is possible.
Section 12.4

1 a Product: 

b Reagents and conditions: Br₂; AlBr₃ or Fe; reflux
c Product: 

d Reactant: 

e Product: 

f Product: 

g Reagents and conditions: CH₃COCl; AlCl₃; reflux
h Product: 

2 a 

b 

c 

d 

3 a Difference in electronegativity between I and Cl

b 

c As the molecule is permanently polarised, a catalyst is not needed.
d Formation of chlorobenzene requires a chlorine with a δ+ charge.

4 a 

b 

c 

d 

5 a The benzene ring is resistant to hydrogenation because this destroys the stable delocalised electron system. The reaction has a high activation enthalpy.

6 a Electrophilic substitution
b Electrophilic addition
c Radical substitution
d Radical addition

Section 13.1

1 a trichloromethane
b 2-chloropropane
c 1,1,1-trichloro-2,2,2-trifluoroethane
d 2-chloro-1,1,1-trifluoropropane
e 2,2-dibromo-3-chlorobutane

2 d 

e 

3 a CH₂CH₂CH₂Cl(l) + NaOH(aq) → CH₂CH₂CH₂OH(aq) + NaCl(aq)
b The chlorine atom in 1-chloropropane has been replaced by a hydroxyl group, –OH.
c 

4 a 

b 

c 

d 

e 

5 a D
b A
c A
d E
e 

cyclohexanol
Explanation along similar lines to that on pages 302–303 in Chemical Ideas. Ammonia is the nucleophile because of its lone pair.

8. a 1-iodopentane (or bromo or chloro); aqueous NaOH; reflux.
   b 2-iodopropane (or bromo or chloro): concentrated aqueous solution of NH₃ (heat under pressure in a sealed tube).
   c 1-iodopropane (or bromo or chloro); alcoholic solution of KCN (or NaCN); reflux.

9. a \( \text{CH}_3\text{I} \xrightarrow{\text{hv}} \text{CH}_3\text{.} + \text{I.} \)
   b \( \text{CH}_3\text{Cl} \xrightarrow{\text{hv}} \text{CH}_3\text{.} + \text{Cl.} \)
   Bond enthalpy of C–I bond is less than that of C–Cl bond. C–I bond can be broken by ultraviolet radiation in the troposphere although this has relatively less energy than the ultraviolet radiation in the stratosphere.
Section 13.2

1a pentan-1-ol
c 2-methylbutan-2-ol
e ethoxypropane
2 methoxybutane
ehtoxypropane

Some students may give this isomer:
ethoxy-2-propane

3 a Hydrogen bonding between ethanol and water molecules (see Chemical Ideas, page 306). As the hydrocarbon chain becomes longer, the importance of the –OH group relative to that of the alkyl group becomes less and hexanol is unable to mix with water.
b No hydrogen bonding occurs.

Section 13.3

1a methanoic acid
c 2-methylbutanoic acid
d ethanoic acid
b pentanoic acid
e 2-octanoic acid
c butanoic acid
d benzene-1,2-dicarboxylic acid

3a CH3–C–C–C–C–C–C–O–H
b CH3–C–C–C–C–C–C–O–H

c O=C=O–H

4 a
CH3–CH2–C–O–CH3
b Cl–C=O

5 a Ethanol has hydrogen bonds between molecules, ethane does not. Hydrogen bonds require more energy to be broken than the weak attractive forces between ethane molecules, so boiling point of ethanol is higher.
b Water forms more hydrogen bonds than ethanol so its boiling point is higher.
c Both have –OH group and form hydrogen bonds between molecules. Boiling point increases down a homologous series as Mr increases. Hence butan-1-ol has a higher boiling point than ethanol.
d Butan-1-ol forms hydrogen bonds, ethoxyethane does not. Hence boiling point of butan-1-ol is higher.
### Section 13.4

| 1 | a | A butan-1-ol |
|   | B | butan-2-ol |
|   | C | 2,4-dichlorophenol |
| b | D | ![Structure of butan-1-ol](image) |
|   | E | ![Structure of butan-2-ol](image) |
| F | G | ![Structure of 2,4-dichlorophenol](image) |

| 2 | a | B |
|   | c | C |
|   | e | G |
| g | E | ![Structure of methyl ethanoate](image) |
| ![Structure of ethanoic acid](image) |
| ![Structure of 2-methylpropanal](image) |
| ![Structure of cyclohexanone](image) |
| ![Structure of 2-hydroxybenzoic acid](image) |

| 3 | a | ![Structure of salicylic acid](image) |
| ![Structure of methyl ethanoate](image) |
| ![Structure of ethanoic acid](image) |
| ![Structure of 2-methylpropanal](image) |
| ![Structure of cyclohexanone](image) |
| ![Structure of 2-hydroxybenzoic acid](image) |

| 4 | a | ![Structure of salicylic acid](image) |
| ![Structure of methyl ethanoate](image) |
| ![Structure of ethanoic acid](image) |
| ![Structure of 2-methylpropanal](image) |
| ![Structure of cyclohexanone](image) |
| ![Structure of 2-hydroxybenzoic acid](image) |

| 5 | a | ![Structure of methyl ethanoate](image) |
| ![Structure of ethanoic acid](image) |
| ![Structure of 2-methylpropanal](image) |
| ![Structure of cyclohexanone](image) |
| ![Structure of 2-hydroxybenzoic acid](image) |

| 6 | a | A F |
|   | b | C |
|   | c | D E |
|   | d | B D E |
|   | e | A |

| 7 | a | ![Structure of salicylic acid](image) |
| ![Structure of methyl ethanoate](image) |
| ![Structure of ethanoic acid](image) |
| ![Structure of 2-methylpropanal](image) |
| ![Structure of cyclohexanone](image) |
| ![Structure of 2-hydroxybenzoic acid](image) |

| ![Structure of ethanol](image) |
| ![Structure of methanoic acid](image) |
| ![Structure of salicylic acid](image) |
| ![Structure of methyl ethanoate](image) |
| ![Structure of ethanoic acid](image) |
| ![Structure of 2-methylpropanal](image) |
| ![Structure of cyclohexanone](image) |
| ![Structure of 2-hydroxybenzoic acid](image) |
| ![Structure of ethanol](image) |
| ![Structure of methanoic acid](image) |
Section 13.5

1a methyl propanoate  
b propyl ethanoate  
c ethyl propanoate  
d methyl methanoate  
e methyl butanoate

2a and b

<table>
<thead>
<tr>
<th>Ester</th>
<th>Alcohol</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl methanoate</td>
<td>ethanol</td>
<td>methanoic acid</td>
</tr>
<tr>
<td>CH₃CH₂OH</td>
<td>CH₃CH₂OH</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>3-methylbutyl ethanoate</td>
<td>3-methylbutanol</td>
<td>ethanoic acid</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₃OH</td>
<td>CH₃CH₂CH₃OH</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>ethyl 2-methylbutanoate</td>
<td>ethanol</td>
<td>2-methylbutanoic acid</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂CH₃OH</td>
<td>CH₃CH₂OH</td>
<td>CH₃CH₂CH₃OH</td>
</tr>
<tr>
<td>phenylmethyl ethanoate</td>
<td>phenylmethanol</td>
<td>ethanoic acid</td>
</tr>
<tr>
<td>CH₃CH₂CH₂OH</td>
<td>CH₃OH</td>
<td>CH₃OH</td>
</tr>
</tbody>
</table>

3a CH₃  
CH₃CH₂CH₂OH + CH₃CH₂CH₂OH → CH₃CH₂CH₂O−CH₂−CH₃ + H₂O

3b HOCH₂CH₂OH + 2CH₃COH → CH₃CH₂CH₂O−CH₂−CH₃ + 2H₂O

4

5a The C–O bond next to the C=O in the ester is broken.

5b The C=O bond is very polar with a δ+ charge on the carbon atom. Hydrolysis occurs by nucleophilic attack on this carbon atom by a lone pair on the oxygen-18 of a water molecule and the C–O bond break.

c A hydrogen ion attaches itself to the oxygen of the carbonyl group, and thus makes the carbon atom in the group more susceptible to attack by a nucleophile (eg water).

A water molecule attacks the positive carbon atom, the CH₂−CH₃−O− group is displaced and combines with H⁺ to form ethanol.
6 a  
\[\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{C} \overset{+}{\text{Cl}} \rightarrow \text{CH}_3\text{CH}_2\text{O} \overset{+}{\text{C}} \text{CH}_3 + \text{HCl}\]

b  
\[\text{CH}_3\overset{+}{\text{OH}} + \text{CH}_3\text{C} \overset{+}{\text{Cl}} \rightarrow \text{CH}_3\overset{+}{\text{C}} \text{O} \overset{+}{\text{C}} \text{CH}_3 + \text{HCl}\]

c  
\[\text{CH}_3\overset{+}{\text{OH}} + \text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \text{CH}_3 \rightarrow \text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \text{CH}_3 + \text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{OH}}\]

d  
\[\text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{C}} \text{CH}_3 + \text{H}_2\text{O} \overset{+}{\text{H}^+} \rightarrow \text{CH}_3\overset{+}{\text{OH}} + \text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{OH}}\]

e  
\[\text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{C}} \text{CH}_3 + 2\text{OH}^- \rightarrow \text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{CH}_3} + \text{H}_2\text{O}\]

(or NaOH as reactant; sodium salts as products)

7  
4-methylphenol

\[\text{CH}_3\text{COCl} \text{ (ethanoyl chloride)} \text{ or } \text{CH}_3\text{CO} \overset{+}{\text{O}} \overset{+}{\text{C}} \text{CH}_3 \text{ (ethanoic anhydride)}\]

Mix the reagents carefully. If the anhydride is used, warm the mixture under reflux.

8 a  Phenylmethanol

b  ethanoic acid, CH$_3$COOH

c  ethanoyl chloride, CH$_3$COCl

d  ethanoic anhydride (CH$_3$CO)$_2$O

c  H$_2$O, water

d  HCl, hydrogen chloride

c  CH$_3$COOH, ethanoic acid

d  
\[\text{CH}_2\overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{C}} \text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_2\overset{+}{\text{OH}} + \text{CH}_3\text{COOH}\]

c  Becomes increasingly vinegary.

Section 13.6

1 a  
\[\text{R} \overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{R}'}\]

b  
\[\text{H} \overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{CH}_3}\]

c  
\[\text{H} \overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{CH}_3}\]

d  
\[\text{H} \overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{CH}_3}\]

e  
\[\text{H} \overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{CH}_3} + 3\text{NaOH} \rightarrow \text{H} \overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{C}} \overset{+}{\text{Na}} + 3\text{CH}_3\overset{+}{\text{C}} \overset{+}{\text{O}} \overset{+}{\text{Na}}\]

200
2. a, b 1 mole glycerol (propane-1,2,3-triol)
    2 moles oleic acid
    1 mole linoleic acid

3. a Saturated fats are esters of fatty acids with no (or few) carbon double bonds.
    b Monounsaturated fats contain fatty acids with one carbon double bond (such as oleic acid).
    c Polyunsaturated fats contain a high proportion of fatty acid groups with two or more carbon double bonds (such as linoleic acid).

4. a
   
   b
   $\text{Na}^+ - O\quad - O$

   c The hydrocarbon chain
   Instantaneous dipole–induced dipole forces
   
   d Soaps are sodium and potassium salts of long chain carboxylic acids. The ions in solution are readily hydrated.

5. a 150°C; pressure (5 atmospheres); nickel as catalyst
    b i $M_r = 882$
    ii $1.13 \times 10^3$ moles of oil react with $2.45 \times 10^3$ moles of hydrogen
    iii 4
    iv 4 moles
    v To fully saturate 1 tonne of oil would require $1.13 \times 10^3 \times 4$ moles hydrogen = $4.52 \times 10^3$ moles
    vi Percentage of double bonds hydrogenated $= \frac{2.45 \times 10^3}{4.52 \times 10^3} \times 100 = 54.2\%$
    vii Easier to spread (less hard); healthier

Section 13.7

1. a methanal
   b propanal
   c 4-methylpentanal

2. a butan-2-one
   b pentan-3-one

3. a
   
   b
   

4. a
   
   b
   

5. a
   
   b
   
   c

ketone

primary

secondary

secondary
Section 13.8

1. a) ethylamine  
   b) dimethylamine  
   c) 2-aminopropane

2. a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \)  
   b) \( \text{NH}_2 \)  
   c) \( \text{CH}_3\text{CH}_2\text{NCH}_2\text{CH}_3 \)

3. a) \( \text{NH}_3^+ \)  
   b) \( \text{NH} \text{CO} \text{CH}_3 \)  
   c) \( \text{NH}_2 \text{CH}_2 \text{CH}_3 \)

4. a) \( \text{CH}_3\text{C}(-\text{CH} \text{C}(-\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{C}(-\text{CH} \text{C}(-\text{CH}_2\text{NH}_3 + \text{Cl}^-) 
   
5. a) Tertiary amines cannot react with acid chlorides because there is no H atom attached to the nitrogen.
   
6. a) Reagents and conditions: HCl(aq) (moderately concentrated); reflux 
   b) Products:
   c) Reactant:
   d) Product:

   (cf \( \text{Cu}(\text{H}_2\text{O})_4\text{H}_2\text{O}^{2+} + 4\text{CH}_3\text{NH}_2 \text{blue} \rightarrow \text{Cu}((\text{C}_4\text{H}_9\text{NH})_4(\text{H}_2\text{O})_2)^{2+} + 4\text{H}_2\text{O} \text{deep blue} \))
Section 13.9

1a

\[
\begin{align*}
N^+ & C\text{C}_\text{H}_2\text{O}^{-} \\
& \text{H}_4\text{N}^{-} \text{CH} \text{CO} \text{O}^{-} + \text{HCl} \rightarrow \text{Cl}^- \text{H}_4\text{N}^{-} \text{CH} \text{CO} \text{O}^{-} \\
& \text{H}_2\text{N} \text{CH}_2\text{O} \rightarrow \text{CH}_3 \\
& \text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} + \text{NaOH} \rightarrow \text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} \text{Na}^+ + \text{H}_2\text{O} \\
& \text{H}_4\text{N}_2 \text{NH}_2 \text{Cl}^- \rightarrow \text{Cl}^- \text{H}_4\text{N}^{-} \text{CH} \text{CO} \text{O}^{-} \\
& \text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} + 2\text{NaOH} \rightarrow \text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} \text{Na}^+ + 2\text{H}_2\text{O}
\end{align*}
\]

2

\[
\begin{align*}
\text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} + 2\text{NaOH} \rightarrow \text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} \text{Na}^+ + 2\text{H}_2\text{O}
\end{align*}
\]

3a

\[
\begin{align*}
\text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{N} \text{CH} \text{CO} \text{O}^{-} + \text{H}_2\text{N} \text{CH}_2\text{C} \text{CO} \text{O}^{-}
\end{align*}
\]

b Key points which should be included are: correct choice of solvent; the container used for the separation should have a lid; authentic samples of the amino acids used alongside the reaction mixture; \( R_f \) values carefully measured.
Section 13.10

1  a  \[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{H}_2\text{N}^- & \quad \text{HSO}_4^- \\
\end{align*}
\]

b  \[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{H}_2\text{N}^- & \quad \text{HSO}_4^- \\
\end{align*}
\]

c  \[
\begin{align*}
\text{N} & \quad \text{N} & \quad \text{OH} \\
\text{(strictly the sodium salt)}
\end{align*}
\]

2  a  \[
\begin{align*}
\text{HO} & \quad \text{N} & \quad \text{N} \\
\text{Cl}^- & \\
\end{align*}
\]

b  i  \[
\begin{align*}
\text{HO} & \quad \text{N} & \quad \text{N} \\
\text{Cl}^- & + & \text{OH} & \rightarrow & \text{HO} & \quad \text{N} & \quad \text{N} & \quad \text{OH} & + & \text{HCl}
\end{align*}
\]

ii  \[
\begin{align*}
\text{HO} & \quad \text{N} & \quad \text{N} \\
\text{Cl}^- & + & \text{OH} & \rightarrow & \text{HO} & \quad \text{N} & \quad \text{N} & \quad \text{OH} & + & \text{HCl}
\end{align*}
\]

iii  \[
\begin{align*}
\text{HO} & \quad \text{N} & \quad \text{N} \\
\text{Cl}^- & + & \text{NH}_2 & \rightarrow & \text{HO} & \quad \text{N} & \quad \text{N} & \quad \text{NH}_2 & + & \text{HCl}
\end{align*}
\]

3  HOO\text{S}^- & \quad \text{N} & \quad \text{N} & \quad \text{X}^- & \quad \text{and} & \text{N} & \quad \text{N} & \quad \text{CH}_3
\]

O\text{N}^- & \quad \text{N} & \quad \text{N} & \quad \text{X}^- & \quad \text{and} & \text{N} & \quad \text{N} & \quad \text{OH}
\]

\text{and} & \quad \text{N} & \quad \text{N} & \quad \text{SO}_2\text{OH}
\]

\text{and} & \quad \text{N} & \quad \text{N} & \quad \text{NH}_2
\]

4  The diazonium salt is a relatively weak electrophile and will only react with particularly electron-rich activated benzene rings.

Section 14.1

1  a  73.9%  b  73.1%

2  Route I (Route I 40%; Route II 30%)

3  16.2 g

4  a  (Selection of starting materials); reaction; extraction of product from reaction mixture; purification of product.

Section 14.2

1  a  A solution of hydrogen bromide (HBr) in a polar solvent at room temperature.  b  Reflux with dilute aqueous sodium hydroxide solution

2  c  Reflux with an acidified solution of potassium dichromate(VI)

d  Treat with hydrogen cyanide solution with a small amount of alkali.
2. a Addition; electrophilic  
b Substitution; nucleophilic  
c Oxidation  
d Addition; nucleophilic  

3. a Radical substitution  
   b The mechanism is:

\[
\text{initiation:} \quad \text{Cl} - \text{Cl} \xrightarrow{h\nu} 2 \text{Cl}^* \\
\text{propagation:} \quad \text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}^* \rightarrow \text{C}_6\text{H}_5\text{C}^* + \text{HCl} \\
\text{C}_6\text{H}_5\text{C}^* + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{C}^* \text{Cl} + \text{Cl}^* \\
\text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2 \\
\text{termination:} \quad \text{C}_6\text{H}_5\text{C}^* + \text{Cl}^* \rightarrow \text{C}_6\text{H}_5\text{C}^* \text{Cl} \\
\]

c. \text{CH}_2\text{Cl} + \text{c. NH}_3(aq) \rightarrow \text{CH}_2\text{NH}_2  

4. a

\[
\text{b Electrophilic substitution}  \\
\text{c AlCl}_3\text{ helps to polarise the chlorine molecule, to produce the electrophile, Cl}^+ \\
\]

\[
\text{initiation:} \quad \text{Cl} - \text{Cl} + \text{AlCl}_3 \xrightarrow{\delta^+ - \delta^-} \text{Cl}^+ + \text{AlCl}_4^- \\
\text{propagation:} \quad \text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}^+ \rightarrow \text{C}_6\text{H}_5\text{C}^* + \text{HCl} + \text{AlCl}_3 \\
\text{termination:} \quad \text{C}_6\text{H}_5\text{C}^* + \text{Cl}^+ \rightarrow \text{C}_6\text{H}_5\text{C}^* \text{Cl} + \text{HCl} + \text{AlCl}_3 \\
\]
5 a i Reagents and condition: treat with a nitrating mixture (conc. HNO₃ and conc. H₂SO₄); keep temperature below 55 °C.

ii Product:

iii Reactant: CH₃Cl (or CH₄)

iv Reactant: CH₃–CH₂–CH₂–X

(v) Products:

vi Products:

6 a i COONa⁺ + H₂O

ii CH₃COONa⁺ + NH₂

iii + H₂O

iv CH₃–CH₂–OH

v + 3H₂ → Pt

6 a vi Electrophilic substitution

ii Electrophilic addition

iii Radical substitution

iv Nucleophilic substitution

v Nucleophilic substitution

vi Electrophilic substitution

7 a React with hydrogen in presence of finely divided nickel at 150 °C and 5 atm.

b Treat with a solution of HBr in a polar solvent at room temperature.

c Hydrolyse by refluxing with a dilute aqueous solution of NaOH.

8 a i Reagents and condition: treat with a nitrating mixture (conc. HNO₃ and conc. H₂SO₄); keep temperature below 55 °C.

ii Product:

iii Reactant: CH₃Cl (or CH₄)

iv Reactant: CH₃–CH₂–CH₂–X

(v) Products:

vi Products:

b i Acid–base

ii Hydrolysis

iii Dehydration

iv Esterification

v Reduction

c Examples may be:

i CH₃COOH + NaOH → CH₃COONa⁺ + H₂O

ii CH₃–C–NH–CH₃ + NaOH

iii CH₃–CH₂–OH → Al₂O₃ → CH₂ ≡ CH₂ + H₂O

iv H–C–OH + CH₃–OH

v H–C–O–CH₃ + H₂O

vi H–C– + H₂ → CH₃–CH₃
d) Dehydrate by heating with Al₂O₃ at 300°C or by heating with concentrated sulphuric acid.

\[
\begin{align*}
\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{COOH} & \quad \rightarrow \quad \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{COOH} + \text{H}_2\text{O} \\
\text{(prepared as in e)} & \\
\text{(prepared as in e)}
\end{align*}
\]

Section 15.1

a) Continuous  
b) Batch  
c) Continuous  
d) Continuous

Section 15.2

a) Conditions: lower pressure, or less separation required.  
Feedstock: methanol can be obtained from a variety of feedstocks.  
Product: higher yield  
Co-products: far fewer.

b) Disadvantages: very expensive catalyst, and more than one stage to process.

Section 15.3

2a) i) As 3 moles of gas form 1 mole of gas, increasing the pressure will cause more methanol to form.  
ii) As the conversion of synthesis gas to methanol is exothermic, an increase in temperature will reduce the equilibrium yield of methanol.

b) i) The pressure of 100 atm will increase the yield.  
The temperature is not too high, otherwise the yield is decreased. It is sufficient to provide a high rate of reaction with the catalyst used. It is carefully controlled to prevent the exothermic reaction raising the temperature and reducing the yield.  
ii) The catalyst lowers the temperature required to give a high rate of reaction. However, some sacrifice in yield is made to maintain this rate. The high pressure also increases the reaction rate.

Section 15.4

a) Thermal energy released from the reaction can be used to pre-heat, via a heat exchanger, the water which will be made into steam as one of the reactants.

b) The unreacted feedstock can be recycled again over the catalyst, saving costs of energy needed in the high temperature and pressure conditions.
Section 15.5

1a Many of the fixed costs for a 200 tonne day<sup>-1</sup> plant are less than double those of a 100 tonne day<sup>-1</sup> plant: for example, the larger plant will require less than twice the area of land for building, and the cost of building access roads will be less than twice as great.

b You have to pay the same fixed costs such as wages and land rental regardless of how much you are producing. But variable costs such as costs of raw materials and energy will double if you double output.

2a Germany $2.2 \times 10^5 \text{ US}\$
France $3.3 \times 10^5 \text{ US}\$
UK $2.1 \times 10^5 \text{ US}\$
Italy $2.6 \times 10^5 \text{ US}\$
Belgium $3.8 \times 10^5 \text{ US}\$
Spain $2.5 \times 10^5 \text{ US}\$

b Ireland

Ireland

The costs of operating in each country (general level of wages; workforce productivity; taxation policies; the age and inherent efficiency of the plant in each of the countries if similar products are being made; the type of product each country produces; some of these factors are controlled by political forces, others are the results of decisions and developments in the past.

d It may be that a country's chemical industry is biased towards products that need a larger number of employees. Thus, one should also look at other statistics such as profits per employee.