11.1 Chemical equilibrium

11.1.1 Equilibrium constant, K_c

1 (a) $\dfrac{[CH_3OH(g)]}{[CO(g)][H_2(g)]^2}$

(b) $\dfrac{2.6 \times 10^{-5}}{3.1 \times 10^{-3} \times (2.4 \times 10^{-2})^2} = 14.6\ dm^6\ mol^{-2}$.

Note: Although positive indices should be put first, you will not be penalised if you write $mol^{-2}\ dm^6$.

2 (a) $\dfrac{[CH_3COOCH_2CH_3(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3CH_2OH(l)]}$

(b) *n*(ethanol) = (12.5 – 5.0) = 7.5 mol.

n(ethyl ethanoate) = 5.0 mol.

n(water) = 5.0 mol.

(c) $\dfrac{(5.0\ /\ V) \times (5.0\ /\ V)}{(1.0\ /\ V) \times (7.5\ /\ V)} = 3.3$ *and* no units.

Note: It is essential to show the division by the volume, V dm^3, even though they cancel, to show that you have understood that the terms in the expression are concentrations. Also, it is essential to state that there are no units, since the question demands that you state the units, if any. Lastly, the answer should be given to only two significant figures since some of the data supplied is given to only two significant figures.

3 *n*(I_2) at equilibrium = (0.20 – 0.16) = 0.04 mol.

n(HI) at equilibrium = (2 × 0.16) = 0.32 mol.

$K_c = \dfrac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

$= \dfrac{(0.32\ /\ V)^2}{(0.14\ /\ V)(0.04\ /\ V)} = 18.29$ *and* no units (answer *must* be to two decimal places).

Note: Two decimal places is correct for the final answer, since all of the data supplied in the question were to two decimal places.

4 (a) Since it is very small, the equilibrium lies well to the left.

(b) $K_c = \dfrac{[NO(g)]^2}{[N_2(g)][O_2(g)]} = 4.8 \times 10^{-31}$.

$[O_2(g)] = \dfrac{[NO(g)]^2}{[N_2(g)](4.8 \times 10^{-31})}$

$= \dfrac{(4.0 \times 10^{-16}\ /\ 1.2)^2}{(1.1\ /\ 1.2)(4.8 \times 10^{-31})} = 0.25\ mol\ dm^{-3}$.

5 $K_c = \dfrac{[H_2(g)][CO(g)]}{[H_2O(g)]} = 4.92 \times 10^{-5}\ mol\ dm^{-3}$.

Let the equilibrium concentration of H_2 and CO = y mol dm^{-3}.

Then, $\dfrac{y^2}{2.00 \times 10^{-2}} = 4.92 \times 10^{-5}$.

$y = (4.92 \times 10^{-5} \times 2.00 \times 10^{-2})^{½} = 9.92 \times 10^{-4}$.

$[H_2(g)] = [CO(g)] = 9.92 \times 10^{-4}\ mol\ dm^{-3}$.

11.1.2 Equilibrium constant, K_p

1 (a) $K_p = \dfrac{(p_{SO_3})^2}{(p_{SO_2})^2(p_{SO_2})}$

(b) $\frac{(p_{SO_3})^2}{(p_{SO_2})^2(p_{SO_2})} = 3.00 \times 10^4$ atm.

$p_{SO_3} = (3.00 \times 10^4 \times 0.100^2 \times 0.500)^{½}$ atm

= 12.2 atm (to 3 significant figures).

Percentage of SO_3 present = $\left(\frac{12.2}{12.2 + 0.1 + 0.5}\right) \times 100 = 95.3\%$.

2 (a) The pressure that an individual gas would exert if it alone occupied the total volume of the gaseous mixture.

(b) $K_p = \frac{(p_{COCl_2})}{(P_{CO})(p_{Cl_2})}$

$= \frac{4.08 \times 10^{-10}}{2.47 \times 10^{-8} \times 2.47 \times 10^{-8}}$ atm^{-1}

$= 6.69 \times 10^5$ atm^{-1}.

3 (a) Mole fraction = $\frac{\text{partial pressure}}{\text{total pressure}}$

Mole fraction of Cl = $\frac{0.030}{0.870} = 0.345$ (to 3 significant figures).

(b) (i) $K_p = \frac{(p_{Cl})^2}{(p_{Cl_2})}$

(ii) $K_p = \frac{(0.030)^2}{0.840} = 1.07 \times 10^{-3}$ atm.

11.1.3 Effect of temperature on equilibrium constants

1 If K_c has decreased, then the position of equilibrium has moved to the left. Since the shift has been caused by an increase in temperature, the reverse reaction must be endothermic. Hence the forward reaction must be exoothermic.

2 If the amount of H_2(g) at equilibrium has increased, then the position of equilibrium has shifted to the left. Since this shift has been caused by an increase in temperature, the reverse reaction must be endothermic. Hence the forward reaction must be exothermic.

3 Since the forward reaction is endothermic, an increase in temperature will increase the value of K_c. This, in turn, will increase the proportion of NO(g) at equilibrium.

11.1.4 Effect of concentration, pressure and catalysts on equilibrium constants

1 The value of K_c will not change, since its value changes only with a change in temperature.

$K_c = \frac{[CH_3OH(g)]}{[CH_3OH(g)][H_2(g)]^2}$

If the pressure is increased then the volume of the reaction mixture will decrease. This will result in an instantaneous equal increase in the concentration of each component.

However, the increase in the magnitude of $[CH_3OH(g)][H_2(g)]^2$ will be greater than the increase in the magnitude of $[CH_3OH(g)]$.

So, the value of the expression $\frac{[CH_3OH(g)]}{[CH_3OH(g)][H_2(g)]^2}$ will temporarily decrease. In order to return its value to that of K_c, the equilibrium has to shift to the right, to increase the magnitude of the numerator.

2 (a) $K_c = \frac{[CH_3COOCH_2CH_3(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3CH_2OH(l)]}$

If more ethanol (CH_3CH_2OH) is added, then its concentration will increase. This will lead to a temporary decrease in the value of the expression $\frac{[CH_3COOCH_2CH_3(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3CH_2OH(l)]}$.

In order to restore its value to that of K_c, the position of equilibrium has to move to the right, so that the magnitude of the denominator decreases.

(b) Since sulfuric acid does not appear in the expression for K_c, changes in its concentration do not affect the value of the ratio $\frac{[CH_3COOCH_2CH_3(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3CH_2OH(l)]}$. Hence, an increase in the concentration of sulfuric acid has no effect on the position of equilibrium.

Note: The question asks for an *explanation*, so the use of qualitative predictions as made at AS level are not sufficient. To answer a question that requires an explanation you *must* refer to the equilibrium constant.

3 $K_p = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

If the volume is reduced, then the concentration of each component will temporarily be increased to the same extent.

However, the value of the ratio $\frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ will not alter, since the increase in $[HI(g)]^2$ will be the same as the increase in $[H_2(g)][I_2(g)]$.

So, there will be no change in the position of equilibrium.

11 Answers to Exam-style questions

1 (a) C (1)

(b) (i) $[N_2] = \frac{1.00}{20.0} = 0.0500\,\text{mol dm}^{-3}$ (1).

$[H_2] = \frac{2.00}{20.0} = 0.100\,\text{mol dm}^{-3}$ (1).

$[NH_3] = \frac{1.00}{20.0} = 0.0500\,\text{mol dm}^{-3}$ (1).

$K_c = \frac{(0.0500)^2}{(0.0500 \times 0.100)^3} = 50.0$ (1) $\text{dm}^6\,\text{mol}^{-2}$ (1).

(ii) $p_{N_2} = \frac{1.00}{4.00} \times 5.00 = 1.25$ atm (1).

$p_{H_2} = \frac{2.00}{4.00} \times 5.00 = 2.50$ atm (1).

$p_{NH_3} = \frac{1.00}{4.00} \times 5.00 = 1.25$ atm (1).

$K_p = \frac{(1.25)^2}{1.25 \times (2.50)^3} = 0.0800$ (1) atm^{-2} (1).

2 (a) (i) $K_p = \frac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})}$ (1).

(ii) atm (1).

(b) p_{PCl_5}, p_{PCl_3} and p_{Cl_2} all instantaneously increase by the same amount (1).

However, the value of $p_{PCl_3} \times p_{Cl_2}$ increases more than that of p_{PCl_5} (1).

Since the magnitude of $\frac{(p_{PCl_3})(p_{Cl_2})}{(p_{PCl_5})}$ has to be constant at a given temperature (1), the equilibrium position moves to the left to decrease the value of $p_{PCl_3} \times p_{Cl_2}$ and increase the value of p_{PCl_5} until a new equilibrium is established (1).

(c) $\Delta n = 1$ (1).

$K_c = \frac{K_p}{0.0821\,T} = \frac{0.801}{0.0821 \times 500}$ (1)

$= 0.0195$ (1).

3 (a) **Concentration**

Using experiments 1, 2 and 3:

As the concentration of steam increases, the percentage of ethene converted increases (1), therefore the equilibrium position moves to the right (1).

Temperature

Using experiments 2, 6 and 7:

As the temperature increases, the percentage of ethene converted decreases (1), therefore the equilibrium moves to the left (1).

Pressure

Using experiments 2, 4 and 5:

As the pressure increases, the percentage of ethene converted increases (1), therefore the equilibrium position moves to the right (1).

(b) (i) $K_p = \dfrac{(p_{C_2H_5OH})}{(p_{C_2H_4})(p_{H_2O})}$ (1).

(ii) Number of moles at equilibrium:

$C_2H_4 = 0.6$; $H_2O = 1.6$; $C_2H_5OH = 0.4$ (1).

Partial pressures:

$C_2H_4 = \dfrac{0.6}{2.6} \times 50 = 11.5$ atm (1).

$H_2O = \dfrac{1.6}{2.6} \times 50 = 30.8$ atm (1).

$C_2H_5OH = \dfrac{0.4}{2.6} \times 50 = 7.69$ atm (1).

$K_p = \dfrac{7.69}{11.5 \times 30.8} = 2.17 \times 10^{-2}$ (1) atm^{-1} (1).

4 (a) (i) $K_p = \dfrac{(p_R)}{(p_P)^2(p_Q)}$ (1).

(ii) atm^{-2} (1).

(b) (i) Total number of moles present at equilibrium = (1.0 + 0.5 + 0.5) = 2.0 (1).

Partial pressures:

P = 250 atm; **Q** = 125 atm; **R** = 125 atm (1).

$K_p = \dfrac{125}{(250)^2 \times 125}$ (1)

$= 1.6 \times 10^{-5}\ \text{atm}^{-2}$ (1).

(ii) High temperature (1) high pressure (1).

(iii) Using high temperatures increases the energy costs (1).

Using high pressures increases the cost of compressing the gases / requires thick walled vessels / increases the maintenance costs / increases the risks of leaks or explosions (1).

5 (a) (i) $K_c = \dfrac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ (1)

(ii) 3.5 hours (1).

(iii) $[HI(g)] = 3.45 \times 10^{-3}$ mol (1).

$[H_2(g)] = [I_2(g)] = 3.00 \times 10^{-4}$ mol (1).

(iv) $K_c = \dfrac{(3.45 \times 10^{-3})^2}{(3.0 \times 10^{-4})\cdot(3.0 \times 10^{-4})}$ (= 132.3) (1)

= 132 *and* no units (1).

(b) (i) The value of K_c does not change (1). Only a change in temperature can change the value of an equilibrium constant (1).

(ii) The value of K_c increases (1). The forward reaction is endothermic so the position of equilibrium shifts to the right, increasing $[HI(g)]$ whilst decreasing $[H_2(g)]$ and $[I_2(g)]$ (1).

(c) C (1)

6 (a) There is a high percentage of SO_3 in the equilibrium mixture (1) since the magnitude of the equilibrium constant is very large (1).

(b) As the temperature increases K_p decreases therefore the equilibrium position moves to the left (1). The reverse reaction is therefore endothermic, making the forward reaction exothermic (1). The sign of the enthalpy change is therefore negative (1).

(c) When the pressure is increased the partial pressure of each gas increases by the same amount (1). In the expression for K_p, the increase in magnitude of the numerator $(p_{SO_3})^2$ is less than the increase in magnitude of the denominator $(p_{SO_2})^2(p_{O_2})$ (1). The ratio of $\frac{(p_{SO_3})^2}{(p_{SO_2})^2(p_{O_2})}$ therefore decreases (1). In order to restore it to the value of K_p the equilibrium shifts to the right producing more SO_3 (1).

12.1 Strong and weak acids

12.1.1 The Brønsted-Lowry theory

1 (a) CH_3COOH
(b) $CH_3NH_3^+$
(c) H_2SO_4

2 (a) ClO_4^-
(b) H_2O
(c) SO_4^{2-}

3 (a) Pair 1: H_2CO_3 and HCO_3^- — H_2CO_3 is acting as the acid.
Pair 2: H_3O^+ and H_2O — H_3O^+ is acting as the acid.
(b) Pair 1: HCO_3^- and CO_3^{2-} — HCO_3^- is acting as the acid.
Pair 2: H_3O^+ and H_2O — H_3O^+ is acting as the acid.
(c) Pair 1: HNO_3 and NO_3^{2-} — HNO_3 is acting as the acid.
Pair 2: CH_3COOH and $CH_3COOH_2^+$ — $CH_3COOH_2^+$ is acting as the acid.

4 NH_4^+ is donating a proton and is therefore acting as a Brønsted-Lowry acid.
NH_2^- is accepting a proton and is therefore acting as a Brønsted-Lowry base.

12.1.2 Hydrogen ion concentration and the pH scale

1 (a) $[H^+(aq)] = 0.0100\ mol\,dm^{-3}$.
pH = $-\lg(0.0100) = 2.00$.
(b) $[H^+(aq)] = 0.500\ mol\,dm^{-3}$.
pH = $-\lg(0.500) = 0.30$.
(c) $[H^+(aq)] = 0.00405\ mol\,dm^{-3}$.
pH = $-\lg(0.00405) = 2.39$.

2 5 cm^3 of 1.00 $mol\,dm^{-3}$ NaOH reacts with 5 cm^3 of 1.00 $mol\,dm^{-3}$ HCl.
So, 15 cm^3 of 1.00 $mol\,dm^{-3}$ HCl is in excess.
n(HCl) in excess = $(15 \times 1.00) \div 1000 = 0.015$ mol.
$[H^+(aq)] = (0.015 \div 25) \times 1000 = 0.60\ mol\,dm^{-3}$.
pH = $-\lg(0.60) = 0.22$.

3 (a) $[H^+(aq)] = (0.100 \times 1.60 \times 10^{-4})^{½} = 4.00 \times 10^{-3}\ mol\,dm^{-3}$.
pH = $-\lg(4.00 \times 10^{-3}) = 2.40$.
(b) $[H^+(aq)] = (1.00 \times 5.62 \times 10^{-4})^{½} = 2.37 \times 10^{-2}\ mol\,dm^{-3}$.
pH = $-\lg(2.37 \times 10^{-2}) = 1.63$.
(c) $[H^+(aq)] = (0.505 \times 5.62 \times 10^{-10})^{½} = 1.68 \times 10^{-5}\ mol\,dm^{-3}$.
pH = $-\lg(1.68 \times 10^{-5}) = 4.77$.

4 $[H^+(aq)] = 10^{-4.97} = 1.07 \times 10^{-5}\ mol\,dm^{-3}$.

$$K_a = \frac{(1.07 \times 10^{-5})^2}{0.0305} = 3.75 \times 10^{-9}\ mol\,dm^{-3}.$$

12.1.3 Ionic product of water, K_w

1 (a) (i) $[H^+(aq)] = (1 \times 10^{-14})^{½} = 1 \times 10^{-7}\ mol\,dm^{-3}$.
pH = $-\lg(1 \times 10^{-7}) = 7.00$.
(ii) $[H^+(aq)] = (6.81 \times 10^{-14})^{½} = 2.63 \times 10^{-7}\ mol\,dm^{-3}$.
pH = $-\lg(2.63 \times 10^{-7}) = 6.58$.
(b) $[H^+(aq)] = [OH^-(aq)]$ in pure water regardless of the temperature.

(c) $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$

$K_w = [H^+(aq)][OH^-(aq)]$.

As the temperature decreases, K_w increases. So the equilibrium shifts to the right. The forward reaction is therefore exothermic.

2 (a) $[OH^-(aq)] = 0.0100\,mol\,dm^{-3}$.

$pOH = -lg\ (0.0100) = 2.00$.

$pH = (14.00 - 2.00) = 12.00$.

(b) $[OH^-(aq)] = 0.100\,mol\,dm^{-3}$ (2 × 0.0500 since, $Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + \mathbf{2}OH^-(aq)$).

$pOH = -lg\ (0.100) = 1.00$.

$pH = (14.00 - 1.00) = 13.00$.

(c) $[OH^-(aq)] = 0.0315\,mol\,dm^{-3}$.

$pOH = -lg\ (0.0315) = 1.50$.

$pH = (14.00 - 1.50) = 12.50$.

12.1.4 Analysing data from pH measurements

1 (a) Acidic. NH_4NO_3 is a salt of a strong acid (HNO_3) and a weak base (NH_3).

(b) Alkaline. CH_3CH_2COOK is a salt of a weak acid (CH_3CH_2COOH) and a strong base (KOH).

(c) Neutral. $NaNO_3$ is a salt of a strong acid (HNO_3) and a strong base (NaOH).

2 The K_a value of HCOOH and the K_b value of NH_3.

3 Molar mass of $CH_2ClCOOH$ is $94.5\,g\,mol^{-1}$.

$n(CH_2ClCOOH) = (1.89\,g \div 94.5\,g\,mol^{-1}) = 0.02\,mol$.

$[CH_2ClCOOH(aq)] = (0.0200 \times 1000/250) = 0.08\,mol\,dm^{-3}$.

$[H^+(aq)] = 10^{-1.99} = 1.02 \times 10^{-2}\,mol\,dm^{-3}$.

$K_a = \frac{(1.02 \text{ x } 10^{-2})^2}{0.0800} = 1.31 \times 10^{-3}\,mol\,dm^{-3}$.

12.2 Acid-base titrations

12.2.1 Acid-base titrations, pH curves and indicators

1 (a) The pH at the equivalence point is less than 7.

(b) The volume of ammonia at the equivalence point is 15 cm^3.

$n(HCl) = n(NH_3) = (0.0250 \times 0.0200) = 5.00 \times 10^{-4}\,mol$.

$[NH_3(aq)] = 5.00 \times 10^{-4}\,mol \times 1000/15\,dm^3 = 0.033\,mol\,dm^{-3}$.

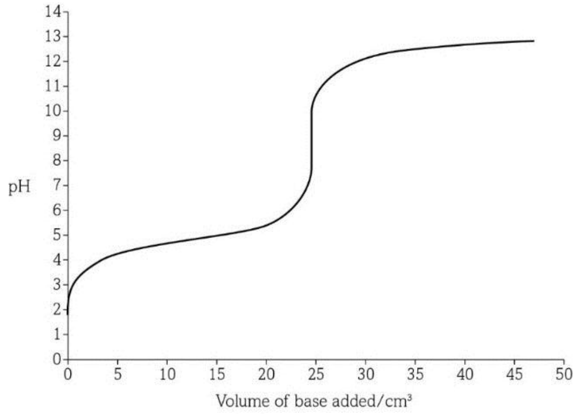
(c) Methyl red.

The pH range of methyl red falls within the sharp rise of the pH curve.

2 (a) $[H^+(aq)] = (0.100 \times 1.74 \times 10^{-5})^{½} = 1.32 \times 10^{-3}\,mol\,dm^{-3}$.

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

(b)



Points to note in order to gain full marks are:

Start the curve at the pH value you have calculated for the acid (2.88 on this occasion).

Make sure the curve starts off steep as the NaOH is first added and then levels out as the buffer mixture is formed.

Make sure the equivalence point is at a pH greater than 7, since this is a titration of a weak acid and a strong base.

Make sure the finishing pH is realistic for the concentration of base taken.

(c) The curve would start at a higher pH.

The volume of sodium hydroxide at the equivalence point would be 12.5 cm^3.

12.2.2 Buffer solutions

1 (a) A buffer solution is one that maintains a fairly constant pH despite the addition of small amounts of either acid or base.

(b) When acid is added, the hydrogen ions added are removed as they react with the methanoate ions:

$HCOO^-(aq) + H^+(aq) \rightarrow HCOOH(aq)$

When base is added, the hydroxide ions added are removed as they react with the methanoic acid molecules:

$HCOOH(aq) + OH^-(aq) \rightarrow HCOO^-(aq) + H_2O(l)$

Since the solution contains a relatively high concentration of both methanoic acid (HCOOH) molecules and methanoate ions ($HCOO^-$), the ratio of the concentration of methanoate ions to methanoic acid molecules does not significantly change. The pH does not change since it is given by the equation:

$\text{pH} = \text{p}K_a + \lg \frac{[\text{HCOO}^-(\text{aq})]}{[\text{HCOOH(aq)}]}$.

(c) $[HCOO^-(aq)]$ will increase with the addition of solid sodium methanoate.

The pH will increase, since $\lg \frac{[\text{HCOO}^-(\text{aq})]}{[\text{HCOOH(aq)}]}$ increases.

(d) $\text{p}K_a = -\lg 1.79 \times 10^{-4} = 3.75$.

$$\text{pH} = \text{p}K_a + \lg \frac{[\text{HCOO}^-(\text{aq})]}{[\text{HCOOH(aq)}]}$$

$$= 3.75 + \lg \frac{0.500}{1.00}$$

$$= 3.75 + (-0.30)$$

$$= 3.45.$$

2 When making solution **A**, 25 cm^3 of the NaOH solution reacts with 25 cm^3 of the CH_3COOH solution. This forms some ethanoate ions, $CH_3COO^-(aq)$, and leaves some unreacted ethanoic acid molecules, CH_3COOH.

$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

So, solution **A** contains a mixture of a weak acid, CH_3COOH, and its conjugate base, CH_3COO^-.

This mixture constitutes a buffer.

When making solution **B**, 50 cm^3 of the NaOH solution will react exactly with 25 cm^3 of the CH_3COOH solution. Solution **B**, therefore, contains only the conjugate base of the acid. This is not a buffer.

3 $[H^+(aq)]$ in the buffer = $10^{-9.55} = 2.82 \times 10^{-10}$ mol dm^{-3}.

$[NH_3(aq)]$ in the buffer = 0.100 mol dm^{-3} (0.200 ÷ 2, as the original solution has been diluted by a factor of 2).

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$

$$K_a = \frac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]}$$

$$[NH_4^+(aq)] \text{ in the buffer} = \frac{[NH_3(aq)][H^+(aq)]}{K_a}$$

$$= \frac{(0.100 \times 2.82 \times 10^{-10})}{5.62 \times 10^{-10}}$$

$$= 0.0502 \text{ mol dm}^{-3}.$$

Original concentration of ammonia solution = 2 × 0.0502 = 0.100 mol dm^{-3} (to 3 significant figures).

4 Molar mass of C_6H_5COOH is 122.0 g mol^{-1}.

$n(C_6H_5COOH) = (12.20 \div 122.0) = 0.100$ mol.

Molar mass of C_6H_5COONa is 144.0 g mol^{-1}.

$n(C_6H_5COONa) = (7.20 \div 144.0) = 0.0500$ mol.

$$pH = pK_a + \lg \frac{0.0500/1.00}{0.100/1.00}$$

$$= 4.20 + \lg 0.500$$

$$= 4.20 + (-0.30)$$

$$= 3.90.$$

5 (a) NH_3 donates a proton to form NH_2^- and accepts a proton to form NH_4^+.

(b) (i) Acidic since the NH_4^+ ion is the acid in liquid ammonia (cf. H_3O^+ in water).

(ii) Basic since the NH_2^- ion is the base in liquid ammonia (cf. OH^- in water).

(iii) Basic; OH^- reacts with NH_4^+ leaving an excess of NH_2^- in solution.

12.2.4 Enthalpy changes of neutralisation for strong and weak acids

1 Both the acid and the base are almost fully ionised. Hence the reaction in each case is essentially the same:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H^\theta \approx -57\,\text{kJ mol}^{-1}$.

2 Ammonia is a weak base and is therefore only partially ionised in aqueous solution. Energy is required to ionise the ammonia molecules and hence less thermal energy is released.

3 Any sensible value less negative than –11.7. The accepted value is –5.4 kJ mol^{-1}.

12 Answers to Exam-style questions

1 (a) pH = – lg (2.50 × 10^{-4}) (1) = 3.60 (1).

(b) (i) $HA + NaOH \rightarrow NaA + H_2O$

or $HA + OH^- \rightarrow A^- + H_2O$ (1)

(ii) $n(NaOH) = n(HA)$ in 25 cm^3 = 0.02670 × 0.0100 = 2.67 × 10^{-4} mol (1).

[HA] = (2.67 × 10^{-4} × 1000/25) mol dm^{-3} (1) = 1.07 × 10^{-2} mol dm^{-3} (1).

(iii) 1.07 × 10^{-2} ≫ 2.50 × 10^{-4} (1) and therefore HA is a weak acid since it is only partially dissociated into ions (1).

(c) (i) $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ (1)

(ii) $K_a = \frac{[\mathrm{H^+(aq)}][\mathrm{A^-(aq)}]}{[\mathrm{HA(aq)}]}$ (1)

(iii) $[\mathrm{HA(aq)}] = \frac{[\mathrm{H^+(aq)}][\mathrm{A^-(aq)}]}{K_a}$ (1)

$= \frac{(2.50 \times 10^{-4})^2}{6.00 \times 10^{-5}} = 1.04 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$ (1).

2 (a) A solution that maintains a fairly constant pH (1) despite the addition of small amounts of either acid or base (1).

(b) The mixture contains relative high concentrations of both ethanoic acid and ethanoate ions (1).

When acid is added, the H^+ ions react with ethanoate ions (to form ethanoic acid) (1).

When base is added, the OH^- ions react with ethanoic acid molecules (to form ethanoate ions and water molecules) (1).

The ratio of $\frac{[\mathrm{CH_3COO^-(aq)}]}{[\mathrm{CH_3COH(aq)}]}$ remains fairly constant and hence the pH remains fairly constant (since pH = pK_a + lg $\frac{[\mathrm{CH_3COO^-(aq)}]}{[\mathrm{CH_3COOH(aq)}]}$ and pK_a is constant) (1).

(c) pH = pK_a + lg $\frac{[\mathrm{CH_3COO^-(aq)}]}{[\mathrm{CH_3COOH(aq)}]}$ (1)

When the acid is half-reacted $[\mathrm{CH_3COOH(aq)}] = [\mathrm{CH_3COO^-(aq)}]$, so lg $\frac{[\mathrm{CH_3COO^-(aq)}]}{[\mathrm{CH_3COOH(aq)}]} = 0$ (1).

Hence, pH = pK_a = 4.77 (1).

3 (a) At 298 K, $[\mathrm{H^+(aq)}] = (1.00 \times 10^{-14})^{1/2} = 1.00 \times 10^{-7}\ \mathrm{mol\,dm^{-3}}$ (1).

pH = – lg (1.00×10^{-7}) = 7.00 (1).

At 323 K, $[\mathrm{H^+(aq)}] = (5.48 \times 10^{-14})^{1/2} = 2.34 \times 10^{-7}\ \mathrm{mol\,dm^{-3}}$ (1).

pH = – lg (2.34×10^{-7}) = 6.63 (1).

(b) Pure water is neutral because $[\mathrm{H^+(aq)}] = [\mathrm{OH^-(aq)}]$ (1). The pH of pure water is temperature dependent, so does not always have a value of 7 (1).

(c) As temperature increases, $[\mathrm{H^+(aq)}]$ increases, hence the extent of dissociation into ions increases (1). Since the position of equilibrium shifts in the endothermic direction with an increase in temperature, the dissociation of water into ions is endothermic (1).

4 (a) A conjugate base is a species formed when an acid loses a proton/hydrogen ion (1).

(b) (i) Equation 1: HF (1).

Equation 2: C_6H_5COOH (1).

(ii) HF is stronger than C_6H_5COOH (1). As the equilibrium of equation 1 is well over to the right-hand side, HF is a better proton donor than C_6H_5COOH (1).

C_6H_5COOH is stronger than HCN (1). As the equilibrium of equation 1 is well over to the right-hand side, C_6H_5COOH is a better proton donor than HCN (1).

(c) (i) Acidic (1); $[\mathrm{NH_4^+}]$ increases and it is an acid since it is a proton donor (1).

(ii) Basic (1); $[\mathrm{NH_2^-}]$ increases and it is a base since it is a proton acceptor (1).

5 (a) $pk_{a(1)}$ = – lg (1.20×10^{-2}) = 1.92 (1).

(b) $[\mathrm{H^+(aq)}] = (1.20 \times 10^{-2} \times 0.500)^{1/2}$ (1) $= 7.75 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ (1).

pH = – lg (7.75×10^{-2}) = 1.11 (1).

(c) HSO_3^- partially dissociates into ions and this increases $[\mathrm{H^+(aq)}]$ (1).

(d) (i) Ionic product (of water) *or* autoprotolysis constant (of water) (1).

(ii) $K_w = [\mathrm{H^+(aq)}][\mathrm{OH^-(aq)}]$ (1)

(e) $[\mathrm{OH^-(aq)}] = 0.500\ \mathrm{mol\,dm^{-3}}$ (1).

pOH = – lg (0.500) = 0.30 (1).

pH = (14.00 – 0.30) = 13.7(0) (1).

6 (a) (i) n(HCl) = 25.0 × 10.00 = 250 mol (1).

Volume of HCl = 250 × 24.0 = 6000 $\mathrm{dm^3}$ (1).

(ii) Pipette 10.0 cm^3 of the stock solution into a 5.00 dm^3 volumetric flask (1).

Make up to the mark with deionised/distilled water (1).

Shake the solution (to produce an even concentration throughout) (1).

(b) pH = – lg (0.0200) = 1.70 (1).

(c) (i) The pH at the equivalence point is approximately 5 / is less than 7 (1), which is consistent with a titration of a strong acid against a weak base (1).

(ii) 25.0 cm^3 of 0.0200 mol dm^{-3} HCl ≡ 15.0 cm^3 of x mol dm^{-3} NH_3.

$\frac{15.0\ x}{25.0 \times 0.0200} = \frac{1}{1}$ (1).

x = 0.0333 mol dm^{-3} (1).

(iii) Methyl red (1), because its pK_a value is the closest to the pH at the equivalence point (1).

13.1 Lattice energy

13.1.1 Lattice energy, $\Delta_{\text{lattice}}H$, and Born-Haber cycles

1 (a) Lattice energy is the energy released when one mole of an ionic compound is formed in its standard state from its ions in their gaseous states.

(b) Lattice energy is more exothermic with:

increasing charge on the ions,
decreasing size of the ions.

The greater the charge on the ions, the larger the electrostatic forces of attraction between the oppositely charged ions in the lattice.

The smaller the ions, the smaller the inter-ionic distance, and the greater the forces of attraction.

2 (a) (i) ΔH_1 is the enthalpy change of formation of magnesium oxide.

ΔH_2 is the enthalpy change of atomisation of magnesium.

ΔH_3 is the first ionisation energy of magnesium.

(ii) $Mg^{2+}(g)$ and $O^{2-}(g)$.

(b) Energy is required to overcome the repulsion between the second added electron and the seven electrons already present in the outer quantum shell. This energy is greater than the energy released when the electron comes under the influence of the attraction to the nucleus.

(c) $\Delta_{\text{lattice}}H\,[\text{MgO(s)}] = -148 - 738 - 1451 - 249 - 657 - 602\ \text{kJ mol}^{-1}$

$= -3845\ \text{kJ mol}^{-1}$.

(d) The lattice energy of barium oxide will be less exothermic.

The force of attraction between barium ions and oxide ions is weaker than that between magnesium ions and oxide ions. The inter-ionic distance between the oppositely charged ions is greater because the barium ion is larger than the magnesium ion.

The barium ion and the magnesium ion have the same charge (2+), so this is not a factor.

However, the charge density of the barium ion is lower than that of the magnesium ion, so barium oxide has less covalent bonding than magnesium oxide.

13.1.2 Experimental and theoretical lattice energy

1 Calculations of theoretical lattice energies are based on the assumption that the bonding in the compound is purely ionic.

The bonding in calcium fluoride is very close to 100% ionic. However, there is significant covalent bonding present in silver fluoride.

2 (a) The cation attracts the electrons in the anion and this leads to a distortion of the electron cloud of the anion.

(b) The sulfide ion is more easily polarised since it is larger. The outer electrons are better shielded from the nucleus as there are more inner quantum shells.

(c) The charge density of each cation is:

$Mg^{2+}\ \frac{2}{0.072^2} = 386 \quad Al^{3+}\ \frac{3}{0.053^2} = 1068 \quad Li^{+}\ \frac{1}{0.074^2} = 183$

$Na^{+}\ \frac{1}{0.102^2} = 96 \quad Ca^{2+}\ \frac{2}{0.100^2} = 200 \quad K^{+}\ \frac{1}{0.138^2} = 53$

The larger the charge density, the greater the polarising power.

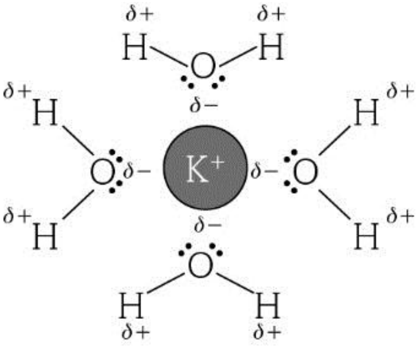
So, the order of increasing polarising power is $K^+ < Na^+ < Ca^{2+} < Li^+ < Mg^{2+} < Al^{3+}$.

3 The second ionisation energy of sodium is very large, since the second electron is removed from a 2p sub-shell. The electrons in the 2p sub-shell have considerably less orbital energy than the first electron removed from the 3s sub-shell.

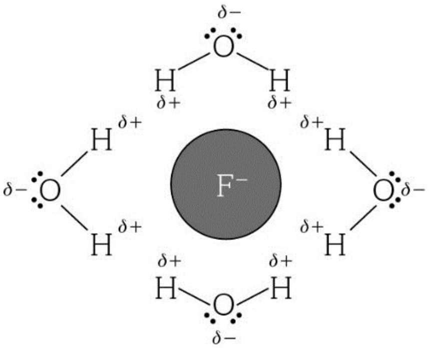
This extra energy required to produce Na^{2+} ions is likely to be much greater than the lattice energy of $Na^{2+}O^{2-}$, so formation of the compound is likely to be highly endothermic.

13.1.3 Enthalpy changes of solution and hydration

1 (a) (i)



(ii)



(b) **Hydrated potassium ion**

Ion-dipole interaction: there is an electrostatic force of attraction between the δ– oxygen atom of the water molecule and the positive potassium ion.

Hydrated fluoride ion

Ion-dipole interaction: there is an electrostatic force of attraction between the δ+ hydrogen atoms of the water molecule and the negative fluoride ion.

Hydrogen bond: between δ+ hydrogen atoms of the water molecule and the negative fluoride ion, using the lone pairs of electrons on the fluoride ion.

2 $\Delta_{sol}H\ [Mg^{2+}(Cl^-)_2(s)] + \Delta_{lattice}H\ [Mg^{2+}(Cl^-)_2(s)] = \Delta_{hyd}H\ [Mg^{2+}(g)] + 2 \times \Delta_{hyd}H\ [Cl^-(g)]$.

$\Delta_{hyd}H\ [Cl^-(g)] = ½(–155 + (–2493) – (–1920) = –364\,kJ\ mol^{-1}$.

3 (a) $Li^+(aq) + F^-(aq)$.

(b) The lattice energy of lithium fluoride.

(c) $\Delta_{sol}H = \Delta H_2 – \Delta H_1$.

(d) $\Delta_{sol}H = –1018 – (–1031) = +13\,kJ\,mol^{-1}$.

4 There will be no measurable change in the reading on the thermometer since there will only be a very small decrease in temperature, and the thermometer is not precise enough to register the change in temperature.

13.2 Entropy

13.2.1 Introduction to entropy

1 (a) $H_2O(g) \rightarrow H_2O(l)$

Decrease, as the molecules in a liquid have less freedom of movement than those in a gas.

(b) $I_2(s) \rightarrow I_2(g)$

Increase, as the molecules in a gas have more freedom of movement than those in a solid.

(c) $Na(l) \rightarrow Na(s)$

Decrease, as the molecules in a solid have less freedom of movement than those in a liquid.

13.2.2 Total entropy

1 (a) $\Delta S^{\ominus}_{\text{system}} = 109.2 + (6 \times 69.9) - 343.0 = +185.6\ \text{J K}^{-1}\ \text{mol}^{-1} = +0.186\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

(b) $\Delta S^{\ominus}_{\text{surroundings}} = -\frac{+88.1}{298} = -0.296\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

(c) $\Delta S^{\ominus}_{\text{total}} = +0.186 + (-0.296) = -0.110\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

(d) It can be stored without decomposing. $\Delta S^{\ominus}_{\text{total}}$ is negative so the reaction is not spontaneous.

2 $\Delta S^{\ominus}_{\text{system}} = 90.0 - ((2 \times 27.2) + (1.5 \times 205)) = -271.9\ \text{J K}^{-1}\ \text{mol}^{-1} = -0.272\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

$\Delta S^{\ominus}_{\text{surroundings}} = -\frac{-822}{298} = +2.76\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

$\Delta S^{\ominus}_{\text{total}} = 2.76 + (-0.272) = +2.49\ \text{kJ K}^{-1}\ \text{mol}^{-1}$ (to 3 significant figures).

13.2.3 Understanding entropy changes

1 (a) $CuSO_4.5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(l)$

Increase in entropy. There is an increase in the number of moles from 1 to 6. Also a liquid is formed from a solid.

(b) $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

Decrease in entropy. There is a decrease in the number of moles from 2 to 1. Also a solid is formed from two gases.

(c) $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

Decrease in entropy. There is a decrease in the number of moles from 1.5 to 1.

(d) $Co(H_2O)_6^{2+}(aq) + EDTA^{2-}(aq) \rightarrow Co(EDTA)(aq) + 6H_2O(l)$

Increase in entropy. There is an increase in number of moles from 2 to 7.

2 (a) There is no change of state or change in the number of moles.

(b) A more sophisticated view of entropy is that it is the number of ways that the molecules can be distributed amongst the energy levels available to them. The number of ways is greater for $2HI(g)$ than for $H_2(g) + I_2(g)$.

13.3 Gibbs energy

13.3.1 The Second Law and Gibbs energy

1 (a) $\Delta S^{\ominus}_{\text{system}} = (2 \times 192) - (191 + (3 \times 132)) = -203\ \text{J K}^{-1}\ \text{mol}^{-1} = -0.203\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}_{\text{system}} = -92.0 - (298 \times -0.203) = -31.5\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

As $\Delta_r G^{\ominus}$ is negative the reaction is thermodynamically feasible.

(b) At high temperatures $T\Delta S^{\ominus}_{\text{system}}$ becomes more negative than $\Delta H^{\ominus}$ and therefore $\Delta G^{\ominus}$ becomes positive.

(c) The activation energy for the reaction is very high and also the catalyst is not active at low temperatures.

2 (a) **$H_2O(s) \rightarrow H_2O(l)$**

Energy is required to overcome the forces of attraction between molecules in the solid in order for the molecules to have sufficient energy to break away from the lattice structure and be free to slide over one another.

$H_2O(l) \rightarrow H_2O(g)$

Energy is required to overcome the forces of attraction between the molecules in the liquid in order for them to have sufficient energy to escape from the liquid.

(b) (i) There is an increase in the degree of disorder of the molecules.

(ii) The molecules are *much* more disordered in a gas than they are in a liquid, so the increase in disorder from liquid to gas is greater than the increase in disorder from solid to liquid.

(c) $\Delta S^{\ominus}_{\text{system}} = (48.0 - 69.9) = -21.9\ \text{J K}^{-1}\ \text{mol}^{-1} = -0.022\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

Water will freeze when $\Delta G^\ominus = 0$, i.e. when $\Delta H^\ominus = T\Delta S^\ominus_{\text{system}}$.

$T = \frac{\Delta H^\ominus}{\Delta S^\ominus} = \frac{6.01}{0.022} = 273\,\text{K}$.

13.3.2 Gibbs energy and equilibrium

1 (a) $\Delta G^\ominus = -RT\ln K$

so $K = e^{\left(-\frac{\Delta G}{RT}\right)}$

$= e^{\left(-\frac{-120.1 \times 1000}{8.31 \times 298}\right)}$

$= 1.15 \times 10^{21}$.

(b) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus_{\text{system}}$

When $\Delta G^\ominus = 0$, $T\Delta S^\ominus_{\text{system}} = \Delta H^\ominus$.

$T = \frac{\Delta H^\ominus}{\Delta S^\ominus_{\text{system}}} = \frac{-172.5 \times 1000}{-175.0} = 986\text{ K }(713\,^\circ\text{C})$.

(c) The activation energy for the reaction is very high.

2 (a) $T = \frac{\Delta H^\ominus}{\Delta S^\ominus_{\text{system}}} = \frac{-135.0 \times 1000}{-142.9} = 945\,\text{K }(672\,^\circ\text{C})$.

Assumptions: $\Delta H^\ominus$ and $\Delta S^\ominus_{\text{system}}$ do not change with temperature.

(b) $K = e^{\left(-\frac{\Delta G}{RT}\right)}$

$= e^{\left(-\frac{+63.3 \times 1000}{8.31 \times 500}\right)}$

$= 2.43 \times 10^{-7}$.

13 Answers to Exam-style questions

1 (a) C (1)

(b) B (1)

(c) (i) ΔH_1 is the first ionisation energy of magnesium (1).

ΔH_2 is the enthalpy change of atomisation of magnesium (1).

ΔH_3 is the enthalpy change of formation of magnesium oxide (1).

(ii) $Mg^{2+}(g)$ (1) + $O^{2-}(g)$ (1)

(iii) Energy is required to overcome the repulsion (1) between the O^- ion and the electron being added (1).

(iv) $\Delta_{\text{lattice}}H[Mg^{2+}O^{2-}(s)] = \Delta H_3 - \Delta H_2 - \Delta H_1 - IE_2[Mg(g)] - \Delta_{\text{at}}H[O_2(g)] - (E_{\text{ea(1)}}[O(g)] + E_{\text{ea(1)}}[O(g)]$ (1)

$= -602 - (+149) - (+736) - (+1450) - (+248) - (+657)$

$= -3842\text{ kJ mol}^{-1}$ (1).

2 (a) Enthalpy change of formation of sodium fluoride.

First ionisation energy of sodium.

Enthalpy change of atomisation of sodium.

Enthalpy change of atomisation of fluorine.

First electron affinity of fluorine.

(All five points = 4 marks; 4 points = 3 marks; 3 points = 2 marks; 2 points = 1 mark).

(b) The difference between the experimental and theoretical lattice energies for both NaF and NaI (0.65% and 2.70% respectively) are very small (1), indicating that the degree of ionic bonding is very high / the ionic model is good (1).

There is a significant difference between the experimental and theoretical lattice energies for AgF and AgI (3.97% and 12.49% respectively) (1), indicating that there is a significant degree of covalent bonding present (1).

(c) (i) ($\Delta_{\text{soln}}H = \Delta_{\text{hyd}}H - \Delta_{\text{lattice}}H$)

$\Delta_{soln}H$ [NaF(s)] = – 406 + (– 506) – (– 918) = + 6 kJ mol^{-1}.

$\Delta_{soln}H$ [NaI(s)] = – 406 + (– 293) – (– 705) = + 6 kJ mol^{-1}.

$\Delta_{soln}H$ [AgF(s)] = – 464 + (– 506) – (– 958) = – 12 kJ mol^{-1}.

$\Delta_{soln}H$ [AgI(s)] = – 464 + (– 293) – (– 889) = + 132 kJ mol^{-1}.

All four calculations correct (1).

$\Delta_{soln}H$[AgF(s)] is the most exothermic, so likely to be the most soluble (1).

(ii) ΔS_{system} (1) and $\Delta S_{surroundings}$ (1) for the addition of the ionic compound to water.

3 (a) (i) Negative. Two molecules are forming from four molecules and so there will be a decrease in disorder (1).

(ii) Positive. A solid is changing into a liquid so there will be an increase in disorder (1).

(iii) Negative. A gas is changing into a solid and three molecules are becoming two, so there will be a decrease in disorder (1).

(iv) Positive. Despite there being no change in the number of molecules, the change of solid into gas will produce a large increase in disorder (1).

(b) (i) ΔS_{system} = (27.0 + 214 – 65.7) = + 175.3 J K^{-1} mol^{-1} / 0.1753 kJ K^{-1} mol^{-1} (1).

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S_{system}$

= (117 – (298 × 0.1753)) = 64.8 kJ mol^{-1} (1).

As $\Delta G^{\ominus}$ is positive the reaction is not feasible (1), so magnesium carbonate does not spontaneously decompose (i.e. is stable) at 298 K (1).

(ii) When $\Delta G^{\ominus} = 0$, $T\Delta S_{system} = \Delta H^{\ominus}$ (1).

$T = \frac{117}{0.1753}$ = 667 K (to 3 significant figures) (1).

4 (a) D (1)

(b) C (1)

(c) (i) $\Delta S^{\ominus}_{system}$ = (69.9 – 131 – (½ × 205)) (1) = – 163.6 J K^{-1} mol^{-1} (1).

(ii) $\Delta S^{\ominus}_{surroundings} = -\frac{-285500}{298}$ (1) = + 958.1 J K^{-1} mol^{-1} (1).

(iii) $\Delta S^{\ominus}_{total}$ = (– 163.6 + 958.1) = + 794.5 J K^{-1} mol^{-1} (1)

= + 795 J K^{-1} mol^{-1} (2).

(1 mark for correct sign; 1 mark for answer to 3 significant figures).

(d) The activation energy of the reaction is high (1).

5 (a) 100 kPa / 1 bar (1).

(b) $\Delta S^{\ominus}_{surroundings}$ (700 K) = $-\frac{-110.2}{700}$ = + 0.1574 kJ K^{-1} mol^{-1} / + 157.4 J K^{-1} mol^{-1} (2).

(1 mark for correct sign; 1 mark for answer).

(c) $\Delta S^{\ominus}_{system}$ (700 K) = $\Delta S^{\ominus}_{total}$ (700 K) – $\Delta S^{\ominus}_{surroundings}$ (700 K) = (– 78.7 – 157.4)

= – 236.1 J K^{-1} mol^{-1} (2).

(1 mark for correct sign; 1 mark for answer).

(d) Since $\Delta S^{\ominus}_{total}$ (700 K) is negative, the equilibrium position lies to the left-hand side, indicating that the proportion of nitrogen and hydrogen is greater than the proportion of ammonia (1).

(e) (i) As temperature increases, $\Delta S^{\ominus}_{surroundings}$ becomes less positive (since $\Delta S^{\ominus}_{surroundings} = -\frac{-110.2}{T}$) (1).

(ii) $\Delta S^{\ominus}_{total}$ becomes more negative / less positive (1) (since $\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surroundings}$) (1), and hence K_p decreases (since $\Delta S^{\ominus}_{total} = R\,T\ln K_p$) (1).

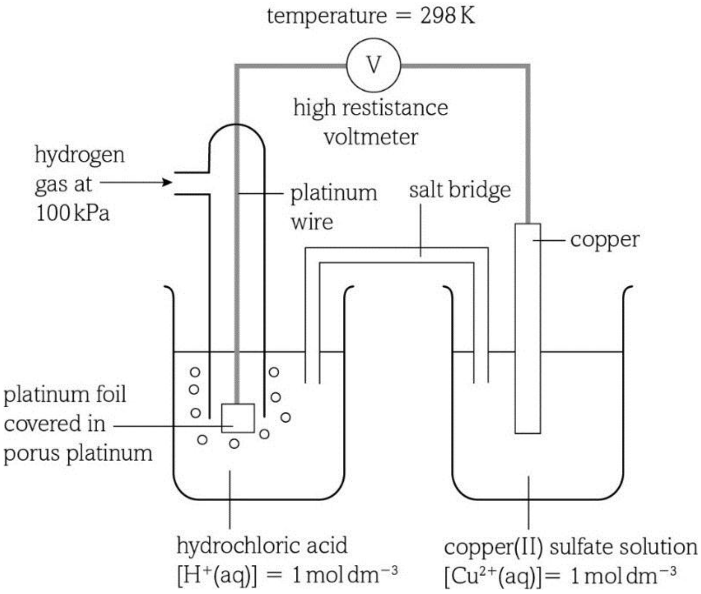
(iii) The yield of ammonia decreases (1).

(iv) The rate of attainment of equilibrium increases (1).

14.1 Standard electrode potential

14.1.1 Standard electrode (redox) potentials

1



2 The standard electrode potential is the emf of a cell formed between the ½Br_2(aq) | Br^-(aq) half-cell and the standard hydrogen electrode.

The concentrations of Br_2(aq) and Br^-(aq) are both 1 mol dm^{-3} and the temperature is 298 K.

The positive sign tells us that the ½Br_2(aq) | Br^-(aq) half-cell forms the positive electrode of the cell.

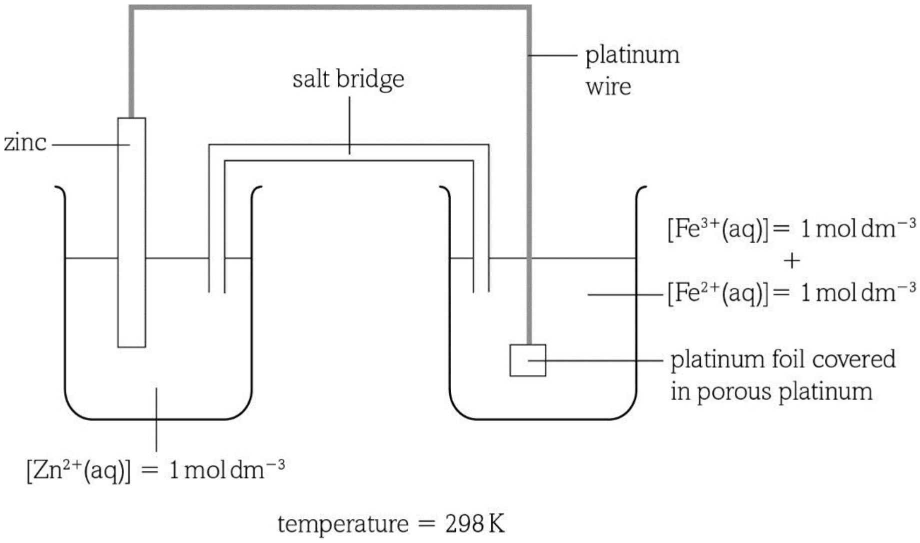
3 Electromotive force is the potential difference of a cell measured when there is no current flowing.

Note: you will find a completely different definition of emf in your physics textbook. This is because physics uses the term in a different way.

Electromotive force is measured using a high resistance voltmeter.

14.1.2 Electrochemical cells

1 (a)



(b) Electrons will flow from the $Zn^{2+} | Zn$ half-cell to the $Fe^{3+}|Fe^{2+}$ half-cell because the electrode potential of $Zn^{2+} | Zn$ is more negative.

(c) $Zn(s) | Zn^{2+}(aq)$ ⁞⁞ $Fe^{3+}(aq), Fe^{2+}(aq) | Pt(s)$

$E^\ominus_{\text{cell}} = 0.77 - (-0.76) = +1.53\,V$.

2 (a) $E^\ominus_{\text{cell}} = (1.51 - 1.36) = (+)\,0.15\,V$.

(b) Electrons will flow from the $\frac{1}{2}Cl_2 | Cl^-$ half-cell to the $MnO_4^- | Mn^{2+}$ half-cell because the electrode potential of $\frac{1}{2}Cl_2 | Cl^-$ is more negative.

(c) $Pt(s) | Cl^-(aq) | \frac{1}{2}Cl_2(g)$ ⁞⁞ $MnO_4^-(aq), 8H^+(aq) | Mn^{2+}(aq), 4H_2O(l) | Pt(s)$

14.1.3 Standard electrode potentials and thermodynamic feasibility

1 (a) VO_2^+/VO^{2+} has the more negative $E^\ominus$ value, so VO^{2+} will release electrons to MnO_4^-.

(b) $MnO_4^-(aq) + 5VO^{2+}(aq) + H_2O(l) \rightarrow Mn^{2+}(aq) + 5VO_2^+(aq) + 2H^+(aq)$

2 $E^\ominus$ (Zn^{2+}/Zn) is more negative than $E^\ominus$ (VO_2^+/VO^{2+}), $E^\ominus$ (VO^{2+}/V^{3+}) and $E^\ominus$ (V^{3+}/V^{2+}) so Zn will reduce VO_2^+ to VO^{2+}, VO^{2+} to V^{3+} and V^{3+} to V^{2+}.

However, $E^\ominus$ (Zn^{2+}/Zn) is less negative than $E^\ominus$ (V^{2+}/V) so Zn will not reduce V^{2+} to V.

3 (a) $E^\ominus$ (O_2/H_2O_2) is more negative than $E^\ominus$ (H_2O_2/H_2O), so one molecule of H_2O_2 will release electrons to (ie. will reduce) another molecule of H_2O_2.

(b) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

(c) The oxidation number of O changes from –1 in H_2O_2 to –2 in H_2O (reduction).

The oxidation number of O changes from –1 in H_2O_2 to 0 in O_2 (oxidation).

The oxygen has been both reduced and oxidised in the same reaction.

4 (a) Emf ($E^\ominus_{\text{cell}}$) = (0.77 – 0.54) = (+) 0.23 V.

(b) $\Delta G^\ominus = nFE^\ominus_{\text{cell}}$

$n = 1\,\text{mol}$

$\Delta G^\ominus = 1\,\text{mol} \times 96\,500\,\text{C mol}^{-1} \times 0.23\,\text{J C}^{-1} = 22\,000\,\text{J mol}^{-1}$ or $22\,\text{kJ mol}^{-1}$ (to 2 significant figures).

Note: $1\,V = 1\,J\,C^{-1}$.

(c) $\Delta G^\ominus = -RT\ln K$

$= -8.31\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298\,\text{K} \times \ln K$.

$$\ln K = \frac{22000}{8.31 \times 298}$$

$K = 7.22 \times 10^3$.

14.2 Redox in action

14.2.1 Storage cells and fuel cells

1 (a) $E^\ominus_{\text{cell}} = 1.40\,V$.

(b) $Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

(c) Cd changes from 0 to +2. Cd is oxidised.

Ni changes from +3 to +2. Ni is reduced.

2 (a) $CH_3OH(l) + 1\frac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(b) $CH_3OH(l) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

(c) Less CO_2 produced overall (some CO_2 is produced when hydrogen is obtained from methane).

Greater efficiency.

(d) Methanol is a liquid and is therefore easier to store and transport.

3 (a) A fuel cell produces electricity by the reaction of a fuel with oxygen.

(b) Any two from:

compressed as a gas
compressed and cooled to form a liquid
adsorbed onto a solid
absorbed into a solid

(c) Energy is required to produce the hydrogen.

14.2.2 Redox titrations

1 $5Fe^{2+} \equiv KMnO_4$

$n(KMnO_4)$ in 24.40 cm^3 = $\frac{24.40 \times 0.0218}{1000}$ = 5.32×10^{-4} mol.

$n(Fe^{2+})$ in 250 cm^3 = $10 \times 2.66 \times 10^{-3} = 2.66 \times 10^{-2}$ mol.

Mass of iron in the nail = $55.8 \times 2.66 \times 10^{-2} = 1.48$ g.

Percentage of iron in the nail = $\frac{1.48}{1.50} \times 100 = 98.7\,\%$

2 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$H_2O_2(aq) \rightarrow 2H^+(aq) + O_2(g) + 2e^-$

$\therefore 5H_2O_2 \equiv 2MnO_4^-$

$n(KMnO_4)$ in 23.90 cm^3 = $\frac{23.90 \times 0.0200}{1000}$ = 4.78×10^{-4} mol.

$n(H_2O_2)$ in 25.0 cm^3 = $\frac{5}{2} \times 4.78 \times 10^{-4} = 1.195 \times 10^{-3}$ mol.

$n(H_2O_2)$ in 1000 cm^3 = $\frac{1000}{25} \times 1.195 \times 10^{-3} = 4.78 \times 10^{-2}$ mol.

Concentration of the original H_2O_2 = $4.78 \times 10^{-2} \times \frac{1000}{50}$

= 0.956 mol dm^{-3}.

3 $n(FeC_2O_4)$ in 1.00 g = $\frac{1.00}{143.8}$ = 6.95×10^{-3} mol.

$5Fe^{2+} \equiv KMnO_4$ and $5C_2O_4^{2-} \equiv 2KMnO_4$

$\therefore 5FeC_2O_4 \equiv 3KMnO_4$

$n(KMnO_4)$ required = $\frac{3}{5} \times 6.95 \times 10^{-3} = 4.17 \times 10^{-3}$ mol.

Volume of $KMnO_4$ required = $\frac{4.17 \times 10^{-3}}{0.0200} \times 1000 = 209$ cm^3 (to 3 significant figures).

4 $5Fe^{2+} \equiv KMnO_4$

$n(KMnO_4)$ in 21.60 cm^3 = $\frac{21.60 \times 0.0210}{1000}$ = 4.536×10^{-4} mol.

$n(Fe^{2+})$ in 25.0 cm^3 = $5 \times 4.536 \times 10^{-4} = 2.268 \times 10^{-3}$ mol.

Concentration of Fe^{2+} = $2.268 \times 10^{-3} \times \frac{1000}{25.0} = 9.07 \times 10^{-2}$ mol dm^{-3}.

Volume of $KMnO_4$ required to react with Fe^{3+} is (44.40 – 21.60) = 22.80 cm^3.

$n(KMnO_4)$ in 22.80 cm^3 = $\frac{22.80 \times 0.0210}{1000}$ = 4.788×10^{-4} mol.

$n(Fe^{3+})$ in 25.0 cm^3 = $5 \times 4.788 \times 10^{-3} = 2.394 \times 10^{-3}$ mol.

Concentration of Fe^{3+} = $2.394 \times 10^{-3} \times \frac{1000}{25.0} = 9.58 \times 10^{-2}$ mol dm^{-3}.

5 $Cl_2 \equiv I_2 \equiv 2Na_2S_2O_3$

$n(Na_2S_2O_3)$ in 23.20 cm^3 = $\frac{22.30 \times 0.105}{1000}$ = 2.342×10^{-3} mol.

$n(I_2)$ in 25.0 cm^3 = $\frac{1}{2} \times 2.342 \times 10^{-3} = 1.171 \times 10^{-3}$ mol.

$n(I_2)$ in 250 cm^3 = 10 × 1.171 × 10^{-3} mol = 1.171 × 10^{-2} mol.

$n(CI_2) = n(I_2)$ = 1.171 × 10^{-2} mol.

Mass of Cl_2 = 1.171 × 10^{-2} mol × 71.0 g mol^{-1} = 0.831 g.

Percentage of ‘available’ chlorine = $\frac{0.831}{2.50}$ × 100 = 33.2 %.

6 $n(Na_2S_2O_3)$ in 21.00 cm^3 = $\frac{21.00 \times 0.0500}{1000}$ = 1.05 × 10^{-3} mol.

$n(I_2) = \frac{1}{2}$ × 1.05 × 10^{-3} = 5.25 × 10^{-4} mol.

$n(K_2S_2O_8)$ in 25.0 cm^3 = $\frac{25.0 \times 0.0210}{1000}$ = 5.25 × 10^{-4} mol.

$\therefore S_2O_8^{2-} \equiv I_2 \equiv 2I^-$

Possible equation: $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$.

14 Answers to exam-style questions

1 (a) $n(S_2O_3^{2-})$ = (0.0223 × 0.200) = 4.46 × 10^{-3} mol (1).

$n(Cu^{2+}) = ½n(I_2) = n(S_2O_3^{2-})$ = 4.46 x 10^{-3} mol (1).

Mass of copper = 4.46 × 10^{-3} mol × 63.5 g mol^{-1} = 0.283(21) g (1).

Percentage of copper = $\frac{0.283(21)}{0.500}$ × 100 (1) = 56.6 % (1).

(b) (i) (Pale) yellow (1) to colourless (1).

(ii) There is an instantaneous change from blue to colourless as opposed to a gradual change from pale yellow to colourless (1).

2 (a)

	$VO_3^-(aq)$	$VO^{2+}(aq)$	$V^{3+}(aq)$	$V^{2+}(aq)$
Oxidation number of vanadium	+5	+4	+3	+2

(1)

(b) Colour changes from yellow (to green) to blue and then to green and then to violet. (1)

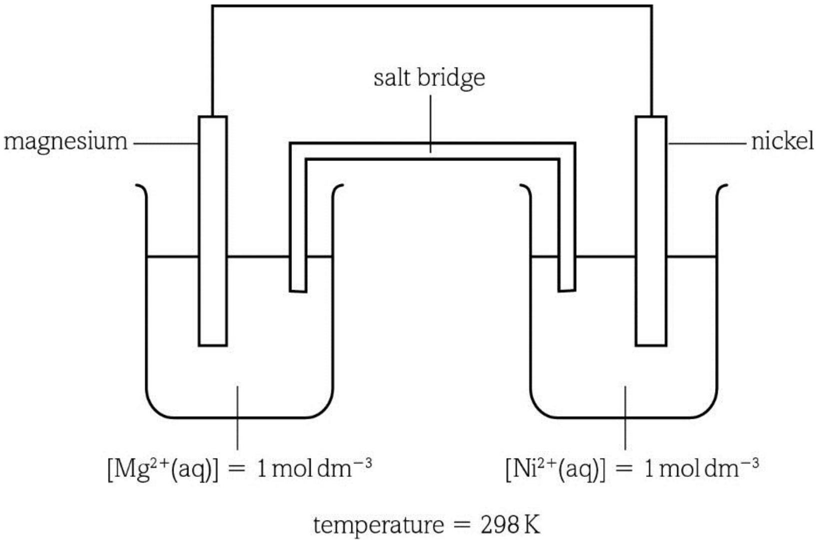
VO_3^- (yellow) is reduced to VO^{2+} (green) (the intermediate green colour is owing to both VO_3^- and VO^{2+} existing in solution together) because the $E^\ominus$ value of half-cell 5 is more negative than that of half-cell 4 (1).

VO^{2+} is then reduced to V^{3+} (blue) because $E^\ominus$ value of half-cell 5 is more negative than that of half-cell 3 (1).

V^{3+} is then reduced to V^{2+} (violet) because $E^\ominus$ value of half-cell 5 is more negative than that of half-cell 2 (1).

The reduction will stop at V^{2+} because $E^\ominus$ value of half-cell 5 is less negative than that of half-cell 1 (1).

3 (a) (i)



Magnesium dipping into Mg^{2+}(aq) *and* nickel dipping into Ni^{2+}(aq) (or named soluble salts) (1).

Salt bridge and wire connecting magnesium to nickel (1).

Both solutions have ion concentration of 1 mol dm^{-3} (1).

Temperature = 298 K (1).

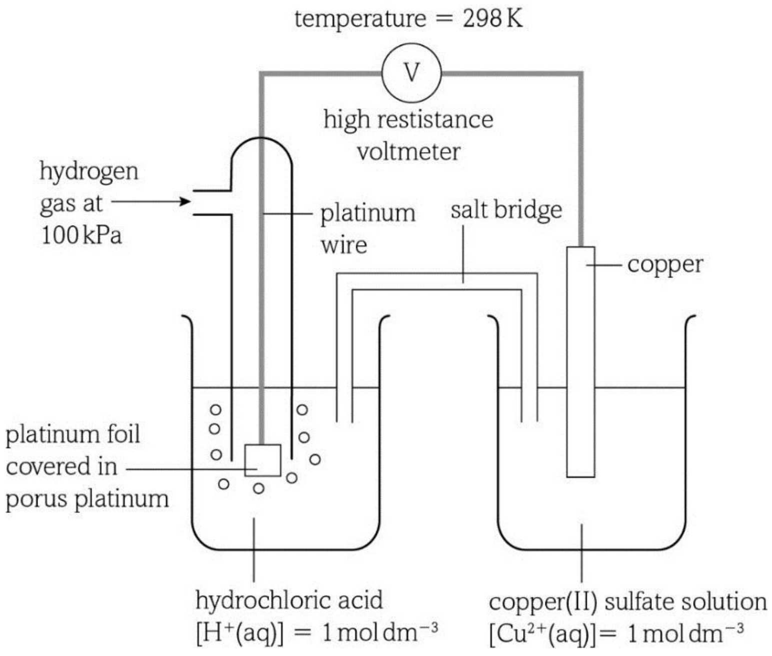
(ii) Magnesium is the negative electrode (1) and so electrons flow from the magnesium electrode to the nickel electrode (1).

(iii) $Mg(s) + Ni^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ni(s)$ (1)

(b) Emf = – 0.25 – (– 2.37) = 2.12 V (1).

(c) When water is added $[Mg^{2+}(aq)]$ decreases (1) and hence the electrode potential of the $Mg^{2+}(aq) | Mg(s)$ half-cell becomes more negative (as the equilibrium shifts to the left-hand side) (1). Hence, the emf of the cell will increase (1).

4 (a)



Platinum dipping into a solution containing H^+ ions / named strong acid (1).

Copper dipping into a solution containin $Cu^{2+}(aq)$ / named soluble copper(II) salt (1).

Hydrogen gas (1).

Complete circuit with salt bridge and voltmeter (1).

Both solutions have an ion concentration of 1 mol dm^{-3} (1).

Temperature of 298 K *and* pressure of hydrogen of 100 kPa (1 bar) (1).

(b) (i) $E^{\ominus}$ of electrode reaction 1 is more negative than that of reaction 3 (1).

Therefore the Cu^{+} ion from reaction 1 will release an electron to the Cu^{+} from reaction 2 (to form Cu^{2+} and Cu (1).

(ii) The oxidation state of copper increases from +1 to +2 (1)

and also decreases from +1 to 0 (1)

therefore the copper is being both oxidised and reduced (in the same reaction) (1).

5 (a) The standard electrode potential of a half-cell is defined as the emf of a cell containing the half-cell

connected to a standard hydrogen electrode (1), measured under standard conditions of 298 K, 100 kPa pressure and concentrations of 1 mol dm^{-3} (1).

(b) Emf = (1.52 – 1.36) = 0.16 V (1).

(c) (i) $MnO_4^{-}(aq) + 8H^{+}(aq) + 5Cl^{-}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 2½Cl_2(g)$

Balanced equation (1) state symbols (1).

(ii) Mn changes from + 7 to + 2, which is reduction *and* H does not change (1)

therefore Cl^{-} is the reducing agent (1).

Or

Cl changes from – 1 to 0, which is oxidised (1)

and therefore Cl^{-} is the reducing agent (1).

(d) As $[Cl^{-}(aq)]$ decreases, the electrode potential of the $Cl_2(g) \mid Cl^{-}(aq)$ half-cell becomes more positive (as the equilibrium moves to the right) (1).

As $[H^{+}(aq)]$ increases, the electrode potential of the $MnO_4^{-}(aq), H^{+}(aq) \mid Mn^{2+}(aq), H_2O(l)$ half-cell becomes less positive (as the equilibrium moves to the left) (1).

Eventually the electrode potential of the $Cl_2(g) \mid Cl^{-}(aq)$ half-cell becomes more positive than the electrode potential of the $MnO_4^{-}(aq), H^{+}(aq) \mid Mn^{2+}(aq), H_2O(l)$ half-cell (and so Cl^{-} can no longer release electrons to MnO_4^{-}) (1).

6 (a) Sulfur dioxide is toxic / poisonous (1).

(b) $n(NH_4VO_3)$ in 25 cm^3 = $\frac{2.24}{116.9 \times 10}$ = 1.92×10^{-3} mol (1).

$n(KMnO_4)$ in 38.10 cm^3 = $(0.03840 \times 0.0200) = 7.68 \times 10^{-4}$ mol (1).

$\frac{1.92 \text{ x } 10^{-3}}{7.68 \text{ x } 10^{-4}}$ = 2.5 (1)

Change in oxidation number of Mn for 1 mol of MnO_4^{-} = – 5.

Change in oxidation number of V for 2.5 mol of VO_3^{-} = + 5 (1).

Change in oxidation number of V for 1 mol of VO_3^{-} = + 2.

Oxidation number of V in solution X = (5 – 2) = + 3 (1).

(c) Not all of the excess sulfur dioxide was removed from solution (1). Extra $KMnO_4$ is required to oxidise the sulfur dioxide. (1) Alternatively, the SO_2 re-reduces the vanadium (V) molecules, which are then re-oxidised by the $MnO4^{-}$.

7 (a) **A** = electrons (1) **B** = hydrogen ions / H^{+} (1).

(b) Platinum / palladium (1).

(c) Any two from:

They offer an alternative to the direct use of fossil fuels such as petrol and diesel, which are a finite resource.

They avoid the production of products that are classified as pollutants, such as carbon monoxide, carbon dioxide and oxides of nitrogen.

The engines are relatively light and more efficient than engines that use fossil fuels (2).

(d) They have a limited lifetime and therefore need regular replacement.

The storage tanks are very large and heavy if the hydrogen is stored under pressure as a liquid (2).

(e) (i) $Zn(s) | Zn^{2+}(aq) ⁞ Ag_2O(s), H_2O(l) | Ag(s), OH^{-}(aq)$ left-hand side (1) right-hand side (1).

(ii) $Zn(s) + Ag_2O(l) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^{-}(aq)$

Equation (1) state symbols (1).

(iii) Emf = (0.34 – – 0.76) = 1.10 V (1).

(iv) $\Delta G^{\ominus} = -nFE$ (1)

$= -2 \times 96\,500 \times 1.10 = 212\,300$ J mol^{-1} or 212.3 kJ mol^{-1} (1).

(v) $\Delta G^{\ominus} = -RT\ln K$ (1)

$K = e^{-\frac{\Delta G^{\ominus}}{RT}} = e^{-\frac{212\,300}{8.31 \times 298}} = 5.86 \times 10^{-38}$ (1).

15.1 Principles of transition metal chemistry

15.1.1 Transition metal electronic configurations

1 (Cr full) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

(Cr abbreviated) $[Ar]4s^1 3d^5$

2 The atom first loses both of its 4s electrons, then two of its five 3d electrons. This forms the Mn^{4+} ion with an oxidation number of +4, and an electronic configuration of $[Ar]3d^3$.

15.1.2 Ligands and complexes

1 A ligand needs a lone pair of electrons that it can use to form a dative bond, and methane has no lone pairs of electrons.

2 It is a complex because there are ligands joined to the metal ion by dative bonds. It is not a complex ion because the 2+ charge on the metal ion is exactly cancelled out by the two negative charges on the OH^- ligands and so the complex is neutral and has no overall charge.

15.1.3 The origin of colour in complexes

1 Violet light, because yellow and violet are complementary colours, opposite each other on a colour wheel.

2 The electronic configuration of an aluminium ion is $1s^2 2s^2 2p^6$, so it has no 3d electrons that could absorb light from the electromagnetic spectrum.

15.1.4 Common shapes of complexes

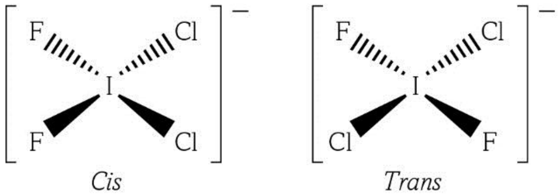
1 As there are six monodentate ligands around the transition metal ion, the shape is octahedral. As the overall charge on the complex is 3–, and each ligand has a 1– charge, then the charge on the transition metal ion must be 3+.

2 As chloride ions are bigger than other ligands, there are four around the central metal ion, giving a tetrahedral shape. Its name is tetrachloronickelate(II) and its formula is $[NiCl_4]^{2-}$.

15.1.5 Square planar complexes

1 An iodine atom has seven electrons in its outer shell, and each chlorine atom brings one electron to form the bonds, then adding one for the 1– charge makes 12 electrons. There are therefore six pairs - four bonding pairs and two lone pairs of electrons, giving an octahedral distribution. The two lone pairs repel most so they are opposite each other, giving a square planar shape for the four chlorines around the iodine.

2 (a)



(b) The $IFCl_3^-$ ion has one F and three Cl atoms, so the only possible arrangement is for two Cl atoms to be opposite each other and one F and one Cl to be opposite.

15.1.6 Multidentate ligands

1 It cannot act as a bidentate ligand because the two lone pairs of electrons are on the same atom. It cannot act as a multidentate ligand because the hydrogen atoms do not have any lone pairs of electrons. It is not a multidentate ligand because it can only use one of its lone pairs at a time to form a dative bond.

2 $[Fe(H_2O)_6]^{3+} + 2en \rightarrow [Fe(H_2O)_2(en)_2]^{3+} + 4H_2O$

15.2 Transition metal reactions

15.2.1 Different types of reaction

1 This is only ligand exchange, as one water ligand is replaced by one $SCN^–$ ligand. This causes the overall charge on the complex to decrease from 3+ to 2+, but the oxidation number of Fe does not change, and there is no change in co-ordination number. It being an acid-base reaction can be ruled out.

2 This is ligand exchange because all six water ligands are replaced by ammonia ligands. It is also redox as the overall charge increases from 2+ to 3+. It is not acid-base and there is no change in co-ordination number.

15.2.2 Reactions of cobalt and iron complexes

1 $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$

2 Ammonia is a weak base, so in aqueous ammonia there are many more NH_3 molecules than $OH^–$ ions.

15.2.3 The chemistry of chromium

1 $[Cr(OH)_6]^{3–} + 6H^+ \rightarrow [Cr(H_2O)_6]^{3+}$

2 The relevant half-equations and E° values are:

$Mn^{2+} + 2e^– \rightarrow Mn$ $E^{\circ} = –1.18\ V$

$Zn \rightarrow Zn^{2+} + 2e^–$ $E^{\circ} = +0.76\ V$

Adding these together gives:

$Mn^{2+} + Zn \rightarrow Mn + Zn^{2+}$ $E^{\circ} = –0.42\ V$

As the E° value is negative, the reaction is not feasible.

15.2.4 The chemistry of vanadium

1 The relevant half-equations and E° values are:

$V^{3+} + e^– \rightarrow V^{2+}$ $E^{\circ} = –0.26\ V$

$Sn \rightarrow Sn^{2+} + 2e^–$ $E^{\circ} = +0.14\ V$

Adding these together gives:

$2V^{3+} + Sn \rightarrow 2V^{2+} + Sn^{2+}$ $E^{\circ} = –0.12\ V$

As the E° value is negative, tin will not act as a reducing agent in this reaction.

2 The relevant half-equations and E° values are:

$VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^–$ $E^{\circ} = –1.00\ V$

$Cu^{2+} + 2e^– \rightarrow Cu$ $E^{\circ} = +0.34\ V$

Adding these together gives:

$2VO^{2+} + 2H_2O + Cu^{2+} \rightarrow 2VO_2^+ + 4H^+ + Cu$ $E^{\circ} = –0.66\ V$

As the E° value is negative, copper(II) ions will not act as an oxidising agent in this reaction.

15.3 Transition metals as catalysts

15.3.1 Heterogeneous catalysis

1 Vanadium(V) oxide chemically changes into vanadium(IV) oxide, and back again, so it does take part in the reaction, even though it is chemically unchanged after the reaction.

2 $4NO + 3O_2 + 2H_2O \rightarrow 4HNO_3$

15.3.2 Homogeneous catalysts

1 The autocatalysis reaction involves the conversion between Fe^{2+} and Fe^{3+} ions. Magnesium only forms one ion - Mg^{2+} so it is not suitable.

2 In alkaline conditions, there would be no H^+ ions, which are needed as reactants. Also Mn^{2+} ions would react with alkali to form a precipitate and so would not be available to act as a catalyst.

15 Answers to exam-style questions

1 (a) $(Sc^{3+} 1s^2 2s^2 2p^6) 3s^2 3p^6$ (1).

$(Ti^{3+} 1s^2 2s^2 2p^6) 3s^2 3p^6 3d^1$ (1).

(b) The ion of a transition metal must have incompletely filled d-orbitals (1).

The Ti^{3+} ion has this but the Sc^{3+} ion does not (1).

(c) $(Sc(OH)_3)$ +3 (1)

$(CaTiO_3)$ +4 (1)

(d) D (1)

2 (a) A species with a lone pair of electrons (1) that forms a dative bond with a metal ion (1).

(b) B (1)

(c) (i) $[Fe(H_2O)_4(OH)_2]$ (1).

(ii) Tetrachlorocobaltate(II) (1).

(d) The 3d energy level splits into two sub-levels with different energy (1).

In the ground state, all the electrons are in the lower energy level (1).

When radiation from the visible spectrum is passed through the solution, some of the radiation is absorbed (1).

The energy of this radiation excites electrons from the lower to the higher energy level (1).

The colour of the solution is in the visible spectrum but without the colour absorbed by the electrons (1).

3 (a) The six water ligands repel each other as far as possible (1)

giving a symmetrical structure with bond angles of 90º (1).

(b) (i) Chloride ions are bigger than water molecules (1)

so only four of them can form bonds with the transition metal ion (1).

(ii) The co-ordination number changes (1).

The oxidation number does not change (1).

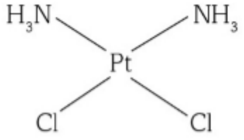
(c) (i) Name: diamminesilver(I) (1).

Reagent: Tollens' reagent / ammoniacal silver nitrate (1).

(ii) Reduction (1).

Silver (1).

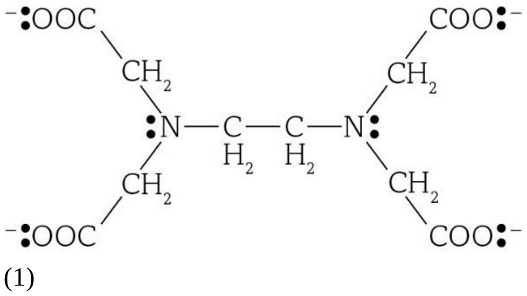
(d) Square planar (1).



(1)

(e) (i) It has more than one lone pair of electrons that can bond to a metal ion (2).

(ii)



(1)

(iii) $[Fe(EDTA)]^-$ (1).

4 (a) Reactant: green solution (1).

Product: green precipitate (1).

(b) Sodium hydroxide (solution) / NaOH (1).

(c) Reaction 3 (1).

Because the oxidation number of Cr changes from +3 to +6 (1).

(d) Yellow to orange (1).

(e) $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$ (1)

5 Sulfur dioxide is adsorbed onto the catalyst (1).

The equation for its reaction with the catalyst is $V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3$ (1)

in which the oxidation number of vanadium decreases from +5 to +4 (1).

Oxygen then reacts as follows: $V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$ (1)

in which the oxidation number of vanadium increases from +4 to +5 (1).

Adding these equations together gives $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ (1).

16.1 Further kinetics

16.1.1 Methods of measuring the rate of reaction

1 (a) Measure the volume of hydrogen given off at regular time intervals.

(b) Withdraw samples at regular time intervals. Quench the reaction in the sample by cooling, and titrate the remaining alkali with standard acid.

(c) Withdraw samples at regular time intervals. Stop the reaction in the sample by adding sodium hydrogencarbonate. Add excess potassium iodide and titrate the liberated iodine with standard sodium thiosulfate(VI) solution.

2 Hydrogen gas has a very low density, so the mass changes would be very small. This would result in a large measurement uncertainty.

3 Collection in a gas syringe because carbon dioxide is slightly soluble in water. Alternatively, the water could be saturated with carbon dioxide before the collection is started.

16.1.2 Rate equations, rate constants and orders of reaction

1 (a) (i) 1

(ii) 1

(b) 2

2 (a) Doubled.

(b) Quadrupled.

(c) Increases by a factor of 8.

3 (a) Order of reaction with respect to R is 2.

Order of reaction with respect to S is 0.

Order of reaction with respect to T is 1.

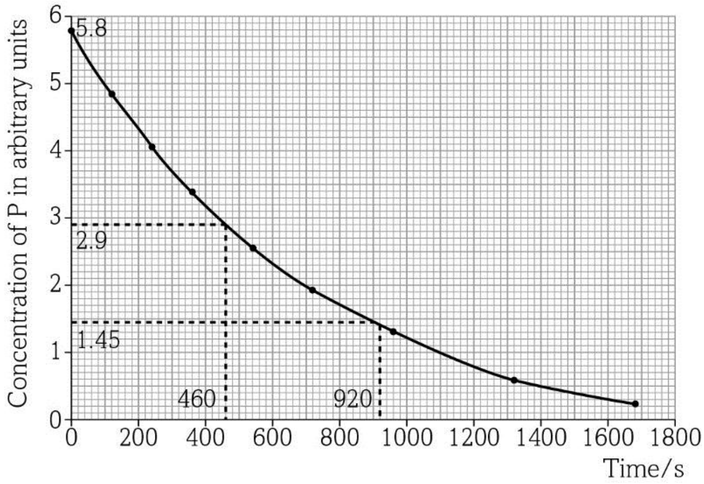
(b) Rate = $k[R]^2[T]$ or rate = $k[R]^2[T][S]^0$.

(c) 3

16.1.3 Determining orders of reaction

1 (a) The half-life of a reaction is the time taken for the concentration of a reactant to fall to half of its original value.

(b)



Time taken for [P] to fall from 5.8 to 2.9 is 460 s (460 – 0).

Time taken for [P] to fall from 2.9 to 1.45 is 460 s (920 – 460).

Since the two half-lives are the same, the reaction is first order.

(c) The half-life for a first order reaction is independent of the initial concentration, so there will be no change.

(d) $k = \frac{0.693}{460\ \text{s}} = 1.51 \times 10^{-3}\ \text{s}^{-1}$.

(e) Rate = k[P].

(f) (i) 1.7×10^{-4} mol dm^{-3}.

(ii) Rate = $1.51 \times 10^{-3}\ \text{s}^{-1} \times 1.7 \times 10^{-4}\ \text{mol dm}^{-3}$
$= 2.6 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$.

(g) Draw a tangent to the curve at t = 800 s. Determine the gradient of the tangent.

2 (a) (i) First order with respect to Br^-. As [Br^-] triples from experiments 1 to 3, the rate also triples.

(ii) First order with respect to BrO_3^-. As [BrO_3^-] doubles from experiments 1 to 2, the rate also doubles.

(iii) Second order with respect to H^+. As [H^+] doubles from experiments 2 to 4, the rate quadruples.

(b) Rate = $k[Br^-][BrO_3^-][H^+]^2$

(c) $$k = \frac{1.2 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{0.10\ \text{mol dm}^{-3} \times 0.10\ \text{mol dm}^{-3} \times 0.10^2\ (\text{mol dm}^{-3})^2}$$
$= 12\ \text{dm}^9\ \text{mol}^{-3}\ \text{s}^{-1}$.

3 (a) The rate equation states that the reaction is first order with respect to HBr and also first order with respect to O_2. This corresponds to the number of molecules of each in step 1, so step 1 is the rate-determining step.

(b) $4HBr + O_2 \rightarrow 2Br_2 + 2H_2O$

16.1.4 Rate equations and mechanisms

1 (a) Mechanism 2 is consistent with the rate equation.

Mechanism 1 has H^+ in the first step. If this were the mechanism then the reaction would be first order with respect to H^+, not zero order.

Mechanism 2 has one molecule of CH_3CHO and one ion of CN^- in the first step and this is consistent with the reaction being first order with respect to each reactant. Also H^+ appears after the rate-determining step, so is consistent with the reaction being zero order with respect to H^+.

(b) Step 1.

2 Yes, because *two* molecules of NO and *one* molecule of H_2 appear either *before* or *in* the rate-determining step (i.e. the slow step). This is consistent with the reaction being *second* order with respect to NO and *first* order with respect to H_2, as stated in the rate equation.

Also, the stoichiometry is consistent with the overall equation for the reaction.

3 (a) $H_2 + Cl_2 \rightarrow 2HCl$

(b) Rate = $k[Cl_2]$.

(c) The rate would double. The mechanism suggests that the reaction is first order with respect to Cl_2.

(d) No change. The mechanism suggests that the reaction is zero order with respect to H_2.

4 The reaction follows an S_N2 mechanism and so one molecule of CH_3Cl and one ion of OH^- appear in the rate-determining step of the mechanism. The rate equation for the reaction is, therefore:

rate = $k[CH_3Cl][OH^-]$.

This is consistent with a second order reaction overall.

However, if the concentration of OH^- is very large, then changes in its concentration become significant. Under these circumstances [OH^-] effectively remains constant. The rate equation then becomes:

rate = $k[CH_3Cl]$.

This is consistent with a first order reaction overall.

Such reactions are known as *pseudo* first order reactions.

16.1.5 Activation energy and catalysis

1 A homogeneous catalyst works by reacting in one step of the reaction mechanism, but then it is regenerated in another step. Hence only a small amount of it is required initially.

2 Some of the lead(II) bromide will attach itself to the catalyst in the catalytic converter as it passes through. This will poison the catalyst and eventually render it inactive.

16.1.6 The effect of temperature on the rate constant

1 $\ln k = -\frac{E_a}{RT} + \ln A$

A plot of $\ln k$ against $\frac{1}{T}$ will give a straight line of negative gradient. This shows that as $\frac{1}{T}$ increases, $\ln k$ decreases. Hence, as T increases, $\ln k$ increases.

As $\ln k$ increases, the rate of reaction increases.

Note: We have assumed that both E_a and A remain constant as T increases. This has shown to be a reasonable assumption.

2 $\ln k = -\frac{E_a}{RT} + \ln A$

$\ln k(300\ \text{K}) = \ln 10.0 = 2.303 = -\frac{E_a}{8.31 \times 300} + \ln A$ Equation 1

$\ln k(400\ \text{K}) = \ln 100.0 = 4.605 = -\frac{E_a}{8.31 \times 400} + \ln A$ Equation 2

Subtracting Equation1 from Equation 2 gives:

$(4.605 - 2.303) = \frac{E_a}{8.31}\left(\frac{1}{300} - \frac{1}{400}\right)$.

$E_a = 22\,956\ \text{J mol}^{-1}$ or $23.0\ \text{kJ mol}^{-1}$ (to 3 significant figures).

16 Answers to exam-style questions

1 (a) (i) Order with respect to NO is 2 (1).

In experiments 1 and 3, [NO] doubles and rate quadruples (1).

Order with respect to O_2 is 1 (1).

In experiments 3 and 4, $[O_2]$ doubles and rate also doubles (1).

(ii) Rate = $k[NO]^2[O_2]$.

(b) The rate equation indicates that two molecules of NO and one molecule of oxygen (1) must occur either *before* or *in* the rate-determining step (1).

Since the rate determining step of this mechanism is the second, slow step, this condition has been met so the proposed mechanism fits with the rate equation (1).

2 (a) $k = \frac{\text{rate}}{[CH_3COCH_3][H^+]} = \frac{1.43 \times 10^{-6}}{0.400 \times 0.200}$ (1) = 1.79×10^{-5} (1) $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ (1).

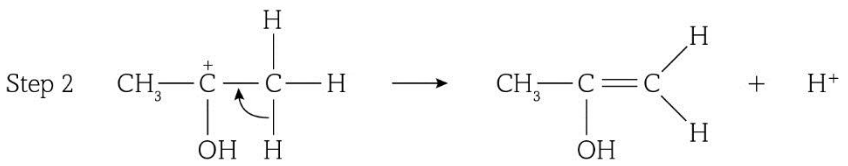
(b) There will be no change in the rate of reaction (1) since the reaction is zero order with respect to iodine (1).

(c) Step 1 could be the rate-determining step (1) since one molecule of CH_3COCH_3 and one H^+ ion appear in it (1) and this agrees with the experimentally determined orders of reaction (1).

Or

Step 2 could be the rate-determining step (1) since one molecule of CH_3COCH_3 and one H^+ ion appear before it (1) and this agrees with the experimentally determined orders of reaction (1).

(d)



(1)

3 (a) The slowest step in the mechanism for the overall reaction (1).

(b) (i) $H_2(g) + ICl(g) \rightarrow HCl(g) + HI(g)$ (1)

(ii) $HI(g) + ICl(g) \rightarrow HCl(g) + I_2(g)$ (1)

(c) (i) A: first order; in experiments 1 and 4, [A] doubles and rate doubles (1).

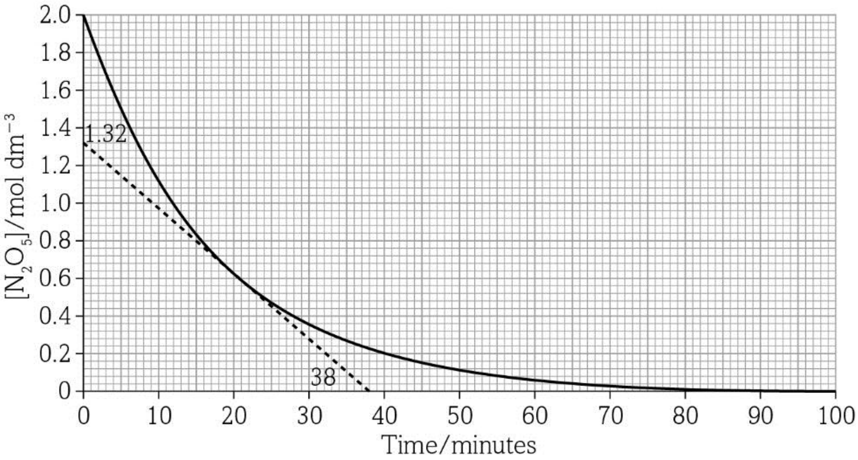
B: zero order; in experiments 1 and 2, [B] doubles but rate does not change (1).

C: second order; in experiments 1 and 3; [C] doubles and rate quadruples (1).

(ii) Rate = $k[A][C]^2$ (1).

(iii) B (since it is zero order) (1).

4 (a) (i)



20 minutes

Tangent drawn to curve at time = 20 minutes (1).

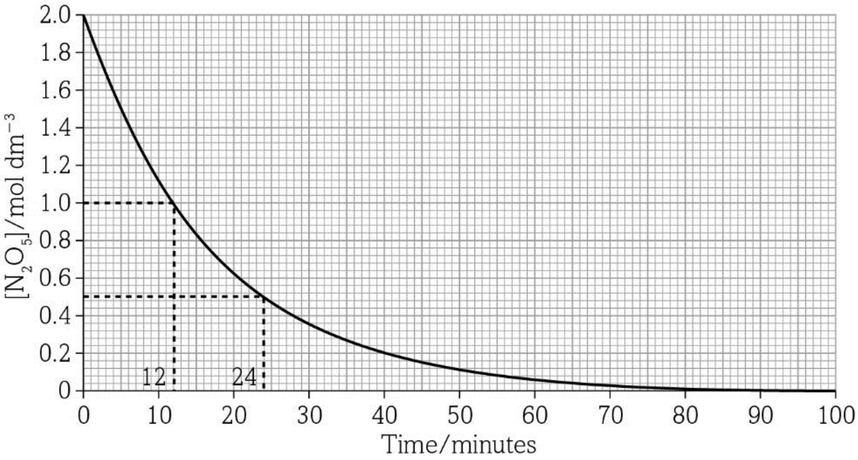
Gradient calculated (1) (e.g. $\frac{1.32}{38}$ = 0.035 mol dm^{-3} min^{-1}).

90 minutes

Rate = 0 (mol dm^{-3} min^{-1}) since the gradient of the curve at time = 90 minutes = 0 (1).

(ii) 0.0175 mol dm^{-3} min^{-1} (1).

(b) (i)

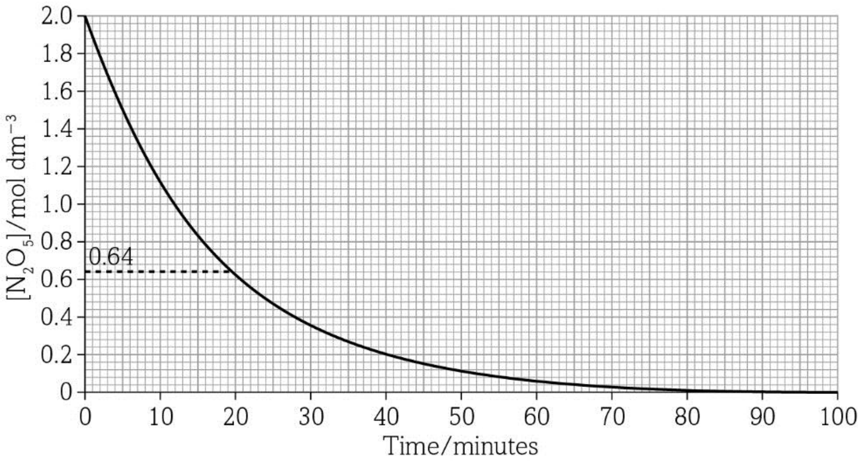


1 mark for each half-life drawn (2).

(ii) First order (1), because the two half-lives are the same (both are 12 minutes) (1).

(iii) Rate = $k[N_2O_5]$ (1).

(c) (i)



$[N_2O_5]$ at 20 mimuntes = 0.64 mol dm^{-3} (1).

$k = \frac{\text{rate}}{[N_2O_5]} = \frac{0.035}{0.64} = 0.55$ (1) s^{-1} (1).

(ii) Rate = 0.55 × 1.50 = 0.82 (1) mol dm^{-3} min^{-1} (1).

5 (a) (i) $2NO_2 \rightarrow 2NO + O_2$ (1)

(ii) Rate = $k[NO_2]^2$ (1).

(b) (i) Gradient of line = $-\frac{(8.5 - 1.1)}{(1.52 - 1.00) \times 10^{-2}}$ = – 1423(.076923) (1).

$-\frac{E_a}{R}$ = – 1423.076923 (1).

E_a = 8.31 × 1423.076923 = 11825(.76923) J mol^{-1}(1)

= 12 000 J mol^{-1} *or* 12 kJ mol^{-1} (1) (final answer to 2 significant figures).

(ii) $[NO_2]$ = (4.00 ÷ 2.00) = 2.00 mol dm^{-3} (1).

12.64 = $k \times (2.00)^2$ (1).

k = 3.16 dm^3 mol^{-1} s^{-1} (1) (units must be included).

17.1 Chirality

17.1.1 Chirality and enantiomers

1 Two optical isomers or two geometric isomers both have the same molecular and structural formulae but with their atoms and groups arranged differently in three dimensions. With optical isomers, the difference is that the atoms and groups are arranged to form an object and its mirror image. With geometrical isomers, the difference is that the atoms and groups are arranged differently on opposite sides of a C=C double bond.

2 (a) None, because all of the carbon atoms are joined to two or more identical atoms.

(b) The first carbon atom is joined to three hydrogen atoms so is not chiral. The third carbon atom is joined by a double bond to oxygen so has only three different groups attached. The second carbon atom is chiral because it is joined to four different atoms or groups (methyl, hydrogen, hydroxyl and carboxylic acid).

(c) The first and last carbon atoms are part of methyl groups so are not chiral. The second carbon atom is chiral (it is joined to CH_2Cl, C, H and $CHFCH_3$). The third carbon atom is also chiral because it is joined to H, F, CH_3 and $CH_2ClCHCl$.

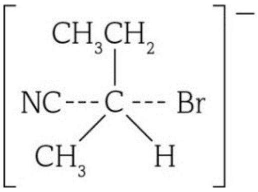
17.1.2 Optical activity

1 When monochromatic light passes through the polariser it absorbs all oscillations except those in one plane.

2 If the mixture had no optical activity, this would indicate that it contained equal amounts of both enantiomers. The fact that the mixture has a rotation with a negative value indicates that it contains more of the laevorotatory enantiomer than the dextrorotatory enantiomer.

17.1.3 Optical activity and reaction mechanisms

1

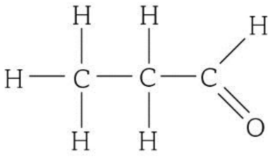


2 2-bromopropane is not a chiral compound and even though the attacking CN^- ion can approach the carbocation from both sides, the resulting products are not chiral. So, neither the reactant nor the product have any optical activity.

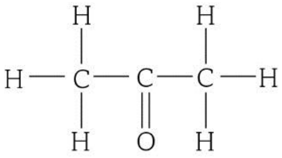
17.2 Carbonyl compounds

17.2.1 Carbonyl compounds and their physical properties

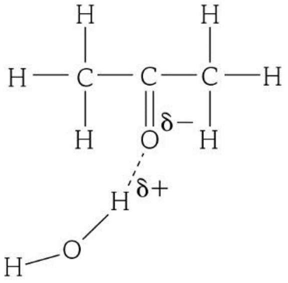
1 (a)



(b)



2



17.2.2 Redox reactions of carbonyl compounds

1 (a) Butan-1-ol.

(b) Pentanoic acid.

2 (a) No change - ketones are not oxidised.

(b) A colourless solution forms a silver mirror.

17.2.3 Nucleophilic addition reactions

1 (a) Hydroxyethanenitrile.

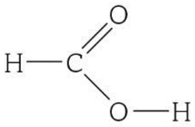
(b) 2-hydroxy-2-methylpropanenitrile.

2 Propan-1-ol and propan-2-ol are not carbonyl compounds so do not give coloured precipitates with 2,4-dinitrophenylhydrazine. Propanal does not react with iodine and alkali because it does not contain the CH_3CO group. Only propanone reacts with both reagents because it is a carbonyl compound and contains the CH_3CO group.

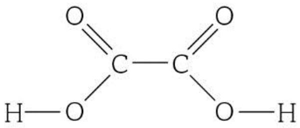
17.3 Carboxylic acids

17.3.1 Carboxylic acids and their physical properties

1 (a)



(b)



2 Both acids are soluble in water because they form hydrogen bonds with water molecules. The solubility of hexanoic acid is lower than that of ethanoic acid because there are more extensive London forces between the hydrocarbon chains in hexanoic acid, and these interfere with the formation of the hydrogen bonds.

17.3.2 Preparations and reactions of carboxylic acids

1 (a) $(CH_3)_2CHCH_2OH + 2[O] \rightarrow (CH_3)_2CHCOOH + H_2O$

(b) $(CH_3)_2CHCN + H^+ + 2H_2O \rightarrow (CH_3)_2CHCOOH + NH_4^+$

2 (a) $(CH_3)_2CHCOOH + PCl_5 \rightarrow (CH_3)_2CHCOCl + POCl_3 + HCl$

(b) $(CH_3)_2CHCOOH + CH_3OH \rightarrow (CH_3)_2CHCOOCH_3 + H_2O$

17.3.3 Acyl chlorides

1	(With water)	propanoic acid
	(With methanol)	methyl propanoate
	(With ammonia)	propanamide
	(With methylamine)	N-methylpropanamide

2 (a) $CH_3CH_2CH_2COCl + CH_3CH_2CH_2OH \rightarrow CH_3CH_2CH_2COOCH_2CH_2CH_3 + HCl$

(b) $CH_3CH_2CH_2COCl + CH_3CH_2NH_2 \rightarrow CH_3CH_2CH_2CONHCH_2CH_3 + HCl$

17.3.4 Esters

1 (a) Propyl propanoate.

(b) Methyl 2-methylpropanoate.

2 (a) $CH_3CH_2CH_2COOCH_2CH_2CH_3 + H_2O \rightleftharpoons CH_3CH_2CH_2COOH + CH_3CH_2CH_2OH$

(b) $CH_3CH_2CH_2COOCH_2CH_2CH_3 + OH^- \rightarrow CH_3CH_2CH_2COO^- + CH_3CH_2CH_2OH$

17.3.5 Polyesters

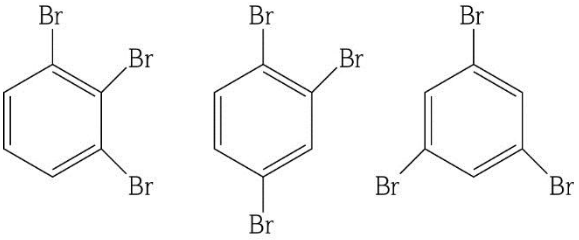
1 Although the first molecule has two reactive COOH groups at both ends of the molecule, the alcohol is not a diol, so with only one OH group the polymerisation reaction cannot proceed.

2 $[–OCCOOCH(CH_3)CH(CH_3)O–]$

17.4 Arenes – benzene

17.4.1 Benzene – a molecule with two models

1

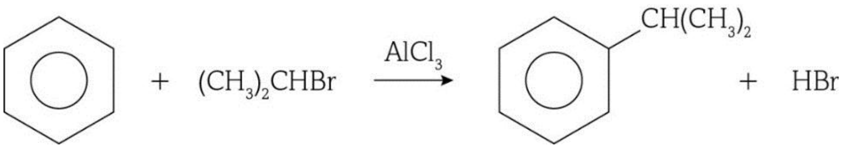


2 (a) Each C–H and C–C bond has two electrons in sigma bonds, and as there are six of each, then 12 × 2 = 24 electrons in sigma bonding.

(b) Each C atom supplies one electron to form the delocalised pi bond, so the answer is 6 electrons in pi bonding.

17.4.2 Some reactions of benzene

1

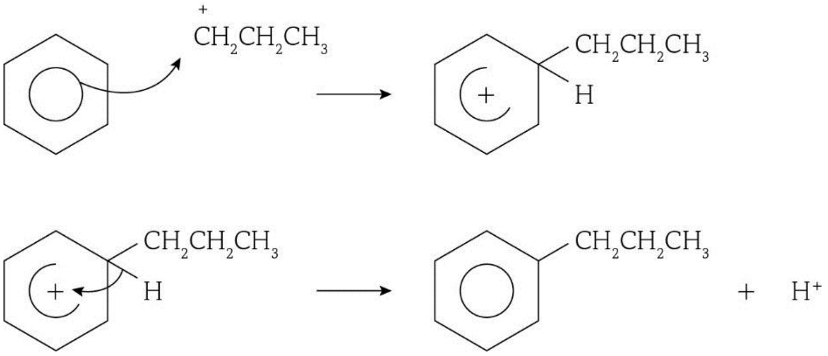


2 Phenylbutanone.

17.4.3 Electrophilic substitution mechanisms

1 $FeBr_3 + Br_2 \rightarrow Br^+ + FeBr_4^-$

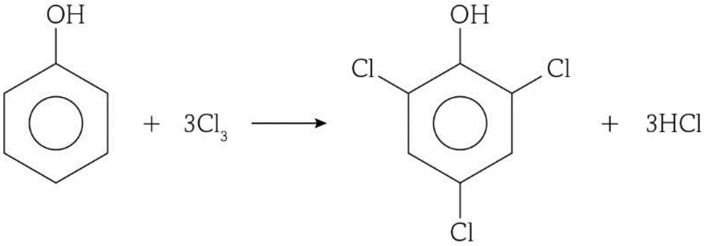
2



17.4.4 Phenol

1 The OH group is polar and can take part in hydrogen bonding. This means that phenol molecules attract each other strongly, and so the melting temperature is above room temperature. Its solubility in water is due to the formation of hydrogen bonds between phenol molecules and water molecules.

2



17.5 Amines, amides, amino acids and proteins

17.5.1 Amines and their preparations

1 (a) $CH_3CH_2CH_2Cl + 2NH_3 \rightarrow CH_3CH_2CH_2NH_2 + NH_4Cl$

(b) $CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$

2 The product will attack some of the halogenoalkanes to form a secondary amine.

17.5.2 Acid-base reactions of amines

1 (a) $CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$

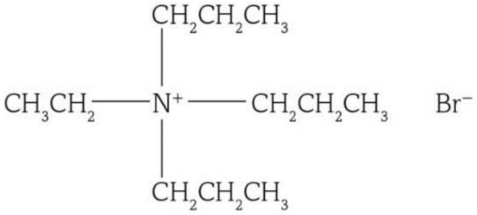
(b) $2CH_3CH_2NH_2 + H_2SO_4 \rightarrow 2CH_3CH_2NH_3^+ + SO_4^{2-}$

2 The second methyl group in dimethylamine is electron-releasing, so compared to methylamine the extra methyl group increases the electron density on the nitrogen atom. This means that the basicity is higher in dimethylamine.

17.5.3 Other reactions of amines

1 $CH_3CH_2COCl + CH_3CH_2CH_2NH_2 \rightarrow CH_3CH_2CONHCH_2CH_2CH_3 + HCl$

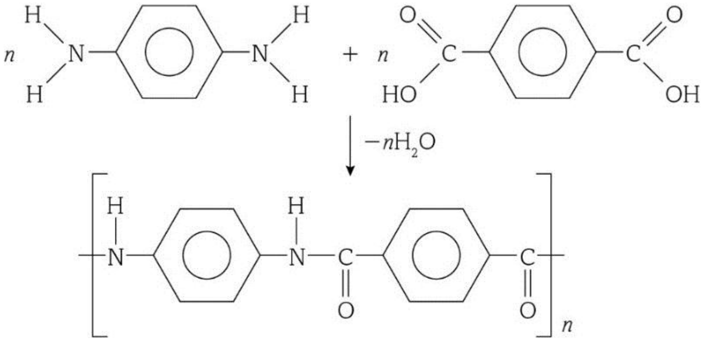
2



17.5.4 Amides and polyamides

1 $CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$

2



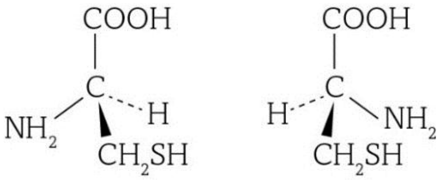
17.5.5 Amino acids

1 (a) $H_3\overset{+}{N}—CH_2—COO^-$

(b) $H_3\overset{+}{N}—CH_2—COOH$

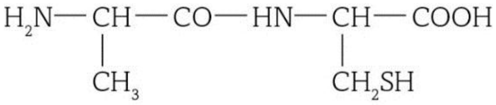
(c) $H_2N—CH_2—COO^-$

2



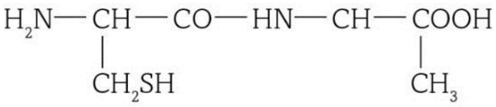
17.5.6 Peptides and proteins

1



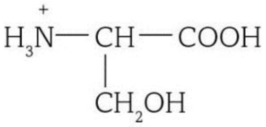
$$H_2N—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CO—HN—\underset{\displaystyle CH_2SH}{\underset{|}{CH}}—COOH$$

and



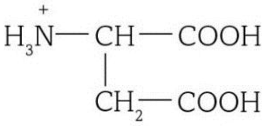
$$H_2N—\underset{\displaystyle CH_2SH}{\underset{|}{CH}}—CO—HN—CH—\underset{\displaystyle CH_3}{\underset{|}{COOH}}$$

2



$H_3\overset{+}{N}-\underset{\displaystyle CH_2OH}{\underset{|}{CH}}-COOH$

and

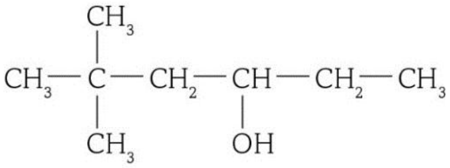


$H_3\overset{+}{N}-\underset{\displaystyle CH_2-COOH}{\underset{|}{CH}}-COOH$

17.6 Organic structures

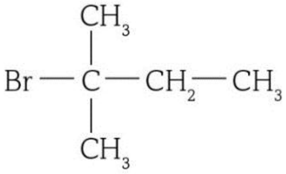
17.6.1 Principles of organic synthesis

1



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$

2



$Br-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-CH_3$

and

CH_3-CH_2-CHO

17.6.2 Hazards, risks and control measures

1 Wear eye protection because aqueous potassium hydroxide is corrosive.

Wear gloves when handling aqueous potassium hydroxide for the same reason.

Make sure that the reflux condenser is set up and used carefully because ethanol in flammable.

2 Sodium hydroxide solution is an alkali and rapidly reacts with the fats on the surface of the skin and hydrolyses them. Dilute hydrochloric acid has the same effect but the reaction is reversible and proceeds very little before the acid is washed off.

17.6.3 Practical techniques in organic chemistry – Part 1

1 In refluxing, the condenser is vertical because the intention is that the condenser should cause all the substances that have evaporated from the flask to return to the flask. In all the methods of distillation, the condenser is nearly horizontal because the intention is that any substance that enters the condenser should travel down it to the receiver.

2 The one with the very small beads, because the greater surface area throughout the column means more distillations and evaporations than with the larger pieces of glass.

17.6.4 Practical techniques in organic chemistry – Part 2

1 If the solvent dissolves the impurities, then there will not be two layers with the substance in one and the impurities in the other.

2 Insoluble impurities must be removed from a hot solution while the substance to be purified is still dissolved. When the solution has been cooled the insoluble impurities will be mixed with the purified solid.

17.6.5 Simple chromatography

1 The stationary phase is the water in the paper, and as water molecules are polar, then the non-polar hexane molecules will not be attracted to them very much and so will travel up the paper easily.

2 $R_f = \frac{20}{75} = 0.27$.

17.7 Organic analysis

17.7.1 Traditional methods of analysis

1

	C	H	O
% of element	40.0	6.67	53.3
Relative atomic mass	12.0	1.0	16.0
Division by A_r	3.33	6.67	3.33
Ratio	1	2	1

The empirical formula is CH_2O.

As this has a mass of 30.0 g mol^{-1} and the M_r = 60.0, the molecular formula is $C_2H_4O_2$.

Effervescence is due to the COOH group, which means that the compound is CH_3COOH, ethanoic acid.

2 As T does not have a COOH group, the same atoms must be arranged differently. The obvious possibility is $HCOOCH_3$, methyl methanoate.

17.7.2 Determining structures using mass spectra

1 The two compounds both have M_r values of 73.0 using the relative atomic masses in the Periodic Table. They have different molecular formulae and when their relative molecular masses are calculated using A_r values to four decimal places, only one of them is 73.0812.

2 Using A_r values to four decimal places, the M_r value of 1,2-diaminoethane is:

$(2 \times 12.0000) + (2 \times 14.0031) + (8 \times 1.0078) = 60.0686$.

Using A_r values to four decimal places, the M_r value of ethanoic acid is:

$(2 \times 12.0000) + (2 \times 15.9949) + (4 \times 1.0078) = 60.0210$.

This value is close to the true value of 60.0213, so the compound is ethanoic acid.

17.7.3 Chromatography – HPLC and GC

1 In traditional column chromatography, a liquid passes down a column by gravity. In HPLC, the liquid is passed through a metal tube under high pressure.

2 The liquids may be different and the pressures of the carrier gases may be different.

17.7.4 Chromatography and mass spectrometry

1 The function of HPLC is to separate a mixture of substances, and the function of MS is to measure the relative molecular mass of each component.

2 (a) Nandrolone, as only this one has a C=C double bond.

(b) Nandrolone and 19-norandrosteron, as they both contain C=O carbonyl groups.

17.7.5 Principles of NMR spectroscopy

1 Both ^{16}O and ^{32}S have even numbers of protons and neutrons so are not suitable. ^{19}F has an odd number of protons and so is suitable.

2 TMS has a strong signal because its molecule contains 12 equivalent protons, and it also mixes easily with organic compounds. Water has only two equivalent protons and so has a weaker signal, and also does not mix with most organic compounds.

17.7.6 ^{13}C NMR spectroscopy

1 CH_4 has only 1.

$CH_3–CH_3$ has only 1.

$CH_3–CH_2–CH_3$ has 2.

$CH_3–CH_2–CH_2–CH_3$ has 2.

$CH_3–CH_2–CH_2–CH_2–CH_3$ has 3.

$CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$ has 3.

17.7.7 ^1H NMR spectroscopy

1 $CH_3–CH_2–CH_2–CH_2–CH_3$ has 3.

$(CH_3)_2CH–CH_2–CH_3$ has 4.

$(CH_3)_4C$ has 1.

2 The integration trace shows only the ratio of numbers of hydrogen atoms. The actual numbers may be a multiple of this ratio.

3 The spectrum of ethylamine has three peaks, while that of ethanamide has two peaks.

17.7.8 Splitting patterns in ^1H NMR spectroscopy

1 The peak on the left is a singlet at $\delta = 4.0$ ppm representing two protons. This suggests a CH_2 group joined to O in an alcohol, ether or ester, so $O–CH_2$.

The peak in the middle is a singlet at $\delta = 3.4$ ppm representing three protons. This suggests a CH_3 group joined to O in an alcohol, ether or ester, so $CH_3–O$.

The peak in the middle is a singlet at $\delta = 2.1$ ppm representing three protons. This suggests a CH_3 group joined to CO in an aldehyde, ketone, ester or acid, so $CH_3–C{=}O$.

The structure that fits these interpretations is $CH_3–CO–CH_2–O–CH_3$.

2 The peak on the left is a singlet at $\delta = 2.3$ ppm representing three protons. This suggests a CH_3 group joined to CO in an aldehyde, ketone, ester or acid, so $CH_3–CO–$.

The peak in the middle is a quartet at $\delta = 1.5$ ppm representing one proton. This suggests a CH group joined to a CH_3 group in an alkyl group, so $CH_3–CH–$.

The peak on the right is a doublet at $\delta = 1.2$ ppm representing six protons. This suggests two CH_3 groups joined to CH in an alkyl group, so $(CH_3)_2–CH–$.

The structure that fits these interpretations is $CH_3–CO–CH(CH_3)_2$.

17 Answers to exam-style questions

1 (a) A and C both have chiral carbon atoms but B does not (1).

A and C have the same four groups in different spatial arrangements (1).

(b) A and C have equal but opposite optical activities so these cancel out (1).

B has no optical activity (1).

(c) If compound A reacts by an S_N1 mechanism, a planar carbocation intermediate will be formed (1)

which will be attacked by $OH^–$ ions in the second step to form an alcohol (1).

This attack has equal probability of forming two different alcohol molecules (1)

giving a racemic mixture (1).

If compound A reacts by an S_N2 mechanism there will be an inversion of stereochemistry (1)

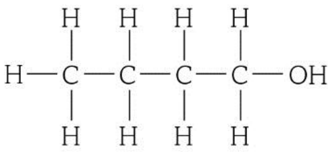
so only one alcohol is formed with an optical activity equal but opposite to that of A (1).

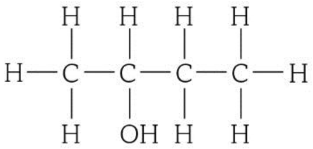
2 (a) They can both form strong intermolecular forces with water molecules (1).

(b) (i) Nucleophilic addition (1).

(ii) The organic products are solids whose melting temperatures can be measured (1), the values can be compared with those in data books to identify which one is which (1).

(c)





(2)

(d) $CH_3CH_2CH_2CH_2CHO + [O] \rightarrow CH_3CH_2CH_2CH_2COOH$ (1)

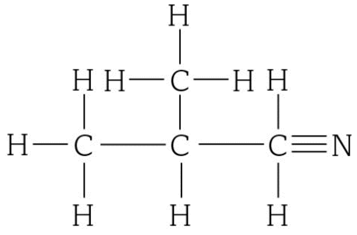
Silver mirror / black precipitate (1).

3 (a) E and F react (1).

Each is either a primary alcohol or a secondary alcohol (1).

Only these have the CHOH group needed for the loss of two hydrogen atoms in oxidation (1).

(b)



(1)

(c) (i) Methanol (1).

(ii) The reagent needed to convert an alcohol into an ester must contain a carboxyl group (1).

It must be an acyl chloride because the other product is hydrogen chloride (1)

(iii) CH_3CH_2COOH (1)

(iv) $CH_3CH_2COOCH_3 + NaOH \rightarrow CH_3CH_2COONa + CH_3OH$

$CH_3CH_2COONa + H^+ \rightarrow CH_3CH_2COOH + Na^+$ (2)

4 (a) (i) $CH_2{=}CHCH_3 + Br_2 \rightarrow CH_2BrCHBrCH_3$ (1)

$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$ (1)

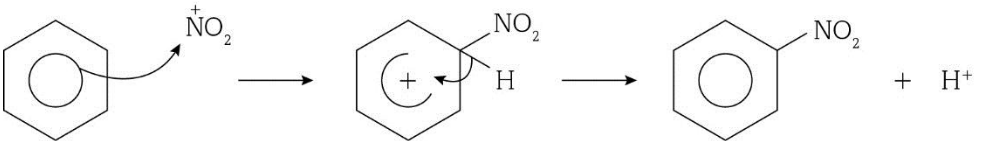
(ii) Propene reacts by electrophilic addition (1).

Benzene reacts by electrophilic substitution (1).

(b) (i) $HNO_3 + H_2SO_4 \rightarrow H_2O + NO_2^+ + HSO_4^-$ (1)

$H^+ + HSO_4^- \rightarrow H_2SO_4$ (1)

(ii)



Curly arrow showing attack by NO_2^+ on benzene (1).

Intermediate showing 4 delocalised electrons, positive charge and NO_2 group (1).

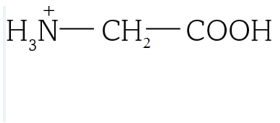
Nitrobenzene and H^+ products (1).

(c) Phenol is much more reactive towards electrophiles because it is more electron-rich (1).

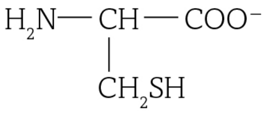
This is because the lone pairs of electrons on oxygen combine with the delocalised electrons of benzene to increase the electron density (1).

Br_2 molecules are polarised as they approach the benzene ring and form Br^+ which readily attacks benzene (1).

5 (a)



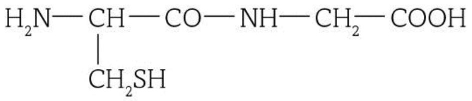
$H_3\overset{+}{N}-CH_2-COOH$



$H_2N-\underset{\underset{\textstyle CH_2SH}{|}}{CH}-COO^-$

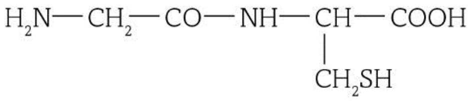
(2)

(b)



$H_2N-\underset{\underset{\textstyle CH_2SH}{|}}{CH}-CO-NH-CH_2-COOH$

and



$H_2N-CH_2-CO-NH-\underset{\underset{\textstyle CH_2SH}{|}}{CH}-COOH$

(2)

(c) Heat the tripeptide with concentrated hydrochloric acid to break it down into the three amino acids (1).

Place a spot of the mixture of amino acids on some chromatography paper (1).

Place the chromatography paper in a tank containing a suitable solvent (1).

Leave until the amino acids have separated then remove and dry (1).

Spray a developing agent on the paper to show the positions of the amino acids (1).

Measure the R_f value of each amino acid and identify them by reference to known R_f values (1).

6 (a) $CH_3CH_2CH_2Br + Mg \rightarrow CH_3CH_2CH_2MgBr$ (1)

(b) Methanal / HCHO (1).

Butan-1-ol (1).

(c) Ethanal / CH_3CHO (1).

Pentan-2-ol (1).

(d) Butanone / $CH_3COCH_2CH_3$ (1).

3-methylhexan-3-ol (1).

7 (a) The spectra are very similar (1)

because they both have the same numbers and types of bond (1).

(b) 2-methypropan-2-ol has two different types of carbon atom / one central C and three identical CH_3 groups (1)

so its spectrum will show two peaks due to ^{13}C atoms (1).

2-methypropan-1-ol has three different types of carbon atom /two identical CH_3 groups, one CH group and one CH_2 group (1)

so its spectrum will show three peaks due to ^{13}C atoms (1).

(c) 2-methylpropan-2-ol has nine identical hydrogen atoms in CH_3 groups and one hydrogen atom in an OH group so two peaks (1) which are singlets because there are no hydrogens on the central C that can affect the CH_3 or OH groups (1).

While 2-methylpropan-1-ol has six identical hydrogen atoms in CH_3 groups, two in a CH_2 group, one in a CH group and one in an OH group (1).

(d) The M_r of both compounds is 74, so the peaks at *m/z* = 74 are due to the molecular ions of both compounds (1).

In the left-hand spectrum the peak at *m/*z = 43 is due to the loss of mass of 31 (CH_2OH) so the peak at *m/z* = 43 is due to $CH(CH_3)_2^+$ (1)

and the peak at *m/*z = 31 is due to CH_2OH^+ (1).

In the right-hand spectrum the peak at *m/*z = 57 is due to the loss of mass of 17 (OH) so the peak at *m/z* = 57 is due to $C(CH_3)_3^+$ (1)

and the peak at *m/*z = 29 is due to COH^+ (1)

so the left-hand spectrum is that of 2-methylpropan-1-ol and the right-hand spectrum is that of 2-methylpropan-2-ol (1).