

Topic 11 Kinetics

11A Further kinetics

11A.1 Techniques for 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. Then 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.

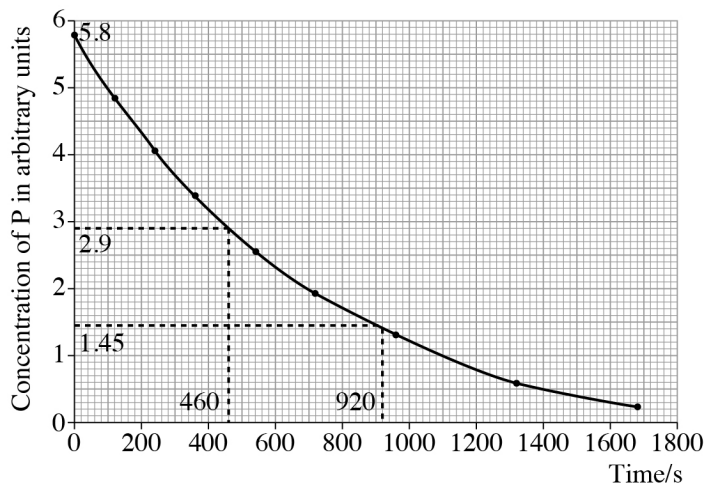
11A.2 Rate equations, rate constants and orders of reaction

- 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) $\text{Rate} = k[\text{R}]^2[\text{T}]$ or $\text{rate} = k[\text{R}]^2[\text{T}][\text{S}]^0$.
 - (c) 3

11A.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) $1.7 \times 10^{-4} \text{ mol dm}^{-3}$.

(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 $t = 800 \text{ s}$. Determine the gradient of the tangent.

- 2 (a) (i) First order with respect to Br^- . As $[\text{Br}^-]$ triples from experiments 1 to 3, the rate also triples.
 (ii) First order with respect to BrO_3^- . As $[\text{BrO}_3^-]$ doubles from experiments 1 to 2, the rate also doubles.
 (iii) Second order with respect to H^+ . As $[\text{H}^+]$ doubles from experiments 2 to 4, the rate quadruples.

(b) Rate = $k[\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$

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

11A.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) $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
 (b) $\text{Rate} = k[\text{Cl}_2]$.
 (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 $\text{S}_{\text{N}}2$ 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:
 $\text{rate} = k[\text{CH}_3\text{Cl}][\text{OH}^-]$.
 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 $[\text{OH}^-]$ effectively remains constant. The rate equation then becomes:
 $\text{rate} = k[\text{CH}_3\text{Cl}]$.
 This is consistent with a first order reaction overall.
 Such reactions are known as *pseudo* first order reactions.
- 5 (a) Step 1 is the rate-determining step since one molecule of HBr and one molecule of O_2 appear in the rate equation.
 (b) $4\text{HBr} + \text{O}_2 \rightarrow 2\text{Br}_2 + 2\text{H}_2\text{O}$

11A.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.

11A.6 Effect of temperature on the rate constant

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

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 been shown to be a reasonable assumption.

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

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

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

Subtracting Equation 1 from Equation 2 gives:

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

$$E_a = 22956 \text{ J mol}^{-1} \text{ or } 23.0 \text{ kJ mol}^{-1} \text{ (to 3 significant figures).}$$

Topic 11 Exam Practice

- 1 A
- 2 C
- 3 B
- 4 D
- 5 A
- 6 (a) $k = \frac{\text{rate}}{[\text{CH}_3\text{COCH}_3][\text{H}^+]} = \frac{1.43 \times 10^{-6}}{0.400 \times 0.200} (1) = 1.79 \times 10^{-5} (1) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} (1).$
 (b) There will be no change in the rate of reaction (1) since the reaction is zero order with respect to iodine (1).

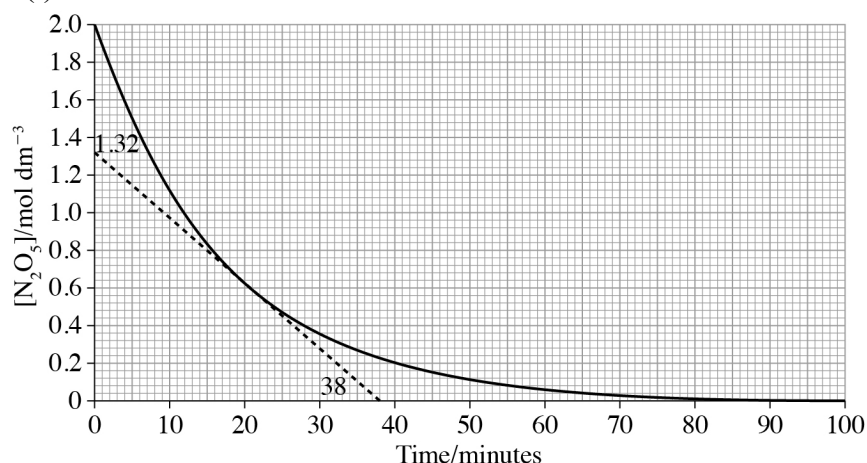
- (c) Step 1 could be the rate-determining step (1) since one molecule of CH_3COCH_3 and one H^+ ion appear in it (1) and this agrees with the experimentally determined orders of reaction (1).

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).

- 7 (a) The slowest step in the mechanism for the overall reaction (1).
 (b) (i) $\text{H}_2(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{HI}(\text{g})$ (1).
 (ii) $\text{HI}(\text{g}) + \text{ICl}(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{I}_2(\text{g})$ (1).
 (c) (i) A: first order; in experiments 1 and 4, $[\text{A}]$ doubles and rate doubles (1).
 B: zero order; in experiments 1 and 2, $[\text{B}]$ doubles but rate does not change (1).
 C: second order; in experiments 1 and 3; $[\text{C}]$ doubles and rate quadruples (1).
 (ii) $\text{Rate} = k[\text{A}][\text{C}]^2$ (1).
 (iii) B (since it is zero order) (1).

- 8 (a) (i)



20 minutes

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

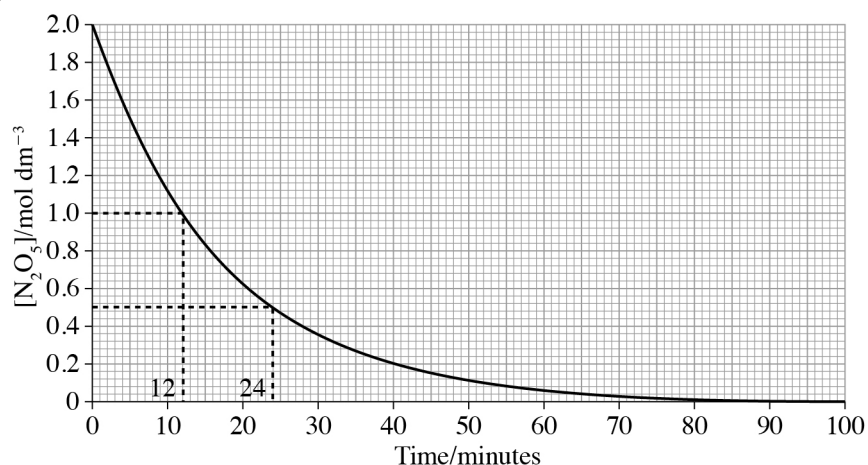
Gradient calculated (1) (e.g. $\frac{1.32}{38} = 0.035 \text{ mol dm}^{-3} \text{ min}^{-1}$).

90 minutes

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

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

(b) (i)

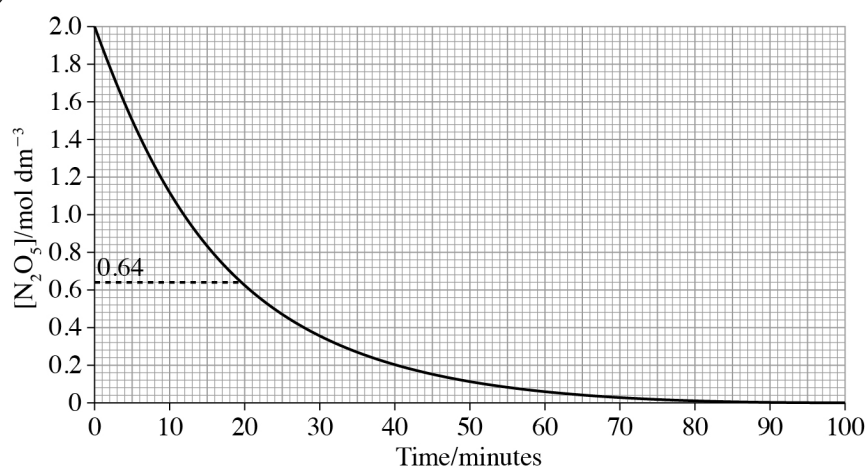


1 mark for each half-life drawn (2).

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

(iii) $\text{Rate} = k[\text{N}_2\text{O}_5]$ (1).

(c) (i)

 $[\text{N}_2\text{O}_5]$ at 20 minutes = 0.64 mol dm^{-3} (1).

$$k = \frac{\text{rate}}{[\text{N}_2\text{O}_5]} = \frac{0.035}{0.64} = 0.55(1) \text{ s}^{-1} (1).$$

(ii) $\text{Rate} = 0.55 \times 1.50 = 0.82 (1) \text{ mol dm}^{-3} \text{ min}^{-1} (1).$

Topic 11 Kinetics

Answers

- 9 (a) (i) $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ (1)
 (ii) $\text{Rate} = k[\text{NO}_2]^2$ (1).
- (b) (i) $\text{Gradient of line} = -\frac{(8.5 - 1.1)}{(1.52 - 1.00) \times 10^{-2}} = -1423(.076923)$ (1).
 $-\frac{E_a}{R} = -1423.076923$ (1).
 $E_a = 8.31 \times 1423.076923 = 11825(.76923) \text{ J mol}^{-1}$ (1)
 $= 12\,000 \text{ J mol}^{-1}$ or 12 kJ mol^{-1} (1) (final answer to 2 significant figures)
- (ii) $[\text{NO}_2] = (4.00 \div 2.00) = 2.00 \text{ mol dm}^{-3}$ (1).
 $12.64 = k \times (2.00)^2$ (1).
 $k = 3.16 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1) (units must be included).

Topic 12 Entropy and energetics

12A Entropy

12A.1 Introduction to entropy

- 1
 - (a) $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
Decrease, as the molecules in a liquid have less freedom of movement than those in a gas.
 - (b) $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$
Increase, as the molecules in a gas have more freedom of movement than those in a solid.
 - (c) $\text{Na}(\text{l}) \rightarrow \text{Na}(\text{s})$
Decrease, as the molecules in a solid have less freedom of movement than those in a liquid.
- 2 ice at -10°C ; water at 30°C ; steam at 110°C

12A.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

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

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

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

12A.3 Understanding entropy changes

- 1
 - (a) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightarrow \text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l})$
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) $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
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) $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$
Decrease in entropy. There is a decrease in the number of moles from 1.5 to 1.
 - (d) $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + \text{EDTA}^{2-}(\text{aq}) \rightarrow \text{Co}(\text{EDTA})(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
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) The entropy change for the system also includes the number of ways that the quanta of energy can be distributed between the molecules for both the reactants and products. This is different for hydrogen iodide molecules than for hydrogen and iodine molecules.

12B Lattice energy

12B.1 Lattice energy, $\Delta_{\text{lattice}}H$, and Born-Haber cycles

- 1
 - (a) Na^+ has a smaller ionic radius than K^+ , and F^- has a smaller ionic radius than Cl^- , so the inter-ionic distance between the ions is smaller for Na^+F^- . Therefore, the electrostatic forces of attraction between the Na^+ and F^- ions are stronger than those between K^+ and Cl^- .
 - (b) The inter-ionic distance between Ca^{2+} and O^{2-} (0.240 nm) is similar to the inter-ionic distance between K^+ and F^- (0.271 nm). However, the product of the ionic charges for $\text{Ca}^{2+}\text{O}^{2-}$ ($2 \times 2 = 4$), is four times larger than the product of the ionic charges for K^+F^- ($1 \times 1 = 2$).
- 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) $\text{Mg}^{2+}(\text{g})$ and $\text{O}^{2-}(\text{g})$.
 - (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) $\Delta_{\text{lattice}}H[\text{MgO}(\text{s})] = -148 - 738 - 1451 - 249 - 657 - 602 \text{ kJ mol}^{-1}$
 $= -3845 \text{ kJ mol}^{-1}$.

- (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.

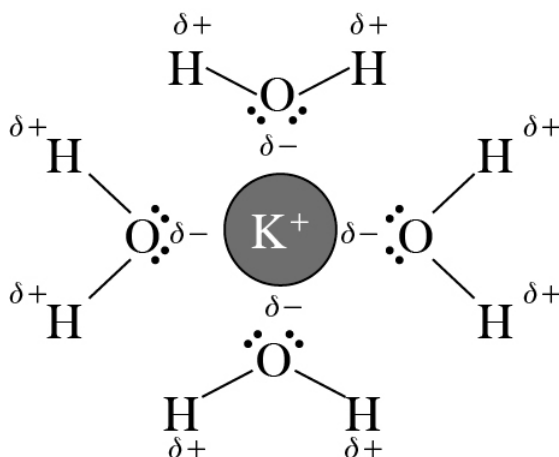
12B.2 Experimental and theoretical lattice energies

- We base calculations of theoretical lattice energies 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.
- The cation attracts the electrons in the anion and this leads to a distortion of the electron cloud of the anion.
 - 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.
 - The charge density of each cation is:

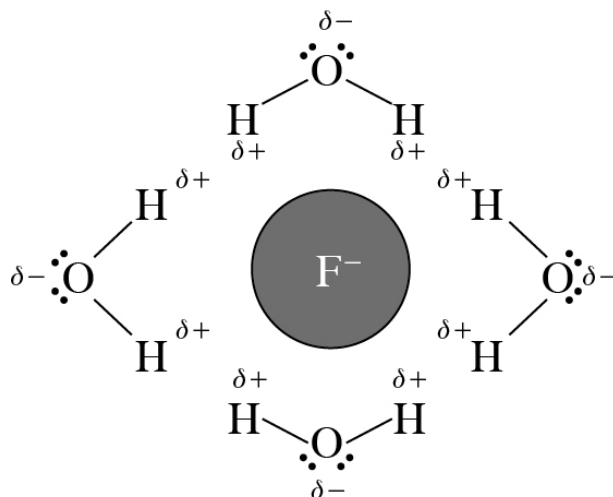
$$\text{Mg}^{2+} \frac{2}{0.072^2} = 386 \quad \text{Al}^{3+} \frac{3}{0.053^2} = 1068 \quad \text{Li}^+ \frac{1}{0.074^2} = 183$$

$$\text{Na}^+ \frac{1}{0.102^2} = 96 \quad \text{Ca}^{2+} \frac{2}{0.100^2} = 200 \quad \text{K}^+ \frac{1}{0.138^2} = 53$$
 The larger the charge density, the greater the polarising power.
 So, the order of increasing polarising power is $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Li}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$.
- 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 $\text{Na}^{2+}\text{O}^{2-}$, so formation of the compound is likely to be highly endothermic.

12B.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 $\Delta_{\text{sol}}H [\text{Mg}^{2+}(\text{Cl}^-)_2(\text{s})] + \Delta_{\text{lattice}}H [\text{Mg}^{2+}(\text{Cl}^-)_2(\text{s})] = \Delta_{\text{hyd}}H [\text{Mg}^{2+}(\text{g})] + 2 \times \Delta_{\text{hyd}}H [\text{Cl}^-(\text{g})].$

$\Delta_{\text{hyd}}H [\text{Cl}^-(\text{g})] = \frac{1}{2}(-155 + (-2493) - (-1920)) = -364 \text{ kJ mol}^{-1}.$

- 3 (a) $\text{Li}^+(\text{aq}) + \text{F}^-(\text{aq}).$
(b) The lattice energy of lithium fluoride.
(c) $\Delta_{\text{sol}}H = \Delta H_2 - \Delta H_1.$
(d) $\Delta_{\text{sol}}H = -1018 - (-1031) = +13 \text{ kJ mol}^{-1}.$

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

Topic 12 Exam Practice

- 1 C
- 2 B
- 3 C
- 4 D
- 5 B
- 6 B
- 7 (a) (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).
 (b) $\text{Mg}^{2+}(\text{g}) (1) + \text{O}^{2-}(\text{g}) (1)$
 (c) Energy is required to overcome the repulsion (1) between the O^- ion and the electron being added (1).
 (d)

$$\Delta_{\text{lattice}} H[\text{Mg}^{2+}\text{O}^{2-}(\text{s})] = \Delta H_3 - \Delta H_2 - \Delta H_1 - IE_2[\text{Mg}(\text{g})] - \Delta_{\text{at}} H[\text{O}_2(\text{g})] - (E_{\text{ea}(1)}[\text{O}(\text{g})] + E_{\text{ea}(2)}[\text{O}(\text{g})])$$

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

$$= -3842 \text{ kJ mol}^{-1} (1).$$
- 8 (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) $(\Delta_{\text{soln}}H = \Delta_{\text{hyd}}H - \Delta_{\text{lattice}}H)$

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

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

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

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

All four calculations correct (1).

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

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

- 9 (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) $\Delta S_{\text{system}} = (27.0 + 214 - 65.7) = +175.3 \text{ J K}^{-1} \text{ mol}^{-1} / 0.1753 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (1).

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

$$= (117 - (298 \times 0.1753)) = 64.8 \text{ kJ mol}^{-1} (1).$$

As ΔG^{\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 $\Delta G^{\ominus} = 0$, $T\Delta S_{\text{system}} = \Delta H^{\ominus}$ (1).

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

- 10 (a) (i) $\Delta S^{\ominus}_{\text{system}} = (69.9 - 131 - (\frac{1}{2} \times 205))(1) = -163.6 \text{ J K}^{-1} \text{ mol}^{-1} (1).$

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

$$\begin{aligned} \text{(iii)} \quad \Delta S^{\ominus}_{\text{total}} &= (-163.6 + 958.1) = +794.5 \text{ J K}^{-1} \text{ mol}^{-1} (1). \\ &= +795 \text{ J K}^{-1} \text{ mol}^{-1} (2). \end{aligned}$$

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

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

- 11 (a) 100 kPa / 1 bar (1).

(b)

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

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

$$\begin{aligned} \text{(c)} \quad \Delta S^{\ominus}_{\text{system}}(700 \text{ K}) &= \Delta S^{\ominus}_{\text{total}}(700 \text{ K}) - \Delta S^{\ominus}_{\text{surroundings}}(700 \text{ K}) = (-78.7 - 157.4) \\ &= -236.1 \text{ J K}^{-1} \text{ mol}^{-1} (2). \end{aligned}$$

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

- (d) Since $\Delta S^{\ominus}_{\text{total}}(700 \text{ K})$ 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).

Topic 13 Chemical equilibria

13A Chemical equilibria

13A.1 Equilibrium constant, K_c

- 1 (a)
$$\frac{[\text{CH}_3\text{OH}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^2}$$
- (b)
$$\frac{2.6 \times 10^{-5}}{3.1 \times 10^{-3} \times (2.4 \times 10^{-2})^2} = 14.6 \text{ dm}^6 \text{ mol}^{-2}.$$

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

- 2 (a)
$$\frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{CH}_3\text{COOH}(\text{l})][\text{CH}_3\text{CH}_2\text{OH}(\text{l})]}$$
- (b) $n(\text{ethanol}) = (12.5 - 5.0) = 7.5 \text{ mol}.$
 $n(\text{ethyl ethanoate}) = 5.0 \text{ mol}.$
 $n(\text{water}) = 5.0 \text{ mol}.$
- (c)
$$\frac{(5.0 / V) \times (5.0 / V)}{(1.0 / V) \times (7.5 / V)} = 3.3 \text{ and no units}.$$

Note: It is essential to show the division by the volume, $V \text{ dm}^3$, even though they cancel, to show you have understood that the terms in the expression are concentrations. Also, as the question demands that you state the units, if any, it is essential to state that there are no units. 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 $n(\text{I}_2) \text{ at equilibrium} = (0.20 - 0.16) = 0.04 \text{ mol}.$
 $n(\text{HI}) \text{ at equilibrium} = (2 \times 0.16) = 0.32 \text{ mol}.$

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

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

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.

$$(b) \quad K_c = \frac{[\text{NO}(\text{g})]^2}{[\text{N}_2(\text{g})][\text{O}_2(\text{g})]} = 4.8 \times 10^{-31}.$$

$$\begin{aligned} [\text{O}_2(\text{g})] &= \frac{[\text{NO}(\text{g})]^2}{[\text{N}_2(\text{g})](4.8 \times 10^{-31})} \\ &= \frac{(4.0 \times 10^{-16} / 1.2)^2}{(1.1 / 1.2)(4.8 \times 10^{-31})} = 0.25 \text{ mol dm}^{-3}. \end{aligned}$$

$$5 \quad K_c = \frac{[\text{H}_2(\text{g})][\text{CO}(\text{g})]}{[\text{H}_2\text{O}(\text{g})]} = 4.92 \times 10^{-5} \text{ mol dm}^{-3}.$$

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

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

$$y = (4.92 \times 10^{-5} \times 2.00 \times 10^{-2})^{1/2} = 9.92 \times 10^{-4}.$$

$$[\text{H}_2(\text{g})] = [\text{CO}(\text{g})] = 9.92 \times 10^{-4} \text{ mol dm}^{-3}.$$

13A.2 Equilibrium constant, K_p

$$1 \quad (a) \quad K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2(p_{\text{SO}_2})}$$

$$(b) \quad \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2(p_{\text{SO}_2})} = 3.00 \times 10^4 \text{ atm}.$$

$$\begin{aligned} p_{\text{SO}_3} &= (3.00 \times 10^4 \times 0.100^2 \times 0.500)^{1/2} \text{ atm} \\ &= 12.2 \text{ atm (to 3 significant figures)} \end{aligned}$$

$$\text{Percentage of } \text{SO}_3 \text{ present} = \left(\frac{12.2}{12.2 + 0.1 + 0.5} \right) \times 100 = 95.3\%.$$

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

$$\begin{aligned} (b) \quad K_p &= \frac{(p_{\text{COCl}_2})}{(p_{\text{CO}})(p_{\text{Cl}_2})} \\ &= \frac{4.08 \times 10^{-10}}{2.47 \times 10^{-8} \times 2.47 \times 10^{-8}} \text{ atm}^{-1} \\ &= 6.69 \times 10^5 \text{ atm}^{-1} \end{aligned}$$

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

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

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

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

13A.3 Factors affecting equilibrium constants 1

- 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 exothermic.
- 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.

13A.4 Factors affecting equilibrium constants 2

- 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.

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

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 $\frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{CH}_3\text{COOH}(\text{l})][\text{CH}_3\text{CH}_2\text{OH}(\text{l})]}$. 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.

$$3 \quad K_p = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

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 $\frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$ will not alter, since the increase in

$[\text{HI}(\text{g})]^2$ will be the same as the increase in $[\text{H}_2(\text{g})][\text{I}_2(\text{g})]$.

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

13A.5 Relating entropy to equilibrium constants

$$1 \quad (a) \quad \Delta S_{\text{total}} = R \ln K = 8.31 \ln 8.54 = +17.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$(b) \quad 17.8 = 225 - \frac{206.1 \times 1000}{T}$$

$$T = 995 \text{ K}$$

- (c) Since $\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$, $\Delta S_{\text{surroundings}}$ becomes less negative as temperature increases.

Since $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$, ΔS_{total} becomes more positive/increases.

As ΔS_{total} increases the value of the equilibrium constant increases.

- 2 (a) Green solution turns yellow/orange/brown.

A grey/black precipitate/solid is formed.

$$(b) \quad (i) \quad \Delta S_{\text{total}} = R \ln K$$

$$47.64 = 8.31 \ln K$$

$$\ln K = (47.64 \div 8.31) = 5.73285 \dots$$

$$K = e^{5.73285 \dots} = 309 \text{ (to 3 sig fig)}$$

- (ii) Two moles of solution react to form one mole of solution and one mole of solid. Hence, the products are more ordered than the reactants.

$$\begin{aligned}
 \text{(iii)} \quad \Delta S^{\ominus}_{\text{surroundings}} &= \Delta S^{\ominus}_{\text{total}} - \Delta S^{\ominus}_{\text{system}} \\
 &= +47.64 - 208.3 \\
 &= +255.9 \text{ J mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{(iv)} \quad \Delta H^{\ominus} &= -\Delta S^{\ominus}_{\text{surroundings}} \times T \\
 &= -255.9 \times 298 = -76258.2 \text{ J mol}^{-1} \\
 &= -76.3 \text{ kJ mol}^{-1} \text{ (to 3 s.f.)}
 \end{aligned}$$

As T increases, $\Delta S_{\text{surroundings}}$ becomes less positive/decreases, therefore ΔS_{total} becomes less positive/decreases.

Topic 13 Exam Practice

- 1 B
- 2 C
- 3 D
- 4 C
- 5 D
- 6 C

$$7 \quad \text{(i)} \quad [\text{N}_2] = \frac{1.00}{20.0} = 0.0500 \text{ mol dm}^{-3} (1).$$

$$[\text{H}_2] = \frac{2.00}{20.0} = 0.100 \text{ mol dm}^{-3} (1).$$

$$[\text{NH}_3] = \frac{1.00}{20.0} = 0.0500 \text{ mol dm}^{-3} (1).$$

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

$$\text{(ii)} \quad p_{\text{N}_2} = \frac{1.00}{4.00} \times 5.00 = 1.25 \text{ atm} (1).$$

$$p_{\text{H}_2} = \frac{2.00}{4.00} \times 5.00 = 2.50 \text{ atm} (1).$$

$$p_{\text{NH}_3} = \frac{1.00}{4.00} \times 5.00 = 1.25 \text{ atm} (1).$$

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

$$8 \quad \text{(a)} \quad \text{(i)} \quad K_p = \frac{(p_{\text{PCl}_3})(p_{\text{Cl}_2})}{(p_{\text{PCl}_5})} (1).$$

$$\text{(ii)} \quad \text{atm} (1).$$

- (b) p_{PCl_5} , p_{PCl_3} and p_{Cl_2} all instantaneously increase by the same amount (1).
However, the value of $p_{\text{PCl}_3} \times p_{\text{Cl}_2}$ increases more than that of p_{PCl_5} (1).

Since the magnitude of $\frac{(p_{\text{PCl}_3})(p_{\text{Cl}_2})}{(p_{\text{PCl}_5})}$ has to be constant at a given

temperature (1), the equilibrium position moves to the left to decrease the value of $p_{\text{PCl}_3} \times p_{\text{Cl}_2}$ and increase the value of p_{PCl_5} until a new equilibrium is established (1).

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

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

$$= 0.0195 (1).$$

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

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

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

Partial pressures:

$P = 250 \text{ atm}$; $Q = 125 \text{ atm}$; $R = 125 \text{ atm}$ (1).

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

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

- (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).

10 (a) (i) $K_c = \frac{[\text{HI(g)}]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} (1)$

(ii) 3.5 hours (1).

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

$[\text{H}_2(\text{g})] = [\text{I}_2(\text{g})] = 3.00 \times 10^{-4} \text{ mol}$ (1).

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

$= 132$ 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 $[\text{HI(g)}]$ while decreasing $[\text{H}_2(\text{g})]$ and $[\text{I}_2(\text{g})]$ (1).

$$11 \quad (a) K_p = \frac{(p\text{CO})(p\text{H}_2)^2}{(p\text{CH}_4)(p\text{H}_2\text{O})} \quad (1)$$

4 correct partial pressures (3)

$$p\text{CH}_4 = 0.25 \quad p\text{H}_2\text{O} = 0.25 \quad p\text{CO} = 0.375 \quad p\text{H}_2 = 1.125$$

$$K_p = \frac{(0.375)(1.125)^2}{(0.25)(0.25)} = 8.54 \text{ atm}^2 \quad (1) \text{ for value of } K_p \quad (1) \text{ for units}$$

$$\begin{aligned} (b) \Delta S^\ominus_{\text{total}} &= R \ln K_p \\ &= 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln(8.54) \\ &= 8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times 2.14 \\ &= 17.8 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

Topic 14 Acid–base equilibria

14A Strong and weak acids

14A.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

<ol style="list-style-type: none"> (a) Pair 1: H_2CO_3 and HCO_3^- Pair 2: H_3O^+ and H_2O (b) Pair 1: HCO_3^- and CO_3^{2-} Pair 2: H_3O^+ and H_2O (c) Pair 1: HNO_3 and NO_3^{2-} Pair 2: CH_3COOH and $\text{CH}_3\text{COOH}_2^+$ acid. 	H_2CO_3 is acting as the acid. H_3O^+ is acting as the acid. HCO_3^- is acting as the acid. H_3O^+ is acting as the acid. HNO_3 is acting as the acid. $\text{CH}_3\text{COOH}_2^+$ 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.

14A.2 Hydrogen ion concentration and the pH scale

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

- 2 5 cm³ of 1.00 mol dm⁻³ NaOH reacts with 5 cm³ of 1.00 mol dm⁻³ HCl.
 So, 15 cm³ of 1.00 mol dm⁻³ HCl is in excess.
 $n(\text{HCl})$ in excess = $(15 \times 1.00) \div 1000 = 0.015$ mol.
 $[\text{H}^+(\text{aq})] = (0.015 \div 25) \times 1000 = 0.60$ mol dm⁻³.
 $\text{pH} = -\lg(0.60) = 0.22$.

- 3 (a) $[\text{H}^+(\text{aq})] = (0.100 \times 1.60 \times 10^{-4})^{1/2} = 4.00 \times 10^{-3}$ mol dm⁻³.
 $\text{pH} = -\lg(4.00 \times 10^{-3}) = 2.40$.
 (b) $[\text{H}^+(\text{aq})] = (1.00 \times 5.62 \times 10^{-4})^{1/2} = 2.37 \times 10^{-2}$ mol dm⁻³.
 $\text{pH} = -\lg(2.37 \times 10^{-2}) = 1.63$.
 (c) $[\text{H}^+(\text{aq})] = (0.505 \times 5.62 \times 10^{-10})^{1/2} = 1.68 \times 10^{-5}$ mol dm⁻³.
 $\text{pH} = -\lg(1.68 \times 10^{-5}) = 4.77$.

- 4 $[\text{H}^+(\text{aq})] = 10^{-4.97} = 1.07 \times 10^{-5}$ mol dm⁻³.
 $K_a = \frac{(1.07 \times 10^{-5})^2}{0.0305} = 3.75 \times 10^{-9}$ mol dm⁻³.

14A.3 Ionic product of water, K_w

- 1 (a) (i) $[\text{H}^+(\text{aq})] = (1 \times 10^{-14})^{1/2} = 1 \times 10^{-7}$ mol dm⁻³.
 $\text{pH} = -\lg(1 \times 10^{-7}) = 7.00$.
 (ii) $[\text{H}^+(\text{aq})] = (6.81 \times 10^{-14})^{1/2} = 2.63 \times 10^{-7}$ mol dm⁻³.
 $\text{pH} = -\lg(2.63 \times 10^{-7}) = 6.58$.
 (b) $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$ in pure water regardless of the temperature.
 (c) $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$
 $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$.
 As the temperature decreases, K_w increases. So the equilibrium shifts to the right. The forward reaction is therefore exothermic.
- 2 (a) $[\text{OH}^-(\text{aq})] = 0.0100$ mol dm⁻³.
 $\text{pOH} = -\lg(0.0100) = 2.00$.
 $\text{pH} = (14.00 - 2.00) = 12.00$.
 (b) $[\text{OH}^-(\text{aq})] = 0.100$ mol dm⁻³ (2×0.0500 since, $\text{Ca}(\text{OH})_2(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$).
 $\text{pOH} = -\lg(0.100) = 1.00$.
 $\text{pH} = (14.00 - 1.00) = 13.00$.
 (c) $[\text{OH}^-(\text{aq})] = 0.0315$ mol dm⁻³.
 $\text{pOH} = -\lg(0.0315) = 1.50$.
 $\text{pH} = (14.00 - 1.50) = 12.50$.

14A.4 Analysing data from pH measurements

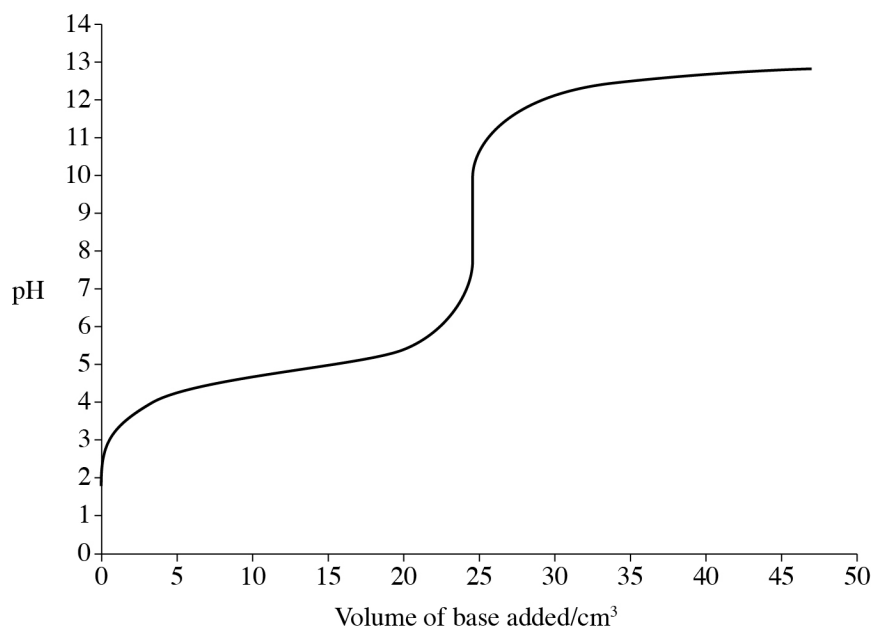
- 1
 - (a) Acidic. NH_4NO_3 is a salt of a strong acid (HNO_3) and a weak base (NH_3).
 - (b) Alkaline. $\text{CH}_3\text{CH}_2\text{COOK}$ is a salt of a weak acid ($\text{CH}_3\text{CH}_2\text{COOH}$) and a strong base (KOH).
 - (c) Neutral. NaNO_3 is a salt of a strong acid (HNO_3) and a strong base (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} .
 $n(\text{CH}_2\text{ClCOOH}) = (1.89 \text{ g} \div 94.5 \text{ g mol}^{-1}) = 0.02 \text{ mol}$.
 $[\text{CH}_2\text{ClCOOH}(\text{aq})] = (0.0200 \times 1000/250) = 0.08 \text{ mol dm}^{-3}$.
 $[\text{H}^+(\text{aq})] = 10^{-1.99} = 1.02 \times 10^{-2} \text{ mol dm}^{-3}$.

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

14B Acid–base titrations

14B.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 .
 $n(\text{HCl}) = n(\text{NH}_3) = (0.0250 \times 0.0200) = 5.00 \times 10^{-4} \text{ mol}$.
 $[\text{NH}_3(\text{aq})] = 5.00 \times 10^{-4} \text{ mol} \times 1000/15 \text{ dm}^3 = 0.033 \text{ mol dm}^{-3}$.
 - (c) Methyl red.
 The pH range of methyl red falls within the sharp rise of the pH curve.
- 2
 - (a) $[\text{H}^+(\text{aq})] = (0.100 \times 1.74 \times 10^{-5})^{1/2} = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$.
 $\text{pH} = -\lg(1.32 \times 10^{-3}) = 2.88$.



(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 cm³.

14B.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:
- $$\text{HCOO}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HCOOH}(\text{aq})$$
- When base is added, the hydroxide ions added are removed as they react with the methanoic acid molecules:
- $$\text{HCOOH}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{HCOO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- 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:
- $$\text{pH} = \text{p}K_{\text{a}} + \lg \frac{[\text{HCOO}^-(\text{aq})]}{[\text{HCOOH}(\text{aq})]}$$
- (c) $[\text{HCOO}^-(\text{aq})]$ will increase with the addition of solid sodium methanoate.
- The pH will increase, since $\lg \frac{[\text{HCOO}^-(\text{aq})]}{[\text{HCOOH}(\text{aq})]}$ increases.
- (d) $\text{p}K_{\text{a}} = -\lg 1.79 \times 10^{-4} = 3.75$.
- $$\begin{aligned} \text{pH} &= \text{p}K_{\text{a}} + \lg \frac{[\text{HCOO}^-(\text{aq})]}{[\text{HCOOH}(\text{aq})]} \\ &= 3.75 + \lg \frac{0.500}{1.00} \\ &= 3.75 + (-0.30) \\ &= 3.45. \end{aligned}$$
- 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, $\text{CH}_3\text{COO}^-(\text{aq})$, and leaves some unreacted ethanoic acid molecules, CH_3COOH .
- $$\text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$$
- 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 $[\text{H}^+(\text{aq})]$ in the buffer $= 10^{-9.55} = 2.82 \times 10^{-10} \text{ mol dm}^{-3}$.
 $[\text{NH}_3(\text{aq})]$ in the buffer $= 0.100 \text{ mol dm}^{-3}$ ($0.200 \div 2$, as the original solution has been diluted by a factor of 2).
 $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}^+(\text{aq})$

$$K_a = \frac{[\text{NH}_3(\text{aq})][\text{H}^+(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

$$[\text{NH}_4^+(\text{aq})] \text{ in the buffer} = \frac{[\text{NH}_3(\text{aq})][\text{H}^+(\text{aq})]}{K_a}$$

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

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

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

4 Molar mass of $\text{C}_6\text{H}_5\text{COOH}$ is 122.0 g mol^{-1} .
 $n(\text{C}_6\text{H}_5\text{COOH}) = (12.20 \div 122.0) = 0.100 \text{ mol}$.
 Molar mass of $\text{C}_6\text{H}_5\text{COONa}$ is 144.0 g mol^{-1} .
 $n(\text{C}_6\text{H}_5\text{COONa}) = (7.20 \div 144.0) = 0.0500 \text{ mol}$.

$$\text{pH} = \text{p}K_a + \lg \frac{0.0500 / 1.00}{0.100 / 1.00}$$

$$= 4.20 + \lg 0.500$$

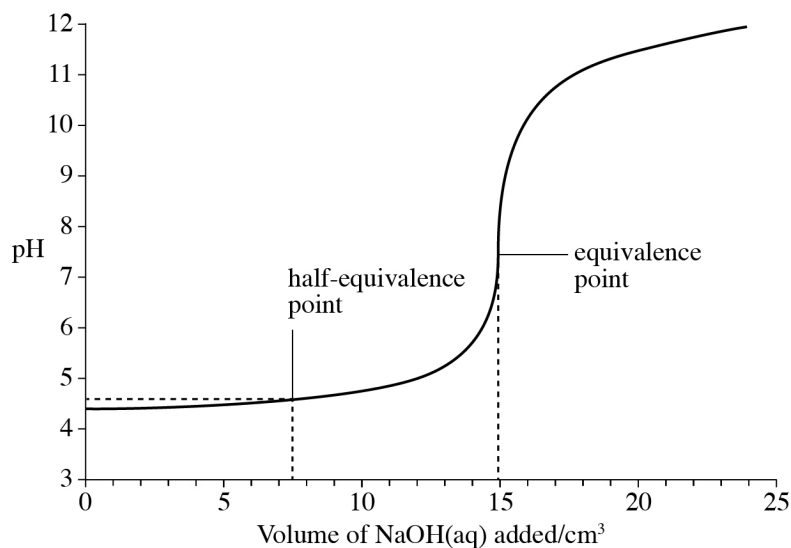
$$= 4.20 + (-0.30)$$

$$= 3.90.$$

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.

14B.3 Buffer solutions and pH curves

- 1 (a) Buffer solution (1)
 (b) This part of the graph is fairly flat (1) so the addition of acid is having very little effect of the pH of the solution (1)

2 $pK_a = 4.6$ 

The pK_a value is equal to the pH of the solution at the half-equivalence point.

The equivalence point is obtained when 15 cm³ of NaOH is added.

The pH of the solution when 7.5 cm³ is added is 4.6

Topic 14 Exam Practice

- 1 C
- 2 A
- 3 C
- 4 A
- 5 D

- 6 (a) $pH = -\lg(2.50 \times 10^{-4}) (1) = 3.60 (1).$
- (b) (i) $HA + NaOH \rightarrow NaA + H_2O$
 or $HA + OH^- \rightarrow A^- + H_2O (1)$
- (ii) $n(NaOH) = n(HA) \text{ in } 25 \text{ cm}^3 = 0.02670 \times 0.0100 = 2.67 \times 10^{-4} \text{ mol}$
 (1).
 $[HA] = (2.67 \times 10^{-4} \times 1000/25) \text{ mol dm}^{-3} (1) = 1.07 \times 10^{-2} \text{ mol}$
 $\text{dm}^{-3} (1).$
- (iii) $1.07 \times 10^{-2} \approx 2.50 \times 10^{-4} (1)$ 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) $K_a = \frac{[H^+(aq)][A^-(aq)]}{[HA(aq)]} (1)$

$$\begin{aligned}
 \text{(iii)} \quad [\text{HA}(\text{aq})] &= \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{K_a} \quad (1) \\
 &= \frac{(2.50 \times 10^{-4})^2}{6.00 \times 10^{-5}} = 1.04 \times 10^{-3} \text{ mol dm}^{-3} \quad (1)
 \end{aligned}$$

- 7 (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 $\frac{[\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$ remains fairly constant and hence the pH

remains fairly constant (since $\text{pH} = \text{p}K_a + \lg \frac{[\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$ and $\text{p}K_a$ is constant) (1).

$$\text{(c)} \quad \text{pH} = \text{p}K_a + \lg \frac{[\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]} \quad (1).$$

When the acid is half-reacted $[\text{CH}_3\text{COOH}(\text{aq})] = [\text{CH}_3\text{COO}^-(\text{aq})]$, so

$$\lg \frac{[\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]} = 0 \quad (1).$$

Hence, $\text{pH} = \text{p}K_a = 4.77$ (1).

- 8 (a) At 298 K, $[\text{H}^+(\text{aq})] = (1.00 \times 10^{-14})^{1/2} = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$ (1).
 $\text{pH} = -\lg (1.00 \times 10^{-7}) = 7.00$ (1).
 At 323 K, $[\text{H}^+(\text{aq})] = (5.48 \times 10^{-14})^{1/2} = 2.34 \times 10^{-7} \text{ mol dm}^{-3}$ (1).
 $\text{pH} = -\lg (2.34 \times 10^{-7}) = 6.63$ (1).
- (b) Pure water is neutral because $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$ (1). The pH of pure water is temperature dependent, so does not always have a value of 7 (1).
- (c) As temperature increases, $[\text{H}^+(\text{aq})]$ increases, so 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).

- 9 (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: $\text{C}_6\text{H}_5\text{COOH}$ (1).
(ii) HF is stronger than $\text{C}_6\text{H}_5\text{COOH}$ (1). As the equilibrium of equation 1 is well over to the right-hand side, HF is a better proton donor than $\text{C}_6\text{H}_5\text{COOH}$ (1).
 $\text{C}_6\text{H}_5\text{COOH}$ is stronger than HCN (1). As the equilibrium of equation 1 is well over to the right-hand side, $\text{C}_6\text{H}_5\text{COOH}$ is a better proton donor than HCN (1).
- (c) (i) Acidic (1); $[\text{NH}_4^+]$ increases and it is an acid since it is a proton donor (1).
(ii) Basic (1); $[\text{NH}_2^-]$ increases and it is a base since it is a proton acceptor (1).
- 10 (a) $\text{p}K_{\text{a}(1)} = -\lg(1.20 \times 10^{-2}) = 1.92$ (1)
(b) $[\text{H}^+(\text{aq})] = (1.20 \times 10^{-2} \times 0.500)^{1/2}$ (1) $= 7.75 \times 10^{-2} \text{ mol dm}^{-3}$ (1)
 $\text{pH} = -\lg(7.75 \times 10^{-2}) = 1.11$ (1)
(c) HSO_3^- partially dissociates into ions and this increases $[\text{H}^+(\text{aq})]$ (1).
(d) (i) Ionic product (of water) *or* autoprotolysis constant (of water) (1).
(ii) $K_{\text{w}} = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$ (1).
(e) $[\text{OH}^-(\text{aq})] = 0.500 \text{ mol dm}^{-3}$ (1).
 $\text{pOH} = -\lg(0.500) = 0.30$ (1).
 $\text{pH} = (14.00 - 0.30) = 13.7(0)$ (1).
- 11 (a) A, phenolphthalein; B, bromophenol blue (2)
(b) There is only a very small change in pH at the equivalence point, so it will be difficult to pass through the complete range of the indicator on the addition of one drop of acid. (1)
(c) $\text{A} - \text{Na}_2\text{CO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaHCO}_3(\text{aq}) + \text{NaCl}(\text{aq})$ (1).
 $\text{B} - \text{NaHCO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ (1).
with a titration of a strong acid against a weak base (1).

Topic 15 Organic chemistry: carbonyls, carboxylic acids and chirality

15A Chirality

15A.1 Chirality and enantiomers

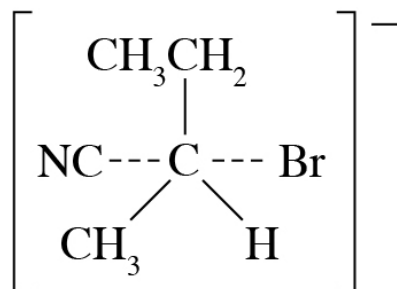
- 1 Two optical isomers or two geometric isomers both have the same molecular and structural formulae but with their atoms and groups arranged differently in three dimensions. With optical isomers, the difference is that the atoms and groups are arranged to form an object and its mirror image. With geometrical 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) One. 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) Two. 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 CH₂Cl, C, H and CHFCH₃). The third carbon atom is also chiral because it is joined to H, F, CH₃ and CH₂ClCHCl.

15A.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.

15A.3 Optical activity and reaction mechanisms

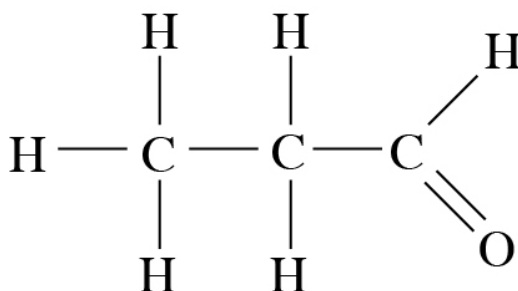
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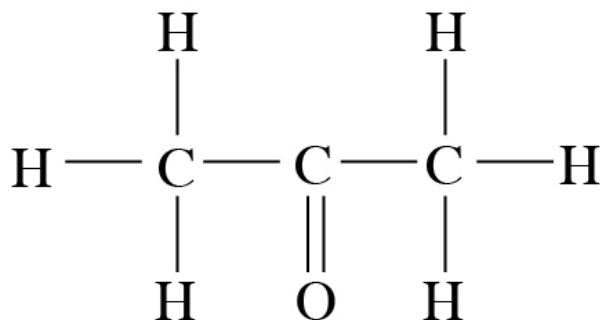
- 2 2-Bromopropane is not a chiral compound and even though the attacking CN^- ion can approach the carbocation from both sides, the resulting products are not chiral. So, neither the reactant nor the product has any optical activity.

15B Carbonyl compounds**15B.1 Carbonyl compounds and their physical properties**

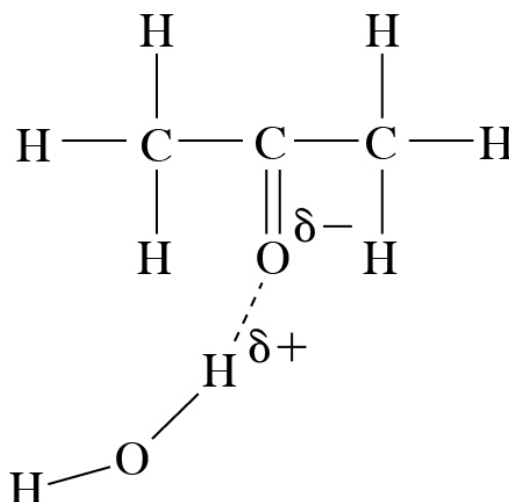
1 (a)



(b)



2



15B.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.

15B.3 Nucleophilic addition reactions

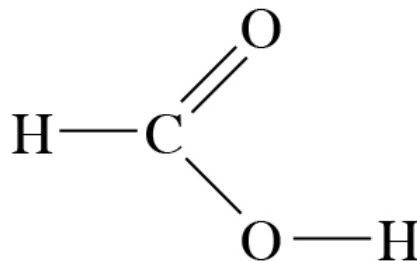
- 1
 - (a) Hydroxyethanenitrile.
 - (b) 2-hydroxy-2-methylpropanenitrile.
- 2

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.

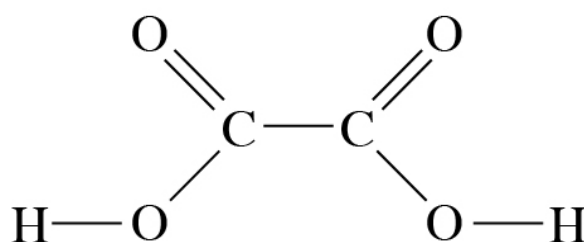
15C Carboxylic acids

15C.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.

15C.2 Preparations and reactions of carboxylic acids

- 1 (a) $(\text{CH}_3)_2\text{CHCH}_2\text{OH} + 2[\text{O}] \rightarrow (\text{CH}_3)_2\text{CHCOOH} + \text{H}_2\text{O}$
 (b) $(\text{CH}_3)_2\text{CHCN} + \text{H}^+ + 2\text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{CHCOOH} + \text{NH}_4^+$
- 2 (a) $(\text{CH}_3)_2\text{CHCOOH} + \text{PCl}_5 \rightarrow (\text{CH}_3)_2\text{CHCOCl} + \text{POCl}_3 + \text{HCl}$
 (b) $(\text{CH}_3)_2\text{CHCOOH} + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3)_2\text{CHCOOCH}_3 + \text{H}_2\text{O}$

15D Carboxylic acid derivatives

15D.1 Carboxylic acid derivatives: acyl chlorides

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

- 2 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3 + \text{HCl}$
- (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl} + \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_3 + \text{HCl}$

15D.2 Carboxylic acid derivatives: esters

- 1 (a) Propyl propanoate.
(b) Methyl 2-methylpropanoate.
- 2 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3 + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^- + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

15D.3 Carboxylic acid derivatives: 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 $[-\text{OCCOOCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{O}-]$

15E Spectroscopy and chromatography

15E.1 Simple chromatography

- 1 The stationary phase is the water in the paper; 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 $R_f = \frac{20}{75} = 0.27$

15E.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.

15E.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.

15E.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-norandrosterone, as they both contain C=O carbonyl groups.

15E.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; it also does not mix with most organic compounds.

15E.6 ^{13}C NMR spectroscopy

- 1 CH_4 has only 1.
 $\text{CH}_3\text{--CH}_3$ has only 1.
 $\text{CH}_3\text{--CH}_2\text{--CH}_3$ has 2.
 $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_3$ has 2.
 $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$ has 3.
 $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$ has 3.
- 2 The four peaks between 110 and 160 ppm are from four carbon atoms in the aromatic ring.
The peak at 190 ppm is from a carbon atom in the ketone group.
The peak at 23 ppm is from a carbon atom in a C–C bond.
The structure of the compound is $\text{CH}_3\text{COC}_6\text{H}_4\text{OH}$.

15E.7 ^1H NMR spectroscopy

- 1 $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_3$ has 3.
 $(\text{CH}_3)_2\text{CH--CH}_2\text{--CH}_3$ has 4.
 $(\text{CH}_3)_4\text{C}$ 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.

15E.8 Splitting patterns in ^1H NMR spectra

- 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 $\text{CH}_3\text{--O}$.
The peak on the right 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 $\text{CH}_3\text{--C=O}$.
The structure that fits these interpretations is $\text{CH}_3\text{--CO--CH}_2\text{--O--CH}_3$
- 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 $\text{CH}_3\text{--CO--}$.
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 $\text{CH}_3\text{--CH--}$.
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 $(\text{CH}_3)_2\text{--CH--}$.
The structure that fits these interpretations is $\text{CH}_3\text{--CO--CH}(\text{CH}_3)_2$

Topic 15 Exam Practice

- 1 D
- 2 D
- 3 B
- 4 C
- 5 C
- 6 B
- 7 (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).

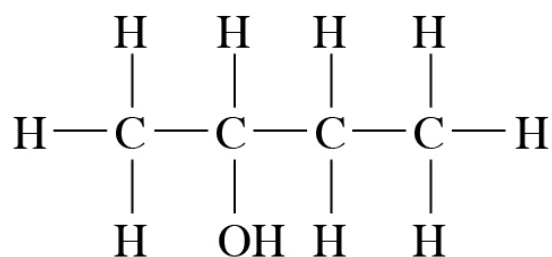
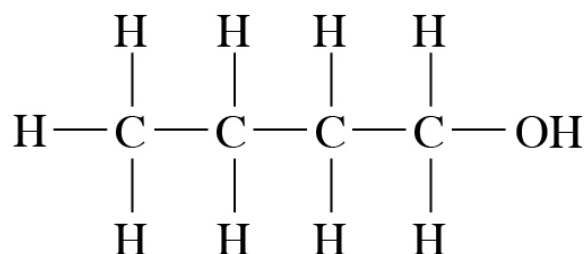
- (c) If compound **A** reacts by an S_N1 mechanism, a planar carbocation intermediate will be formed (1) which will be attacked by OH^- ions in the second step to form an alcohol (1).

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).

- 8 (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)

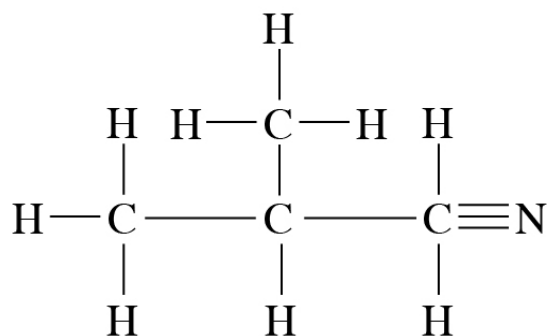


(2)

- (d) $CH_3CH_2CH_2CH_2CHO + [O] \rightarrow CH_3CH_2CH_2CH_2COOH$ (1).
 Silver mirror / black precipitate (1).

- 9 (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) $\text{CH}_3\text{CH}_2\text{COOH}$ (1).
 (iv) $\text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{CH}_3\text{OH}$
 $\text{CH}_3\text{CH}_2\text{COONa} + \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{Na}^+$ (2).

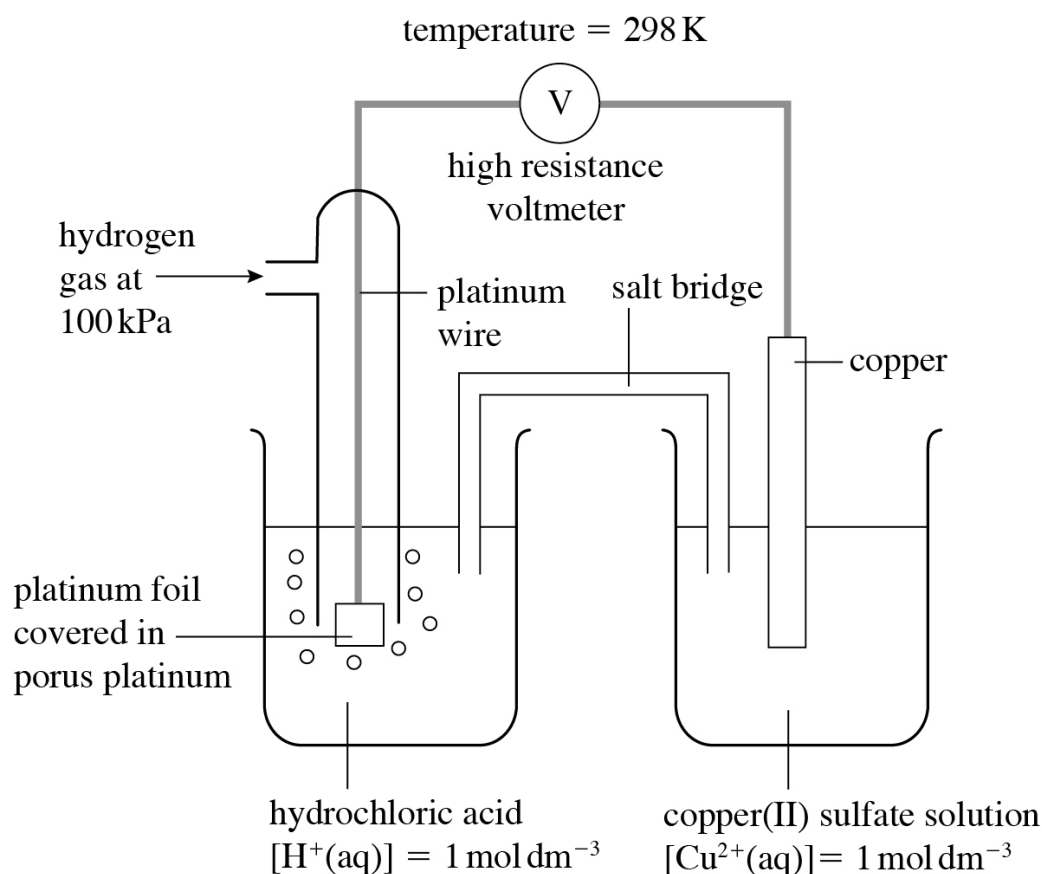
- 10 (a) The spectra are very similar (1) because they both have the same numbers and types of bond (1).
- (b) 2-methylpropan-2-ol has two different types of carbon atom / one central C and three identical CH_3 groups (1) so its spectrum will show two peaks due to ^{13}C atoms (1).
 2-methylpropan-1-ol 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 $\text{CH}(\text{CH}_3)_2^+$ (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 $\text{C}(\text{CH}_3)_3^+$ (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).

Topic 16 Redox equilibria

16A Standard electrode potential

16A.1 Standard electrode (redox) potentials

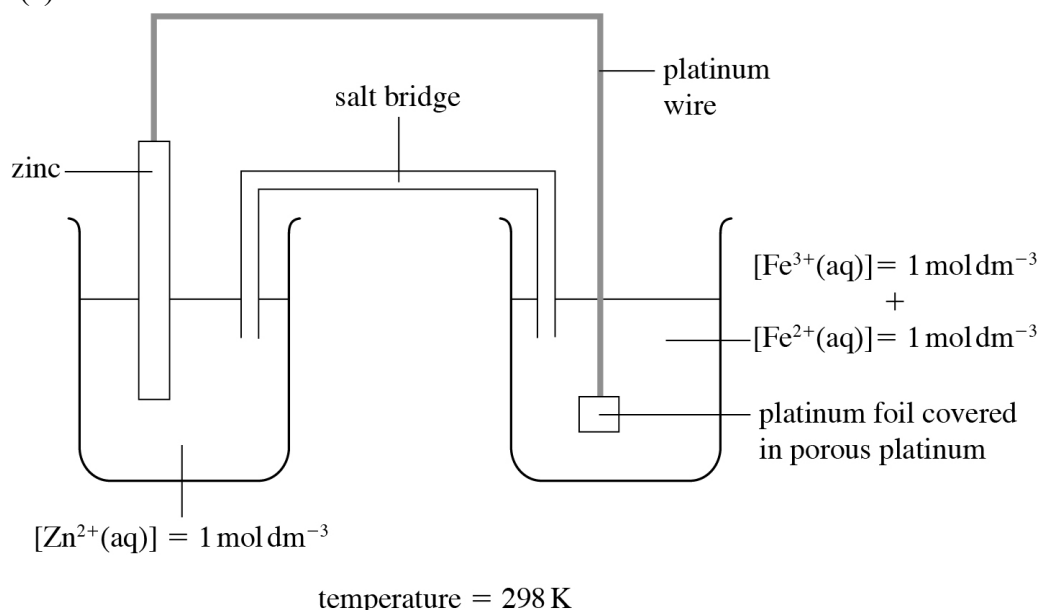
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- 2 The standard electrode potential is the emf of a cell formed between the $\frac{1}{2}\text{Br}_2(\text{aq}) \mid \text{Br}^-(\text{aq})$ half-cell and the standard hydrogen electrode. The concentrations of $\text{Br}_2(\text{aq})$ and $\text{Br}^-(\text{aq})$ are both 1 mol dm⁻³ and the temperature is 298 K. The positive sign tells us that the $\frac{1}{2}\text{Br}_2(\text{aq}) \mid \text{Br}^-(\text{aq})$ 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.

16A.2 Electrochemical cells

1 (a)



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

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

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

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

(b) Electrons will flow from the $\frac{1}{2}\text{Cl}_2 | \text{Cl}^-$ half-cell to the $\text{MnO}_4^- | \text{Mn}^{2+}$ half-cell because the electrode potential of $\frac{1}{2}\text{Cl}_2 | \text{Cl}^-$ is more negative.

(c) $\text{Pt}(\text{s}) | \text{Cl}^-(\text{aq}) | \frac{1}{2}\text{Cl}_2(\text{g}) :: \text{MnO}_4^-(\text{aq}), 8\text{H}^+(\text{aq}) | \text{Mn}^{2+}(\text{aq}), 4\text{H}_2\text{O}(\text{l}) | \text{Pt}(\text{s})$

16A.3 Standard electrode potentials and thermodynamic feasibility

 1 (a) $\text{VO}_2^+ / \text{VO}^{2+}$ has the more negative E^{\ominus} value, so VO^{2+} will release electrons to MnO_4^-

(b) $\text{MnO}_4^-(\text{aq}) + 5\text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 5\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq})$

 2 $E^{\ominus}(\text{Zn}^{2+} / \text{Zn})$ is more negative than $E^{\ominus}(\text{VO}_2^+ / \text{VO}^{2+})$, $E^{\ominus}(\text{VO}^{2+} / \text{V}^{3+})$ and $E^{\ominus}(\text{V}^{3+} / \text{V}^{2+})$ so Zn will reduce VO_2^+ to VO^{2+} , VO^{2+} to V^{3+} and V^{3+} to V^{2+}

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

 3 (a) $E^{\ominus}(\text{O}_2 / \text{H}_2\text{O}_2)$ is more negative than $E^{\ominus}(\text{H}_2\text{O}_2 / \text{H}_2\text{O})$, so one molecule of H_2O_2 will release electrons to (i.e. will reduce) another molecule of H_2O_2 .

(b) $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

Topic 16 Redox equilibria

Answers

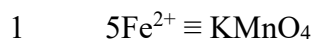
- (c) The oxidation number of O changes from -1 in H_2O_2 to -2 in H_2O (reduction).
The oxidation number of O changes from -1 in H_2O_2 to 0 in O_2 (oxidation).
The oxygen has been both reduced and oxidised in the same reaction.
- 4 (a) $\text{Emf } (E^\ominus_{\text{cell}}) = (0.77 - 0.54) = (+)0.23 \text{ V}$
- (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 kJ mol^{-1} (to 2 significant figures).
Note: $1 \text{ V} = 1 \text{ J C}^{-1}$

16B Redox in action

16B.1 Fuel cells

- 1 (a) $E^\ominus_{\text{cell}} = 1.40 \text{ V}$
- (b) $\text{Cd(s)} + 2\text{NiO(OH)(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Cd(OH)}_2\text{(s)} + 2\text{Ni(OH)}_2\text{(s)}$
- (c) Cd changes from 0 to $+2$. Cd is oxidised.
Ni changes from $+3$ to $+2$. Ni is reduced.
- 2 (a) $\text{CH}_3\text{OH(l)} + 1\frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$
- (b) $\text{CH}_3\text{OH(l)} + \text{H}_2\text{O(l)} \rightarrow \text{CO}_2\text{(g)} + 6\text{H}^+\text{(aq)} + 6\text{e}^-$
- (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.

16B.2 Redox titrations

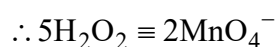
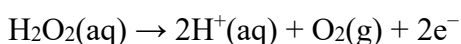
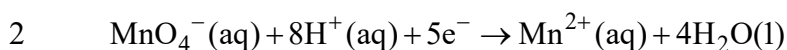


$$n(\text{KMnO}_4) \text{ in } 24.40 \text{ cm}^3 = \frac{24.40 \times 0.0218}{1000} = 5.32 \times 10^{-4} \text{ mol.}$$

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

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

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



$$n(\text{KMnO}_4) \text{ in } 23.90 \text{ cm}^3 = \frac{23.90 \times 0.0200}{1000} = 4.78 \times 10^{-4} \text{ mol.}$$

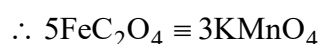
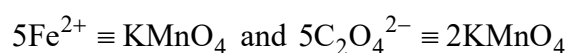
$$n(\text{H}_2\text{O}_2) \text{ in } 25.0 \text{ cm}^3 = \frac{5}{2} \times 4.78 \times 10^{-4} = 1.195 \times 10^{-3} \text{ mol.}$$

$$n(\text{H}_2\text{O}_2) \text{ in } 1000 \text{ cm}^3 = \frac{1000}{25} \times 1.195 \times 10^{-3} = 4.78 \times 10^{-2} \text{ mol.}$$

$$\begin{aligned} \text{Concentration of the original } \text{H}_2\text{O}_2 &= 4.78 \times 10^{-2} \times \frac{1000}{50} \\ &= 0.956 \text{ mol dm}^{-3}. \end{aligned}$$

3

$$n(\text{FeC}_2\text{O}_4) \text{ in } 1.00 \text{ g} = \frac{1.00}{143.8} = 6.95 \times 10^{-3} \text{ mol.}$$



$$n(\text{KMnO}_4) \text{ required} = \frac{3}{5} \times 6.95 \times 10^{-3} = 4.17 \times 10^{-3} \text{ mol.}$$

$$\text{Volume of } \text{KMnO}_4 \text{ required} = \frac{4.17 \times 10^{-3}}{0.0200} \times 1000 = 209 \text{ cm}^3 \text{ (to 3 significant figures).}$$

Topic 16 Redox equilibria Answers

4 $5\text{Fe}^{2+} \equiv \text{KMnO}_4$

$$n(\text{KMnO}_4) \text{ in } 21.60 \text{ cm}^3 = \frac{21.60 \times 0.0210}{1000} = 4.536 \times 10^{-4} \text{ mol}$$

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

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

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

$$n(\text{KMnO}_4) \text{ in } 22.80 \text{ cm}^3 = \frac{22.80 \times 0.0210}{1000} = 4.788 \times 10^{-4} \text{ mol}$$

$$n(\text{Fe}^{3+}) \text{ in } 25.0 \text{ cm}^3 = 5 \times 4.788 \times 10^{-4} = 2.394 \times 10^{-3} \text{ mol}$$

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

5 $\text{Cl}_2 \equiv \text{I}_2 \equiv 2\text{Na}_2\text{S}_2\text{O}_3$

$$n(\text{Na}_2\text{S}_2\text{O}_3) \text{ in } 23.20 \text{ cm}^3 = \frac{22.30 \times 0.105}{1000} = 2.342 \times 10^{-3} \text{ mol}$$

$$n(\text{I}_2) \text{ in } 25.0 \text{ cm}^3 = \frac{1}{2} \times 2.342 \times 10^{-3} = 1.171 \times 10^{-3} \text{ mol.}$$

$$n(\text{I}_2) \text{ in } 250 \text{ cm}^3 = 10 \times 1.171 \times 10^{-3} \text{ mol} = 1.171 \times 10^{-2} \text{ mol.}$$

$$n(\text{Cl}_2) = n(\text{I}_2) = 1.171 \times 10^{-2} \text{ mol.}$$

$$\text{Mass of } \text{Cl}_2 = 1.171 \times 10^{-2} \text{ mol} \times 71.0 \text{ g mol}^{-1} = 0.831 \text{ g.}$$

$$\text{Percentage of 'available' chlorine} = \frac{0.831}{2.50} \times 100 = 33.2\%.$$

6 $n(\text{Na}_2\text{S}_2\text{O}_3) \text{ in } 21.00 \text{ cm}^3 = \frac{21.00 \times 0.0500}{1000} = 1.05 \times 10^{-3} \text{ mol.}$

$$n(\text{I}_2) = \frac{1}{2} \times 1.05 \times 10^{-3} = 5.25 \times 10^{-4} \text{ mol.}$$

$$n(\text{K}_2\text{S}_2\text{O}_8) \text{ in } 25.0 \text{ cm}^3 = \frac{25.0 \times 0.0210}{1000} = 5.25 \times 10^{-4} \text{ mol.}$$

$$\therefore \text{S}_2\text{O}_8^{2-} \equiv \text{I}_2 \equiv 2\text{I}^-$$

Possible equation: $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq}).$

Topic 16 Exam Practice

1 A

2 B

3 D

4 D

5 C

6 (a)

	$\text{VO}_3^- (\text{aq})$	$\text{VO}^{2+} (\text{aq})$	$\text{V}^{3+} (\text{aq})$	$\text{V}^{2+} (\text{aq})$
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)

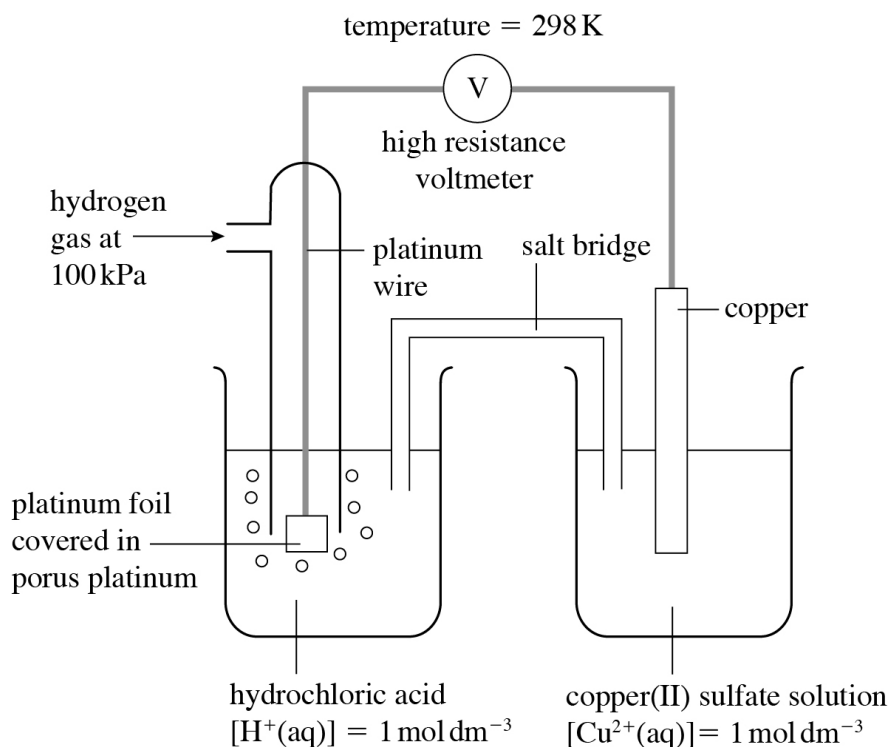
VO_3^- (yellow) is reduced to VO^{2+} (green) (the intermediate green colour is owing to both VO_3^- and VO^{2+} existing in solution together) because the E^\ominus value of half-cell 5 is more negative than that of half-cell 4 (1).

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).

7 (a)



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

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

Hydrogen gas (1).

Complete circuit with salt bridge and voltmeter (1).

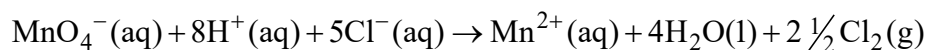
Both solutions have an ion concentration of 1 mol dm^{-3} (1).

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).

Topic 16 Redox equilibria Answers

- 8 (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) $\text{Emf} = (1.52 - 1.36) = 0.16 \text{ V}$ (1).
- (c) (i)



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 Cl₂(g) | Cl⁻(aq) half-cell becomes more positive (as the equilibrium moves to the right) (1).
As [H⁺(aq)] increases, the electrode potential of the MnO₄⁻(aq), H⁺(aq) | Mn²⁺(aq), H₂O(l) half-cell becomes less positive (as the equilibrium moves to the left) (1).
Eventually the electrode potential of the Cl₂(g) | Cl⁻(aq) half-cell becomes more positive than the electrode potential of the MnO₄⁻(aq), H⁺(aq) | Mn²⁺(aq), H₂O(l) half-cell (and so Cl⁻ can no longer release electrons to MnO₄⁻) (1).

- 9 (a) Sulfur dioxide is toxic / poisonous (1).

(b) $n(\text{NH}_4\text{VO}_3) \text{ in } 25 \text{ cm}^3 = \frac{2.24}{116.9 \times 10} = 1.92 \times 10^{-3} \text{ mol (1)}.$

$$n(\text{KMnO}_4) \text{ in } 38.10 \text{ cm}^3 = (0.03840 \times 0.0200) = 7.68 \times 10^{-4} \text{ mol (1)}.$$

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

Change in oxidation number of Mn for 1 mol of MnO₄⁻ = -5

Change in oxidation number of V for 2.5 mol of VO₃⁻ = +5 (1).

Change in oxidation number of V for 1 mol of VO₃⁻ = +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 KMnO₄ is required to oxidise the sulfur dioxide (1). Alternatively, the SO₂ re-reduces the vanadium (V) molecules, which are then re-oxidised by the MnO₄⁻

Topic 16 Redox equilibria

Answers

- 10 (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) $\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Ag}_2\text{O(s)}, \text{H}_2\text{O(l)} \mid \text{Ag(s)}, \text{OH}^-(\text{aq})$ left-hand side (1)
 right-hand side (1).
 (ii) $\text{Zn(s)} + \text{Ag}_2\text{O(l)} + \text{H}_2\text{O(l)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)} + 2\text{OH}^-(\text{aq})$
 Equation (1) state symbols (1).
 (iii) $\text{emf} = (0.34 - -0.76) = 1.10 \text{ V}$ (1).
 (iv)

$$\ln K = \frac{nFE_{\text{cell}}^{\ominus}}{RT}$$

$$= \frac{2 \times 96\,500 \times 1.10}{8.31 \times 298}$$

$$= 85.73$$

$$K = e^{85.73} = 1.71 \times 10^{37}$$

Topic 17 Transition metals and their chemistry

17A Principles of transition metal chemistry

17A.1 Transition metal electronic configurations

- | | | |
|---|------------------|--------------------------------------|
| 1 | (Cr full) | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ |
| | (Cr abbreviated) | $[\text{Ar}] 4s^1 3d^5$ |
- 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 $[\text{Ar}] 3d^3$.

17A.2 Ligands and complexes

- 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.
- 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, so the complex is neutral and has no overall charge.

17A.3 The origin of colour in complexes

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

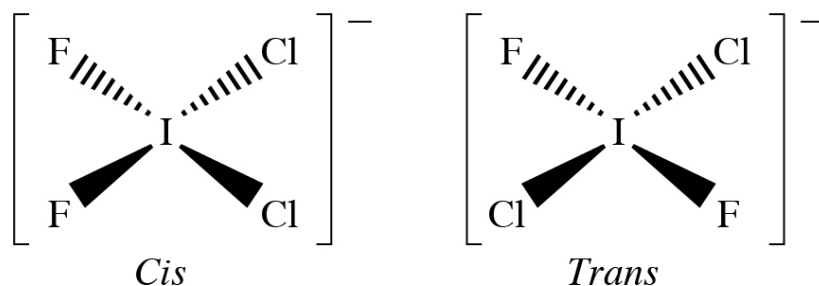
17A.4 Common shapes of complexes

- 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+.
- 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 $[\text{NiCl}_4]^{2-}$.

17A.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.

17A.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 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 2\text{en} \rightarrow [\text{Fe}(\text{H}_2\text{O})_2(\text{en})_2]^{3+} + 4\text{H}_2\text{O}$

17B Transition metal reactions

17B.1 Different types of reactions

- 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 coordination 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 coordination number.

17B.2 Reactions of cobalt and iron complexes

- $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \rightarrow [\text{Co}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$
- Ammonia is a weak base, so in aqueous ammonia there are many more NH_3 molecules than OH^- ions.

17B.3 The chemistry of chromium

- $[\text{Cr}(\text{OH})_6]^{3-} + 6\text{H}^+ \rightarrow [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- The relevant half-equations and E° values are:
 $\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn} \quad E^\circ = -1.18 \text{ V}$
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad E^\circ = +0.76 \text{ V}$
 Adding these together gives:
 $\text{Mn}^{2+} + \text{Zn} \rightarrow \text{Mn} + \text{Zn}^{2+} \quad E^\circ = -0.42 \text{ V}$
 As the E° value is negative, the reaction is not feasible.

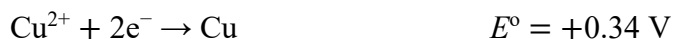
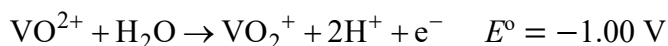
17B.4 Reactions of manganese complexes

- Percentage by mass of **T** = 63.18%
 $n(\text{O}) = (36.82 \div 16) = 2.30125 \text{ mol}$
 $n(\text{T}) = (2.30125 \div 2) = 1.150625 \text{ mol}$
 molar mass of **T** = $(63.18 \div 1.150625) = 54.9 \text{ g mol}^{-1}$
 Hence **T** is manganese, Mn
 (b) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
 (c) **Q** = $[\text{Mn}(\text{H}_2\text{O})_4(\text{OH}_2)]$
S = $\text{MnO}_2 \cdot x\text{H}_2\text{O}$
- $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow [\text{Mn}(\text{H}_2\text{O})_4(\text{OH}_2)](\text{s}) + 2\text{H}_2\text{O}$
 - $\text{MnO}_2 \cdot x\text{H}_2\text{O} \rightarrow \text{MnO}_2 + x\text{H}_2\text{O}$

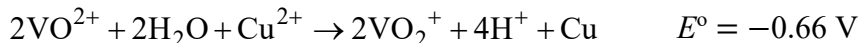
17B.5 The chemistry of vanadium

- The relevant half-equations and E° values are:
 $\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+} \quad E^\circ = -0.26 \text{ V}$
 $\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^- \quad E^\circ = +0.14 \text{ V}$
 Adding these together gives:
 $2\text{V}^{3+} + \text{Sn} \rightarrow 2\text{V}^{2+} + \text{Sn}^{2+} \quad E^\circ = -0.12 \text{ V}$
 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:



Adding these together gives:



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

17B.6 Reactions of nickel and zinc complexes

- In each atom the 3d orbitals are filling.
[**Note:** some texts describe d-block elements as those in which the 3d orbitals are the last to fill. This is not correct as was explained in Book 1, Topic 2A.3, page 51. With the elements Sc to Zn, the 4s orbital starts to fill before the 3d].
 - Nickel forms an ion with a partially filled 3d sub-shell. The Ni^{2+} ion has the electronic configuration of $[\text{Ar}] 3\text{d}^8$
The only ion formed by zinc is the Zn^{2+} ion. It has the electronic configuration of $[\text{Ar}] 3\text{d}^{10}$. In this ion the 3d sub-shell is completely full.
- $(1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6) 3\text{d}^8$
 - The ion will be blue. The spectrum shows that it absorbs in the yellow region of the electromagnetic spectrum.
 - Rings drawn around the N and the O^-
 - They have a lone pair of electrons.

17C Transition metals as catalysts

17C.1 Heterogeneous catalysis

- 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.
- $4\text{NO} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3$

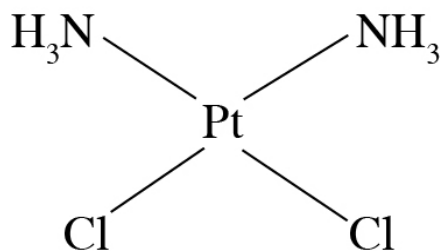
17C.2 Homogeneous catalysts

- 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.
- 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.

Topic 17 Exam Practice

- 1 D
- 2 C
- 3 B
- 4 C
- 5 D
- 6 B
- 7 B
- 8
 - (a) $\text{Sc}^{3+} (1s^2 2s^2 2p^6) 3s^2 3p^6$ (1).
 $\text{Ti}^{3+} (1s^2 2s^2 2p^6) 3s^2 3p^6 3d^1$ (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) $(\text{Sc}(\text{OH})_3) \quad +3$ (1).
 $(\text{CaTiO}_3) \quad +4$ (1).
- 9
 - (a) A species with a lone pair of electrons (1) that forms a dative bond with a metal ion (1).
 - (b) (i) $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]$ (1).
 (ii) Tetrachlorocobaltate(II) (1).
 - (c) 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).
- 10
 - (a) The six water ligands repel each other as far as possible (1)
 giving a symmetrical structure with bond angles of 90° (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).

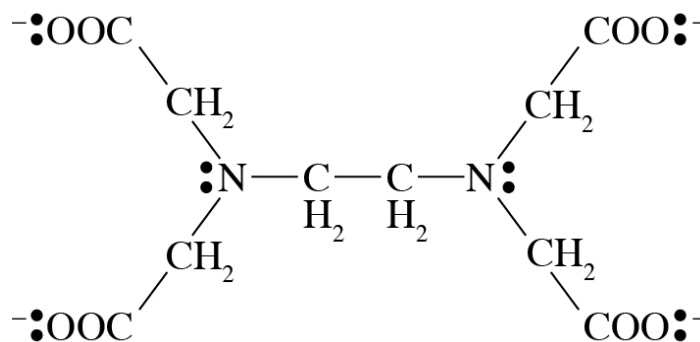
- (d) Square planar (1).



(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).

- 11 (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) $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}(l)$.

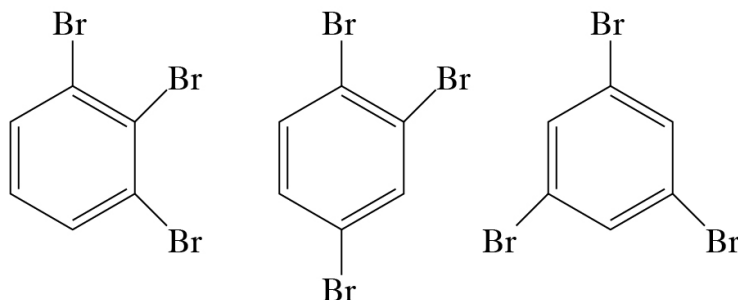
- 12 Sulfur dioxide is adsorbed onto the catalyst (1).
The equation for its reaction with the catalyst is $\text{V}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{V}_2\text{O}_4 + \text{SO}_3$ (1).
in which the oxidation number of vanadium decreases from +5 to +4 (1).
Oxygen then reacts as follows: $\text{V}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{V}_2\text{O}_5$ (1).
in which the oxidation number of vanadium increases from +4 to +5 (1).
Adding these equations together gives $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ (1).

Topic 18 Organic chemistry: arenes

18A Arenes: benzene

18A.1 Benzene: a molecule with two models

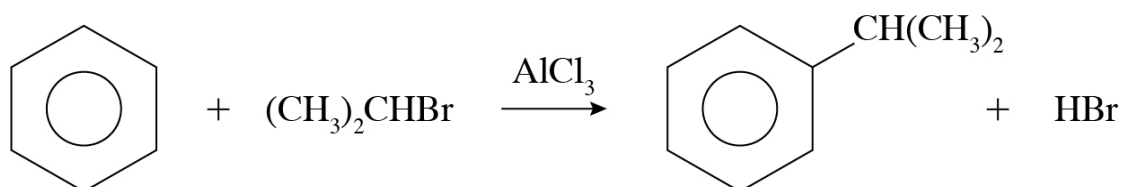
1



- 2
- Each C–H and C–C bond has two electrons in sigma bonds, and as there are six of each, then $12 \times 2 = 24$ electrons are involved in sigma bonding.
 - Each C atom supplies one electron to form the delocalised pi bond, so the answer is 6 electrons in pi bonding.

18A.2 Some reactions of benzene

1

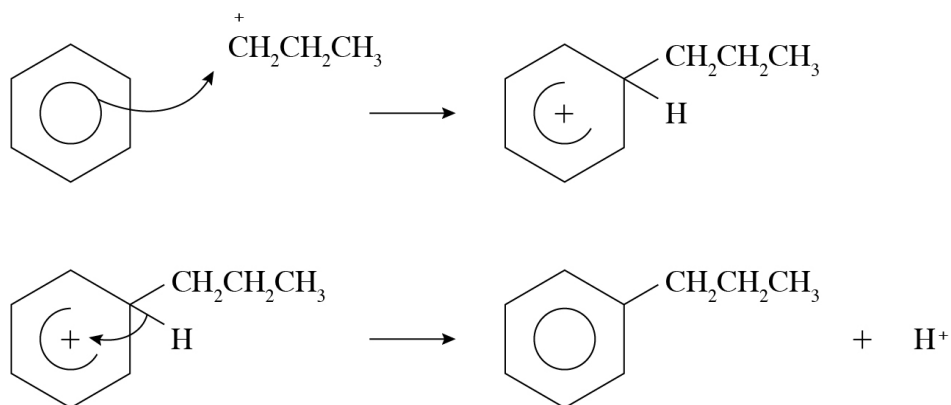


- 2 Phenylbutanone.

18A.3 Electrophilic substitution mechanisms

- 1 $\text{FeBr}_3 + \text{Br}_2 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$

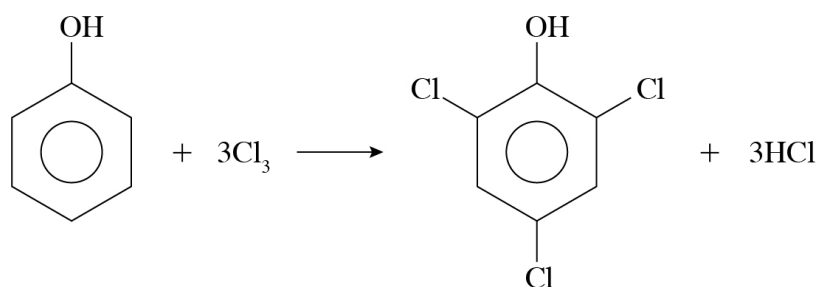
2



18A.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

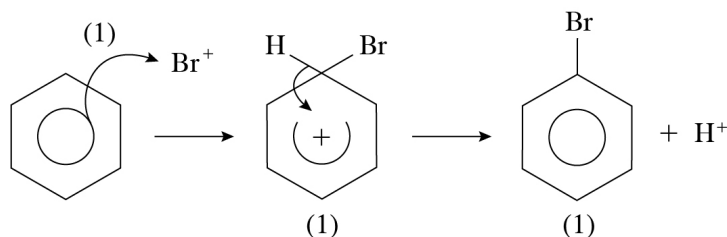


Topic 18 Exam Practice

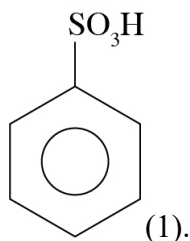
- 1 D
- 2 C
- 3 C
- 4 A
- 5 A
- 6 C

- 7 (a) (i) $\text{C}_3\text{H}_8 + \text{Br}_2 \rightarrow \text{C}_3\text{H}_8\text{Br}_2$ (1).
 $\text{C}_6\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$ (1).
 (ii) Propene – nucleophilic addition (1).
 Benzene – electrophilic substitution (1).
 (b) (i) $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$ (1)
 $\text{HSO}_4^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4$

- 8 (a) (i) $(3 \times -120) = -360 \text{ kJ mol}^{-1}$ (1)
 (ii) The bonding in benzene is more stable than in the Kekulé structure by 152 kJ mol^{-1} (1). The π double bond electrons are delocalised around the ring (1). Benzene undergoes substitution reactions rather than addition (1) in order to maintain its delocalised system of electrons (1).
 (b) (i) Concentrated nitric acid (1), concentrated sulfuric acid (1).
 (ii) Electrophile (1).
 (iii) $\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{FeBr}_4^- + \text{Br}^+$ (1).

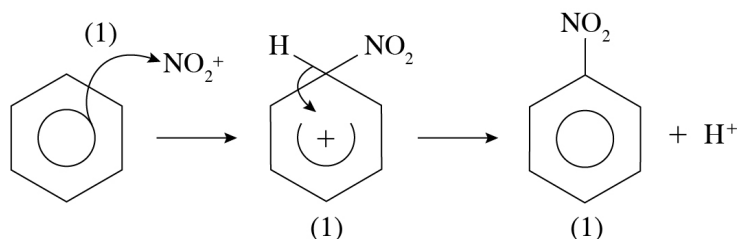


(iv)



Benzenesulfonic acid (1)

- 9 (a) $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$ (1).



- (b) Higher temperatures lead to the formation of dinitrobenzene, and possibly trinitrobenzene (1).
 At lower temperatures the reaction is too slow (1).

- 10
- (a) X-ray diffraction – all of the carbon to carbon bond lengths are the same (1). In structure A the carbon to carbon bonds lengths would alternate between ‘short’ and ‘long’ (1).
 - (b) Enthalpy change of hydrogenation – the enthalpy change of hydrogenation of benzene -208 kJ mol^{-1} (1). The enthalpy change for structure A would be -360 kJ mol^{-1} (1).
 - (c) Reaction with bromine – benzene undergoes a substitution reaction with bromine (1). Structure A would undergo an addition reaction with bromine (1).

Topic 19 Organic nitrogen compounds: amines, amides, amino acids and proteins

19A Amines, amides, amino acids and proteins

19A.1 Amines and their preparations

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Cl}$
 - $\text{CH}_3\text{CH}_2\text{CN} + 4[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- The product will attack some of the halogenoalkanes to form a secondary amine.

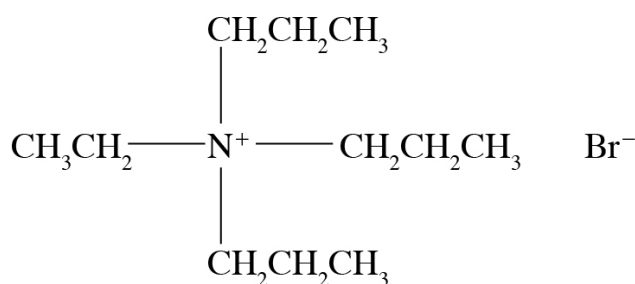
19A.2 Acid–base reactions of amines

- $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{OH}^-$
 - $2\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{SO}_4^{2-}$
- 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.

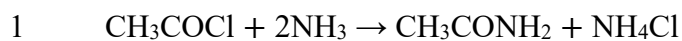
19A.3 Other reactions of amines

- $\text{CH}_3\text{CH}_2\text{COCl} + \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3 + \text{HCl}$

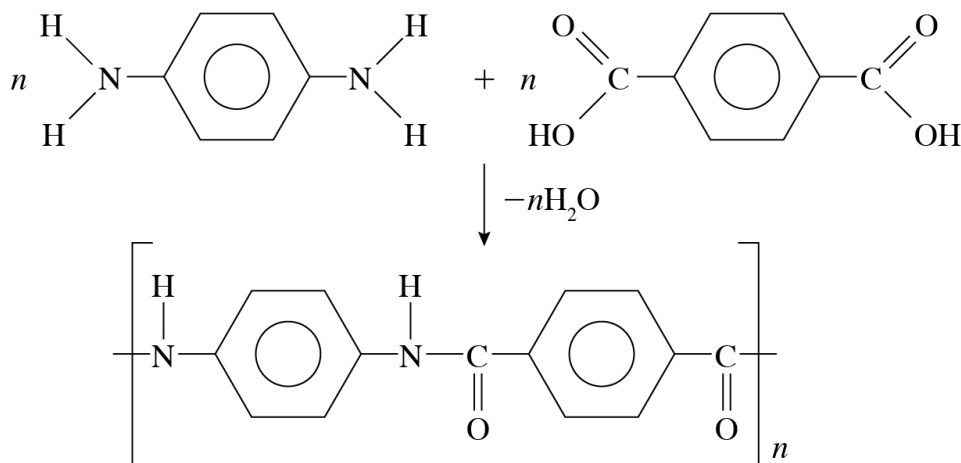
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19A.4 Amides and polyamides



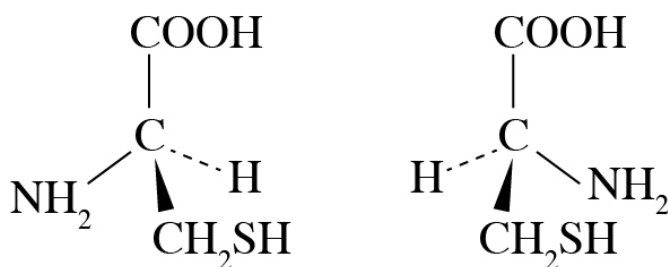
2



19A.5 Amino acids

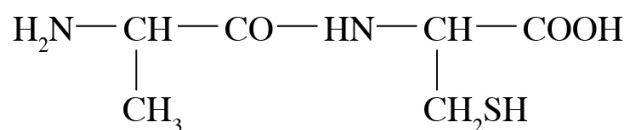
- 1 (a) $\text{H}_3\text{N}^+\text{---CH}_2\text{---COO}^-$
 (b) $\text{H}_3\text{N}^+\text{---CH}_2\text{---COOH}$
 (c) $\text{H}_2\text{N---CH}_2\text{---COO}^-$

2

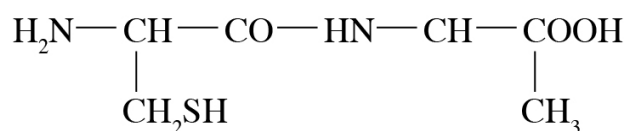


19A.6 Peptides and proteins

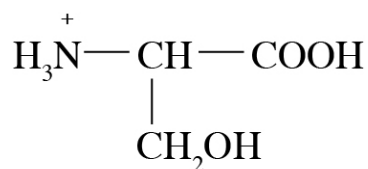
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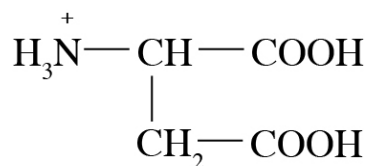
and



2



and



Topic 19 Exam Practice

1 B

2 C

3 C

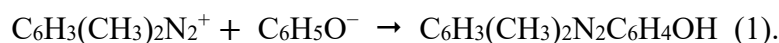
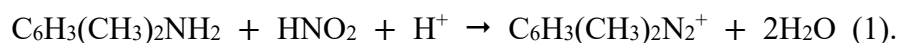
4 D

5 C

6 B

- 7 (a) (i) Concentrated nitric acid (1), concentrated sulfuric acid (1).
 (ii) The benzene ring is more susceptible to electrophilic attack (1) because the two methyl groups release electrons and hence increase the electron density of the benzene ring (1).
 (b) Reduction (1) [Accept redox]

- (c) Sodium nitrite and dilute hydrochloric acid (1), temperature between 0°C and 5°C (1). Add a solution of phenol dissolved in sodium hydroxide (1).

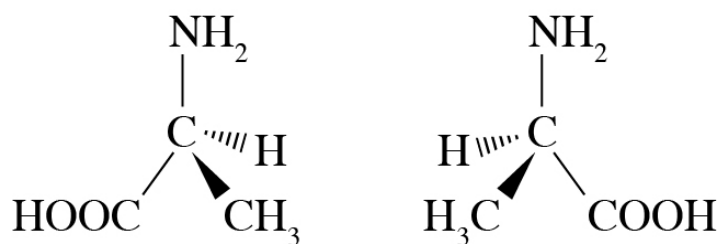


- 8 (a) 2-aminoethanoic acid (1).

- (b) (i) $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$ (1).

- (ii) A large amount of energy is required to overcome (1) the strong electrostatic forces of attraction between the zwitterions (1).

- (c) (i)



(1).

(1).

- (ii) A solution of one isomer will rotate the plane of plane-polarised monochromatic light to the right (dextrarotation) (1).

A solution of the other isomer will rotate the plane of plane-polarised monochromatic light to the left (laevorotation) (1).

- (d) (i) Water molecules are eliminated in the reaction (1).

- (ii) $\text{H}_2\text{NCH}(\text{CH}_3)\text{CONHCH}_2\text{COOH}$ (1).



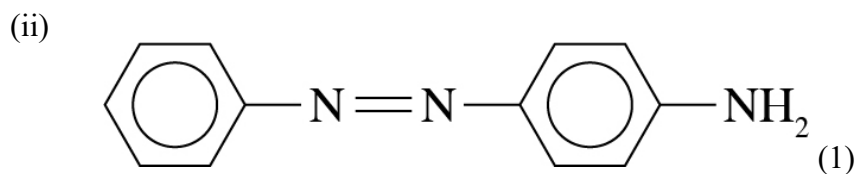
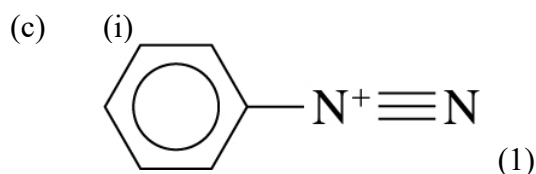
- 9 (a) (i) The lone pair of electrons on the nitrogen atom of the amine group (1).

- (ii) In phenylamine, the lone pair of electrons on the nitrogen atom of the amine group is incorporated into the delocalised electrons of the benzene ring (1). This results in the lone pair being less readily available for donation (1).

- (iii) $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{SO}_4$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{HSO}_4$ (1),
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3\text{OOCCH}_3$ or $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3$ (1).

[Accept formulae with correct charges shown on the ions.]

- (b) Tin (1) and concentrated hydrochloric acid (1).

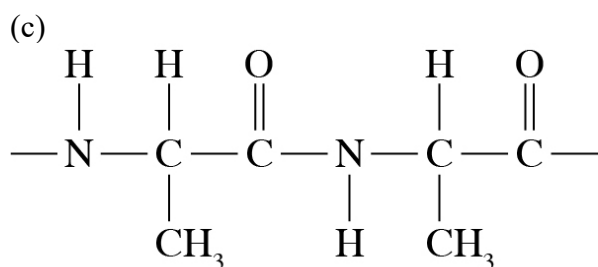


(iii) A dye (1).

10 (a) $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$ (1).

(b) pH 1.0 $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{OH})\text{COOH}$ (1).

pH 10.0 $\text{H}_2\text{NCH}(\text{CH}_2\text{OH})\text{COO}^-$ (1).



CONH displayed (1).

rest of structure correct with extension bonds from C and N shown (1).

(d) (i) (2-)aminoethanoic acid (1).

(ii) sodium nitrite (1).

(iii) esterification (1), neutralisation (1).

(iv) ethanol/ $\text{C}_2\text{H}_5\text{OH}$ (1).

(v) hydrolysis (1).

(vi) carbon dioxide/ CO_2 (1) ammonium chloride/ NH_4Cl (1).

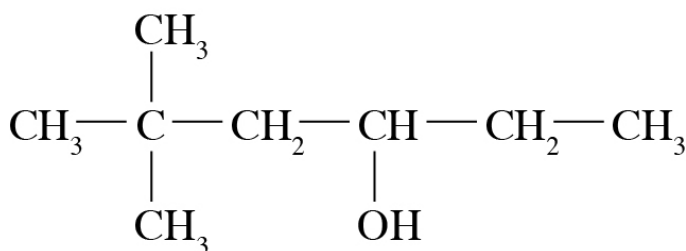
Topic 20 Organic synthesis

20A Organic structures

20A.1 Organic analysis

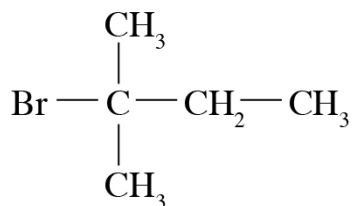
- 1 (a) **T** does not contain a C=C (no immediate decolourisation of bromine water). **T** does not contain a –COOH group (does not react with aqueous sodium carbonate). **T** contains one –OH group (produces 1 mol of HCl per mole of compound). **T** contains a carbonyl group (orange precipitate with 2,4-DNPH). The possible structural formulae are:
- | | | |
|-------------------------------------|-----------------------------|--------------------------------------|
| $\text{CH}_3\text{COCH}_2\text{OH}$ | $\text{CH}_3\text{CHOHCHO}$ | $\text{CH}_2\text{OHCH}_2\text{CHO}$ |
| Isomer A | Isomer B | Isomer C |
- (b) Relative molecular mass of **T** is 74.
 A m/z value of 29 suggests a $\text{CH}_3\text{CH}_2\text{—}$ group or a —CHO group, so **T** cannot be isomer A. A m/z value of 59 ($74 - 15$) suggests a $\text{CH}_3\text{—}$ group, so **T** cannot be isomer C.
T is isomer B – $\text{CH}_3\text{CHOHCHO}$
- 2 C ($52.17 \div 12.0$) = 4.35
 H ($13.04 \div 1.0$) = 13.04
 O ($34.78 \div 16.0$) = 2.17
 Dividing by 2.17 gives the whole number ratio of C:H:O of 2:6:1
 The empirical formula is $\text{C}_2\text{H}_6\text{O}$
 The empirical formula mass = $(12.0 \times 2) + (1.0 \times 6) + (16.0 \times 1) = 46$
 The empirical formula mass = the relative molecular mass, so the molecular formula is $\text{C}_2\text{H}_6\text{O}$
 The peak at chemical shift 1.2 ppm is caused by the protons in a CH_3 group in an alkane chain. It is a triplet, so it is attached to a CH_2 group.
 The peak at 3.7 is caused by the protons in a CH_2 group attached to an oxygen atom. It is a quartet, so it is also attached to a CH_3 group.
 The peak at 2.6 is caused by the protons in an OH group.
 The structural formula of the compound is $\text{CH}_3\text{CH}_2\text{OH}$.

20A.2 Organic synthesis



Topic 20 Organic synthesis Answers

2

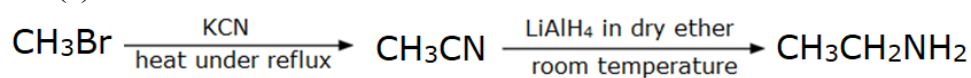


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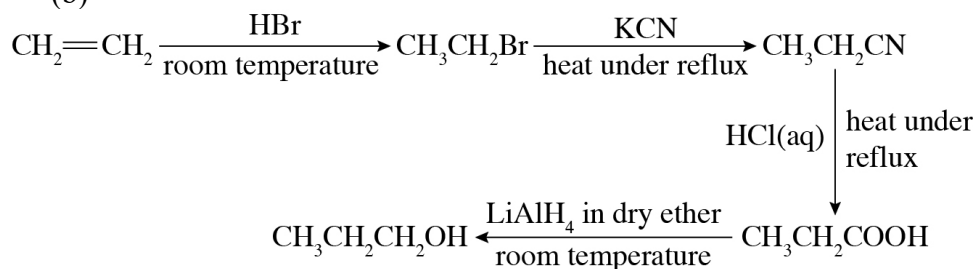


3

(a)



(b)



20A.3 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 is 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.

20A.4 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.

20A.5 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.

Topic 20 Exam Practice

- 1 D
- 2 B
- 3 B
- 4 (a) C
(b) B
(c) A
- 5 (a) B
(b) D
(c) B
(d) B
- 6 (a) Orange/yellow precipitate (1).

Topic 20 Organic synthesis Answers

- (b) Heat with Benedict's or Fehling's solution (1), observation with **P** – no change (1), observation with **Q** – red precipitate forms (1).
- Or*
- heat with Tollens' reagent (1), observation with **P** – no change (1), observation with **Q** – silver mirror forms (1).
- Or*
- heat with acidified potassium dichromate(VI) solution (1), observation with **P** – no change (1), observation with **Q** – orange solution turns green (1).
- (c) (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ and $(\text{CH}_3)_2\text{CHCHO}$ (1).
 (ii) Recrystallisation (1).
 (iii) Measure the melting temperature (1) and compare the value with a known value from a database (1).
- 7 (a) Concentrated nitric acid (1) and concentrated sulfuric acid (1).
 (b) Heat – to increase the rate of reaction (because the activation energy for the reaction is high as covalent bonds need to be broken) (1).
 Under reflux – to prevent the escape of the reactants and/or products (because they may be volatile and/or flammable and/or harmful) (1).
 (c) $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{OH}$
 (d) Reduction.
- 8 (a) Molar mass of 2-hydroxybenzoic acid = 138 g mol^{-1}
and molar mass of aspirin = 180 g mol^{-1} (1).
 138 g of 2-hydroxybenzoic acid produce 180 g of aspirin (1).
 9.40 g 2-hydroxybenzoic acid produce $(180 \div 138) \times 9.40 \text{ g}$ of aspirin
 = 12.26 g (1).
 % yield = $(7.77 \div 12.26) \times 100 = 63.4\%$ (1).
 (b) (i) Dissolve the impure solid in the minimum volume (1) of hot water (1).
 Filter while hot (1). Allow the filtrate to cool and filter to obtain the crystals that form (1). Wash the crystals with a small volume of cold water (1).
 (ii) It reduces the yield (1) because some of the pure substance does not crystallise/remains in solution on cooling (1).
- 9 (a) Hazard – methanol is flammable (1). ion – use electrical heating source or water bath (1). *Or* hazard – methanol is toxic by inhalation of vapour (1).
 Precaution – carry out reaction in well ventilated area (1). *Or* hazard – methanol is toxic by skin absorption (1). Precaution – wear gloves (1). *Or* hazard – NaOH is corrosive (1). Precaution – wear gloves and/or goggles (1).
 (b) Any two from:
 Vegetable oils are a renewable resource (1).
 Reduces the need to dispose of waste vegetable oils (1).
 Reduces the use of fossil fuels (1).
- 10 (a) Step 1 – dilute nitric acid (1).
 Step 2 – tin and concentrated hydrochloric acid (1).
 Step 3 – ethanoyl chloride or ethanoic anhydride (1).

Topic 20 Organic synthesis Answers

- (b) Pass steam into the mixture (1).
The 2-nitrophenol is distilled off with the water and condensed (1).
The 2-nitrophenol is then separated from the water (using a separating funnel) (1).
Advantage – the 2-nitrophenol is distilled at a lower temperature than its boiling temperature, thus reducing the chance of it decomposing (1).
- (c) (i) Hot filtration – to remove the insoluble impurities (1).
Cold filtration – to remove the soluble impurities (1).
(ii) 5°C and 95°C (1).
The lowest proportion of paracetamol remains in solution after the cold filtration (1).
(iii) Measure its melting temperature (1).