



- (ii) Nucleophilic addition. [1]  
 (iii) Nucleophiles attack the positively charged carbon atom in



This arises because the oxygen is more electronegative than the carbon and attracts electrons from the C=O bond. [1]

- (iv) C=C is not polar. It has no positive carbon atom for nucleophiles to attack.

- 85 (a) (i) A biological catalyst [1] made from protein/with an active site [1].  
 (b) (i) One primary [1], four secondary [1].  
 (ii) The large number of —OH groups [1] mean that glucose is strongly hydrogen-bonded to water [2].  
 (c) (i) Nucleophile. [1]  
 (ii)  $\text{HCN} + \text{NaOH} \rightarrow \text{NaCN} + \text{H}_2\text{O}$   
 (iii) Excess  $\text{H}^+$  ions will protonate  $\text{CN}^-$  ions [1] so they cannot act as nucleophiles [1].  
 (d) (i) Step 1 is the slow, rate-determining step, so the rate equation for the overall reaction is the same as the rate equation for step 1:  
 $\text{rate} = k[\text{C}_6\text{H}_5\text{CHO}] [\text{CN}^-]$  [2]  
 (ii) The overall order is the same as the order for step 1: two [1]  
 (iii)  $k = \frac{\text{rate}}{[\text{C}_6\text{H}_5\text{CHO}] [\text{CN}^-]}$

$$\text{Units of } k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} [2]$$

- (e) (i) It has four different groups [1] attached to the central carbon atom [1].  
 (ii) Laboratory synthesis produces equal amounts of the two chiral forms, which cancel each other out.  
 (f) (i) A: hydrochloric acid, HCl (aq) [1]  
 B: acidified potassium dichromate or potassium manganate(VII),  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{KMnO}_4$   
 C: lithium tetrahydridoaluminate,  $\text{LiAlH}_4$  [1]

D: ethanoic acid,  $\text{CH}_3\text{COOH}$ , with  $\text{H}^+$  catalyst or ethanoyl chloride,  $\text{CH}_3\text{COCl}$  [1]

- 86 (a) (i) A yellow-orange ppt. [1]  
 (ii) A yellow ppt. [1]  
 (iii)



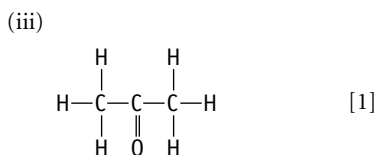
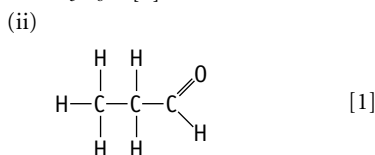
Use for the reaction: to detect the  $\text{CH}_3\text{CO}-$  or  $\text{CH}_3\text{CH}(\text{OH})-$  group in a compound. [1]

- (b) (i) C:H:O  
 mass ratio: 62.04 : 10.41 : 27.55

$$\text{mol ratio: } \frac{62.04}{12} : \frac{10.41}{1} : \frac{27.55}{16}$$

$$= 5.17 : 10.41 : 1.72 \\ = 3 : 6 : 1$$

Empirical formula =  $\text{C}_3\text{H}_6\text{O}$  [1]  
 $M_r = 58.08 \text{ g mol}^{-1}$ , therefore molecular formula is also  $\text{C}_3\text{H}_6\text{O}$ . [1]



- (iv)  $\text{CH}_3\text{CH}_2\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$   
 $M_r = 58.08 \rightarrow M_r = 74.08$

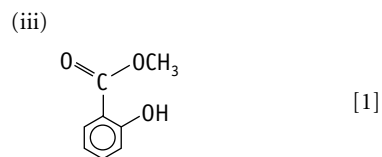
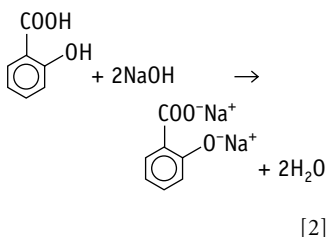
$$\frac{11.6}{58.08} = 0.200 \text{ mol} \rightarrow$$

$$\frac{10.6}{74.08} = 0.143 \text{ mol}$$

$$\text{so yield} = \frac{0.143}{0.200} \times 100$$

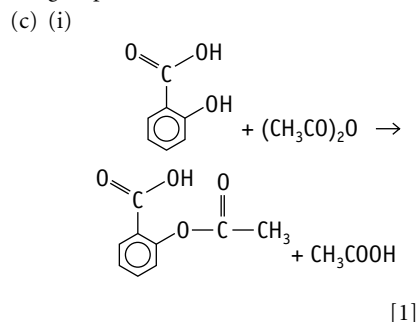
$$= 71.5\% [1]$$

- 87 (a) (i) 2-Hydroxybenzoic acid. [1]  
 (ii)



Conditions: heat/warm [1] with concentrated  $\text{H}_2\text{SO}_4$  [1].

- (b) Complex ion: central metal ion bonded to one or more ligands. [1]  
 Ligand: ion/molecule/species with lone pair of electrons [1] capable of forming a dative bond with a metal ion [1].  
 The negatively charged O atom [1] and the oxygen atom of the —OH group [1] could bond to a metal atom.



- (ii) Number of moles of NaOH

$$= 0.1 \times \frac{27.60}{1000} [1]$$

$$= 2.76 \times 10^{-3}$$

= moles of aspirin in the sample [1]

Mass of aspirin present

$$= 180 \times 2.76 \times 10^{-3} [1]$$

$$= 0.497 \text{ g}$$

% purity

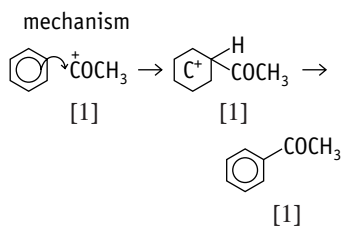
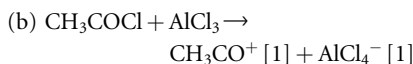
$$= \frac{0.497}{0.500} \times 100 = 99.4\% [1]$$

- (iii) Aspirin is a covalent molecule and is therefore more soluble in ethanol than in water. [1]

- (iv) Phenolphthalein or bromothymol blue. [1]  
 Weak acid titrated against strong base, so the equivalence point will be in the range  $\text{pH} = 8-10$ . [1]

- (d) Dissolve the tablet and a separate sample of pure aspirin in ethanol. [1]  
 Place a spot of each solution near one end of a TLC plate. [1] Stand the plate in a container with a small amount of a suitable solvent. [1] Leave until the solvent has risen almost to the top of the plate. [1] Dry and develop the plate. [1] Compare the positions of the spots. [1]



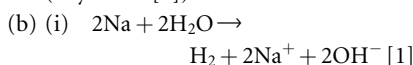


- 95 (a) Both sodium and magnesium have metallic bonding. [1] They have a regular arrangement [1] of positive ions [1] in a 'cloud' of delocalised electrons. [1] The electrical conductivity arises as the delocalised electrons are free to move through the structure. [1]

The strength of the metallic bond depends on the number of electrons per atom in the cloud. [1] Magnesium has two electrons per atom whereas sodium only has one, therefore magnesium has a higher melting point. [1]

The density is related to the packing of atoms. [1] Magnesium ions are smaller, so they pack together more closely. Magnesium has a higher density. [1] Sodium ions are larger, so sodium has a more open structure, and a lower density. [1]

(any 9 for [9])



Na has lost electrons (oxidation). [1]

$\text{H}_2\text{O}$  has gained electrons (reduction). [1]

or

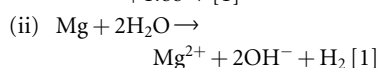
Na: oxidation number has changed from 0 to +1 (oxidation). [1]

H: oxidation number has changed from +1 to 0 (reduction). [1]

The e.m.f. of the cell:

$$E_{\text{cell}}^{\ominus} = (2.71) + (-0.83)$$

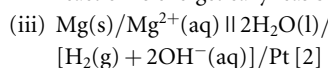
$$= +1.88 \text{ V} [1]$$



$$E_{\text{cell}}^{\ominus} = 2.38 + (-0.83)$$

$$= +1.55 \text{ V} [1]$$

A positive e.m.f. suggests that the reaction is energetically feasible. [1]



(iv) Magnesium is coated with a layer of oxide. [1] The activation energy is high, so the reaction is slow. [1]

(c) (i) The thermal stability of the Group 2 carbonates increases from  $\text{BeCO}_3$  to  $\text{BaCO}_3$ . [1] This is because the smaller the ion, the greater the charge density and the greater the polarising power. [1] The high charge density distorts the carbonate ion, making it unstable. [1]

(ii) Sodium carbonate is more thermally stable. [1] This is because magnesium has a higher charge density and distorts the carbonate ion, making it relatively unstable. [1]

96 (a) (i) Billingham is close to North Sea gas fields. [1]

(ii) If the gas supplies run out or if methane becomes more expensive. [1]

(iii) Argon is present in the air which is used to make synthesis gas. [1]

(b) Advantage: a high pressure increases the yield of ammonia/increases the rate. [1]

Disadvantages: high pressures are expensive to maintain [1]; increased risk of explosions/leaks [1].

(c) (i) As the temperature increases the yield decreases but the rate increases. [2]  $450^\circ\text{C}$  represents a compromise, chosen to achieve a reasonable yield at an acceptable rate. [1] A catalyst also speeds up the reaction. [1]

(ii) Iron/iron oxide [1]; heterogeneous catalysis [1].

(d) (i) The mixture is cooled [1] and ammonia condenses [1].

(ii) Recycled. [1]

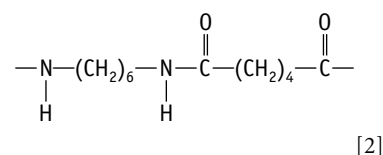
(e) (i)  $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} [2]$

(ii)  $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 [1]$

(f) (i) This saves on transport costs [1]; engineering facilities can be shared [1]; whole process can be kept going continuously [1]; the ammonia is used to make both nitric acid and ammonium nitrate [1]. (any 3 for [3])

(ii) No naked flames; prevent leaks into water supply; use rubber tools etc. (any 1 for [1])

(g) Nylon [1]; condensation polymerisation [1].



Clothing/textiles/tent fabric; ropes/string/thread; carpets; fishing line. (any 2 for [2])

97 (a) (i)  $\Delta H^{\ominus} = 2(-395) - 2(-297) [1]$   
 $= -196 \text{ kJ mol}^{-1} [1]$

(ii) Oxygen is an element.  $\Delta H_f^{\ominus}$  of all elements is zero. [1]

(b) (i)  $K_p = \frac{p(\text{SO}_3)^2}{p(\text{SO}_2)^2 \times p(\text{O}_2)}$

(ii) The sign of  $\Delta H$ . [1] (If  $\Delta H$  is positive,  $K_p$  increases with temperature)

(iii) Effect of increasing the temperature:  
 The value of the equilibrium constant:  $K_p$  decreases. [1]  
 The rate of the forward reaction: increases. [1]

The rate of the backward reaction: increases. [1]

(c) (i)  $\text{H}_2\text{O}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 [1]$

(ii) Number of moles of NaOH =  $15 \times 10^{-3} \times 0.1$   
 $= 1.5 \times 10^{-3} [1]$   
 Number of moles of  $\text{H}_2\text{SO}_4$   
 $= \frac{1.5 \times 10^{-3}}{2}$

$$= 7.5 \times 10^{-4} [1]$$

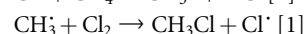
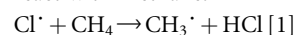
$\therefore$  number of moles of  $\text{SO}_2$  in  $200 \text{ m}^3$  of air  
 $= 7.5 \times 10^{-4}$

Mass of  $\text{SO}_2$  in  $200 \text{ m}^3$  of air  
 $= 7.5 \times 10^{-4} \times 64$   
 $= 0.048 \text{ g} [1]$

$$\therefore \text{concentration of } \text{SO}_2 = \frac{0.048}{200}$$

$$= 2.4 \times 10^{-4} \text{ g m}^{-3} [1]$$

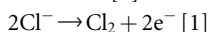
98 (a) Light provides energy [1] to break the Cl-Cl bond [1] and to generate free radicals ( $\text{Cl}^\cdot$ ) [1]. The free radicals react with methane:



Other products are generated by further reaction or by termination steps: e.g.  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_6$  [1], so the product is not pure [1].

(b) The first ionisation energy (I.E.) is the energy required to remove 1 mole of electrons from 1 mole of gaseous atoms. [1] The first I.E. for P is greater than for Si, as the nuclear charge in P is greater [1] and the shielding by inner shells is the same [1]. The first I.E. for P is greater than for S, as S has a paired electron in the 3p shell. [1] The repulsion between the paired electrons makes them easier to remove. [1]

(c) The liberation of chlorine is oxidation. [1]



The reaction between  $\text{MnO}_4^-/\text{H}^+$  and  $\text{Cl}^-$  has a positive  $E^\ominus$ :  $1.52 - 1.36 = +0.16$  V, so the reaction takes place. [1]

The reaction between  $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$  and  $\text{Cl}^-$  has a negative  $E^\ominus$ :

$1.33 - 1.36 = -0.03$  V and so does not take place. [1]

$E^\ominus$  values refer to  $1.0 \text{ mol dm}^{-3}$  solutions/standard conditions. [1]

Concentrated HCl is not

$1.0 \text{ mol dm}^{-3}$ . [1] The change in concentration of  $\text{H}^+$  and  $\text{Cl}^-$  is enough to change  $E^\ominus$ , so it becomes positive and the reaction takes place. [1]

(d) Bonds broken: C—O and H—O [1]

Bonds made: C—O and H—O [1]

So  $\Delta H$  is likely to be approximately zero. [1] So  $K_c$  will be unaffected by temperature. [1]

The relationship between  $K_c$  and  $T$  depends on the sign of  $\Delta H$  [1] and since  $\Delta H \approx 0$ , changing the temperature will not affect the position of equilibrium [1].

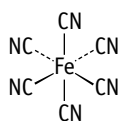
99 (a) Pale green. [1]

(b) To oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  [1]

(c)  $[(\text{Fe}(\text{H}_2\text{O})_6)^{3+}]$  or  $\text{Fe}^{3+}(\text{aq})$  [1]

(d) (i)  $[(\text{Fe}(\text{CN})_6)^{3-}]$  [1]

(ii) Octahedral. [1]



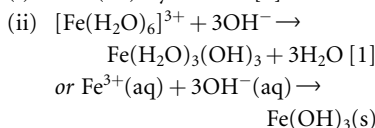
[1]

(iii) To check all  $\text{Fe}^{2+}$  had changed to  $\text{Fe}^{3+}$  [1]

(iv) Add more concentrated nitric acid [1] and reheat [1].

(e) So the ammonia was in excess [1] to ensure all  $\text{Fe}^{3+}$  has precipitated [1].

(f) (i) Iron(III) hydroxide. [1]



(g)  $2\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$  [1]  
or  $2\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3 \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}_2\text{O}$

(h) Mass Fe =  $\frac{112}{160} \times 0.245$  [1]  
= 0.1715 g [1]

(i) %Fe =  $\frac{0.175}{1.20} \times 100$  [1]  
= 14.3% [1]

100 (a) Atomic radius increases [1], so ionisation energies fall [1], making it easier to form positive ions [1]. As the atoms become larger, they become less electronegative and form weaker covalent bonds. [1]

(b) (i) Lead(II) oxide is amphoteric. [1]  
 $\text{PbO} + 2\text{H}^+ \rightarrow \text{Pb}^{2+} + \text{H}_2\text{O}$  [1]  
 $\text{PbO} + 2\text{OH}^- \rightarrow \text{PbO}_2^{2-} + \text{H}_2\text{O}$   
or  $\text{PbO} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow$   
 $\text{Pb}(\text{OH})_4^{2-}$  [1]

(ii)  $\text{PbO}_2 + 4\text{HCl} \rightarrow$   
 $\text{Cl}_2 + \text{PbCl}_2 + 2\text{H}_2\text{O}$  [1]  
This is a redox reaction as Pb(IV) changes to Pb(II) and Cl(-I) changes to  $\text{Cl}_2(\text{O})$ . [1] Pb(II) is more stable than Pb(IV) [1] owing to the inert pair effect. The 6s electrons are difficult to lose as a result of a high nuclear charge and poor shielding by the 4f electrons. [1]

(c) (i) Trigonal planar. [1]  
Boron has 3 bonding pairs of electrons which position themselves as far apart as possible. [1]  
(ii)  $\text{BCl}_3 + \text{H}_2\text{O} \rightarrow$   
 $\text{B}(\text{OH})_3 + 3\text{HCl}$  [1]  
B only has six electrons so it can accept electrons from the attacking water molecule. [1] C is saturated, so in order to react with water a C—Cl bond has to be broken first. [1]

(iii) Addition of  $\text{AgNO}_3(\text{aq})$  produces a white [1] precipitate [1] which dissolves in dilute ammonia [1].

(d) (i)  $\Delta H_{\text{soln}} = 876 - 464 - 293$   
= +119  $\text{kJ mol}^{-1}$  [1]  
A large, positive value of  $\Delta H_{\text{soln}}$  suggests dissolving is not likely to occur. [1]

(ii)  $\Delta H$  is not the only driving force for a reaction. [1] Entropy must also be considered.

(iii) As the concentration of  $\text{Ag}^+$  ions rises [1] the equilibrium moves towards the left. [1] This ensures that precipitation is complete. [1]

101 (a) The equation given can be obtained by adding together equations I, II and III. [1]

$$\begin{aligned} \therefore \Delta H &= \Delta H_{\text{I}} + \Delta H_{\text{II}} + \Delta H_{\text{III}} \quad [1] \\ \Delta H &= +181 + (-113) + (-128) \quad [1] \\ &= -60 \text{ kJ mol}^{-1} \quad [1] \end{aligned}$$

Although  $\Delta H$  is favourable overall [1], the first stage is endothermic, so the reaction is unlikely to proceed under normal conditions [1].

(b) Temperature: since  $\Delta H$  is positive, a high temperature will move the equilibrium position to the right. [2] A high temperature will also increase the rate [1] as more molecules will have sufficient energy to react [1]. Pressure: there are equal numbers of molecules on both sides of the equation, so pressure has no effect on the position of equilibrium. [2] Increasing the pressure will increase the rate. [1] For the process to be economical, the equilibrium must move as far as possible to the right [1] and the reaction must be as fast as possible [1].

(c) Points to consider:

- Nitrates and urea are both soluble and are therefore leached from soil quickly. [1]
- Urea releases nitrogen more slowly. [1]
- Nitrates drain into rivers and can cause eutrophication. [1]
- If nitrates get into the water supply they are harmful to humans. [1]
- % Nitrogen:  
Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ :  
 $\frac{28}{80} \times 100 = 35\%$   
Urea,  $\text{CO}(\text{NH}_2)_2(\text{aq})$ :  
 $\frac{28}{60} \times 100 = 47\%$  [1]
- Urea is more expensive than ammonium nitrate. [1]  
(any 4 for [4])

(d) The epoxy groups are very reactive [1] owing to highly strained rings [1]. The

