

# Answers to self-assessment questions in Chapters 1 to 21

## 1 Stoichiometric relationships

- 1 a Heat produced; colour change  
 b Magnesium + iodine → magnesium iodide  
 c Compounds can be decomposed; elements cannot be decomposed.  
 Elements contain one type of atom; compounds have two or more different atoms bonded together.

- 2 a Melting  
 b Freezing or solidifying  
 c Boiling  
 d Boiling  
 e Vapour deposition  
 f Sublimation

- 3 a 40°C and 90°C  
 b Solid, liquid and gas.  
 c There is no change in temperature; the thermal energy (heat) is used to separate the particles and overcome the intermolecular forces or chemical bonds.

- 4  $\text{C(s)} + 2\text{H}_2\text{O(g)} \rightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{(g)}$   
 12      $[2 \times 18]$      44      $[2 \times 2]$

Recall that the  $A_r$  or  $M_r$  in grams is one mole, so:

Total mass of products = 44 g + 4 g = 48 g, note that this is the same as the reactants: 12 + 36 = 48 g.

Mass of hydrogen = 4 g

$$\% \text{ atom economy} = \frac{4}{48} \times 100 = 8.3\%$$

- 5 a Element  
 b Compound  
 c Compound  
 d Element  
 e Mixture of compounds  
 f Mixture of elements with a compound
- 6 Homogenous; heterogeneous; homogenous; heterogeneous; homogenous; homogenous; homogenous; homogenous;
- 7  $\text{Fe}_2(\text{PO}_4)_3$ ,  $\text{NH}_4\text{I}$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{CaBr}_2$  and  $\text{Fe}_2\text{O}_3$ .
- 8  $\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4 + 4\text{HCl}$   
 $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$

- 9  $\text{Ag}(\text{NO}_3)_2(\text{aq}) + 2\text{NaCl}(\text{aq}) \rightarrow \text{AgCl(s)} + 2\text{NaNO}_3(\text{aq})$   
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl(s)}$   
 $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O(l)}$   
 $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$   
 $\text{Zn(s)} + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu(s)}$   
 $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$   
 $\text{Na}_2\text{CO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$   
 $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$

10 2:1

11  $0.01 \text{ mol} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 6.02 \times 10^{21}$

12  $\frac{9 \times 10^{23}}{6.02 \times 10^{23}} = 1.5 \text{ mol}$

13 Number of oxygen atoms =  $(9 \times 10^{23} \times 3) = 2.7 \times 10^{24}$

15  $\frac{35.45}{9.01} = 3.93 = 4$

16 Molar mass of magnesium carbonate,  $\text{MgCO}_3$   
 $= [24.31 + 12.01 + (3 \times 16.00)]$   
 $= 84.32 \text{ g mol}^{-1}$

17 Molar mass of carbon dioxide,  $\text{CO}_2$   
 $= [12.01 + (2 \times 16.00)]$   
 $= 44.01 \text{ g mol}^{-1}$

18 Molar mass of hydrated iron(II) sulfate crystals,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$   
 $= 55.85 + 32.07 + (4 \times 16.00) + 7 \times [(2 \times 1.01) + 16.00]$   
 $= 278.06 \text{ g mol}^{-1}$

19 Amount of water molecules =  $\frac{54 \text{ g}}{18 \text{ g mol}^{-1}} = 3.0 \text{ mol}$

20 Amount of calcium =  $\frac{500 \text{ g}}{40 \text{ g mol}^{-1}} = 12.5 \text{ mol}$

21 Amount of water =  $\frac{0.18 \text{ g}}{18 \text{ g mol}^{-1}} = 0.010 \text{ mol}$

22 Mass of calcium carbonate(g) =  $0.40 \text{ mol} \times 100 \text{ g mol}^{-1}$   
 $= 40 \text{ g}$

23 Molar mass ( $\text{g mol}^{-1}$ ) =  $\frac{1.00 \text{ g}}{0.00200 \text{ mol}} = 500 \text{ g mol}^{-1}$

24 Mass of a single molecule of  $\text{CO}_2$  =  $\left( \frac{44.01 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} \right) \times 1000$   
 $= 7.31 \times 10^{-20} \text{ kg}$

$$25 \text{ Amount of propane} = \frac{22 \text{ g}}{44 \text{ g mol}^{-1}} = 0.50 \text{ mol}$$

Hence, 22 g of propane contains  $(6 \times 10^{23} \times 0.50 = 3 \times 10^{23})$  molecules of propane and since each molecule of propane contains 11 atoms (3 carbon atoms and 8 hydrogen atoms), the total number of atoms is  $(11 \times 3 \times 10^{23}) = 3.3 \times 10^{24}$ .

The total number of carbon atoms is  $(3 \times 3 \times 10^{23}) = 9 \times 10^{23}$  and the total number of hydrogen atoms is  $(8 \times 3 \times 10^{23}) = 2.4 \times 10^{24}$ .

$$26 \text{ Amount of atoms: C: } \frac{39.13}{12.01} = 3.258 \text{ mol;}$$

$$\text{O: } \frac{52.17}{16.00} = 3.261 \text{ mol and H: } \frac{8.70}{1.01} = 8.61 \text{ mol}$$

Dividing through by smallest: 1 : 1 : 2.6 and then multiplying through by 3:  $\text{C}_3\text{H}_8\text{O}_3$

27	Lead	Oxygen
Combining masses:	41.4 g	$(44.6 \text{ g} - 41.4 \text{ g}) = 3.2 \text{ g}$
Amount of atoms:	$\frac{41.4 \text{ g}}{207 \text{ g mol}^{-1}}$	$\frac{3.2 \text{ g}}{16 \text{ g mol}^{-1}}$
Ratio of amounts:	0.2	0.2
Empirical formula: $\text{PbO}$		

$$28 \text{ Mass of carbon in } \text{CO}_2 = \frac{12.01}{44.01} \times 0.6875 \text{ g} = 0.1876 \text{ g}$$

$$\text{Mass of hydrogen in } \text{H}_2\text{O} = \frac{2.02}{18.02} \times 0.5625 \text{ g} = 0.06305 \text{ g}$$

$$\text{Amount of carbon atoms} = \frac{0.1876 \text{ g}}{12.01 \text{ g mol}^{-1}} = 0.01562 \text{ mol}$$

$$\text{Amount of hydrogen atoms} = \frac{0.06305 \text{ g}}{1.01 \text{ g mol}^{-1}} = 0.06243 \text{ mol}$$

Empirical formula is  $\text{CH}_4$ .

$$29 \text{ Percentage by mass of carbon} = \frac{12}{16} \times 100 = 75\%$$

$$\text{Percentage by mass of hydrogen} = \frac{4}{16} \times 100 = 25\%$$

$$\text{Sum of percentages by mass} = (75\% + 25\%) = 100\%$$

$$30 \text{ Percentage by mass of sodium} = \frac{46}{322} \times 100 = 14.3\%$$

$$\text{Percentage by mass of sulfur} = \frac{32}{322} \times 100 = 9.9\%$$

$$\text{Percentage by mass of oxygen} = \frac{64}{322} \times 100 = 19.9\%$$

$$\text{Percentage by mass of water} = \frac{180}{322} \times 100 = 55.9\%$$

31	Carbon	Hydrogen	Oxygen
Combining masses:	73.47 g	10.20 g	16.33 g
Amount of atoms:	$\frac{73.47}{12}$	$\frac{10.20}{1}$	$\frac{16.33}{16}$
Ratio of amounts:	6.1225	10.20	1.020

Dividing through by smallest number:

$\frac{6.1225}{1.020}$	$\frac{10.20}{1.020}$	$\frac{1.020}{1.020}$
6	10	1

Empirical formula:  $\text{C}_6\text{H}_{10}\text{O}$

To determine the molecular formula:

$$196 = [(6 \times 12) + (10 \times 1) + 16] \times n = 98 \times n$$

Hence  $n$  equals two and the molecular formula is  $\text{C}_{12}\text{H}_{20}\text{O}_2$ .

$$32 \text{ Amount of hexan-1-ol} = \frac{20.4 \text{ g}}{102 \text{ g mol}^{-1}} = 0.200 \text{ mol}$$

Hence, the theoretical amount of hex-1-ene produced is 0.200 mol (since there is excess phosphoric(v) acid).

$$\text{Amount of hex-1-ene} = \frac{\text{mass(g)}}{\text{molar mass(g mol}^{-1}\text{)}} = 0.200 \text{ mol}$$

$$\text{Rearranging, mass of hex-1-ene} = 84 \text{ g mol}^{-1} \times 0.200 \text{ mol} = 16.8 \text{ g}$$

Since only 10.08 g of hex-1-ene was produced, the

$$\text{percentage yield is } \frac{10.08 \text{ g}}{16.8 \text{ g}} \times 100 = 60\%.$$

$$33 \text{ Volume occupied} = 1.35 \text{ mol} \times 22.7 \text{ dm}^3 \text{ mol}^{-1} = 30.6 \text{ dm}^3$$

$$34 \text{ Amount of gas} = \frac{\left(\frac{175}{1000}\right) \text{ dm}^3}{22.7 \text{ dm}^3 \text{ mol}^{-1}} = 7.71 \times 10^{-3} \text{ mol}$$

$$35 \text{ Amount of carbon dioxide} = \frac{2.85 \text{ dm}^3}{22.7 \text{ dm}^3 \text{ mol}^{-1}} = 0.126 \text{ mol}$$

$$\text{Number of molecules} = 0.126 \times 6.02 \times 10^{23} \text{ mol}^{-1} = 7.59 \times 10^{22}$$

$$36 \text{ Density} = \frac{\text{mass}}{\text{volume}} = \frac{39.95 \text{ g}}{22.7 \text{ dm}^3} = 1.76 \text{ g dm}^{-3}$$

$$37 \text{ Amount of gas} = \frac{7.44 \text{ dm}^3}{22.7 \text{ dm}^3 \text{ mol}^{-1}} = 0.328 \text{ mol}$$

$$\text{Molar mass} = \frac{20.8 \text{ g}}{0.328 \text{ mol}} = 63.4 \text{ g mol}^{-1}$$

$$38 \text{ Amount of } \text{KClO}_3 = \frac{3.06 \text{ g}}{122.5 \text{ g mol}^{-1}} = 0.025 \text{ mol}$$

$$\text{Amount of } \text{O}_2 = \frac{0.84 \text{ dm}^3}{22.7 \text{ dm}^3 \text{ mol}^{-1}} = 0.0370 \text{ mol}$$

The simplest molar ratio is 2 : 3 and hence the balanced equation must be



$$39 \text{ } V_2 = \frac{V_1 \times T_2}{T_1} = \frac{4.50 \text{ dm}^3 \times 350 \text{ K}}{300 \text{ K}} = 5.25 \text{ dm}^3$$

$$40 \quad \frac{97\,000\text{ Pa}}{298\text{ K}} = \frac{101\,325\text{ Pa}}{T_2}$$

$$T_2 = 101\,325\text{ Pa} \times \frac{298\text{ K}}{97\,000\text{ Pa}}$$

$$T_2 = 311.3\text{ K} = (311.3 - 273) = 38.3^\circ\text{C}$$

$$41 \quad \frac{T_2}{T_1} = \frac{P_2}{P_1} = \frac{3000\text{ K}}{300\text{ K}} = 10$$

$$\frac{P_2}{P_1} = 10:1$$

$$42 \quad \frac{1.05 \times 10^5\text{ Pa} \times 60\text{ cm}^3}{333\text{ K}} = \frac{1.01 \times 10^5\text{ Pa} \times V_2}{273\text{ K}}$$

$$V_2 = \frac{1.05 \times 10^5\text{ Pa} \times 60\text{ cm}^3 \times 273\text{ K}}{(1.01 \times 10^5\text{ Pa} \times 333\text{ K})} = 51\text{ cm}^3$$

$$43 \quad PV = nRT; n = \frac{PV}{RT}; n = \frac{101\,325\text{ Pa} \times 4 \times 10^{-3}\text{ m}^3}{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 273\text{ K}} = 0.1786\text{ mol}$$

$$\text{Amount of gas} = \frac{\text{mass(g)}}{\text{relative molecular mass}};$$

$$\text{relative molecular mass} = \frac{\text{mass(g)}}{\text{amount (mol)}}$$

$$\text{Relative molecular mass (M}_r\text{)} = \frac{12.64}{0.1786} = 70.7$$

$$44 \quad M_r = d \frac{RT}{P}; M_r = \frac{2.615\text{ kg m}^{-3} \times 8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 298\text{ K}}{101.325\text{ kPa}} = 63.9$$

$$45 \quad \text{Concentration} = \frac{0.5\text{ mol}}{5.0\text{ dm}^3} = 0.1\text{ mol dm}^{-3}$$

$$46 \quad \text{Amount of sodium hydroxide} = \frac{4.00\text{ g}}{40.0\text{ g mol}^{-1}} = 0.100\text{ mol}$$

$$\text{Concentration of sodium hydroxide} = \frac{0.100\text{ mol}}{0.200\text{ dm}^3} = 0.50\text{ mol dm}^{-3}$$

$$47 \quad \text{Amount of hydrated copper(II) sulfate} = 0.50\text{ mol dm}^{-3} \times 0.0250\text{ dm}^3 = 0.0125\text{ mol}$$

$$\text{Mass of hydrated copper(II) sulfate} = 0.0125\text{ mol} \times 249.7\text{ g mol}^{-1} = 3.12\text{ g}$$

$$48 \quad \text{Molar mass of hydrogen chloride} = (1.00\text{ g mol}^{-1} + 35.5\text{ g mol}^{-1}) = 36.5\text{ g mol}^{-1}$$

$$\text{Amount of hydrogen chloride in } 100\text{ cm}^3 = \frac{14.6\text{ g}}{36.5\text{ g mol}^{-1}} = 0.400\text{ mol}$$

$$\text{Hence, the concentration of hydrogen chloride} = 0.400 \times 10 = 4\text{ mol dm}^{-3}$$

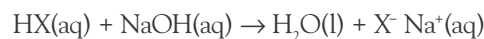
$$49 \quad M_1 \times V_1 = M_2 \times V_2; 5.0\text{ mol dm}^{-3} \times 25.0\text{ cm}^3 = 1.5\text{ mol dm}^{-3} \times V_2$$

$$V_2 = 25.0 \times \frac{5.0}{1.5} = 83.3\text{ cm}^3$$

50 Amount of sodium hydroxide

$$= \frac{0.100\text{ mol dm}^{-3} \times 41.0\text{ cm}^3}{1000} = 4.10 \times 10^{-3}\text{ mol}$$

Amount of HX equals  $4.1 \times 10^{-3}\text{ mol}$  because the acid and base are reacting in a 1:1 molar ratio:



Hence, molar mass of HX =

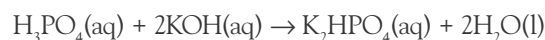
$$\frac{\text{mass(g)}}{\text{amount (mol)}} = \frac{0.558\text{ g}}{4.10 \times 10^{-3}\text{ mol}} = 136\text{ g mol}^{-1}$$

51 Amount of potassium hydroxide

$$= \frac{17.5\text{ dm}^3}{1000} \times 0.150\text{ mol dm}^{-3} = 2.63 \times 10^{-3}\text{ mol}$$

$$\text{Amount of phosphoric acid} = \frac{20.0\text{ dm}^3}{1000} \times 0.0656\text{ mol dm}^{-3} = 1.31 \times 10^{-3}\text{ mol}$$

The two chemicals react in a 2 to 1 molar ratio and hence the equation is:



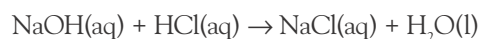
52 a  $2\text{NaOH(aq)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O(l)}$

$$\text{b Amount of sodium hydroxide used in the titration} = \frac{25.0\text{ dm}^3}{1000} \times 1.00\text{ mol dm}^{-3} = 0.0250\text{ mol NaOH}$$

$$\text{c From the equation, amount of H}_2\text{SO}_4 = \text{amount of NaOH} \div 2 = 0.0125\text{ mol in } 20.0\text{ cm}^3, \text{ so 'scaling up' to } 1000\text{ cm}^3 \text{ to obtain the concentration of diluted sulfuric acid} = \frac{1000 \times 0.0125\text{ mol dm}^{-3}}{20.0} = 0.625\text{ mol dm}^{-3}$$

$$\text{d 'Scaling up' from } 50.0 \text{ to } 1000\text{ cm}^3 \text{ gives the concentration of the original concentrated sulfuric acid solution} = \frac{0.625 \times 0.0125\text{ mol dm}^{-3} \times 1000}{50.0} = 12.5\text{ mol dm}^{-3}$$

53 a  $\text{MgO(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O(l)}$



$$\text{b Amount of hydrochloric acid added to the magnesium oxide} = \frac{100\text{ dm}^3}{1000} \times 2.00\text{ mol dm}^{-3} = 0.200\text{ mol}$$

$$\text{c Amount of excess hydrochloric acid titrated} = \frac{19.7\text{ dm}^3 \times 0.200\text{ mol dm}^{-3}}{1000} = 0.00394\text{ mol HCl,}$$

since the mole ratio of NaOH to HCl is 1:1

$$\text{d Amount of hydrochloric acid reacting with the magnesium oxide} = 0.200\text{ mol} - 0.00394\text{ mol} = 0.196\text{ mol}$$

- e Amount of magnesium oxide that reacted  

$$= \frac{0.196 \text{ mol}}{2} = 0.098 \text{ mol (1:2 molar ratio in equation). The molar mass of magnesium oxide is } 40.3 \text{ g mol}^{-1}, \text{ hence the mass of magnesium oxide reacting with acid} = 0.098 \text{ mol} \times 40.3 \text{ g mol}^{-1} = 3.95 \text{ g}$$
  
 and hence percentage purity =  $\frac{3.95 \text{ g}}{4.08 \text{ g}} \times 100 = 97\%$ .

- 54 The amount of solution made with distilled water should be  $500 \text{ cm}^3$ .

$$\text{Amount of } \text{Cr}_2\text{O}_7^{2-} = \left( \frac{24.00}{1000} \right) \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3} = 0.0024 \text{ mol}$$

$$\text{Amount of } \text{Fe}^{2+} \text{ in } 20.00 \text{ cm}^3 = 6 \times 0.0024 \text{ mol} = 0.0144 \text{ mol}$$

$$\text{Amount of } \text{Fe}^{2+} \text{ in } 500 \text{ cm}^3 \text{ solution}$$

$$= \left( \frac{500}{20} \right) \times 0.0144 \text{ mol} = 0.36 \text{ mol}$$

$$\text{Amount of } \text{Fe}^{2+} = \text{amount of } \text{FeSO}_4 \cdot x\text{H}_2\text{O}$$

$$\text{Molar mass} = \frac{\text{mass}}{\text{amount}}$$

$$\text{Molar mass} = \frac{101.2 \text{ g}}{0.36 \text{ mol}} = 281.1 \text{ g mol}^{-1}$$

$$\text{Molar mass of } \text{FeSO}_4 = 151.91 \text{ g mol}^{-1}$$

$$\text{Molar mass of water molecules} = 281.1 \text{ g mol}^{-1} - 151.91 \text{ g mol}^{-1} = 129.2 \text{ g mol}^{-1}$$

$$\text{Number of water molecules} = \frac{129.2 \text{ g mol}^{-1}}{18.02 \text{ g mol}^{-1}} = 7; x = 7$$

- 55 Amount of  $\text{S}_2\text{O}_3^{2-} = \left( \frac{26.20}{1000} \right) \text{ dm}^3 \times 0.500 \text{ mol dm}^{-3} = 0.0131 \text{ mol}$

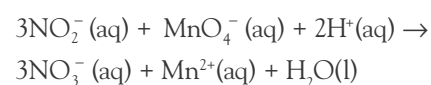
$$\text{Amount of } \text{I}_2 \text{ reacting with } \text{S}_2\text{O}_3^{2-} = \frac{1}{2} \times 0.0131 \text{ mol} = 0.00655 \text{ mol}$$

$$\text{Amount of } \text{MnO}_4^-/\text{KMnO}_4 = \frac{2}{5} \times 0.00655 \text{ mol} = 0.00262 \text{ in } 25.00 \text{ cm}^3$$

$$\text{Concentration of } \text{KMnO}_4 = \left( \frac{1000}{25.00} \right) \times 0.00262 \text{ mol} = 0.105 \text{ mol dm}^{-3}$$

- 56 Amount of  $\text{KMnO}_4$  solution

$$= \left( \frac{12.15}{1000} \right) \text{ dm}^3 \times 0.0100 \text{ mol dm}^{-3} = 0.0001215 \text{ mol}$$



$$\text{Amount of } \text{NO}_2^- = 0.0001215 \text{ mol} \times 3 = 0.0003645 \text{ mol}$$

$$\text{Mass of } \text{NaNO}_2 = 0.0003645 \text{ mol} \times 69.00 \text{ g mol}^{-1} = 0.02515 \text{ g}$$

$$\text{Percentage by mass of } \text{NaNO}_2 = \left( \frac{0.025}{1.00} \right) \times 100 = 2.5\%$$

## 2 Atomic structure

- 1 Mass of one mole of electrons  

$$= 9.109383 \times 10^{-31} \text{ g} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 5.48 \times 10^{-7} \text{ g} = 5.48 \times 10^{-5} \text{ kg}$$

$$\text{Charge on one mole of electrons} = 1.602189 \times 10^{-19} \text{ C} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 9.64 \times 10^4 \text{ C}$$

- 2 Volume of atom =  $4 \times \pi \times (10^{-10} \text{ m})^3/3 = 4.2 \times 10^{-30} \text{ m}^3$

$$\text{Volume of nucleus} = 4 \times \pi \times (10^{-16} \text{ m})^3/3 = 4.2 \times 10^{-48} \text{ m}^3$$

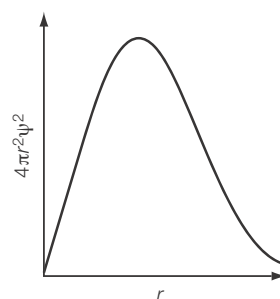
$$\text{Percentage of atom that is nucleus} = 4.2 \times 10^{-48} \text{ m}^3/4.2 \times 10^{-30} \text{ m}^3 \times 100 = 10^{-16}\%$$

- 3 A hydrogen atom consists of one proton and one electron. Mass of hydrogen atom is the sum of the proton and electron masses (ignoring the mass defect).

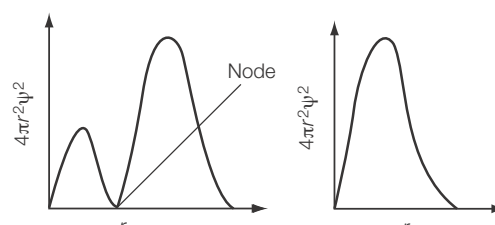
$$\frac{1.672622 \times 10^{-27} + 9.109383 \times 10^{-31} \text{ g}}{9.109383 \times 10^{-31} \text{ g}} = 1837 \text{ times heavier}$$

- 4 A probability density curve is a plot prepared by plotting the calculated electron probability ( $|\psi|^2$ ) against the distance from the nucleus ( $r$ ). Radial probability electron distribution curves give the probability of finding the electron at a given distance from the nucleus (regardless of the angular position). The probability of finding an electron at a node is zero.

Radial probability density curves for three atomic orbitals:



For 1s orbital



For 2s orbital

For 2p orbital

The particles (atoms or molecules) are identical in terms of physical properties but distinguishable in terms of position, path or trajectory. The equilibrium distribution is the most probable way of distributing the particles among various allowed energy states. There is no theoretical limit on the number of particles in a given energy state, but the density of particles is sufficiently low and the temperature sufficiently high that no more than one particle is likely to be in a given state at one time.

- 5 The third hydrogen species listed in the question should be  ${}^2_1\text{H}$ . Protons, neutrons and electrons: 1, 2, 2; 1, 2, 0; 1, 1, 2; and 2, 0, 0.
- 6  $A_r = (\text{mass isotope 1})(\text{abundance isotope 1}) + (\text{mass isotope 2})(\text{abundance isotope 2})$   
 $= 192.22 = (191)x + (193)(1 - x)$   
 $= 191x + 193 - 193x$   
 $= -2x + 193; 2x = 193 - 192.22; x = 0.39$   
 Therefore the abundance of  ${}^{191}\text{Ir}$  is 39% and that of  ${}^{193}\text{Ir}$  is 61%.
- 7 Carbon-60 was first detected as an unusually abundant species in mass spectra recorded on carbon clusters produced by laser vaporization of graphite in a flow of helium gas. The most abundant carbon cluster had a molecular mass of 720.
- 8 Ultraviolet radiation: higher frequency, smaller wavelength, greater energy and higher wave number.  
 Infrared radiation: lower frequency, greater wavelength, lower energy and lower wave number.
- 9 a Frequency, energy or wavelength.  
 b Frequency: decreasing; wavelength: increasing, left to right.  
 c When sufficient energy (thermal or electrical) is supplied, electrons can be promoted (excited) to higher energy levels in an atom. The electrons are unstable in higher levels and rapidly emit radiation and fall back into lower energy levels. As the energy levels are fixed, the energy lost between any higher level and a lower level is also of a certain fixed value so the radiation emitted will only have certain fixed frequencies (i.e. specific colours). This means that the atomic spectrum of an element will consist of a series of lines of different colours (on a black background),  
 d Main energy level 2 (second shell) i.e.  $n = 2$   
 e Each element has its own characteristic line spectrum. Therefore an element can be identified by its line spectrum just as a criminal can be identified from a fingerprint.  
 f An unknown yellow emission line was observed in the solar spectrum during an eclipse.  
 g In a continuous spectrum the radiations corresponding to all the wavelengths (within a certain range) are present. In an emission spectrum only a limited number of radiations corresponding to a small number of wavelengths (within a certain range) are present.
- 10 This is a thought experiment illustrating the principles of quantum mechanics. A cat is placed in a sealed box along with a Geiger counter, a vial of poison, a hammer and a radioactive substance. When the substance undergoes decay, the Geiger counter detects the ionizing particle and triggers the hammer to release the poison which kills the cat. Radioactive decay is a random process and the atom exists in a state known as

superposition, both decayed and not decayed at the same time. Until the box is opened, an observer does not know whether the cat is dead or alive. It is considered to be both alive and dead at the same time until it is observed.

- 11  $\text{Ti}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$   
 $\text{Cr}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$   
 $\text{Cu}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$   
 $\text{P}^{3-}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6$   
 $\text{Cl}$ :  $1s^2 2s^2 2p^6 3s^2 3p^5$   
 $\text{Ga}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$
- 12 i Li atom is  $1s^2 2s^1$  atom (excited state)  
 ii H atom is  $1s^1 \text{H}^-$  (hydride ion) (ground state)  
 iii S atom is  $1s^2 2s^2 2p^6 3s^2 3p^4$  atom (ground state)  
 iv N atom is  $1s^2 2s^2 2p^3 \text{N}^+$  (unipositive ion) (excited state)  
 v F atom is  $1s^2 2s^2 2p^5 \text{F}^-$  (fluoride ion) (excited state)
- 13 The electrons in atoms are uniquely described by four electron numbers. The principal quantum number ( $n$ ) describes the energy of the orbital – the shell. The angular quantum number ( $l$ ) describes the shape of the orbital: s, p, d and f. The third quantum number, known as the magnetic quantum number ( $m$ ), describes the orientation in space of a particular orbital. (It is called the *magnetic* quantum number because the effect of different orientations of orbitals was first observed in the presence of a magnetic field).  
 Rules governing the allowed combinations of quantum numbers:  
 The three quantum numbers ( $n$ ,  $l$ , and  $m$ ) that describe an orbital are integers: 0, 1, 2, 3, and so on. The principal quantum number ( $n$ ) cannot be zero. The allowed values of  $n$  are therefore 1, 2, 3, 4, and so on. The angular quantum number ( $l$ ) can be any integer between 0 and  $n - 1$ . If  $n = 3$ , for example,  $l$  can be either 0, 1, or 2. The magnetic quantum number ( $m$ ) can be any integer between  $-l$  and  $+l$ . If  $l = 2$ ,  $m$  can be either  $-2$ ,  $-1$ , 0,  $+1$ , or  $+2$ .

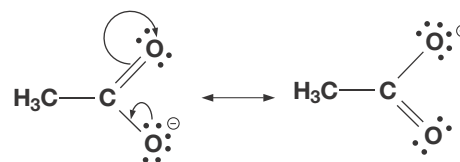
### 3 Periodicity

- 1 The periodic table is a tabular arrangement of the chemical elements organized in the basis of their atomic number, electron configurations and recurring chemical properties. Elements are presented in order of increasing atomic number into groups, periods and blocks.

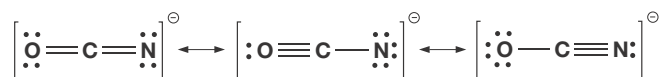
There are many alternative forms of the periodic table, including spiral and helical, many of which highlight or emphasize chemical or physical properties of the elements that are not as apparent in the long form of the periodic table.

- 2 X is magnesium:  $1s^2 2s^2 2p^6 3s^1$ ; Y is phosphorus:  $1s^2 2s^2 2p^6 3s^2 3p^3$  and Z is argon:  $1s^2 2s^2 2p^6 3s^2 3p^3$ .

- 3 P is argon (group 18; period 3); Q is bromine (group 17; period 4) and R is calcium (group 2 and period 4).
- 4 Graphs can be plotted as line graphs (with smooth curves). The physical property on the vertical axis and the halogen along the horizontal axis. The data for fluorine, chlorine, bromine and iodine can be extrapolated to astatine.
- 5 There is generally a correlation between electron affinity and electronegativity, because they both are measures of an affinity of an atom for electrons. However, the electron affinities of nitrogen and phosphorus are relatively low. This is due to the presence of half-filled p sub-shells which increases inter-electron repulsion and decreases electron affinity.
- 6 Indium is classified as a metal. It is in group 13 and hence expected to form indium(III) ions,  $\text{In}^{3+}$ . It is expected to be a relatively unreactive metal that is not expected to react with water. It is expected to be an excellent thermal and electrical conductor.
- 7 Volumes, concentrations and temperatures of chemicals including the catalyst must be controlled. The reacting mixtures should be made homogenous by stirring.
- 3 Chlorine–chlorine: 0; covalent (non-polar)  
Hydrogen–fluorine: 1.8; covalent (highly polar)  
Carbon–chlorine: 0.6; covalent (polar)  
Beryllium–chlorine: 1.6; covalent (polar)  
Carbon–hydrogen: 0.4 covalent (polar)
- 4 Phosphorus tribromide or phosphorus(III) bromide; phosphorus pentachloride or phosphorus(V) chloride; lead(II) chloride, lead(IV) chloride, iodine monochloride or iodine(I) chloride and sulfur hexafluoride or sulfur(VI) fluoride.
- 5
- $$\begin{array}{ccc} \begin{array}{c} \text{H} \\ \times \\ \oplus \text{C} \times \text{H} \\ \times \\ \text{H} \end{array} & \begin{array}{c} \text{H} \\ \times \\ \ominus \text{C} \times \text{H} \\ \times \\ \text{H} \end{array} & \begin{array}{c} \text{H} \\ \times \\ \cdot \text{C} \times \text{H} \\ \times \\ \text{H} \end{array} \\ {}^+\text{CH}_3 & {}^-\text{CH}_3 & \bullet\text{CH}_3 \end{array}$$
- 6 Resonance structures for the ethanoate ion:



Resonance structures for the cyanate ion:



## 4 Chemical bonding and structure

- 1 Ca:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$   
Ca<sup>2+</sup>:  $1s^2 2s^2 2p^6 3s^2 3p^6$   
F:  $1s^2 2s^2 2p^5$   
F<sup>-</sup>:  $1s^2 2s^2 2p^6$   
Each calcium atom loses two electrons; each fluorine atom gains one electron.  
Na:  $1s^2 2s^2 2p^6 3s^1$   
Na<sup>+</sup>:  $1s^2 2s^2 2p^6$   
O:  $1s^2 2s^2 2p^4$   
O<sup>2-</sup>:  $1s^2 2s^2 2p^6$   
Each sodium atom loses one electron; each oxygen atom gains two electrons.  
Al:  $1s^2 2s^2 2p^6 3s^2 3p^1$  Al<sup>3+</sup>:  $1s^2 2s^2 2p^6$   
O:  $1s^2 2s^2 2p^4$  O<sup>2-</sup>:  $1s^2 2s^2 2p^6$   
Each aluminium atom loses three electrons; each oxygen atom gains two electrons.
- 2
- 7 <sup>+</sup>CH<sub>3</sub> (trigonal planar); <sup>-</sup>CH<sub>3</sub> (tetrahedral); PH<sub>3</sub> (trigonal pyramidal); AsH<sub>3</sub> (trigonal bipyramidal) and NH<sub>2</sub><sup>-</sup> (bent, V-shaped or non-linear)
- 8 Colourless (when pure), very hard, high melting and boiling (or sublimation) points, chemically unreactive, poor thermal and electrical conductor.  
It can be used as an abrasive, in cutting tools and brakes. Grains of silicon carbide can be sintered together to form very hard ceramics.
- 9 Iodine monochloride molecules are associated in the solid and liquid states by dipole–dipole forces and London (dispersion) forces. The non-polar bromine molecules are only associated via London (dispersion) forces.

Group	1	2	13	14	15	16	17	18
Element	Li	Be	B	C	N	O	F	Ne
Electron arrangement	2,1	2,2	2,3	2,4	2,5	2,6	2,7	2,8
Electron configuration	$1s^2 2s^1$	$1s^2 2s^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^4$	$1s^2 2s^2 2p^5$	$1s^2 2s^2 2p^6$
Number of electrons in outer shell	1	2	3	4	5	6	7	8
Common simple ion	Li <sup>+</sup>	Be <sup>2+</sup>	None	None	N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	None
Electron arrangement of ion	2	2	—	—	2,8	2,8	2,8	—
Electron configuration of ion	$1s^2$	$1s^2$	—	—	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6$	—



- 10 Carbon disulfide has a higher boiling point than carbon dioxide because molecules of  $\text{CS}_2$  have more electrons than molecules of  $\text{CO}_2$ . This results in the London (dispersion) forces being stronger between molecules of  $\text{CS}_2$ , hence more thermal energy is required to separate them.

Hydrogen peroxide has more electrons than water, which gives a greater polarizability and hence stronger (London) dispersion forces. The hydrogen peroxide has a much greater dipole moment than does the water molecule. The greater dipole–dipole attraction also contributes to the expected increased boiling point. Hydrogen peroxide exhibits hydrogen bonding and with one additional oxygen atom, compared to water, there are more sites available to form hydrogen bonds. With potentially more hydrogen bonding in hydrogen peroxide, the boiling point will be greater (unless decomposition occurs).

## 5 Energetics/thermochemistry

- 1  $^{\circ}\text{C} \times \frac{9}{5} + 32 = ^{\circ}\text{F}$  and  $(^{\circ}\text{F} - 32) \times \frac{5}{9} = ^{\circ}\text{C}$
- 2 A perpetual motion machine is a hypothetical device that produces work without consuming energy (i.e. it creates energy). Such a device would violate the first law of thermodynamics (law of conservation of energy).

## 6 Chemical kinetics

- 1 Sketch a similar graph to Figure 6.6, but the 'products' level on the right should be higher than the 'reactants'. The other labelled items are the same as in Figure 6.6.

- 2 *Collision 1* is the only successful type of collision because the orientation of the molecule is correct both in terms of the H–Cl molecule interacting with the pi electron cloud of the carbon–carbon double bond and the polarization of the attacking molecule. The hydrogen atom is slightly positive ( $\delta^+$ ) and interacts with the negative pi cloud.

*Collision 2:* the H–Cl molecule is wrongly orientated with the Cl atom ( $\delta^-$ ) towards the pi cloud; resulting in repulsion.

*Collisions 3 & 4:* in both the H–Cl molecule is colliding with the wrong region of the ethene molecule.

- 3
  - a Base your sketch on Figure 6.6, but put the actual reactants ( $\text{N}_2 + 3\text{H}_2$ ) and products ( $2\text{NH}_3$ ) on the appropriate levels. You can label the activation energy at this stage.
  - b Using a broken line sketch in a peak that is below that in (a).
  - c Note that the activation energy is lower in the presence of a catalyst.
- 4
  - a The sketch of the energy profile for the uncatalysed reaction will as drawn in 3(a). The energy difference between reactants and products will be  $-92 \text{ kJ mol}^{-1}$ .

The energy difference between the transition state peak and the products will be  $335 \text{ kJ mol}^{-1}$ .

$$E_a = 335 - 92 = +243 \text{ kJ mol}^{-1}$$

- b The activation energy will be lowered to a value less than  $+243 \text{ kJ mol}^{-1}$ .
  - 5
    - a Molybdenum(vi) oxide and silicon(iv) oxide.
    - b The traditional method uses concentrated nitric acid whereas the new method uses only dilute nitric acid. The traditional method uses concentrated sulfuric acid in a powerful mixture with nitric acid; this is not used at all in the new method.
- The temperature used in the new method is higher than that of the traditional method.
- 6 In answering this question refer to Figures 6.17, 6.18 and 6.19 on page 207.
    - a Sketch a graph similar to Figure 6.17.
    - b Activation energy is the minimum combined kinetic energy the colliding molecules must have in order to react.
    - c See Figure 6.17.
    - d See Figure 6.19; draw a line at a lower energy value than your first  $E_a$ .
    - e Shade the area under the graph between the two values for activation energy; see Figure 6.19.
    - f See Figure 6.18.

- 7
  - a At higher pressure the same number of molecules are packed closer together and will collide more frequently (the concentration of the gases is effectively increased) and so there is more chance of reaction.
  - b At higher concentration there are more particles in a given volume and so the collision frequency is increased and so there is more chance of reaction.
  - c There is a greater surface area of the solid exposed for the same mass of solid when it is finely divided and so there is more chance of reaction.
  - d There are two factors here: the molecules have greater combined kinetic energy and so collide more frequently; also when they do collide the combined kinetic energy is more likely to equal or exceed the activation energy and so there is more chance of the collision producing a reaction. This second factor is the more significant of the two.
- 8
  - a Sample B has the highest value of mean kinetic energy.
  - b Convert the temperatures of the samples to Kelvin: A 298 K; B 323 K; C 273 K; D 149 K

The mean kinetic energy of a sample of particles is proportional to the absolute temperature. Sample A has double the mean kinetic energy of sample D.

- 9 22 g of  $\text{CO}_2$  ( $= 0.5 \text{ mol}$ ) produced in a volume of  $4 \text{ dm}^3$  in 15 s

$$\text{Rate} = \frac{\frac{0.5}{4}}{15} = 8.3 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

- 10  $0.06 \text{ mol dm}^{-3}$  of iodine produced in 30 s

$$\text{Rate} = \frac{0.06}{30} = 2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$$

- 11 a Sketch a diagram similar to Figure 6.31 on page 214 without the small tube on the string. Show a strip of magnesium ribbon in the acid. Draw the graph, labelling the axes and plotting the points accurately.
- b Draw a tangent to the curve at time zero and calculate the slope using  $\text{slope} = \Delta y / \Delta x$  (see Figure 6.26 on page 212).
- c Reaction is fastest at the start as the concentration of the acid is greatest at this point. The graph curves as the rate decreases because the acid (and magnesium) is being used up and the collision frequency decreases. Eventually the curve flattens to a plateau as the magnesium is all used up and there is no further reaction (see Figure 6.25 on page 611).
- d Volume of gas produced in  $150 \text{ s} = 75.6 \text{ cm}^3$ .  
Average rate of reaction  $= \frac{75.6}{150} = 0.504 \text{ cm}^3 \text{ s}^{-1}$
- e The magnesium has all been reacted and no more gas is produced. The acid ( $15 \times 10^{-3} \text{ mol}$ ) is in excess of the magnesium ( $4.17 \times 10^{-3} \text{ mol}$ ).
- f Sketch a line on your graph which lies beneath the first line and levels out at  $38 (37.8) \text{ cm}^3$  of hydrogen gas.
- g This graph should be steeper initially but should level out at  $75.6 \text{ cm}^3$  of gas. The reaction will be faster than in the first experiment as the magnesium is powdered, but the same amount of gas is produced. Sketch a curve to show this.
- h This graph will start more slowly (less steep gradient) than the first graph and move towards levelling at the same volume of gas – it probably will not level off on your scale.
- i Sketch a diagram similar to Figure 6.18 on page 207; remember that the first experiment is at the higher temperature.  
Draw in the areas representing the activation energy. At the higher temperature more particles will have energy greater than or equal to the activation energy and therefore more collisions will result in product formation. Hence the rate of reaction will increase.
- 12 a Average temperatures: A 24; B 32; C 39; D 49; E 57
- b Draw the graph, labelling the axes and plotting the points accurately. Draw a smooth best-fit curve using the points.
- c The rate is fastest in experiment E.
- d The rate is fastest at the highest temperature. The particles are moving fastest and therefore collide more

frequently and, more importantly, a greater proportion of collisions will result in a reaction as more collisions involve particles whose total kinetic energy is equal to or greater than the activation energy for the reaction.

- e These factors, including the dimensions of the flask, must be kept constant so that the experiments are comparable, with only one variable changed; the cross must be viewed through the same depth of solution each time.
- f Extrapolate your curve and estimate a value for the time taken at  $70^\circ\text{C}$ .
- g Sketch a curve on your graph which is steeper than the experimental curve.
- h Use an ice-water bath to achieve a temperature between  $0^\circ\text{C}$  and  $5^\circ\text{C}$ ; equilibrate the solutions to this temperature before mixing them to react.

## 7 Equilibrium

- 1 a The rates of the forward and reverse reactions are equal; there is no change in the concentrations of the components of the equilibrium mixture even though reactions are taking place.
- b The reaction must be taking place in a closed system.
- 2 a Sketch a graph using Figure 7.9b on page 227 for guidance; the two curves do not meet.
- b Sketch a graph in which the rate of the forward reaction decreases and that of the reverse reaction increases until they meet at a shared value.
- 3 a i  $K_c = \frac{[\text{Fe}(\text{SCN})]^{2+}}{[\text{Fe}^{3+}][\text{SCN}^-]}$
- ii  $K_c = \frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^5}$
- b  $K_c$  for the reverse reaction  $= \frac{1}{4.0}$  or 0.25.
- 4 a The equilibrium will shift to the left, favouring reactants, to restore equilibrium concentrations that fit the same value of  $K_c$ .
- b The equilibrium position will shift to the left, to replace ethanol and restore the equilibrium at the constant value of  $K_c$ .
- 5 a If the concentration of  $\text{Fe}^{2+}$  ions is increased then the equilibrium position will shift to use the added ions and restore equilibrium concentrations that fit the same  $K_c$ .
- b The addition of water reduces the concentration of all the ions in solution equally; there will be no change in the equilibrium position.
- 6 a i Increasing pressure will shift the equilibrium to the left as the reactants occupy less volume (there are fewer moles of gas on the reactants side of the equation).



- ii There will be no change in the equilibrium position as there are equal numbers of moles of gas on the two sides of the equation.
- iii Increasing the pressure will favour the reactants side of the equation. The equilibrium position will shift to the left as there are fewer moles of gas on this side of the equation; the reactants occupy less volume than the products.
- b Decreasing the pressure will favour the products, shifting the equilibrium to the right, as this represents an expansion (the products will occupy a greater volume).
- 7 a Increasing the temperature always favours the endothermic process (that absorbs the heat), so the equilibrium will shift to the left (favouring the reactants) as the reverse reaction is endothermic.
- b The forward reaction is endothermic, so this will be favoured by increasing the temperature; the equilibrium position will shift to the right.
- 8 a Moles of ester =  $\frac{44}{88} = 0.50 \text{ mol CH}_3\text{COOC}_2\text{H}_5$
- Moles of water =  $\frac{36}{18} = 2.0 \text{ mol}$
- b Moles of NaOH used in titration =  $\left(\frac{1.0}{1000}\right) \times 29.5$   
 $= 2.95 \times 10^{-3} \text{ mol}$
- Mol of acid in 25 cm<sup>3</sup> of equilibrium mixture =  $2.95 \times 10^{-3} \text{ mol}$
- Mol of acid in 250 cm<sup>3</sup> of equilibrium mixture =  $2.95 \times 10^{-2} \text{ mol}$  (or 0.0295 mol)

c

	Ethyl ethanoate	Water	Ethanoic acid	Ethanol
Start / mol	0.50	2.0	–	–
At equilibrium / mol	0.4705	1.9705	$2.95 \times 10^{-2}$	$2.95 \times 10^{-2}$
At equilibrium / mol dm <sup>-3</sup>	0.4705 / V	1.9705 / V	$2.95 \times 10^{-2} / V$	$2.95 \times 10^{-2} / V$

$$d \quad K_c = \frac{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}$$

Note that the volume, V, will cancel out in the expression when the values are fed in. Therefore

$$K_c = \frac{(2.95 \times 10^{-2})^2}{(0.4705)(1.9705)} = 9.38 \times 10^{-4}$$

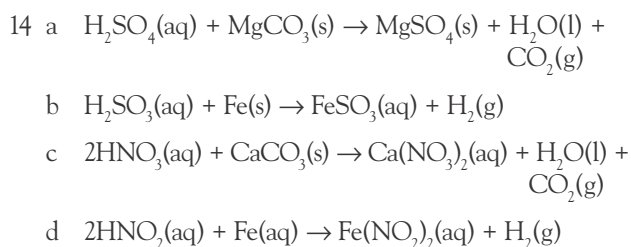
- e The H<sup>+</sup> ions added will still be available to titrate with the alkali and interfere with the result.
- f Add a defined volume of acid as a catalyst using a microsyringe.
- g Phenolphthalein would be a suitable indicator.

## 8 Acids and bases

- 1 a Base and acid  
 b Base and acid  
 c Base and acid  
 d Base and acid  
 e Acid and base
- 2 a H<sub>2</sub>O is the acid; OH<sup>-</sup> is the conjugate base; CO<sub>3</sub><sup>2-</sup> is the base and HCO<sub>3</sub><sup>-</sup> is the conjugate acid.  
 b H<sub>2</sub>SO<sub>4</sub> is the acid and SO<sub>4</sub><sup>2-</sup> is the conjugate base; H<sub>2</sub>O is the base and H<sub>3</sub>O<sup>+</sup> is the conjugate acid.
- 3 a H<sub>2</sub>SO<sub>4</sub>(aq) + CuCO<sub>3</sub>(s) → CuSO<sub>4</sub>(aq) + H<sub>2</sub>O(l) + CO<sub>2</sub>(g)  
 b 2HBr(aq) + Ca(HCO<sub>3</sub>)<sub>2</sub> (s or aq) → CaBr<sub>2</sub>(aq) + 2H<sub>2</sub>O(l) + 2CO<sub>2</sub>(g)  
 c 2H<sub>3</sub>PO<sub>4</sub>(aq) + 3Na<sub>2</sub>CO<sub>3</sub> (s or aq) → 2Na<sub>3</sub>PO<sub>4</sub>(aq) + 3H<sub>2</sub>O(l) + 3CO<sub>2</sub>(g)  
 d 2CH<sub>3</sub>COOH(aq) + Ca(s) → Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq) + H<sub>2</sub>(g)  
 e 2(NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>(aq) + 3Ba(OH)<sub>2</sub> (aq) → 6NH<sub>3</sub>(g) + 3H<sub>2</sub>O(l) + Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(aq)
- 4 a Sulfuric acid and silver(I) nitrate  
 b Magnesium oxide and nitric acid  
 c Potassium hydroxide and hydrochloric acid  
 d Barium hydroxide and ethanoic acid
- 5 pH = -log<sub>10</sub>(0.1) = 1
- 6 pH = -log<sub>10</sub>(3.00 × 10<sup>-7</sup>) = 6.52
- 7 pH = -log<sub>10</sub>(2 × 0.0100) = 1.70
- 8 pOH = -log<sub>10</sub>(2.50 × 10<sup>-3</sup>) = 2.60; pH + pOH = 14.00; pH = 11.40
- 9 pOH = -log<sub>10</sub>(0.0100 × 2) = 1.70; pH = 14.00 - 1.70 = 12.30
- 10 Amount of hydrogen chloride =  $\frac{3.646 \text{ g}}{36.46 \text{ g mol}^{-1}} = 0.1 \text{ mol}$   
 0.1 mol H<sup>+</sup>(aq) in 250 cm<sup>3</sup> solution, hence concentration is 0.4 mol dm<sup>-3</sup>.
- 11 Amount of HCl(aq) = 2.5 × 10<sup>-3</sup> mol;  
 amount of NaOH = 1.5 × 10<sup>-3</sup> mol;  
 amount of excess HCl(aq)/H<sup>+</sup>(aq) = 1 × 10<sup>-3</sup> mol in 40 cm<sup>3</sup>;  
 concentration =  $\left(\frac{1000}{40}\right) \times 1 \times 10^{-3} \text{ mol} = 0.025 \text{ mol dm}^{-3}$ ;  
 pH = -log<sub>10</sub>(0.025) = 1.60

12  $[\text{OH}^-(\text{aq})] = 0.01 \text{ mol dm}^{-3}$ ;  $\text{pOH} = 2$ ;  $\text{pH} = 12$ ;  
 $\text{H}^+(\text{aq}) = 10^{-12} \text{ mol dm}^{-3}$

13 Individual answers.



15 Individual answers.

## 9 Redox processes

- 1 a +5 d +5  
 b +2 e +5  
 c +3 f +4
- 2 a Ammonium dichromate(vi)  
 b Potassium chromate(vi)  
 c Vanadium(v) oxide  
 d Ammonium vanadate(v)  
 e Copper(II) sulfate(vi)-1-water  
 f Copper(I) sulfate  
 g Zinc nitrate(v)  
 h Scandium(III) chloride
- 3 Two arsenic atoms are oxidized from +3 to +5 per mole of  $\text{As}_2\text{O}_3$  (loss of  $4\text{e}^-$ ); therefore if 5 moles is oxidized, a total of  $20\text{e}^-$  are lost/change in oxidation number = 20 and if 4 moles  $\text{MnO}_4^-$  is reduced, a total  $20\text{e}^-$  are gained/change in oxidation number = 20. Therefore each Mn(vii) gains  $5\text{e}^-$ /change in oxidation number is 5; hence Mn(II)/Mn $^{2+}$ .
- 4  $\text{Fe}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$   
 $8\text{H}^+(\text{aq}) + \text{MnO}_4^-(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) \rightarrow 5\text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + \text{Mn}^{2+}(\text{aq})$   
 Amount of  $\text{MnO}_4^- = 0.00068 \text{ mol}$ ;  
 Amount of  $\text{Fe}^{2+} = 0.0034 \text{ mol}$   
 Mass of iron =  $0.0034 \text{ mol} \times 55.85 \text{ g mol}^{-1} = 0.1899 \text{ g}$   
 Percentage purity =  $\frac{0.1899}{0.200} = 95\%$
- 5  $6\text{H}^+(\text{aq}) + 5\text{H}_2\text{O}_2(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) \rightarrow 5\text{O}_2(\text{g}) + 10\text{H}^+(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$   
 Amount of  $\text{H}_2\text{O}_2 = 0.001 \text{ mol}$ ;  
 Amount of  $\text{MnO}_4^- = 0.0004 \text{ mol}$ ;  
 Volume of  $\text{H}_2\text{O}_2 = 20 \text{ cm}^3$ ;  
 volume of  $\text{O}_2 = 0.001 \text{ mol} \times 22.7 \text{ dm}^3 \text{ mol}^{-1} = 22.7 \text{ cm}^3$ .

- 6 a  $\text{H}_2\text{O}_2 + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$   
 b  $6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$   
 c  $4\text{Cl}_2 + \text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O} \rightarrow 8\text{Cl}^- + 2\text{SO}_4^{2-} + 10\text{H}^+$
- 7 Individual answers.
- 8 a Lithium and bromine  
 b Caesium and nitrogen  
 c Iron and bromine

## 10 Organic chemistry

- 1 a  $\text{C}_8\text{H}_{18}$   
 b  $\text{C}_{16}\text{H}_{34}$  and  $\text{C}_{17}\text{H}_{36}$   
 c i 198 K and 372 K  
 ii 218 K and 402 K.
- 2 Draw the graph, labelling the axes and plotting the points accurately. Draw a smooth best-fit curve using the points.  
 The curve shows a smooth trend of increasing density (see Figure 10.8 on page 326).
- 3 Five chain isomers to be found:  
 $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$   $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$   
 $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$   $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_3$   
 $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_3$
- 4 a i Hex-2-ene  
 ii 3-Methylpent-1-ene  
 iii 2-Methylpent-1,4-ene.  
 b a(i) and a(ii) (hex-2-ene and 3-methylpent-1-ene).  
 c Pent-1-yne,  $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$   
 Pent-2-yne,  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$   
 3-Methylbut-1-yne,  $\text{CH}\equiv\text{CCH}(\text{CH}_3)\text{CH}_3$
- 5 a Tertiary  
 b Secondary  
 c Primary
- 6 1,1-dibromoethane,  $\text{CHBr}_2\text{CH}_3$   
 1,2-dibromoethane,  $\text{CH}_2\text{BrCH}_2\text{Br}$   
 A 50:50 mixture of these products is formed.
- 7  $M_r$  of ethanol = 46;  $M_r$  of octane = 114  
 Enthalpy per g of ethanol =  $\frac{1371}{46} = 29.8 \text{ kJ g}^{-1}$   
 Enthalpy per g of octane =  $\frac{5512}{114} = 48.4 \text{ kJ g}^{-1}$   
 % increase for burning octane =  $\left[ \frac{(48.3 - 29.8)}{29.8} \right] \times 100 = 62\%$

## 11 Measurement and data processing

- 1 a  $25 \times 10^{-9} \text{ m}$  e  $6 \times 10^{-6} \text{ m}^3$   
 b  $245 \text{ s}$  f  $4 \times 10^6 \text{ kg m}^{-1} \text{ s}^{-2}$   
 c  $8 \times 10^{-6} \text{ kg}$  g  $14 \times 10^6 \text{ s}^{-1}$   
 d  $275 \text{ K}$  h  $295 \times 10^{-6} \text{ m}$
- 2 a Systematic d Random  
 b Random e Systematic  
 c Systematic f Systematic
- 3 More readings could be obtained by carrying out more titrations. Then the consistent values can be selected and the average taken. The Dixon's Q-test, or simply Q test, establishes whether one (and only one) measurement from a small set of replicated measurements (typically 3 to 10) can be statistically rejected or not.
- 4 a  $\pm 0.01 \text{ g}$   
 b  $\pm 0.001 \text{ s}$   
 c  $\left(\frac{5}{100}\right) \times 60 = \pm 3 \text{ mph}$   
 d  $\pm 0.05 \text{ mm}$   
 e  $0.005$
- 5 a  $29.72 \pm 0.04$   
 b  $10.06 \pm 0.02$   
 c  $1.119 \pm 0.07$   
 d  $2.5 \pm 0.7$
- 6 a  $7.78\%$   
 b  $0.23\%$   
 c  $1.2\%$   
 d  $0.21\%$
- 7 a  $8.0 \text{ m}^3 \pm 3.0 \text{ m}^3$   
 b  $1.4 \text{ m}^{\frac{1}{2}} \pm 0.5 \text{ m}$   
 c  $3.0 \pm 0.3 \text{ m}$   
 d  $3.0 \text{ m} \pm 1.0 \text{ m}$
- 8  $\frac{6.75 \times 10^{-3} \text{ cm}}{2.27 \times 1000 \text{ cm mol}^{-1}} = 2.97 \times 10^{-7} \text{ moles of helium atoms};$   
 $\text{He}^{2+}(\text{g}) + 2\text{e}^- \rightarrow \text{He}(\text{g});$  number of helium atoms =  $1.82 \times 10^{17};$   
 Avogadro constant =  $6.1 \times 10^{23} \text{ mol}^{-1}$
- 9 Random errors include: measurement errors in the measurement of masses. Systematic errors include: loss of magnesium oxide; incomplete oxidation of magnesium; presence of oxide layer on magnesium; side reactions involving magnesium reacting with nitrogen and carbon dioxide in the air and the silica in the crucible.

- 10 Stopwatch (a) has poor resolution (only two digits and  $\Delta t = 1 \text{ s}$ ), but it is accurate within its limits since its reading matches the true reading rounded off to two digits.

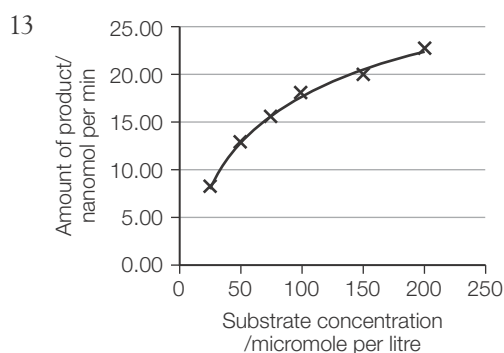
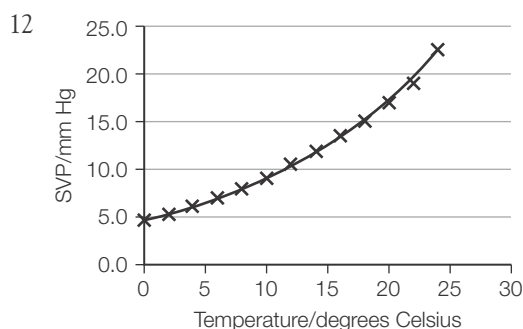
Stopwatch (b) is not very accurate since it displays an inaccurate reading compared to the true value, and it has poor resolution (only two digits of display and  $\Delta t = 1 \text{ s}$ ).

Stopwatch (c) has excellent resolution with 5 digits and  $\Delta t = 0.001 \text{ s}$ , but the reading is very inaccurate.

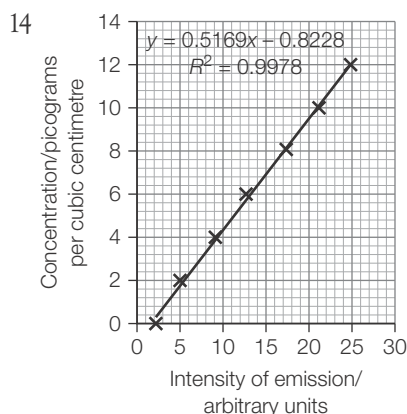
Stopwatch (d) is both accurate (reading close to true value) and has excellent resolution. Nothing can be concluded about precision because we have only one reading.

If we repeat the measurement many times, it is expected that stopwatch (c) or (d) would be the most precise as well – they have the most potential to be precise – but we cannot tell from the given information.

- 11 a  $13.5 \text{ cm}^3$  (1 dp)  
 b  $1900 \text{ J}$  (2 sf)  
 c  $1.01 \text{ g cm}^{-3}$  (3 sf)  
 d  $1.99 \text{ kJ mol}^{-1}$  (2 dp)  
 e  $268.1 \text{ cm}$  (1 dp)  
 f  $1.7 \times 10^2 \text{ cm}^3$  (2 sf)  
 g  $4$  (1 sf)  
 h  $0.1712$  (4 dp)



Maximum rate of enzyme activity approximately  $25.00 \text{ nmol min}^{-1}$



15 Individual answers.

16 Individual answers.

17 a 0

b 1

c 0

18  $c = v \times \lambda$ ;  $3.00 \times 10^8 \text{ ms}^{-1} = v \times 1515 \text{ m}$ ;  $v = 198020 \text{ Hz}$

19  $E = hv$ ;  $E = 6.63 \times 10^{-34} \text{ Js} \times 4.60 \times 10^9 \text{ s}^{-1} = 3.05 \times 10^{-24} \text{ J}$

$E = 3.05 \times 10^{-24} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 1.84 \text{ J mol}^{-1}$

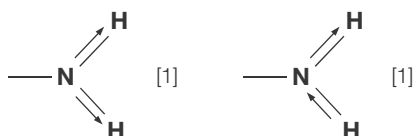
20 Wavenumber =  $\frac{5.0 \times 10^{13} \text{ s}^{-1}}{3.00 \times 10^8 \text{ ms}^{-1}} = 1.67 \times 10^5 \text{ m}^{-1}$

21 Wavelength =  $\frac{1}{17.50 \text{ m}} = 0.05714 \text{ m}$ ;

$c = v \times \lambda$ ;  $3.00 \times 10^8 \text{ ms}^{-1} = v \times 0.05714 \text{ m}$ ;

$v = 5.25 \times 10^9 \text{ s}^{-1} \text{ (Hz)}$ .

22 Symmetrical and asymmetrical stretching of the primary amine group:



23 There are three sets of hydrogen atoms (protons) in the ratio 2:3:3. From the chemical shift values and the molecular formula these peaks could be due to  $\text{CH}_2\text{-O-C=O}$ ,  $\text{CH}_3\text{-C=O}$  and  $\text{CH}_3\text{-C}$ . The only structure consistent with this data is ethyl ethanoate,  $\text{CH}_3\text{COOC}_2\text{H}_5$ .

## 12 Atomic structure

1 Individual answers.

2  $c = v \times \lambda$ ;  $3.00 \times 10^8 \text{ ms}^{-1} = v \times 2.42 \times 10^{-9} \text{ m}$ ;  
 $v = 1.24 \times 10^{15} \text{ Hz}$

$E = hv$ ;  $E = 6.63 \times 10^{-34} \text{ Js} \times 1.24 \times 10^{15} \text{ s}^{-1}$   
 $= 8.22 \times 10^{-20} \text{ J}$

$E = 8.22 \times 10^{-20} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 49491.6 \text{ J mol}^{-1}$   
 $= 49 \text{ kJ mol}^{-1}$

$$3 \quad \Delta x \times \Delta p = \frac{h}{4\pi}$$

$$\Delta p = \frac{h}{4\pi \Delta x} = \frac{6.63 \times 10^{-34} \text{ Js}}{4\pi \times 1.00 \times 10^{-11} \text{ m}}$$

$$= 5.28 \times 10^{-24} \text{ kg ms}^{-1}$$

$$\Delta p = 5.28 \times 10^{-24} \text{ kg ms}^{-1} = m \Delta v$$

$$\Delta v = \frac{p}{m} = \frac{5.25 \times 10^{-24} \text{ kg ms}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 5.79 \times 10^6 \text{ ms}^{-1}$$

4 Kinetic energy =  $\frac{1}{2}mv^2$ ;

$$\frac{1}{2} \times 9.109383 \times 10^{-31} \text{ kg} \times v^2 = 3.00 \times 10^{-25} \text{ J}$$

$$v = \sqrt{\frac{2 \times 3.00 \times 10^{-25} \text{ J}}{9.109383 \times 10^{-31} \text{ kg}}} = 8.12 \times 10^2 \text{ ms}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{9.109383 \times 10^{-31} \text{ kg} \times 8.12 \times 10^2 \text{ ms}^{-1}}$$

$$= 8.96 \times 10^{-7} \text{ m}$$

$$5 \quad \lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{9.109383 \times 10^{-31} \text{ kg} \times 1.600 \times 10^2 \text{ ms}^{-1}}$$

$$= 4.55 \times 10^{-6} \text{ m}$$

6 Individual answers.

$$7 \quad c = v \times \lambda$$

$$\lambda = \frac{c}{v}; \lambda = \frac{3.00 \times 10^8 \text{ ms}^{-1}}{1368 \times 10^3 \text{ Hz}} = 219 \text{ m}; \text{radio waves}$$

$$8 \quad c = v \times \lambda$$

$$v = \frac{c}{\lambda}; v = \frac{3.00 \times 10^8 \text{ ms}^{-1}}{5.800 \times 10^7 \text{ Hz}} = 5.17 \times 10^{14} \text{ s}^{-1}$$

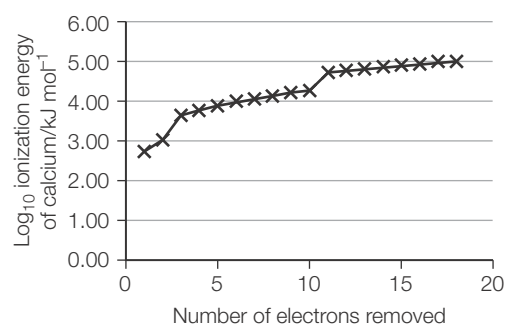
$$9 \quad E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ ms}^{-1}}{780 \times 10^{-9} \text{ m}}$$

$$= 2.55 \times 10^{-19} \text{ J}$$

10 The hydrogen atom has 1 proton, but the helium ion ( $\text{He}^+$ ) has 2 protons. The effective nuclear charge (electrostatic force experienced by the electron) will be greater in the helium ion ( $\text{He}^+$ ), hence it will have the greater ionization energy.

The increase in shielding (electron–electron repulsion) is less than the increase in nuclear charge.

11 Successive ionization energies of calcium:

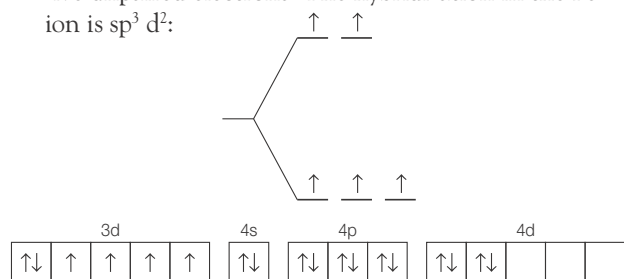


The only stable oxidation state relates to the removal of the two 4s electrons. The next eight electrons to be removed are from the third shell (3p and then 3s). The increase in ionization energy occurs because the next eight electrons are removed from the inner second





- 13 Splitting diagram for  $[\text{FeF}_6^{3-}]$ , a high-spin complex, five unpaired electrons. The hybridization in the  $\text{Fe}^{3+}$  ion is  $\text{sp}^3 \text{d}^2$ :



$$14 \quad \nu = \frac{c}{\lambda}; \quad \nu = \frac{3 \times 10^8 \text{ ms}^{-1}}{410 \times 10^{-9} \text{ m}} = 7.32 \times 10^{14} \text{ s}^{-1}$$

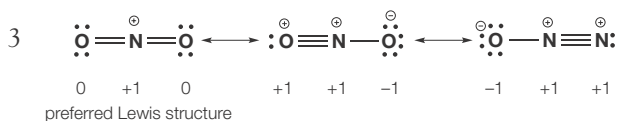
$$E = h\nu, \text{ so}$$

$$E = \frac{6.6 \times 10^{-34} \text{ Js} \times 7.32 \times 10^{14} \text{ s}^{-1}}{\lambda} = 4.83 \times 10^{-19} \text{ J}$$

$$E = \frac{4.83 \times 10^{-19} \times 6.02 \times 10^{23}}{1000} = 290.8 \text{ kJ mol}^{-1}$$

## 14 Chemical bonding and structure

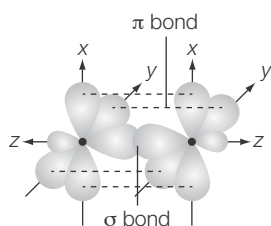
- Individual answers.
- Individual answers.



- $\text{H}_2$ :  $(\sigma 1s)^2$ ,  $\text{H}_2^+$ :  $(\sigma 1s)^1$ ,  $\text{H}_2^-$ :  $(\sigma 1s)^2 (\sigma^* 1s)^1$
- $\text{He}_2^+$  has the configuration  $(\sigma 1s)^2 (\sigma^* 1s)^1$  and hence a bond order of  $(1 - \frac{1}{2}) = \frac{1}{2}$ . As the bond order is positive, this ion can be formed (in the gaseous state at low pressure).

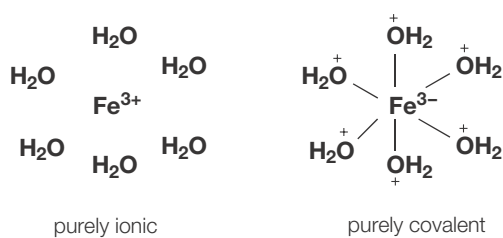
$\text{He}_2$  has the configuration  $(\sigma 1s)^2 (\sigma^* 1s)^1$  and hence a bond order of zero. Hence this molecule is unstable with respect to its atoms and cannot be prepared.

- The electronic configuration of a nitrogen atom is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ . Hence a nitrogen atom has three singly occupied orbitals. One  $2p_x-2p_x$  sigma bond is formed. The other two pi bonds are  $2p_y-2p_y$  and  $2p_z-2p_z$ . Thus the nitrogen molecule has three bonds: one sigma and two pi bonds that are perpendicular to each other and perpendicular to the z-axis, that is, the axis of the sigma bond. Hence, a triple bond is formed.



formation of a nitrogen molecule

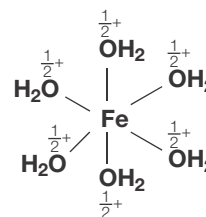
- The limiting ionic and dative covalent descriptions of the hexaaquairon(III) ion are shown below.



The purely ionic structure does match with the observed chemical properties of coordination complexes. However, there are objections to the covalent description because the charge distribution is such that the iron(III) centre bears a three minus charge and the oxygen atoms of the water ligands each carry a single positive charge. This would be unrealistic in view of the electronegativity values of these elements (iron, 1.8; oxygen, 3.4), which predicted that the iron–oxygen bond would be polarized in the sense  $\text{Fe}^{\delta+}-\text{O}^{\delta-}$ .

The problem was addressed by Pauling via his electroneutrality principle which suggested that the actual distribution of charges within a molecule is such that the charges on any single atom are within the range +1 to -1. Consider the hexaaquairon(III) ion.

An ionic description results in a +3 charge on the metal centre, whilst a covalent description gives the metal a -3 charge. The electroneutrality principle suggests that the ideal charge on the metal centre is zero. That would be achieved if the iron centre gains a total of three electrons from the six oxygen donor atoms; in other words, if each oxygen loses one half of an electron rather than the whole electron which the fully covalent model demands. Pauling described this situation as 50% covalent (or 50% ionic).



## 15 Energetics/thermochemistry

- $\frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{O}(\text{g}); \frac{1}{4} \text{P}_4(\text{s}) \rightarrow \text{P}(\text{g}); \text{B}(\text{s}) \rightarrow \text{B}(\text{g})$
- Enthalpy change =  $6.04 \times 2.38/28.01 = 0.513 \text{ kJ} = 513 \text{ J}$
- $Q = mc\Delta T$ ;  $Q = 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1} \times 0.91^\circ \text{C} = 380.38 \text{ J} = 400 \text{ J}$

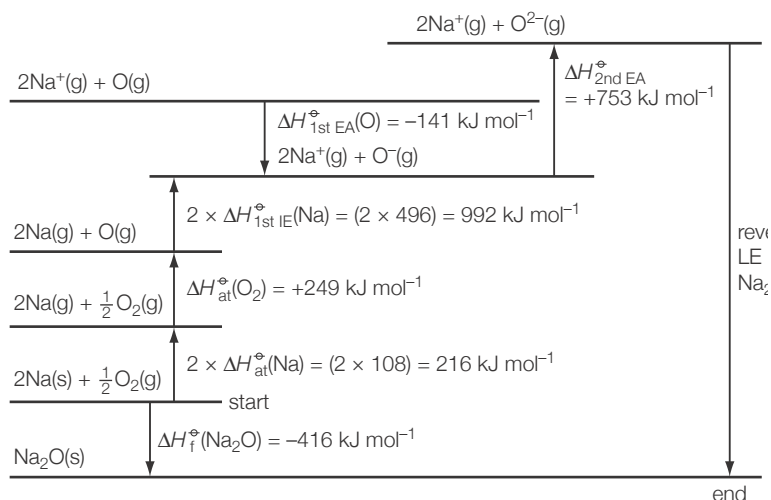
Amount of  $\text{Ag}^+$  = 0.005 mol; amount of  $\text{Cl}^-$  = 0.005 mol

Enthalpy change =  $-400 \text{ J}/0.005 \text{ mol} = -80000 \text{ J mol}^{-1} = -80 \text{ kJ mol}^{-1}$

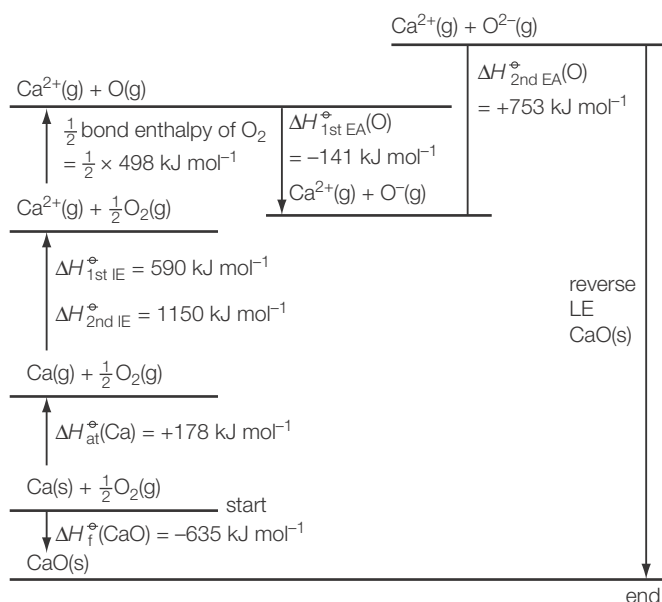
- Percentage error =  $(80 - 70)/70 \times 100 = 14\%$ ; provide a lid for the cup; provide thermal insulation around the beaker.
- $\text{N}^{2-}(\text{g}) + \text{e}^- \rightarrow \text{N}^{3-}(\text{g})$ ; the repulsion between the incoming electron and the electrons in the anion is greater than the attraction between the incoming electron and the protons in the nucleus.

$\text{Al}_2\text{O}_3(\text{s}) \rightarrow 2\text{Al}^{3+}(\text{g}) + 3\text{O}^{2-}(\text{g})$ ; work has to be done to overcome the electrostatic forces of attraction between the highly charged ions.

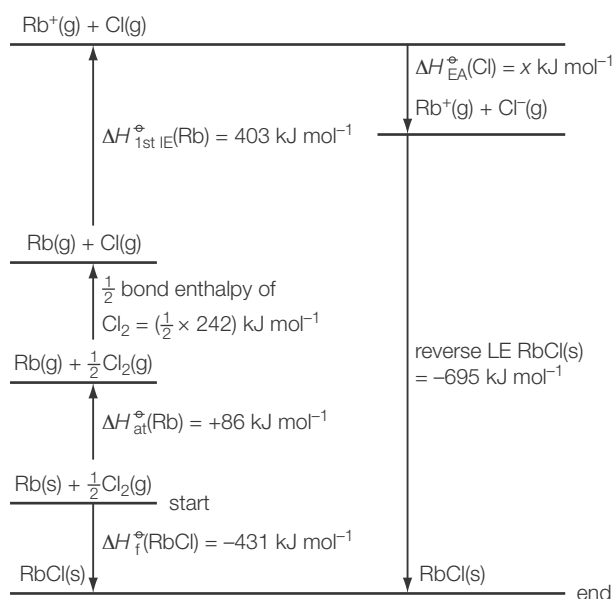
6  $-416 = 216 + 249 + 992 + (-141) + 753 + x$ ;  $x = -2485$ ; lattice enthalpy of sodium oxide =  $+2485 \text{ kJ mol}^{-1}$



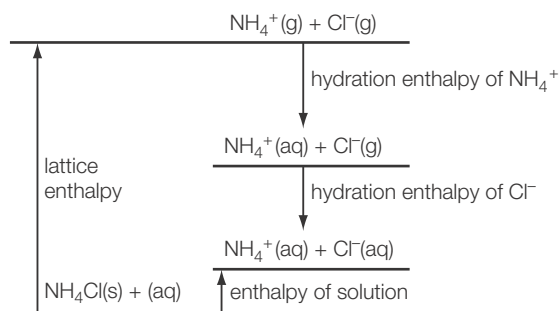
$-635 = 178 + 1150 + 590 + 249 + (-141) + 753 + x$ ;  $x = -3414$ ; lattice enthalpy of calcium oxide =  $+3414 \text{ kJ mol}^{-1}$



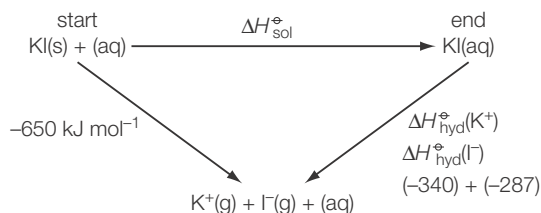
7  $-431 = 861 + 121 + 403 + x + -9695$ ;  $x = -1121$ ; first electron affinity of chlorine =  $-1121 \text{ kJ mol}^{-1}$



8



9  $\Delta H_{\text{sol}}^{\ominus} = (-650 + 340 + 287) = -23 \text{ kJ mol}^{-1}$



- 10 a Little change                      f Decrease  
 b Decrease                                g Decrease  
 c Decrease                                h Little change  
 d Increase                                i Decrease  
 e Increase                                j Increase
- 11  $\Delta S^{\ominus} = [2 \times 87.4 \text{ J K}^{-1} \text{ mol}^{-1}] - [(4 \times 27.3 \text{ J K}^{-1} \text{ mol}^{-1}) + (3 \times 205.0 \text{ J K}^{-1} \text{ mol}^{-1})] = -549.4 \text{ J K}^{-1} \text{ mol}^{-1}$
- 12  $\Delta G^{\ominus} = (-569 \text{ kJ mol}^{-1} + -394 \text{ kJ mol}^{-1}) - (-1012 \text{ kJ mol}^{-1}) = +49 \text{ kJ mol}^{-1}$
- 13  $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ ;  $\Delta G^{\ominus} = +49100 \text{ J mol}^{-1} - (298 \text{ K} \times 198 \text{ J K}^{-1} \text{ mol}^{-1}) = 431996 \text{ J mol}^{-1} = +432 \text{ kJ mol}^{-1}$  (hence not spontaneous)  
 $0 = \Delta H^{\ominus} - T\Delta S^{\ominus}$ ;  $0 = +49100 \text{ J mol}^{-1} - (T \times 198 \text{ J K}^{-1} \text{ mol}^{-1})$ ;  $T = 2479 \text{ K} = 2206^{\circ}\text{C}$
- 14  $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ ;  $0 = 457.9 - T \times 0.56$ ;  $T = \frac{457.9}{0.56}$   
 $= 818 \text{ K}$  (since  $\Delta H^{\ominus}$  is positive (endothermic) the reaction proceeds in the forward direction above this temperature.

## 16 Chemical kinetics

- 1 Overall order = 2; units of  $k$  are  $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- 2 Rate =  $k[\text{propene}][\text{bromine}]$   
 $= 30(0.040)^2 = 30(1.6 \times 10^{-3}) = 0.048 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
- 3 Rate =  $k[\text{HI}]^2$   
 $25 \times 10^{-5} = k(2.00)^2$   
 $k = \frac{25 \times 10^{-5}}{4.00} = 6.25 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$   
 $25 \times 10^{-5} \text{ mol} = (25 \times 10^{-5}) \times (6.02 \times 10^{23})$   
 $= 1.505 \times 10^{20} \text{ molecules}$   
 $1.505 \times 10^{20} \text{ molecules of HI decompose per second}$

- 4 The methanol should be present in a large excess so that this concentration remains effectively unchanged (effectively constant).

5 a 5 minutes = 300 seconds  
 Average rate of reaction =  $\frac{0.27}{300}$   
 $= 9.00 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

- b Plot the graph, labelling the axes and plotting the points accurately. Draw a smooth curve of best fit using the points.

Draw a tangent to the curve at time zero and calculate the slope using slope =  $\Delta y/\Delta x$  (see Figure 6.26 on page 212).

- c Draw tangents and find their slopes for the other specified concentrations.
- d The concentrations of cyclopropane are 1.50, 1.20, 0.90, and 0.60  $\text{mol dm}^{-3}$ , respectively
- e Plot the graph accurately and draw a line of best fit through the points. The graph is a straight line of slope  $k$ . Find the slope of your graph.
- 6 a Connect the reaction flask to a gas syringe and follow the increase in volume of nitrogen released with time.  
 b Plot the graph accurately and draw a line of best fit through the points. See Figure 16.7 on page 561 for the method of finding successive half-lives. The reaction is first order if the half-lives are constant.
- c The reaction is first order with respect to [benzenediazonium chloride] as successive half-lives are equal.
- 7 a  $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2$   
 $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2$   
 Sum of the two equations gives  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$   
 b Draw diagram similar to Figure 16.18 on page 572 but the first peak is lower than the second as the activation energy for the second step is greater than that of the first step.

- 8 Carry out the exercise to visualize the steps in the mechanism for this reaction.

- 9 Sketch a diagram similar to that for the catalysed reaction in Figure 16.20 on page 573. The activation energy for the combined later fast steps is lower than that of the slow, rate-determining, first step.

- 10 a  $2\text{XY}_2 \rightarrow \text{X}_2 + 2\text{Y}_2$   
 b Rate =  $k[\text{XY}_2]^2$   
 c Units of  $k$  are  $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ .  
 d Draw diagram similar to Figure 16.18 on page 572.

## 17 Equilibrium

- 1
- $$2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$$
- |                                    |       |        |       |
|------------------------------------|-------|--------|-------|
| Initial/mol:                       | 2     | 1.4    | 0     |
| Equilibrium/mol:                   | 1.7   | 1.25   | 0.3   |
| Equilibrium/mol dm <sup>-3</sup> : | 1.7/3 | 1.25/3 | 0.3/3 |
- $$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.1)^2}{(0.566)^2(0.416)} = \frac{0.01}{0.311 \times 0.416} = 0.075$$
- 2
- $$\text{SO}_3 + \text{NO} \rightleftharpoons \text{NO}_2 + \text{SO}_2$$
- |                                    |             |             |   |   |
|------------------------------------|-------------|-------------|---|---|
| Initial/mol dm <sup>-3</sup> :     | 0.030       | 0.030       | 0 | 0 |
| Equilibrium/mol dm <sup>-3</sup> : | (0.030 - x) | (0.030 - x) | x | x |
- $$K_c = 6.78 = \frac{[\text{NO}_2][\text{SO}_2]}{[\text{SO}_3][\text{NO}]} = \frac{x^2}{(0.030 - x)^2}$$
- Taking square roots of both sides:  $\sqrt{6.78} = \frac{x}{(0.030 - x)}$
- $$2.60(0.030 - x) = x$$
- $$0.078 - 2.60x = x$$
- Therefore  $3.60x = 0.078$
- $$x = 0.022$$
- $[\text{SO}_3] = [\text{NO}] = 8 \times 10^{-3} \text{ mol dm}^{-3}$  and  $[\text{NO}_2] = [\text{SO}_2] = 0.022 \text{ mol dm}^{-3}$
- 3
- $$\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$$
- |                                    |                         |                         |                         |                         |
|------------------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Initial/mol:                       | 2.00                    | 2.00                    | 1.00                    | 1.00                    |
| Equilibrium/mol:                   | (2.00 - x)              | (2.00 - x)              | (1.00 + x)              | (1.00 + x)              |
| Equilibrium/mol dm <sup>-3</sup> : | $\frac{(2.00 - x)}{10}$ | $\frac{(2.00 - x)}{10}$ | $\frac{(1.00 + x)}{10}$ | $\frac{(1.00 + x)}{10}$ |
- $$K_c = 2.10 = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]}$$
- Note that the volumes will cancel out
- Therefore:  $2.10 = \frac{(1.00 + x)^2}{(2.00 - x)^2}$
- Taking square roots of both sides:  $\sqrt{2.10} = \frac{(1.00 + x)}{(2.00 - x)}$
- $$1.45(2.00 - x) = (1.00 + x)$$
- $$1.90 = 2.45x$$
- $$x = 0.78$$
- $$[\text{H}_2\text{O}] = [\text{CO}] = \frac{1.78}{10} = 0.178 \text{ mol dm}^{-3}$$
- $$[\text{H}_2] = [\text{CO}_2] = \frac{1.22}{10} = 0.122 \text{ mol dm}^{-3}$$
- 4 a  $\Delta G^\ominus = -RT \ln K_p$  for a gas phase reaction
- $$1.38 \times 1000 = -(8.31 \times 298 \times \ln K_p); \text{ note the conversion of kJ to J}$$
- $$\ln K_p = -\frac{(8.31 \times 298)}{1380} = -\left(\frac{2476}{1380}\right) = -1.79$$
- $$K_p = e^{-1.79} = 0.166$$

b  $K_c = 0.166$ ; in this case, for a reaction where there are the same number of moles of gas on both sides of the equation,  $K_p = K_c$ .

c The equilibrium constant value is less than 1.00 and so the equilibrium is well to the reactants side of the equation.

5 a Zero

b  $\Delta G^\ominus = -RT \ln K_c$

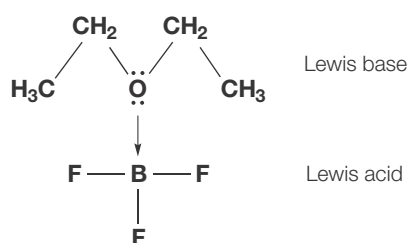
$$\Delta G^\ominus = -(8.31 \times 298) \ln (1.7 \times 10^{12})$$

$$= -2476 \times (-28.16) = +69728.2 \text{ J mol}^{-1}$$

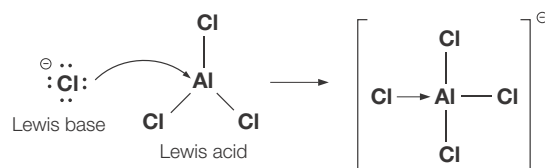
$$\Delta G^\ominus = +69.73 \text{ kJ mol}^{-1}$$

## 18 Acids and bases

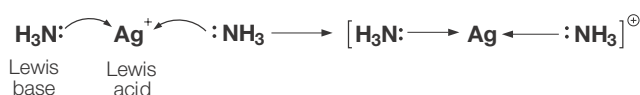
1 a



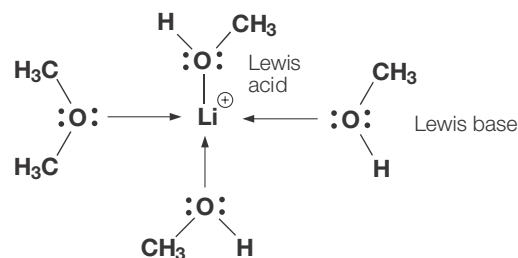
b



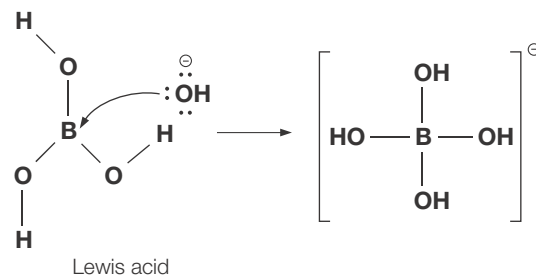
c

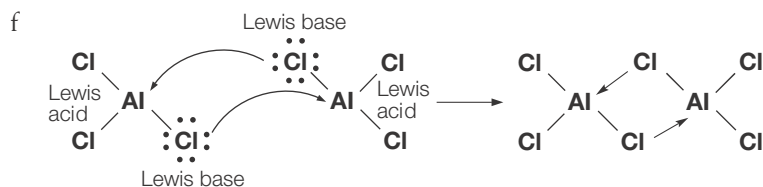


d



e





2 a III

b IV

c V

d I

e II

3 The Lux–Flood theory is used in geochemistry and the electrochemistry of molten salts. This definition describes an acid as an oxide ion acceptor and a base an oxide ion donor, for example,  
 $\text{CaO (base)} + \text{SiO}_2 \text{ (acid)} \rightarrow \text{CaSiO}_3$

4  $K_w = [\text{H}^+(\text{aq})] \times [\text{OH}^-(\text{aq})];$   
 $1.00 \times 10^{-14} = 5.4 \times 10^{-4} \times [\text{OH}^-(\text{aq})];$   
 $[\text{OH}^-(\text{aq})] = 2 \times 10^{-4} \text{ mol dm}^{-3}$

5  $\text{H}^+(\text{aq}) = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7} \text{ mol dm}^{-3}; \text{pH} = 6.5$

6 a  $\text{pH} = -\log_{10}(0.01) = 2$

b  $\text{pOH} = -\log_{10}(0.01) = 2; \text{pH} = 12$

c  $\text{pOH} = -\log_{10}(0.02) = 1.7; \text{pH} = 12.3$

d  $\text{pH} = -\log_{10}(0.02) = 1.7$

7  $\text{H}^+(\text{aq}) = 10^{-\text{pH}}; \text{H}^+(\text{aq}) = 10^{-2.80} = 1.58 \times 10^{-3} \text{ mol dm}^{-3}$

8 Amount of  $\text{HNO}_3 = \frac{1.26 \text{ g}}{68.02 \text{ g mol}^{-1}} = 0.02 \text{ mol}$  in  $100 \text{ cm}^3$  of solution.

Concentration of  $\text{HNO}_3 = 0.2 \text{ mol dm}^{-3};$   
 $\text{pH} = -\log_{10}(0.2) = 0.69$

9 Dilution factor is  $\frac{1000}{10} = \times 100$ ; this will be an increase in pH of 2; since a change of one pH unit corresponds to a change in  $\text{H}^+$  of 10.

10  $\text{pOH} = -\log_{10}(0.100) = 1$

11  $[\text{OH}^-(\text{aq})] = 10^{-\text{pOH}}; [\text{OH}^-(\text{aq})] = 10^{-2};$   
 $[\text{OH}^-(\text{aq})] = 0.01 \text{ mol dm}^{-3}$

12  $\text{pH} + \text{pOH} = 14; \text{pH} + 1 = 14; \text{pH} = (14 - 1) = 13$

13  $\text{pH} + \text{pOH} = 14; 2 + \text{pOH} = 14; \text{pOH} = (14 - 2) = 12$

14  $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$

$[\text{H}^+(\text{aq})] = -\text{antilog}(3.10) \text{ or } 10^{-3.10} = 7.94 \times 10^{-4} \text{ mol dm}^{-3}$

$K_a = \frac{[\text{H}^+(\text{aq})] \times [\text{C}_6\text{H}_5\text{COO}^-(\text{aq})]}{[\text{C}_6\text{H}_5\text{COOH}(\text{aq})]}$

but since  $[\text{H}^+(\text{aq})] = [\text{C}_6\text{H}_5\text{COO}^-(\text{aq})]$

$K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{C}_6\text{H}_5\text{COOH}(\text{aq})]}$

$K_a = \frac{(7.94 \times 10^{-4})^2}{0.1} = 6.3 \times 10^{-6} \text{ mol dm}^{-3}$

15  $K_a = \frac{[\text{H}^+(\text{aq})] \times [\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$

but since  $[\text{H}^+(\text{aq})] = [\text{CH}_3\text{COO}^-(\text{aq})];$

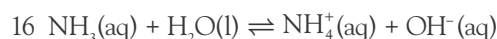
$K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{CH}_3\text{COOH}(\text{aq})]}$

then rearranging,  $[\text{H}^+(\text{aq})] = \sqrt{[\text{CH}_3\text{COOH}(\text{aq})] \times K_a}$

$[\text{H}^+(\text{aq})] = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$

and then  $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$

$= -\log_{10}(1.34 \times 10^{-3} \text{ mol dm}^{-3}) = 2.87$



$K_b = \frac{([\text{OH}^-] \times [\text{NH}_4^+])}{[\text{NH}_3(\text{aq})]}$

$K_b = \frac{[\text{OH}^-]^2}{[\text{NH}_3(\text{aq})]}; 1.8 \times 10^{-5} = \frac{[\text{OH}^-]^2}{[0.50]};$

$[\text{OH}^-(\text{aq})] = \sqrt{\frac{1.8 \times 10^{-5}}{0.50}} = 6 \times 10^{-3} \text{ mol dm}^{-3};$

$\text{pOH} = 2.22; \text{pH} = 11.8$

17  $[\text{H}^+(\text{aq})] = 10^{-\text{pH}}; [\text{H}^+(\text{aq})] = 10^{-6.80} = 1.58 \times 10^{-7} \text{ mol dm}^{-3};$   
 $K_w = 1.58 \times 10^{-7} \text{ mol dm}^{-3} \times 1.58 \times 10^{-7} \text{ mol dm}^{-3}$   
 $= 2.51 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}; [\text{OH}^-(\text{aq})]$   
 $= 1.58 \times 10^{-7} \text{ mol dm}^{-3}$

18  $[\text{H}^+(\text{aq})] = 10^{-3.20} = 6.3 \times 10^{-4} \text{ mol dm}^{-3};$   
 $K_w = 1.00 \times 10^{-14};$   
 $1.00 \times 10^{-14} = 6.3 \times 10^{-4} \times [\text{OH}^-(\text{aq})];$   
 $[\text{OH}^-(\text{aq})] = 1.58 \times 10^{-11}$

19  $[\text{OH}^-(\text{aq})] = 10^{-1.0} = 0.10 \text{ mol dm}^{-3};$   
molar mass of  $\text{NaOH} = (22.99 + 16.00 + 2.02)$   
 $= 41.01 \text{ g mol}^{-1};$   
mass of  $\text{NaOH}$  required  $= \frac{44.01 \text{ g}}{5} = 8.202 \text{ g}$

20  $[\text{H}^+(\text{aq})] = 0.05 \text{ mol dm}^{-3} \times 2 = 0.10 \text{ mol dm}^{-3};$   
 $[\text{OH}^-(\text{aq})] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$

21  $[\text{OH}^-(\text{aq})] = 2 \times 0.25 \text{ mol dm}^{-3} = 0.50 \text{ mol dm}^{-3};$   
 $\text{pOH} = 0.30; \text{pH} = 14.00 - 0.30 = 13.70$

22  $\text{p}K_a = -\log_{10} K_a; K_a = 1.74 \times 10^{-5};$   
 $\text{H}^+(\text{aq}) = \sqrt{([\text{CH}_3\text{COOH}(\text{aq})] \times K_a)};$

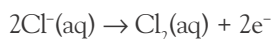
$\text{H}^+(\text{aq}) = \sqrt{0.125 \times 1.74 \times 10^{-5}} = 1.47 \times 10^{-3} \text{ mol dm}^{-3};$   
 $\text{pH} = 2.83$



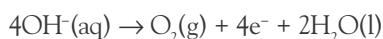
- 23  $K_b = \text{antilog } 9.13 = 7.41 \times 10^{-10}$ ;  
 $\text{OH}^- = \sqrt{0.50 \times 7.41 \times 10^{-10}} = 1.925 \times 10^{-5}$ ;  
 $\text{pOH} = 4.71$ ;  $\text{pH} = 9.28$
- 24  $[\text{H}^+(\text{aq})] = 10^{-\text{pH}} = 10^{-5.74} = 1.82 \times 10^{-6}$ ;  
 $1.82 \times 10^{-6} = \sqrt{0.025 \times K_a}$ ;  $K_a = 1.325 \times 10^{-10}$
- 25  $K_a \times K_b = K_w$ ;  $1.8 \times 10^{-4} \times K_b = 1.00 \times 10^{-14}$ ;  
 $K_b = 5.56 \times 10^{-11}$
- 26 Amount of  $\text{Sr}(\text{OH})_2 = \frac{19.23 \text{ g}}{121.64 \text{ mol}^{-1}} = 0.158 \text{ mol}$   
 $[\text{Sr}^{2+}(\text{aq})] = 0.158 \text{ mol dm}^{-3}$ ;  $[\text{OH}^-(\text{aq})] = 0.316 \text{ mol dm}^{-3}$   
 $\text{pOH} = -\log_{10}[\text{OH}^-(\text{aq})] = 0.5$ ;  $\text{pH} = 13.5$
- 27 Amount of  $\text{H}^+(\text{aq}) = 2.5 \times 10^{-3}$ ;  
amount of  $\text{OH}^-(\text{aq}) = 1.5 \times 10^{-3}$ ;  
amount of excess  $\text{H}^+(\text{aq})$  after neutralization =  
 $1 \times 10^{-3} \text{ mol}$  in  $40 \text{ cm}^3$  of solution  
 $[\text{H}^+(\text{aq})] = 25 \times 1 \times 10^{-3} \text{ mol} = 0.025 \text{ mol dm}^{-3}$ ;  $\text{pH} = 1.6$

## 19 Redox processes

- 1 Zinc atoms > lead(II) ions > sulfate ions > iodide ions
- 2  $\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$   $x\text{V}$   
 $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$   $+0.34 \text{ V}$   
 $E^\circ_{\text{cell}} = (+0.34) - x = +0.62$   
 $x = (+0.34) - (+0.62) = -0.28 \text{ V}$
- 3 a  $\text{Fe}(\text{s}) + \text{Ni}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Ni}(\text{s})$ ;  
 $E^\circ_{\text{cell}} = (0.45 \text{ V}) + (-0.26 \text{ V}) = +0.19 \text{ V}$
- b  $2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) + 10\text{I}^-(\text{aq}) \rightarrow 5\text{I}_2(\text{s}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$ ;  
 $E^\circ_{\text{cell}} = (-0.54 \text{ V}) + (1.51 \text{ V}) = +0.97 \text{ V}$
- c  $2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) + 3\text{F}_2(\text{g}) \rightarrow 6\text{F}^-(\text{g}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq})$ ;  
 $E^\circ_{\text{cell}} = (2.87 \text{ V}) + (-1.36 \text{ V}) = +1.51 \text{ V}$
- d  $2\text{Ag}^+(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$ ;  
 $E^\circ_{\text{cell}} = (0.80 \text{ V}) + (-0.34 \text{ V}) = +0.46 \text{ V}$
- 4  $E_{\text{cell}} = (0.059/1) \times (\log_{10} 0.100/0.001) = 0.118 \text{ V}$
- 5  $E^\circ_{\text{cell}} = (-0.80 \text{ V}) + (1.23 \text{ V}) = +0.43 \text{ V}$ ;  
 $\Delta G^\circ = -nFE^\circ = -4 \times 96500 \text{ C mol}^{-1} \times 0.43 \text{ V}$   
 $= -165980 \text{ J mol}^{-1} = -166 \text{ kJ mol}^{-1}$
- 6 The  $E^\circ$  value for this related reaction will not change and standard electrode potential is an intensive property independent of amount (see page 655). The standard electrode potentials of the two half equations are not halved even though the stoichiometry in this reaction is halved. The  $\Delta G^\circ$  value will be halved as the amount of electrons transferred in the reaction is halved.
- 7 a A reduction process takes place on the cathode surface and hence for competing reduction processes, the one with the higher reduction potential will occur.
- Hydrogen ions have greater electrode potential and hence are a stronger oxidizing agent than lithium ions. Hydrogen gas is discharged at the cathode.
- $$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$$
- An oxidation process takes place on the anode surface and hence for competing oxidation processes, the one with the lower reduction potential will occur.
- Hydroxide ions (from the ionization of water) have a lower electrode potential and hence a stronger reducing agent than iodide ions. However, iodide ions are present in high concentration and will be discharged at the anode. Carbon (graphite) is an inert electrode. (In practice there will be a mixture of iodine and oxygen).
- $$2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{e}^-$$
- b Hydrogen ions have a greater electrode potential and hence are a stronger oxidizing agent than barium ions. (Barium is more reactive than calcium and should therefore have a more negative standard electrode potential). Hydrogen gas is discharged at the cathode. Hydroxide ions are the only anion present and hence discharged as oxygen molecules at the anode. Carbon (graphite) and platinum are inert electrodes.
- $$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g});$$
- $$4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 4\text{e}^- + 2\text{H}_2\text{O}(\text{l})$$
- c The copper electrode is an active electrode: copper dissolves at the anode and it deposits at the cathode. At the cathode copper(II) ions undergo reduction. At the anode copper atoms dissolve to release copper(II) ions.
- $$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s}); \text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$$
- Carbon (graphite) is an inert electrode. Copper(II) ions have a more positive electrode potential and hence are a stronger oxidizing agent than hydrogen ions. (Nitrate ions are stable and not discharged. They resist oxidation at the anode because the nitrogen is in +5 oxidation state). Hydroxide ions from the dissociation of water are discharged as oxygen. Copper atoms have a less positive electrode potential and hence are a stronger reducing agent than hydroxide ions.
- $$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s});$$
- $$4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 4\text{e}^- + 2\text{H}_2\text{O}(\text{l})$$
- d At the cathode hydrogen ions undergo reduction. Hydrogen ions have a more positive electrode potential and hence are a stronger oxidizing agent than sodium ions. Hydrogen gas is discharged.
- $$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$$
- Hydroxide ions have a more negative electrode potential and hence a stronger reducing agent than chloride ions. However, chloride ions are present in high concentration and will be discharged at the anode. Carbon (graphite) is an inert electrode.



With a dilute solution of chloride ions, hydroxide ions will be discharged as oxygen gas. (In practice a mixture of chlorine and oxygen will be formed).



- 8 Amount of aluminium atoms =  $\frac{5.4 \text{ g}}{26.98 \text{ g mol}^{-1}}$   
 $= 0.20 \text{ mol}$ ;  
 amount of electrons =  $0.60 \text{ mol}$ ;  
 charge transferred =  $5.00 \text{ A} \times 11580 \text{ s} = 57900 \text{ C}$ ;  
 amount of electrons =  $\frac{57900 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.60 \text{ mol}$ ,  
 hence  $\text{Al}^{3+}$ .
- 9 Charge (C) =  $2.00 \text{ A} \times (15 \times 60) \text{ s} = 1800 \text{ C}$ ;  
 amount of electrons =  $\frac{1800 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.0187 \text{ mol}$ ;  
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ ;  
 amount of copper atoms =  $9.326 \times 10^{-3} \text{ mol}$ ;  
 mass of copper =  $9.326 \times 10^{-3} \text{ mol} \times 63.55 \text{ g mol}^{-1} = 0.593 \text{ g}$
- 10 Charge (C) =  $4.00 \text{ A} \times 370 \text{ s} = 1480 \text{ C}$ ;  
 amount of electrons =  $\frac{1480 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.0153 \text{ mol}$ ;  
 $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ ; amount of  $\text{H}_2 = 7.67 \times 10^{-3} \text{ mol}$ ;  
 volume of  $\text{H}_2 = 7.67 \times 10^{-3} \text{ mol} \times 2.27 \text{ m}^3 \text{ mol}^{-1}$   
 $= 1.74 \times 10^{-2} \text{ m}^3 = 174 \text{ cm}^3$
- 11  $3.00 \text{ A}$  passed for 30 minutes (1800 s)  
 Charge =  $3.00 \text{ A} \times 1800 \text{ s} = 5400 \text{ C}$   
 Amount of lead produced =  $\frac{5.60 \text{ g}}{207.2 \text{ g mol}^{-1}} = 0.027 \text{ mol}$   
 $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$   
 Therefore, moles of electrons passed =  $0.027 \text{ mol} \times 2$   
 $= 0.054 \text{ mol}$   
 $0.054 \text{ mol electrons} = 5400 \text{ C}$   
 $1 \text{ mol electrons} = 100000 \text{ C}$   
 Charge on one electron =  $-1.602 \times 10^{-19} \text{ C}$   
 Number of electrons in  $1 \text{ mol} = \frac{100000}{1.602 \times 10^{-19}}$   
 $= 6.24 \times 10^{23}$ ;  
 Avogadro constant =  $6.24 \times 10^{23}$

f Aprotic polar

g Non-polar

h Aprotic polar

- 2 a The mechanism is a nucleophilic substitution ( $\text{S}_{\text{N}}2$ ).  $\text{OH}^-$  is the nucleophile that attacks at the electron-deficient carbon atom ( $\delta^+$ ) to which the bromine atom is attached. The molecule inverts its tetrahedral structure as a result of the attack. See Figure 20.3 on page 673 for detail of the movement of electrons in this mechanism, and Figure 20.5 on page 674 for an illustration of the inversion which takes place.
- b Rate =  $k [\text{C}_2\text{H}_5\text{Br}] [\text{OH}^-]$   
 The reaction takes place in a single concerted step involving both of the reacting species in this rate-determining step. The reaction is therefore bimolecular.  $\text{S}_{\text{N}}2$  stands for substitution, nucleophilic, bimolecular.
- c Polar aprotic solvents will not interact with the attacking nucleophile forming a 'solvent shell'. The nucleophile remains 'naked'. A nucleophile with a solvent shell is going to be slower in attacking the target molecule. By using an aprotic solvent and allowing the nucleophile to react all of the time, we are greatly speeding up the reaction.  $\text{S}_{\text{N}}2$  reactions performed with nucleophiles in polar aprotic solvents occur about 1000 times faster than those in regular protic solvents.
- d DMF is a better solvent for this reaction as it is a polar aprotic solvent whereas water is a polar protic solvent which will shield the nucleophile by forming a solvent shell. Water has hydrogen atoms that are attached to a highly electronegative element, oxygen.
- 3 a Chlorine is more electronegative than bromine and so the Cl atom will be  $\delta^-$  and the Br atom  $\delta^+$ .
- b 1-Bromo-2-chloropropane,  $\text{CH}_3\text{CHClCH}_2\text{Br}$   
 2-Bromo-1-chloropropane,  $\text{CH}_3\text{CHBrCH}_2\text{Cl}$
- c 1-Bromo-2-chloropropane is the more likely product as the bromine is added first on the terminal carbon atom. This produces a secondary carbocation intermediate that is more stable than the possible primary carbocation. This means that the chlorine is likely to be added to the second carbon atom in the chain.

- 4 Pent-1-ene: the major product will be 2-bromopentane as this involves the formation of the more stable secondary carbocation intermediate, as predicted by Markovnikov's rule. The other product is 1-bromopentane.

Pent-2-ene: a 50:50 mixture of 2-bromopentane and 3-bromopentane is formed, as both would involve the formation of a secondary carbocation as an intermediate.

## 20 Organic chemistry

- 1 a Non-polar  
 b Polar protic  
 c Aprotic polar  
 d Protic polar  
 e Aprotic polar

- 5 M1: free radical substitution  
M2: electrophilic addition  
M3: nucleophilic substitution  
M4: electrophilic substitution
- 6 a Reduction with  $\text{LiAlH}_4$  in diethyl ether; reflux; add dilute acid to complete reaction.  
b Not a possible route.  
c Reaction with bromine vapour (or in an organic solvent) in sunlight (UV light).  
d Reaction with chlorine or bromine in an organic solvent (in dark).  
e Heat with concentrated sulfuric acid and then add water.  
f Reaction under reflux ( $50^\circ\text{C}$ ) with a nitrating mixture of concentrated nitric acid and concentrated sulfuric acid.  
g Reflux with tin and concentrated hydrochloric acid.  
h Warm with sodium dichromate(VI)/concentrated sulfuric acid in distillation apparatus.

- 7 **But-1-ene**  $\rightarrow$  react with  $\text{HBr}$   $\rightarrow$  **2-bromobutane**  $\rightarrow$  react with  $\text{NaOH}$  solution  $\rightarrow$  **butan-2-ol**  $\rightarrow$  oxidation with  $\text{Na}_2\text{Cr}_2\text{O}_7$  / concentrated  $\text{H}_2\text{SO}_4$   $\rightarrow$  **butanone**

OR

**But-1-ene**  $\rightarrow$  react with conc.  $\text{H}_2\text{SO}_4$  / add water **butan-2-ol**  $\rightarrow$  oxidation with  $\text{Na}_2\text{Cr}_2\text{O}_7$  / concentrated  $\text{H}_2\text{SO}_4$   $\rightarrow$  **butanone**

The second method may give the greater yield as it involves fewer stages

- 8 **1-Chlorobutane**  $\rightarrow$  react with  $\text{NaOH}$  solution  $\rightarrow$  **butan-1-ol**  $\rightarrow$  oxidation with  $\text{Na}_2\text{Cr}_2\text{O}_7$  / concentrated  $\text{H}_2\text{SO}_4$  under reflux  $\rightarrow$  **butanoic acid**
- $$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$$
- $$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + 2[\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O}$$

- 9 Just b and c can show *cis-trans* isomerism.

For b see the example of 1,3-dichlorocyclobutane in Figure 20.52 on page 701; in this case the two methyl groups can be on the same side of the plane, or one above and one below.

For c see Figure 20.51 on page 701 as a guide; note that in this case there are complex examples involving the substituents on all three carbon atoms.

- 10 *Cis*-but-2-ene-1,4-dioic acid and *trans*-but-2-ene-1,4-dioic acid.

See Figure 20.53 for the structures of these two isomers.

- 11  $\text{CHBr}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$

*Z*-1-Bromo-2-methylbut-1-ene drawn with the  $-\text{Br}$  and the  $-\text{CH}_2\text{CH}_3$  groups on carbons 1 and 2 on the same side of the double bond.

*E*-1-Bromo-2-methylbut-1-ene drawn with the  $-\text{Br}$  and the  $-\text{CH}_2\text{CH}_3$  groups on carbons 1 and 2 on opposite sides of the double bond.

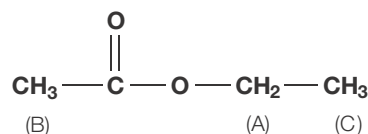
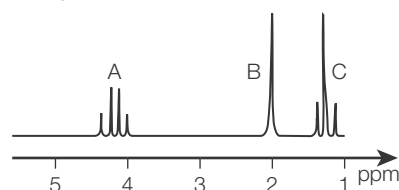
- 12  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$

*Z*-3-Methylpent-2-ene drawn with the methyl group on carbon 2 and the ethyl group on carbon 3 on the same side of the double bond (*trans*-3-methylpent-2-ene).

*E*-3-Methylpent-2-ene drawn with the methyl group on carbon 2 and the ethyl group on carbon 3 on opposite sides of the double bond (*cis*-3-methylpent-2-ene).

## Chapter 21 Measurement and analysis

- 1  **$\text{C}_4\text{H}_8\text{O}_2$**



- 2 The high C:H ratio in the molecular formula suggests the presence of a benzene ring and this is confirmed by the peak at  $\delta = 7.6$ . The broad peak at 10.8 is typical of the  $-\text{O}-\text{H}$  of a carboxylic acid (which reacts with sodium). The two proton single peak at  $\delta = 3.7$  is a  $-\text{CH}_2-$  group flanked by a benzene ring and a  $-\text{COOH}$  group, both of which cause a high field resonance. The structure is therefore  $\text{C}_6\text{H}_5-\text{CH}_2-\text{COOH}$ .
- 3 There are three times as many combinations giving a net magnetic moment of +1 or -1 compared with +3 or -3.

	↑↑↑	↑↑↓	↑↓↑	↓↓↓
		↑↑↑	↑↓↑	
		↓↑↑	↓↑↑	
net moment	+3	+1	-1	-3
		+1	-1	
		+1	-1	

- 4 Functional magnetic resonance imaging can detect changes in blood oxygenation caused by increased metabolism of activated parts of the brain. It has become a powerful tool for cognitive neuroscience research and brain activity mapping to preserve critical functions in patients requiring neurosurgery. Oxyhemoglobin is paramagnetic (due to the presence of unpaired electrons in the iron(III) ion,  $\text{Fe}^{3+}$ ) and gives an enhanced relaxation, and hence a signal, close to the blood supply.

# Answers to self-assessment questions in Chapters 22 to 25 (Options A to D)

## 22 Option A Materials

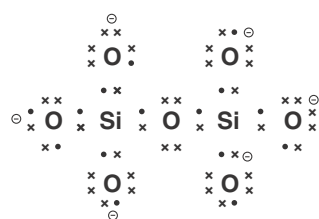
- 1 The softness of large crystals of pure metals is due to the presence of dislocations in the crystals. These are irregularities of the crystal structure that allow atomic planes to slip much more easily than they would in a perfect crystal. A dislocation is caused by an extra plane of atoms within the crystal. Dislocations can be viewed using high resolution transmission electron microscopy (TEM) which allows the crystal planes and atomic positions within materials to be imaged.

- 2 An amorphous (non-crystalline) solid is formed when a liquid is cooled rather rapidly, that is, super-cooled. The rapid cooling process does not give the atoms sufficient time to arrange themselves into an ordered lattice. The atoms are bonded in a short-range structure. Since the material is cooled, the movement of the atoms is reduced and this accounts for the fixed shape of glass. Glass flows very slowly under the force of gravity.

The glass-liquid transition (or glass transition for short) is the reversible transition in amorphous materials, such as glass (or in amorphous regions within semi-crystalline materials, such as some polymers) from a hard and relatively brittle state into a molten or rubber-like state. It is not a phase transition and extends over a range of temperatures.

- 3 Individual answers.

- 4 Dot-and-cross diagram for the ion,  $\text{Si}_2\text{O}_7^{6-}$



- 5 Individual answers.

- 6 Gold: metal; jewelry

Polyurethane: synthetic polymer; foam for home furnishings

Solder: alloy; joining metals

Nitrocellulose nitrate: synthetic polymer; propellant or explosive or plastic film

Silicon: metalloid; transistors, photovoltaic cells

Brass: alloy; musical instruments

Gutta percha: natural polymer; dentistry, core of a golf ball

Polystyrene: synthetic polymer; disposable cutlery

Titanium: metal; aerospace alloys, replacement hip joints

Plywood: composite; fencing

Silicon nitride: ceramic; induction coils

Porcelain: ceramic; dishes and vases

Carbon-fibre reinforced epoxy resin: composite; oars

Terracotta: ceramic; flower pots, sculptures and bricks

Talcum powder: mineral; keeps skin dry

Magnadur: ceramic; permanent magnets

Borosilicate glass: glass; laboratory glassware

Nylon: synthetic polymer; ropes

Muntz metal: alloy; corrosion-resistant machine parts

Pyrex: glass; measuring cup, baking dishes

Rayon: semi-synthetic polymer; clothing

Silicone rubber: polymer (elastomer); sportswear and footwear

Bronze: alloy; statues, bearing and electrical connectors

Silk: natural polymer (protein); clothing

Nitinol: alloy; medical applications

Thinsulate: synthetic polymer; clothing

Kevlar: synthetic polymer; body armour

Mica: mineral; wall boards, cladding, car manufacture

Rayon: semi-synthetic fibre; sportswear

Teflon (PTFE): synthetic polymer; containers, pipe work, insulating cables

Polycetylene: conducting polymer; battery electrodes

Asbestos: mineral; ceiling insulation, fire proofing material

Bakelite: synthetic plastic; jewelry and billiard balls

Carbon fibre: composite material; the body of formula one racing cars

Cellophane: natural polymer; food packaging

Dacron: synthetic plastic; to replace or repair blood vessels

Ebonite: vulcanized rubber (elastomer); bowling balls and smoking mouthpieces

Cement: composite; used to make concrete, building construction

- 7 Individual answers

- 8 GaN, polar covalent, HF, polar covalent; CsH, ionic;  $\text{AlCl}_3$ , polar covalent;  $\text{SCl}_2$ , covalent and KCl, ionic.

- 9 (i) Lead(II) oxide, gold(I) oxide, manganese(IV) oxide and zinc oxide can all be reduced by heating with carbon.  
(ii) Gold(I) oxide can be reduced by heating with hydrogen gas.
- 10  $\text{HgO(s)} + \text{C(s)} \rightarrow \text{Hg(l)} + \text{CO(g)}$ ;  
 $2\text{HgO(s)} + \text{C(s)} \rightarrow 2\text{Hg(l)} + \text{CO}_2\text{(g)}$   
 $\text{HgO(s)} + \text{H}_2\text{(g)} \rightarrow \text{Hg(l)} + \text{H}_2\text{O(l)}$   
 $3\text{HgO(s)} + 2\text{Cr(s)} \rightarrow \text{Cr}_2\text{O}_3\text{(s)} + 3\text{Hg(l)}$
- 11 Mass of cadmium electrolysed =  $\frac{(A_r \times I \times t)}{(z \times 96\,500 \text{ C mol}^{-1})}$   
 $= \frac{(112.41 \text{ g mol}^{-1} \times 0.755 \text{ A} \times 10\,800 \text{ s})}{(2 \times 96\,500 \text{ C mol}^{-1})} = 4.75 \text{ g}$
- 12 Mass of gold electrolysed =  $\frac{(A_r \times I \times t)}{(z \times 96\,500 \text{ C mol}^{-1})}$   
 Time to deposit gold =  $\frac{(5.00 \text{ g} \times 1 \times 96\,500 \text{ C mol}^{-1})}{(196.97 \text{ g mol}^{-1} \times 2.68 \text{ A})}$   
 $= 914 \text{ s (15 minutes 4 seconds)}$
- 13 Quantity of charge passed =  $0.500 \text{ A} \times 1800 \text{ s} = 900 \text{ C}$ ;  
 mass of copper deposited =  $2.299 \text{ g}$ ;  
 amount of copper atoms =  $\frac{2.299 \text{ g}}{63.55 \text{ g mol}^{-1}} = 0.0362 \text{ mol}$ ;  
 $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ ; amount of electrons =  $0.0724 \text{ mol}$ ;  
 Faraday constant =  $\frac{900 \text{ C}}{0.0724 \text{ mol}} = 12\,430 \text{ C mol}^{-1}$
- 14 Quantity of charge passed = mass of silver deposited  
 $= \frac{(A_r \times z \times 96\,500 \text{ C mol}^{-1})}{A_r}$   
 $= \frac{(0.785 \text{ g} \times 1 \times 96\,500 \text{ C mol}^{-1})}{107.87 \text{ g mol}^{-1}}$   
 $= 702 \text{ C (which will be the same quantity of charge for cell 2)}$   
 Mass of chromium electrolysed =  $\frac{(52 \text{ g mol}^{-1} \times 702 \text{ C})}{3 \times 96\,500 \text{ C mol}^{-1}}$   
 $= 0.126 \text{ g}$
- 15 Sodium (paramagnetic), magnesium (diamagnetic), tin (diamagnetic), lead (diamagnetic); all first row transition metals are paramagnetic except zinc, which is diamagnetic. Iron, cobalt and nickel are also ferromagnetic.
- 16 Anti-ferromagnetism is a type of magnetism in solids where adjacent ions that behave as tiny magnets spontaneously align themselves at relatively low temperatures into opposite, or antiparallel, arrangements throughout the material so that it exhibits almost no gross external magnetism. In anti-ferromagnetic materials, which include certain metals and alloys in addition to some ionic solids, the magnetism from magnetic atoms or ions oriented in one direction is canceled out by the set of magnetic atoms or ions that are aligned in the reverse direction.
- 17 The gas could be collected in a gas syringe or via displacement of water in a measuring cylinder (or eudiometer). The temperature of the reactants could be controlled via a water bath with a thermostat. Total volumes of oxygen gas and times should be recorded at five or more different temperatures. Tangents should be drawn against various points on graphs of total volume of oxygen versus time to generate values of rate, which should be plotted against time for the different temperatures.
- 18 Individual answers.
- 19 Individual answers.
- 20 A monotropic liquid crystal is a type of material that exhibits the liquid crystalline state only when the temperature changes in one direction. This is generally a result of the liquid crystal phase being below the melting temperature of the solid, where the liquid crystal phase is only observed if the liquid is supercooled below the melting point. Enantiotropic liquid crystals exhibit the liquid crystal state when the temperature rises from the solid state side or when it falls from the liquid state. Monotropic liquid crystals exhibit the liquid crystalline state only when the temperature changes in one direction.
- 21 Individual answers.
- 22 Cold drawing causes the polymer chains to become orientated along the length of the fibre. This means that the chains can get closer together and so there are more points where intermolecular forces can act, thus leading to a large increase in the polymer's tensile strength.
- 23 The atom economy of nylon synthesis should be calculated. Weighed quantities of reactants should be left to react until the reaction has gone to completion. The dried and purified product should be weighed and the atom economy calculated.
- 24 Individual answers.
- 25 In the laser ablation technique, a high-power laser is used to vaporize carbon from a graphite target at high temperature. Both multiple and single-walled carbon nanotubes can be produced with this technique. In order to generate single-walled nanotubes, metal particles as catalysts must be added to the graphite targets in a similar way to the arc discharge technique. The quantity and quality of produced carbon nanotubes depend on several factors such as the amount and type of catalysts, laser power and wavelength, temperature, pressure, type of inert gas, and the fluid dynamics near the carbon target. Carbon nanotubes produced by laser ablation are purer (up to 90% purity) than those produced in the arc discharge process and have a very narrow distribution of diameters.



26 Individual answers.

27 Individual answers.

28 Individual answers.

29 The C–H bonds are causing the peaks at  $3000\text{ cm}^{-1}$ ; the benzene ring is responsible for the peaks between  $2800$  and  $3200\text{ cm}^{-1}$  and  $600$  to  $1000\text{ cm}^{-1}$ .

30 Individual answers.

31  $\text{YBa}_2\text{Cu}_3\text{O}_6$  [ $\text{Y}^{3+}$   $2\text{Ba}^{2+}$   $3\text{Cu}^{n+}$   $6\text{O}^{2-}$ ];  $(+7 + -12) = -5$ ,  
hence average oxidation number of copper  $= +\frac{5}{3} = 1.6$ .

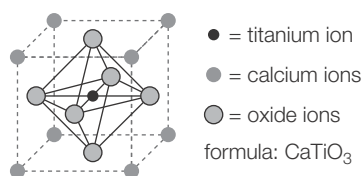
32 Individual answers.

33  $T_c = 92\text{ K}$  (This is experimental data that shows the curved low-temperature tail of a transition).

34 Frequency (Hz)  $= \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1.00 \times 10^{-9} \text{ m}} = 3.00 \times 10^{17} \text{ Hz (s}^{-1}\text{)}$

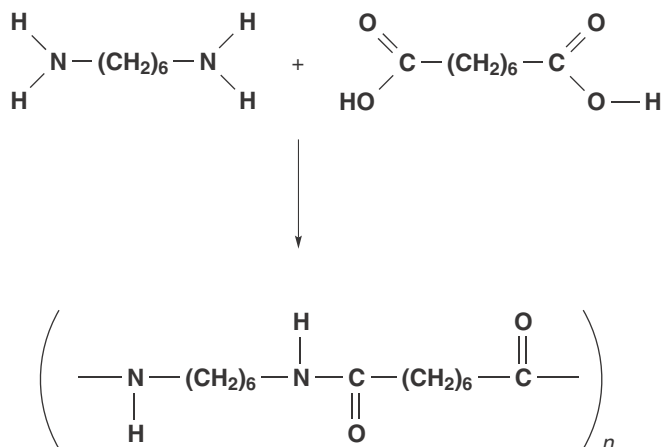
35  $a = \frac{4r}{\sqrt{3}} = \frac{4 \times 0.124 \text{ nm}}{\sqrt{3}} = 0.2864 \text{ nm}$

36 Unit of cell of the perovskite structure:



37 Individual answers.

38



39 Individual answers.

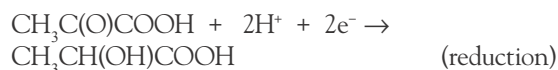
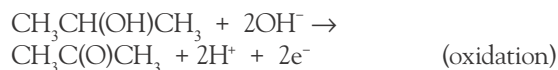
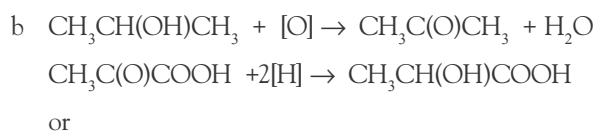
40 Individual answers.

## 23 Option B Biochemistry

- 1 a Reduction is the loss of electrons; oxidation the gain.  
b Reduction is the gain of hydrogen; oxidation the loss.  
c Reduction is the loss of oxygen; oxidation the gain.

d Reduction is a lowering of oxidation state; oxidation is an increase in oxidation state.

- 2 a Propan-2-ol has been oxidized to propanone; 2-oxopropanoic acid has been reduced to 2-hydroxypropanoic acid.



- 3 a 2-Aminopropanoic acid  
b See Figure 23.14. It does not contain a chiral centre as there are not four different substituents on the central carbon atom.  
c Optical isomerism. It is a white crystalline solid at room temperature.  
d  $\text{NH}_2\text{CH}_2\text{COOH} + \text{HCl} \rightarrow [\text{NH}_3^+\text{CH}_2\text{COOH}] \text{Cl}^-$   
 $\text{NH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{NH}_2\text{CH}_2\text{COOCH}_3 + \text{H}_2\text{O}$

- 4 a The amino group,  $-\text{NH}_2$ , and the carboxylic acid group,  $-\text{COOH}$ .  
b Proline, the amino group is cyclised (becomes an imino group).  
c Alanine, valine, phenylalanine, leucine, isoleucine  
d Serine, threonine, tyrosine  
e Aspartic acid, glutamic acid

- 5 a The lone pair of (non-bonding) electrons on the nitrogen atom (the amino group acts as a Lewis base).  
b The R group can act as a base and gain a proton; becoming positively charged.

- 6 a Re-draw in the zwitterion form; see Figure 23.17.  
b The overall charge = 0.

- 7 a The amino acid is in the zwitterion form in the solid so there are ionic interactions between the molecules resulting in a relatively high melting point.  
b The ionic nature of the zwitterion form means that the molecules can interact with water as a polar solvent.

- 8 Solid state: draw the zwitterion form.

In water at  $\text{pH} = 1$ : draw the molecule with a charged  $-\text{NH}_3^+$  group.

At  $\text{pH} = 5.7$ : draw the zwitterion.

At  $\text{pH} = 14$ : draw the molecule with a charged  $-\text{COO}^-$  group.

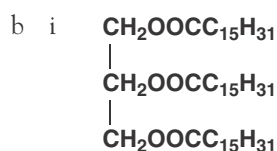
See Figure 23.18.

- 9 Estimate the  $R_f$  of the middle spot in the right-hand diagram (it has moved furthest in the second solvent:  $R_f = 0.8$ ).
- 10 a 5
- b Spraying with the locating agent, ninhydrin; or observing the chromatogram under UV light.
- c Sketch showing just four spots (take guidance from the movement to the right); the first two spots move well up the chromatogram, spots three and four are quite close together – the fourth spot (closest to the origin) is made up of two solutes.
- 11 a Condensation polymerization.
- b See Figure 23.26 for the bonding and 23.27 for the bond angles.
- The peptide bond region is arranged in the *trans* conformation (Figure 23.27).
- c i The peptide link region is planar and rigid because of the formation of a delocalized pi ( $\pi$ ) bond over the region.
- ii Most R groups are bulky and steric factors favour the *trans* conformation to accommodate their presence.
- 12 a Covalent bonding
- b Polypeptide chains have an amino-terminal (N-terminal) and a carboxy-terminal (C-terminal) end; they are linear polymers and synthesised from the N-terminal end to the C-terminal end.
- 13 Look closely at the R groups along the chain; the sequence is Phe-Ser-His-Ala.
- 14 a The amide (or peptide) link.
- b Both N terminus and C terminus: draw the structure of alanine.
- c Two; alanine and lysine (glycine is the third residue but this is not optically active).
- 15 Secondary structure: Hydrogen-bonding between the peptide link regions formed between any of these amino acids can contribute to the formation of an alpha helix (see Figure 23.39, particularly the simplified sketch on the right).
- Tertiary structure: Describe the different interactions the R groups of these amino acids can participate in:
- Valine: hydrophobic, non-polar interactions via London forces.
- Glutamic acid: ionic or charged group interactions.
- Cysteine: covalent disulfide bridging.
- These interactions can take place between amino acid residues in the same chain (tertiary structure); see Figure 23.46.
- 16 The R groups of aspartic acid, asparagine and lysine will contribute to hydrogen bonding; the R group of valine will not.
- 17 a and b See Figure 23.58
- 18 a The substrate must be in excess so that molecules of the substrate are freely available and their accessibility is not limiting on enzyme activity.
- b For many enzymes a fall in temperature of  $10^\circ\text{C}$  halves the rate of reaction or turnover number (this generalisation applies to reactions where the activation energy is around  $+50\text{ kJ mol}^{-1}$ ).
- 19 a  $1.5\text{ g of iodine} = 0.59 \times 10^{-2}\text{ moles iodine}$
- This reacted with  $1.0 \times 10^{-2}\text{ moles of linoleic acid}$
- Molar ratio of fatty acid:iodine (to nearest whole number) = 2:1
- There are two C=C double bonds in a molecule of linoleic acid
- b Iodine number = number of grams of iodine reacting with 100 g of lipid
- $0.01\text{ mol of linoleic acid (C}_{17}\text{H}_{31}\text{COOH})$
- $= 0.01 \times 280.5 = 2.8\text{ g}$
- $\text{Iodine number} = \left(\frac{100}{2.8}\right) \times 1.5 = 53.5$
- 20 a Improved solubility of fat/oil (and iodine) in ethanol compared with water.
- b Soft margarine: 7 drops; polyunsaturated margarine: 11 drops.
- c Olive oil
- 21 a  $\text{Mol iodine reacting} = \frac{0.5 \times 19}{1000} = 9.5 \times 10^{-3}\text{ mol}$
- $\text{Mass of iodine} = 9.5 \times 10^{-3} \times 253.8 = 2.41\text{ g}$
- $\text{Iodine number} = \frac{100}{25} \times 2.41 = 9.64$
- b  $\text{Mol vegetable oil} = \frac{2.5}{865} = 2.89 \times 10^{-3}\text{ mol}$
- Molar ratio of oil: iodine (to nearest whole number) = 3:1.
- An average of three C=C double bonds in a molecule of the oil.
- c The vegetable oil will contain a mixture of different long-chain acid molecules.
- 22 a i Stearic acid
- ii Oleic acid
- b i To prevent the chocolate manufactured melting too readily in the hotter climate.
- ii They are likely to be made of longer chains and a higher proportion of saturated fats.
- 23 a Lipid: a varied group of non-polar molecules containing carbon, hydrogen and oxygen; they have a lower proportion of oxygen than carbohydrates.

Triglyceride: a molecule consisting of three long-chain fatty acids linked by ester links to a glycerol molecule.

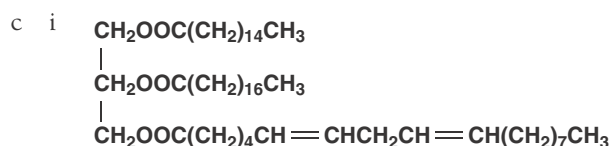
Saturated fatty acid: a long-chain carboxylic acid containing only C–C single bonds in the molecule (no double bonds).

Polyunsaturated fatty acid: a long-chain carboxylic acid containing more than one C=C double bond in the hydrocarbon chain.

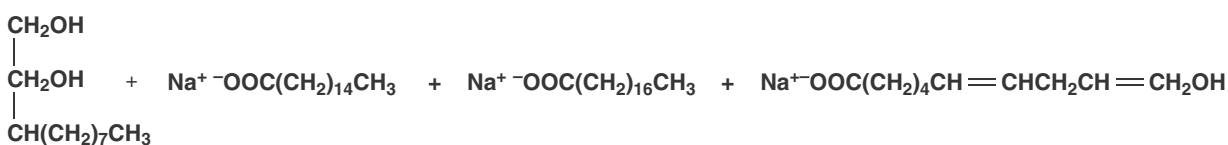
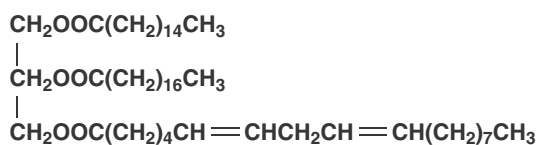


ii The ester link.

iii Solid



ii



24 a They have long, non-polar chains ('tails') that enable them to sit across the membrane, but a polar end ('head') to the molecule which interacts with the aqueous environment.

b i The fluid mosaic model.

ii A = hydrophobic 'tail' of the phospholipid molecule (long-chain hydrocarbon tail)

B = hydrophilic 'head' of the phospholipid molecule

C = transmembrane protein

D = carbohydrate side-chain on the protein

E = non-membrane protein

iii W = 7 to 10 nm for the plasma membrane (the bilayer is estimated to be 4 to 5 nm thick).

iv Cholesterol gives some rigidity to the membrane.

25 Ketone = B

Aldehyde = A and C

Triose = C

Pentose = A

Hexose = B

26 a They are isomers.

b The molecule contains a number of hydroxyl groups (–OH) which can interact with water molecules through hydrogen bonding – see Figure 23.114.

c A is  $\alpha$ -glucose.

27 a  $\alpha$ -1,4 and  $\alpha$ -1,6 glycosidic links.

b Hydrolysis

c See the structure of  $\alpha$ -glucose in Figure 23.108.

d Amylopectin.

e The polymer contains many glucose molecules which are not able to react while they are 'stored' in the polymer, whereas the monomer is readily able to react.

28 Starch contains  $\alpha$ -glycosidic links which enzymes present in humans are able to hydrolyse – hence starch is a useful dietary source of energy; cellulose contains  $\beta$ -glycosidic links and humans do not have enzymes capable of hydrolysing such bonds. Cellulose is useful in human diet as 'dietary fibre'.

29 a Hydroxyl group and amide group

b Hydroxyl group and ketone group

c I is water soluble as it has several hydroxyl groups to hydrogen bond with water

II is lipid soluble as it has a long, hydrophobic hydrocarbon chain.

30 a i 17%

ii 8%

iii 10%

b 0.13%

c i  $4 \times 10^6$  times more concentrated.

ii 5.8 times; 9.0 times; 6.7 times.

31 Vancomycin is a glycopeptide antibiotic most effective against Gram-positive bacteria.

32 Research the location and nature of the Grand Pacific garbage patch, and the impact of plastic waste on the oceans in general including the leaching out of environmentally harmful chemicals.

- 33 a i See Figure 23.143.  
 ii See Figure 23.144.  
 b i See Figure 23.151.  
 ii The inhibitor competes with the substrate for active sites on the enzyme thus slowing the rate of reaction / the rate will eventually reach the same plateau value ( $V_{\max}$ ) as that achieved without inhibitor.  
 c i See Figure 23.153.  
 ii The inhibitor binds to a site on the enzyme other than the active site, altering the conformation of the enzyme and reducing its activity / the rate will not reach the same plateau value ( $V_{\max}$ ) as the uninhibited enzyme.

34 a Solid state:  $\text{NH}_3^+\text{CH}(\text{CH}_2\text{OH})\text{COO}^-$

pH = 1:  $\text{NH}_3^+\text{CH}(\text{CH}_2\text{OH})\text{COOH}$

pH = 14:  $\text{NH}_2\text{CH}(\text{CH}_2\text{OH})\text{COO}^-$

pH = 5.7:  $\text{NH}_3^+\text{CH}(\text{CH}_2\text{OH})\text{COO}^-$

b  $\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]}} \right)$   
 $\text{pH} = 9.1 + \log_{10} \left( \frac{[\text{anionic form}]}{[\text{zwitterion}]} \right) = 9.1 + \log_{10} \left( \frac{0.2}{0.8} \right)$   
 $\text{pH} = 9.1 + \log_{10} 0.25 = 9.1 - 0.6 = 8.5$

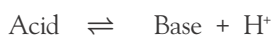
35 Glycine species are  $\text{NH}_3^+\text{CH}_2\text{COOH}$  and  $\text{NH}_3^+\text{CH}_2\text{COO}^-$

$$\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

$$3.0 = 2.31 + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

$$\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 0.69$$

$$\frac{[\text{base}]}{[\text{acid}]} = 4.9$$



Initial concentrations: 0.500      0      0

Equilibrium: (0.500 - x)      x      x

$$\text{Therefore: } \frac{x}{(0.500 - x)} = 4.9$$

$$x = 0.415 \text{ mol dm}^{-3}$$

$$[\text{NH}_3^+\text{CH}_2\text{COOH}] = 0.085 \text{ mol dm}^{-3}$$

$$[\text{NH}_3^+\text{CH}_2\text{COO}^-] = 0.415 \text{ mol dm}^{-3}$$

36 a Equilibrium is  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$\text{Therefore } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Making the approximation that the equilibrium concentrations of ethanoic acid and ethanoate ions are the same as their initial concentrations. This is a reasonable assumption because the dissociation of ethanoic acid in pure water is very low, and

therefore the dissociation is going to be even lower if some  $\text{CH}_3\text{COO}^-$  is already present.

$$K_a = 1.74 \times 10^{-5} = \frac{0.250 \times [\text{H}^+]}{0.200}$$

$$[\text{H}^+] = (1.74 \times 10^{-5}) \times \left( \frac{0.200}{0.250} \right) = 1.39 \times 10^{-5}$$

$$\text{pH} = -\log_{10}(1.39 \times 10^{-5}) = 4.86$$

Could also use the equation  $\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$  directly if you work out the  $\text{p}K_a$  first.

b  $\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 7.21 + \log_{10} \left( \frac{0.045}{0.055} \right)$

$$\text{pH} = 7.21 - 0.09 = 7.12$$

c  $\text{pH} = \text{p}K_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 8.30 + \log_{10} \left( \frac{0.750}{0.650} \right)$

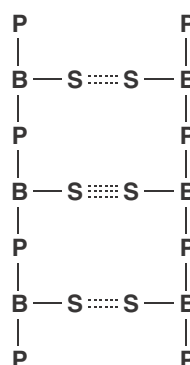
$$\text{pH} = 8.30 + 0.06 = 8.36$$

37 Concentration =  $\frac{A}{\epsilon} = \frac{0.29}{0.08} = 3.6 \text{ ppm}$

38 a Concentration =  $\frac{A}{\epsilon} = \frac{0.31}{500} = 6.2 \times 10^{-4} \text{ mol dm}^{-3}$

b Concentration =  $\frac{A}{\epsilon} = \frac{0.23}{63.5} = 3.6 \times 10^{-3} \text{ mol dm}^{-3}$

39 a Based on Figure 23.169.



b i Each strand has direction / the two strands run in opposite directions / the 5'-3' phosphodiester linkages run in opposite directions.

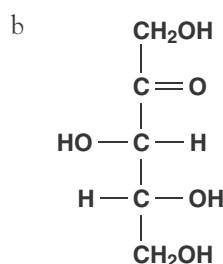
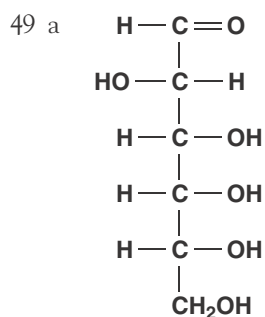
ii The strands are antiparallel.

iii The ends of each strand are designated 5' ('5-prime') and 3' ('3-prime').

c The gentle heating disrupts the hydrogen bonding between the bases / the number of hydrogen bonds between strands depends on the proportion of GC base pairs as they have three hydrogen bonds between them compared to AT base pairs with only two.

40 a Hydrogen bonds play a part in the recognition of the possible base pairs that can form / A always pairs with T, and G with C / AT pairing involves two hydrogen bonds whereas GC pairing involves three.

- b After replication the daughter molecules contain one parent strand and one new strand / each new molecule contains one old strand and one new strand.
- c i Hydrogen bonding (and London forces referred to as 'base stacking')
- ii Phosphodiester links
- 41 a RNA contains the sugar, ribose / DNA the sugar, deoxyribose.
- RNA is single stranded / DNA is double stranded.
- RNA contains the base uracil / DNA contains thymine.
- b i Purine: adenine or guanine
- Pyrimidine: cytosine or thymine
- ii I is a purine (with two rings); II is a pyrimidine (with one ring).
- 42 A is D-form / B is L-form / C is D-form.
- 43 A is L-alanine / B is D-phenylalanine / C is D-serine.
- 44 a Isomerism
- b The several hydroxyl groups can all participate in hydrogen bonding with the water molecules.
- c A is  $\alpha$ -glucose as the  $-\text{OH}$  on carbon-1 is on the opposite side of the plane of the ring to the carbon-6 / C is  $\beta$ -glucose.
- 45 a They all contain an aldehyde group.
- b They are all D-form as the  $-\text{OH}$  on carbon-5 is to the right in this representation.
- c Carbon-2 in A is different from B and C / carbon-4 in B is different from A and C optical isomers.
- 46 Research the origins of chirality and the importance of molecular shape in biochemical processes.
- 47 a See Figure 23.251.
- b The presence of several  $-\text{OH}$  groups in the structure of glucose leads to hydrogen bonding with water molecules and the enhanced solubility of glucose: see Figure 23.114.
- 48 a The  $\beta$ -form.
- b It is a reducing sugar.
- c See structure on left in Figure 23.247.



## 24 Option C Energy

- 1 Specific energy:  $49.9 \text{ MJ kg}^{-1}$   
Energy density:  $24.7 \text{ MJ dm}^{-3}$
- 2  $4800000 \text{ MJ per hour}$ ;  $1333 \text{ MW}$
- 3 a  $\text{C}_{10}\text{H}_{22} \rightarrow 5\text{C}_2\text{H}_4 + \text{H}_2$   
b  $\text{C}_{20}\text{H}_{42} \rightarrow \text{C}_8\text{H}_{18} + 4\text{C}_3\text{H}_6$
- 4 Total volume of fuel =  $70000 \text{ dm}^3 = 70000000 \text{ cm}^3$   
Mass of fuel =  $70000000 \text{ cm}^3 \times 0.703 \text{ g cm}^{-3} = 49210000 \text{ g}$   
Amount of fuel =  $430800 \text{ mol}$   
Equation for combustion is:  
 $\text{C}_8\text{H}_{18} + 12.5\text{O}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O}$   
Amount of  $\text{CO}_2 = 8 \times 430800 \text{ mol} = 3446400 \text{ mol}$   
Mass of  $\text{CO}_2 = 3446000 \text{ mol} \times 44 \text{ g mol}^{-1} = 151641600 \text{ g} = 152 \text{ tonnes CO}_2$
- 5  ${}^{14}_7\text{N} + {}^4_2\text{He} \rightarrow {}^{17}_8\text{O} + {}^1_1\text{H}$ ; oxygen-17
- 6  ${}^{12}_6\text{C} + {}^1_1\text{H} \rightarrow {}^{13}_7\text{N}$   
 ${}^{13}_7\text{N} \rightarrow {}^{13}_6\text{C} + {}^0_1\text{e}$   
 ${}^{13}_6\text{C} + {}^1_1\text{H} \rightarrow {}^{14}_7\text{N}$   
Unknown:  ${}^{13}_6\text{C}$
- 7  $t = t_{\frac{1}{2}} \frac{\ln\left(\frac{N_0}{N}\right)}{\ln 2} = 2.14 \times 10^6 \times \frac{\ln\left(\frac{100}{10}\right)}{\ln 2}$   
 $= 2.14 \times 10^6 \times 3.32$   
 $= 7.11 \times 10^6 \text{ years}$
- 8 Carbon in  $\text{CO}_2$ : +4  
Carbon in glucose: 0
- 9  $(\text{C}_{17}\text{H}_{31}\text{COO})_3\text{CH}(\text{CH}_2)_2 + 3\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons 3\text{C}_{17}\text{H}_{31}\text{COOCH}_2\text{CH}_3 + (\text{CH}_2\text{OH})_2\text{CHOH}$
- 10  $\frac{-237}{-286} \times 100 = 82.9\%$
- 11  $E_{\text{cell}} = 0.78 \text{ V} - \frac{0.0257}{2} \ln \frac{0.0200}{0.100} = 0.76 \text{ V}$
- 12  $E = \frac{0.0257}{2} \ln \frac{0.1}{0.0005} = 0.0681 \text{ V}$



- 13 Mass difference: mass of reactants – mass of products  
 $= 2.2 \times 10^{-3} \text{ amu}$

$$\text{Mass difference in kg: } 2.2 \times 10^{-6} \times 1.660539 \times 10^{-27} \\ = 3.65319 \times 10^{-30} \text{ kg}$$

$$\text{Energy} = 3.65319 \times 10^{-30} \times (299792500)^2 \\ = 3.28332 \times 10^{-13} \text{ J/nucleus}$$

Expressed in electronvolts this becomes 2.05 MeV.

## 25 Option D Medicinal chemistry

- 1 Amount of 2-hydroxybenzoic acid  $= \frac{9.40 \text{ g}}{138.13 \text{ g mol}^{-1}}$   
 $= 0.0681 \text{ mol}$

1:1 molar ratio, hence amount of aspirin  $= 0.0681 \text{ mol}$

$$\text{Mass of aspirin} = 0.0681 \text{ mol} \times 180.17 \text{ g mol}^{-1} = 12.3 \text{ g}$$

$$\text{Percentage yield} = \frac{7.77 \text{ g}}{12.3 \text{ g}} \times 100 = 63.4\%$$

- 2 The sharp peaks at  $1690 \text{ cm}^{-1}$  and  $1750 \text{ cm}^{-1}$  indicate the presence of carbonyl groups. (The peak at  $1690 \text{ cm}^{-1}$  is due to the carbonyl in the carboxylic acid group; the peak at  $1750 \text{ cm}^{-1}$  is due to the carbonyl in the ester group.) The broad peak at approximately  $3000 \text{ cm}^{-1}$  is typical of an –OH group in a phenol and/or carboxylic acid. The broadness is due to hydrogen bonding.
- 3 At 2.2 ppm, the –CH<sub>3</sub> group, and at 13.1 ppm the –COOH group.
- 4 At 180: the molecular ion; at 163: loss of OH (–17); at 120: the loss of C<sub>2</sub>H<sub>4</sub>O<sub>2</sub> (actually loss of CH<sub>2</sub>CO followed by H<sub>2</sub>O) from the molecular ion; and at 43: the appearance of the CH<sub>3</sub>CO<sup>+</sup> ion.
- 5 Morphine: ether, alcohol, benzene ring, tertiary amine  
 Codeine: ether, alcohol, ester, tertiary amine  
 Diamorphine (heroin): tertiary amine, benzene ring, ester, ether
- 6 Sodium alginate has a relatively large number of hydroxyl groups, –OH, which are able to form hydrogen bonds with water molecules.
- 7 Smallpox was an infectious disease caused by either of two virus variants, *Variola major* and *Variola minor*. Smallpox was localized in small blood vessels of the

skin and in the mouth and throat. In the skin it caused a rash and fluid-filled blisters. Smallpox was eradicated by inoculation or vaccination using the live virus preparation of infectious *vaccinia* virus.

- 8 Capsid proteins are an important mechanism by which viruses infect host cells. The viral proteins interact with host cell proteins in the cell membrane, and this interaction initiates biochemical processes which allow the virus to enter the cell.

Enfuvirtide (a polypeptide) binds to viral proteins and can inhibit the protein–protein interaction and hence acts as an antiviral agent (fusion inhibitor).

- 9 a  ${}^{13}_6\text{C} + {}^1_0\text{n} \rightarrow {}^4_2\text{He} + {}^{10}_4\text{Be}$   
 b  ${}^{14}_7\text{N} + {}^4_2\text{He} \rightarrow {}^1_0\text{n} + {}^{17}_9\text{F}$   
 c  ${}^{253}_{99}\text{Es} + {}^4_2\text{He} \rightarrow {}^1_0\text{n} + {}^{256}_{101}\text{Md}$   
 d  ${}^{53}_{24}\text{Cr} + {}^4_2\text{He} \rightarrow {}^1_0\text{n} + {}^{56}_{26}\text{Fe}$   
 e  ${}^{250}_{98}\text{Cf} + {}^{11}_5\text{B} \rightarrow {}^{257}_{103}\text{Lr} + {}^4_1\text{n}$
- 10 a  ${}^{239}_{94}\text{Ra} \rightarrow {}^4_2\text{He} + {}^{235}_{92}\text{U}$   
 b  ${}^{40}_{19}\text{K} \rightarrow {}^0_{-1}\text{e} + {}^{40}_{20}\text{Ca}$   
 c  ${}^{99}_{43}\text{Tc} \rightarrow {}^{99}_{44}\text{Ru} + {}^0_{-1}\text{e}$   
 d  ${}^{218}_{84}\text{Po} \rightarrow {}^{214}_{82}\text{Pb} + {}^4_2\text{He}$
- 11  ${}^{231}_{92}\text{U}$
- 12  ${}^{235}_{92}\text{U} \rightarrow {}^{231}_{90}\text{Th} + {}^4_2\text{He}$ ;  ${}^{210}_{82}\text{Pb} \rightarrow {}^{210}_{83}\text{Bi} + {}^0_{-1}\text{e}$
- 13  ${}^{131}_{54}\text{Xe}^* \rightarrow {}^{131}_{54}\text{Xe} + {}^0_0\gamma$
- 14 Polonium
- 15 Alexander Litvinenko was poisoned by polonium-210, a highly toxic radioactive heavy metal with a physical half-life of 138 days. It decays to stable lead-206 giving off 5.3 MeV alpha particles that have a range of 40–50 μm in tissue.
- 16 a Fractional distillation  
 b Suction filtration  
 c Distillation  
 d Recrystallization