

Answers to self-assessment questions in Chapters 1 to 21

1 Stoichiometric relationships

- 1 a Heat produced; colour change
 b Magnesium + iodine \rightarrow 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 = $44\text{ g} + 4\text{ g} = 48\text{ g}$, note that this is the same as the reactants: $12 + 36 = 48\text{ g}$.
 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 $\text{Fe}_2(\text{PO}_4)_3$, NH_4I , $\text{Al}(\text{NO}_3)_3$, CaBr_2 and Fe_2O_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 $\text{Ag}(\text{NO}_3)_2(\text{aq}) + 2\text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + 2\text{NaNO}_3(\text{aq})$
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$
 $\text{Zn}(\text{s}) + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu}(\text{s})$
 $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
 $\text{Na}_2\text{CO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
 $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- 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, MgCO_3
 $= [24.31 + 12.01 + (3 \times 16.00)]$
 $= 84.32\text{ g mol}^{-1}$
- 17 Molar mass of carbon dioxide, 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 (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:	PbO	

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

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

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

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

Empirical formula is 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:

$$\frac{6.1225}{1.020} \quad \frac{10.20}{1.020} \quad \frac{1.020}{1.020}$$

$$6 \quad 10 \quad 1$$

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

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

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

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

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

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

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

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

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

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

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



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

$$40 \quad \frac{97000 \text{ Pa}}{298 \text{ K}} = \frac{101325 \text{ Pa}}{T_2}$$

$$T_2 = 101325 \text{ Pa} \times \frac{298 \text{ K}}{97000 \text{ Pa}}$$

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

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

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

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

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

$$43 \quad PV = nRT; n = \frac{PV}{RT}; n = \frac{101325 \text{ Pa} \times 4 \times 10^{-3} \text{ m}^3}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 273 \text{ K}} = 0.1786 \text{ mol}$$

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

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

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

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

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

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

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

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

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

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

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

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

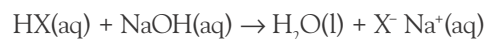
$$49 \quad M_1 \times V_1 = M_2 \times V_2; 5.0 \text{ mol dm}^{-3} \times 25.0 \text{ cm}^3 = 1.5 \text{ mol dm}^{-3} \times V_2$$

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

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 4.1×10^{-3} mol because the acid and base are reacting in a 1:1 molar ratio:



Hence, molar mass of HX =

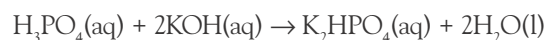
$$\frac{\text{mass(g)}}{\text{amount (mol)}} = \frac{0.558 \text{ g}}{4.10 \times 10^{-3} \text{ mol}} = 136 \text{ g mol}^{-1}$$

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

b Amount of sodium hydroxide used in the titration

$$= \frac{25.0 \text{ dm}^3}{1000} \times 1.00 \text{ mol dm}^{-3} = 0.0250 \text{ mol NaOH}$$

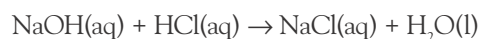
c From the equation, amount of H_2SO_4 = amount of NaOH $\div 2 = 0.0125 \text{ mol}$ in 20.0 cm^3 , so 'scaling up' to 1000 cm^3 to obtain the concentration of diluted sulfuric acid

$$= \frac{1000 \times 0.0125 \text{ mol dm}^{-3}}{20.0} = 0.625 \text{ mol dm}^{-3}$$

d 'Scaling up' from 50.0 to 1000 cm^3 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 $\text{MgO(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O(l)}$



b Amount of hydrochloric acid added to the magnesium oxide

$$= \frac{100 \text{ dm}^3}{1000} \times 2.00 \text{ mol dm}^{-3} = 0.200 \text{ mol}$$

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

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 g mol^{-1} , 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 cm^3 .

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

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

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

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

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

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

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

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

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

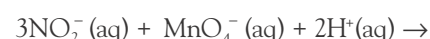
$$\text{Amount of } \text{MnO}_4^-/\text{KMnO}_4 = \frac{2}{5} \times 0.00655 \text{ mol} = 0.00262 \text{ in } 25.00 \text{ cm}^3$$

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

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

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

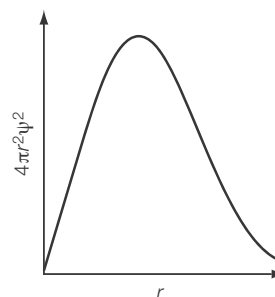
$$\text{Percentage of atom that is nucleus} = 4.2 \times 10^{-48} \text{ m}^3/4.2 \times 10^{-30} \text{ m}^3 \times 100 = 10^{-16}\%$$

- 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).

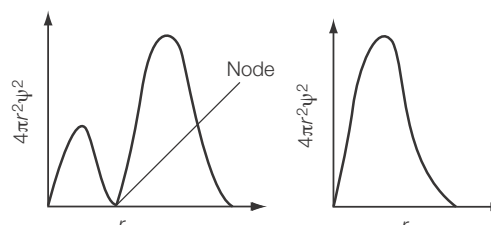
$$\frac{1.672622 \times 10^{-27} + 9.109383 \times 10^{-31} \text{ g}}{9.109383 \times 10^{-31} \text{ g}} = 1837 \text{ times heavier}$$

- 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 Ti^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$
 Cr^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$
 Cu : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
 P^{3-} : $1s^2 2s^2 2p^6 3s^2 3p^6$
 Cl : $1s^2 2s^2 2p^6 3s^2 3p^5$
 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 $1s^1$ 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 $1s^2 2s^2 2p^3$ N^+ (unipositive ion) (excited state)
 v F atom is $1s^2 2s^2 2p^5$ 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 $+2$.

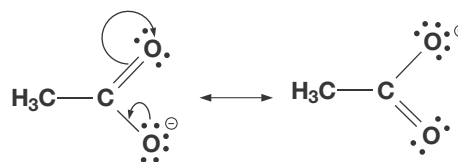
3 Periodicity

- 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.

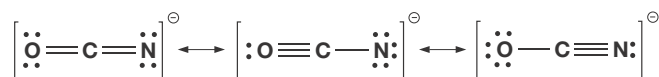
There are many alternative forms of the periodic table, including spiral and helical, many of which highlight or emphasize chemical or physical properties of the elements that are not as apparent in the long form of the periodic table.

- 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, 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
- $$\begin{array}{ccc} \begin{array}{c} \text{H} \\ \times \\ \oplus \text{C} \times \text{H} \\ \times \\ \text{H} \end{array} & \begin{array}{c} \text{H} \\ \times \\ \ominus \text{C} \times \text{H} \\ \times \\ \text{H} \end{array} & \begin{array}{c} \text{H} \\ \times \\ \cdot \text{C} \times \text{H} \\ \times \\ \text{H} \end{array} \\ +\text{CH}_3 & -\text{CH}_3 & \cdot\text{CH}_3 \end{array}$$
- 6 Resonance structures for the ethanoate ion:

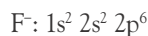
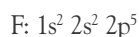
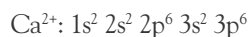


Resonance structures for the cyanate ion:

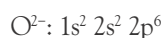
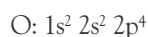
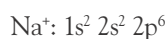
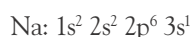


4 Chemical bonding and structure

- 1 Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$



Each calcium atom loses two electrons; each fluorine atom gains one electron.



Each sodium atom loses one electron; each oxygen atom gains two electrons.



Each aluminium atom loses three electrons; each oxygen atom gains two electrons.

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^+	Be^{2+}	None	None	N^{3-}	O^{2-}	F^-	None
Electron arrangement of ion	2	2	—	—	2,8	2,8	2,8	—
Electron configuration of ion	$1s^2$	$1s^2$	—	—	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6$	—

- 7 $^+\text{CH}_3$ (trigonal planar); $^-\text{CH}_3$ (tetrahedral); PH_3 (trigonal pyramidal); AsH_3 (trigonal bipyramidal) and NH_2^- (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.

10 Carbon disulfide has a higher boiling point than carbon dioxide because molecules of CS_2 have more electrons than molecules of CO_2 . This results in the London (dispersion) forces being stronger between molecules of 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

- $^{\circ}\text{C} \times \frac{9}{5} + 32 = ^{\circ}\text{F}$ and $(^{\circ}\text{F} - 32) \times \frac{5}{9} = ^{\circ}\text{C}$
- 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 (δ^+) and interacts with the negative pi cloud.

Collision 2: the H–Cl molecule is wrongly orientated with the Cl atom (δ^-) 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.

- Base your sketch on Figure 6.6, but put the actual reactants ($\text{N}_2 + 3\text{H}_2$) and products (2NH_3) on the appropriate levels. You can label the activation energy at this stage.
 - Using a broken line sketch in a peak that is below that in (a).
 - Note that the activation energy is lower in the presence of a catalyst.
- 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 kJ mol^{-1} .

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

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

- The activation energy will be lowered to a value less than $+243 \text{ kJ mol}^{-1}$.
- Molybdenum(vi) oxide and silicon(iv) oxide.
 - 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.

- Sketch a graph similar to Figure 6.17.
 - Activation energy is the minimum combined kinetic energy the colliding molecules must have in order to react.
 - See Figure 6.17.
 - See Figure 6.19; draw a line at a lower energy value than your first E_a .
 - Shade the area under the graph between the two values for activation energy; see Figure 6.19.
 - See Figure 6.18.
- 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.
 - 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.
 - 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.
 - 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.
 - Sample B has the highest value of mean kinetic energy.
 - 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 CO_2 (= 0.5 mol) produced in a volume of 4 dm^3 in 15 s

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

- 10 0.06 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 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 s = 75.6 cm^3 .

$$\text{Average rate of reaction} = \frac{75.6}{150} = 0.504 \text{ cm}^3 \text{ s}^{-1}$$

- 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) cm^3 of hydrogen gas.

- g This graph should be steeper initially but should level out at 75.6 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°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°C and 5°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.

$$3 \text{ a i } K_c = \frac{[\text{Fe}(\text{SCN})]^{2+}}{[\text{Fe}^{3+}][\text{SCN}^-]}$$

$$\text{ii } K_c = \frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^5}$$

- 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 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 cm³ of equilibrium mixture = $2.95 \times 10^{-3} \text{ mol}$

Mol of acid in 250 cm³ 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	2.95×10^{-2}	2.95×10^{-2}
At equilibrium / mol dm ⁻³	0.4705 / V	1.9705 / V	$2.95 \times 10^{-2} / V$	$2.95 \times 10^{-2} / V$

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

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⁺ 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 H₂O is the acid; OH⁻ is the conjugate base; CO₃²⁻ is the base and HCO₃⁻ is the conjugate acid.
 b H₂SO₄ is the acid and SO₄²⁻ is the conjugate base; H₂O is the base and H₃O⁺ is the conjugate acid.
- 3 a $\text{H}_2\text{SO}_4(\text{aq}) + \text{CuCO}_3(\text{s}) \rightarrow \text{CuSO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
 b $2\text{HBr}(\text{aq}) + \text{Ca}(\text{HCO}_3)_2(\text{s or aq}) \rightarrow \text{CaBr}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{CO}_2(\text{g})$
 c $2\text{H}_3\text{PO}_4(\text{aq}) + 3\text{Na}_2\text{CO}_3(\text{s or aq}) \rightarrow 2\text{Na}_3\text{PO}_4(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + 3\text{CO}_2(\text{g})$
 d $2\text{CH}_3\text{COOH}(\text{aq}) + \text{Ca}(\text{s}) \rightarrow \text{Ca}(\text{CH}_3\text{COO})_2(\text{aq}) + \text{H}_2(\text{g})$
 e $2(\text{NH}_4)_3\text{PO}_4(\text{aq}) + 3\text{Ba}(\text{OH})_2(\text{aq}) \rightarrow 6\text{NH}_3(\text{g}) + 3\text{H}_2\text{O}(\text{l}) + \text{Ba}_3(\text{PO}_4)_2(\text{aq})$
- 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 $\text{pH} = -\log_{10}(0.1) = 1$

6 $\text{pH} = -\log_{10}(3.00 \times 10^{-7}) = 6.52$

7 $\text{pH} = -\log_{10}(2 \times 0.0100) = 1.70$

8 $\text{pOH} = -\log_{10}(2.50 \times 10^{-3}) = 2.60$; $\text{pH} + \text{pOH} = 14.00$;
 $\text{pH} = 11.40$

9 $\text{pOH} = -\log_{10}(0.0100 \times 2) = 1.70$; $\text{pH} = 14.00 - 1.70$
 $= 12.30$

10 Amount of hydrogen chloride = $\frac{3.646 \text{ g}}{36.46 \text{ g mol}^{-1}} = 0.1 \text{ mol}$
 0.1 mol H⁺(aq) in 250 cm³ solution, hence concentration is 0.4 mol dm⁻³.

11 Amount of HCl(aq) = $2.5 \times 10^{-3} \text{ mol}$;
 amount of NaOH = $1.5 \times 10^{-3} \text{ mol}$;
 amount of excess HCl(aq)/H⁺(aq) = $1 \times 10^{-3} \text{ mol}$ in 40 cm³;
 concentration = $\left(\frac{1000}{40}\right) \times 1 \times 10^{-3} \text{ mol} = 0.025 \text{ mol dm}^{-3}$;
 $\text{pH} = -\log_{10}(0.025) = 1.60$

11 Measurement and data processing

- 1 a $25 \times 10^{-9} \text{ m}$ e $6 \times 10^{-6} \text{ m}^3$
 b 245 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 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 ± 0.04
 b 10.06 ± 0.02
 c 1.119 ± 0.07
 d 2.5 ± 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.

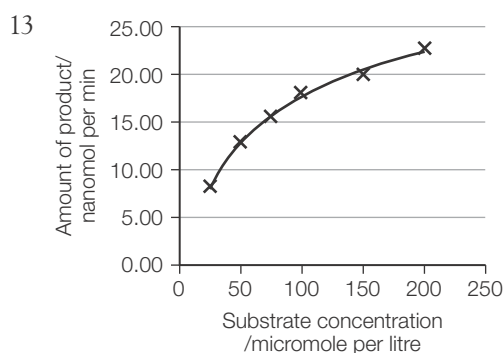
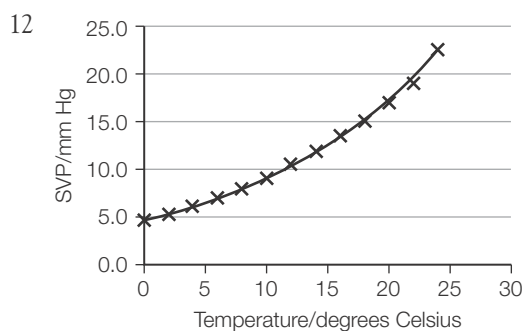
Stopwatch (b) is not very accurate since it displays an inaccurate reading compared to the true value, and it has poor resolution (only two digits of display and $\Delta t = 1 \text{ s}$).

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

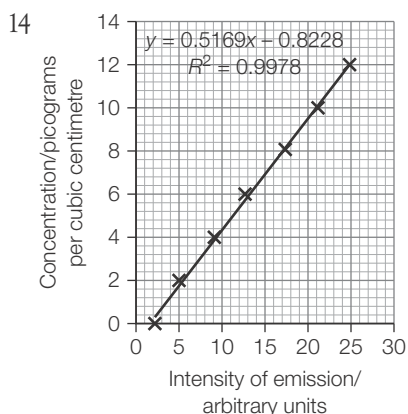
Stopwatch (d) is both accurate (reading close to true value) and has excellent resolution. Nothing can be concluded about precision because we have only one reading.

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 cm^3 (1 dp)
 b 1900 J (2 sf)
 c 1.01 g cm^{-3} (3 sf)
 d 1.99 kJ mol^{-1} (2 dp)
 e 268.1 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 $25.00 \text{ nanomol min}^{-1}$



15 Individual answers.

16 Individual answers.

17 a 0

b 1

c 0

18 $c = v \times \lambda$; $3.00 \times 10^8 \text{ ms}^{-1} = v \times 1515 \text{ m}$; $v = 198\,020 \text{ Hz}$

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

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

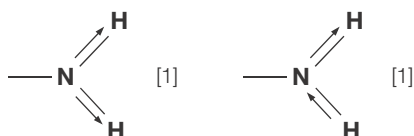
20 Wavenumber = $\frac{5.0 \times 10^{13} \text{ s}^{-1}}{3.00 \times 10^8 \text{ ms}^{-1}} = 1.67 \times 10^5 \text{ m}^{-1}$

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

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

$$E = 8.22 \times 10^{-20} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 49\,491.6 \text{ J mol}^{-1} \\ = 49 \text{ kJ mol}^{-1}$$

$$3 \quad \Delta x \times \Delta p = \frac{h}{4\pi} \\ \Delta p = \frac{h}{4\pi \Delta x} = \frac{6.63 \times 10^{-34} \text{ Js}}{4\pi \times 1.00 \times 10^{-11} \text{ m}} \\ = 5.28 \times 10^{-24} \text{ kg ms}^{-1} \\ \Delta p = 5.28 \times 10^{-24} \text{ kg ms}^{-1} = m \Delta v \\ \Delta v = \frac{p}{m} = \frac{5.25 \times 10^{-24} \text{ kg ms}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 5.79 \times 10^6 \text{ ms}^{-1}$$

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 $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{9.109383 \times 10^{-31} \text{ kg} \times 1.600 \times 10^2 \text{ ms}^{-1}} \\ = 4.55 \times 10^{-6} \text{ m}$

6 Individual answers.

7 $c = v \times \lambda$; $\lambda = \frac{c}{v}$; $\lambda = \frac{3.00 \times 10^8 \text{ ms}^{-1}}{1368 \times 10^3 \text{ Hz}} = 219 \text{ m}$; radio waves

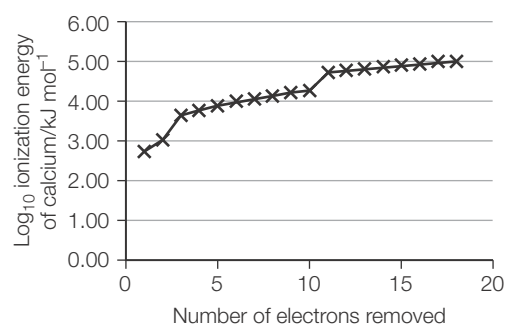
8 $c = v \times \lambda$; $v = \frac{c}{\lambda}$; $v = \frac{3.00 \times 10^8 \text{ ms}^{-1}}{5.800 \times 10^7 \text{ Hz}} = 5.17 \times 10^{14} \text{ s}^{-1}$

9 $E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ Js} \times 3.00 \times 10^8 \text{ ms}^{-1}}{780 \times 10^{-9} \text{ m}} \\ = 2.55 \times 10^{-19} \text{ J}$

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

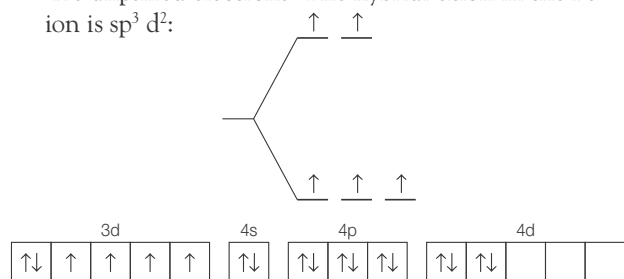
The increase in shielding (electron–electron repulsion) is less than the increase in nuclear charge.

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 Fe^{3+} ion is $\text{sp}^3 \text{d}^2$:



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

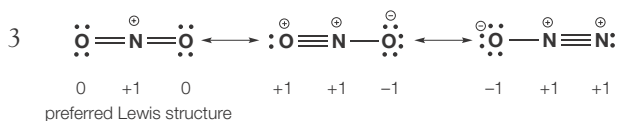
$$E = h\nu, \text{ so}$$

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

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

14 Chemical bonding and structure

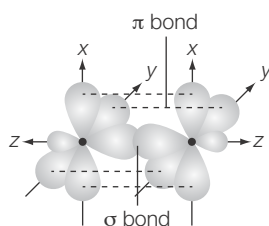
- Individual answers.
- Individual answers.



- H_2 : $(\sigma 1s)^2$, H_2^+ : $(\sigma 1s)^1$, H_2^- : $(\sigma 1s)^2 (\sigma^* 1s)^1$
- 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).

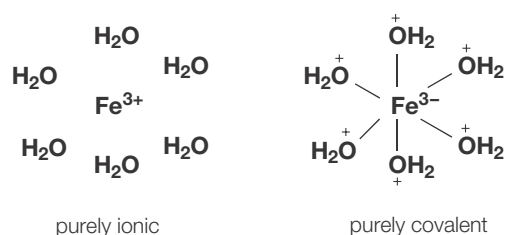
He_2 has the configuration $(\sigma 1s)^2 (\sigma^* 1s)^1$ and hence a bond order of zero. Hence this molecule is unstable with respect to its atoms and cannot be prepared.

- 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 $2p_z$ - $2p_z$ sigma bond is formed. The other two pi bonds are $2p_x$ - $2p_x$ and $2p_y$ - $2p_y$. 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

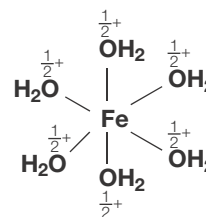
- The limiting ionic and dative covalent descriptions of the hexaquairon(III) ion are shown below.



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 hexaquairon(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).

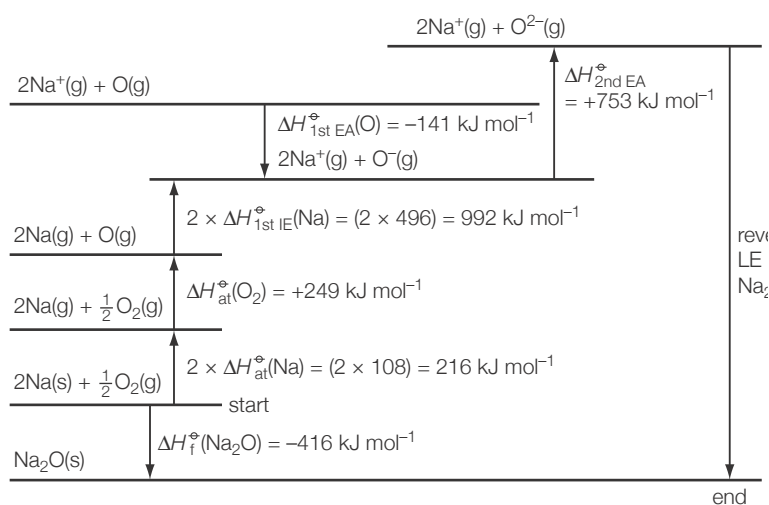


15 Energetics/thermochemistry

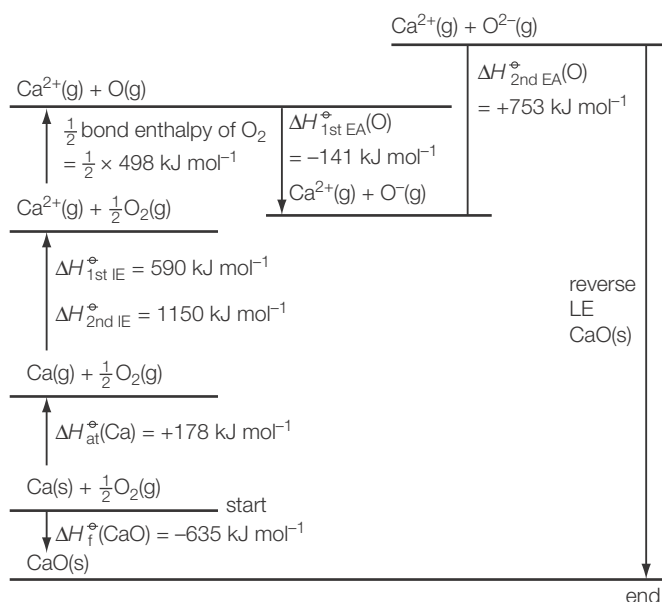
- $\frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{O}(\text{g}); \frac{1}{4} \text{P}_4(\text{s}) \rightarrow \text{P}(\text{g}); \text{B}(\text{s}) \rightarrow \text{B}(\text{g})$
- Enthalpy change = $6.04 \times 2.38/28.01 = 0.513 \text{ kJ} = 513 \text{ J}$
- $Q = mc\Delta T; Q = 100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{K}^{-1} \times 0.91^\circ\text{C} = 380.38 \text{ J} = 400 \text{ J}$
Amount of Ag^+ = 0.005 mol; amount of 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.

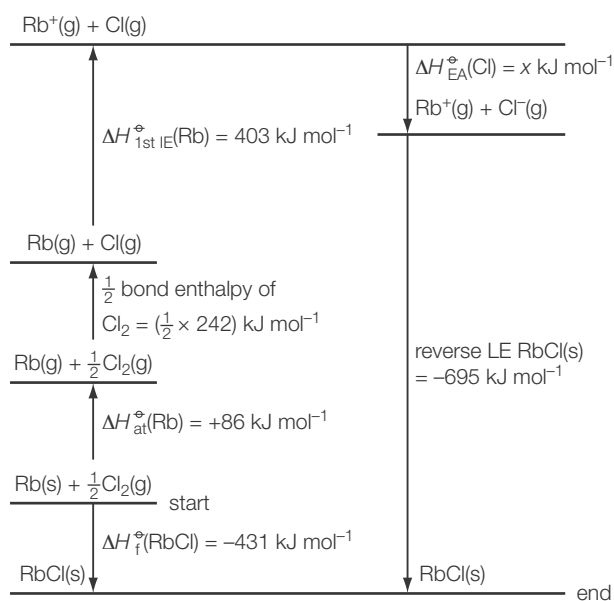
6 $-416 = 216 + 249 + 992 + (-141) + 753 + x$; $x = -2485$; lattice enthalpy of sodium oxide = $+2485 \text{ kJ mol}^{-1}$



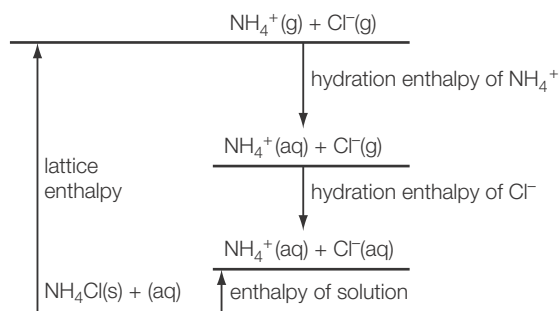
$-635 = 178 + 1150 + 590 + 249 + (-141) + 753 + x$; $x = -3414$; lattice enthalpy of calcium oxide = $+3414 \text{ kJ mol}^{-1}$



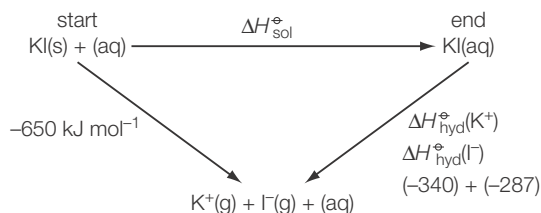
7 $-431 = 861 + 121 + 403 + x + -9695$; $x = -1121$; first electron affinity of chlorine = $-1121 \text{ kJ mol}^{-1}$



8



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



- 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 ΔH^{\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.

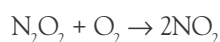
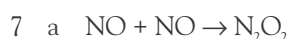
d The concentrations of cyclopropane are 1.50, 1.20, 0.90, and 0.60 mol dm^{-3} , respectively

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.

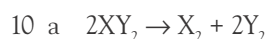


Sum of the two equations gives $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

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.

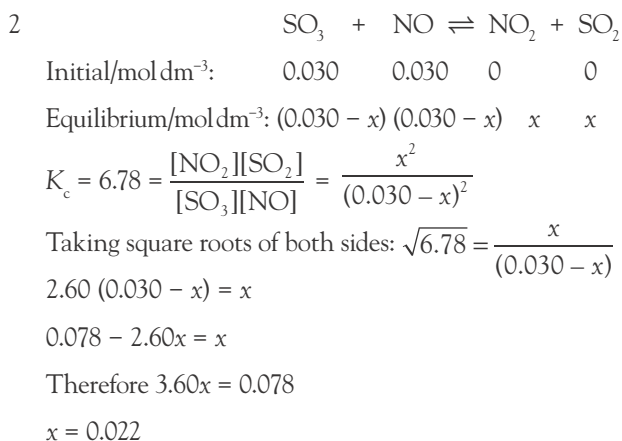
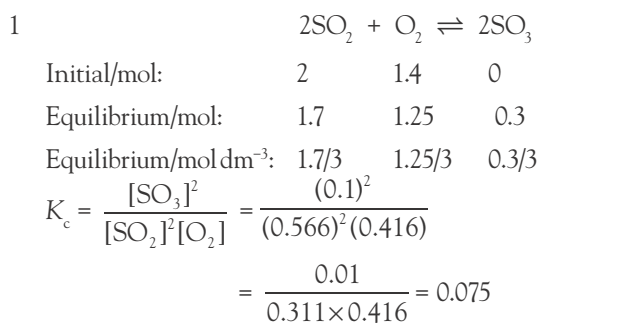


b Rate = $k[\text{XY}_2]^2$

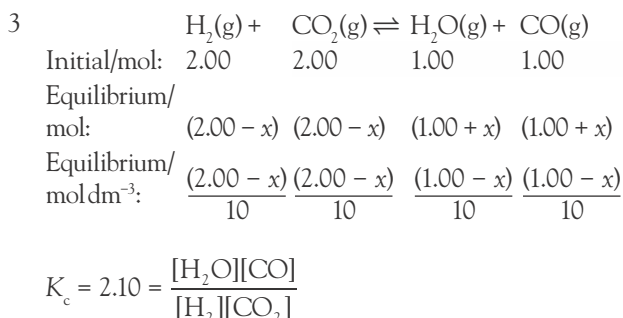
c Units of k are $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

d Draw diagram similar to Figure 16.18 on page 572.

17 Equilibrium



$$[\text{SO}_3] = [\text{NO}] = 8 \times 10^{-3} \text{ mol dm}^{-3} \text{ and } [\text{NO}_2] = [\text{SO}_2] = 0.022 \text{ mol dm}^{-3}$$



Note that the volumes will cancel out

$$\text{Therefore: } 2.10 = \frac{(1.00 + x)^2}{(2.00 - x)^2}$$

$$\text{Taking square roots of both sides: } \sqrt{2.10} = \frac{(1.00 + x)}{(2.00 - x)}$$

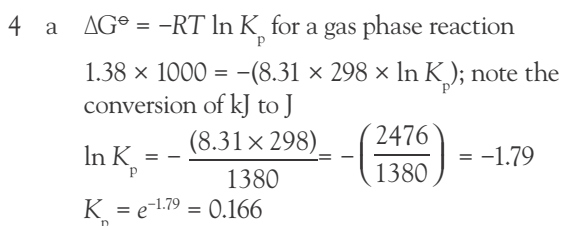
$$1.45(2.00 - x) = (1.00 + x)$$

$$1.90 = 2.45x$$

$$x = 0.78$$

$$[\text{H}_2\text{O}] = [\text{CO}] = \frac{1.78}{10} = 0.178 \text{ mol dm}^{-3}$$

$$[\text{H}_2] = [\text{CO}_2] = \frac{1.22}{10} = 0.122 \text{ mol dm}^{-3}$$



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

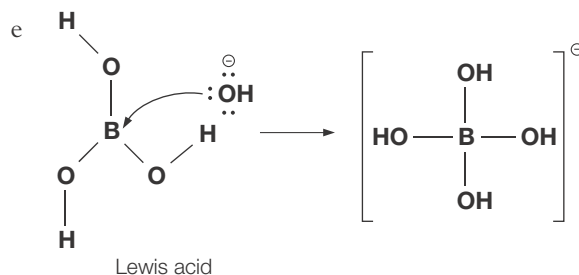
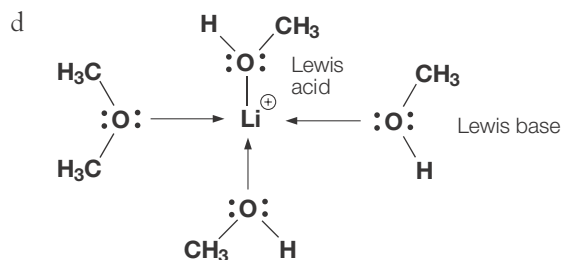
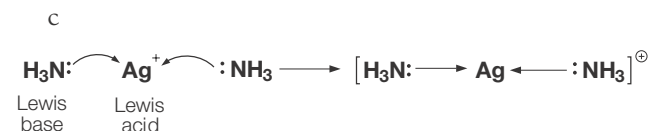
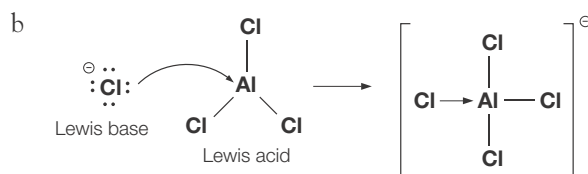
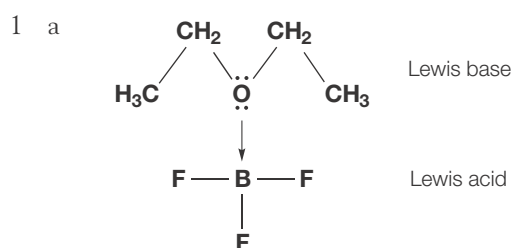
$$\text{b } \Delta G^\ominus = -RT \ln K_c$$

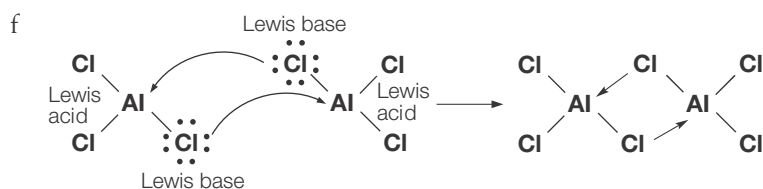
$$\Delta G^\ominus = -(8.31 \times 298) \ln (1.7 \times 10^{12})$$

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

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

18 Acids and bases





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

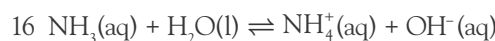
$K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{CH}_3\text{COOH}(\text{aq})]}$

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 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 $\text{p}K_a = -\log_{10}K_a; K_a = 1.74 \times 10^{-5};$

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

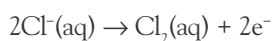
$[\text{H}^+(\text{aq})] = \sqrt{0.125 \times 1.74 \times 10^{-5}} = 1.47 \times 10^{-3} \text{ mol dm}^{-3};$

$\text{pH} = 2.83$

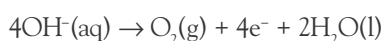
- 23 $K_b = \text{antilog } 9.13 = 7.41 \times 10^{-10}$;
 $\text{OH}^- = \sqrt{0.50 \times 7.41 \times 10^{-10}} = 1.925 \times 10^{-5}$;
 $\text{pOH} = 4.71$; $\text{pH} = 9.28$
- 24 $[\text{H}^+(\text{aq})] = 10^{-\text{pH}} = 10^{-5.74} = 1.82 \times 10^{-6}$;
 $1.82 \times 10^{-6} = \sqrt{0.025 \times K_a}$; $K_a = 1.325 \times 10^{-10}$
- 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 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 $\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$ $x\text{V}$
 $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ $+0.34\text{V}$
 $E^\ominus_{\text{cell}} = (+0.34) - x = +0.62$
 $x = (+0.34) - (+0.62) = -0.28\text{V}$
- 3 a $\text{Fe}(\text{s}) + \text{Ni}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Ni}(\text{s})$;
 $E^\ominus_{\text{cell}} = (0.45\text{V}) + (-0.26\text{V}) = +0.19\text{V}$
- b $2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) + 10\text{I}^-(\text{aq}) \rightarrow 5\text{I}_2(\text{s}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l})$;
 $E^\ominus_{\text{cell}} = (-0.54\text{V}) + (1.51\text{V}) = +0.97\text{V}$
- c $2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) + 3\text{F}_2(\text{g}) \rightarrow 6\text{F}^-(\text{g}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq})$;
 $E^\ominus_{\text{cell}} = (2.87\text{V}) + (-1.36\text{V}) = +1.51\text{V}$
- d $2\text{Ag}^+(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$;
 $E^\ominus_{\text{cell}} = (0.80\text{V}) + (-0.34\text{V}) = +0.46\text{V}$
- 4 $E_{\text{cell}} = (0.059/1) \times (\log_{10} 0.100/0.001) = 0.118\text{V}$
- 5 $E_{\text{cell}} = (-0.80\text{V}) + (1.23\text{V}) = +0.43\text{V}$;
 $\Delta G^\ominus = -nFE^\ominus = -4 \times 96500 \text{ C mol}^{-1} \times 0.43\text{V}$
 $= -165980 \text{ J mol}^{-1} = -166 \text{ kJ mol}^{-1}$
- 6 The E^\ominus 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 ΔG^\ominus 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 mol;
 amount of electrons = 0.60 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 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 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 mol
 0.054 mol electrons = 5400 C
 1 mol electrons = 100000 C
 Charge on one electron = $-1.602 \times 10^{-19} \text{ C}$
 Number of electrons in 1 mol = $\frac{100000}{1.602 \times 10^{-19}}$
 = 6.24×10^{23} ;
 Avogadro constant = 6.24×10^{23}

20 Organic chemistry

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

- f Aprotic polar
 g Non-polar
 h Aprotic polar

- 2 a The mechanism is a nucleophilic substitution ($\text{S}_{\text{N}}2$). OH^- is the nucleophile that attacks at the electron-deficient carbon atom (δ^+) 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 general 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 δ^- and the Br atom δ^+ .
 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.

- 5 M1: free radical substitution
M2: electrophilic addition
M3: nucleophilic substitution
M4: electrophilic substitution
- 6 a Reduction with 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°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 HBr \rightarrow **2-bromobutane** \rightarrow react with NaOH solution \rightarrow **butan-2-ol** \rightarrow oxidation with $\text{Na}_2\text{Cr}_2\text{O}_7$ / concentrated H_2SO_4 \rightarrow **butanone**

OR

But-1-ene \rightarrow react with conc. H_2SO_4 / add water **butan-2-ol** \rightarrow oxidation with $\text{Na}_2\text{Cr}_2\text{O}_7$ / concentrated H_2SO_4 \rightarrow **butanone**

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

- 8 **1-Chlorobutane** \rightarrow react with NaOH solution \rightarrow **butan-1-ol** \rightarrow oxidation with $\text{Na}_2\text{Cr}_2\text{O}_7$ / concentrated H_2SO_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.

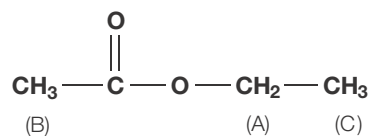
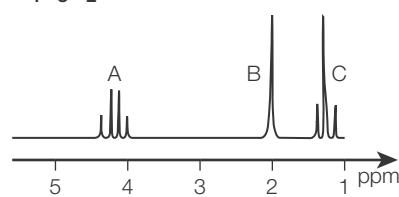
- 12 $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$

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, Fe^{3+}) and gives an enhanced relaxation, and hence a signal, close to the blood supply.

