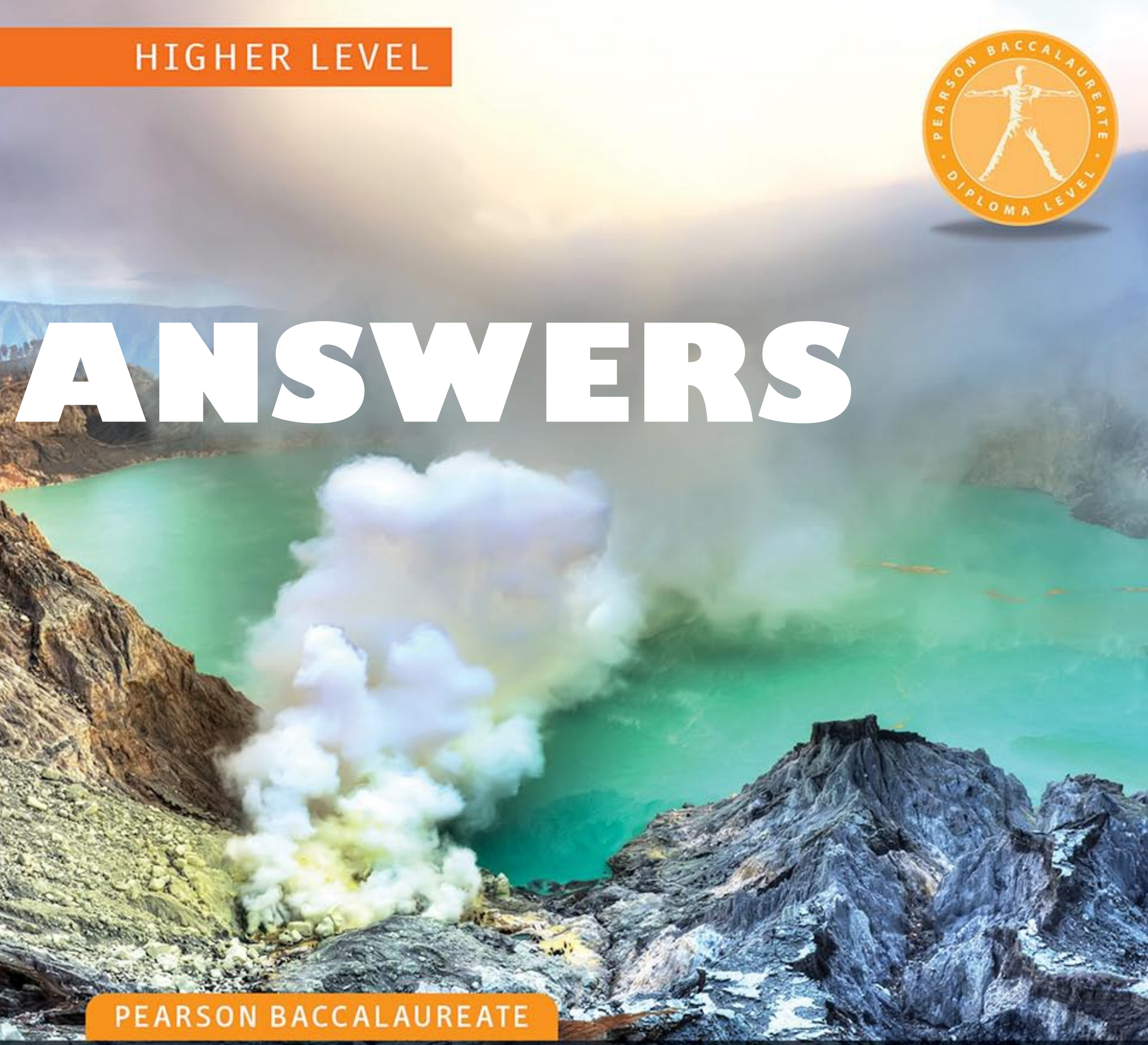
HIGHER LEVEL



ANSWERS

PEARSON BACCALAUREATE

HIGHER LEVEL

Chemistry

2nd Edition

CATRIN BROWN • MIKE FORD

Supporting every learner across the IB continuum

ALWAYS LEARNING
PEARSON

Answers

Chapter 1

Exercises

1 **(a)** $CuCO_3 \rightarrow CuO + CO_2$
(b) $2Mg + O_2 \rightarrow 2MgO$
(c) $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
(d) $N_2 + 3H_2 \rightarrow 2NH_3$
(e) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

2 **(a)** $2K + 2H_2O \rightarrow 2KOH + H_2$
(b) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
(c) $Cl_2 + 2KI \rightarrow 2KCl + I_2$
(d) $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$
(e) $Fe_2O_3 + 3C \rightarrow 3CO + 2Fe$

3 **(a)** $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$
(b) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
(c) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
(d) $6H_2O_2 + 2N_2H_4 \rightarrow 2N_2 + 10H_2O + O_2$
(e) $4C_2H_7N + 15O_2 \rightarrow 8CO_2 + 14H_2O + 2N_2$

4 **(a)** Sand and water: heterogeneous
(b) Smoke: heterogeneous
(c) Sugar and water: homogeneous
(d) Salt and iron filings: heterogeneous
(e) Ethanol and water: homogeneous
(f) Steel: homogeneous

5 **(a)** $2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$
(b) $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$
(c) $2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$
(d) $Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$
(e) $2C_3H_6(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

6 X has diffused more quickly, so it must be a lighter gas. Its particles have greater velocity than the particles of Y at the same temperature. (Note though that they will both have the same value for average kinetic energy.)

7 From the kinetic molecular theory we would expect a solid to be more dense than its liquid, and therefore that ice would sink in water.

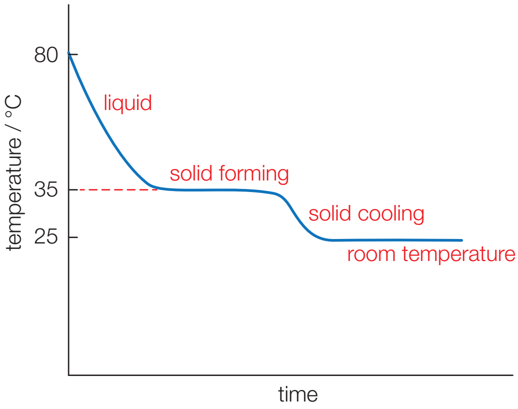
8 Bubbles will be present through the volume of the liquid. A brown gas is visible above the brown liquid. As the two states are at the same temperature, the particles have the same average kinetic energy and are moving at the same speed. The inter-particle distances in the gas are significantly larger than those in the liquid.

9 At certain conditions of low temperature and low humidity, snow changes directly to water vapour by sublimation, without going through the liquid phase.

10 Steam will condense on the skin, releasing energy as it forms liquid at the same temperature (e–d on Figure 1.4). This is additional to the energy released when both the boiling water and the condensed steam cool on the surface of the skin.

11 B

12



13 These calculations have used $L = 6.02 \times 10^{23}$
(a) 7.2×10^{22} **(b)** 3.01×10^{24}
(c) 1.2×10^{23}

14 0.53 mol H

15 0.250 mol

16 **(a)** 262.87 g mol^{-1} **(b)** 176.14 g mol^{-1} **(c)** 164.10 g mol^{-1} **(d)** 248.22 g mol^{-1}

17 189.1 g

18 1.5 mol

19 0.0074 mol Cl^-

20 1.83×10^{24} C atoms

21 171 g (integer value because no calculator)

22 10.0 g H_2O

23 2.0 mol N_2 > 3.0 mol NH_3 > 25.0 mol H_2 > 1.0 mol N_2H_4

24 **(a)** CH **(b)** CH_2O **(c)** $C_{12}H_{22}O_{11}$ **(d)** C_4H_9 **(e)** C_4H_7 **(f)** CH_2O

25 $Na_2S_2O_3$

26 $CoSO_4.7H_2O$

27 $C_{17}H_{25}N$

28 NH_3

29 6.94 Li

30 CdS

31 empirical formula CH; molecular formula C_6H_6

32 empirical formula H_2PO_3; molecular formula $H_4P_2O_6$

33 $C_{10}H_{16}N_5P_3O_{13}$ for both empirical and molecular formulas

34 C_3H_8O

35 Let y = mass of chalk in grams.

$$\text{moles of chalk used} = \frac{\text{mass used}}{M_r(CaCO_3)}$$

$$= \frac{y \text{ g}}{100.09 \text{ g mol}^{-1}}$$

This is the same as the number of moles of carbon atoms used.

Therefore the number of carbon atoms used = moles of chalk × (6.02×10^{23} mol^{-1})

$$= \frac{6.02 \times 10^{23}\, y}{100.09}$$

36 **(a)** 2.50 mol **(b)** 5.63 mol **(c)** 665.5 g

37 **(a)** $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

(b) 1.59 g

38 4.355 kg

39 **(a)** $CaCO_3 \rightarrow CaO + CO_2$

(b) 92.8%

(c) $CaCO_3$ is the only source of CO_2; all the $CaCO_3$ undergoes complete decomposition; all CO_2 released is captured; heating does not cause any change in the mass of the other minerals present.

40 **(a)** 85.2 g **(b)** 1.3 g H_2

41 5.23 g $C_2H_4Cl_2$

42 254 g theoretical $CaSO_3$; 77.9%

43 3.16 g ester

44 107 g of C_6H_6 needed

45 **(a)** 2.40 mol **(b)** 0.0110 mol **(c)** 44 mol

46 **(a)** 35.65 dm^3 **(b)** 5.7 dm^3

47 0.652 dm^3

48 0.138 mol Br_2 and 0.156 mol Cl_2, so more molecules of Cl_2

49 0.113 dm^3

50 0.28 dm^3

51 90 kPa

52 16 °C

53 3.0 dm^3

54 2.8 dm^3

55 M = 133 g mol^{-1} so gas is Xe

56 90.4 g mol^{-1}

57 Helium

58 311 dm^3

59 empirical formula and molecular formula = SO_3

60 At higher altitude the external pressure is less. As the air in the tyre expands on heating (due to friction with the road surface), the internal pressure increases.

61 **(a)** Particles are in constant random motion and collide with each other and with the walls of the container in perfectly elastic collisions. The kinetic energy of the particles increases with temperature. There are no inter-particle forces and the volume of the particles is negligible relative to the volume of the gas.

(b) At low temperature, the particles have lower kinetic energy, which favours the formation of inter-particle forces and reduces gas pressure. $\frac{PV}{nRT} < 1$

62 NH_3 shows greater deviation than CH_4 due to stronger intermolecular attractions, especially at low temperature.

63 B

64 2.81 g

65 4.93 g

66 0.0100 mol

67 0.400 mol dm^{-3}

68 3.1 cm^3

69 0.178 mol dm^{-3}

70 0.0220 mol dm^{-3}, 0.0802% HCl

71 0.106 mol dm^{-3} Na_2SO_4 and 0.115 mol dm^{-3} $Pb(NO_3)_2$; assume no side reactions, all $PbSO_4$ precipitates

Challenge problems

72 1217 tonnes

73 52% NH_3 by mass; assuming no side reactions occur and gases behave as ideal gases

74 3.20×10^5 kg

75 0.225 mol dm^{-3} (or round to 0.23 mol dm^{-3})

76 $[Na_2CO_3] = \frac{YP}{X}$ mol dm^{-3}

$[NaHCO_3] = \frac{Y(Q - P)}{X}$ mol dm^{-3}

77 100 mol O_2; 3.2 kg

Practice questions

The answers to the practice questions below are as given to the IB examiners. The following notes may help you to interpret these and make full use of the guidance given.

- There are no half marks awarded. Each mark is shown by the number in square brackets [1].
- Points worth single marks are separated from each other by a semicolon (;).
- Alternative possible answers are separated from each other by a dash (/).
- Any answer given in **bold** or underlined *must* be present to score the mark.
- Information in brackets (   ) is not needed to score the mark.
- Notes given in italics are to guide the examiner on what to accept/reject in their marking.
- OWTTE means 'or words to that effect', so alternative wording that conveys the same meaning can be equally rewarded.
- ECF means 'error carried forward', so examiners must award a mark for an incorrect answer from an earlier part of a question used correctly in a subsequent step.
- M1, M2 etc. represent method marks to be awarded by an examiner for answers showing the appropriate steps of the working (method) necessary for answering the question.

You may notice occasional differences between the calculations or wordings given in the answers and those in the worked solutions. This is because the answers give the final solution with the minimum of working, and the worked solutions provide the extra reasoning and working needed to understand how the answers are attained.

1 D

2 D

3 B

4 C

5 A

6 B

7 D

8 D

9 D **10** D **11** A **12** C

13 D **14** C **15** D **16** A

17 **(a)** temperature: 4

mass: 3

pressure: 3 [1]

(b) 0.0650 kg = 65.0 g

$n = \frac{65.0}{65.02} = 1.00$ (mol) [1]

No penalty for using whole number atomic masses.

(c) $n(N_2) = \frac{3}{2} \times 1.00 = 1.50$ (mol)

$T = 25.00 + 273.15 = 298.15$ K *or* $25.00 + 273 = 298$ K

$P = 1.08 \times 1.01 \times 10^5$ Pa *or* $1.08 \times 1.01 \times 10^2$ kPa *or* 1.09×10^5 Pa *or* 1.09×10^2 kPa

$R = 8.31$ J K^{-1} mol^{-1} (from IB Data booklet)

Use $PV = nRT$ (from IB Data booklet)

$V = \frac{nRT}{P} = \frac{1.50 \times 8.31 \times 298.15}{1.08 \times 1.01 \times 10^5} =$

0.034.1 m^3 = 34.1 dm^3 [4]

Award ***[4]*** *for correct final answer.*

Award ***[3]*** *(max) for 0.0341 dm^3 or 22.7 dm^3.*

Award ***[3]*** *(max) for 34.4 dm^3.*

Award ***[2]*** *(max) for 22.9 dm^3.*

Award ***[2]*** *(max) for 0.0227 dm^3.*

Award ***[2]*** *(max) for 0.034 dm^3.*

18 **(a)** $\left(\left(\frac{2 \times 1.01}{18.02}\right)(0.089) = \right)1.0 \times 10^{-2}$ g H **and**

$\left(\left(\frac{12.01}{44.01}\right)(0.872) = \right)2.38 \times 10^{-1}$ g C

$\left(\left(\frac{0.238}{1.30}\right)(100) = \right)18.3\%$ C

$\left(\frac{1.0 \times 10^{-2}}{1.30}\right)(100) = 0.77\%$ H [3]

Award ***[3]*** *for correct final answer of 18.3% C and 0.77% H without working.*

Allow whole numbers for molar masses.

(b) $\left((1.75)\left(\frac{35.45}{143.32}\right) = \right)0.433$ g (Cl) **and**

$\left(\left(\frac{0.433}{0.535}\right)(100) = \right)80.9\%$ (Cl) [1]

Allow whole numbers for molar masses.

(c) $\left(\frac{18.3}{12.01}\right) = 1.52$ mol C **and**

$\left(\frac{0.77}{1.01}\right) = 0.76$ mol H **and**

$\left(\frac{80.9}{35.45}\right) = 2.28$ mol Cl

Allow whole numbers for atomic masses.

Empirical formula = C_2HCl_3;

Award ***[2]*** *for correct empirical formula without working.*

$M_r = (24.02 + 1.01 + 106.35) = 131.38$

so molecular formula is C_2HCl_3 [3]

Award ***[3]*** *for correct final answer without working.*

Allow whole numbers for atomic masses.

19 NH_3/ammonia in excess, by 10 dm^3 [1]

volume of N_2 produced = 25.0 dm^3 [2]

20 **(a)** $n(HCl) = 0.200$ mol dm^{-3} × 0.02720 dm^3 = 0.00544 *or* 5.44×10^{-3} (mol) [1]

(b) $n(HCl)$ excess is 0.100 mol dm^{-3} × 0.02380 dm^3 = 0.00238 *or* 2.38×10^{-3} mol [1]

Penalize not dividing by 1000 once only in (a) and (b).

(c) $n(HCl)$ reacted = 0.00544 – 0.00238 = 0.00306 *or* 3.06×10^{-3} (mol) [1]

(d) $2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ *or*

$2H^+(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$ [2]

Award ***[1]*** *for correct reactants and products.*

Award ***[1]*** *if the equation is correctly balanced.*

Award ***[1]*** *(max) for the following equations:*

$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$

$2H^+(aq) + CaCO(s) \rightarrow Ca^{2+}(aq) + HCO(aq)$

Ignore state symbols.

(e) $n(CaCO_3) = \frac{1}{2}n(HCl) = \frac{1}{2} \times 0.00306$

$= 0.00153$ *or* 1.53×10^{-3} mol [2]

Award ***[2]*** *for correct final answer.*

(f) $M_r(CaCO_3) = 40.08 + 12.01 + 3 \times 16.00 = 100.09$ *or* 100.1 g mol^{-1}

Accept 100.

$m(CaCO_3) = n \times M = 0.00153$ mol × 100.09 g mol^{-1} = 0.153 g

$\%CaCO_3 = \frac{0.153}{0.188} \times 100 = 81.4\%$ *or* 81.5% [3]

Ignore state symbols.

Accept answers in the range 79.8% to 81.5%.

Award ***[3]*** *for correct final answer.*

(g) only $CaCO_3$ reacts with acid *or* impurities are inert *or* non-basic *or* impurities do not react with the acid *or* nothing else in the eggshell reacts with acid *or* no other carbonates. [1]

Do not accept 'all calcium carbonate reacts with acid'.

21 NaCl 62.9%, $CaCl_2$ 37.1%

22 **(a)** 0.115 mol H_2O

(b) 0.0574 mol K_2CO_3

(c) $K_2CO_3.2H_2O$

(d) Heat to constant mass – when further heating does not lead to further decrease in mass.

23 **(a)** NH_3 is in excess

(b) HCl is limiting

(c) 1.64 g ammonium chloride forms

Challenge yourself

1 In cold climates, temperature may approach or go below the boiling point of butane so the butane stays liquid even when it is released from the pressure it is under when stored in its canister. This makes it ineffective as a fuel.

2 $FeCl_3.6H_2O$, $CuSO_4.5H_2O$, $Co(NO_3)_2.6H_2O$

3 N = 18%, P = 22%, K = 17%

4 Many reactions with 'useless' by-products could have high stoichiometric yield under optimum conditions, but low atom economy, for example methanoic acid production:

$$2NaCOOH + H_2SO_4 \rightarrow 2HCOOH + Na_2SO_4$$

For 100% conversion with stoichiometric reactants, the yield = 100%.

$$\text{atom economy} = \frac{2 \times 46.03}{(2 \times 68.01) + 98.08} \times 100\%$$
$$= 39.33\%$$

5 $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

$10Na(s) + 2KNO_3(s) \rightarrow K_2O(s) + 5Na_2O(s) + N_2(g)$

$K_2O(s) + Na_2O(s) + SiO_2(s) \rightarrow Na_2K_2SiO_4$ (alkaline silicate glass)

6 As NaOH dissolves, the separated Na^+ and OH^- ions become hydrated, i.e. they are surrounded by H_2O molecules. This involves breaking the hydrogen bonds between the H_2O molecules in pure water and allows closer packing, which reduces the volume.

Answers

Chapter 2

Exercises

1 Examples are density (related to mass) or, for gases, rate of diffusion.

2 Tellurium has a greater proportion of heavier isotopes (with more neutrons).

3

	Species	No. of protons	No. of neutrons	No. of electrons
(a)	^{7}Li	3	4	3
(b)	^{1}H	1	0	1
(c)	^{14}C	6	8	6
(d)	$^{19}F^{-}$	9	10	10
(e)	$^{56}Fe^{3+}$	26	30	23

4

	Species	No. of protons	No. of neutrons	No. of electrons
	$^{40}Ca^{2+}$	20	20	18
(a)	$^{40}_{18}Ar$	18	22	18
(b)	$^{39}_{19}K^{+}$	19	20	18
(c)	$^{35}_{17}Cl^{-}$	17	18	18

5 C

	Species	No. of protons	No. of neutrons	No. of electrons
A	$^{2}_{1}H$	1	1	1
B	$^{11}_{5}B$	5	6	5
C	$^{16}_{8}O^{2-}$	8	8	10
D	$^{19}_{9}F^{-}$	9	10	10

6 B 7 B

8 Let x atoms be ^{20}Ne atoms. The remaining atoms are ^{22}Ne.

number of ^{22}Ne atoms $= 100 - x$

total mass $= 20 \times x + (100 - x) \times 22 = 2200 - 2x$

average mass $= \dfrac{2200 - 2x}{100}$

From the Periodic Table we see that the relative atomic mass of neon = 20.18

$$20.18 = \frac{2200 - 2x}{100}$$

$$2018 = 2200 - 2x$$

$$2x = 2200 - 2018 = 182$$

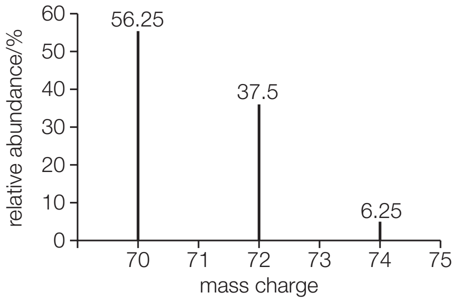
$x = 91$; abundance $^{20}Ne = 91\%$

9 probability of $^{35}Cl = \frac{3}{4}$ probability of $^{37}Cl = \frac{1}{4}$

probability of $^{35}Cl–^{35}Cl$ $(M = 70) = \frac{3}{4} \times \frac{3}{4} = \frac{9}{16} =$ 56.25%

probability of $^{35}Cl–^{37}Cl/^{37}Cl–^{35}Cl$ $(M = 72) = 2 \times \frac{3}{4} \times \frac{1}{4} = \frac{6}{16} =$ 37.5%

probability of $^{37}Cl–^{37}Cl$ $(M = 74) = \frac{1}{4} \times \frac{1}{4} = \frac{1}{16} =$ 6.25%



10 Let the abundance of ^{25}Mg be x. Consider 100 atoms.

$$24.31 = \frac{(78.90 \times 24) + (x \times 25) + (100 - 78.90 - x) \times 26}{100}$$

$$= 1893.6 + 25x + 2600 - 2051.4 - 26x$$

$$= 2442.2 - x$$

$x = 11.20$

^{25}Mg 11.20% and ^{26}Mg 9.90%

11 B 12 C 13 A 14 A

15 4s < 4p < 4d < 4f

16

Sub-level	4s	4p	4d	4f
No. of orbitals	1	3	5	7

17 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

18 $1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^13p_z^1$, so three unpaired electrons

19 C **20** C

21 **(a)** V is $1s^22s^22p^63s^23p^63d^34s^2$

(b) K is $1s^22s^22p^63s^23p^64s^1$

(c) Se is $1s^22s^22p^63s^23p^63d^{10}4s^24p^4$

(d) Sr is $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^2$

22 D **23** B **24** B

25 **(a)** O^{2-} is $1s^22s^22p^6$

(b) Cl^- is $1s^22s^22p^63s^23p^6$

(c) Ti^{3+} $1s^22s^22p^63s^23p^63d^1$

(d) Cu^{2+} is $1s^22s^22p^63s^23p^63d^9$

26

	Ion	3d					4s
(a)	Ti^{2+}	↑	↑				
(b)	Fe^{2+}	↑↓	↑	↑	↑	↑	
(c)	Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	
(d)	Zn^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	

27 **(a)** Ne is $1s^22s^22p^6$

(b) Negatively charged ions would be F^-, O^{2-} or N^{3-}; positively charged ions would be Na^+, Mg^{2+} or Al^{3+}.

28 **(a)** Cl is $1s^22s^22p^63s^23p^5$

(b) Nb is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^35s^2$

(c) Ge is $1s^22s^22p^63s^23p^63d^{10}4s^24p^2$

(d) Sb is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^3$

29 **(a)** Si **(b)** Mn **(c)** Sr **(d)** Sc

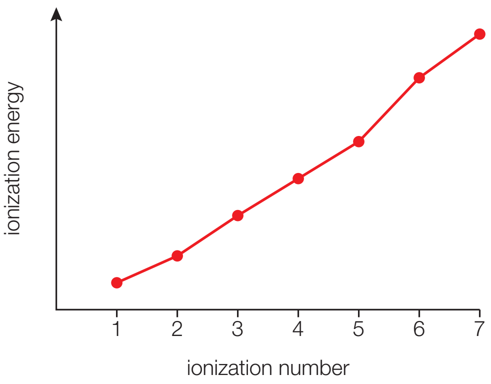
30 11 **31** 20 **32** [Kr]$4d^{10}$

33 B **34** B

35 **(a)** C has the electronic configuration $1s^22s^22p^2$. The 4th electron is removed from a 2s orbital, the 5th electron from the 1s orbital. Electrons in 1s orbitals are closer to the nucleus and experience a stronger electrostatic force of attraction.

(b) The 2nd electron is removed from a 2p orbital, the 3rd electron from the 2s orbital. Electrons in 2s orbitals are closer to the nucleus and so experience a stronger electrostatic force of attraction.

36



37 **(a)** The ionization energy rises from Na to Ar because the charge of the nucleus increases but the number of inner 'shielding' electrons remains the same. The increase in effective nuclear charge makes it progressively more difficult to remove an outer shell electron.

(b) Mg has the electron configuration [Ne]$3s^2$, Al has the electron configuration [Ne]$3s^23p^1$. The 3p electron, removed from Al, has more energy and is further away from the nucleus than the 3s electron removed from Mg.

(c) P has the configuration [Ne]$3s^23p_x^13p_y^13p_z^1$, S has the configuration [Ne]$3s^23p_x^23p_y^13p_z^1$. The electron removed from S comes from a doubly occupied 3p orbital, which is repelled by its partner and is easier to remove than the electron removed from P which comes from a half-filled orbital.

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 D **2** A **3** A **4** B

5 D **6** A **7** C **8** B

9 B **10** D

11 $\frac{(54 \times 5.95) + (56 \times 91.88) + (57 \times 2.17)}{100} = 55.90$ [2]

*Award **[2]** for correct final answer.*

Answer must be to 2 d.p.

12 **(a)** the electron configuration (of argon) *or* $1s^22s^22p^63s^23p^6$ [1]

(b) $x = 1$ and $y = 5$ [1]

(c) [1]

Accept all six arrows pointing down rather than up.

13 **(a)** Cobalt has a greater proportion of heavier isotopes (*OWTTE*) *or* cobalt has a larger number of neutrons. [1]

(b) 27 protons and 25 electrons [1]

(c) $1s^22s^22p^63s^23p^63d^7$ *or* $[Ar]\ 3d^7$ [1]

14 B

15 $1s^22s^22p^63s^1$ [1]

Do not accept $[Ne]3s^1$

First electron easy/easiest to remove *or* 1 electron in outermost/$n = 3$ energy level/furthest from nucleus [1]

large increase between 1st and 2nd I.E. as electron now removed from $n = 2$ [1]

next 8 electrons slightly more difficult to remove *or* show (relatively) small increase as these electrons are in the same energy level/second energy level/$n = 2$ [1]

large increase between 9th and 10th I.E. as electron now removed from $n = 1$ *or* last two electrons very hard/most difficult to remove *or* innermost/lowest/closest to the nucleus/energy level (*OWTTE*) [1]

electron 11 also comes from 1s, so shows a small increase [1]

max [4]

Challenge yourself

1 In 1827 Robert Brown dropped grains of pollen into water and examined them under a microscope. The pollen moved around erratically in the water. This so-called 'Brownian motion' was explained in 1905 by Albert Einstein. He realized that the pollen was being jostled by something even smaller: water molecules. Einstein didn't just base this theory on his observations – he used complex mathematics to show that an atomic model could explain Brownian motion.

2 Potash, soda, magnesia and barytes are compounds of Group 1 and 2 elements. In order to obtain the Group 1 and 2 elements (which are metals) from these compounds (which are ionic compounds) it is necessary to reduce them from their ions. This was not possible using the chemical methods available at the time and these compounds were later broken down into their component elements by electrolysis.

3 The Schrödinger model:

- does not have well-defined orbits for the electrons
- does not treat the electron as a localized particle but gives a probability wave description
- predicts the relative intensities of various spectral lines.

4 **(a)** $[Rn]7s^25f^{14}6d^7$

(b) The first g block element would be $[Rn]7s^25f^{14}6d^{10}7p^68s^28g^1$

$Z = 86 + 2 + 14 + 10 + 6 + 2 + 1 = 121$

5 $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^65f^4$

6 **(a)** There would be two types of p orbital and two types of d orbitals.

(b) Four groups in the p and d blocks.

7 1290 kJ mol^{-1}

8 The convergence limit corresponds to the transition $n = 2$ to $n = \infty$. To obtain the ionization energy, we have to add the energy which corresponds to the $n = 2$ to $n = 1$ transition. This is the first line in the Lyman series.

I.E. = 1310 kJ mol^{-1}

Answers

Chapter 3

Exercises

1

	Element	Period	Group
(a)	helium	1	18
(b)	chlorine	3	17
(c)	barium	6	2
(d)	francium	7	1

2 **(a)** Periods are rows and groups are columns.

(b) $1s^22s^22p^63s^23p^3$

The valence energy level is the third principal energy level, so the element is in period 3. It has the $3p^3$ configuration, so it is in the third group of the p block, which is Group 15.

3 Element 51 is antimony (Sb), which is in Group 15. Its valence electrons are $5s^25p^3$, and so it has five valence electrons.

4 C **5** B **6** C

7 **(a)** Half the distance between the nuclei of neighbouring atoms of the same element.

(b) **(i)** The noble gases do not form stable ions and engage in ionic bonding so the distance between neighbouring ions cannot be defined.

(ii) The atomic radii decrease from Na to Cl. This is because the number of inner, shielding, electrons is constant (10) but the nuclear charge increases from +11 to +17. As we go from Na to Cl, the increasing effective nuclear charge pulls the outer electrons closer.

8 Si^{4+} has an electronic configuration of $1s^22s^22p^6$ whereas Si^{4-} has an electronic configuration of $1s^22s^22p^63s^23p^6$. Si^{4+} has two occupied energy levels and Si^{4-} has three and so Si^{4-} is larger.

9 A **10** B **11** C **12** D

13 **(a)** The electron in the outer electron energy level (level 4) is removed to form K^+. The net attractive force increases as the electrons in the third energy level experience a greater effective nuclear charge.

(b) P^{3-} has an electronic configuration of $1s^22s^22p^63s^23p^6$ whereas Si^{4+} has an electronic configuration of $1s^22s^22p^6$. P^{3-} has one more principal energy level than Si^{4+} so its valence electrons will be further from the nucleus and it will have a larger ionic radius.

(c) The ions have the same electron configuration, $1s^22s^22p^63s^23p^6$: both have two complete shells; the extra protons in Na^+ attract the electrons more strongly.

14 Phosphorus exists as molecules with four atoms: P_4. Sulfur exists as molecules with eight atoms: S_8. There are stronger London dispersion forces between the larger S_8 molecules as there are more electrons.

15 D **16** C **17** $Cl^- > Cl > Cl^+$

18 B **19** C **20** D **21** B

22 Sodium floats on the surface; it melts into a sphere; there is fizzing/effervescence/bubbles; sound is produced; solution gets hot; white smoke is produced.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

23 D

24 The reactivities of the alkali metals increase but those of the halogens decrease.

25 C **26** D **27** D **28** A

29 A **30** B **31** D

32

	(a) State under standard conditions	(b) Structure and bonding
MgO	(s)	giant structure ionic bonding; strong attraction between oppositely charged ions
SiO_2 (quartz)	(s)	giant structure covalent bonding; strong covalent bonds throughout structure
P_4O_{10}	(s)	molecular, covalent bonding; weak intermolecular forces between molecules; P_4O_{10} is larger molecule and so has stronger London dispersion forces and a higher melting point than SO_2
SO_2	(g)	molecular, covalent bonding; weak intermolecular forces between molecules; SO_2 is smaller molecule and so has weaker London dispersion forces and a higher melting point than P_4O_{10}

(c)

Oxide	pH of solution	Equations
MgO	alkaline	$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$
SiO_2 (quartz)	neutral – oxide is insoluble	
P_4O_{10}	acidic	$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
SO_2	acidic	$SO_2(l) + H_2O(l) \rightarrow H_2SO_3(aq)$

(d) **(i)** $Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

(ii) $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$

33 The oxides of Na and Mg are basic; the oxide of Al is amphoteric; the oxides of Si to Cl are acidic. Ar forms no oxide.

$Na_2O + H_2O \rightarrow 2NaOH$

$SO_3 + H_2O \rightarrow H_2SO_4$

34

	3d					4s
Sc^{3+}						
Ti^{3+}	↑					
Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	
Zn^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	

35 D **36** B **37** D

38 **(a)** $1s^22s^22p^63s^23p^63d^{10}4s^2$

(b) $1s^22s^22p^63s^23p^63d^{10}$

(c) The element does not form ions with partially filled d orbitals.

39 Calcium has one oxidation state: +2 (typical of Group 2). Chromium has common oxidation states of +2, +3 and +6. Calcium(II) and chromium(VI) have noble gas electron configurations, which are typically stable. However, the extremely high charge density of chromium(VI) makes it unstable and other oxidation states are more common. The chromium(II) oxidation state has lost its outer 4s electron and one 3d electron. Chromium(III) forms when the atom loses its 4s electron and two 3d electrons.

40 C **41** C **42** D **43** C

44 **(a)** Zn

(b) **(i)** Fe_3O_4: +2.67

(ii) MnO_4^-: +7

(iii) CrO_4^{2-}: +6

(iv) $[FeCN_6]^{4-}$: +2

45 **(a)** +2

(b) The N atoms adopt a square planar arrangement.

(c) The planar structure allows oxygen molecules easy access to the iron ion, which can accept a lone pair of electrons from an oxygen molecule and form a coordinate bond. This bond is not strong, so the process is easily reversible. This allows the complex to absorb oxygen where oxygen is in high concentrations (i.e. in the lungs) but release oxygen in tissues with low oxygen concentrations.

46 **(a)** Ni **(b)** V_2O_5

(c) Pt or Pd

47 **(a)** Homogeneous catalysts are in the same state of matter as the reactants; heterogeneous catalysts are in a different state from the reactants.

(b) They provide a surface for the reactant molecules to come together with the correct orientation.

(c) They can be easily removed by filtration from the reaction mixture and re-used.

48 D **49** D

50 Chromium has the electron configuration $[Ar]3d^5 4s^1$; it has six unpaired electrons, which is the maximum number for the series. Zn has the $[Ar]3d^{10}$ configuration with no unpaired electrons.

51 In a complex the d sub-level splits into two energy levels due to the presence of the ligand's lone pair of electrons. The energy difference between the two sets of d orbitals depends on the oxidation state of the central metal, the number of ligands and the identity of the ligand. Electron transitions between d orbitals result from the absorption of energy from the visible region of the electromagnetic spectrum. The wavelength (colour) of light absorbed depends on the size of the splitting between the two sets of d orbitals.

As the two complexes both contain a cobalt ion in the +2 oxidation state the difference in colour is due to the identity of the ligands (H_2O vs Cl^-) and the coordination number (6 in $[Co(H_2O)_6]^{2+}$ and 4 in $[CoCl_4]^{2-}$), which changes from H_2O to Cl^-.

52 **(a)** difference in nuclear charge of metal (ion)

(b) difference in oxidation number

(c) difference in ligand

53 Fe^{2+} has configuration $[Ar]3d^6$ and Zn^{2+} is $[Ar]3d^{10}$. Colour in transition metal complexes is due to the splitting of the d subshell into two sets of d orbitals with different energy levels; the absorption of visible light results in electrons being excited from the lower energy set to the higher energy set and the colour observed is complementary to the colour (wavelength) of light absorbed. Light can only be absorbed if the d orbitals are partially filled and the higher energy set has an empty or partially filled orbital that can accept an electron from the lower energy set. Fe^{2+} has partially filled d orbitals and so electronic transitions can occur from the lower energy set to the higher energy set with the absorption of visible light and it appears coloured in solution. In Zn^{2+} all of the d orbitals are fully occupied so an electronic transition cannot occur from the lower energy set to the higher energy set so it is unable to absorb visible light and Zn^{2+} is not coloured in solution.

Fe^{2+} not in its highest oxidation state and so can be oxidized by removal of d electron; Zn^{2+} in its highest oxidation state and so can't be oxidized (and so can't act as reducing agent).

54 λ_{max}= 525 nm. The colour absorbed is green; the colour transmitted is red.

55 **(a)** $[Ar]3d^6$

↑↓	↑	↑	↑	↑

(b) The splitting would be greater for $[Fe(CN)_6]^{4-}$.

56 **(a)** $[Fe(H_2O)_6]^{3+}$ is yellow and $[Cr(H_2O)_6]^{3+}$ is green; the colours they show are complementary to the colours of light they absorb; colour is caused by transitions between the two sets of d orbitals in the complex; the different metals in the two complexes cause the d orbitals to split differently as they have different nuclear charges and this results in different wavelengths (colours) of light being absorbed.

(b) The oxidation state of the central ion is different in the two complexes and this affects the size of the d orbital splitting due to the different number of electrons present in d orbitals. Fe^{2+} has the electron configuration $[Ar]3d^6$ and Fe^{3+} has the electron configuration $[Ar]3d^5$.

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1	C	**2**	A	**3**	B	**4**	B
5	A	**6**	B	**7**	D	**8**	C
9	D	**10**	D	**11**	C	**12**	C

13 **(a)** the amount of energy required to remove one (mole of) electron(s) [1]

from (one mole of) an atom(s) in the gaseous state [1]

(b) greater positive charge on nucleus / greater number of protons / greater core charge [1]

greater attraction by Mg nucleus for electrons (in the same shell) / smaller atomic radius [1]

14 $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ [1]

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ [1]

State symbols are not needed.

Na_2O is basic and SO_3 is acidic [1]

15 **(a)** solution becomes yellow/orange/brown/darker [1]

chlorine is more reactive than iodine (and displaces it from solution) / *OWTTE* [1]

Allow correct equation $Cl_2(g) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(s)$ *for second mark or stating that iodine/*I_2 *is formed.*

(b) no colour change / nothing happens as fluorine is more reactive than chlorine / *OWTTE* [1]

16 **(a)** atomic number / Z [1]

Accept nuclear charge / number of protons.

(b) Across period 3: increasing number of protons / atomic number / Z / nuclear charge [1]

(atomic) radius/size decreases / same shell/energy level / similar shielding/screening (from inner electrons) [1]

No mark for shielding/screening or shielding/screening increases.

Noble gases: do not form bonds (easily) / have a full/stable octet/shell/energy level / cannot attract more electrons [1]

Do not accept 'inert' or 'unreactive' without reference to limited ability/inability to form bonds or attract electrons.

17 **(a)** Na: 11 p, 11/2.8.1 e^- and Na^+: 11 p, 10/2.8 e^- *OR* Na^+ has 2 shells/energy levels, Na has 3 / *OWTTE* [1]

Na^+ has greater net positive charge/same number of protons pulling smaller number of electrons [1]

(b) Si^{4+}: 10 e^- in 2 (filled) energy levels / electron arrangement 2.8 / *OWTTE* [1]

P^{3-}: 18 e^- in 3 (filled) energy levels / electron arrangement 2.8.8, thus larger / *OWTTE* [1]

OR Si^{4+} has 2 energy levels whereas P^{3-} has 3 / P^{3-} has one more (filled) energy level [1]

Si^{4+} has 10 e^- whereas P^{3-} has 18 e^- / Si^{4+} has fewer electrons / P^{3+} has more electrons [1]

18 **(a)** in the solid state ions are in fixed positions / there are no moveable ions / *OWTTE* [1]

Do not accept answer that refers to atoms or molecules.

(b) $2O^{2-} \rightarrow O_2 + 4e^- / O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$ [1]

Accept e instead of e^-*.*

(c) **(i)** basic [1]

Allow alkaline.

(ii) $Na_2O + H_2O \rightarrow 2NaOH / Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$ [1]

Do not accept $\rightleftharpoons$

19 **(a)** first ionization energy: $M(g) \rightarrow M^+(g) + e^-/e$ *OR* the (minimum) energy (in kJ mol^{-1}) to remove one electron from a gaseous atom *OR* the energy required to remove one mole of electrons from one mole of gaseous atoms [1]

periodicity: repeating pattern of (physical and chemical) properties [1]

(b) 2.8.8 [1]

Two of: the outer energy level/shell is full; the increased charge on the nucleus; great(est) attraction for electrons [2]

(c) 17 p in Cl nucleus attract the outer level more than 11 p in Na nucleus / greater nuclear charge attracts outer level more [1]

Allow converse for Na. Do not accept 'has larger nucleus'.

(d) S^{2-} has one proton less/smaller nuclear charge so outer level held less strongly / *OWTTE* [1]

Allow converse for chloride. Do not accept 'has larger nucleus'.

(e) the radii of the metal atoms increase (from Li → Cs) (so the forces of attraction are less between them) / *OWTTE* [1]

the forces of attraction between halogen molecules are van der Waals forces [1]

these forces increase with increasing mass/ number of electrons [1]

20 **(a)** complex (ion) / the charge is delocalized over all that is contained in the brackets [1]

(b) colour is due to energy being absorbed when electrons are promoted within the split d orbitals *OR* the colour observed is the complementary colour to the energy absorbed / *OWTTE* [1]

Accept either answer for the first mark.

changing the ligand / coordination number / geometry [1]

changes the amount the d orbitals are split/ energy difference between the d orbitals / *OWTTE* [1]

Challenge yourself

1 Ytterbium, yttrium, terbium, erbium

2 Two liquids, 11 gases

3 Metalloids are elements that have chemical and physical properties intermediate to those of metals and non-metals, and include the elements boron, silicon, germanium, arsenic, antimony and tellurium.

Semi-conductors are materials (elements or compounds) that have electrical conductivity between those of conductors and insulators.

Some metalloids are also semi-conductors. Silicon and germanium are two examples.

4 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^7 6s^2$ or $[Xe]4f^7 6s^2$

5 EDTA acts as a hexadentate ligand and is attached to the central metal ion by six coordination bonds, therefore the complex formed (the chelate) is very stable as to break it apart involves breaking all six of these coordination bonds. The entropy change is positive as there are more particles on the right-hand side. See Chapter 6 for more details regarding energy and entropy.

6 The broad absorption spectrum of the complex ions should be contrasted with the sharp lines of atomic spectra (discussed in Chapter 2). Both phenomena are due to electronic transitions, but the spectrum of a complex ion is affected by the surrounding ligands as the complex ion also has vibrational and rotational energy levels. This allows the complex ion to absorb a wider range of frequencies due to the large number of vibrational and rotational excited states also available. Because the absorption of complex ions is measured in solution, interactions with the solvent further increase the number of energy levels present in the complex ion and the number of associated frequencies it can absorb, resulting in the broad absorption bands observed.

The isolated gaseous ions do not have vibrational or rotational energy levels available to them and will only absorb energy of the exact wavelength required to move an electron from a lower energy to a higher energy atomic orbital, generating discrete line spectra.

Answers

Chapter 4

Exercises

1 lead nitrate, $Pb(NO_3)_2$
barium hydroxide, $Ba(OH)_2$
potassium hydrogencarbonate, $KHCO_3$
magnesium carbonate, $MgCO_3$
copper sulfate, $CuSO_4$
calcium phosphate, $Ca_3(PO_4)_2$
ammonium chloride, NH_4Cl

2 **(a)** KBr **(b)** ZnO
(c) Na_2SO_4 **(d)** $CuBr_2$
(e) $Cr_2(SO_4)_3$ **(f)** AlH_3

3 **(a)** tin(II) phosphate
(b) titanium(IV) sulfate
(c) manganese(II) hydrogencarbonate
(d) barium sulfate
(e) mercury sulfide

4 **(a)** Sn^{2+} **(b)** Ti^{4+}
(c) Mn^{2+} **(d)** Ba^{2+}
(e) Hg^{+}

5 A_3B_2

6 Mg 12: electron configuration $[Ne]3s^2$

Br 35: electron configuration $[Ar]3d^{10}4s^24p^5$

The magnesium atom loses its two electrons from the 3s orbital to form Mg^{2+}. Two bromine atoms each gain one electron into their 4p sub-shell to form Br^-. The ions attract each other by electrostatic forces and form a lattice with the empirical formula $MgBr_2$.

7 B **8** D

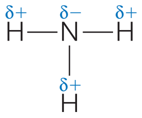
9 Test the melting point: ionic solids have high melting points.

Test the solubility: ionic compounds usually dissolve in water but not in hexane.

Test the conductivity: ionic compounds in aqueous solution are good conductors.

10 D **11** C

12 **(a)** $\overset{\delta+}{H}—\overset{\delta-}{Br}$ **(b)** $\overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$
(c) $\overset{\delta+}{Cl}—\overset{\delta-}{F}$ **(d)** $O=O$
(e)

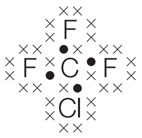


13

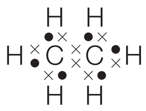
(a)	C 2.6	H 2.2	difference = 0.4
	C 2.6	Cl 3.2	difference = 0.6, more polar
(b)	Si 1.9	Li 1.0	difference = 0.9
	Si 1.9	Cl 3.2	difference = 1.3, more polar
(c)	N 3.0	Cl 3.2	difference = 0.2
	N 3.0	Mg 1.3	difference = 1.7, more polar

14 **(a)**

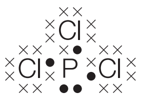
(b)



(c)



(d)

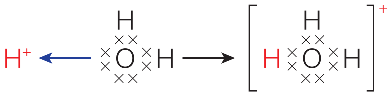


(e)

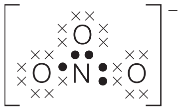
(f)

15 **(a)** 16 **(b)** 24
(c) 32 **(d)** 8
(e) 20 **(f)** 26

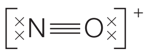
16



17 **(a)**



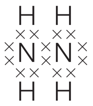
(b)



(c)

(d)

(e)



18 **(a)** 105° bond angle, shape is bent

(b) 109.5° bond angle, shape is tetrahedral

(c) 180° bond angle, shape is linear

(d) 107° bond angle, shape is trigonal pyramidal

(e) 120° bond angle, triangular planar

(f) 107° bond angle, trigonal pyramidal

(g) 105° bond angle, shape is bent

19 **(a)** 120° bond angle, shape is trigonal planar

(b) 120° bond angle, shape is trigonal planar

(c) 180° bond angle, shape is linear

(d) 120° bond angle, shape is bent

(e) 105° bond angle, shape is bent

(f) 107° bond angle, shape is trigonal pyramidal

20 **(a)** 4 **(b)** 3 or 4

(c) 2 **(d)** 4

(e) 3

21 **(a)** polar **(b)** non-polar

(c) polar **(d)** non-polar

(e) non-polar **(f)** polar

(g) non-polar **(h)** non-polar

22 *cis* isomer has a net dipole moment

23 $CO < CO_2 < CO_3^{2-} < CH_3OH$

24 The N–O bonds in the nitrate(V) ion all have a bond order of 1.33 and will be longer than two bonds in nitric(V) acid, which have a bond order of 1.5 and are shorter than the N–OH bond with a bond order of 1.

25 Similarities: strong, high melting points, insoluble in water, non-conductors of electricity, good thermal conductors.

Differences: diamond is stronger and more lustrous; silicon can be doped to be an electrical conductor.

26 Graphite and graphene have delocalized electrons that are mobile and so conduct electrical charge. In diamond all electrons are held in covalent bonds and are not mobile.

27 A metal B giant molecular

C polar molecular D non-polar molecular

E ionic compound

28 A

29 **(a)** London dispersion forces

(b) H bonds, dipole—dipole, London dispersion forces

(c) London dispersion forces

(d) dipole—dipole, London dispersion forces

30 **(a)** C_2H_6 **(b)** H_2S

(c) Cl_2 **(d)** HCl

31 B

32 **(a)** malleability, thermal conductivity, thermal stability

(b) light, strong, forms alloys

(c) thermal conductivity, thermal stability, non-corrosive

(d) light, strong, non-corrosive

33 **(i)** anodizing: increasing the thickness of the surface oxide layer helps resist corrosion

(ii) alloying: mixing Al with other metals such as Mg and Cu increases hardness and strength

34 **(a)** linear, 180°

(b) triangular pyramidal, 107°

(c) bent, 105°

(d) tetrahedral, 109.5°

(e) octahedral, 90°

(f) seesaw, 117°

35 **(a)** 6 **(b)** 6

(c) 6 **(d)** 5

(e) 2 or 5

36 **(a)** 90° **(b)** 107°

(c) 90°

37 **(a)** polar **(b)** polar

(c) non-polar **(d)** polar

(e) non-polar **(f)** non-polar

38 **(a)** polar

(b) polar or non-polar does not apply to molecular ions

(c) non-polar

(d) polar or non-polar does not apply to molecular ions

(e) polar or non-polar does not apply to molecular ions

(f) polar or non-polar does not apply to molecular ions

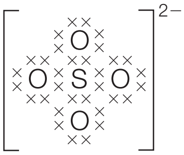
39 In BF_3 all the atoms have formal charge of 0.

B: FC = 3 – 3 = 0

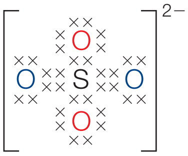
each F: FC = 7 – (1 + 6) = 0

Zero formal charge represents the most stable, preferred structure, so this is favoured despite violating the octet rule by having fewer than 8 electrons around Be.

40 **(i)** S: FC = 6 – 4 = +2 each O: FC = 6 – (1 + 6) = –1



(ii) S: FC = 6 – 6 = 0 each O: FC = 6 – (1 + 6) = –1 each O: FC = 6 – (2 + 4) = 0



The structure with 12 electrons round the S atom has FC = 0 and so is the preferred structure.

41 O—O bonds in O_3 are weaker than in O_2, due to lower bond order, therefore dissociation occurs with lower energy light (longer wavelength).

42 O_3 breakdown is catalysed by NO_x and CFCs in the atmosphere, e.g.

$CCl_2F_2(g) \rightarrow CClF_2{\bullet}(g) + Cl{\bullet}(g)$

CFCs break down in upper atmosphere.

$Cl{\bullet}(g) + O_3(g) \rightarrow O_2(g) + ClO{\bullet}(g)$

Chlorine radical reacts with ozone and another radical is produced.

$ClO{\bullet}(g) + O{\bullet}(g) \rightarrow O_2(g) + Cl{\bullet}(g)$

Chlorine radical is regenerated and so acts as a catalyst for ozone destruction.

43 Electrons in a sigma bond are most concentrated in the bond axis, the region between the nuclei. Electrons in a pi bond are concentrated in two regions, above and below the plane of the bond axis.

44 **(b)** H—F in HF **(c)** Cl—Cl in Cl_2
(d) C—H in CH_4 **(e)** C—H in C_2H_4
(f) C—H in C_2H_2 **(g)** C—Cl in C_2H_3Cl

45 **(a)** sp^2 **(b)** sp^3
(c) sp^2 **(d)** sp
(e) sp^2

46 In C_6H_{12} (cyclohexane) the carbon atoms are sp^3 hybridized, each forming a tetrahedral arrangement with two neighbouring carbon atoms and two hydrogen atoms. The bond angles of 109.5° give the puckered shape. In C_6H_6 (benzene) the carbon atoms are all sp^2 hybridized, forming a planar triangular arrangement with bond angles of 120°.

Practice questions

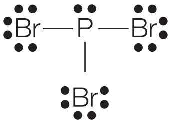
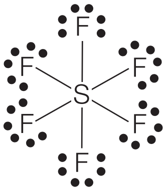
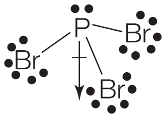
For advice on how to interpret the marking below please see Chapter 1.

1	C	**2**	A	**3**	A	**4**	A
5	B	**6**	A	**7**	B	**8**	D
9	C	**10**	A	**11**	B	**12**	C
13	D	**14**	B	**15**	A		

16 Hydrogen bonding in butan-1-ol; stronger than dipole—dipole attractions in butanal. [2]

Accept converse argument. Do not penalize ‘dipole—dipole bonding’ instead of ‘dipole—dipole attractions’.

17 **(a)**

PBr$_3$	SF$_6$
(i) *Lewis structure:*  *Allow x's, dots or lines to represent electrons.* *Penalize missing lone pairs on terminal atoms once only for the two Lewis structures.*	**(i)** *Lewis structure:*  *Allow x's, dots or lines to represent electrons.* *Penalize missing lone pairs on terminal atoms once only for the two Lewis structures.*
(ii) *Shape:* trigonal/triangular pyramidal *Bond angle:* less than 109.5° *Allow any angle less than 109.5° but greater than or equal to 100° (experimental value is 101°).*	**(ii)** *Shape:* octahedral *Bond angle:* 90° *Ignore extra correct bond angles (e.g. 90° and 180° scores but not 90° and 120°).*
(iii) *Polarity:* polar **and** *Explanation:* net dipole (moment) / polar PBr bonds **and** molecule not symmetrical/ bond dipoles do not cancel / asymmetric distribution of electron cloud /  / *OWTTE*	**(iii)** *Polarity:* non-polar **and** *Explanation:* no net dipole (moment) / polar SF bonds but molecule symmetrical/ bond dipoles cancel / symmetric distribution of electron cloud / *OWTTE*

[8]

Do not allow ECF in this question from incorrect Lewis structure.

Allow ***[1]*** *max for stating that PBr is polar and SF is non-polar without giving a reason or if explanations are incorrect.*

Allow polar bonds do not cancel for PBr$_3$ and polar bonds cancel for SF$_6$.

Do not allow asymmetric molecule as reason for PBr$_3$ or symmetric molecule for SF$_6$ as reason alone.

(b) **(i)** *σ bond:*

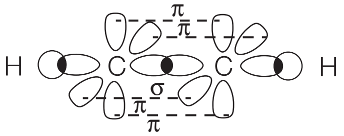
end-on/axial overlap with electron density between the two carbon atoms/nuclei / end-on/axial overlap of orbitals so shared electrons are between atoms / *OWTTE*

π bond:

sideways/parallel overlap of p orbitals with electron density above **and** below internuclear axis/σ bond / sideways/ parallel overlap of p orbitals so shared electrons are above **and** below internuclear axis/σ bond / *OWTTE* [2]

Marks can be scored from a suitable diagram.

*Award **[1 max]** for stating end-on/axial overlap for σ and sideways/parallel overlap for π only i.e. without mentioning electron density **OR** stating electron density between the two atoms/nuclei for σ and above and below internuclear axis for π.*



(ii) 11 σ **and** 3 π [1]

(iii) (strong) intermolecular hydrogen bonding in *trans* but (strong) intramolecular hydrogen bonding in *cis* so attraction between different molecules is less (hence lower melting point) [1]

Allow between molecules for intermolecular and within molecules for intramolecular.

(iv) in *cis* two carboxylic acid groups close together so on heating cyclic anhydride forms (with elimination of water) / *OWTTE* [1]

Allow converse argument for trans.

(c) O of OH *sp*^{3} **and** O of C=O *sp*^{2} [1]

Oxygens must be identified.

18 **(a)** *Award **[2 max]** for three of the following features:*

Bonding
*Graphite **and** C$_{60}$ fullerene*: covalent bonds **and** van der Waals'/London/dispersion forces
Diamond: covalent bonds (and van der Waals'/London/dispersion forces)

Delocalized electrons
*Graphite **and** C$_{60}$ fullerene*: delocalized electrons
Diamond: no delocalized electrons

Structure
Diamond: network/giant structure / macromolecular / three-dimensional structure **and** *Graphite*: layered structure / two-dimensional structure / planar
C$_{60}$ fullerene: consists of molecules / spheres made of atoms arranged in hexagons/pentagons

Bond angles
Graphite: 120° **and** *Diamond*: 109°
C$_{60}$ fullerene: bond angles between 109–120°

*Allow Graphite: sp^2 **and** Diamond: sp^3.*
*Allow C$_{60}$ fullerene: sp^2 **and** sp^3.*

Number of atoms each carbon is bonded to
*Graphite **and** C$_{60}$ fullerene*: each C atom attached to 3 others
Diamond: each C atom attached to 4 atoms / tetrahedral arrangement of C (atoms) [6 max]

(b) **(i)** network/giant structure / macromolecular

each Si bonded covalently to 4 oxygen atoms **and** each O atom bonded covalently to 2 Si atoms / single covalent bonds [2]

*Award **[1 max]** for answers such as network-covalent, giant-covalent or macromolecular-covalent.*

Both M1 and M2 can be scored by a suitable diagram.

(ii) *Silicon dioxide*: strong/covalent bonds in network/giant structure/macromolecule

Carbon dioxide: weak/van der Waals'/dispersion/London forces between molecules [2]

(c) triple (covalent) bond

one electron pair donated by oxygen to carbon atom / dative (covalent)/coordinate (covalent) bond [2]

*Award **[1 max]** for representation of* C≡O.

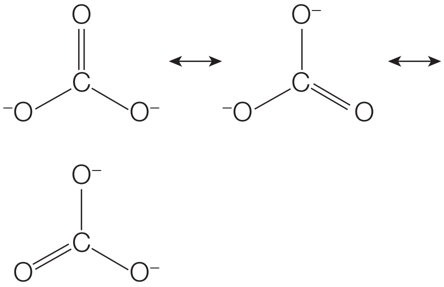
*Award **[2]** if CO shown with dative covalent bond.*

(d) delocalization/spread of pi/π electrons over more than two nuclei

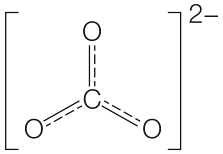
equal bond order/strength/length / spreading charge (equally) over all three oxygens gives carbonate ion a greater stability/lower potential energy [3]

M3 can be scored independently.

Accept suitable labelled diagrams for M1 and M2 e.g.



OR



Do not penalize missing brackets on resonance structure but 2– charge must be shown.

Allow –2 for charge on resonance structure.

(e) mixing/combining/merging of (atomic) orbitals to form new orbitals (for bonding)

Allow molecular or hybrid instead of new.

Do not allow answers such as changing shape/symmetries of atomic orbitals.

Carbon dioxide: sp

Diamond: sp^3

Graphite: sp^2

Carbonate ion: sp^2 [5]

19 Methoxymethane is very weakly polar/weak van der Waals'/dipole–dipole forces exist between methoxymethane molecules.

Accept alternatives to van der Waals' such as London and dispersion forces

Ethanol contains a hydrogen atom bonded directly to an electronegative oxygen atom / hydrogen bonding can occur between two ethanol molecules / intermolecular hydrogen bonding in ethanol; the forces of attraction between molecules are stronger in ethanol than in methoxymethane / hydrogen bonding stronger than van der Waals'/dipole-dipole attractions. max [3]

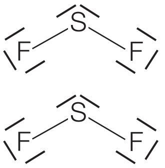
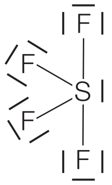
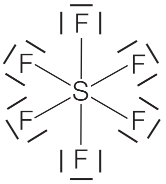
Award **[2]** *max if covalent bonds breaking during boiling is mentioned in the answer.*

Penalize only once if no reference given to intermolecular nature of hydrogen bonding or van der Waals'.

20 **(a)** (bond formed by) sideways overlap of p orbitals. [2]

(b) C1 is sp^3 and C2 is sp^2. [1]

21

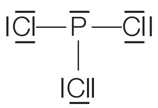
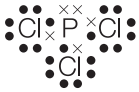
	Lewis structure	Name of shape
SF_2	 *2 lone pairs on S required for the mark*	bent/angular/V shaped
SF_4	 *1 lone pair on S required for the mark*	Seesaw/ distorted tetrahedral
SF_6		octahedral *Accept square bipyrimidal*

[6]

Penalise missing lone pairs on fluorine atoms once in correct structures only.

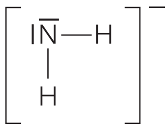
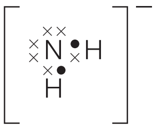
For Lewis structures candidates are not expected to draw exact shapes of molecules.

Do not allow ECF for wrong Lewis structures.

22 **(a)** **(i)**  / 

trigonal pyramid

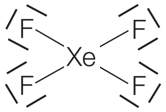
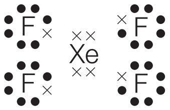
in the range of 100–108° [3]

(ii)  / 

Must include minus sign for the mark.

bent/V-shaped

in the range of 100–106° [3]

(iii)  / 

square planar

90° [3]

Penalize once only if electron pairs are missed off outer atoms

(b) **(i)** sigma bonds are formed by end on/axial overlap of orbitals with electron density between the two atoms/nuclei

pi bonds are formed by sideways overlap of parallel p orbitals with electron density above **and** below internuclear axis/σ bond [2]

Accept suitably annotated diagrams

(ii) 8 sigma/σ

1 pi/π [2]

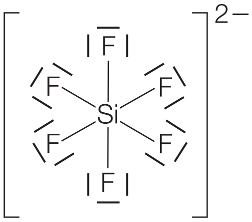
(iii) 109°/109.5°

120° [2]

(iv) sp hybridization

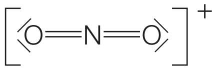
1 sigma and 2 pi

sigma bond formed by overlap between the two sp hybrid orbitals (on each of the two carbon atoms) / pi bonds formed by overlap between remaining p orbitals (on each of the two carbon atoms) / diagram showing 2 sp hybrid orbitals and 2 p orbitals [3]

23 **(a)** **(i)** 

octahedral/octahedron/square bipyramidal

90° / 90° **and** 180° [3]

(ii) 

linear

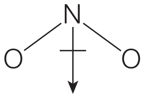
180° [3]

Allow dots, crosses or lines in Lewis structures.

Penalize missing charge, missing bracket once only in (i) and (ii).

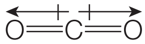
Lone pairs required for BOTH (i) and (ii).

(b) *NO_2*:



*Award **[1]** for correct representation of the bent shape **and [1]** for showing the net dipole moment, or explaining it in words (unsymmetrical distribution of charge).*

CO_2:



*Award **[1]** for correct representation of the linear shape **and** for showing the two equal but opposite dipoles or explaining it in words (symmetrical distribution of charge).* [3]

For both species, allow either arrow or arrow with bar for representation of dipole moment.

Allow correct partial charges instead of the representation of the vector dipole moment.

Ignore incorrect bonds.

Lone pairs not needed.

(c) *Structure*:

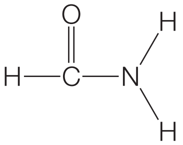
network/giant lattice / macromolecular / repeating tetrahedral units

Bonding:

(single) covalent (bonds) [2]

It is not necessary to identify which part refers to structure and bonding specifically.

(d) (i) methanamide



[2]

(ii) mixing/joining together/combining/ merging of atomic orbitals to form molecular/new orbitals / orbitals of equal energy [1]

(iii) σ *bond*:

end-on/axial overlap with electron density between the two atoms/nuclei

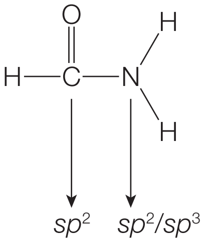
π *bond*:

sideways/parallel overlap with electron density above **and** below internuclear axis/σ bond [2]

Marks can be scored from a suitable diagram.

Award ***[1 max]*** *for stating end-on/ axial overlap for σ and sideways/parallel overlap for π only i.e. without mentioning electron density OR stating electron density between the two atoms/nuclei for σ above and below internuclear axis/σ bond for π i.e. without mentioning overlap.*

(iv)



[2]

Correct answer is actually sp² for nitrogen because of delocalization/planar geometry.

Accept sp³.

24 **(a) (i)** from left N = +1, N = –1, all others = 0 [1]

(ii) from left C = +1, 2nd N = –1 [1]

formal charges show same differences but structure (i) will be more important because C has stable octet [1]

(b) (i) from left O = –1, Cl = +1, O = –1 [1]

(ii) O = –1, Cl = 0, O = 0 [1]

structure (ii) is preferred due to less difference in formal charge [1]

Challenge yourself

1 Aluminium oxide is less ionic than MgO due to a smaller difference in electronegativity. It has some partially covalent character, which means the comparison with more ionic oxides is not fully valid.

2 F_2 has lower bond enthalpy than expected from its atomic radius due to repulsion. The bond length is so short that the lone pairs in the two atoms repel each other, weakening the bond.

3 When bonded to F, e.g. in OF_2

4 Run each solution out from separate burettes, and see whether the stream of liquid is deflected in the presence of a charged rod. Only the polar solution will show deflection.

Test solubility with ionic and covalent solutes. The polar solution will be a better solvent for polar/ionic solutes; the non-polar solution for covalent/non-polar solutes.

5 The high thermal conductivity of diamond is because of its strong covalent bonds. When heated the bonds becoming vibrationally excited, and as they are all connected heat energy could be readily transferred through the network from one bond to the next. Silicon is similarly a good thermal conductor – which is why computer chips need to be cooled.

6 Diamonds are kinetically stable with respect to graphite, as the conversion has a very high activation energy (see Chapter 6). So the reaction generally occurs too slowly to be observed.

7 It is difficult to know the number of valence electrons a transition metal has. Treating bonds from ligands as pure covalent molecules results in transition metals in complex ions with large negative formal charges. The formal charge model may not be useful for complex ions, as the values obtained do not make much sense.

8 In the polar winter small amounts of water vapour freeze into ice crystals in the atmosphere, which provide a reactive surface. Reactions on the crystals' surfaces produce species such as Cl_2• which later dissociate into Cl•, which breaks down ozone.

Answers

Chapter 5

Exercises

1 B **2** B **3** A

4 D **5** C

6 $q = mc\Delta T$, so $\Delta T = \dfrac{q}{mc} = \dfrac{100}{100 \times 0.138} = 7.25\ °\mathrm{C}$

$T = 25.0 + 7.25 = 32.3\ °\mathrm{C}$

7 A **8** A **9** C

10 **(a)** $\Delta T = 36.50 - 25.85 = 10.65\ °\mathrm{C}$ (or K)

$q = mc\Delta T$

$q = m(\mathrm{H_2O}) \times c(\mathrm{H_2O}) \times \Delta T(\mathrm{H_2O}) + m(\mathrm{Cu}) \times c(\mathrm{Cu}) \times \Delta T(\mathrm{Cu})$

$= (200.00\ \mathrm{g} \times 4.18\ \mathrm{J\ g^{-1}\ K^{-1}} \times 10.65\ \mathrm{K}) + (120.00\ \mathrm{g} \times 0.385\ \mathrm{J\ g^{-1}\ K^{-1}} \times 10.65\ \mathrm{K})$

$= 8900\ \mathrm{J} + 492\ \mathrm{J}$

$q = 9392\ \mathrm{J}$

$$n(\mathrm{C_6H_{12}O_6}) = \frac{1.10\ \mathrm{g}}{180.18\ \mathrm{g\ mol^{-1}}} = 6.11 \times 10^{-3}\ \mathrm{mol}$$

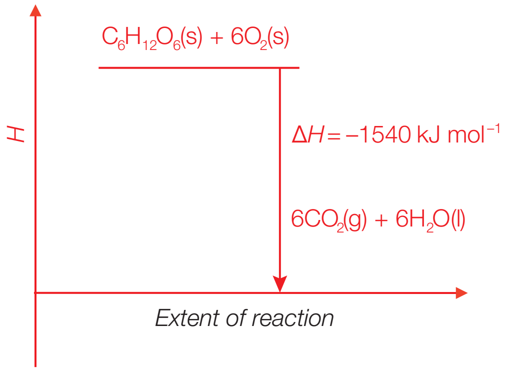
In calculating the enthalpy change of combustion, ΔH_c, we have to recognize that this is an exothermic reaction and that ΔH_c will therefore be a negative value.

$$\Delta H_c = -\frac{9392\ \mathrm{J}}{6.11 \times 10^{-3}\ \mathrm{mol}}$$

$= -1.54 \times 10^{6}\ \mathrm{J\ mol^{-1}}$

$= -1540\ \mathrm{kJ\ mol^{-1}}$

(b)



11 $q = mc\Delta T$

$q = 150.00\ \mathrm{g} \times 4.18\ \mathrm{J\ g^{-1}\ K^{-1}} \times (31.5 - 25.0)\ \mathrm{K}$

$= 4075.5\ \mathrm{J} = 4100\ \mathrm{J}$ (to 2 s.f.)

$$n(\mathrm{P}) = \frac{0.0500\ \mathrm{g}}{30.97\ \mathrm{g\ mol^{-1}}} = 1.61 \times 10^{-3}\ \mathrm{mol}$$

$$\Delta H_c = \frac{-4100\ \mathrm{J}}{1.61 \times 10^{-3}\ \mathrm{mol}}$$

$= -2525 \times 10^{3}\ \mathrm{J\ mol^{-1}}$

$= -2500\ \mathrm{kJ\ mol^{-1}}$

The precision of the answer is limited by the precision of measurement of the temperature difference. The value is lower than the literature value owing to heat losses and incomplete combustion.

12 $q = mc\Delta T$

$= 1000\ \mathrm{g} \times 4.18\ \mathrm{J\ g^{-1}\ K^{-1}} \times (70.0 - 20.0)\ \mathrm{K}$

$= 209\ \mathrm{kJ}$, for 1 mole of 1 mol $\mathrm{dm^{-3}}$ solution

$\Delta H = -209\ \mathrm{kJ\ mol^{-1}}$

13 $\Delta T = 32.3 - 24.5 = 7.8\ \mathrm{K}$

$q = m(\mathrm{H_2O}) \times c(\mathrm{H_2O}) \times \Delta T(\mathrm{H_2O})$

$= 100.00\ \mathrm{g} \times 4.18\ \mathrm{J\ g^{-1}\ K^{-1}} \times 7.8\ \mathrm{K}$

$= 3300\ \mathrm{J}$

$$n(\mathrm{NaOH}) = \frac{50.00}{1000} \times 0.950 = 0.0475\ \mathrm{mol}$$

$$\Delta H = \frac{-3300\ \mathrm{J}}{0.0475\ \mathrm{mol}} = 69 \times 10^{3}\ \mathrm{J\ mol^{-1}}$$

$= -69\ \mathrm{kJ\ mol^{-1}}$

Assumptions: no heat loss, $c(\text{solution}) = c(\text{water})$, $m(\text{solution}) = m(\mathrm{H_2O})$, density$(\mathrm{H_2O}) = 1.00$

14 If the mass of the solution is taken as 105.04 g (mass of water + mass of $\mathrm{NH_2Cl}$ dissolved), $\Delta H = +16.5\ \mathrm{kJ\ mol^{-1}}$.

If the mass of the solution is instead assumed to be 100.00 g (mass of water only), $\Delta H = +15.7\ \mathrm{kJ\ mol^{-1}}$.

$q = mc\Delta T$

$= 100.00\ \mathrm{g} \times 4.18\ \mathrm{J\ g^{-1}\ K^{-1}} \times (21.79 - 25.55)$

$= -1570\ \mathrm{J}$ for 5.35 g

$q = 293.6$ J per g

$n(\mathrm{NH_4Cl}) = 53.50\ \mathrm{g\ mol^{-1}}$

$\Delta H = 293.6\ \mathrm{J\ g^{-1}} \times 53.50\ \mathrm{g\ mol^{-1}}$

$= 15.7\ \mathrm{kJ\ mol^{-1}}$

15 ΔH is change in enthalpy, the heat content of a system. Enthalpy cannot be measured directly but enthalpy changes can be calculated for chemical reactions and physical processes from measured temperature changes using the equation $q = mc\Delta T$, where q is the heat change, m is the mass of the substance(s) changing temperature, c is the specific heat capacity of the substance(s) changing temperature and ΔT is the measured temperature change occurring in the substance(s).

16 A

17 $\Delta H^\ominus = -394\ \mathrm{kJ} - (-283)\ \mathrm{kJ} = -111\ \mathrm{kJ}$

18 $\Delta H^\ominus = -180.5\ \mathrm{kJ} + (+66.4\ \mathrm{kJ}) = -114.1\ \mathrm{kJ}$

19 $\Delta H^\ominus = (2 \times (-33.2\ \mathrm{kJ\ mol^{-1}})) + (+9.16\ \mathrm{kJ\ mol^{-1}}) = -57.24\ \mathrm{kJ\ mol^{-1}}$

20 B **21** C **22** D **23** D

24 **(a)** $3\mathrm{C(graphite)} + 3\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CH_3COCH_3(l)}$

$\Delta H_f^\ominus = -248\ \mathrm{kJ\ mol^{-1}}$

(b) Under standard conditions of 298 K (25 °C) and 1.00×10^5 Pa. If the reaction involves solutions these have a concentration of 1.00 $\mathrm{mol\ dm^{-3}}$.

25 $+330\ \mathrm{kJ\ mol^{-1}}$

26 $-57.2\ \mathrm{kJ\ mol^{-1}}$

27 D

28 $2\mathrm{MgO(s)} + \mathrm{C(s)} \rightarrow \mathrm{CO_2(g)} + 2\mathrm{Mg(s)}$

$\Delta H^\ominus_{\text{reaction}} = (-394) - 2(-602) = +810\ \mathrm{kJ\ mol^{-1}}$

Such a highly endothermic reaction is unlikely to be feasible.

29 B **30** A **31** C

32 1 × C—C + 6 × C–H

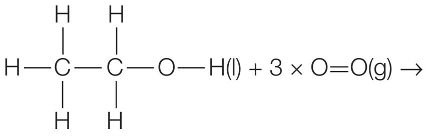
33 B

34 $-125\ \mathrm{kJ\ mol^{-1}}$

35 $-486\ \mathrm{kJ\ mol^{-1}}$

36 B **37** C

38 $\mathrm{C_2H_5OH(l)} + 3\mathrm{O_2(g)} \rightarrow 2\mathrm{CO_2(g)} + 3\mathrm{H_2O(g)}$



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H(l)} + 3 \times \mathrm{O{=}O(g)} \rightarrow$

$2 \times \mathrm{O{=}C{=}O(g)} + 3 \times \mathrm{H{-}O{-}H(g)}$

Bonds broken	ΔH / kJ mol^{-1}	Bonds formed	ΔH / kJ mol^{-1}
C—C	+346	4 C=O	4 × (–804)
3 O=O	3 × (+498)	6 H—O	6 × (–463)
O—H	+463		
C—O	+358		
5 C—H	5 × (+414)		
Total	+4731		–5994

$\Delta H^\ominus = +4731 - 5994\ \mathrm{kJ\ mol^{-1}} = -1263\ \mathrm{kJ\ mol^{-1}}$

The calculated value is less exothermic than the enthalpy of combustion in Table 13. This is because the bond enthalpy calculation assumes all species are in the gaseous state: water and ethanol are liquids.

39 **(a)** Step II, as bonds are formed.

(b) $\mathrm{O_2}$ has a double bond. $\mathrm{O_3}$ has resonance structures/delocalization with bonding intermediate between double and single bonds; the bond order is 1.5. The bonding in $\mathrm{O_2}$ is stronger therefore reaction I needs more energy.

40 $L \times E_{\text{photon}} = 498\ \mathrm{kJ} = 498\,000\ \mathrm{J}$

$$E_{\text{photon}} = \frac{498\,000}{6.02 \times 10^{23}}\ \mathrm{J}\ (= 8.272 \times 10^{-19}\ \mathrm{J})$$

$$\lambda = hc/E_{\text{photon}}$$

$$= 6.63 \times 10^{-34} \times 3.00 \times 10^{8} \times \frac{6.02 \times 10^{23}}{498\,000}$$

$$= 2.41 \times 10^{-7}\ \mathrm{m}$$

$$= 241\ \mathrm{nm}$$

Any radiation in the UV region with a wavelength shorter than 241 nm breaks the O=O bond in oxygen.

41 The oxygen double bond is stronger than the 1.5 bond in ozone. Thus, less energy is required to dissociate O_3 than O_2. Longer wavelength radiation of lower energy is needed to dissociate O_3.

42 A **43** C **44** D

45 **(a)** $K_2O(s) \rightarrow 2K^+(g) + O^{2-}(g)$

(b) **W** = $\Delta H^\ominus_{atom}(O)$, the enthalpy of atomization of oxygen (which also corresponds to $\frac{1}{2}E(O{=}O)$, the O=O bond enthalpy)

X = $2\Delta H^\ominus_i(K)$, 2 × the first ionization energy of potassium

Y = $\Delta H^\ominus_{e1}(O) + \Delta H^\ominus_{e2}(O)$, the sum of the first and second electron affinities of oxygen

Z = $\Delta H^\ominus_f(K_2O(s))$, the standard enthalpy of formation of $K_2O(s)$

(c) $\Delta H^\ominus_{latt}(K_2O) = 361 + 2(89.2) + 2(419) + \frac{1}{2}(498) + (-141) + 753$

$= +2238 \text{ kJ mol}^{-1}$

46 B

47 They decrease down Group 17 as the ionic radius of the halide ion increases.

48 Consider first the effect of increased ionic charge (Na^+/Mg^{2+} and Cl^-/O^{2-}). The charge of both the positive and negative ions is doubled. This leads to a quadrupled increase in the lattice energy. This effect is further enhanced by the decrease in ionic radius of the Mg^{2+} compared to Na^+ due to the increased nuclear charge of the metal and the decreased ionic radius of the oxide ion because of a decrease in the number of energy levels occupied.

49 C **50** A

51 Bonding in AgBr is stronger because Ag^+ has smaller ionic radius and more covalent character, which makes bonding stronger than that based on the ionic model.

52 They have similar ionic radii but the enthalpy of hydration of the F^- ion is significantly more exothermic. This suggests that there is an additional interaction to the electrostatic attraction between the charged ion and the polar molecules. F^- ions form hydrogen bonds with the water.

53 **(a)** $\Delta H^\ominus_{sol}(KCl) = \Delta H^\ominus_{lattice}(KCl) + \Delta H^\ominus_{hyd}(K^+) + \Delta H^\ominus_{hyd}(Cl^-)$

$= +720 - 340 - 359 \text{ kJ mol}^{-1}$

$= +21 \text{ kJ mol}^{-1}$

(b) $\Delta H^\ominus_{sol}(KCl) = +17.22 \text{ kJ mol}^{-1}$ (from data booklet)

$$\% \text{ accuracy} = \frac{21 - 17.22}{17.22} \times 100\% = 22\%$$

The large inaccuracy is based on the calculated value being found by the difference between two large values.

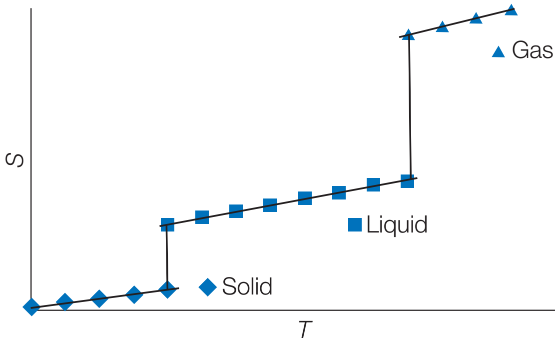
54 B **55** C **56** A **57** D

58 **(a)** ΔS is negative. The number of moles of gas decreases from reactants to products.

(b) ΔS is negative. Three moles of solid and four moles of gas change into one mole of solid and four moles of gas. There is a small decrease in disorder.

(c) ΔS is positive. A solid reactant is being converted into an aqueous solution so there is a large increase in disorder.

59



60

$N_2(g)$	+	$3H_2(g)$	→	$2NH_3(g)$	
191		3 × 131		2 × 193	$S^\ominus$/J K^{-1} mol^{-1}

$\Delta S^\ominus_{reaction} = 2 \times 193 - (191 + (3 \times 131))$

$= -198 \text{ J K}^{-1} \text{ mol}^{-1}$

61

C(graphite)	+	$2H_2(g)$	→	$CH_4(g)$	
5.7		2 × 131		186	$S^\ominus$/J K^{-1} mol^{-1}

$\Delta S^\ominus_{reaction} = 186 - (5.7 + (2 \times 131)) = -82 \text{ J K}^{-1} \text{ mol}^{-1}$

When adding figures, the figure with the smallest number of decimal places determines the precision.

62 C

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

$\Delta H^{\ominus}_{reaction} = -286 - (-292) = +6\ \text{kJ mol}^{-1}$

(b) $T = \dfrac{\Delta H^{\ominus}_{reaction}}{\Delta S^{\ominus}_{reaction}}$

$= \dfrac{6000}{22.0} = 273\ \text{K}$

64 A **65** D **66** B

67 **(a)** ΔH is positive as heat is needed to break up the carbonate ion.

(b) ΔS is positive as there is an increase in the amount of gas produced.

(c) At low temperature: $\Delta G = \Delta H$ and so is positive.

At high temperature: $\Delta G = -T\Delta S$ and so is negative.

The reaction is not spontaneous at low temperature but becomes spontaneous at high temperatures.

68 D **69** C

70 $\Delta G_{reaction} = (-604 + -394) - (-1129) = 131\ \text{kJ mol}^{-1}$

As $\Delta G_{reaction}$ is very positive, the reaction is not spontaneous under standard conditions. This accounts for the stability of calcium carbonate in the form of limestone, chalk and marble.

71 $\Delta H^{\ominus}_{reaction} = 178\ \text{kJ mol}^{-1}$

$\Delta S^{\ominus}_{reaction} = 160.8\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Delta G^{\ominus}_{reaction} = +178 - (2000 \times 160.8 \times 10^{-3})\ \text{kJ mol}^{-1}$

$= -144\ \text{kJ mol}^{-1}$

72 B

73 **(a)** $2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$

(b) $\Delta S^{\ominus}_{reaction} = +161 - (2 \times 5.7) - (3 \times 63.5) - (\frac{1}{2} \times 102.5)$

$= -98\ \text{J K}^{-1}\ \text{mol}^{-1}$

(c) $\Delta G_{reaction} = -278 - (500 \times -98 \times 10^{-3})$

$= -229\ \text{kJ mol}^{-1}$

(d) The reaction is spontaneous as ΔG is negative.

(e) At high temperature: $\Delta G = -T\Delta S$ and so is positive. The reaction will stop being spontaneous at higher temperature.

74 C **75** D **76** B

77 When $\Delta G = -30\ \text{kJ mol}^{-1}$

$-30\ \text{kJ mol}^{-1} = -123 - (T_1 \times -128 \times 10^{-3})\ \text{kJ mol}^{-1}$

$93 = (T_1 \times 128 \times 10^{-3})$

$T_1 = 727\ \text{K}$

When $\Delta G = +30\ \text{kJ mol}^{-1}$

$+30\ \text{kJ mol}^{-1} = -123 - (T_2 \times - 128 \times 10^{-3})\ \text{kJ mol}^{-1}$

$153 = (T_2 \times 128 \times 10^{-3})$

$T_2 = 1195\ \text{K}$

78 When $\Delta G = -30\ \text{kJ mol}^{-1}$

$-30\ \text{kJ mol}^{-1} = -93 - (T_1 \times -198 \times 10^{-3})\ \text{kJ mol}^{-1}$

$63 = (T_1 \times 198 \times 10^{-3})$

$T_1 = 318\ \text{K}$

When $\Delta G = +30\ \text{kJ mol}^{-1}$

$+30\ \text{kJ mol}^{-1} = -93 - (T_2 \times -198 \times 10^{-3})\ \text{kJ mol}^{-1}$

$123 = (T_2 \times 198 \times 10^{-3})$

$T_2 = 621\ \text{K}$

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 D **2** D **3** A **4** C

5 B **6** C **7** B **8** B

9 **(a)** amount of energy required to break bonds of reactants

$3 \times 414 + 358 + 463 + 1.5 \times 498\ (\text{kJ mol}^{-1})$
$= 2810\ (\text{kJ mol}^{-1})$ [1]

amount of energy released during bond formation of products

$4 \times 463 + 2 \times 804\ (\text{kJ mol}^{-1}) = 3460\ (\text{kJ mol}^{-1})$ [1]

$\Delta H = 2810 - 3460 = -650\ (\text{kJ mol}^{-1})$ [1]

Award ***[3]*** *for correct final answer. Award* ***[2]*** *for (+)650.*

(b) **(i)** m(methanol) = 80.557 – 80.034 = 0.523 (g) [1]

$n(\text{methanol}) = \dfrac{0.523\text{ g}}{32.05\text{ g mol}^{-1}}$

$= 0.0163$ (mol) [1]

*Award **[2]** for correct final answer.*

(ii) $\Delta T = 26.4 - 21.5 = 4.9$ (K) [1]

$q = (mc\Delta T =)\ 20.000 \times 4.18 \times 4.9$ (J) *or* $20.000 \times 4.18 \times 4.9 \times 10^{-3}$ (kJ) [1]

$= 410$ J *or* 0.41 kJ [1]

*Award **[3]** for correct final answer.*

(iii) $\Delta H^{\ominus}_{c} = -\dfrac{410\text{ (J)}}{0.0163\text{ (mol)}}$ *or* $-\dfrac{0.41\text{ (kJ)}}{0.0163\text{ (mol)}}$ [1]

$= -25153\text{ J mol}^{-1}$ *or* -25 kJ mol^{-1} [1]

*Award **[2]** for correct final answer. Award **[1]** for (+)25 (kJ mol^{-1}).*

(c) (i) bond enthalpies are average values/ differ (slightly) from one compound to another (depending on the neighbouring atoms) / methanol is liquid not gas in the reaction [1]

(ii) not all heat produced transferred to water / heat lost to surroundings/ environment / *OWTTE* / incomplete combustion (of methanol) / water forms as $H_2O(l)$ instead of $H_2O(g)$ [Do not allow just 'heat is lost'] [1]

10 (a) all heat is transferred to water/copper sulfate solution / no heat loss;

specific heat capacity of zinc is zero/ negligible / no heat is absorbed by the zinc;

density of water/solution = 1.0 / density of solution = density of water;

heat capacity of cup is zero / no heat is absorbed by the cup;

specific heat capacity of solution = specific heat capacity of water;

temperature uniform throughout solution;

*Award **[1]** each for any two. Accept 'energy' instead of 'heat'* [2]

(b) (i) $T_{\text{final}} = 73.0$ (°C) [1]

Allow in the range 72 to 74 (°C).

$\Delta T = 48.2$ (°C) [1]

*Allow in the range 47 to 49 (°C). Award **[2]** for correct final answer. Allow ECF if T_{final} or T_{initial} correct.*

(ii) temperature decreases at uniform rate (when above room temperature) / *OWTTE* [1]

(iii) 10.1 (kJ) [1]

Allow in the range 9.9 to 10.2 (kJ).

(c) Complete colour change shows all the copper has reacted, so $n(\text{Zn}) = n(\text{CuSO}_4)$

$= \dfrac{1.00 \times 50.0}{1000} = 0.0500$ (mol) [1]

(d) -201 kJ mol^{-1} [1]

Allow in the range –197 to –206 (kJ mol^{-1}). Value must be negative to award mark.

11 (a) energy required = C=C + H—H

= 614 + 436 = 1050

energy released = C—C + 2(C—H)

= 346 + 2(414) = 1174 [1]

Allow full consideration of breaking all bonds and forming all the new bonds, which gives values of 2706 and 2830.

energy required = C=C + H—H + 4(C—H)/612 + 436 + 4(413)

and

energy released = C—C + 6(C—H)/347 + 6(413);

$\Delta H = (1050 - 1174)$ *or* $(2706 - 2830) = -124\text{ kJ mol}^{-1}$ [1]

(b) $\Delta H = -1411 + (-286) - (-1560) = -137\text{ kJ mol}^{-1}$ [1]

(c) the actual values for the specific bonds may be different to the average values / the combustion values referred to the specific compounds / *OWTTE* [1]

(d) (i) -124 kJ mol^{-1} [1]

(ii) average bond enthalpies do not apply to the liquid state / *OWTTE*; [1]

the enthalpy of vaporization/ condensation of cyclohexene and cyclohexane / *OWTTE* [2]

12 bonds broken: 4 × N—H, 1 × N—N, 1 × O=O = +2220 (kJ mol^{-1}) [1]

bonds formed: 1 × N≡N, 4 × O—H = –2797 (kJ mol^{-1}) [1]

enthalpy change = 2797 + 2220 = –577 kJ mol^{-1} [1]

Award ***[3]*** *for correct final answer.*

13 reaction II (requires a shorter wavelength) [1]

O_2 has double bond/bond order 2 **and** O_3 intermediate between double and single bonds/ bond order of $1\frac{1}{2}$ [1]

Do not accept stronger/weaker bonding without justification for the second marking point.

14 A **15** A **16** C **17** D

18 B **19** B **20** B

21 **(a)** I is atomization/sublimation (of Mg) / $\Delta H^{\ominus}_{\text{atomization}}(\text{Mg})$ / $\Delta H^{\ominus}_{\text{sublimation}}(\text{Mg})$ [1]

V is enthalpy change of formation of ($MgCl_2$) / $\Delta H^{\ominus}_{\text{formation}}(MgCl_2)$ [1]

(b) Energy value for II is +242 [1]

Energy value for III: is 738 + 1451 = 2189 [1]

Energy value for IV is 2 × (–349) [1]

$\Delta H^{\ominus}_{\text{lat}}(MgCl_2)$ = 642 + 148 + 243 + 2189 + 2 × (–349) = (+)2523 kJ [1]

(c) theoretical value assumes ionic model [1]

experimental value greater due to (additional) covalent character [1]

(d) oxide has greater charge [1]

oxide has smaller radius [1]

Accept opposite arguments.

Challenge yourself

1 N_2(g): $N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H^{\ominus}_{c} = 90$ kJ mol^{-1}

2 The specific heat capacities depend on the number of atoms in the unit mass. So *c* is approximately inversely proportional to the relative atomic mass.

3 The temperature of the Bunsen flame is 5748 °C

4 The difference in the values is largely to due to the assumption that H_2O is gaseous in the bond enthalpy calculation (1), whereas it is actually formed as a liquid in combustion reactions (2).

(1) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -891$ kJ mol^{-1}

(2) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -808$ kJ mol^{-1}

(2) – (1) $2H_2O(l) \rightarrow 2H_2O(g)$ $\Delta H = 891 - 808 = +83$ kJ mol^{-1}

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H = +41.5$ kJ mol^{-1}

There are (on average) two hydrogen bonds between each molecule so a hydrogen bond is approximately 20 kJ mol^{-1}.

This assumes that all other molecular interactions such as dipole–dipole and London dispersion forces are negligible, which is an approximation.

5 Within the sheets of graphite the C=C bond order is 1.33 and the coordination number is 3, and there are weak intermolecular forces between the layers. In diamond each carbon is bonded to four other atoms by single covalent bonds and the C–C bond order is 1. The total bonding is slightly stronger in graphite (higher bond orders) and this makes it more stable.

6 It has two unpaired electrons in the 2p sub-level.

7 With positive ions, there is generally a loose electrostatic attraction with the partially negatively charged oxygen atoms of the water molecules. Positive ions with higher charge densities, such as d block ions, may form complex ions with formal covalent coordinate bonds with the water molecules. There is increased covalent interaction between the Ag^+ ions and the water molecules, which leads to more exothermic hydration enthalpies.

8 Sodium chloride is an ionic substance that contains alternating sodium and chlorine ions. When salt is added to water, the partial charges on the water molecule are attracted to the Na^+

and Cl⁻ ions. The water molecules work their way into the crystal structure and between the individual ions, surrounding them and slowly dissolving the salt – but as we have seen the enthalpy change is very small. The aqueous solution is more disordered and so has a higher entropy, as discussed later in the chapter.

9 When $K_c = 1$, $\Delta G^{\ominus}_{\text{reaction}} = 0$

When $K_c > 1$, $\Delta G^{\ominus}_{\text{reaction}} < 0$

When $K_c < 1$, $\Delta G^{\ominus}_{\text{reaction}} < 0$

Possible function: $\Delta G^{\ominus}_{\text{reaction}} = -A \ln K_c$ where A is a constant with units kJ mol^{-1}.

The precise relationship discussed in Chapter 7 is $\Delta G^{\ominus}_{\text{reaction}} = -RT \ln K_c$

Chapter 6

Exercises

1 Reaction gives off a gas: change in volume could be measured. Reaction involves purple MnO_4^- ions being reduced to colourless Mn^{2+} ions: colorimetry could be used. Reaction involves a change in the concentration of ions (23 on the reactants side and 2 on the products side): conductivity could be used.

All these techniques enable continuous measurements to be made from which graphs could be plotted of the measured variable against time.

2 C

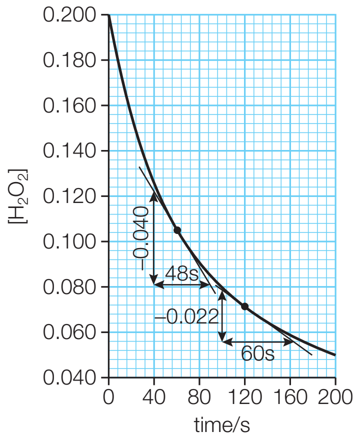
3 **(a)** **(i)** Measure the decrease in the mass of flask + contents.

(ii) Measure the increase in pH of the reaction mixture.

(iii) Measure the increase in volume of gas collected.

(b) The rate of the reaction decreases with time because the concentration of the acid decreases.

4



At 60 s, rate = 8.3×10^{-4} mol dm^{-3} s^{-1}

At 120 s, rate = 3.7×10^{-4} mol dm^{-3} s^{-1}

5 D

6 A

7 The reaction requiring the simultaneous collision of two particles is faster. The simultaneous collision of three particles is statistically less likely.

8 B **9** B **10** B

11 The ashes must contain a catalyst that speeds up the reaction between sugar and oxygen. (Deduced from the fact that all other factors that affect reaction rate can be ruled out.)

12 **(a)** $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$

(b) CO is a toxic gas: it combines with haemoglobin in the blood and prevents it from carrying oxygen. NO is a primary air pollutant: it is oxidized in the air to form acidic oxides, leading to acid rain. It also reacts with other pollutants in the atmosphere, forming smog.

(c) The increased surface area of the catalyst in contact with exhaust gases will increase catalyst efficiency.

(d) Catalytic activity involves the catalyst interacting with the gases, and the reaction occurring on its surface. As temperature increases, the increased kinetic energy of the gases increases the frequency with which they bind to the catalyst.

(e) Catalytic converters reduce pollution from cars but do not remove it completely. As in (d), they are not effective when the engine first starts from cold, when an estimated 80% of pollution occurs. Other pollutants in car exhausts are not removed by the catalyst, e.g. ozone, sulfur oxides and particulates. Also the catalytic converter increases the output of CO_2, a serious pollutant because of its greenhouse gas properties.

13 Experiment 1: rate = $k[H_2][I_2]$

Experiment 2: rate = $k[H_2O_2]$

Experiment 3: rate = $k[S_2O_8^{2-}][I^-]$

Experiment 4: rate = $k[N_2O_5]$

14 1st order with respect to NO; 1st order with respect to O_3; 2nd order overall.

15 Rate = $k[CH_3Cl]^2$

Rate = $k\,[CH_3Cl][OH^-]$

Rate = $k\,[OH^-]^2$

16 **(a)** $mol^{-1}\,dm^3\,s^{-1}$ **(b)** s^{-1}

(c) $mol\,dm^{-3}\,s^{-1}$ **(d)** $mol^{-2}\,dm^6\,s^{-1}$

(e) $mol^{-1}\,dm^3\,s^{-1}$

17 From the units of *k*, it must be 1st order.
Rate = $k[N_2O_5]$

18 $k = 4.5 \times 10^{-4}/(2.0 \times 10^{-3})^2 = 1.1 \times 10^2\ mol^{-1}\,dm^3\,min^{-1}$

19 C

20 NO: 2nd order; O_2: 1st order

Rate = $k[NO]^2[O_2]$

21 Experiment 2: rate = $1.5 \times 10^{-2}\ mol\,dm^{-3}\,s^{-1}$

Experiment 3: rate = $1.5 \times 10^{-2}\ mol\,dm^{-3}\,s^{-1}$

22 Rate = $k[NO_2][CO]$

23 Yes, it fits the kinetic data and the overall stoichiometry.

24 C

25 **(a)** $2AB_2 \rightarrow A_2 + 2B_2$

(b) Rate = $k\,[AB_2]^2$

(c) $mol^{-1}\,dm^3\,s^{-1}$

26 C **27** D **28** B

29 134 kJ mol^{-1}

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 A **2** B **3** C **4** C

5 A **6** A **7** B **8** C

9 C **10** D

11 **(a)** catalyst; regenerated at end of reaction / *OWTTE* [2]

(b) **(i)** N_2O_2 [1]

(ii) ([H_2] appears in rate expression so) step 2 rate-determining/rds/slow step [1]

Allow 'since step 1 involves 2NO and step 2 involves H_2 and as all 3 molecules are involved in rate expression, then two steps must have approximately same rate' / OWTTE.

(c) ($k_2 >> k_1$ so) step 1 rate-determining / rds / slow step; two molecules of NO_2 involved in step 1 consistent with rate expression / rate of overall reaction must equal rate of step 1 which is rate = $k_1[NO_2]^2$ / *OWTTE* [2]

(d) $E_a = -R \times m$; measurement of gradient from **two** points on line

Accept a gradient in range -2.14×10^4 K to -2.27×10^4 K.

correct answer for E_a;

correct units kJ mol^{-1} / J mol^{-1} corresponding to answer [4]

Allow kJ or J.

A typical answer: $E_a = 1.85 \times 10^2$ kJ mol^{-1}.

Allow answers for E_a in range 1.75×10^2 kJ mol^{-1} to 1.91×10^2 kJ mol^{-1}.

*Award **[4]** for correct final answer with some working shown.*

*Award **[2 max]** for correct final answer without any working shown.*

12 **(a)** the concentration (of nitrogen(II) oxide) [1]

*Award **[0]** if reference made to equilibrium.*

(b) $mol^{-2}\,dm^6\,s^{-1}$ / $dm^6\,mol^{-2}\,s^{-1}$ [1]

Accept $(mol^{-1}\,dm^3)^2\,s^{-1}$.

13 **Note:** The *y*-axis of the graph is incorrectly labelled as log *k*. This should be labelled as ln *k*.

(a) *k* increases with increase in *T* / *k* decreases with decrease in *T* [1]

Do not allow answers giving just the Arrhenius equation or involving ln k relationships.

(b) gradient = $-E_a/R$;

-30000 (K) = $-E_a/R$

Allow value in range −28800 to −31300 (K).

E_a = (30000 × 8.31=) 2.49×10^5 J mol^{-1}/ 249 kJ mol^{-1}

Allow value in range 240–260 kJ mol^{-1}.

*Allow **[3]** for correct final answer.*

(c) 0.9 × 0.200 = 0.180 (mol dm^{-3});

rate = (0.244 × $(0.180)^2$ =) 7.91×10^{-3} mol dm^{-3} s^{-1}

*Award **[2]** for correct final answer.*

*Award **[1 max]** for either 9.76×10^{-3} mol dm^{-3} s^{-1} or 9.76×10^{-5} mol dm^{-3} s^{-1}.*

14 **(a)** to maintain a constant volume / *OWTTE* [1]

(b) **(i)** $[H^+]$ order 1, $[CH_3COCH_3]$ order 1, $[I_2]$ order 0;

(rate =) $k[H^+][CH_3COCH_3]$ [2]

*Award **[2]** for correct rate expression.*

Allow expressions including $[I_2]^0$.

(ii) neither were correct / Alex was right about propanone and wrong about iodine / Hannah was right about propanone and hydrogen ions but wrong about iodine / *OWTTE* [1]

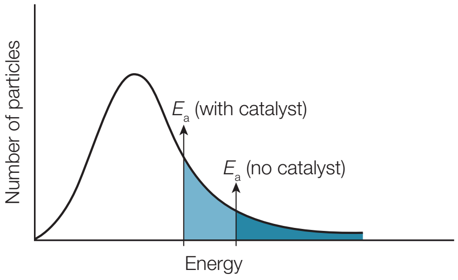
(c) $[CH_3COCH_3]$ = 0.100 mol dm^{-3} **and** $[H^+]$ = 0.100 mol dm^{-3}

$$k = \frac{4.96 \times 10^{-6}}{(0.100 \times 0.100)} = 4.96 \times 10^{-4}\ \text{mol}^{-1}\ \text{dm}^{-3}\ \text{s}^{-1}$$

Ignore calculation of $[I_2]$.

No ECF here for incorrect units.

(d) **(i)**



axes correctly labelled x = energy/ velocity/speed, y = number/% of molecules/particles/probability

graph showing correct curve for Maxwell-Boltzmann distribution

If two curves are drawn, first and second marks can still be scored, but not third.

Curve(s) must begin at origin and not go up at high energy.

two activation energies shown with E_{cat} shown lower [3]

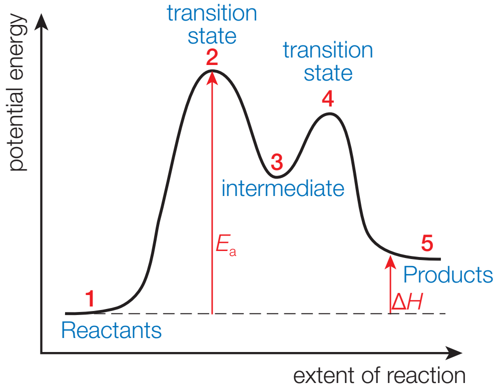
Award the mark for the final point if shown on an enthalpy level diagram.

(ii) catalyst provides an alternative pathway of lower energy / *OWTTE* [1]

Accept catalyst lowers activation energy (of reaction).

15 **(a)** XY + Z → X + YZ [1]

(b)



*Award **[3]** for all 5 correct, **[2]** for 4 correct, **[1]** for 3 correct.*

(c)
1 X–Y + Z, W
2 X–Y–W
3 W–Y
4 W–Y–Z
5 W, Y–Z + X

*Award **[3]** for all 5 correct, **[2]** for 4 correct, **[1]** for 3 correct.*

(d) 1st step is rate-determining step (highest energy of transition state);

rate equation = $k[W][XY]$ [2]

(e) reaction is catalysed by W, which is not chemically changed at the end of the reaction [1]

(f) see graph in (b) above [2]

Challenge yourself

1 Collecting a gas over warm water will cause its temperature and therefore its volume to increase.

2 If the partially made/broken bonds are treated as containing only one electron, we can calculate formal charges which have fractional values. The distribution of these formal charges in the transition state may help to interpret its stability and how it will react in the next step of the reaction mechanism.

Answers

Chapter 7

Exercises

1 A **2** C **3** B

4 **(a)** $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$ **(b)** $K_c = \frac{[NO_2]^4\,[H_2O]^6}{[NH_3]^4[O_2]^7}$

(c) $K_c = \frac{[CH_3OH][Cl^-]}{[CH_3Cl][OH^-]}$

5 **(a)** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(b) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

6 **(a)** $3F_2(g) + Cl_2(g) \rightleftharpoons 2ClF_3(g)$

$K_c = \frac{[ClF_3]^2}{[F_2]^3[Cl_2]}$

(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

$K_c = \frac{[N_2][O_2]}{[NO]^2}$

(c) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$

7 **(a)** Mostly reactants **(b)** Mostly reactants

(c) Mostly products

8 **(a)** $\frac{[HOCl]^2}{[H_2O][Cl_2O]} > K$; not at equilibrium; reaction proceeds to the left

(b) At equilibrium

(c) $\frac{[HOCl]^2}{[H_2O][Cl_2O]} > K$; not at equilibrium; reaction proceeds to the left

9 **(a)** 7.73×10^4 **(b)** 3.60×10^{-3}

(c) 6.00×10^{-2}

10 B **11** D **12** C

13 **(a)** Shift to the left **(b)** Shift to the right

(c) No shift in equilibrium

14 **(a)** Shift to the left **(b)** Shift to the right

(c) This is equivalent to an increase in pressure, so shifts to the left

(d) Shift to the right **(e)** Shift to the right

15 **(a)** Amount of CO will decrease

(b) Amount of CO will decrease

(c) Amount of CO will increase

(d) No change in CO

16 C **17** B

18 The Haber process is exothermic in the forward direction. Therefore, increasing temperature will decrease the value of K_c. This represents a decrease in the reaction yield.

19 **(a)**

	$2HI(g)$ $\rightleftharpoons$	$H_2(g)$ +	$I_2(g)$
Initial:	1.0	0.0	0.0
Change:	–0.22	+0.11	+0.11
Equilibrium:	0.78	0.11	0.11

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.11)^2}{(0.78)^2} = 2.0 \times 10^{-2}$$

(b) At the higher temperature, the value of K_c is higher, so the reaction must be endothermic.

20

	$N_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2NO(g)$
Initial:	1.6	1.6	0.0
Change:	$-x$	$-x$	$2x$
Equilibrium:	$1.6 - x$	$1.6 - x$	$2x$

As K_c is very small, $1.6 - x \approx 1.6$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2x)^2}{(1.6)^2} = 1.7 \times 10^{-3}$$

$x = 0.03298$, so $2x = 0.066$

$[NO]_{eqm} = 0.066\ mol\ dm^{-3}$

21 **(a)**

	$CO(g)$ +	$H_2O(g)$ =	$H_2(g)$ +	$CO_2(g)$
Initial:	4.0	6.4	0.0	0.0
Change:	–3.2	–3.2	+3.2	+3.2
Equilibrium:	0.8	3.2	3.2	3.2

$$K_c = \frac{[H_2][CO_2]}{[CO][H_2O]} = \frac{(3.2)^2}{(0.8)(3.2)} = 4.0$$

(b) Put the values into the equilibrium expression to determine Q:

$$Q = \frac{(3.0)^2}{(4.0)^2} = 0.56$$

This is not equal to the value of K_c so the reaction is not at equilibrium. As the value of this mixture is lower than K_c, the reaction will move to the right before equilibrium is established.

22 C

23 **(a)** 0 **(b)** Negative

(c) Positive

24 **(a)** 79.8 kJ

(b) Increasing temperature has increased the value of K so it must be an endothermic reaction.

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1	C	**2**	D	**3**	D	**4**	A
5	D	**6**	C	**7**	D	**8**	A
9	D						

10 **(a)** **(i)** (K =) $[SO_3]^2/[O_2][SO_2]^2$ [1]

(ii) yield (of SO_3) increases / equilibrium moves to right / more SO_3 formed;

3 gaseous molecules → 2 gaseous molecules / decrease in volume of gaseous molecules / fewer gaseous molecules on right hand side [2]

Do not allow ECF.

(iii) yield (of SO_3) decreases;

forward reaction is exothermic / reverse/ backwards reaction is endothermic / equilibrium shifts to absorb (some of) the heat [2]

Do not accept exothermic reaction or Le Châtelier's principle.

Do not allow ECF.

(iv) rates of both forward and reverse reactions increase equally; no effect on position of equilibrium; no effect on value of K_c [3]

(b) $2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$

	$NO(g)$	$H_2(g)$	$N_2(g)$	$H_2O(g)$
Initial/ mol dm^{-3}	0.100	0.051	0.000	0.100
Change/ mol dm^{-3}	−0.038	−0.038	+0.019	+0.038
Equilibrium/ mol dm^{-3}	0.062	0.013	0.019	0.138

$[H_2]$ at equilibrium = 0.013 (mol dm^{-3});

$[N_2]$ at equilibrium = 0.019 (mol dm^{-3});

$[H_2O]$ at equilibrium = 0.138 (mol dm^{-3});

$K_c = [N_2][H_2O]^2/[NO]^2[H_2]^2 = (0.019)(0.138)^2/(0.062)^2(0.013)^2 = 5.6 \times 10^2$ [4]

Award ***[4]*** *for final correct answer.*

Accept any value also in range 557–560.

Do not penalize significant figures.

11 **(a)** $(K_c =) \dfrac{[SO_2Cl_2]}{[Cl_2][SO_2]}$ [1]

Ignore state symbols.

Square brackets [ ] required for the equilibrium expression.

(b) 7.84×10^{-3} mol of SO_2 and 7.84×10^{-3} mol of Cl_2;

7.84×10^{-3} mol dm^{-3} of SO_2, 7.84×10^{-3} mol dm^{-3} of Cl_2 **and** 7.65×10^{-4} mol dm^{-3} of SO_2Cl_2;

12.5 [3]

Award ***[1]*** *for 10.34.*

Award ***[3]*** *for the correct final answer.*

(c) value of K_c increases;

$[SO_2Cl_2]$ increases;

decrease in temperature favours (forward) reaction which is exothermic [3]

Do not allow ECF.

(d) no effect on the value of K_c / depends only on temperature;

$[SO_2Cl_2]$ decreases;

increase in volume favours the reverse reaction which has more gaseous moles [3]

Do not allow ECF.

(e) no effect;

catalyst increases the rate of forward and reverse reactions (equally) / catalyst decreases activation energies (equally) [2]

12 **(a)** exothermic

Accept either of the following for the second mark.

increasing temperature favours endothermic/ reverse reaction; as yield decreases with increasing temperature [2 max]

(b) yield increases / equilibrium moves to the right / more ammonia;

increase in pressure favours the reaction which has fewer moles of gaseous products [2]

(c) $(K_c =) \dfrac{[NH_3]^2}{[N_2][H_2]^3}$ [1]

(d) $[N_2]$: (at equilibrium = 1.00 – 0.031 =) 0.969 (mol dm^{-3});

$[H_2]$: (at equilibrium = 3.00 – 3(0.031) =) 2.91 (mol dm^{-3});

$\left(K_c = \dfrac{(0.062)^2}{(0.969)(2.91)^3}\right) = 1.6(1) \times 10^{-4}$ [3]

Ignore units.

Award ***[1]*** *for* $K_c = 1.4 \times 10^{-4}$

(e) no effect [1]

13 **(a)** reactants and products in same phase/state;

rate of forward reaction = rate of reverse reaction;

concentrations of reactants and products remain constant / macroscopic properties remain constant [2 max]

Do not accept concentrations are equal.

(b) $(K_c =) \dfrac{[HI]^2}{[H_2][I_2]}$ [1]

(c) no change to position of equilibrium [1]

(d) the reaction is exothermic / heat is given out / ΔH is negative [1]

(e) amount of H_2 remaining at equilibrium

$= 1.60 - \dfrac{1.80}{2} = 0.70$ mol

amount of I_2 remaining at equilibrium

$= 1.0 - \dfrac{1.80}{2} = 0.10$ mol

$$K_c = \frac{(1.80/4.0)^2}{(0.70/4.00) \times (0.10/4.00)} \Big/ \frac{1.80^2}{0.70 \times 0.10}$$

$$K_c = \frac{(1.80)^2}{0.70 \times 0.10} = 46.3$$ [4]

Award ***[4]*** *for correct final answer.*

(f) no effect (on the value of the equilibrium constant)

as it speeds up forward and reverse reaction / concentrations of reactants and products do not change / position of equilibrium does not change / no change in yield [2]

14 **(a)** $\Delta G^{\ominus} = 0$

(b) $\Delta G = -70$ kJ mol^{-1}

The reaction has a very high value for K, so will go essentially to completion – from the equilibrium yield, this reaction is likely to give a high production of methanol. However, kinetic data are not available, so the rate cannot be deduced.

15 **(a)** $[H_2(g)] = 4.0$ mol dm^{-3}

$[I_2(g)] = 1.0$ mol dm^{-3}

$[HI] = 4.0$ mol dm^{-3}

(b) **(i)** HI originally placed = 2.0 mol dm^{-3}

(ii) I_2 at equilibrium = 0.218 mol dm^{-3}; HI at equilibrium = 1.56 mol dm^{-3}

Challenge yourself

1 Earth receives energy from the Sun and disperses energy, largely as heat. But exchange of matter is minimal – the only exceptions to Earth being a closed system are matter received from space such as asteroids and space dust, and matter lost to space such as spacecraft.

2 The different values of K_c indicate different stabilities of the hydrogen halides. The bonding in HCl is the strongest and in HI the weakest.

This is largely because of the size of the atoms. As I has a larger atomic radius than Cl, in HI the bonding pair is further from the nucleus than the bonding pair in HCl, and so experiences a weaker pull. The HI bond breaks more easily and so the dissociation reaction is favoured.

3 The concentration of a pure solid or pure liquid is a constant, effectively its density, which is independent of its amount. These constant values therefore do not form part of the equilibrium expression.

4 The value for K_c at 298 K for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is extremely low, so the equilibrium mixture lies to the left with almost no production of NO. But at higher temperatures, such as in vehicle exhaust fumes, the reaction shifts to the right and a higher concentration of NO is produced. This gas is easily oxidized in the air, producing the brown gas NO_2 which is responsible for the brownish haze: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$.

5 The atom economies of the Haber process and the Contact process reactions described are both 100% as there is only one product. In other words, there is no waste. But this does not mean that all reactants are converted to product, so the stoichiometric yield is less than 100%. It is the goal of these industries to maximize yield and efficiency by choosing the optimum conditions, taking equilibrium and kinetic considerations into account.

Answers

Chapter 8

Exercises

1 **(a)** HSO_3^- **(b)** $CH_3NH_3^+$
(c) C_2H_5COOH **(d)** HNO_3
(e) HF **(f)** H_2SO_4

2 **(a)** $H_2PO_4^-$ **(b)** CH_3COO^-
(c) HSO_3^- **(d)** SO_4^{2-}
(e) O^{2-} **(f)** Br^-

3 **(a)** CH_3COOH (acid)/CH_3COO^- (base)
NH_3 (base)/NH_4^+ (acid)
(b) CO_3^{2-} (base)/HCO_3^- (acid)
H_3O^+ (acid)/H_2O (base)
(c) NH_4^+ (acid)/NH_3 (base)
NO_2^- (base)/HNO_2 (acid)

4 $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$ (acid behaviour)

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$ (base behaviour)

5 **(a)** $H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$
(b) $HNO_3(aq) + NaHCO_3(s) \rightarrow NaNO_3(aq) + H_2O(l) + CO_2(g)$
(c) $H_3PO_4(aq) + 3KOH(aq) \rightarrow K_3PO_4(aq) + 3H_2O(l)$
(d) $6CH_3COOH(aq) + 2Al(s) \rightarrow 2Al(CH_3COO)_3(aq) + 3H_2(g)$

6 B **7** B

8 **(a)** nitric acid + sodium carbonate / sodium hydrogencarbonate / sodium hydroxide

$2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$

(b) hydrochloric acid + ammonia solution

$HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$

(c) copper(II) oxide + sulfuric acid

$H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$

(d) methanoic acid + potassium hydroxide

$HCOOH(aq) + KOH(aq) \rightarrow KCOOH(aq) + H_2O(l)$

9 pH increases by 1 unit

10 pH = 4.72

11 $[H^+] = 1.0 \times 10^{-9}$ mol dm^{-3}, $[OH^-] = 1.0 \times 10^{-5}$ mol dm^{-3}

12 **(a)** $[OH^-] = 2.9 \times 10^{-6}$ mol dm^{-3}; basic
(b) $[H^+] = 1.0 \times 10^{-12}$ mol dm^{-3}; basic
(c) $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}; acidic
(d) $[OH^-] = 1.2 \times 10^{-10}$ mol dm^{-3}; acidic

13 pH = 2.0

14 **(a)** pH = 6.9 **(b)** pH = 2
(c) pH = 4.8

15 pH = 13.17

16 B **17** A

18 **(a)** H_2CO_3 **(b)** HCOOH

19 **(a)** Lewis acid Zn^{2+}; Lewis base NH_3
(b) Lewis acid $BeCl_2$; Lewis base Cl^-
(c) Lewis acid Mg^{2+}; Lewis base H_2O

20 D, CH_4 because it does not possess a lone pair.

21 C, there is no exchange of H^+.

22 $[H^+] = [OH^-] = 1.55 \times 10^{-7}$ mol dm^{-3}
pH = pOH = 6.81
pH + pOH = pK_w = 13.62
neutral

23 pOH = 7.23
$[H^+] = 1.7 \times 10^{-7}$ mol dm^{-3}
$[OH^-] = 5.9 \times 10^{-8}$ mol dm^{-3}
acidic

24 **(a)** 0.40 **(b)** 10.57
(c) 10.00

25 B

26 **(a)** $K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]}$

(b) $K_b = \frac{[H_2SO_4][OH^-]}{[HSO_4^-]}$

(c) $K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$

27 $HNO_2 < H_3PO_4 < H_2SO_3$

28 Strong acids and bases are fully dissociated, so it is not useful to think of them in terms of an equilibrium mixture. The pH of their solutions can be derived directly from their concentration.

29 B

30 $K_b = 5.6 \times 10^{-4}$

31 $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}; $[OH^-] = 1.0 \times 10^{-10}$ mol dm^{-3}

32 pH = 3.22; $[H^+] = 6.0 \times 10^{-4}$ mol dm^{-3}

33 A

34 HF is the stronger acid.

35 pK_b CN^- = 4.79; pK_b F^- = 10.83
CN^- is the stronger base.

36 **(a)** pK_b CH_3COO^- = 9.24

(b) Methanoic acid is a stronger acid than ethanoic acid from its lower pK_a. Therefore, its conjugate base is weaker.

37 B **38** B

39 **(i)** Because it has a higher concentration of the acid and its conjugate base.

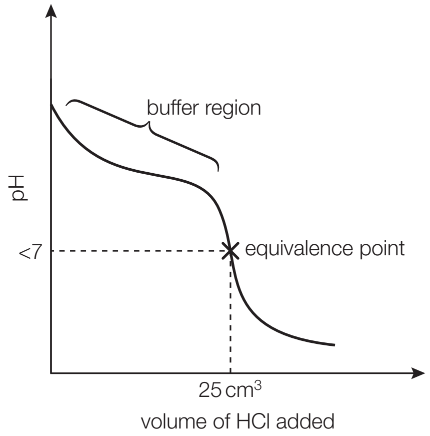
40 **(a)** equal to 7 **(b)** less than 7
(c) less than 7 **(d)** greater than 7

41 B; salt of strong base and weak acid

42 **(a)** less than 7 **(b)** greater than 7
(c) equal to 7

43 D (III only)

44



45 Initial pH of acid ⇒ K_a of acid ⇒ pK_a of acid.
At half equivalence, pH = pK_a, so this can be read directly off the curve.

46 D

47 **(a)** Strong acid–strong base and strong acid–weak base

(b) pK_a = 4.6 (midway in endpoint range)

(c) Yellow at all pHs below 3.8

48 **(a)** Contains dissolved carbon dioxide which reacts with water to form carbonic acid:

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

(b) Sulfuric acid:

$S(s) + O_2(g) \rightarrow SO_2(g)/2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$

(c) Nitric acid:

reduced by use of catalytic converters, recirculation of exhaust gases

(d) $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$

(e) Effects on materials, plant life and human health (see text for details).

(f) Use alternative energy source to fossil fuels or use coal with a low sulfur content.

49 **(a)** SO_2 and NO

(b) SO_2 and particulates

(c) Particulates act as catalysts in the production of secondary pollutants.

(d) SO_2(g): $CaO(s) + SO_2(g) \rightarrow CaSO_3(g)$

(e) NO: formed from the combination of nitrogen and oxygen at the high temperature of internal combustion engines.

50 **(a)** Dry acid deposition typically occurs close to the source of emission.

Wet acid deposition is dispersed over a much larger area and distance from the emission source.

(b) The acid is formed in the air from sulfur dioxide (SO_2) and nitrogen oxide (NO) which are emitted by thermal power stations, industry and motor vehicles. A major source is the burning of fossil fuels, particularly in coal-fired power stations. Pollutants are carried by prevailing winds and converted (oxidized) into sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These are then dissolved in cloud droplets (rain, snow, mist, hail) and this precipitation may fall to the ground as dilute forms of sulfuric acid and nitric acid. The dissolved acids consist of sulfate ions, nitrate ions and hydrogen ions.

51 The hydroxyl free radical $^\bullet OH$.

It is formed by the reaction between water and either ozone or atomic oxygen:

$H_2O + O^\bullet \rightarrow 2^\bullet OH$

$O_2 + O^\bullet \rightarrow O_3$; $O_3 + H_2O \rightarrow 2^\bullet OH + O_2$

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1	D	**2**	B	**3**	C	**4**	C
5	B	**6**	C	**7**	C	**8**	B
9	C	**10**	D	**11**	A	**12**	A
13	C						

14 **(a)** (K_w =)$[H^+(aq)][OH^-(aq)]$ [1]

Do not penalize if (aq) not stated.

H_3O^+ may be given instead of H^+.

Do not award mark if square brackets are omitted or are incorrect.

(b) **(i)** (pK_b =(14.00 – 7.52 =) 6.48 and) K_b = ($10^{-6.48}$) = 3.3×10^{-7} [1]

Do not award mark if answer just left as $10^{-6.48}$.

(ii) $K_b = \frac{[HOCl][OH^-]}{[OCl^-]} = \frac{x^2}{0.705} = 3.3 \times 10^{-7}$

$[OH^-] = 4.8 \times 10^{-4}$ (mol dm^{-3})

*Award **[2]** for correct value of $[OH^-]$.*

OCl^- only partially hydrolysed / x negligible (compared to $[OCl^-]$) / *OWTEE* [3]

Accept $[HOCl] = [OH^-]$.

(iii) $[H_3O^+]/[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{4.8 \times 10^{-4}} = 2.1 \times 10^{-11}$

pH = ($-\log_{10}[H_3O^+]/-\log_{10}[H^+]$ = $-\log_{10}(2.1 \times 10^{-11})$ =)10.68 [2]

*Award **[2]** for correct final answer.*

15 **(a)** **(i)** *Acid*: proton/H^+ donor **and** *Base*: proton/H^+ acceptor

Do not accept OH^- for base.

Weak base: (base/electrolyte) partially dissociated/ionized (in solution/water) **and** *Strong base*: (base/electrolyte assumed to be almost) completely/100% dissociated/ionized (in solution/water) / *OWTTE*

NH_3 / $CH_3CH_2NH_2$ [3]

Allow either name or formula or other suitable example.

(ii) sulfurous acid/H_2SO_3

corrodes marble/limestone buildings/statues / leaching in soils / harms/kills plants

OR

nitrous acid/HNO_2

corrodes marble/limestone buildings/statues / leaching in soils / harms/kills plants

OR

carbonic acid/H_2CO_3

corrodes marble/limestone buildings/ statues / acidification of lakes [2]

Do not allow oxides (e.g. CO_2 etc.).

Do not accept just corrodes or damages.

(iii) *Volume of KOH*: 20 (cm^3)

Allow any value between 20 and 21 (cm^3).

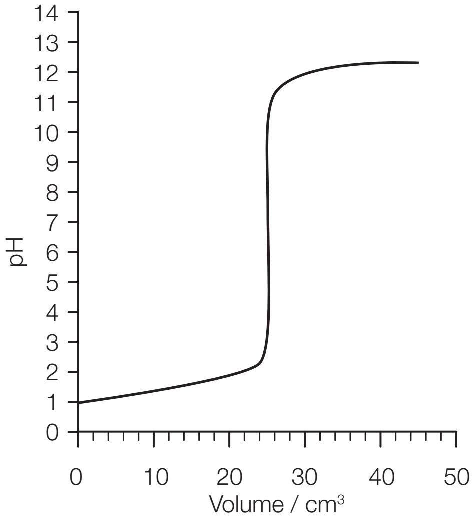
pH at the equivalence point: 8.0–10.0 [2]

(iv) At half-equivalence point, $[CH_3COOH] = [CH_3COO^-]$ so $pH = pK_a$;

$pK_a = 4.7$ [2]

Accept in range 4.2 to 5.2. M2 can only be scored if M1 correct (i.e. no marks for just Data Booklet value of 4.76).

(v)



Starting pH: 1

Equivalence point: pH = 7 **and** 25 cm^3

Final pH reached: 12–13

correct curve shape [4]

Do not award M4 if turn in curve is seen at low volumes (suggesting weak acid–strong base titration).

*Award **[4]** if values corresponding to M1, M2 and M3 are labelled on graph (e.g. using X) and correct shape of curve shown.*

(b) (i) HIn is a weak acid / weak base

$$\underset{\text{colour 1}}{HIn} \rightleftharpoons H^+ + \underset{\text{colour 2}}{In^-}$$

$\rightleftharpoons$ required.

*Award **[2]** for M2 alone.*

in base equilibrium moves to right / in acid equilibrium moves to left [3]

(ii) phenolphthalein

indicator colour change occurs in range of pH at the equivalence point / *OWTTE* [2]

M2 can be scored independently even if indicator is incorrect.

16 (a) strong acid completely dissociated/ionized **and** weak acid partially dissociated/ionized

$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ [3]

Insist on both arrows as shown.

State symbols not needed.

Accept H_2O and H_3O^+.

(b) $K_a = \dfrac{[H^+][CN^-]}{[HCN]}$

Allow H_3O^+ instead of H^+.

$K_a = 10^{-9.21} = 6.17 \times 10^{-10}$

(c) $[H^+] = \sqrt{K_a[HCN]}$ / $\sqrt{(6.17 \times 10^{-10} \times 0.108}$

$= 8.16 \times 10^{-6}$

Allow in the range 8.13×10^{-6} to 8.16×10^{-6}.

pH = 5.09

OR

$pH = \frac{1}{2}(pK_a - \log[HCN])/\frac{1}{2}(9.21 - \log 0.108)$

$= 5.09$

$[H^+] = 10^{-5.09} = 8.16 \times 10^{-6}$

Allow in the range 8.13×10^{-6} to 8.16×10^{-6}.

*If expression for $[H^+]$ missing but both answer correct, award **[3]**, if one answer correct, award **[2]**.*

assume $[H^+] << 0.108$/negligible dissociation [4]

Challenge yourself

1 Increasing the length of the carbon chain increases the donation/push of electrons towards the carbonyl C atom, known as a positive inductive effect. This causes less electron withdrawal from the O—H bond, so weakening acid strength. The basic strength of amines depends largely on the availability of the lone pair electrons on nitrogen. C_2H_5 pushes electrons towards N more than CH_3 does, so it is a stronger base.

(This will make more sense after studying inductive effects in Chapter 10.)

2 **(a)** pH increases on dilution of a strong acid as $[H^+]$ decreases.

(b) pH increases on dilution of a weak acid as $[H^+]$ decreases, but the change is less than for a strong acid, as acid dissociation increases with dilution.

(c) pH of a buffer stays the same with dilution, as K_a or K_b and [acid]/[salt] ratio stay constant.

3 [acid] = initial concentration of acid; [HA] = equilibrium concentration of acid. These will be equal only for weak acids, in which the extent of dissociation is so low that the acid is considered to be undissociated at equilibrium.

[salt] = initial concentration of salt solution; $[A^-]$ = concentration of anion/conjugate base at equilibrium. These will be equal for fully soluble salts in which the formula unit contains a single anion.

4 Titration needs to add acid from burette to base (see exam hint on page 400). The pH at half equivalence when half the base has been neutralized and half remains unreacted is recorded. At this point, $pOH = pK_b$. (pOH is usually calculated from the measured pH by assuming the temperature is 298 K, so pH + pOH = 14.)

5 Indicators usually contain structures with delocalized electrons, either benzene rings and/or multiple bonds. Conjugation of the electrons influences the absorption of light in the visible region, giving rise to specific colours. The gain or loss of H^+ changes the delocalization within the structure, which causes changes in absorption maxima and so different colours. Colour is discussed in Topic 13, Chapter 3.

6 Sulfur is present in proteins in living cells (a component of two out of the twenty amino acids). Decomposition of plant material to peat and then coal conserves this sulfur. Additional sources are the depositional environment such as sea water, where sulfates are reduced by bacteria to form H_2S, which can react further to form organic sulfur structures.

7 Combustion of nitrogen involves the highly endothermic step (+942 kJ mol^{-1}) of breaking the triple N≡N bond, as well as the O═O bond (+498 kJ mol^{-1}). The exothermic step of forming the triple N≡O bond releases less energy – approximately 630 kJ mol^{-1}. Therefore enthalpy change (*bonds broken minus bonds formed*) is endothermic. So the stability and strength of the nitrogen triple bond creates an unusual situation where the products of combustion are less stable than the reactants.

8 HNO_2: N = +3, nitric(III) acid
HNO_3: N = +5, nitric(V) acid
H_2SO_3: S = + 4, sulfuric(IV) acid
H_2SO_4: S = +6, sulfuric(VI) acid

Answers

Chapter 9

Exercises

1 (a) NH_4^+ = N −3, H +1

(b) $CuCl_2$ = Cu +2, Cl −1

(c) H_2O = H +1, O −2

(d) SO_2 = S +4, O −2

(e) Fe_2O_3 = Fe +3, O −2

(f) NO_3^- = N +5, O −2

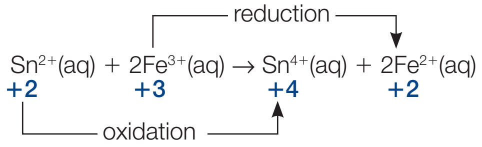
(g) MnO_2 = Mn +4, O −2

(h) PO_4^{3-} = P +5, O −2

(i) $K_2Cr_2O_7$ = K +1, Cr +7, O −2

(j) MnO_4^- = Mn +7, O −2

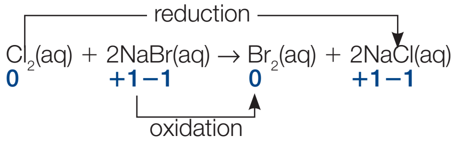
2 (a)



$Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

+2 +3 +4 +2

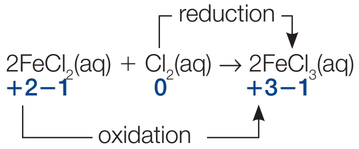
(b)



$Cl_2(aq) + 2NaBr(aq) \rightarrow Br_2(aq) + 2NaCl(aq)$

0 +1 −1 0 +1 −1

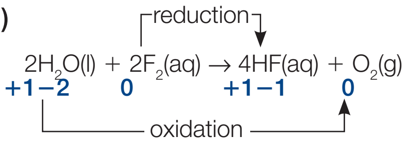
(c)



$2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

+2 −1 0 +3 −1

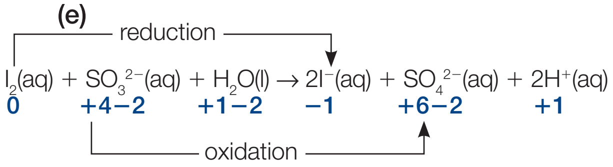
(d)



$2H_2O(l) + 2F_2(aq) \rightarrow 4HF(aq) + O_2(g)$

+1 −2 0 +1 −1 0

(e)



$I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

0 +4 −2 +1 −2 −1 +6 −2 +1

3 (a) $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$

0 +1 +2 0

oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$

reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

(b) $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

+2 0 +3 −1

oxidation: $2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2e^-$

reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

(c) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

+2 +3 +4 +2

oxidation: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

reduction: $2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$

(d) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

0 −1 −1 0

oxidation: $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

reduction: $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

4 (a) $Zn(s) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + SO_2(g) + 2H_2O(l)$

(b) $2I^-(aq) + HSO_4^-(aq) + 3H^+(aq) \rightarrow I_2(aq) + SO_2(g) + 2H_2O(l)$

(c) $NO_3^-(aq) + 4Zn(s) + 10H^+(aq) \rightarrow NH_4^+(aq) + 4Zn^{2+}(aq) + 3H_2O(l)$

(d) $I_2(aq) + 5OCl^-(aq) + H_2O(l) \rightarrow 2IO_3^-(aq) + 5Cl^-(aq) + 2H^+(aq)$

(e) $2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5SO_4^{2-}(aq) + 4H^+(aq)$

5 B 6 D

7 (a) chromium(III) oxide (b) copper(I) chloride

(c) nitric(V) acid (d) nitric(III) acid

(e) lead(IV) oxide

8 (a) reducing agent = $H_2(g)$; oxidizing agent = $Cl_2(g)$

(b) reducing agent = Al(s); oxidizing agent = $Pb^{2+}(s)$

(c) reducing agent = $I^-(aq)$; oxidizing agent = $Cl_2(aq)$

(d) reducing agent = $CH_4(g)$; oxidizing agent = $O_2(g)$

9 (a) $CuCl_2(aq) + Ag(s)$

No reaction, Cu is a more reactive metal than Ag.

(b) $3Fe(NO_3)_2(aq) + 2Al(s) \rightarrow 2Al(NO_3)_3(aq) + 3Fe(s)$

Al is a more reactive metal than Fe, so is able to reduce Fe^{2+}.

(c) $2NaI(aq) + Br_2(aq) \rightarrow 2NaBr(aq) + I_2(aq)$

Br is a more reactive non-metal than I, so is able to oxidize I^-.

(d) $KCl(aq) + I_2(aq)$

No reaction, Cl is a more reactive non-metal than I.

10 **(a)** $W > X > Y > Z$

(b) **(i)** no reaction

(ii) no reaction

11 **(a)** Solution changes from purple to colourless

(b) $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$

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

(d) $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

(e) 6.16×10^{-3} **(f)** 6.16×10^{-3}

(g) 24.7%

12 **(a)** 0.117%

(b) Solution changes from orange to green

13 **(a)** Zn / Zn^{2+} anode; Fe / Fe^{2+} cathode

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

(b) Fe / Fe^{2+} cathode; Mg / Mg^{2+} anode

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

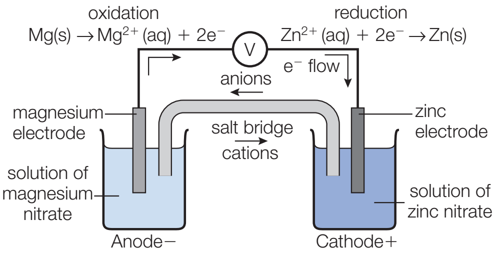
$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

(c) Mg / Mg^{2+} anode; Cu / Cu^{2+} cathode

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

14 **(a)**



(b) $Mg(s)|Mg^{2+}(aq)||Zn^{2+}(aq)|Zn(s)$

15 The iron spatula would slowly dissolve as it is oxidized to Fe^{2+} ions. Copper metal would precipitate as Cu^{2+} ions are reduced. The blue colour of the solution would fade as Cu^{2+} ions are removed.

16 $$E^\ominus_{cell} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$$
$$= E^\ominus_{Cd^{2+}} - E^\ominus_{Cr^{3+}} = -0.40 - (-0.75) = +0.35\text{ V}$$

17 BrO_3^- will be reduced (higher $E^\ominus$ value); I^- will be oxidized.

Cell reaction:

$BrO_3^-(aq) + 6H^+ + 6I^- \rightarrow Br^-(aq) + 3H_2O(l) + 3I_2(s)$

$E^\ominus_{cell} = E^\ominus_{BrO_3^-} - E^\ominus_{I_2} = +1.44 - (+0.54) = +0.90\text{ V}$

18 Strongest oxidizing agent Cu^{2+}; strongest reducing agent Mg.

19 **(a)** No reaction

(b) Reaction occurs

$BrO_3^-(aq) + 6H^+(aq) + 3Cd(s) \rightarrow Br^-(aq) + 3H_2O(l) + 3Cd^{2+}(aq)$

$E^\ominus_{cell} = E^\ominus_{BrO_3^-} - E^\ominus_{Cd^{2+}} = +1.44 - (-0.40) = 1.84\text{ V}$

(c) No reaction

20 −270 kJ

21 **(a)** At anode: $2Br^-(l) \rightarrow Br_2(l) + 2e^-$

At cathode: $2K^+(l) + 2e^- \rightarrow 2K(l)$

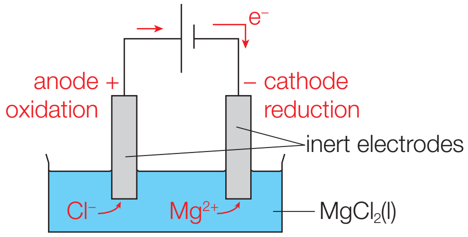
(b) At anode: $2F^-(l) \rightarrow F_2(g) + 2e^-$

At cathode: $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$

(c) At anode: $S^{2-}(l) \rightarrow S(l) + 2e^-$

At cathode: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$

22 **(a)**



(b) Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Cathode: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$

Overall: $Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(s) + Cl_2(g)$

23 D

24 Ions present: $K^+(aq)$, $F^-(aq)$

At anode: $F^-(aq)$ and $H_2O(l)$; $H_2O(l)$ will be oxidized.

Reaction occurring is $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

$H^+(aq)$ and $O_2(g)$ will be discharged at the anode.

At cathode: $K^+(aq)$ and $H_2O(l)$; $H_2O(l)$ will be reduced.

Reaction occurring is $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

$OH^-(aq)$ and $H_2(g)$ will be discharged at the cathode.

Products will be $O_2(g)$ and $H_2(g)$

This is because H_2O has a higher $E^\ominus$ than K^+ so is preferentially reduced at the cathode; H_2O has a higher $E^\ominus$ than F^- so is preferentially oxidized at the anode (assuming the concentration of F^- is not high enough to cause it to be discharged).

25 **(a)** At the anode, bubbles of gas emitted; at the cathode, pinky brown layer of copper metal deposited. The blue colour of the solution fades.

Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

or

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

depending on the concentration of the solution.

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Blue colour fades as the concentration of Cu^{2+} ions in solution decreases.

(b) Reaction at the cathode would be the same with copper deposited on the copper electrode.

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Reaction at the anode would be different:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

The copper electrode disintegrates as it is oxidized, releasing Cu^{2+} ions into the solution. The blue colour of the solution would not change as Cu^{2+} ions are produced and discharged at an equal rate.

26 During electrolysis of NaCl(aq) at the cathode H_2O is reduced (rather than Na^+, which is reduced in molten NaCl) and $H_2(g)$ is discharged:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

27 $AlCl_3(l) \rightarrow Al^{3+}(l) + 3Cl^-(l)$

$2Cl^-(l) \rightarrow \underset{\text{1 mole of } Cl_2}{Cl_2(g)} + \underset{\text{2 moles of electrons}}{2e^-}$ $\quad Al^{3+}(l) + \underset{\text{3 moles of electrons}}{3e^-} \rightarrow \underset{\text{1 mole of Al}}{Al(l)}$

So the same quantity of electricity will produce $Cl_2 : Al\ 3 : 2$

Therefore, yield of Al = 0.2 mol × 2/3 = 0.13 mol Al

Mass Al = 0.13 × *M*(Al) = 3.5 g

28 C

29 The mass of the silver anode will decrease as Ag is oxidized to Ag^+ ions that are released into the solution. The mass of the cathode (spoon) will increase as a layer of Ag is deposited. Impurities may be visible collecting as a sludge at the bottom of the electrolyte as they fall from the decomposing anode.

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1	B	**2**	B	**3**	D	**4**	C
5	C	**6**	C	**7**	A	**8**	A
9	B	**10**	A	**11**	C		

12 **(a)** **(i)** The voltage obtained when the half-cell is connected to the standard hydrogen electrode;

Under standard conditions of 298K and 1 mol dm^{-3} solutions;

Electrons flow (in the external circuit) from the half-cell to the hydrogen electrode / the metal in the half-cell is above hydrogen in the ECS / Fe is a better reducing agent than H_2 / Fe is oxidized more readily than H_2 [3]

(ii) −0.28 V [1]

(iii) Co^{2+} / cobalt(II) ion [1]

(iv) $2Al + 3Fe^{2+} \rightarrow 3Fe + 2Al^{3+}$ [2]

*Award **[1]** for correct reactants and products and **[1]** for correctly balanced; ignore states. Do not accept ⇌.*

(v) To complete the electrical circuit / *OWTTE*;

by allowing the movement of ions [2]

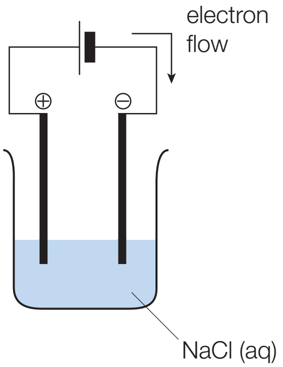
(b) **(i)** +2 [1]

(ii) +3 [1]

(iii) +2 [1]

Only penalize once if roman numerals are used or if written as 2+ or 3+.

(c) **(i)**



battery / source of electricity connected to two electrodes in the solution with positive **and** negative electrodes correctly labelled;

electrons / current flowing from the cell to the negative electrode;

labelled solution of sodium chloride [3]

*If the connecting wires to electrodes are immersed in the solution **[1 max]**.*

(ii) Na^+, H^+/H^3O^+, Cl^-, OH^- [2 max]

*All four correct **[2]**, any 3 correct **[1]**.*

(iii) hydrogen at (–)/cathode **and** oxygen at (+)/anode

$2H^+ + 2e^- \rightarrow H_2$ / $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ / $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ [3]

*Accept e instead of e⁻; if electrodes omitted or wrong way round **[2 max]**.*

(iv) ratio of $H_2 : O_2$ is 2 : 1 [1]

(d) **(i)** (–)/(cathode) $2H^+ + 2e^- \rightarrow H_2$ / $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

(+)/(anode) $2Cl^- \rightarrow Cl_2 + 2e^-$ [2]

*Accept e instead of e⁻; if electrodes omitted or wrong way round **[1 max]**.*

(ii) (–)/(cathode) $Na^+ + e^- \rightarrow Na$

(+)/(anode) $2Br^- \rightarrow Br_2 + 2e^-$ [2]

*Accept e instead of e⁻; if electrodes omitted or wrong way round **[1 max]**.*

13 **(a)** Electrolytic cell converts electrical energy to chemical energy **and** voltaic cell converts chemical energy to electrical energy / electrolytic cell uses electricity to carry out a (redox) chemical reaction **and** voltaic cell uses a (redox) chemical reaction to produce electricity / electrolytic cell requires a power supply **and** voltaic cell does not.

Electrolytic cell involves a non-spontaneous (redox) reaction **and** voltaic cell involves a spontaneous (redox) reaction.

In an electrolytic cell, cathode is negative and anode is positive **and** *vice versa* for a voltaic cell / electrolytic cell, anode is positive and voltaic cell, anode is negative / electrolytic cell, cathode is negative and voltaic cell cathode is positive.

Voltaic cell has two separate solutions and electrolytic cell has one solution / voltaic cell has salt bridge and electrolytic cell has no salt bridge.

Electrolytic cell, oxidation occurs at the positive electrode/anode **and** voltaic cell, oxidation occurs at the negative electrode/anode and vice versa. [2 max]

(b) (solid) ions in a lattice / ions cannot move

(molten) ions mobile / ions free to move [2]

(c) Reduction occurs at the cathode / negative electrode **and** oxidation occurs at the anode / positive electrode

Cathode / negative electrode: $Na^+ + e^- \rightarrow Na$

Anode / positive electrode: $2Cl \rightarrow Cl_2 + 2e^-$/ $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

*Award **[1 max]** if the two electrodes are not labelled/labelled incorrectly for the two half-equations.*

Overall cell reaction: $Na^+(l) + Cl^-(l) \rightarrow Na(s) + \frac{1}{2}Cl_2(g)$ [5]

*Award **[1]** for correct equation and **[1]** for correct state symbols.*

Allow NaCl(l) instead of $Na^+(l)$ and $Cl^-(l)$.

(d) Al does not corrode / rust; Al is less dense / better conductor / more malleable [1]

Accept Al is lighter (metal compared to Fe).

Accept converse argument.

(e) Cathode / negative electrode

Object to be plated

Allow a specific example here, e.g. spoon.

Accept inert metal / graphite.

Do not accept silver halides or their formulae.

Anode / positive electrode

Silver / Ag

Electrolyte: $[Ag(CN)_2]^-$ [3]

Allow silver nitrate / $AgNO_3$ / silver cyanide / any other suitable silver salt/solution.

Do not accept AgCl.

14 **(a)** $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ [2]

*Correct reactants and products, award **[1]**.*

*Balancing award **[1]**.*

Ignore state symbols and equilibrium sign.

(b) (+) 1.40 (V) [1]

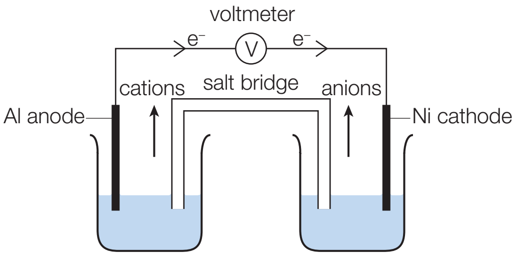
(c) aluminium anode / negative electrode

nickel cathode / positive electrode

electron movement from Al to Ni

correct movement of cations and anions through salt bridge [4]

If electron movement shown correctly but not labelled, award the mark.



Challenge yourself

1 H_2O_2 : H = +1, O = −1

Oxygen is halfway between 0 (element) and −2 (usual oxidation state in compounds), so can be oxidized (to 0) or reduced (to −2). It will more easily be reduced from −1 to −2 as it is a very electronegative element, and so acts mainly as an oxidizing agent.

2 $Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$

Cl changes from 0 to −1 (reduction)

Cl changes from 0 to +1 (oxidation)

Both changes occur simultaneously.

3 Iodine solution contains the triiodide ion, I_3^-, in which the central atom has five electron domains with two bonding and three non-bonding pairs in the equatorial plane. This gives a linear ion with a low charge density, which is able to slip into the coils of the hydrophobic interior of the amylose helix.

4 Solubility of gases decreases with increasing temperature as evaporation is higher. So the discharge of hot water will lower the dissolved O_2 content.

5 Charge per e^- = 1.602189×10^{-19} C

Electrons per mole = 6.02×10^{23} mol⁻¹

Therefore, charge per mole = $1.602189 \times 10^{-19}\ C \times 6.02 \times 10^{23}\ mol^{-1} = 96451.78\ C\ mol^{-1}$

6 $\Delta G = -RT \ln K_c$ and $\Delta G = -nFE_{cell}$

Therefore $E_{cell} = \dfrac{RT \ln K_c}{nF}$

Expressing in terms of $\log_{10}$ and combining all constants at 298 K:

$$E_{cell} = \frac{0.0592}{n} \log_{10} K_c$$

Answers

Chapter 10

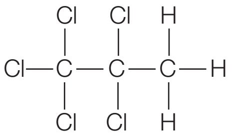
Exercises

1 **(a)** carboxylic acid; butanoic acid
  (b) halogenoalkane; 1,1-dichloropropane
  (c) ketone; butanone
  (d) ester; methyl ethanoate
  (e) ether; methoxyethane
  (f) ester; ethyl pentanoate

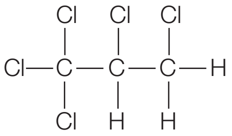
2 **(a)** $CH_3(CH_2)_4COOH$
  (b) $CH_3CH_2CH_2CHO$
  (c) $CH_2CH(CH_2)_2CH_3$
  (d) $CH_2BrCH(CH_3)C_2H_5$
  or $CH_2BrCH(CH_3)CH_2CH_3$
  (e) $HCOOCH_2CH_3$
  (f) $CH_3OCH_2CH_2CH_3$
  (g) $CH_3C{\equiv}CCH_3$

3 A **4** D

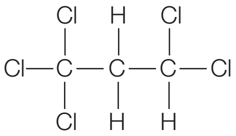
5



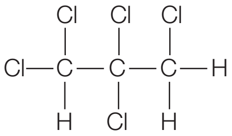
1,1,1,2,2-pentachloropropane



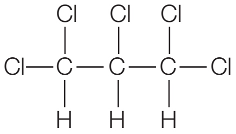
1,1,1,2,3-pentachloropropane



1,1,1,3,3-pentachloropropane



1,1,2,2,3-pentachloropropane



1,1,2,3,3-pentachloropropane

6 B

7 Benzene is a cyclic molecule with a planar framework of single bonds between the six carbon atoms and six hydrogen atoms. The carbon atoms are also bonded to each other by a delocalized cloud of electrons which forms a symmetrical region of electron density above and below the plane of the ring. This is a very stable arrangement, so benzene has much lower energy than would be expected.

8 **(a)** Similar molar mass will mean molecules have approximately equal London (dispersion) forces and so differences in boiling point can be attributed to differences in dipole–dipole or hydrogen bonding.
  (b) Solubility in hexane will increase with increasing chain length as the non-polar part of the molecule makes a larger contribution to its structure.

9 **(a)** $C_5H_{14}(l) + 6O_2(g) \rightarrow 5CO(g) + 7H_2O(l)$
  (b) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$
  (c) $C_3H_4(g) + O_2(g) \rightarrow 3C(s) + 2H_2O(l)$

10 Bromine + ethane

initiation

$Br_2 \xrightarrow{\text{UV light}} 2Br^{\bullet}$ bromine radicals

propagation

$Br^{\bullet} + C_2H_6 \rightarrow C_2H_5^{\bullet} + HBr$
$C_2H_5^{\bullet} + Br_2 \rightarrow C_2H_5Br + Br^{\bullet}$
$C_2H_5Br + Br^{\bullet} \rightarrow C_2H_4Br^{\bullet} + HBr$
$C_2H_4Br^{\bullet} + Br_2 \rightarrow C_2H_4Br_2 + Br^{\cdot}$

termination

$Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$
$C_2H_5^{\bullet} + Br^{\bullet} \rightarrow C_2H_5Br$
$C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_4H_{10}$

Overall, these reactions show how a mixture of products is formed.

11 **(a)** $CH_3CH_2CH_2CH_3$ butane

(b) $CH_3CH_2CH(OH)CH_3$ butan-2-ol

(c) $CH_3CH_2CHBrCH_3$ 2-bromobutane

12 **(a)** No observable change.

(b) Burns with very smoky flame.

(c) The bromine water changes from brown to colourless.

13 **(a)** $C_2H_5OH(l) + 3O_2 \rightarrow 2CO_2(g) + 3H_2O(l)$

$2C_3H_7OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)$

(b) $C_2H_5COOH(aq) + C_4H_9OH(aq) \rightarrow C_2H_5COOC_4H_9(aq) + H_2O(l)$

14 **(a)** butanone; orange → green

(b) methanal; orange → green

(c) no reaction; no colour change

15 Nucleophilic substitution involves an electron-rich species (e.g. OH^-) attacking an electron-deficient carbon atom (e.g. in chloroethane), leading to substitution of the halogen functional group by the nucleophile.

$C_2H_5Cl + OH^- \rightarrow C_2H_5OH + Cl^-$

16 Benzene has a very stable structure as a result of its symmetrical ring of delocalized electrons. Addition reactions would involve breaking this ring and therefore decreasing its stability. Substitution reactions in which one or more hydrogen atoms of the ring are replaced by other atoms or groups preserves the aromatic ring structure and therefore its stability.

17 **(a)** $CH_3CH_2CH_2CH_2Br$ primary

$CH_3CH_2CHBrCH_3$ secondary

$C(CH_3)_3Br$ tertiary

(b) The tertiary halogenoalkane reacts by an S_N1 mechanism.

S = substitution; N = nucleophilic; 1 = unimolecular

(c) $RBr \rightarrow R^+ + Br^-$

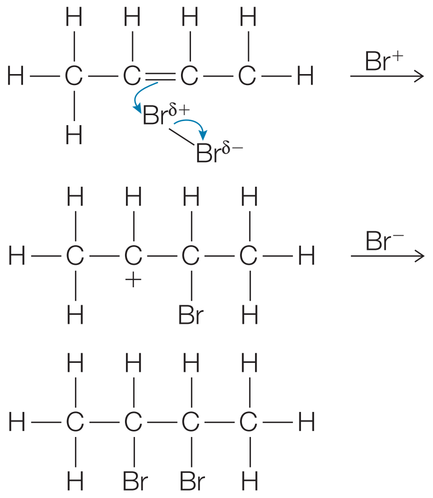
18 C

19 **(a)** The carbon–halogen bond breaks more easily in the iodo- and bromo- derivatives than in the chloro- derivatives, so these compounds more readily undergo substitution reactions.

(b) The substitution reaction of OH for Cl occurs in both these compounds, displacing Cl^- and forming the white precipitate of AgCl, which darkens on exposure to air. The tertiary halogenoalkane $C(CH_3)_3Cl$ isomer reacts more quickly than the primary isomer $CH_3CH_2CH_2CH_2Cl$ because it undergoes an S_N1 mechanism, which is faster.

20 Alkenes have a double bond which is an electron-dense region and so is susceptible to attack by electrophiles which are themselves electron deficient. They undergo addition reactions because they are unsaturated; one of the bonds in the double bond breaks and incoming groups can add to the two carbon atoms.

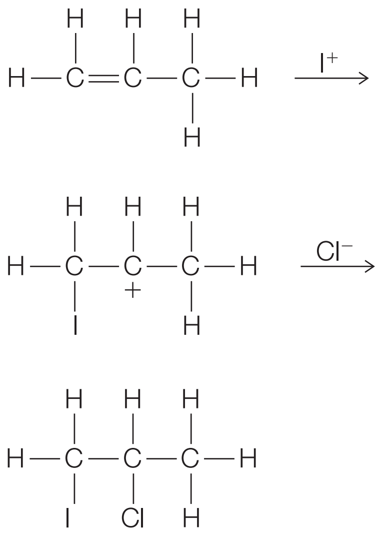
When bromine approaches but-2-ene, it is polarized by the electron density in the double bond. Electrons in the bromine–bromine bond are repelled away from the double bond, leading to the heterolytic fission of the bromine molecule. The Br^+ product now attaches itself to one of the carbon atoms as the carbon–carbon bond breaks. This produces an unstable carbocation which then rapidly reacts with the Br^- ion. The product is 2,3-dibromobutane.



21 But-1-ene + HBr → 2-bromobutane

Application of Markovnikov's rule enables us to predict that the electrophile H^+ will add to the terminal carbon, forming a secondary carbocation, as this is stabilized by the positive inductive effect of the alkyl groups. Br^- will then add to carbon 2, forming 2-bromobutane.

22 ICl is polarized: $I^{\delta+}Cl^{\delta-}$ owing to the greater electronegativity of Cl than I. So when it undergoes heterolytic fission it will form I^+ and Cl^-. By application of Markovnikov's rule, the I^+ will attach to the terminal carbon, while Cl^- will add to carbon 2. The product is therefore 1-iodo-2-chloropropane.



23 Concentrated H_2SO_4 and concentrated HNO_3. The stronger acid H_2SO_4 protonates the HNO_3, leading to production of the nitronium ion NO_2^+. This is a strong electrophile which reacts with the π electrons of the benzene ring, substituting for H.

24 **(a)** Use $LiAlH_4$ in dry ether and heat. The acid is reduced first to the aldehyde and then to the alcohol.

$$CH_3CH_2COOH \xrightarrow{[+H]} C_2H_5CH_2OH$$

(b) Nitrobenzene is heated under reflux with tin and concentrated HCl, and the product is reacted with NaOH.

$$C_6H_5NO_2 \xrightarrow{[+H]} C_6H_5NH_2$$

(c) Ethanal is heated with $NaBH_4$(aq).

$$CH_3CHO \xrightarrow{[+H]} CH_3CH_2OH$$

25 Start with ethanol. Take one portion and oxidize it using acidified potassium(VI) dichromate solution and heat under reflux to allow the reaction to go to completion.

$$C_2H_5OH \xrightarrow{[+O]} CH_3COOH$$

The product is ethanoic acid.

React the ethanoic acid product with another portion of the ethanol by warming it in the presence of some concentrated H_2SO_4. The esterification reaction yields ethyl ethanoate.

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5$$

26 React the 1-chlorobutane with NaOH in warm aqueous solution to convert it into butan-1-ol.

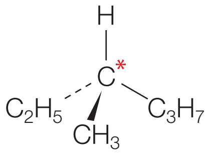
$$C_4H_9Cl + NaOH \rightarrow C_4H_9OH + NaCl$$

Oxidize the butan-1-ol using acidified potassium(VI) dichromate solution and heat under reflux to allow the reaction to go to completion.

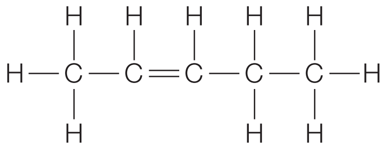
$$C_4H_9OH \xrightarrow{[+O]} C_3H_7COOH$$

27 C

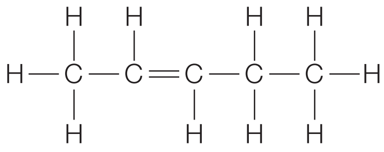
28 3-methylhexane: $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$



29 **(a)**

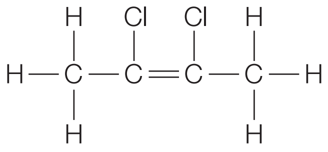


Z-pent-2-ene

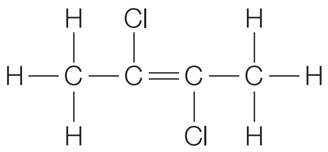


E-pent-2-ene

(b)



Z-2,3-dichlorobut-2-ene



E-2,3-dichlorobut-2-ene

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1	C	**2**	C	**3**	D	**4**	A
5	A	**6**	A	**7**	B	**8**	C
9	B	**10**	B	**11**	A	**12**	C
13	A	**14**	D				

15 **(a)** A: 1-bromobutane

B: 2-bromobutane

C: 2-bromo-2-methylpropane

D: 1-bromo-2-methylpropane [4]

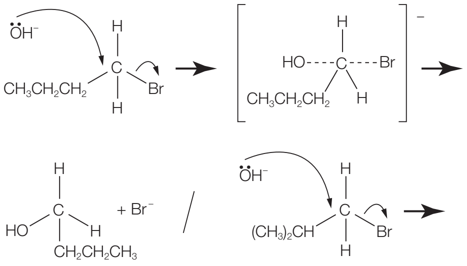
Penalize incorrect punctuation, e.g. commas for hyphens, only once. Accept 2-bromomethylpropane and 1-bromomethylpropane for C and D respectively.

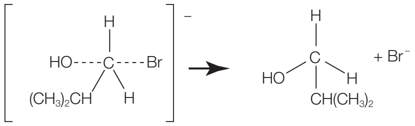
(b) **(i)** C / 2-bromo-2-methylpropane; unimolecular nucleophilic substitution [2]

(ii) $RBr \rightarrow R^+ + Br^-$ [1]

Allow use of 2-bromo-2-methylpropane instead of RBr.

(iii) A / 1-bromobutane / D / 1-bromo-2-methylpropane





curly arrow going from lone pair/negative charge on O in OH^- to C

Do not allow curly arrow originating on H in OH^-.

curly arrow showing Br leaving

Accept curly arrow either going from bond between C and Br to Br in 1-bromobutane or in the transition state.

representation of transition state showing negative charge, square brackets and partial bonds [4]

Do not penalize if HO and Br are not at 180° to each other.

Do not award fourth mark if OH–C bond is represented.

(c) (b) (i) no change as $[OH^-]$ does not appear in the rate equation / in the rate determining step

(b) (iii) rate doubles as the rate is proportional to $[OH^-]$ / OH^- appears in the rate-determining / slow step / first order with respect to OH^- [2]

Award [1] if correctly predicts no rate change for S_N1 and doubling of rate for S_N2 without suitable explanation.

(d) rate of 1-bromobutane is faster; C–Br bond is weaker / breaks more easily than C–Cl bond [2]

(e) 2-bromobutane / B; (plane-) polarized light shone through; enantiomers rotate plane of plane-polarized light to left or right / opposite directions (by same amount)

Accept 'turn' instead of 'rotate' but not 'bend'/'reflect'.

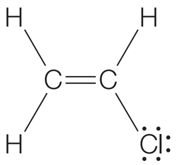
Physical properties identical (apart from effect on plane-polarized light); chemical properties are identical (except with other chiral compounds) [5]

Do not accept 'similar' in place of 'identical'.

16 **(a)** Colour change from yellow / orange / rust colour / red / brown to colourless [1]

No mark for change to clear, or for decolorized with no reference to original colour.

(b) Chloroethene:



No mark if the lone pairs are missing on Cl. Accept lines, dots or crosses for e⁻ pairs.

Poly(chloroethene):

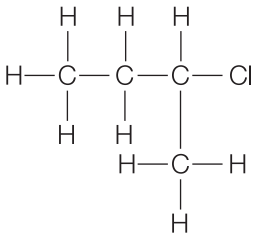
$-\!\!\left[CH_2 - CHCl \right]\!\!-_n$ [2]

n and square brackets are not required. Continuation bonds must be shown.

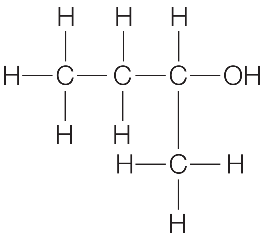
(c) (hydration of ethene for the manufacture of) ethanol / $C_2H_4 + H_2O \rightarrow C_2H_5OH$; (synthesis of) CH_3COOH / ethanoic / acetic acid; (synthesis of) ethylene glycol / 1,2-ethanediol / ethane-1,2-diol; (synthesis of) drugs / pesticides; (hydrogenation of unsaturated oils in the manufacture of) margarine [2 max]

Accept other commercial applications.

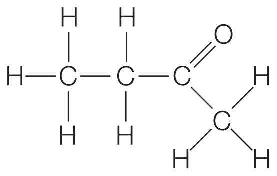
17 **(a)** **A:**



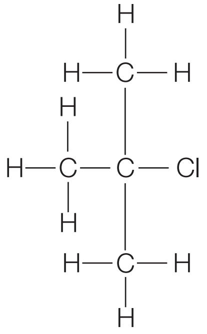
B:



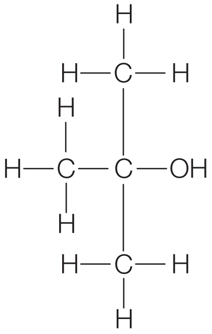
C:



D:



E:



Accept condensed formulas. [5]

*Award **[1 max]** if **A** and **D** are other way round (and nothing else correct). Award **[2 max]** if **A** and **D** are other way round but one substitution product **B** or **E** is correct based on initial choice of **A** and **D**. Award **[3 max]** if **A** and **D** are other way round but both substitution products **B** and **E** are correct based on initial choice of **A** and **D**. M2 (for **B**) and M5 (for **E**) may also be scored for substitution product if primary chloroalkane used. Penalize missing hydrogens once only.*

(b) $CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$

***[1]** for reactants and **[1]** for products.*

(concentrated) sulfuric acid / H_2SO_4

Do not accept just H^+ or acid.

methyl propanoate [4]

Challenge yourself

1 All four C atoms in the molecule are sp^3 hybridized because they form four single bonds which are tetrahedrally arranged. The nitrogen atom is also sp^3 hybridized, as its four electron domains are also tetrahedrally arranged. Note that here the hybridization also includes the lone pair on the nitrogen atom.

2 Complete combustion:

$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

C: $-3 \rightarrow +4$

Incomplete combustion:

$2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$

C: $-3 \rightarrow +2$

3 *Hetero*lytic describes breaking of the bond, producing two *different* products. The products are ions, and the reaction mechanism involves attraction of the electron density of the C=C double bond to the positive ion.

4 The repeating unit in polystyrene is

$-CH(C_6H_5)-CH_2-$

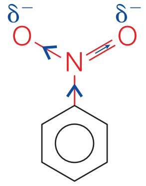
5 The cyanide ion, CN^-, and ammonia, NH_3, are nucleophiles that react with halogenoalkanes in substitution reactions. They act as ligands with transition metal ions, forming complexes such as $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(CN)_4]^{3-}$. They act as Lewis bases by donating a lone pair of electrons. For example:

$NH_3 + BCl_3 \rightarrow NH_3BCl_3$

6 The order of the reaction with respect to each reactant can be deduced from experiments in which the concentration of each reactant in turn is changed, and the initial rate of the reaction then measured. If, for example, the concentration of halogenoalkane is doubled while the concentration of OH^- remains constant, and the rate is found to have doubled, then it indicates that the reaction is first order with respect to halogenoalkane. Examples of this type of experiment and the interpretation of the results are given in Chapter 6.

7 With bromine water, the water can also take part in the second part of the reaction because of its lone pairs. The carbocation is attacked by water in competition with Br^-, and the major product is 2-bromoethanol, CH_2BrCH_2OH. The bromine water is decolorized from brown. The relative concentration of bromoethanol and 1,2-dibromoethane depends on the strength of the bromine water used.

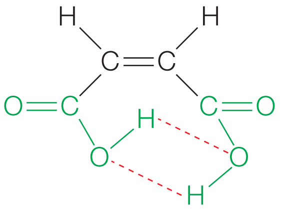
8 The $-NH_2$ group in phenylamine is electron donating due to conjugation of the lone pair of electrons on N with the ring electrons. As a result, the electron density of the ring is increased, making it more susceptible to electrophilic attack. In contrast, the $-NO_2$ group in nitrobenzene is electron withdrawing due to the electronegativity of the nitrogen and oxygen atoms.



Also, the electrons in its double bond conjugate with the π electrons in the ring, causing the electron density of the ring to be decreased, making it less susceptible to electrophilic attack.

9 In both square planar and octahedral compounds, geometric isomers can arise due to groups having the possibility of being in adjacent (*cis*) or in across (*trans*) positions. In tetrahedral compounds, all positions are adjacent to each other, so these isomers are not possible.

10



cis-butenedioic acid
melting point 139 °C

The *cis* isomer, maleic acid, has a lower melting point as it forms fewer intermolecular bonds. The *cis* isomer is much more soluble in water than the *trans* isomer, and its density is less. *cis*-Butenedioic acid is a stronger acid because when H^+ is lost, the *cis* anion is more stable than the *trans* form.

Answers

Chapter 11

Exercises

1 The smallest division is 1 so the uncertainty is ±0.5.

2 The missing diamond has a mass of between 9.87 and 9.97 g.

The found diamond has a mass between 9.9 and 10.3 g.

As the ranges overlap, it **could** be the missing diamond.

3 **(a)** 4×10^{-2} g **(b)** 2.22×10^{2} cm^3

(c) 3.0×10^{-2} g

(d) 3×10 or 3.0×10 °C (unspecified)

4 **(a)** 4 **(b)** unspecified

(c) 3 **(d)** 4

5 A **6** A **7** D **8** A

9 A **10** D **11** C

12 The average value = 49.0 s

The uncertainty in the measurements is given as ±0.1 s but the results show that there is additional uncertainty, suggesting that the value could be anywhere between 48.8 and 49.2 s. So the value could be quoted as 49.0 s ± 0.2 s.

13 Note that the correct solution to this question is not one of the possible answers listed. The temperature change expressed to the appropriate precision is 2.050 ± 0.050 K.

14 D **15** B **16** B **17** C

18 A **19** C

20 Number of moles = concentration × volume/1000

= 1.00 × 10.0/1000 = 0.0100 mol

% uncertainty in concentration = (0.05/1.00) × 100 = 5%

% uncertainty in volume = (0.1/10.0) × 100 = 1%

% uncertainty in number of moles = 5% + 1% = 6%

Absolute uncertainty in number of moles = (6/100) × 0.0100 = 0.0006

Number of moles = 0.0100 ± 0.0006 mol

21 **(a)** $\Delta T = 43.2 - 21.2\,°C = 22.0\,°C$

absolute uncertainty = (±)0.2 °C

(b) % uncertainty = 0.2/22.0 × 100% ≈ 1%

(c) $\Delta H = -4.18 \times 22.0/0.500 = -184$ kJ mol^{-1}

(d) 1%

(e) Absolute uncertainty = 1/100 × 184 = (±) 2 kJ mol^{-1}

(f) Experimental value for $\Delta H = -184$ (±) 2 kJ mol^{-1}

The literature value is outside this range.

The random errors involved in reading the thermometer do not account for this difference.

There are systematic errors. The assumptions on which the calculation is based are not strictly valid. Some of the heat of reaction passes into the surroundings and the other uncertainties in the measurements cannot be ignored. It should also be noted that the standard value for ΔH refers to standard conditions of 298 K and 100 kPa.

22 B

23 The scale of the graph does not allow us to distinguish whether A or B is the best answer and both are acceptable.

24 B

25 Concentration of chromium (from graph for absorbance of 0.215) = 3.34 μg dm^{-3}

26 B **27** C **28** C

29 A (the spectrum on the left) corresponds to CH_3CH_2CHO

B (the spectrum on the right) corresponds to CH_3COCH_3

Similarities

Both have a molecular ion corresponding to 58.

Differences

A has peaks corresponding to 29 ($CH_3CH_2^+$) and 28 (loss of CH_3CH_2).

B has a peak corresponding to 43 (loss of CH_3).

30 **(a)**

Mass / charge	Fragment
15	CH_3^+
29	$C_2H_5^+$
43	$C_3H_7^+$ (loss of CH_3)
58	$C_4H_{10}^+$

(b) $CH_3CH_2CH_2CH_3$

31

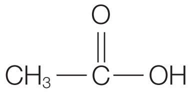
Molecule	Corresponding saturated non-cyclic molecule	IHD
C_6H_6	C_6H_{14}	4
CH_3COCH_3	C_3H_8O	2
$C_7H_6O_2$	$C_7H_{16}O$	5
C_2H_3Cl	C_2H_5Cl	1
C_4H_9N	$C_4H_9NH_2$	1
$C_6H_{12}O_6$	$C_6H_{14}O_6$	1

32 B **33** D **34** B

35 **(a)** Empirical formula CH_2O. Molecular formula $C_2H_4O_2$.

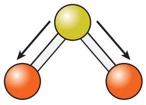
(b) IHD = 1

(c)

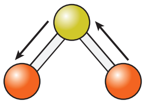


$CH_3-\overset{\overset{O}{\|}}{C}-OH$

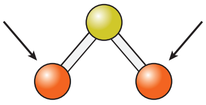
36



symmetric stretch
IR active



asymmetric stretch
IR active



symmetric bend
IR active

37 B

38 The polarity (of bond or molecule) changes as the bonds are bent or stretched.

39 Hex-1-ene shows an absorption in the range 1610–1680 cm^{-1} due to the presence of the C=C bond.

40 C—H bond

41 CH_3OCH_3

42 C **43** A

44 **(a)** 2 **(b)** 1

(c) 1 **(d)** 2

45 The H atoms are in three different environments so there will be three peaks in the ^1H NMR spectrum with integrated areas in the ratio 3:2:1.

46 **(a)** $CH_3COCH_2CH_3$

(b)

Type of hydrogen atom	Chemical shift / ppm	No. of H atoms	Splitting pattern
CH_3CO	2.2–2.7	3	1
$COCH_2CH_3$	2.2–2.7	2	4
CH_2CH_3	0.9–1.0	3	3

47

Compound	Number of peaks	Chemical shift / ppm	No. of H atoms	Splitting pattern
CH_3CHO	2	2.2–2.7	3	2
		9.4–10.0	1	4
CH_3COCH_3	1	2.1	6	1

48 Possible structures: CH_3CH_2COOH, CH_3COOCH_3, $HCOOCH_2CH_3$.

The peak at 8.0 ppm corresponds to R—COO**H**. There is no splitting as there are no hydrogen atoms bonded to neighbouring carbon atoms.

The peak at 1.3 ppm corresponds to a CH_3 group. The peak is split into a triplet because there is a neighbouring CH_2 group.

The peak at 4.3 ppm corresponds to the R—**CH_2**—COO group. The peak is split into a quartet as there is a neighbouring CH_3 group.

Molecular structure: CH_3CH_2COOH

49 X-ray crystallography.

50 Monochromatic means all the X-rays have the same wavelength.

The angle of diffraction depends on the wavelength. If the X-rays have different wavelengths, different diffraction angles/pattern would be obtained. It would be impossible to match the angles with the wavelengths.

51 Hydrogen atoms have a low electron density.

52 The atoms must have a regular arrangement if an ordered diffraction pattern is to be produced.

53 **(a)** $C_6H_5CH_3$

(b) Hydrogen atoms do not appear because of their low electron density

(c) The saturated non-cyclic compound is C_7H_{16}

IHD = $\frac{1}{2}(16 - 8) = 4$ (the IHD of a benzene ring = 4)

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 B **2** C **3** C **4** A

5 **(a)** *Compound:*

$CH_3—CH_2—CHO$

Explanation: ***[1 max]***

only this compound would give 3 peaks / *OWTTE*

only this compound has H atoms in 3 different chemical environments / *OWTTE*

only this compound has protons in ratio 3:2:1 in each environment / *OWTTE*

only this compound would give a peak in the 9.4–10 ppm region / *OWTTE* [2 max]

(b) 2.5 ppm peak

$CH_3—CO—CH_3$ also has hydrogen atoms on a carbon next to the >C=O group [2]

(c) **(i)** 1700–1750 cm^{-1} (>C=O) [1]

(ii) 1610–1680 cm^{-1} (>C=C<) / 3200–3600 cm^{-1} (—O—H) [1]

(d) $C_3H_6O^+$ **and** $m/z = 58$

$C_2H_5^+$ **and** $m/z = 29$

CHO^+ **and** $m/z = 29$

CH_3^+ **and** $m/z = 15$ [2 max]

Penalize missing + sign once only.

6 **(a)** (stretches/vibrations in) HBr involve change in bond dipole / (stretches/vibrations in) Br_2 do not involve change in bond dipole [1]

(b) **(i)** I: O—H

II: C—H

III: C=O [3]

Award ***[2]*** *for C—H for I and O—H for II.*

(ii) *m/z 102:* molecular ion peak / $(CH_3)_3CCOOH^+$ / $C_5H_{10}O^+$ / M^+

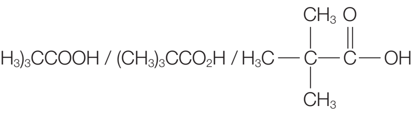
m/z 57: $(CH_3)_3C^+$ / $(M—COOH)^+$ / $C_4H_9^+$

m/z 45: $COOH^+$ [3]

Penalize missing + once only.

(iii) (H of) COOH group [1]

(iv) nine hydrogens in the same environment / $(CH_3)_3C–$ (group) [1]

(v) $(CH_3)_3CCOOH$ / $(CH_3)_3CCO_2H$ /  [1]

$H_3C—C(CH_3)_2—C(=O)—OH$

(vi) no peak at 11.5 ppm in spectrum of isomer / different chemical shift values

four peaks (instead of two) / different number of peaks;

Three of these peaks can be split in actual spectrum, so allow for this in answers if exactly four peaks is not stated.

different integration trace / different areas under the peaks / integration trace would have a 3:2:2:3 peak area ratio [2 max]

Do not award mark if incorrect peak area ratios are given for the structure drawn in (v).

7 change in bond length / bond stretching / asymmetric stretch

change in bond angle / bending (of molecule)

Allow ***[1 max]*** *for only stating vibrations.*

induces molecular polarity / dipole moment / *OWTTE* [3]

8 **(a)** A: O—H

B: C═O

C: C—O

*Award **[2]** for three correct, **[1]** for two correct.* [2]

(b) *m/z* = 74: $C_2H_5COOH^+$ / $C_3H_6O_2^+$

m/z = 45: $COOH^+$

m/z = 29: $C_2H_5^+$

Penalize missing + charge once only.

Do not award mark for m/z = 29: CHO^+. [3]

(c) —COOH [1]

(d) CH_3CH_2COOH / $CH_3CH_2CO_2H$

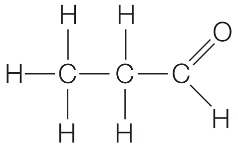
More detailed structural formula may be given. [1]

9 **(a)** absence of peak between 3200 and 3600 cm^{-1} / above 3000 cm^{-1} / peak for OH

presence of peak between 1700 and 1750 cm^{-1} / peak for C═O

absence of peak between 1610 and 1680 cm^{-1} / peak for C═C [2 max]

(b)



Accept CH_3CH_2CHO.

3:2:1

Ignore order.

ECF if structure is incorrect only if its NMR spectrum contains three peaks. [2]

10 **(a)** **(i)** (2-)methylpropan-2-ol

the (H atoms in the three) —CH_3 groups are responsible for the peak at 1.3 ppm

the —O**H** hydrogen atom is responsible for the peak at 2.0 ppm

Accept explanations with suitable diagram. [3]

(ii) (2-)methylpropan-1-ol

the first peak (at 0.9 ppm) is due to the (H atoms in the) two —CH_3 groups (bonded to the second carbon atom) / $(C\mathbf{H}_3)_2CHCH_2OH$

the peak at 3.4 ppm is due to the (H atoms in the) —CH_2— group / $(CH_3)_2CHC\mathbf{H}_2OH$

Accept explanations with suitable diagram. [3]

(b) **(i)** butan-1-ol and butan-2-ol

74: M^+ / $C_4H_{10}O^+$ / $CH_3CH_2CH_2CH_2OH^+$ **and** $CH_3CH_2CH(OH)CH_3^+$

59: $C_3H_7O^+$ / $(M - CH_3)^+$ / $CH_2CH_2CH_2OH^+$ **and** $CH_2CH(OH)CH_3^+$ / $CH_3CH_2CH(OH)^+$

45: $C_2H_5O^+$ / $(M - C_2H_5)^+$ / $CH_2CH_2OH^+$ **and** $CH(OH)CH_3^+$

Accept explained answers instead of formulas. [4]

(ii) butan-1-ol

CH_2OH^+ / $(M - C_3H_7)^+$

Penalize missing + signs once only in parts (b)(i) and (ii). [2]

(c) they all contain O—H

they all contain C—H

they all contain C—O

*Award **[1 max]** for same functional groups/ bonds.* [2 max]

11 D could be $CH_3CH_2COOCH_3$ or $CH_3COOCH_2CH_3$

this is because there are 3 peaks / 3:2:3 ratio

explanation of splitting into a singlet, a triplet and a quartet

methyl propanoate / $CH_3CH_2COOCH_3$ is correct isomer because of higher chemical shift value of singlet (3.6 instead of 2.0–2.5) [4]

12 **(a)** **(i)** 88

Do not award mark if units are given.

$C_4H_8O_2^+$ [2]

(ii) $CH_3CH_2^+$ /$C_2H_5^+$ / CHO^+

Only penalize once for missing charge in (a)(i) and (ii). [1]

(iii) $C_2H_3O_2$ produced has no charge / fragment produced after loss of C_2H_5 from molecular ion has no charge

Accept fragment(s) too unstable, fragment breaks up etc.

Do not accept answers with reference to $^{13}C/^{14}C$ isotopes and peak at m/z = 61.

Do not accept $C_2H_3O_2^+$ / $C_3H_7O^+$ does not exist. [1]

(b) (i) A: C=O **and** B: C—O

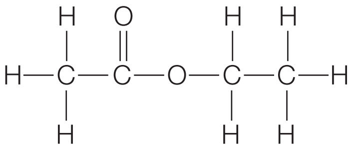
No mark if two bonds are given for A or B.

Ignore names if incorrect. [1]

(ii) ester

Do not accept COO. [1]

(c) (i) [1]



/

$CH_3CO_2CH_2CH_3$

(ii) [3]

Peak	Chemical shift / ppm	Relative peak area	Splitting pattern
first	2.0	3	singlet
second	4.1	2	quartet
third	0.9–1.0	3	triplet

(iii) (quartet means) neighbouring C:

has 3 H atoms [2]

Challenge yourself

1 $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2\times(-2)) + (-1\times(-1)) + 0 + (1\times 1) + (2\times 2)}{(-2)^2 + (-1)^2 + 0^2 + 1^2 + 2^2}$$

$$= 1$$

2 $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2\times 2) + (-1\times 1) + 0 + (1\times(-1)) + (2\times(-2))}{(-2)^2 + (-1)^2 + 0^2 + 1^2 + 2^2}$$

$$= -1$$

3 $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2\times(-2)) + (-1\times 2) + 0 + (1\times 1) + (2\times(-1))}{2^2 + 1^2 + 0^2 + 1^2 + 2^2}$$

$$= \frac{4 - 2 + 1 - 2}{10} = 0.10$$

4 Saturated hydrocarbons have the general formula C_nH_{2n+2}

For C_nH_p:

H atoms needed = $2n + 2 - p$

H_2 molecules needed = IHD = $\frac{1}{2}(2n + 2 - p)$

For $C_nH_pO_q$:

Oxygen forms two covalent bonds. Comparing ethane, C_2H_6: C–H, to ethanol, C_2H_5OH: C–O–H, we see that the presence of O has no impact on the IHD:

IHD = $\frac{1}{2}(2n + 2 - p)$

For $C_nH_pO_qN_r$:

Nitrogen forms three covalent bonds. Comparing C—H to C—N—H, we see that the presence of one N increases the IHD by 1:

IHD = $\frac{1}{2}(2n + 2 - p + r)$

For $C_nH_pO_qN_rX_s$:

A halogen, X, forms one bond, like hydrogen, so can be treated in the same way:

IHD = $\frac{1}{2}(2n + 2 - p + r - s)$

5 $E = h\nu$

$E = 6.63 \times 10^{-34}$ J s $\times 3.0 \times 10^{14}$ s^{-1} $= 2.0 \times 10^{-19}$ J

The energy of one mole of photons = 6.02×10^{23} mol^{-1} $\times 2.0 \times 10^{-19}$ J

= 120 kJ mol^{-1}

6 $1/\lambda = 2100$ cm^{-1} = 210000 m^{-1}

$\lambda = 1/210000$ m $= 4.76 \times 10^{-6}$ m

$$\nu = \frac{3.00 \times 10^{8}\text{ m s}^{-1}}{4.762 \times 10^{-6}\text{ m}} = 6.30 \times 10^{13}\text{ s}^{-1}$$

7 The answer to this question involves the derivation of the Bragg Equation, $n\lambda = 2d\sin\theta$, which is discussed in Chapter 12. A simple derivation is provided in the worked solutions.

Answers

Chapter 12

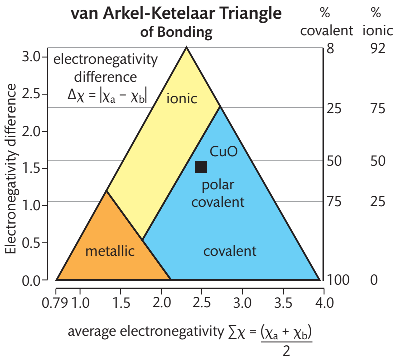
Exercises

1 A

2

Substance	$\chi_{average}$	$\Delta\chi$	% ionic character	Bonding
Cl_2O	3.3	0.2	6	(Polar) covalent
$PbCl_2$	2.5	1.4	44	Polar covalent
Al_2O_3	2.5	1.8	56	Ionic
HBr	2.6	0.8	25	Polar covalent
NaBr	1.95	2.1	66	Ionic
The % ionic character is taken from the bonding triangle (Figure 12.1).				

3

Substance	$\chi_{average}$	$\Delta\chi$	% ionic character	Bonding	
CuO	2.65	1.5	47		Polar covalent

4 Metal atoms can slide across each other with the metallic bonding not breaking as the delocalized electrons can move to accommodate the changes in the lattice.

The ionic and covalent bonds are directional and more rigid in ceramics. They resist changes in the atomic arrangement but will break if the applied forces are too strong.

5 Concrete can contain iron or carbon fibres. If these are connected into a network within the concrete the material will conduct electricity along the network.

6 **(a)** Bauxite

(b) Aluminium is more reactive than carbon.

(c) Aluminium ions are attracted towards the negative electrode where they are reduced to aluminium atoms: $Al^{3+} + 3e^- \rightarrow Al$

(d) Aluminium is more reactive than hydrogen. Hydrogen gas would be produced as the hydrogen from the water is reduced in preference to the aluminium.

(e) Aluminium oxide is only 56% ionic based on electronegativity values. The ions are not completely free in the molten compound.

(f) Oxygen is produced at the anode from the oxide ions:

$2O^{2-} \rightarrow O_2 + 4e^-$

The oxygen reacts with the carbon to produce carbon dioxide:

$C + O_2 \rightarrow CO_2$

7 **At the cathode**

$Cu^{2+} + 2e^- \rightarrow Cu$

1 mol 2 mol 1 mol

$n(Cu)/n(e^-) = 1/2$

$n(Cu) = (1/2)n(e^-)$

0.100 F = 0.100 mol of e^-

$n(Cu) = 0.050$ mol

$m(Cu) = 0.050 \text{ mol} \times 63.55 \text{ g mol}^{-1}$
$= 3.2$ g

At the anode

$2Cl^- \rightarrow Cl_2 + 2e^-$

2 mol 1 mol 2 mol

$n(Cl_2)/n(e^-) = 1/2$

$n(Cl_2) = (1/2)n(e^-)$

0.100 F = 0.100 mol of e^-

$n(Cl_2) = 0.050$ mol

$V(Cl_2) = 0.050 \text{ mol} \times 22.4 \text{ dm}^3 \text{ mol}^{-1}$
$= 1.1 \text{ dm}^3$

8 $n(e^-) = 0.0965 \text{ A} \times 1000 \text{ s}/96\,500 \text{ C mol}^{-1} = 96.5/96\,500 = 0.00100$ mol

$n(Ti) = 0.011975/47.9 = 0.000250$ mol

$n(e^-)/n(Ti) = 4$

Ti is in the +4 state. Formula: $TiCl_4$

9 $Fe_2O_3(s) + CH_4(g) + O_2 \rightarrow 2Fe(l) + CO_2(g) + H_2O(l)$ Unbalanced

Balance the elements only present in a combined state first.

Balance the C and H:

$Fe_2O_3(s) + CH_4(g) + O_2 \rightarrow Fe(l) + CO_2(g) + 2H_2O(l)$ Unbalanced

Balance the Fe and O:

$Fe_2O_3(s) + CH_4(g) + \frac{1}{2}O_2 \rightarrow 2Fe(l) + CO_2(g) + 2H_2O(l)$ Balanced

$2Fe_2O_3(s) + 2CH_4(g) + O_2 \rightarrow 4Fe(l) + 2CO_2(g) + 4H_2O(l)$ Balanced

10 **(a)** $TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$

(b) $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

11 The alloy is stronger than the pure metal.

Adding atoms of different size disrupts the regular metal lattice so that it is difficult for one layer to slide over another. Alloying can make the metal harder, stronger and more resistant to corrosion.

12 All of the electron spins are paired in diamagnetic elements.

Atoms are paramagnetic if they have unpaired electrons. So, to determine whether the elements are paramagnetic or diamagnetic, we need to consider the electron configuration for each element.

Element	Electron config.	No. of unpaired electrons	Magnetic behaviour
Na	$[Ne]3s^1$	1	Para
Mg	$[Ne]3s^2$	0	Dia
Al	$[Ne]3s^23p^1$	1	Para
Si	$[Ne]3s^23p^2$	2	Para
P	$[Ne]3s^23p^3$	3	Para
S	$[Ne]3s^23p^4$	2	Para
Cl	$[Ne]3s^23p^5$	1	Para
Ar	$[Ne]3s^23p^6$	0	Dia

Phosphorus has the most unpaired electrons and so is the most paramagnetic.

13

Atom	K	Sc	V	Mn	Ga	As
Electron configuration	$[Ar]4s^1$	$[Ar]3d^14s^2$	$[Ar]3d^34s^2$	$[Ar]3d^54s^2$	$[Ar]3d^{10}4s^24p^1$	$[Ar]3d^{10}4s^24p^3$
No. of unpaired electrons	1	1	3	5	1	3

$K \approx Sc \approx Ga < V \approx As < Mn$

14 **(a)** Positive argon ions and (free) electrons.

(b) Argon, as it is present in the plasma.

(c) ICP-MS

(d) ICP-AES , ICP-MS is less effective with non-metals as they have higher ionization energies and so form positive ions less readily.

15 **(a)** Different calibrations are produced for each electron transition so three transitions are analysed.

(b) It produced 3.00×10^7 counts in one minute = 0.0500×10^7 c s^{-1} = 5.00×10^5 c s^{-1} = 500 kc s^{-1}

From the graph and line II, [Hg] is between 1.9 and 2.0 µg dm^{-3}

(c) 798 kc s^{-1}

(d) Series I, as it has the steepest gradient; small differences in concentration can be detected with large differences in count rate.

16 0.37% by mass

17 Transition metals are effective heterogeneous catalysts as they form weak bonds to small reactant molecules which allow them to come together with the correct orientation.

The ability of transition metals to show variable oxidation states allows them to be particularly effective homogeneous catalysts.

18 **(a)** Lower temperatures needed so reduced energy costs.

Catalysts act selectively, increasing the yield of the desired product. They are not used up and so can be reused over long periods of time.

(b) Sulfur impurities block the active sites of the catalyst; the impurities are adsorbed on the catalyst surface more strongly than reactant molecules.

19 **(a)** An activated complex is an unstable combination of reactant molecules that can go on to form products or fall apart to form reactants. A reaction intermediate is a species that is produced and consumed during a reaction but does not occur in the overall equation.

An activated complex corresponds to a maximum in the energy and a reaction intermediate corresponds to a local minimum in energy. Reaction intermediates can in theory be isolated.

(b) Heterogeneous catalysts are in a different phase from the reactants; they can be easily removed by filtration.

(c) They have a large surface area per unit mass for reactants to be adsorbed and their surface structure can be modified to improve effectiveness.

(d) Toxicity of the nanoparticles is dependent on their size, so need to regulate for type of material and size of particles.

20 **(a)**

	Liquid	Liquid crystal
Molecular arrangement	disordered	disordered
Molecular orientation	disordered	ordered

(b) The phase transitions of thermotropic liquid crystals depend on temperature.

The phase transitions of lyotropic liquid crystals depend on both temperature and concentration.

(c) The molecules/ions group together to form a spherical arrangement; the hydrophilic heads are exposed to water, shielding the non-polar tails.

21 Thermotropic liquid crystal materials are pure substances that show liquid crystal behaviour over a temperature range between the solid and liquid states. Example: biphenyl nitriles.

Lyotropic liquid crystals are solutions that show the liquid crystal state at certain concentrations. Examples: soap and water, Kevlar® in solution.

22 **(a)** Low reactivity of C—H and C—C bonds due to high bond energy and low polarity.

(b) Increases polarity. Molecule can change orientation when an electric field is applied.

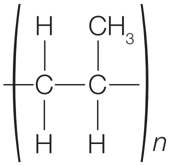
23 **(a)** $C_{24}H_{23}N$

(b) The addition of a benzene ring makes the molecule more rigid and rod-shaped.

24 A

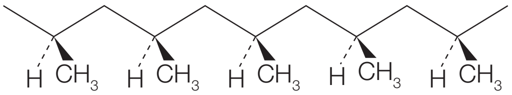
There are strong C—C covalent bonds within the chains and relatively strong intermolecular forces between the large polymer chains.

25 **(a)**



$$\left[-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}- \right]_n$$

(b)



isotactic polypropene

(c) Isotactic polypropene has a regular structure with the methyl groups pointing in the same direction and so is crystalline and tough.

(d) $M_r = (3 \times 12.01) + (6 \times 1.01) = 42.09$

$n = 2.1 \times 10^6/42.09 = 50\,000$

(e) The chains in a polymer are not all the same length.

26 **(a)** The pure form, which has strong dipole–dipole interactions between the chains, is hard and brittle. The addition of plasticizers allows the chains to slip across each other and makes the plastic more flexible.

(b) The non-expanded form of polystyrene is a colourless, transparent, brittle plastic. The expanded form is opaque with a lower density. It is a better insulator and shock absorber.

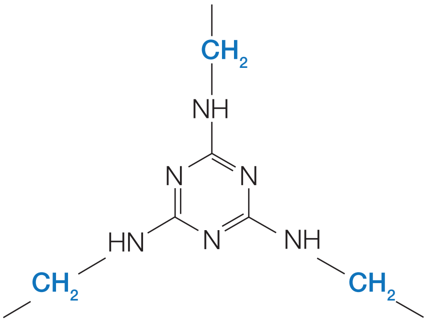
The expanded form is produced by heating polystyrene beads with a volatile hydrocarbon such as pentane. The pentane evaporates and causes bubbles to form in the plastic.

27 **(a)** Relative molar mass of reactant = $(6 \times 12.01) + (24 \times 1.01) + (12 \times 14.01) + (6 \times 16.00) = 360.42$

Relative molar mass of desired product = $(3 \times 12.01) + (6 \times 1.01) + (6 \times 14.01) = 126.15$

$$\text{Atom economy} = \frac{126.15}{360.42} \times 100\% = 35.0\%$$

(b)



(c) There are relatively weak intermolecular forces between the chains in polyethene. These forces are broken when the solid melts but are reformed when the liquid is cooled. The crosslinks between the chains in the thermosetting resin are made from strong covalent bonds. When heated to high temperature the resin does not melt but burns.

(d) There is extensive cross-linking in thermosetting plastics which means they cannot be reshaped and do not melt when heated.

Elastomers have very limited cross-links which knot some chains together and prevent molecules slipping across each other without restricting the freedom of the molecules to coil and uncoil.

28 **(a)** Polystyrene can act as a good shock absorber. Its low density will reduce transport costs and make it easier to handle.

(b) A volatile hydrocarbon is added during the polymerization process. The volatile hydrocarbon turns into a gas, forming bubbles that force the surrounding polymer to expand and take the shape of the mould.

29 **(a)** No. of diameters $= 10 \times 10^{-6}\text{ m}/1 \times 10^{-9}\text{ m}$
$= 10^{-5}/10^{-9} = 10^4 = 10\,000$

(b) Strong covalent C—C bonds must be broken.

(c) Range of tube lengths with different structures lead to a less regular structure in the solid, which reduces strength. As properties are sensitive to tube length, it is difficult to produce tubes with required properties.

(d) Large surface area for reactants to be adsorbed; the shape and size of the tubes make them shape-selective catalysts, only reactants of the appropriate geometry are able to interact effectively with the active sites.

(e) Quantum effects predominate and the electrons behave like waves; the length of the tube affects the behaviour of electrons; the tubes are conductors or semiconductors depending on the length.

30 **(a)** The size of the nanoparticles is similar to the wavelength of harmful UV radiation. UV is scattered and not absorbed.

(b) Toxicity of the nanoparticles is dependent on their size, so need to regulate for type of material and size of particles.

31 **(a)** Approx. 25 atoms high

Each C atom has a diameter of $2 \times 75 \times 10^{-12}$ m and each O atom has a diameter of $2 \times 64 \times 10^{-12}$ m

Approximate length $= 25 \times 2 \times 70 \times 10^{-12}$ m

$= 3.5 \times 10^{-9}$ m

(b) Scanning tunnelling microscope (STM) or atomic force microscope (AFM).

32 **(a)** Plastics are easily moulded; they are non-biodegradable; they have low density.

(b)

Method	Advantages	Disadvantages
landfill	simple method to deal with large volumes	plastics are not biodegradable; limited sites
incineration	reduces volume; plastics are concentrated energy source	CO_2 is a greenhouse gas; CO is poisonous; HCl produced from combustion of PVC causes acid rain
recycling	conserves natural resources	plastics need to be sorted

(c) Bacteria do not have the enzymes needed to break the C—C bonds present.

(d) Natural polymers (e.g. starch, cellulose or protein) can be added. Bacteria can break down the natural polymers and so the bag is broken down into smaller pieces.

33

Method	Advantages	Disadvantages
landfill	efficient method to deal with large volumes	not popular with locals; needs to be maintained and monitored after use
incineration	reduces volume; energy source	can cause pollutants such as greenhouse gases and dioxins

34 *Advantages:* saves natural resources; saves energy; reduces pollution

Disadvantages: materials need to be sorted

35 **(a)** 1–5

(b) 1–4

36 Both molecules have C—H bonds so they have strong absorptions between 2850 and 3090 cm^{-1}.

The monomer has a C=C bond not found in the polymer so it will have a weak absorption at 1620–1680 cm^{-1}.

37 **(a)** A

(b) A: The resistance is zero at very low temperature due to the formation of Cooper electron pairs. The crystal structure is distorted at low vibrational energies by the presence of electrons that form pairs, which are more difficult to impede than single electrons.

B: The resistance decreases as the reduced vibrational energies of the ions in the lattice offer reduced resistance to the passage of single electrons.

38 The electrons are given energy as they are accelerated by the power source.

They collide with the ions in the lattice and pass on some of their kinetic energy.

The average vibrational energy and thus temperature of the ions increases.

39 Type 1 superconductors are metals or alloys.

They only exhibit superconductivity at very low temperatures (<20 K).

They lose their superconductivity suddenly as the temperature or magnetic field strength is increased.

Type 2 superconductors are ceramic metal compounds.

Some can exhibit superconductivity at higher temperatures (<100 K).

They lose their superconductivity gradually as the temperature or magnetic field strength is increased.

40

Location of atoms	Number of atoms	Contribution	Total atoms
Corner	8	8 × (1/8)	1

There is one atom.

41 **(a)** The diagonal of the cube = $4r_M$

The length of a unit cell = $4r_M / \sqrt{3} = (4 \times 220 / \sqrt{3}) \times 10^{-12}$ m

$= 508 \times 10^{-12}$ m

(b) The volume of a cube = $(508 \times 10^{-12})^3$ m^3

No. of atoms = 2

Mass of individual atom = $39.10/6.02 \times 10^{23}$ g

Mass of unit cell = $2 \times 39.10/6.02 \times 10^{23}$ g

Density = $(2 \times 39.10/6.02 \times 10^{23})/(508 \times 10^{-12})^3$ g m^{-3}

$= 9.91 \times 10^5$ g m^{-3}

$= 991$ kg m^{-3}

42 **(a)** The diagonal of a face = $4r_M$

The length of a unit cell = $4r_M / \sqrt{2} = (4 \times 144 / \sqrt{2}) \times 10^{-12}$ m

$= 407 \times 10^{-12}$ m

(b) The volume of a cube = $(407 \times 10^{-12})^3$ m^3

No. of atoms = 4

Mass of individual atom = $196.97/6.02 \times 10^{23}$ g

Mass of unit cell = $4 \times 196.97/6.02 \times 10^{23}$ g

Density = $(4 \times 196.97/6.02 \times 10^{23})/(407 \times 10^{-12})^3$ g m^{-3}

$= 19.4 \times 10^3$ kg m^{-3}

43 $n\lambda = 2d \sin \theta$

With $n = 1$ ($\theta = 17.9°$)

$d = \lambda/2 \sin \theta$

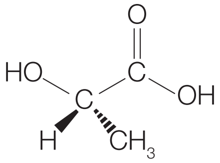
$d = 150 \times 10^{-12}$ m$/(2 \times \sin(17.9°)) = 244 \times 10^{-12}$ m

Assuming the atoms are touching

$r = d/2 = 122 \times 10^{-12}$ m

44 $-(-NH-(CH_2)_6-NH-CO-(CH_2)_8-CO-)_n-$

45



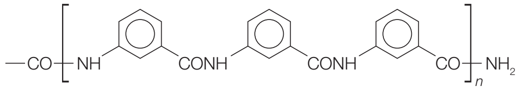
46 **(a)** $\left[O-CH_2-CH_2-CH_2-O-CO-CH_2-CH_2-CO\right]_n + H_2O$

(b) $\left[HN-CH_2-(CH_2)_4-CH_2-NH-CO-CH_2-CH_2-CO\right]_n + HCl$

47 **(a)** The primary amine and carboxylic acid groups.

(b) H_2O

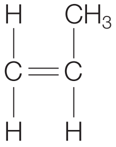
(c)



(d) The polymer formed has straight chains. Hydrogen bonds can form between the closely packed chains.

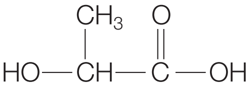
(e) The C, H, N and O atoms have a lower relative atomic mass than Fe. The atoms in Kevlar® are not close packed, unlike in a metal.

48 **(a)**



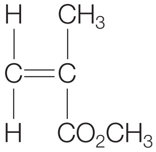
$H_2C=CH(CH_3)$

(b)



$HO-CH(CH_3)-C(=O)-OH$

(c)



$H_2C=C(CH_3)CO_2CH_3$

49 Heavy metal ions interfere with the function of key enzymes. They bind to the proteins instead of essential ions such as Mg^{2+} or Ca^{2+} and so interfere with key biochemical processes.

50 **(a)** The ligand has two O atoms which can form dative coordinate bonds. It is a bidentate ligand.

(b) Each ox forms two bonds. Coordination number = 6. Oxidation state = +3

51 $NiS(s) \rightleftharpoons Ni^{2+}(aq) + S^{2-}(aq)$

If the solubility is s: $[Ni^{2+}(aq)] = s$; $[S^{2-}(aq)] = s$

$K_{sp} = [Ni^{2+}(aq)]\,[S^{2-}(aq)] = s^2 = 2.0 \times 10^{-26}$

$s = \sqrt{2.0 \times 10^{-26}}$

$= 1.4 \times 10^{-13}$ mol dm^{-3}

52 **(a)** $K_{sp} = [Pb^{2+}(aq)]\,[S^{2-}(aq)]$

(b) $K_{sp} = [Cu^{+}(aq)]^2\,[S^{2-}(aq)]$

(c) $K_{sp} = [Al^{3+}(aq)]\,[PO_4^{\ 3-}(aq)]$

(d) $K_{sp} = [Ni^{2+}(aq)]\,[OH^{-}(aq)]^2$

53 **(a)** 1.3×10^{-5} mol dm^{-3}

(b) $[Ag^{+}(aq)]\,[Cl^{-}(aq)] = 1.6 \times 10^{-10}$

$[Ag^{+}(aq)] = \dfrac{1.6 \times 10^{-10}}{0.100}$

$= 1.6 \times 10^{-9}$ mol dm^{-3}

54 **(a)** s^2 **(b)** $4s^3$

(c) $4s^3$ **(d)** $108s^5$

(e) $27s^4$

55 **(a)** $K_{sp} = [Pb^{2+}]\,[S^{2-}] = 1.30 \times 10^{-28}$

(b) $[Pb^{2+}] = [S^{2-}]$

$[Pb^{2+}] = \sqrt{1.30 \times 10^{-28}}$

$= 1.14 \times 10^{-14}$ mol dm^{-3}

(c) As the product of the concentrations is constant, an increase in $[S^{2-}]$ will lead to a decrease in $[Pb^{2+}]$ and Pb^{2+} will be precipitated out of solution.

56 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}$

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-}$

$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^{-}$

57 **(a)** $O_2^{-\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+}$

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet}$

(b) The second step.

(c) Oxidation number = $-\frac{1}{2}$

One electron is transferred to Fe^{3+}, which is reduced to Fe^{2+}.

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 **(a)** **(i)** melting point of the cryolite solution is much lower than the melting point of alumina / Al_2O_3 / it lowers the melting point of the mixture / cell operates at lower temperature [1]

Allow lowers melting point or lowers melting point of aluminium oxide.

Do not allow lowers melting point of aluminium.

(ii) Positive electrode:

$2O^{2-} \rightarrow O_2 + 4e^{-}$ / $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^{-}$

Negative electrode:

$Al^{3+} + 3e^{-} \rightarrow Al$ [2]

*Award **[1]** for correct equations but wrong electrodes.*

Allow e instead of e⁻.

(b) use of fossil fuels (to provide energy)

oxidation of the (graphite) positive electrode / anode [2]

2 **(a)** Al is more reactive than Fe / Al is higher than Fe in the reactivity series / it is harder to reduce aluminium ores compared to iron ores / Fe^{3+} is a better oxidizing agent than Al^{3+} / *OWTTE* [2]

(b) **(i)** $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$ [1]

(ii) $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$ [1]

3 **(a)** **homogeneous** mixture of metals / a metal and non-metal [1]

(b) alloying element(s) disrupts regular / repeating (metal) lattice

difficult for one layer to slide over another / atoms smaller than the metal cations can fit into the (holes of) metal lattice disrupting bonding

can make metal harder / stronger / more corrosion resistant / brittle [2 max]

4 *Mode of action of homogeneous catalysis:*

catalyst reacts in one step (of the mechanism) and is regenerated at a later step /ability to form a range of oxidation states (for transition metals) / reaction steps with catalyst have lower activation energies than for reaction without catalyst / *OWTTE*

Example using chemical equation:

$CH_3COOH(aq) + C_2H_5OH(aq) \xrightleftharpoons{H^+(aq)} CH_3COOC_2H_5(aq) + H_2O(l)$ / other suitable example

Mode of action of heterogeneous catalysis:

catalyst provides the reactive surface / presence of active sites / adsorb reactant molecule(s) (on surface)

Example using chemical equation:

$2SO_2(g) + O_2(g) \xrightleftharpoons{V_2O_3(g)} 2SO_3(g)$ / $N_2(g) + 3H_2(g) \xrightleftharpoons{Fe(s)} 2NH_3(g)$ / $C_2H_4(g) + H_2(g) \xrightleftharpoons{Ni(s)} C_2H_6(g)$ / other suitable example

Reversible sign not required for mark.

Catalyst and states must be specified to score mark. [4]

5 **(a)** biphenyl nitriles / cyanobiphenyls [1]

(b) nitrile groups make molecule polar

intermolecular forces are strong enough to align in a common direction

biphenyl groups make molecules more rigid/ rod-shaped

(long) alkane chain ensures that molecules cannot pack together closely (to maintain liquid-crystal state) [4]

6 **(a)** C–Cl bond / molecule is polar

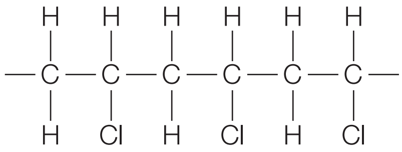
stronger intermolecular / van der Waals / London / dispersion forces / dipole–dipole attraction [2]

(b) addition of **plasticizers**

Allow misspelling within reason.

gets between polymer chains / keeps chains further apart **and** reduces attraction (between the chains) [2]

(c)



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$$

Accept any structure with all the Cl atoms shown on the same side.

Continuation bonds at end of structure not needed.

Hydrogen atoms must be included. [1]

7 **(a)** *Landfill:*

can be used to deal with large volumes/ amounts / filled ground can be re-used / low cost

Do not accept 'no air pollution'.

Incineration:

reduces volume / requires minimal space / source of energy

Do not accept 'no land pollution'

Apply list principle, i.e. award ***[0]*** *when one correct and one incorrect advantage given.* [2]

(b) limited supply of oxygen (prevents the bacteria from acting)

Do not accept air. [1]

8 **(a)** *Positive electrode:*

graphite / carbon

Negative electrode:

graphite / carbon (on a steel liner) [2]

(b) much less energy required to recycle than to produce Al from ore / *OWTTE* less production of CO_2/greenhouse gases (graphite used in the electrolysis is converted into CO_2) / the more that is recycled the less there will be in landfill sites / *OWTTE* [2]

9 **(a)** walls have rolled/single sheets of graphite / carbons bonded in hexagons

ends have half a buckyball (fullerene) / carbons in pentagons (and hexagons) [2]

(b) **covalent** bonds are very strong [1]

(c) **(i)** large surface area

Do not accept 'reactive surface'.

high selectivity related to dimensions of tube [2]

(ii) unknown health effects

Accept potentially harmful as easily ingested/inhaled.

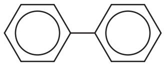
Accept difficulty of preparing nanotubes in required amounts. [1]

10 **(a)** **(i)** CN

makes molecule polar, ensures common orientation which can be changed by electric field

(ii) C_5H_{11}

prevents close packing of molecules

(iii) 

molecules rigid **and** rod-shaped

Accept chemical stability for second or third mark not both. [3]

(b) liquid crystal between two glass plates which have scratches at 90° to each other

molecules form a twisted arrangement between plates due to **intermolecular** bonds

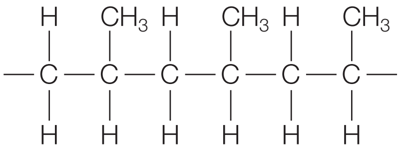
when polarizers are aligned with scratches, light will pass through film and pixel will appear bright

applied voltage aligns polar molecules **and** pixel appears dark [4]

11 (rod-shaped) molecules aligned in the same direction

increasing temperature causes arrangement to lose its directional order / molecules to become more randomly arranged until normal liquid state occurs [3]

12 **(a)** **(i)** CH_2CHCH_3 [1]

(ii) 

harder / more rigid / higher melting point / stronger / denser

crystalline / chains closer together [3]

(b) polystyrene beads contain pentane / volatile hydrocarbon

heating causes pentane to evaporate

white / opaque / lower density / better insulator / (better) shock absorber [4]

Any two properties, ***[1]*** *each.*

(c) carbon dioxide is a greenhouse gas / CO_2 causes global warming, climate change etc.

produces toxic chlorine compounds / causes acid rain due to HCl [2]

13 HDPE:

no / very few branches

chains pack closer together

stronger intermolecular forces

Allow converse argument, e.g. LDPE has more branches, so its chains are further apart and the intermolecular forces are weaker. [4]

14 **(a)** addition of plasticizers

more flexible / flexibility [2]

(b) *polymer disadvantages*

difficult to dispose of polymer properly

fills up landfill sites

litter

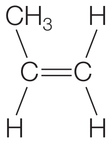
lack of biodegradability

use of natural resources

Award ***[1]*** *each for any two.*

PVC disadvantages

burning produces toxic gases / HCl [3 max]

15 **(a)** 

/ $CH_3 – CH = CH_2$ [1]

(b) melting point

Do not accept boiling point.

softness / hardness / flexibility / strength / rigidity / density [2]

(c) atactic

methyl groups arranged randomly / *OWTTE* [2]

16 coke / carbon / C **and** limestone / calcium carbonate / $CaCO_3$

(coke)

to produce heat

$C + O_2 \rightarrow CO_2$

OR

to act as a reducing agent / to produce carbon monoxide

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$ / $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$ / $C + CO_2 \rightarrow 2CO$

(limestone)

to remove impurities / silica

$CaCO_3 \rightarrow CaO + CO_2$ **and** $CaO + SiO_2 \rightarrow CaSiO_3$ / $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$ [5]

17 (metal)

does not rust / corrode

low density

thermal insulator / poor conductor of heat

electrical insulator / poor conductor of electricity

Accept any answer above for ***[1]***.

(wood)

easily moulded

non-biodegradable / does not rot

low density

Accept any answer above for ***[1]***.

Do not accept reference to cost. [2]

18 **(a)** lyotropic liquid crystal

rigid rod-shaped molecules

alignment of molecules depends on concentration of solution [3]

(b) (Kevlar has) strong hydrogen bonds between chains creating a very ordered / strong structure [2]

(c) acid donates a proton to the O and N atoms, breaking the hydrogen bonds [2]

19 $K_{sp} = [Ag^+][Cl^-]/1.8 \times 10^{-10} = 8.0 \times 10^{-3} \times [Cl^-]$

$[Cl^-] = 2.3 \times 10^{-8}$ mol dm^{-3}

$K_{sp} = [Pb^{2+}][Cl^-]^2 / 1.7 \times 10^{-5} = 1.9 \times 10^{-2} \times [Cl^-]^2$

$[Cl^-] = 3.0 \times 10^{-2}$ mol dm^{-3}

AgCl will precipitate first (because it is less soluble) [5]

20 **(a)** $K_{sp} = [Ni^{2+}] \times [OH^-]^2$

$[OH^-] = 2[Ni^{2+}]$, hence $K_{sp} = 4[Ni^{2+}]^3$

$[Ni^{2+}] = \left(\frac{6.50 \times 10^{-18}}{4}\right) = 1.18 \times 10^{-6}$ mol dm^{-3}

Mass of Ni^{2+} in 1 dm^3 = $58.71 \times 1.18 \times 10^{-6}$ = 6.90×10^{-5} g

Award ***[4]*** *for correct final answer.*

Accept

$K_{sp} = [Ni^{2+}] \times [OH^-]^2$

$pH = pOH = 7 \rightarrow [OH^-] = 10^{-7}$ *mol dm*$^{-3}$

$[Ni^{2+}] = \frac{6.50 \times 10^{-18}}{(10^{-7})^2} = 6.50 \times 10^{-4}$ *mol dm*$^{-3}$

Mass of Ni^{2+} *in 1 dm*^{3} = $6.50 \times 10^{-4} \times 58.71$ = 3.82×10^{-2} *g*

Award ***[4]*** *for correct final answer.* [4]

(b) add excess hydroxide ions / increase the pH

more $Ni(OH)_2$ will precipitate due to common ion effect / *OWTTE* [2]

Challenge yourself

1 **(a)** The molecule is rigid and rod-shaped.

(b) Thermotropic.

2 **(a)** The observer can see nothing. The whole area would appear dark as the polarizer and analyser are crossed.

(b) The whole area would appear light as the liquid crystal rotates the plane of polarization, so light is now transmitted by the analyser.

(c) In regions where there is no applied voltage the liquid crystal rotates the plane of polarization so light is now transmitted by the analyser. In regions where there is voltage applied the liquid crystal molecules align with the electric field and no longer rotate the plane of polarization. The observer would see a dark circle surrounded by light.

3 The halogen atoms have a larger mass and so C—X bonds vibrate at a lower frequency.

4 OS = oxidation state

OS(Ca) = +2

OS(O) = −2

OS(Ti) = 6 − 2 = +4

5 OS = oxidation state

OS(Ba) = +2

OS(O) = −2

OS(Y) = +3

3 × OS(Cu) = 14 − 4 − 3 = +7

OS(Cu) = +7/3 = $+2\frac{1}{3}$

Two of the Cu ions are Cu^{2+} and one is Cu^{3+}.

6 There are four atoms in the unit cell so the volume occupied = 4 × volume of one atom

Assuming the atoms are spherical:

Volume = $4 \times (4/3)\pi r^3$

Edge of a unit cell = $(4/\sqrt{2})r$

Volume of unit cell = $((4/\sqrt{2})r)^3$

$$\text{Volume occupied} = [(16/3)\pi r^3/((2/\sqrt{2})r)^3] \times 100\%$$
$$= [(\sqrt{2})^3 \times \pi/12] \times 100\%$$
$$= 74\%$$

7 There are two atoms in the unit cell so the volume occupied = 2 × volume of one atom

Assuming the atoms are spherical:

Volume occupied = $2 \times (4/3)\pi r^3$

Edge of a unit cell = $(4/\sqrt{3})r$

Volume of unit cell = $((4/\sqrt{3})r)^3$

$$\text{Volume occupied} = [(8/3)\pi r^3/((4/\sqrt{3})r)^3] \times 100\%$$
$$= [(\sqrt{3})^3 \times \pi/24] \times 100\%$$
$$= 68\%$$

8

Element	No. of atoms	Position	Total number of atoms
Ca	1	Centre	1 × 1 = 1
O	12	Edges	12/4 = 3
Ti	8	Corners	8 × 1/8 = 1
Formula:	$CaTiO_3$		

9 Polyesters have similar linkages to biopolymers and so can be broken down by bacteria. They are broken down by hydrolysis.

10 Hg^{2+} binds to sulfur

Cysteine

11 There are two particles on the left and seven particles on the right.

There will be an increase in the number of ways the energy can be distributed and an increase in entropy. This means ΔG (= $\Delta H - T\Delta S$) is more likely to be negative and the reaction more likely to be spontaneous.

12 $[H_2O] = n(H_2O)/V(H_2O)$

Consider a 1 dm^3 sample of H_2O with a mass of 1.000×10^3 g

$$n(H_2O) = m(H_2O)/M(H_2O)$$
$$= 1.000 \times 10^3/(16.00 + 2(1.01))$$
$$= 55.49 \text{ mol dm}^{-3}$$

13 If the solubility is s: $[M^{m+}(aq)] = ps$; $[X^{n-}(aq)] = qs$

$$K_{sp} = [M^{m+}(aq)]^p\,[X^{n-}(aq)]^q$$
$$= (ps)^p(qs)^q$$
$$= p^p q^q s^{p+q}$$

Answers

Chapter 13

Exercises

1 $C_{18}H_{32}O_{16} + 2H_2O \rightarrow 3C_6H_{12}O_6$

2 Monomers must each have two functional groups. A molecule of water is given off for each bond that forms between the monomers.

3 **(a)** anabolic **(b)** catabolic
(c) catabolic **(d)** anabolic

4 Sunlight, photosynthetic pigments to absorb light energy, water and carbon dioxide.

Carbon dioxide is reduced by the hydrogen from water, forming carbohydrate. The oxidation state of carbon decreases from +4 in CO_2 to 0 in $C_6H_{12}O_6$. Oxygen is oxidized from –2 in H_2O to 0 in O_2.

5 Aerobic respiration yields a great deal more energy than anaerobic respiration, as in the presence of oxygen the oxidation of glucose to CO_2 and H_2O is complete. In anaerobic respiration, oxidation is incomplete, and much of the energy remains in the end products such as ethanol.

6 **(a)** Tyr—Val—His; Tyr—His—Val; His—Tyr—Val; His—Val—Tyr; Val—His—Tyr; Val—Tyr—His

There are six different tripeptides possible from three amino acids: 3 × 2 × 1

(b) There are 24 different peptides that can be synthesized from four amino acids: 4 × 3 × 2 × 1

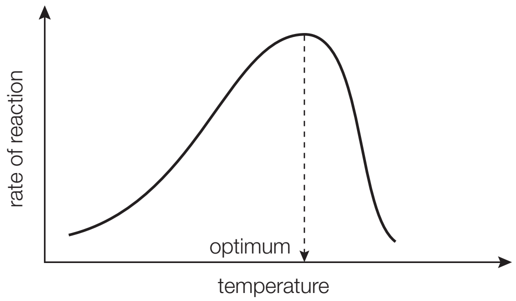
7 **(a)** leucine **(b)** threonine
(c) glutamic acid **(d)** lysine

8 Fibrous proteins are usually elongated molecules with a well-defined secondary structure. They are structural materials and insoluble in water. Globular proteins have a well-defined tertiary structure and are compact spherical molecules, soluble in water. They are functional as enzymes, carriers, hormones and receptors.

9 Hydrogen bonds in the secondary structure are between groups that are part of the peptide bonds of amino acids four residues apart in a polypeptide chain. Hydrogen bonds in the tertiary structure are between groups such as –OH in the side chains of amino acids.

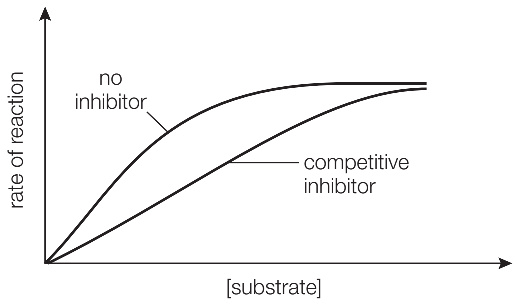
10 **(a)** Enzymes are biological catalysts; they are made of proteins; they are very specific in their action; they are affected by changes in temperature and pH; during the reaction they form an enzyme–substrate complex in which the reaction occurs.

(b)



The shape shows increasing rate with increasing temperature as a result of the increase in average kinetic energy leading to more successful collisions between enzyme and substrate. This continues to a maximum point (close to 40 °C in humans), known as the optimum. At temperatures higher than this, the rate of the reaction falls dramatically as the enzyme is denatured. This means that it loses its specific tertiary structure and can no longer bind the substrate at the active site.

11 **(a)** and **(b)**



(c) **(i)** no effect on V_{max}

(ii) K_m increases

12 *Similarities:* both increase rate of reaction by providing pathway of lower E_a; both have no effect on K_c or yield.

Differences: enzymes are proteins, inorganic catalysts have a varied structure; enzymes show saturation kinetics, inorganic catalysts usually do not; enzymes are regulated by inhibitors, inorganic catalysts are usually not; enzymes are sensitive to pH and temperature, inorganic catalysts usually work well at a wide range of temperature and pressure.

13 **(a)** Hands are likely to carry free amino acids that could be deposited on the paper and interfere with the chromatogram.

(b) Isoleucine has an isoelectric point = 6.0

Therefore, at pH < 6.0 it will be positively charged and so attracted to the cathode; at pH > 6.0 it will be negatively charged and so attracted to the anode.

(c) Glutamic acid has an isoelectric point = 3.2

Histidine has an isoelectric point = 7.6

Therefore, pH between 3.2 and 7.6 would achieve separation, e.g. pH 5.0.

Glutamic acid will be negatively charged and attracted to the anode.

Histidine will be positively charged and attracted to the cathode.

14 75 cm^3 of 0.05 mol dm^{-3} NaOH

15 A series of dilutions (at least five) is prepared of a protein standard solution. These are treated with a reagent (such as Biuret solution) which generates colour according to the protein content. Absorbance of each solution is measured under carefully controlled conditions of temperature, wavelength and volume of reagent added. The calibration curve is plotted of absorbance versus protein concentration. The same conditions are applied to the experimental solution, whose protein concentration can then be read from the calibration curve.

16 $10.16 \text{ g } I_2 = \frac{10.16}{254} \text{ moles } I_2$

$= 0.04 \text{ moles } I_2$

Therefore, 0.02 moles fat react with 0.04 moles I_2 so there are two double bonds in the fat.

17 **(a)** Melting point above 25 °C: lauric, myristic, palmitic and stearic acids are solids at room temperature.

(b) Melting point increases as London dispersion forces increase with size of the R group, due to an increase in number of electrons.

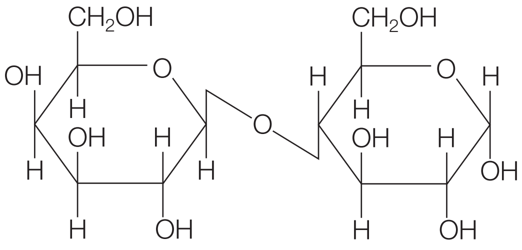
(c) An increase in the number of the C=C double bonds adds kinks to the structure which reduces the ability of the molecules to pack together. The intermolecular forces are weaker and the melting points decrease.

18 Fats and oils; hydrolytic and oxidative rancidity.

19 **(a)** CH_2O

(b) Monosaccharides are water soluble as they are small molecules with many free —OH groups which can form hydrogen bonds. Polysaccharides are insoluble as they are much larger molecules.

20



Lactose

$C_{12}H_{22}O_{11}$. Glycosidic bond.

21 **(a)** Carbon—carbon double bonds and hydroxyl groups.

(b) Water-soluble: vitamin C; fat-soluble vitamin A / vitamin D.

Vitamin C has many —OH and polar groups able to form hydrogen bonds with water. Vitamins A and D are predominantly non-polar/have hydrophobic groups and so cannot form hydrogen bonds with water.

22 Fortification of certain staple foods such as rice and flour with micronutrients; supply of nutritional supplements particularly in places where certain deficiencies are known (e.g. iodine); possible changes and improvements in nutrient content through genetic modification.

23 **(a)** Polynucleotides form by the condensation reactions between nucleotides. Phosphate groups react with ribose sugar molecules at C_3 and C_5 forming phosphodiester links between the sugar molecules. The backbone of the polynucleotide strand is an alternating sequence of sugar and phosphate groups.

(b) The double helix of the DNA molecule is stabilized by hydrogen bonds between the complementary pairs of bases. Guanine and cytosine pairs are held together by three hydrogen bonds, and adenine and thymine pairs by two hydrogen bonds. The molecule is also stabilized by hydrophobic interactions between the stacked bases in the interior of the helix.

24 **(a)** TTAGCGTATATTAAGCGATCG

(b) UUAGCGUAUAUUAAGCGAUCG

(c) There are seven base triplets so seven amino acids can be inserted.

25

Benefits	Concerns
Improved flavour, texture and nutritional value	Uncertainties about the outcomes
Longer shelf-life	Links to increased allergies (for people involved in their processing)
Increased crop yields in plants and feed efficiency in animals	Pollen from GM crops may escape to contaminate 'normal' crops

26 When a substance is oxidized, electrons are transferred and the oxidation number of the substance is increased. This happens to Fe in cytochromes when they act as electron carriers. Oxygenation does not involve transfer of electrons and there is no change in oxidation number; it involves the bonding of a molecule of oxygen as a ligand. This happens in hemoglobin when it forms oxyhemoglobin.

27

pH	λ_{max}	Colour absorbed	Colour of pigment
1	550	Green	Red
7	350	Absorbs outside of visible region	Colourless

28 **(a)** The carotenoids are coloured due to the presence of an extended π system of electrons in their molecules. They are not water soluble as the molecules contain a non-polar hydrocarbon chain. They are soluble in non-polar fats and oils.

(b) The colour is due to the presence of anthocyanins. These are water soluble as the molecules contain polar hydroxyl groups which form hydrogen bonds with water.

The colour changes in the presence of acid as the degree of conjugation of the π system is reduced when anthocyanins are protonated. This changes the wavelength of the light absorbed.

29 A: 0.17; B: 0.50; C: 0.67

Polar molecules interact fairly strongly with the polar Si—O bonds of the stationary phase and so have smaller R_f values.

30 Oxygen dissociation curve of hemoglobin is sigmoidal, representing cooperative binding between the four heme groups within the quaternary structure. Oxygen dissociation curve of myoglobin is hyperbolic, representing saturation kinetics with no cooperative binding, as myoglobin contains a single heme group and no quaternary structure.

31 The carbon–carbon double bonds that remain in partially hydrogenated fats are changed from *cis* to *trans* configurations. *Trans* fats are associated with a number of negative health effects, including cardiovascular disease. Complete hydrogenation results in fats that have no carbon–carbon double bonds.

32 Cellulose is a polymer of β-glucose. It has –OH groups sticking out on both sides of its chains, so hydrogen bonds between them form microfibrils, which give it rigidity. It is used for support. Starch is a polymer of α-glucose, forming compact and spiral molecules.

33 Light activates the conversion of 11-*cis*-retinal to the all-*trans* isomer, which causes its dissociation from opsin and the triggering of a nervous impulse.

34 Ionic bonds, hydrogen bonds, London dispersion forces, hydrophobic interactions.

35 Biomagnification refers to the increasing concentration of a xenobiotic substance at different levels in a food web. It is often associated with toxic effects for organisms that feed at a high trophic level, as their cells contain the highest concentrations.

36 Break down oil spills, help break down some plastics, in biological detergents that improve energy efficiency, in Green Chemistry involving less toxic chemical pathways and solvents.

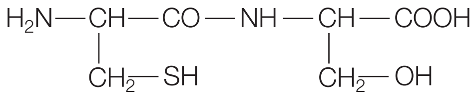
Practice questions

For advice on how to interpret the marking below please see Chapter 1.

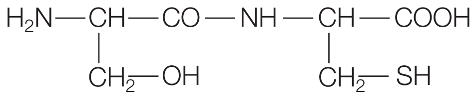
1 **(a)** condensation

water / H_2O [2]

(b)



$H_2N-CH(CH_2-SH)-CO-NH-CH(CH_2-OH)-COOH$ [2]



$H_2N-CH(CH_2-OH)-CO-NH-CH(CH_2-SH)-COOH$

(c) Arg—His—Leu

Arg—Leu—His

His—Arg—Leu

His—Leu—Arg

Leu—Arg—His

Leu—His—Arg [3 max]

Award ***[3]*** *for all six correct,* ***[2]*** *for five or four,* ***[1]*** *for three.*

(d) **(i)** hydrogen bonding [1]

(ii) van der Waals forces / hydrophobic interactions / dispersion forces

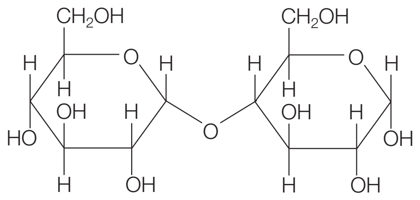
ionic bonding / (formation of) salt bridges / electrostatic attractions

covalent bonding / (formation of) disulfide bridges [2 max]

Award ***[1]*** *each for any two.*

Do not accept sulfur bridges or hydrogen bonding.

2 **(a)** **(i)** [3]

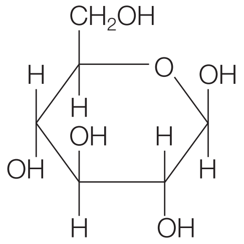


(ii) $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$ [2]

(iii) catabolism [1]

Accept hydrolysis.

(b) **(i)** [1]



Accept structures given as repeating unit with open bonds at the —OH groups at positions 1 and 4.

(ii) starch forms a compact spiral structure / granular / amorphous

cellulose forms microfibrils / cables / rigid structure

cellulose can form hydrogen bonds between chains due to β-glycosidic links (and starch cannot) [3]

3 **(a)** rate of reaction increases with temperature from approximately 0 to 35°C

increasing kinetic energy of enzyme and substrate increases the probability of a successful collision forming an enzyme–substrate complex

catalytic action / alternative pathway of lower activation energy occurs due to binding of substrate to enzyme

at 40°C tertiary structure / conformation of enzyme starts to break down / denature and less enzyme–substrate complex forms

above 40°C enzyme is denatured / unable to bind to substrate [5]

(b) optimum temperature / maximum rate of reaction at temperature lower than 40°C

graph rises more quickly at low temperatures [2]

4 **(a)** **(i)** linoleic acid $C_{17}H_{31}COOH$ so has two C═C bonds

2 moles I_2 react with 1 mole linoleic acid

2 × 254 g react with 280 g

100 g linoleic acid reacts with $\dfrac{508 \times 100}{280}$

$= 181$ g I_2 [3]

(ii) X has fewer C═C double bonds / is less unsaturated / more saturated [1]

(iii) X has higher melting point as molecules pack more closely

unsaturation puts kinks in the hydrocarbon chains / less close packed / weaker intermolecular forces [2]

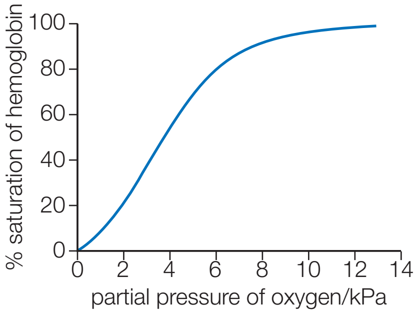
(b) Hydrolytic rancidity: fat breaks down by hydrolysis at the ester links between glycerol and fatty acids, releasing the free acids. Favoured by high temperature and enzyme lipase. [3]

Oxidative rancidity: unsaturated fat is oxidized at the carbon—carbon double bonds forming volatile aldehydes and ketones. Favoured by light and enzymes or metal ions. [3]

(c) Lipids release more energy per unit mass on oxidation than carbohydrates, as they are more reduced. Lipids are insoluble and difficult to transport so their breakdown is more difficult and slower than carbohydrates. [3]

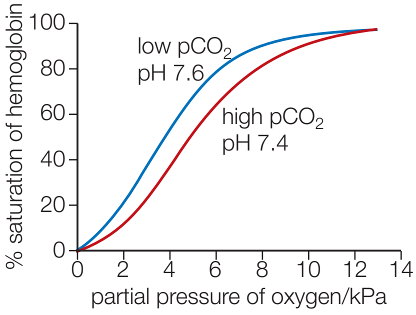
5 **(a)** Hemoglobin has a compact structure and a specific three-dimensional conformation. Its shape is determined by both its tertiary and quaternary structures. [3]

(b) [4]



(c) Binding of O_2 to the first subunit causes a conformational shift, which facilitates the binding of O_2 to the subsequent subunits. [2]

(d)



Actively respiring cells release CO_2 / lower pH. This shifts the O_2 dissociation curve to the right, so that the blood is less saturated with O_2. Oxyhemoglobin dissociates more readily at low pH. [3]

(e) In the presence of O_2 from the air, hemoglobin in the meat is converted to oxyhemoglobin, which helps give meat a bright red colour. [2]

(f) The oxygen dissociation curve for myoglobin: (i) lies to the left of hemoglobin – it has a greater affinity for O_2; (ii) is not a sigmoidal shape but hyperbolic as there is no cooperative binding. [4]

6 *Benefit:*

enhanced taste/flavour/quality/nutrients/vitamin A / longer shelf life / greater yield / greater resistance to pesticides/disease

Concern:

increased allergies / changed composition of balanced diet / unknown health consequences in food chain / risk of escape to wild population / lack of knowledge of potential consequences to ecosystem

7 **(a)** deoxyribose sugar, phosphoric acid, nitrogenous base (purine/pyrimidine) [2]

these components combine through condensation reactions to form nucleotides

(b) phosphate groups negatively charged / anionic attracted to positive electrode

(c) **(i)** CGGATGAATCGAT

(ii) GCCUACUUAGCUA [2]

8 **(a)** pigments absorb visible light

and scatter/reflect/transmit the remaining light [2]

(b) **(i)** no effect as it lies outside the visible regions/is in the UV / *OWTTE* [2]

(ii) the colour will be the complementary colour to the colour absorbing at 530 nm / it will be red as 530 nm is blue-green / *OWTTE* [1]

(c) oxidation

temperature

pH/acidity/basicity

presence of metal ions [2 max]

9 Anthocyanins: water soluble due to their —OH groups, which allow formation of hydrogen bonds with H_2O.

Carotenoids: fat soluble due to long non-polar hydrocarbon structure [4]

10 **(a)** Vitamin A: not soluble in water, non-polar molecule.

Vitamin C: soluble in water due to several —OH groups able to form hydrogen bonds with H_2O. [2]

(b) Vitamin A will be stored in fat deposits. [1]

(c) processed food / cooking destroys vitamins

depletion of nutrients in soil and water cultures

lack of education / understanding about balanced diet

poor distribution of global resources [3]

11 **(a)** substance foreign to organisms / not naturally found in the environment [2]

(b) starch absorbs water and swells, causing plastic to break into small pieces which can be broken down by bacteria [2]

(c) PVC contains the C—Cl bond for which no enzyme exists in the environment [2]

Challenge yourself

1 The entropy of the environment increases. Energy is returned as less useful forms such as heat and other forms which quickly become randomized. Order is created at the expense of the environment, which becomes more disordered.

2 In $C_6H_{12}O_6$ the oxidation state of C = 0

In CO_2 the oxidation state of C = +4

3 Threonine and isoleucine have two chiral carbon atoms.

4 Proline is a secondary amine; all other amino acids are primary amines. In peptides, proline does not have any hydrogens bonded to N, so cannot be a hydrogen bond donor, but can be a hydrogen bond acceptor. The presence of proline leads to a bend or kink in the polypeptide chain.

5 **(a)** first order
(b) mixed order
(c) zero order

6 succinate = butanedioate
fumarate = *trans*-butenedioate
malonate = propanedioate

7 Oxidation state of carbon will be higher in a carbohydrate than in a lipid, e.g. glucose and palmitic acid.

8 Threonine and isoleucine have four stereoisomers, as they each have two chiral C atoms.

9 β-Glucose is more stable because there is less steric hindrance in the *trans* position.

Answers

Chapter 14

Exercises

1 **(a)** Solar heating, solar electricity, hydroelectricity, wind power, biomass.

(b) Fossil fuels.

(c) Tidal is due to the presence of the moon, nuclear fission due to presence of radioactive elements found in the earth.

(d) Renewable sources are generally derived from recent solar energy.

2 **(a)** $\dfrac{\text{useful output energy}}{\text{total input energy}} = \dfrac{\text{useful heat energy}}{\text{total input heat energy}} = 0.85$

Heat energy produced by combustion

$= 4.00 \times 10^7$ kJ/0.85

$= 4.71 \times 10^7$ kJ

Moles of $CH_4 = 4.71 \times 10^7/891 = 5.28 \times 10^4$ mol

Mass $= 5.28 \times 10^4$ mol $\times$ 16.05 g mol^{-1}

$= 8.48 \times 10^5$ g $= 8.48 \times 10^2$ kg

(b) Energy produced by combustion $= 4.00 \times 10^7$ kJ/0.5

$= 8.00 \times 10^7$ kJ

Moles of $CH_4 = 8.00 \times 10^7/891 = 8.98 \times 10^4$ mol

Mass $= 8.98 \times 10^4$ mol $\times$ 16.05 g mol^{-1}

$= 1.44 \times 10^6$ g $= 1.44 \times 10^3$ kg

3 **(a)**

Formula	***M* / g mol^{-1}**	**DH_c / kJ mol^{-1}**	**Specific energy / kJ g^{-1}**
H_2	= 2 × 1.01 = 2.02	–286	= 286/2.02 = 142
CH_4	= 12.01 + (4 × 1.01) = 16.05	–891	= 891/16.05 = 55.5

(b) Assuming ideal behaviour: $PV = nRT$

$PV = (m/M)RT$

$\rho = m/V = PM/RT$

With everything in SI units, the units of density are kg m^{-3}

With the molar mass in g mol^{-1}, the units of density are g m^{-3}

STP conditions: $T = 273$ K and $P = 100$ kPa

3 **(b)** ***cont'd***

Formula	**Specific energy / kJ g^{-1}**	**Density / g m^{-3}**	**Energy / kJ cm^{-3}**
H_2	= 286/2.02 = 142	= 1.00 × 10^5 × 2.02/8.13 × 273 = 91.0	= (286/2.02) × 1.00 × 10^5 × 2.02/(8.13 × 273) = 12 900
CH_4	= 891/16.05 = 55.5	= 1.00 × 10^5 × 16.05/8.13 × 273 = 723	= (891/16.05) × 1.00 × 10^5 × 16.05/(8.13 × 273) = 40 100

Note: energy density of a gas is not determined by the molar mass.

3 **(c)** Hydrogen is the best fuel.

It is dangerous to store and burn.

4 **(a)** Empirical formula: $C_{135}H_{96}O_9NS$. (It typically also contains trace elements of silicon, sodium, calcium, aluminium, nickel, copper, zinc, arsenic, lead and mercury.)

(b) $S + O_2 \rightarrow SO_2$ and $2SO_2 + O_2 \rightarrow 2SO_3$ and $H_2O + SO_2 \rightarrow H_2SO_3$ and $H_2O + SO_3 \rightarrow H_2SO_4$

$2N + O_2 \rightarrow 2NO$ and $2NO + O_2 \rightarrow 2NO_2$ and $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$

5 **(a)** $$\frac{\text{useful output energy}}{\text{total input energy}} =$$

$$\frac{\text{useful heat energy}}{\text{total input heat energy}} = 0.38$$

Heat energy produced by combustion = 5.00×10^5 kJ s^{-1}/0.38

Mass = 5.00×10^5 kJ s^{-1}/(0.38 × 33.0 kJ g^{-1})

= 39 900 g s^{-1} = 39.9 kg s^{-1}

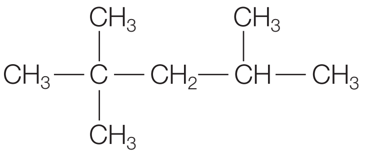
(b) We have the unbalanced equation: $CH + (5/4)O_2 \rightarrow CO_2 + \frac{1}{2}H_2O$

no. of moles of CO_2 = no. of moles of CH

no. of moles of C H = 39 900/(12.01 + 1.01) = 3062 mol

mass of CO_2 = 3062 × 44.01 = 135 000 g = 135 kg

6



$$\begin{array}{ccccccccc} & & CH_3 & & & & CH_3 & & \\ & & | & & & & | & & \\ CH_3 & - & C & - & CH_2 & - & CH & - & CH_3 \\ & & | & & & & & & \\ & & CH_3 & & & & & & \end{array}$$

7 **(a)** $C_{11}H_{24} \rightarrow C_2H_6 + 3C_3H_6$ or $C_{11}H_{24} \rightarrow C_5H_{12} + 3C_2H_4$

(b) Increases the yield of the more useful lower fractions used as fuels for cars.

Produces the more reactive alkenes, which can be used as chemical feedstock, to make useful products such as plastics.

(c) Lower temperatures needed. Catalysts act selectively, increasing the yield of the desired product.

8 **(a)** Octane is one of the main components of petroleum: C_8H_{18}

Any compound between pentane and decane would be acceptable as an answer.

(b) They are isolated from crude oil by fractional distillation.

- The mixture of hydrocarbons is heated, causing them to vaporize.
- As the vapour travels up the fractionating column the hydrocarbons condense at different heights, resulting in their separation.
- The different compounds have different boiling points: the lowest boiling point compounds condense at the top and the highest boiling point compounds condense at the bottom.
- As the relative molar mass increases, the attractive London dispersion forces between the molecules increase, leading to an increase in the boiling point.

(c) The components of gasoline have boiling points above normal temperatures. They are volatile liquids.

They can be easily vaporized in the car cylinder for reaction with oxygen.

Lower molar mass compounds are gases which occupy too much volume, while higher molar mass compounds do not vaporize or burn easily.

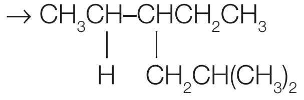
(d) Higher fractions can be cracked into smaller molecules; the larger molecules are heated with a catalyst and broken into smaller molecules.

Alkenes formed in the cracking process can undergo alkylation reactions with lower molecular mass alkanes to further increase the yield of gasoline.

(e) *Cracking*: $C_{16}H_{34} \rightarrow C_6H_{12} + C_{10}H_{22}$

$C_6H_{10} + C_{10}H_{24}$

Alkylation: $(CH_3)_3CH + CH_3CH{=}CHCH_2CH_3$



$$\begin{array}{lcccl} \rightarrow CH_3 & CH & – & CH & CH_2CH_3 \\ & | & & | & \\ & H & & & CH_2CH(CH_3)_2 \end{array}$$

9 The general pattern is:

straight-chain alkanes < cycloalkanes < alkenes < aromatics

pentane < cyclopentane < pentene < benzene

10 The general pattern is that the octane number of straight-chain alkanes decreases with an increase in chain length. Alcohols have very high octane numbers.

heptane < hexane < pentane < ethanol

11 **(a)** High specific energy / energy density.

As a liquid it is convenient to handle and deliver.

Easy to vaporize, which assists combustion.

(b) It is formed by the partial decomposition of marine plants millions of years ago.

(c) Compounds are separated by fractional distillation.

Increase of petrol fraction by cracking.

Further refining: reforming, alkylation, isomerization to increase octane number.

12 *Coal gasification*

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

$CO(g) + 3H_2(g) \rightarrow CH_4 + H_2O$

Coal liquefaction

Direct: $5C(s) + 6H_2(g) \rightarrow C_5H_{12}(l)$

$11H_2(g) + 5CO(g) \rightarrow C_5H_{12}(l) + 5H_2O(l)$

13 Carbon-containing fuels are non-renewable.

They are needed as chemical feedstocks.

Their combustion adds carbon dioxide to the atmosphere, which contributes to global warming.

14 **(a)** $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$: $\Delta H_c^{\ominus} = -283\ \text{kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$: $\Delta H_c^{\ominus} = -286\ \text{kJ mol}^{-1}$

$CO(g) + H_2(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$: $\Delta H_c^{\ominus} = -283 + (-286)\ \text{kJ mol}^{-1} = -569\ \text{kJ mol}^{-1}$

(b) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$: $\Delta H_c^{\ominus} = -891\ \text{kJ mol}^{-1}$

(c) One mole of synthesis gas has the same volume as two moles of methane. One mole of synthesis gas produces 569 kJ and two moles of methane produce 2 × 891 kJ.

15 **(a)** Methane is the major component of natural gas. It has the formula CH_4.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

(b) Natural gas is the cleanest of the fossil fuels to burn as it has a high H : C ratio.

The combustion of natural gas produces minimal amounts of carbon monoxide, hydrocarbons and particulates. It does contribute to global warming but does not contribute to acid rain, unlike coal and oil.

(c) Natural gas is the fossil fuel in the shortest supply and it is unevenly distributed around the world.

Oil is expected to last a little longer and coal, which is distributed more evenly around the world, longer still.

(d) Supplies of methane can be increased as a result of the cracking of larger hydrocarbons from oil or by coal gasification.

Cracking

$C_4H_{10} \rightarrow CH_4\ (g) + C_3H_6(g)$

Coal gasification

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

$CO(g) + 3H_2(g) \rightarrow CH_4 + H_2O$

16 **(a)** Wide availability

Relatively cheap compared to other sources

Ease of transportation

Power stations can be built close to the source

High energy density

Can be used with existing technology

Concern over nuclear

Limited productivity of other sources

Not possible to generate sufficient electrical energy without it

Many transport systems rely on fossil fuels

(b) Oil used to power internal combustion engines

17 It is more efficient

It produces more thermal energy per unit of mass / has a higher specific energy / energy density

It produces less CO_2 per unit of output energy

18 **(a)**

Fuel	$\Delta H_c^\ominus$ / kJ mol^{-1}	Moles needed to produce 10 000 kJ	Molar mass / g mol^{-1}	Mass needed to produce 10 000 kJ
Methylbenzene	–3910	10 000/3910 = 2.56	$(12.01 \times 7) + (8 \times 1.01)$ = 92.15	2.56×92.15 = 236
Ethanol	–1367	10 000/1367 = 7.31	$(12.01 \times 2) + (6 \times 1.01) + 16.00$ = 46.08	7.31×46.08 = 337

(b)

Fuel	Moles of CO_2 produced / mol	Mass of CO_2 produced / g
Methylbenzene	$7 \times 2.56 = 17.92$	$17.92 \times 44.01 = 789$
Ethanol	$2 \times 7.31 = 14.62$	$14.62 \times 44.01 = 643$

18 **(c)** They produce less carbon dioxide / have a smaller carbon footprint.

19 **(a)** Predicted mass of deuterium nucleus = 2 (1.008 665 + 1.007 265) amu

= 2.01593 amu

$\Delta m = 2.01593 - 2.01355$ amu $= 0.00238$ amu $= 0.00238 \times 1.66 \times 10^{-27}$ kg

$\Delta E = 0.00238 \times 1.66 \times 10^{-27} \times (3.00 \times 10^{8})^2$ J

$\Delta E = 0.00238 \times 1.66 \times 10^{-27} \times (3.00 \times 10^{8})^2 \times 6.02 \times 10^{23}$ J mol^{-1}

$= 2.14 \times 10^{11}$ J mol^{-1}

$= 2.14 \times 10^{8}$ kJ mol^{-1}

(b)

Nuclide	No. of nucleons	Binding energy / kJ mol^{-1}	Binding energy / kJ mol^{-1} per nucleon
$^{4}_{2}He$	4	2.73×10^{9}	$2.73 \times 10^{9}/4$ $= 6.825 \times 10^{8}$
$^{2}_{1}H$	2	2.14×10^{8}	$2.14 \times 10^{8}/2$ $= 1.07 \times 10^{8}$

(c) We have the following energy changes as the nuclei of the two elements are formed:

$2p + 2n \rightarrow 2\,^{2}_{1}H$: $\Delta E = 2 \times 2.14 \times 10^{8}$ kJ mol^{-1}

$2p + 2n \rightarrow \,^{4}_{2}He$: $\Delta E = 2.73 \times 10^{9}$ kJ mol^{-1}

Using Hess' law we have for the following:

$2\,^{2}_{1}H \rightarrow 2p + 2n$: $\Delta E = -2 \times 2.14 \times 10^{8}$ kJ mol^{-1}

$2p + 2n \rightarrow \,^{4}_{2}He$: $\Delta E = 2.73 \times 10^{9}$ kJ mol^{-1}

Adding the equations:

$2\,^{2}_{1}H \rightarrow \,^{4}_{2}He$: $\Delta E = (-2 \times 2.14 \times 10^{8}) + (2.73 \times 10^{9})$ kJ mol^{-1}

$\Delta E = 2.30 \times 10^{9}$ kJ mol^{-1}

(d) $^{4}_{2}He$ is more stable than $^{2}_{1}H$

20 **(a)** $^{1}_{0}n$

(b) $^{17}_{8}O$

21 **(a)** $\Delta E = hc/\lambda$

$= 6.63 \times 10^{-34} \times 3.00 \times 10^{8}/\lambda$ J

$= 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3.00 \times 10^{8}/\lambda$ J mol^{-1}

$= 6.02 \times 10^{20} \times 6.63 \times 10^{-34} \times 3.00 \times 10^{8}/\lambda$ kJ mol^{-1}

$= 0.00012/\lambda$ kJ mol^{-1}

λ / m	ΔE / kJ mol^{-1}
656×10^{-9}	$0.00012/656 \times 10^{-9}$ $= 183$
486×10^{-9}	$0.00012/486 \times 10^{-9}$ $= 247$
434×10^{-9}	$0.00012/434 \times 10^{-9}$ $= 276$

(b) By inspection we can see that transitions from $n = 2$ fall into this range

ΔE / kJ mol^{-1}	Transition
183	$n = 2 \rightarrow n = 3$
247	$n = 2 \rightarrow n = 4$
276	$n = 2 \rightarrow n = 5$

(c) At higher energy, energy levels become closer together; the energy differences between higher energy levels and the lower level ($n = 2$) become closer together and the difference in wavelength decreases.

22 **(a)** Energy produced from 1 g $= 6.72 \times 10^{-6} \times (3.00 \times 10^{8})^{2}$ J g^{-1}

$= 6.05 \times 10^{11}$ J

$= 6.05 \times 10^{8}$ kJ

(b) Mass of coal needed $= 6.05 \times 10^{8}$ kJ/ 30 kJ g^{-1} $= 20 \times 10^{6}$ g

$= 20 \times 10^{3}$ kg

23 $E = \Delta mc^2$

$\Delta m = 0.018884$ amu

$= 0.018884$ g mol^{-1}

$E = 0.018884 \times 10^{-3}$ kg $\times (3.00 \times 10^{8})^{2}$

$= 1.70 \times 10^{12}$ J mol^{-1}

$= 1.70 \times 10^{9}$ kJ mol^{-1}

24 **(a)** W: atomic number = 90, mass number = 233 – 4 = 229: ${}^{229}_{90}\text{Th}$

X: atomic number = 0, mass number = 236 – 233 = 3: $3{}^{1}_{0}\text{n}$

Y: atomic number = 93, mass number = 239: ${}^{239}_{93}\text{Np}$

Z: atomic number = 34, mass number = 92: ${}^{92}_{34}\text{Se}$

(b) Process II (fission) is used to produce electricity in nuclear power plants. (Process IV is also a fission reaction and is another potential reaction.)

This process can be initiated as required by controlling the input of neutrons, whereas the other processes are natural ones and occur randomly.

Process II is self-sustaining if the critical mass is available. It produces more neutrons than are needed initially and so a chain reaction occurs which can lead to the fission of more nuclei.

(c) The mass of the products is less than the mass of the reactants. The difference is converted to energy according to the equation $\Delta E = \Delta mc^2$.

25 Less than 1% of uranium is the fissionable isotope: ${}^{235}_{92}\text{U}$

There is less than the critical mass present. There is insufficient ${}^{235}_{92}\text{U}$ to sustain the chain reaction.

26 **(a)** UO_2 is a giant ionic; UF_6 is molecular covalent.

The +4 oxidation state forms ionic compounds but the +6 state forms covalent compounds as the U^{6+} ion would be too polarizing.

(b) Both compounds would have similar radioactivity as its depends on the nucleus of the atoms and not on the electron arrangements.

(c) For fission reactors, the fuel (typically based on uranium) is usually based on the metal oxide; oxides are used rather than the metals themselves because the oxide melting point is much higher than that of the metal and because it cannot burn, being already in the oxidized state.

27 **(a)** The elements all have non-polar molecular covalent structures. The intermolecular forces are due to the interaction between an instantaneous dipole and induced dipole and so depend on the number of electrons. The boiling points increase as the number of electrons increase.

(b) UF_6 has a lower boiling point than expected based on the trend in (a). Although it is a non-polar molecule it does contain polar bonds. The fluorine atoms all have a partial negative charge so repel the fluorine atoms in other molecules, which reduces the intermolecular forces.

(c) It is volatile and the fluorine atoms only have one mass number so the mass difference is due to mass differences in the uranium atoms.

(d) The separation depends on the ratio of the masses of the compounds containing the two isotopes = 352/349.

As the ratio is close to one, the molecules have very similar physical properties and so are hard to separate.

28 **(a)** Fuel enrichment means that the amount of ^{235}U in the fuel is increased, which means more than the critical mass of ^{235}U is available for fission so the reaction can be sustained.

(b) Enriched fuel can be used in the manufacture of nuclear weapons.

29 **(a)** Mass which is converted to energy = 1/1000 × 1.0 kg

$= 1.0 \times 10^{-3}$ kg

$\Delta E = \Delta mc^2$

$= 1.0 \times 10^{-3}\ \text{kg} \times (3.00 \times 10^8\ \text{m s}^{-1})^2$

$= 9.0 \times 10^{13}$ J

$= 9.0 \times 10^{10}$ kJ

(b) Mass of coal which produces this energy = $9.0 \times 10^{10}\ \text{kJ}/30\ \text{kJ g}^{-1} = 3.0 \times 10^9$ g

30 $\Delta m = 5.2 \times 10^{-3}$ amu

$\Delta E = \Delta mc^2$

$= 5.2 \times 10^{-3} \times 1.661 \times 10^{-27} \times (3.00 \times 10^8)^2$

$= 7.77 \times 10^{-13}$ J

$= 4.7 \times 10^8\ \text{kJ mol}^{-1}$

31 **(a)** The first neutron is needed to initiate a chain reaction and the reaction would not happen without it.

(b) Mass of reactants = 235.0439 + 1.0087 = 236.0526 amu

mass of products = 95.9342 + 137.9112 + (2 × 1.0087) = 235.8628 amu

$\Delta m = 0.1898$ amu

$\Delta E = 0.1898 \times 1.661 \times 10^{-27} \times (3.00 \times 10^8)^2$ J

$= 0.1898 \times 1.661 \times 10^{-27} \times (3.00 \times 10^8)^2 \times 6.02 \times 10^{23}\ \text{J mol}^{-1}$

$= 1.71 \times 10^{13}\ \text{J mol}^{-1}$

$= 1.71 \times 10^{10}\ \text{kJ mol}^{-1}$

32 **(a)** $^{228}_{90}Th \rightarrow {}^{224}_{88}Rn + {}^{4}_{2}He$

(b) Mass of products = 228.022800 amu

$\Delta m = 0.005926$ amu

(c) $\Delta E = \Delta mc^2$

$\Delta m = 0.005926 \times 1.66 \times 10^{-27}$ kg

$\Delta E = 0.005926 \times 1.66 \times 10^{-27} \times (3.0 \times 10^8)^2$ J

$= 8.860 \times 10^{-13}$ J

$= 8.860 \times 10^{-13} \times 6.02 \times 10^{23}\ \text{J mol}^{-1}$

$= 5.33 \times 10^{11}\ \text{J mol}^{-1} = 5.33 \times 10^8\ \text{kJ mol}^{-1}$

(d) Mass of coal burned = $5.33 \times 10^8\ \text{kJ mol}^{-1}/28\ \text{kJ g}^{-1}$

$= 1.9 \times 10^7$ g

$= 1.9 \times 10^4$ kg

33 **(a)**

Time / half-lives	Fraction remaining
0	1
1	0.5
2	0.25
3	0.125
4	0.0625
5	0.03125
6	0.015625
7	0.0078125
8	0.00390625
9	0.001953125
10	0.000976563

(b) 99.9%

34 First notice that 96.0 s = 96.0/19.2 = $5t_{1/2}$

Use the information in the question to compile a table:

Time / half-lives	Time / s	Activity / s^{-1}
0	0	1200
1	19.2	600
2	38.4	300
3	57.6	150
4	76.8	75
5	96.0	37.5

The count rate would be 37 or 38 disintegrations per second.

35 $^{235}_{92}U + ^{1}_{0}n \rightarrow \ldots\ldots\ldots \rightarrow ^{90}_{38}Sr + ^{144}_{54}Xe + 2^{1}_{0}n$

36 High level: contains fission products

Low level: clothing / fuel cans / other

Stored under water

Buried underground

Encased in steel/concrete

Vitrified / made into glass

37 Use the information in the question to compile a table:

Time / years	Activity / $hr^{-1}\ g^{-1}$
0	60.0
5730	30.0
5730 × 2	15.0
5730 × 3	7.5
5730 × 4	3.75

The shell is approximately 5730 × 4 years = 22 920 years old.

38 **(a)** $^{238}_{94}Pu \rightarrow ^{234}_{92}U + ^{4}_{2}He$

(b) One year is short compared to the half-life and so the number of plutonium nuclei does not change significantly.

(c) $\lambda = \ln 2/t_{1/2}$

$= \ln 2/(88\ yr) = 0.007877\ yr^{-1}$

$\ln([A]_t)/([A]_0) = -0.007877\ yr^{-1} \times 20\ yr = -0.157533$

$([A]_t)/([A]_0) = e^{-0.157} = 0.854$

$= 85.4\%$

39 **(a)** $\lambda = \ln 2/(28.4\ yr) = 0.0244\ yr^{-1}$

$A = A_0 e^{-0.0244 \times 80}$

$= 5.1 \times 10^{16} \times e^{-0.0244 \times 80}$

$= 7.24 \times 10^{15}\ s^{-1}$

(b) Initial activity is very high and still highly radioactive after 80 years. This poses severe health risks and problems of disposal.

40 $E_{needed} = 1216\ kJ\ mol^{-1}$

$= 1216 \times 1000\ J\ mol^{-1}/(6.02 \times 10^{23}\ mol^{-1})$

$E = h\nu$

$\nu = 1216 \times 1000\ J\ mol^{-1}/(6.02 \times 10^{23}\ mol^{-1} \times 6.63 \times 10^{-34}\ J\ s)$

$= 3.05 \times 10^{15}\ s^{-1}$

$\lambda = 3.00 \times 10^{8}\ m\ s^{-1}/3.05 \times 10^{15}\ s^{-1}$

$= 9.85 \times 10^{-8}\ m$

This is in the UV region of the electromagnetic spectrum, as displayed in section 4 of the IB data booklet.

41 **(a)** $CH_2{=}CH{-}CH{=}CH_2$ is a conjugated system with two double bonds separated by a single bond which extends along the full length of the molecule.

(b) The double bonds disappear as the molecules undergo an addition reaction with bromine.

(c) Benzene absorbs radiation in the UV region.

In nitrobenzene, conjugation between the benzene ring and the nitro group allows radiation of longer wavelength to be absorbed. This radiation occurs in the visible region of the spectrum and so the compound is coloured.

42 **(a)** Increased conjugation (increased *n*) moves the absorption band λ_{max} towards longer wavelength.

(b) The first members of the series are colourless as they absorb in the UV region, but the later members ($n > 2$) are coloured as they absorb in the visible region.

(c) $C_6H_5{-}(CH{=}CH)_5{-}C_6H_5$ absorbs in the purple region and is probably yellow.

C_6H_5—(CH═CH)$_6$—C_6H_5 absorbs in purple/blue region and is probably orange.

(d) Only λ_{max} and not the full spectrum is given so it is not possible to give a precise answer.

43 The conjugated system includes eleven C═C bonds and so absorbs in the visible region.

The molecule absorbs blue light and so appears orange.

44 **(a)** Fossil fuels and biomass are derived from the sun through photosynthesis.

Other sources: wind and hydroelectricity.

(b) Advantage: renewable and has little environmental impact.

Disadvantages: photosynthesis is not very efficient so relatively little of the available solar energy is trapped.

45 **(a)** $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(b) Chlorophyll

(c) Conjugated system of double and single bonds

(d) Process: fermentation

Equation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

Conditions: acidity / absence of oxygen / below 40 °C

Yeast provides enzyme

46 **(a)** Methane

(b) Carbon monoxide and hydrogen

(c) Particulates (soot), hydrocarbons, carbon monoxide

(d) Fossil fuels are running out. Biomass is a renewable source.

47 **(a)** 1%

(b) Wavelength of radiation not absorbed by chlorophyll

Some radiation is reflected or heats the surface of the earth

Plants do not cover all the earth

(c) Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(d) Production of biogas

Production of ethanol / fermentation

48 Biodiesel is renewable.

Biodiesel is carbon neutral. Plants use the same amount of CO_2 to make the oil that is released when the fuel is burned.

Biodiesel is rapidly biodegradable and completely non-toxic, meaning spillages represent far less risk than petroleum diesel spillages.

Biodiesel has a higher flash point than petroleum diesel, making it safer in the event of a crash.

Blends of 20% biodiesel with 80% petroleum diesel can be used in unmodified diesel engines. Biodiesel can be used in its pure form but engines may require certain modifications to avoid maintenance and performance problems.

Biodiesel can be made from recycled vegetable and animal oils or fats.

49 **(a)** Distant from localized areas of pollution; data present an accurate measure of global levels of CO_2.

(b) % increase = (increase/initial value) × 100%

$= [(384 - 316)/316] \times 100\% = 21.5\%$

(c) Combustion of fossil fuels.

(d) The annual variation is due to CO_2 uptake by growing plants. The uptake is highest in the northern hemisphere springtime.

(e) Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

CO_2 dissolves in water: $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

(f) Decreased level of photosynthesis: less CO_2 taken in by plants.

(g) CO_2 absorbs infrared radiation, which leads to increased vibrations and bending and stretching of the bonds.

50 **(a)** Carbon dioxide has polar C═O bonds and the oxygen atoms have lone pairs. It can form hydrogen bonds with water molecules.

(b) Relatively strong hydrogen bonds are formed: ΔH is negative. The solubility decreases with increasing temperature, as the equilibrium shifts to the endothermic (reverse) direction as the temperature increases.

(c) Increased temperatures due to increased atmospheric carbon dioxide concentrations could result in reduced solubility of carbon dioxide. More carbon dioxide is then released, which amplifies the initial change.

(d) Increased carbon dioxide increases the rate of photosynthesis, producing more phytoplankton, which further reduce levels of carbon dioxide.

51 The removal of $CO_3^{2-}(aq)$ will cause the equilibrium $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ to shift to the right. The resulting decreased levels of $HCO_3^-(aq)$ will cause $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ to shift to the right and so on until $CO_2(g) \rightleftharpoons CO_2(aq)$ shifts to the right with the absorption of $CO_2(g)$.

52 pH = 8.2: $[H^+] = 10^{-8.2}$

pH = 8.1: $[H^+] = 10^{-8.1}$

% increase = $(10^{-8.1} - 10^{-8.2})/10^{-8.2} \times 100\%$

$= (10^{0.1} - 1) \times 100\% = 26\%$

53 **(a)** Respiration, volcanic eruption, complete aerobic decomposition of organic matter, forest fires

(b) Methane produced from anaerobic decomposition

(c) Smoke particulates: block out sunlight

(d) High-energy short-wavelength radiation passes through the atmosphere

Lower energy / longer wavelength radiation from the earth's surface is absorbed by vibrating bonds in CO_2 molecules

(e) Melting of polar ice caps; thermal expansion of oceans will lead to rise in sea levels, which can cause coastal flooding; crop yields reduced; changes in flora and fauna distribution; drought; increased rainfall; desertification

54 **(a)** Incoming radiation from the sun is of short wavelength

Long-wavelength infrared radiation leaves earth's surface and some is absorbed by gases in the atmosphere

Results in increased vibration of bonds in molecules which then re-radiate heat back to the earth

(b) *Natural:* (evaporation from) oceans

Artificial: burning (any specified) fossil fuel

(c) CO_2 is more abundant but CH_4 absorbs the radiation more effectively / has a larger greenhouse factor

55 **(a)** coal / diesel (fuel) / wood

(b) $CH_4 + O_2 \rightarrow C + 2H_2O$

56 **(a)** $E = E^\ominus - (RT/nF)\ln Q$

Cell reaction: $Zn(s) + Ni^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Ni(s)$; $Q = [Zn^{2+}(aq)]/[Ni^{2+}(aq)]$

$E^\ominus = -0.26 - (-0.76) = +0.50$ V

$Q = 0.100/0.00100 = 100$

$E = 0.50 - (8.31 \times 298/(2 \times 9.65 \times 10^4)) \times \ln 100$ V

$= 0.50 - 0.059$

$= 0.441$ V

(b) $E = E^\ominus - (RT/nF)\ln Q$

Cell reaction: $Mn(s) + Pb^{2+}(aq) \rightleftharpoons Mn^{2+}(aq) + Pb(s)$; $Q = [Mn^{2+}(aq)]/[Pb^{2+}(aq)]$

$E^\ominus = -0.13 - (-1.18) = 1.05$ V

$Q = 0.100/0.00010 = 1.0 \times 10^3$

$E = 1.05 - (8.31 \times 298/(2 \times 9.65 \times 10^4)) \times \ln(1.0 \times 10^3)$ V

$= 1.05 - 0.088633$

$= 0.96$ V

(c) $E = E^\ominus - (RT/nF)\ln Q$

Cell reaction: $Zn(s) + Fe^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Fe(s)$; $Q = [Zn^{2+}(aq)]/[Fe^{2+}(aq)]$

$E^\ominus = -0.45 - (-0.76) = +0.31$ V

$Q = 1.50/0.100 = 15.0$

$E = 0.31 - (8.31 \times 298/(2 \times 9.65 \times 10^4)) \times \ln 15.0$ V

$= 0.31 - 0.035 = 0.28$ V

57 **(a)** $E = E^\ominus - (RT/nF)\ln Q$

Cell reaction: $Zn(s) + Pb^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Pb(s)$; $Q = [Zn^{2+}(aq)]/[Pb^{2+}(aq)]$

$E^\ominus = -0.13 - (-0.76) = +0.63$ V

$Q = [\mathrm{Zn^{2+}(aq)}]/0.100$

$0.60 = 0.63 - (8.31 \times 298/(2 \times 9.65 \times 10^4)) \times \ln Q$

$-0.03 = -8.31 \times 298/(2 \times 9.65 \times 10^4) \times \ln Q$

$0.03 \times 2 \times 9.65 \times 10^4/(8.31 \times 298) = \ln Q$

$2.34 = \ln Q$

$Q = e^{2.34} = 10.1$

$10.1 = [\mathrm{Zn^{2+}(aq)}]/0.100$

$\mathrm{Zn^{2+}(aq)}] = 1.01\ \mathrm{mol\ dm^{-3}}$

(b) The equilibrium needs to be shifted to the right.

$[\mathrm{Zn^{2+}(aq)}]$ could be decreased or $[\mathrm{Pb^{2+}(aq)}]$ could be increased

In detail:

$0.65 = 0.63 - (8.31 \times 298/(2 \times 9.65 \times 10^4)) \times \ln Q$

$-0.02 = 8.31 \times 298/(2 \times 9.65 \times 10^4) \times \ln Q$

$-0.02 \times 2 \times 9.65 \times 10^4/(8.31 \times 298) = \ln Q$

$-1.55873 = \ln Q$

$Q = e^{-1.55873}$

$Q = 0.210 = [\mathrm{Zn^{2+}(aq)}]/0.100$

$\mathrm{Zn^{2+}(aq)}] = 0.021\ \mathrm{mol\ dm^{-3}}$

(c) Increase the temperature. This would increase the size of the second negative term in the Nernst equation.

58 **(a)** The half reaction at the cathode is: $\mathrm{Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)}$

The equilibrium will be to the right for high $[\mathrm{Zn^{2+}(aq)}]$

Solution B should be used at the cathode.

(b) $E = E^\ominus - (RT/nF)\ln Q$

$E = -(RT/nF)(\ln 2)$

$= 0.0089\ \mathrm{V}$

59 **(a)** $\underset{-167}{\mathrm{CH_3OH(l)}} + \underset{0}{\mathrm{(3/2)O_2(g)}} \rightarrow \underset{-394.4}{\mathrm{CO_2(g)}} + \underset{2(-237.1)}{\mathrm{2H_2O(l)}}$

$\Delta G_f^\ominus$ / kJ mol^{-1}

$\Delta G_{\text{reaction}} = \sum \Delta G_f^\ominus\ \text{(products)} - \sum \Delta G_f^\ominus\ \text{(reactants)}$

$= (-394.4 + 2(-237.1) - (-167)\ \mathrm{kJ\ mol^{-1}}$

$= -702\ \mathrm{kJ\ mol^{-1}}$

(b) $\text{Efficiency} = \dfrac{-\Delta G_{\text{sys}}}{-\Delta H_{\text{sys}}} \times 100\% = \dfrac{-702}{-726} \times 100\%$

$= 97\%$

60 **(a)** Oxidation number increases from 0 to +2. Pb(s) is oxidized.

(b) $\mathrm{Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-}$

(c) $\mathrm{PbSO_4}$ is insoluble: the $\mathrm{Pb^{2+}}$ ions do not disperse into solution.

(d) Advantage: delivers large amounts of energy over short periods.

Disadvantage: heavy mass; lead and sulfuric acid could cause pollution.

61 **(a)** Bacteria oxidize the substrate: they live at the negative electrode or cathode.

(b) Sucrose is oxidized by the bacteria. 12 Cs are oxidized from 0 to + 4 so 48 electrons are released

24 Os are needed so 13 $\mathrm{H_2O}$ are needed

48 Hs are needed on both sides

Check that the charges are balanced: zero on both sides

$\mathrm{C_{12}H_{22}O_{11}(aq) + 13H_2O(l) \rightarrow 12CO_2(g) + 48H^+(aq) + 48e^-}$

(c) 48 electrons will reduce 12 $\mathrm{O_2}$ molecules

48 Hs are needed on both sides:

$\mathrm{48H^+(aq) + 12O_2(g) + 48e^- \rightarrow 24H_2O(l)}$

(d) $\mathrm{C_{12}H_{22}O_{11}(aq) + 13H_2O(l) \rightarrow 12CO_2(g) + 48H^+(aq) + 48e^-}$

$\mathrm{48H^+(aq) + 12O_2(g) + 48e^- \rightarrow 24H_2O(l)}$

$\mathrm{C_{12}H_{22}O_{11}(aq) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)}$

62 **(a)** $\mathrm{H_2 + 2OH^- \rightarrow 2H_2O + 2e^-}$

$\mathrm{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-}$

(b) Less waste heat produced and more chemical energy converted to useful energy. They use a renewable energy source which is more efficient.

63 Metals conduct electricity well, insulators do not; semiconductors have intermediate conductivities. The conductivity of metals decreases with temperature; the conductivity of semiconductors increases with temperature. Conductors have low ionization energies; insulators have high ionization energies.

64 **(a)** Ionization energies decrease down a group so the electrons are easier to remove in germanium compared to diamond, resulting in more free electrons.

(b) Boron has only three outer electrons so it produces a positive hole in the lattice to give a p-type semiconductor.

65 Arsenic, as it has five outer electrons and a similar atomic radius.

66 Si is doped with As to produce an n-type semiconductor and with Ga to produce a p-type semiconductor. Light stimulates electron flow from the n-type to the p-type semiconductor through an external circuit.

67

Advantages	Disadvantages
no pollution no moving parts so no maintenance no need for refuelling as sunlight is unlimited produces less noise conserves petroleum for other uses	low power output needs a large surface area battery / storage facilities needed in absence of light high capital cost easily damaged

68 Conductivity increases as the gallium has one less electron than silicon.

Electron holes are introduced, which make it a p-type conductor so electrons can move into these holes. Arsenic has one more electron than silicon. An extra electron is introduced so it is a n-type conductor. The extra electrons are free to move.

69 **(a)**

Process	Photovoltaic	DSSC
Light absorption	Silicon atom is ionized to create hole and electron (Si^+ and e^-) pair	Electron excited in conjugated organic molecule
Charge separation	Electron and hole move in opposite directions due to electric field in p–n semiconductor	Election is accepted by semiconductor. Positive ion loses its charge as the ion is reduced by electrolyte

(b) If the electron directly recombines with an ion the light energy is converted to useless heat energy.

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 **(a)** long wavelength / infrared / IR radiation from Earth's surface

(some of this radiation) is absorbed (by gas)

Do not accept 'trapped' or 'blocked'.

Do not award mark for 'IR from sun'.

causes (increased) vibration in bonds

re-radiates heat back to the Earth

Accept 're-transmits'

Do not accept 'reflects/bounces' [2 max]

(b) melting of polar ice caps / glaciers melting

thermal expansion of oceans / rise in sea levels / coastal flooding

stated effect on agriculture (e.g. crop yields changed)

changes in flora / plant / fauna / animal / insect distribution / biodiversity

Accept specific example.

stated effect on climate (e.g. drought / increased rainfall / desertification)

Do not accept 'climate change' alone.

Do not allow 'increased temperature / global warming' (given in question).

*Award **[1]** each for any three.* [3 max]

2 high-level waste has longer half-life / low-level waste has shorter half-life

high-level waste is vitrified / made into glass / buried underground / in granite / in deep mines / under water / in steel containers / in cooling ponds / *OWTTE*

low-level waste is stored under water / in steel containers / in cooling ponds /filtered / discharged directly into sea / *OWTTE*

Accept cooling ponds/steel containers/under water/concrete containers only once. [3]

3 *Catalytic cracking:*

used to produce moderate length alkanes for fuels

lower temperature / lower energy consumption / more control of product [2]

4 light nuclei for fusion and heavy nuclei for fission

more massive nucleus produced in fusion as nuclei joined together and two lighter nuclei produced in fission as nuclei split apart [2]

5 6.25% remains

4 half-lives = 6400 years [2]

6 **(a)** energy transferred to surroundings / from system which is no longer available for use / cannot be used again [2]

(b) $^{235}_{92}U$ undergoes a fission reaction due to neutron capture

reaction produces neutrons so chain reaction occurs

mass of products less than reactants

corresponding energy released according to $E = mc^2$ [4]

(c) the mass needed that allows fission to be sustained [1]

7 **(a)** wide availability

produce energy at appropriate rate

ease of transportation

current technology is based on fossil fuels

high energy density / specific energy [2 max]

(b) energy produced per unit mass / kg / stored per unit mass / kg [1]

(c) uranium / hydrogen [1]

(d) Efficiency = $600 \times 10^6/\text{energy}_{\text{input}}$

$\text{Energy}_{\text{input}} = 600 \times 10^6/0.30\ \text{J s}^{-1} = 2000 \times 10^6\ \text{J s}^{-1}$

Mass of fuel = $2000 \times 10^6/60 \times 10^3 = 33.3 \times 10^3\ \text{g s}^{-1}$ [3]

8 **(a)** coal about 90% and petroleum about 84% and natural gas 75% [1]

(b) they have higher specific energy

liquid or gaseous state make them more convenient to use / easier to transport

produce less pollution / smaller carbon foot print [2 max]

(c) hydrogen has a very high specific energy / energy density

it is clean burning producing only H_2O when it is burned [2]

9 **(a)**

Formula	M /g mol^{-1}	ΔH_c / kJ mol^{-1}	Specific energy / kJ g^{-1}
C_3H_8	44.11	−2219	2219/44.11 = 50.31
C_4H_{10}	58.14	−2878	2878/58.14 = 49.50

[2]

(b) $\rho = PM/RT$

Formula	Specific energy
C_3H_8	$(2219/44.11) \times 1.00 \times 10^5 \times 44.11/(8.13 \times 273)$ $= 2219 \times 1.00 \times 10^5/(8.31 \times 273)$ $= 97\,800$ kJ m^{-3} $= 0.978$ kJ cm^{-3}
C_4H_{10}	$(2878/58.14) \times 1.00 \times 10^5 \times 58.14/(8.13 \times 273)$ $= (2878 \times 1.00 \times 10^5)/(8.31 \times 273)$ $= 127\,000$ kJ m^{-3} $= 0.127$ kJ cm^{-3}

[3]

(c) propane as it the smallest molar mass [1]

10 **(a)** photosynthesis [1]

(b) chlorophyll

conjugated structure [2]

(c) $6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$ [1]

(d) $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ [1]

(e) **(i)** fermentation

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ [2]

(ii) $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$$\begin{array}{cccc} -175 & 0 & 2(-394.4) & 3(-237.1) \end{array}$$

$\Delta G_f^{\ominus}$ /kJ mol^{-1}

$\Delta G = 2(-394.4) + 3(-237.1) - (-175) = -1325.1$ kJ mol^{-1}

thermodynamic efficiency = $-1325.1/-1367 = 97\%$ [3]

(f) bacteria live at the anode

they oxidize the biomass [2]

11 **(a)** the octane number indicates the resistance of a motor fuel to knock / premature ignition

octane numbers are based on a scale on which 2,2,4-trimethylpentane (isooctane) is 100 (minimal knock) and heptane is 0 (maximum knock) [2]

(b) octane number of straight-chain alkanes decrease with an increase in chain length

straight chain alkanes < aromatics

alcohols have very high octane numbers:

hexane (24.8) < pentane (61.7) < benzene (105.8) < ethanol (108) [4]

The octane numbers are given for reference and are not expected to be recalled.

12 **(a)** $^{235}_{92}U \rightarrow ^{231}_{90}Th + ^{4}_{2}He$

atomic number = 90 and element = Th

mass number = 231 [2]

(b) *To answer this question you need to know that the half-life of $^{235}_{92}U$ is 704 million years.*

After one half-life the amount of $^{235}_{92}U$ will have decayed to 50% of its original amount.

After two half-lives the amount of $^{235}_{92}U$ will have decayed to 25% of its original amount, i.e. 75% will have decayed.

2 × 704 million years = 1408 million years

It will take 1408 million years for 75% of the $^{235}_{92}U$ to decay. [2]

13 **(a)** effects due to: increased carbon dioxide levels, global warming

non-metal / sulfur / nitrogen oxides produce acid rain

unburned hydrocarbons and carbon monoxide

particulates cause global dimming [3 max]

13 **(b)**

Strategy	Action
Increased energy efficiency and conservation	• Use of insulation and more efficient appliances • Reducing personal energy use by turning off lights and electronics when not in use • Reducing distance travelled in vehicles or using more efficient modes of transport such as hybrid cars or public transport *Award **[1 max]** for action*
Reduced dependence on carbon-based energy resources	• Use alternative sources such as solar, wind, geothermal, hydropower, wave, tidal or nuclear power • Use reduced-carbon fuels such as natural gas. The potential use of biomass depends on the processes by which it is converted to energy *Award **[1 max]** for action*
Capture and storage of carbon from fossil fuels or from the atmosphere	• Carbon dioxide can be removed from the atmosphere and stored within plants and soil supporting the plants. Alternatively, carbon dioxide can be captured either before or after fossil fuel is burned and then be stored (sequestered) within the earth • Reduce deforestation and plant more trees *Award **[1 max]** for action*

[6]

(c) countries with cheaper gasoline on average:

use more gasoline

have less efficient vehicles

produce more CO_2 and have higher carbon footprint [3]

14 **(a)** octane C_8H_{18}

any other compound with C_5–C_{10} [2]

(b) fractional distillation

mixture of hydrocarbons is heated causing them to vaporize

different compounds have different boiling points; the lowest boiling point compounds condense higher up the column

as the size of the molecule increases the attractive van der Waals forces increase [4]

(c) larger molecules can be cracked into smaller molecules when heated with a catalyst and broken into smaller molecules

equation for cracking: $C_{14}H_{30} \rightarrow C_7H_{14} + C_7H_{16}$ [2]

15 **(a)**

Fuel	Formula	Standard enthalpy of combustion ΔH / kJmol^{-1}	Relative molecular mass	Specific energy / kJ g^{-1}
methane	CH_4	–891	16.05	55.5
methanol	CH_3OH	–726	32.05	22.7

[2]

(b) CH_4: Ox (C) = –4; CH_3OH: Ox (C) = –2 [1]

(c) the more oxidized the C the lower the specific heat [1]

(d)

Fuel	Formula	Standard enthalpy of combustion ΔH / kJmol^{-1}	Relative molecular mass	Specific energy / kJ g^{-1}
methanol	$C_6H_{12}O_6$	–2803	180.18	15.6

oxidation number of C = 0

the result supports the hypothesis [3]

16 **(a)** they are too viscous

as there are strong intermolecular forces between the triglyceride molecules [2]

(b) transesterification

reaction with methanol or ethanol with strong acid or base catalyst produces a methyl / ethyl ester [2]

17 **(a)** *Cathode:*

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

Anode:

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

If both equations given but at wrong electrodes award ***[1]****.* [2]

(b) *Cathode:*

nickel hydroxide / $Ni(OH)_2$

Anode:

cadmium hydroxide / $Cd(OH)_2$

Cell equation:

$Cd + 2H_2O + 2NiO(OH) \rightarrow Cd(OH)_2 + 2Ni(OH)_2$ [3]

18 **(a)** contains no lithium / metal / uses lithium salt in an organic solvent (as electrolyte)

involves movement of lithium ions (between electrodes) [2]

(b) *Anode:*

$LiC_6 \rightarrow Li^+ + 6C + e^-$ / Li^+ ions dissociate from anode (and migrate to cathode)

Cathode:

$Li^+ + e^- + MnO_2 \rightarrow LiMnO_2$ / $Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$ / $Li^+ + e^- + FePO_4 \rightarrow LiFePO_4$ / $Li^+ + e^- + NiO_2 \rightarrow LiNiO_2$ / Li^+ ions are inserted into metal oxide / phosphate (structure)

Award ***[1]*** *if electrodes are reversed.* [2]

(c) *Similarity:*

both convert chemical energy **directly** into electrical energy / both use spontaneous redox reactions (to produce energy) / both are electrochemical cells / voltaic cells / galvanic cells

Difference:

fuel cells are energy conversion devices **and** rechargeable batteries are energy storage devices / fuel cells require constant supply of reactants **and** batteries have stored chemical energy / provide power until stored

chemicals are used up / batteries can be recharged **and** fuel cells do not need recharging (have a continuous supply of fuel) / fuel cells are more expensive than rechargeable batteries / the reactions in a rechargeable battery are reversible **and** in a fuel cell are not [2]

19 Si has a lower ionization energy (than P or S)

so electrons can flow through the material more easily

(p-type) has small amount of / is doped with a group 3 element / B / In / Ga

which produces electron holes / positive holes

sun / photons cause release of electrons

electrons move from n-type to p-type material [5 max]

20 **(a)** ^{56}Fe [1]

(b) the energy released when nuclides form from separate nuclei into separate nucleons [1]

(c) $^{235}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{141}_{56}\text{Ba} + ^{92}_{36}\text{Kr} + 2\ ^{1}_{0}\text{n}$

two neutrons produced may cause two further fissions

producing four neutrons which may produce four further fissions [3]

(d) one reaction: $\Delta E = 3.1 \times l0^{-28} \times [3 \times 10^8]2/2.8 \times l0^{-11}$ (J)

$= 2.8 \times 10^{-11} \times 6.02 \times 10^{23} = 1.69 \times 10^{13}$ (J mol^{-1})

$= 1.69 \times 10^{10}$ (kJ mol^{-1}) [3]

(e) mass of $^{235}_{92}$U in 1 g = 3.00×10^{-2} g

$n = 3.00 \times 10^{-2}/235 = 0.000128$ mol

specific energy = $1.69 \times 10^{10} \times 0.000128 = 2.16 \times 10^{9}$ kJ g^{-1} [3]

(f) enrichment process

converted to gaseous UF_6

position in centrifuge / diffusion rate depends on the masses [3]

21 **(a)** nuclear fusion [1]

(b) $\Delta m = 0.00535$ amu

$= 1.66 \times 10^{-27} \times 0.00535$ kg $= 8.88 \times 10^{-30}$ kg

$\Delta E = \Delta mc^2 = 8.88 \times 10^{-30} \times (3.00 \times 10^8)^2$ J $= 7.99 \times 10^{-13}$ J

$= 4.18 \times 10^{11}$ J mol^{-1} $= 4.18 \times 10^{8}$ kJ mol^{-1} [4]

(c) $^{3}_{2}$He

this is the source of the energy produced [2]

(d) confining the hot plasma [1]

22 *Photovoltaic cell:*
an impurity such as arsenic and gallium added to dope silicon layers to produce p–n junction

electron emitted as photon ionizes Si atom

when p-type and n-type silicon are put together, an electric field is produced which prevents recombination

electrons need to pass through external circuit

Dye sensitized cell:
highly conjugated organic molecules absorb electrons

excited electron injected into TiO_2 semiconductor

ionized dye reduced by electrode at anode

electrons pass through external circuit and reduce electrolyte at cathode [8]

23 **(a)** 42% efficient so $2.00 \times 10^4/0.42$ kJ $= 4.76 \times 10^4$ kJ required every second

$4.76 \times 10^7/2.8 \times 10^{-11} = 1.70 \times 10^{18}$ fissions each second $= 6.12 \times 10^{21}$ fissions each hour

moles needed $= 6.12 \times 10^{21}/6.02 \times 10^{23} = 1.02 \times 10^{-2}$ so mass needed $= 235 \times 1.02 \times 10^{-2}$

= 2.39 g [3]

(b) U-238 is present

U-238 captures a neutron (to produce plutonium)

plutonium can be used as fuel for (fast breeder) reactors [3]

(c) $0.693/(2.40 \times 10^4 \text{ yr}) = 2.89 \times 10^{-5} \text{ yr}^{-1}$ [1]

(d) $-\ln(0.01)/2.89 \times 10^{-5}$

$= 1.59 \times 10^5$ yr [2]

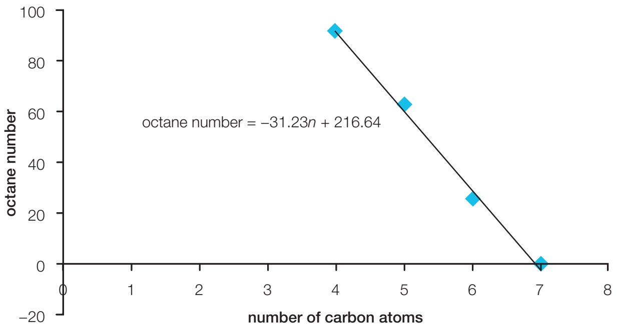
Challenge yourself

1 680 kJ of heat is given out. Energy efficiency is 32%.

2 The decrease in entropy in your brain is accompanied by increases elsewhere in the universe.

3 Coal and oil are fossilized decayed plants or animals that contain amino acids. The amino acid *cysteine* contains sulfur. Coal and oil with a higher percentage of sulfur are considered 'dirty' because of the sulfur dioxide pollution that they produce on combustion. Sulfur dioxide results in acid rain.

4 **(a)** Plotting a graph we see that the data follow an approximate straight-line relationship:



This suggests an octane number of −33.

In practise the graph is a curve rather than a straight line and octane has an octane number of −19.

(b) Assuming the same straight-line trend, for an octane number of 100, $n = 3.73$. So propane has an octane number above 100.

5 The isomers of octane have the essentially the same number of C—C and C—H bonds.

This suggests that they are not a key factor in a molecule's octane number.

6 The ratio between the values is approximately 4

This corresponds to $2^2 = Z^2$, where Z is the atomic number of helium.

This is a general result: the energy level is proportional to the square of the atomic number.

7 The 1% difference in molecular mass between the molecules formed from the two isotopes is due only to the difference in masses of the uranium isotopes.

8 As many stages are involved (up to 4000), a large area of ground is needed.

9 Other covalent fluorides with the non-metal in a high oxidation state. An example is SF_6.

10 $C_{40}H_{56}$

The position of the double bond in the hexagon on the right is different in the two isomers.

11 **(a)**

$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow xH_2 + yCO + zCO_2$

−1/16 +1 −2 +1 −2 0 0 +2 −2 +4 −2

(b) C is oxidized

O and H are reduced

(c) Balancing the H atoms:

$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow 42H_2 + yCO + zCO_2$

$x = 42$

(d) Total change of oxidation number of H = −84

Total change of oxidation number of O = −2

Total increase in oxidation number of C =+86

Balancing the change in oxidation numbers: $2y + 4z - 2 = +86$

Balancing the C atoms: $y + z = 32$

Solving the equations: $2z = 88 - 64 = 22$

$z = 11$ and $y = 21$

$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow 42H_2 + 21CO + 11CO_2$

(e) $42H_2 + 21CO \rightarrow 21CH_3OH$

2 molecules of wood produce 21 molecules of methanol

1 molecule produces 10.5 molecules

12 The solubility of carbon dioxide increases at lower temperatures and higher pressures.

Increased levels of $CO_2(g)$ will lead to the formation of the more soluble $Ca(HCO_3)_2(aq)$.

$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$

13 $$\text{Efficiency} = \frac{-\Delta G_{sys}}{-\Delta H_{sys}} \times 100\% = \frac{-\Delta H_{sys} + T\Delta S_{sys}}{-\Delta H_{sys}} \times 100 = 1 + \frac{T\Delta S_{sys}}{-\Delta H_{sys}} \times 100$$

The entropy decrease is smaller for the reaction which produces one mole of gaseous water, which leads to a larger efficiency.

Answers

Chapter 15

Exercises

1 intramuscular / into muscles

intravenous / into veins

subcutaneous / into fat

The fastest will be intravenous as the drug can be transported quickly all over the body in the bloodstream.

2 Tolerance occurs when repeated doses of a drug result in smaller physiological effects. It is potentially dangerous because increasing doses of the drug are used in response and this might get close to or exceed the toxic level.

3 **(a)** Lethal doses can be determined for animals; in humans the upper limit is the toxic dose.

(b) Bioavailability, side-effects, possibility of tolerance and addiction of the drug; age, sex, diet and weight of patient.

(c) Low therapeutic index means a low margin of safety, so small changes in dosage may produce adverse side-effects.

4 Method of administration of drug, solubility (in water and lipid) and functional group activity.

5 **(a)** 84.94%

(b) melting point determination: melting point of asprin is 138–140°C

6 Increase its solubility in water by converting to sodium salt.

7 **(a)** Mild analgesic blocks transmission of impulses at site of injury, not in the brain; anticoagulant acts to prevent coagulation / thickening of the blood and so reduces risk of coronary disease.

(b) Alcohol has synergistic effect with other drugs; can cause stomach bleeding with aspirin.

8 **(a)** $R{-}C_9H_{11}N_2O_4S$

(b) At the R group. Modification prevents the binding of the penicillinase enzyme and so maintains the action of the drug / prevents resistant bacteria rendering it inactive.

(c) Beta-lactam ring undergoes cleavage and binds irreversibly to the transpeptidase enzyme in bacteria. This inactivates the enzyme, which interrupts the synthesis of bacterial cell walls.

9 Overuse of antibiotics in animal stocks / food chain; over-prescription; failure of patients to complete treatment regimen.

10 **(a)** The functional groups in common are ether linkage (–C–O–C–), tertiary amine linkage (R–N(R′) – R″), alkene (–C=C–) and a benzene ring.

(b) main effect: pain relief

side-effect: constipation

11 Diamorphine has two ester groups in place of two –OH groups in morphine. The less polar diamorphine is more soluble in lipids and so crosses the blood–brain barrier more easily, and enters the brain where it blocks the perception of pain.

12 In favour: strongest pain killer known; the only effective analgesic against extreme pain.

Against: addictive drug; leads to dependence and serious side-effects.

13 H_2-receptor antagonists: block the binding of histamine, which prevents the reactions leading to stomach acid secretion.

Proton-pump inhibitors: directly prevent the release of acid into the stomach lumen.

14 **(a)** $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$

(b) $Al(OH)_3$ reacts with H^+ in a mole ratio of 1:3

$Mg(OH)_2$ reacts with H^+ in a mole ratio of 1:2

So 0.1 mol $Al(OH)_3$ will neutralize the greater amount.

(c) KOH is a strong alkali so would be dangerous for body cells; it is corrosive and would upset the stomach pH.

15 **(a)** pH changes from 5.12 to 5.11 (assuming no volume change on mixing).

(b) No change in pH on dilution of buffer.

16 Viruses lack a cellular structure and so are difficult to target. Antibiotics specifically interfere with bacterial cell walls or internal structures. Viruses replicate inside host cells and so treatment may involve killing host cells.

17 Subunits in hemagglutinin (H) and neuraminidase (N) can mutate and mix and match, so forming different strains. These change the specific nature of the glycoprotein–host interactions, and alter the body's immune response. This is why it is possible to suffer from flu several times during a lifetime.

18 Tamiflu and Relenza do not prevent the flu virus from entering cells, but act to stop it from being released from the host cells. So if the infection is not stopped early, too many new viral particles may have already been released.

19 Challenges: antiretroviral costs, distribution and availability; patient compliance to regimen and multiple drug treatments; sociocultural issues.

Successes: new and more effective antivirals that can be used in combination; better screening of HIV-positive; controlling infection through drugs.

20 **(a)** Bark of Pacific yew tree. Harvesting has depleted the trees which grow slowly.

(b) Taxol has 11 chiral carbon atoms, giving rise to a very large number of possible stereoisomers. At many stages in its synthesis, different enantiomers could be produced, which may have different physiological properties, so these steps need to be controlled by chiral auxiliaries.

21 A chiral auxiliary is itself an enantiomer which bonds to the reacting molecule to create the stereochemical environment necessary to follow a certain pathway. The reaction then takes place, forming the desired enantiomer and the chiral auxiliary is then removed.

Different enantiomers may have different biological effects, some of which may be harmful. An example are the genetic deformities caused by the (*S*)-enantiomer of the drug thalidomide in the racemic mixture.

22 **(a)** ${}^{90}_{39}\text{Y} \rightarrow {}^{90}_{40}\text{Zr} + {}^{0}_{-1}\beta$

(b) 23 g

23 6.12 hours

24 **(a)** Half-life is 6 hours – long enough for diagnosis but decays quickly.

Radiation is gamma rays used for detection, and low-energy electrons which minimize radiation dose. The isotope is chemically able to bond to various biomolecules.

(b) Strong beta emitters that also emit gamma radiation to enable imaging.

25 **(a)** Targeted alpha therapy uses alpha emitters attached to carriers such as antibodies, which specifically target certain cells.

(b) Very high ionizing density and so a high probability of killing cells along their track.

Short range and so minimize unwanted irradiation of normal tissue surrounding the targeted cancer cells.

26 B – immiscible liquids

27 **(a)** An ideal solution contains fully miscible components. Each component exerts the same vapour pressure in the mixture, according to its relative concentration, as it does when pure. The intermolecular forces between the particles of the different components are the same as those between the particles in the pure substances.

(b) Boiling point of a mixture decreases with increasing height in a fractionating column as the mixture becomes enriched in the more volatile component.

28 **(a)** 2850–3090 cm^{-1} is characteristic of the C—H bond

3200–3600 cm^{-1} is characteristic of the O—H bond

(b) The peak at 2850–3100 cm^{-1} is used to characterize ethanol in the presence of water vapour.

(c) Propanone also contains C—H bonds, which give the same characteristic band at 2950 cm^{-1} as ethanol.

29 **(a)** molecular ion at $m/z = 194$

(b) C—H in methyl groups: 2850–3090 cm^{-1}

C=O: 1700–1750 cm^{-1} (two different peaks)

(c) four peaks, relative areas 3:3:3:1

(d) amine, amide, alkene

30 Solvents cause problems of disposal. Organic solvents can be incinerated, causing release of pollutants, greenhouse gases and toxins. Solvents can contaminate ground water and soil. Some solvents can be hazardous to health of workers.

31 Protective shoe-covers, clothing, gloves, paper towels and contaminated implements. Interim storage in sealed containers for radioactivity to decay, before conventional disposal.

32 The success of antibiotics in treating disease has led to their widespread use, and in some cases over-use. Exposure of bacteria to antibiotics increases the spread of resistant strains. Antibiotic resistance renders some antibiotics ineffective, especially with multiply resistant strains, e.g. MRSA.

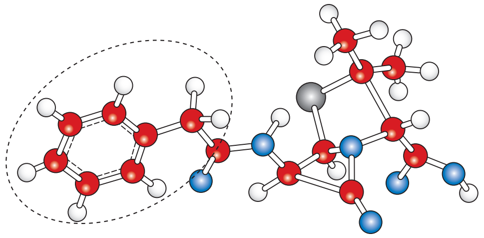
33 Patient compliance refers to the importance of patients following medical instructions, in particular to completing the course of an antibiotic treatment. This helps prevent the spread of antibiotic-resistant bacteria.

34 Green Chemistry principles seek to reduce toxic emissions and waste substances in the manufacture of drugs. This includes reduction in the amount of solvent used, the adoption of synthesis pathways with shorter routes, the replacement of inorganic catalysts with enzymes and the recycling of waste.

Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 **(a)** [1]



No mark if circle includes CO or just O.

*Award **[1]** if it includes 7 C atoms but misses out on attached H atoms*

(b) overprescription can lead to allergic reaction

may wipe-out harmless/helpful/beneficial bacteria (in the alimentary canal)/destroyed bacteria may be replaced by more harmful bacteria

(may pass on genetic) resistance/immunity

***[1]** each for any two.*

modify R group/side chain to change penicillin effectiveness / form penicillin that is more resistant to penicillinase enzyme [3 max]

2 chiral auxiliaries are enantiomers/optically active

auxiliary creates stereochemical condition necessary to follow a certain pathway / is used to manufacture one enantiomer (so avoids need to separate a racemic mixture)

attaches/connects itself to non-chiral molecule / makes it optically active

only desired/one enantiomer/molecule formed (and chiral auxiliary removed) [2 max]

3 **(a)** $Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$ / $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$ [1]

Accept ionic equations.

(b) less effect **and** (magnesium hydroxide) 2/0.2 mol OH^- ions available as compared to (aluminium hydroxide) 3/0.3 mol OH^- ions for neutralization / neutralizes $2H^+$/0.2 mol acid as compared to $3H^+$/0.3 mol acid [1]

Do not accept aluminium hydroxide can neutralize more acid.

4 **(a)** viruses do not have cell/cellular structure

viruses do not have nucleus

viruses do not have cell wall

viruses do not have cytoplasm [2]

Accept opposite statements for bacteria.

(b) stops virus replication

Accept reproduction / multiplication.

becomes part of DNA of virus / alters virus DNA / blocks polymerase which builds DNA

changes the cell membrane that inhibits the entry of virus into the cells

prevents viruses from leaving the cell (after reproducing) [2 max]

(c) HIV mutates (rapidly)

Accept AIDS mutates

HIV metabolism linked to that of host cell / HIV uses host cell / drugs harm host cell as well as HIV / difficult to target HIV without damaging host cell

HIV destroys helper cells of the immune system [2 max]

5 **(a)** fast delivery / *OWTTE* [1]

(b) diamorphine has (2) ester/acetyl/$COOCH_3$ groups instead of hydroxyl/OH groups

diamorphine is less polar/non-polar [2]

6 if concentration is too high it will have harmful side effects / determination of the lethal dose (to 50% of the population / *OWTTE*

if concentration is too low it has little or no beneficial effect / determination of the effective dose / dose which has a noticeable effect (on 50% of the population) / *OWTTE*

therapeutic window is the range between these doses / range over which a drug can be safely administered / ratio of LD_{50}:ED_{50}

for minor ailments a large window is desirable, for serious conditions a smaller window may be acceptable / *OWTTE*

(therapeutic window) depends on the drug/age/sex/weight

a small therapeutic window means that an overdose is a high risk / *OWTTE* [4 max]

7 **(a)** amine

ether

alkene

benzene ring [2 max]

Do not allow arene.

Allow phenyl (ring or group) or benzene.

Allow structural representation of functional group instead of name (e.g. C=C instead of alkene).

(b) phenol / alcohol / hydroxyl (group) [1]

Allow OH.

(c) (di)esterification / condensation / (di) acetylation [1]

8 **(a)** penicillins interfere with the enzymes that bacteria need to make cell walls / interfere with formation of bacterial cell walls / *OWTTE*

the increased osmotic pressure causes the bacterium to die / the bacterial cells absorb too much water and burst / *OWTTE* [2]

(b) resistance to penicillinase enzyme / more resistance to bacteria breaking it down / effective against bacteria that are resistant (to penicillin G)

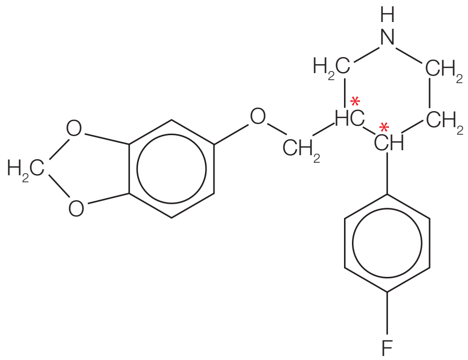
resistance to breakdown by stomach acid (so can be taken orally / *OWTTE* [2]

(c) amide group / —CONH— / peptide

ring is strained /

ring breaks easily so (the two fragments similar to cysteine and valine) then bond(s) covalently to the enzyme that synthesizes the bacterium cell wall (so blocking its action) [3]

9 **(a)** [2]



Award [1] for each correctly placed asterisk.

(b) different enantiomers can cause different (physiological) effects in the body

thalidomide – one isomer prevented morning sickness, the other caused fetal abnormalities / ibuprofen – one isomer is more effective than the other / DOPA – one isomer helps manage Parkinson disease, the other has no physiological effects [2]

Accept other correct examples.

(c) chiral auxiliaries are themselves chiral

attach to the non-chiral molecule (to enable the desired enantiomer to be formed)

after the desired enantiomer is formed the chiral auxiliary is removed/recycled [2 max]

(d) **(i)** it turns the (relatively non-polar) molecule into an ionic/polar species

it increases its solubility in aqueous solutions / facilitates distribution around the body [2]

(ii) (secondary) amine group / non-bonding pair of electrons on (electronegative) N atom [1]

10 **(a)** C [1]

(b) A / B/ A **and** B [1]

(c) A [1]

11 **(a)** intravenous / into veins

transported/pumped via blood (to various parts of the body) [2]

(b) intramuscular/intermuscular/into muscles **and** subcutaneous/into fat [1]

(c) inhalation/breathing it in [1]

12 **(a)** **(i)** *Oxidation:*

$C_2H_5OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$

Reduction:

$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Accept balanced equation with molecular formulas.

*If both equations are wrong, award **[1]** for $C_2H_5OH \rightarrow CH_3COOH$ and $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$.*

*If correct equations are used but oxidation and reduction reversed, award **[1]**.*

(ii) orange to green [1]

(b) peak at 2950 cm^{-1} / absorption occurs due to C—H bonds in ethanol

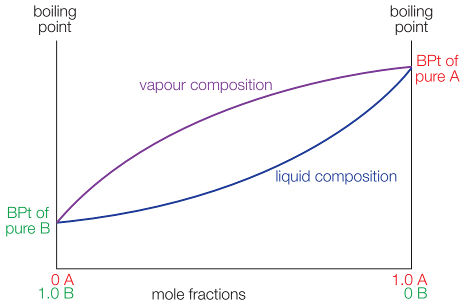
No mark for absorption due to just ethanol, or O—H bond in ethanol (water vapour in breath also contributes).

intensity / height to peak / absorption / amount of transmittance depends on amount of ethanol / compare absorption to standard / reference/control sample / sample containing no alcohol [2]

13 **(a)** shorter half-life means the body is exposed to radiation for a shorter time [1]

(b) $^{131}_{53}I \rightarrow ^{131}_{54}Xe + ^{0}_{-1}\beta + ^{0}_{0}\gamma$ [1]

14 **(a)** [3]



(b) as vapour rises up the column, it cools, condenses and falls back down. It is re-boiled by ascending vapour in a repeating cycle until vapour exits the top of the column [3]

15 obtained from needles of Pacific yew tree / obtained from fungus / fermentation process avoids production of waste / hazardous by-products / (fermentation) avoids use of solvents / reagents / resources used renewable [2]

Challenge yourself

1 Two top C atoms in beta lactam ring: sp^3

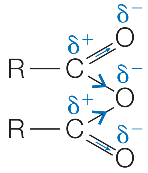
Lower C atom in beta lactam ring: sp^2

C in COOH group: sp^2

All other C atoms: sp^3

lower C atom in beta lactam ring (amide carbon): sp^2

2 Ethanoic anhydride is more susceptible to nucleophilic attack due to two electron-withdrawing carbonyl groups:



This enables it to react more vigorously than CH_3COOH with the —OH groups in morphine.

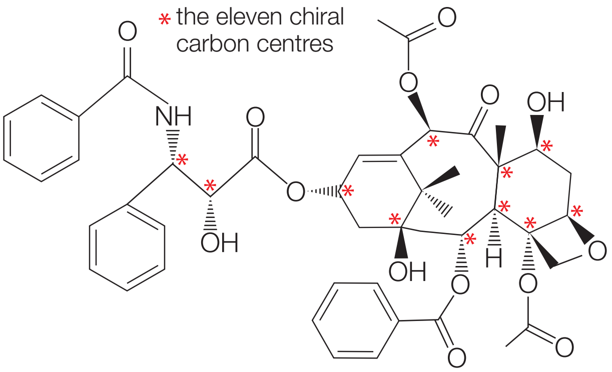
3 Na_2CO_3 and $NaHCO_3$ contain the conjugate bases CO_3^{2-} and HCO_3^- of weak acids. They are able to hydrolyse water and release OH^- ions:

$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

4 Neuraminidase inhibitors compete with the substrate sialic acid for binding to the enzyme neuraminidase. They have a chemical structure similar to the substrate and so bind in the same way at the active site of the enzyme.

5 Red asterisks mark the position of chiral carbon atoms.



6 K_2CO_3 dissolves readily in water, but not easily in ethanol as it is less polar. The presence of the ions in water reduces the solubility of the ethanol, so it forms a separate layer on top of the water. This process is used in biochemistry to precipitate proteins from solution.