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 the 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 <u>underlined</u> *must* be present to score the mark.
- Information in brackets ( ) is not needed to score the mark. You may also find «» brackets to indicate that the information inside the 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.

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.

S1.1 Introduction to the particulate nature of matter

Exercises

Q1 C

Q2 B

Q3 C

Q4 (a) Fertilizers are soluble.

(b) Large energy requirement and so is expensive.

Q5 The solvent evaporates. The oil has changed chemically by reacting with oxygen in the air.

Q6 Both coins are made from a homogeneous mixture with the same composition: Cu 89%, Al 5%, Zn 5%, Sn 1%.

Q7 X has moved more quickly, therefore the particles of X have smaller mass.

Q8 The average kinetic energy increases with temperature. The particles will move faster and the rate of diffusion increases.

Q9 D

Q10 (a) Bubbles will be present throughout the volume of the liquid. A brown gas will be visible above the brown liquid.

(b) As the two states are at the same temperature, the particles have the same average kinetic energy and are moving at the same average speeds. The inter-particle distances in the gas are significantly larger than those in the liquid.

Q11 D

Q12 C

Q13 B

Q14 At certain conditions of low temperature and low humidity, snow changes directly to water vapour by sublimation, without going through the liquid state.

Q15 (a) Ice, as it has a melting point of $0\,°C$.

(b) They are vibrating with increasing frequency.

(c) They are moving freely in a fixed volume as it is the liquid state.

(d) The heat energy is used to separate the particles and not increase their movement.

(e) $52.5\,°C$

(f) Temperature predicted = $127.5\,°C$. Water boils at $100\,°C$, which would be reached after around $980\,s$, and so the temperature does not follow the predicted pattern. The temperature is likely to be $100\,°C$.

Q16 D

Q17 B

Q18 C

Q19 D

Q20 Steam will condense on the skin, releasing energy as it forms liquid at the same temperature (portion e−d on S1.1 Figure 5). This is additional to the energy released when both the boiling water and the condensed steam cool on the surface of the skin.

Challenge yourself

1 The molecules of ethanol can partly fit between the spaces between the water molecules, and vice versa.

2 A mixture may appear to be homogeneous with the naked eye but on closer inspection with a microscope may be heterogeneous. The classification depends on the scale on which the components are analysed.

3 In 1827 Robert Brown dropped pollen grains into water and examined them under a microscope. The pollen grains 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 than the pollen grains: water molecules. Einstein didn't just base this theory on his observations – he used complex mathematics to show that a particle model could explain Brownian motion.

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

5 $\Delta E = mc\Delta T$

gradient of graph $= \dfrac{\Delta T}{\Delta E} = \dfrac{1}{mc}$

The gradient is determined by the mass and the specific heat capacity of the substance as solid, liquid and gas.

Practice questions

1 D

2 A

3 B

4 B

5 D

6 A

7 C

8 B

9 B

10 B

11 A

12 (a) Smoke: heterogeneous – the solid particles are suspended in the air. [1]

(b) Sugar and water: homogeneous – the sugar dissolves in the water. (If it is a saturated solution with excess sugar that cannot dissolve, the overall mixture is then heterogeneous.) [1]

(c) Steel: homogeneous – it is an alloy of iron and carbon (+ other components) with the same properties throughout. [1]

13 (At certain conditions of low temperature and low humidity), snow changes directly to water vapour by sublimation, without going through the liquid phase. [1]

14 (a) Any two from:

forces between gas particles are smaller than between liquid particles

speed of gas particles greater than speed of liquid particles

movement of gas particles is less restricted than that for liquid particles

separation of particles (generally) much greater in a gas than in a liquid [2]

(b) the gas particles do not have the same speed [1]

the speed of individual particles changes with each collision [1]

(c) (i) increased kinetic energy of the particles [1]

(ii) heat energy used to separate the particles [1]

no increase in kinetic energy (as indicated by temperature) [1]

15 (a) Any value between −15 °C and +10 °C. (The experimental value = −7.2 °C.) [1]

(b) boiling points increase [1]

(c) gas [1]

(d) (i) liquid [1]

the molecules are close together but have an irregular arrangement [1]

(ii) increased movement of molecules [1]

with increased separation between particles [1]

(Note the molecules do not break into individual atoms.)

(iii) The bromine molecule break into atoms or ions, which then combine with atoms or ions of other elements. [1]

(iv) Temperature is a measure of the average kinetic energy: increase in temperature results in increase in movement / rate of diffusion. [1]

S1.2 The nuclear atom

Exercises

Q1 Tellurium has a greater proportion of heavier isotopes (those with more neutrons).

Q2

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

Q3

	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

Q4 D

Q5 Examples are density (related to mass) and, as chlorine is a gas, rate of diffusion.

Q6 C

Q7 C

Q8 B

Q9 A

Q10 C

Q11 No individual atom with this mass exists. Silicon has a number of isotopes and this is an average value. The claim is true.

Q12 D

Q13 B

Q14
$$RAM = \frac{(50 \times 4.31) + (52 \times 83.76) + (53 \times 9.55) + (54 \times 2.38)}{100}$$
$$= 52.0569 \approx 52.06$$

Q15 $RAM = \dfrac{(20 \times x) + (22 \times y)}{100} = 20.18$ and $x + y = 100$;

$y = 100 - x$

$(20 \times x) + (22 \times 100) - (22 \times x) = 2018$

$2x = 2200 - 2018 = 182$

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

Q16 Let the abundance of ^{25}Mg be x. Consider 100 atoms.

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

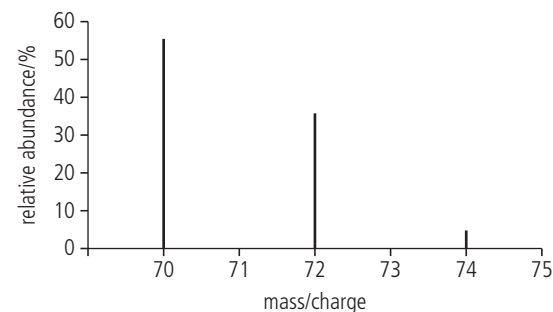$2431 = 1893.6 + 25x + 548.6 - 26x$

$2431 = 2442.2 - x$

$x = 11.20$

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

Q17 $^{35}Cl-^{35}Cl$ is present at an abundance of $75\% \times 75\% = 56.25\%$

$^{35}Cl-^{37}Cl$ is present at an abundance of $2 \times 75\% \times 25\% = 37.5\%$

$^{37}Cl-^{37}Cl$ is present at an abundance of $5\% \times 25\% = 6.25\%$

ratio is 9 : 6 : 1

Challenge yourself

1 Potash, soda, magnesia and barytes are compounds of group 1 and 2 elements. These compounds were later broken down into their component elements by electrolysis. (See Reactivity R3.2.)

2 High energy alpha particles can get so close to the nucleus that the strong nuclear force, not included in the Rutherford model, begins to act on them.

3 $^{0}_{+1}e + ^{0}_{-1}e \rightarrow 2\gamma$
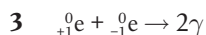
Note the left-hand subscripts which represent the charges are balanced.

The negligible masses of the position and electron are converted into energy in the form of two photons.

4 The nucleons are attracted to each other by the short-range strong nuclear force, which is stronger than the electrostatic repulsive forces.

5 $V_{\text{nucleus}} = \dfrac{4\pi}{3} \times R^3 = \dfrac{4\pi}{3} \times (1.2 \times 10^{-15} \times A^{1/3})^3$

$= 7.24 \times 10^{-45} \times A\,\text{m}^3$

the mass of the nucleus is A u, i.e. $A \times 1.67 \times 10^{-27}$ kg

$\text{density}\,(\rho) = \dfrac{\text{mass}}{\text{volume}} = \dfrac{A \times 1.67 \times 10^{-27}\,\text{kg}}{7.24 \times 10^{-45} \times A\,\text{m}^3}$

$\approx 2.3 \times 10^{17}\,\text{kg m}^{-3}$

The density is independent of mass number and so all nuclei have the same density.

This is to be expected as all nuclei are composed of protons and neutrons packed closely together and so have similar densities.

The density of the nucleus is extremely high compared to the bulk density of an element. For example, the density of mercury is 1.35×10^4 kg m^{-3} (so the nucleus is denser by 13 orders of magnitude).

6 mass of H atom = mass of proton (H$^+$) plus mass of electron

$= 1.672622 \times 10^{-27}$ kg $+ 9.109383 \times 10^{-31}$ kg

$= 1.67353 \times 10^{-27}$ kg

The mass of a hydrogen atom is the same as the mass of a hydrogen ion to 3 significant figures (1.67) and the 4th significant figure only differs by 0.001. The mass of the atom is 1.673 and the ion 1.674.

7 The difference in mass between the molecules is very small. The molecules can only be separated over large distances. A large area of ground is needed.

8 Technetium, Tc, has no stable isotopes. Note that its relative mass is an integer and given in parentheses.

9 Double-charged ions could be formed so some ions could be detected with $\dfrac{m}{z} = \dfrac{69}{2} = 34.5$ and $\dfrac{71}{2} = 35.5$.

10 Sample 1

$\text{RAM} = \dfrac{(16 \times 99.759) + (18 \times 0.241)}{100}$

$= 16.00482$

Sample 2

$\text{RAM} = \dfrac{(16 \times 99.757) + (18 \times 0.243)}{100}$

$= 16.00486$

Ice core sample 2 has a higher abundance of the heavier isotopes, which suggests it originated from lower temperatures as heavier water molecules need more energy to evaporate.

11 mass contributed by BrCl = 12 − 14 = 114

$^{35}_{17}$Cl and $^{79}_{35}$Br present; other isotope combinations give a greater mass probability 75% × 50% = 37.5%

Practice questions

1 A

2 C

3 B

4 D

5 no. of protons = 25   [1]

no. of electrons = 25 − 2 = 23   [1]

no. of neutrons = 55 − 25 = 30   [1]

6 $\text{RAM} = \dfrac{(54 \times 5.95) + (56 \times 91.88) + (57 \times 2.17)}{100}$ [1]

$= 55.90$ [1]

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

(b) 27 protons and 25 electrons   [1]

8 **(a)** different number of neutrons   [1]

(b) Same chemical properties because they have the same number of electrons; it is electrons that are responsible for chemical properties. [1]

(c) mass spectrometer [1]

(d) RAM $= \dfrac{(28 \times 92.18) + (29 \times 4.70) + (30 \times 3.12)}{100}$ [1]

$= 28.11$ [1]

9 A

10 (a) RAM $= \dfrac{(124 \times 2) + (126 \times 4) + (128 \times 6) + (130 \times 5)}{17}$

$= 127.65$ [1]

The element is likely to be tellurium (Te), assuming it is a typical sample of the element. [1]

(b) Te has an atomic number of 52; the remaining mass is due to neutrons $= 127.68 - 52 = 75.68$ [1]

% mass due to neutrons $= \dfrac{75.68}{127.68} \times 100 = 59\%$ [1]

S1.3 Electron configurations

Exercises

Q1 C

Q2 D

Q3 (a) C

(b) B

Q4 The transition corresponds to a larger energy change in the atom. The emitted photon has more energy and corresponds to a lower wavelength.

Q5 4s < 4p < 4d < 4f

Q6

Sublevel	4s	4p	4d	4f
No. of orbitals	1	3	5	7

Q7 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Q8 $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^1 3p_y^1 3p_z^1$, so three unpaired electrons

Q9 Number of orbitals $= n^2 = 4^2 = 16$
$= (1 \times s) + (3 \times p) + (5 \times d) + (7 \times f) = 16$

Q10 C

Q11 C

Q12 (a) V is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

(b) K is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(c) Se is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

(d) Sr is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$

Q13 D

Q14 B

Q15 B

Q16 D

Q17 (a) O^{2-} is $1s^2 2s^2 2p^6$

(b) Cl^- is $1s^2 2s^2 2p^6 3s^2 3p^6$

(c) Ti^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

(d) Cu^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

Q18

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

Q19 (a) Ne is $1s^2 2s^2 2p^6$

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

Q20 (a) [Ar] $3d^8$

(b) [Xe] $5d^{10} 6s^2$

(c) [Ne] $3s^2 3p^6$

(d) [Ne]

Q21 (a) Cl is $1s^2 2s^2 2p^6 3s^2 3p^5$

(b) Nb is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^3 5s^2$

(c) Ge is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$

(d) Sb is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$

Q22 (a) Si

(b) Mn

(c) Sr

(d) Sc

Q23 11

Q24 20

Q25 [Kr] $4d^{10}$

Q26 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 5f^4$

Q27 $E = h\nu = \dfrac{hc}{\lambda} = \dfrac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{590 \times 10^{-9}}$
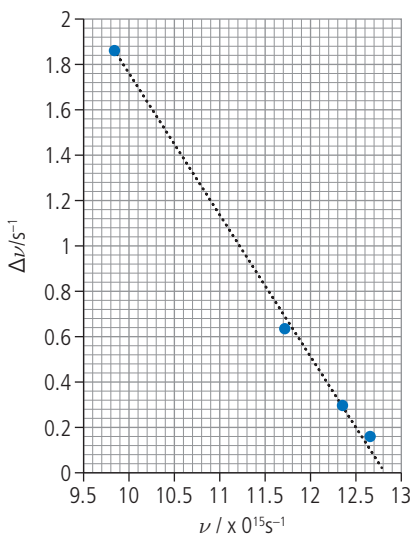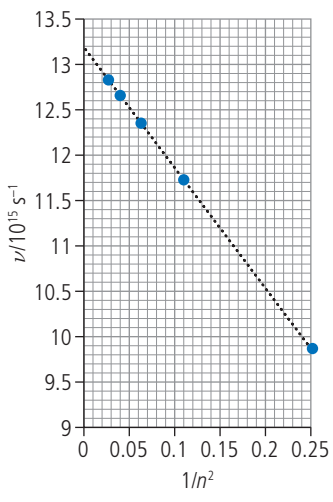
For one mole:

$$E = 6.02 \times 10^{23} \times \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{590 \times 10^{-9}}$$

$$= 203 \text{ kJ mol}^{-1}$$

experience a stronger force of electrostatic force of attraction.

Q28 The convergence can be found graphically

Method 1	Method 2
The equation of the best fit line $\Delta\nu = -0.613\nu + 7.884$ When $\Delta\nu = 0$, $\nu = 12.86 \times 10^{-15}\text{ s}^{-1}$ Ionization energy = 5132 kJ mol^{-1}	The equation of the best fit line $\nu = \frac{-13.278}{n^2} + 13.191$ When $n = \nu$, $\frac{1}{n^2} = 0$ $\nu = 13.19 \times 10^{-15}\text{ s}^{-1}$ Ionization energy = 5264 kJ mol^{-1}

Q29 Li^{2+}: 11 900 kJ mol^{-1}

Be^{3+}: 21 000 kJ mol^{-1}

Q30 From the graph $\lambda = 233.0$ nm

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{233.0 \times 10^{-9}}$$

For one mole:

$$E = 6.02 \times 10^{23} \times \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{233.0 \times 10^{-9}}$$

$$= 514 \text{ kJ mol}^{-1}$$

Q31 B

Q32 B

Q33 **(a)** C has the electronic configuration 1s^{2}2s^{2}2p^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

(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.

Q34
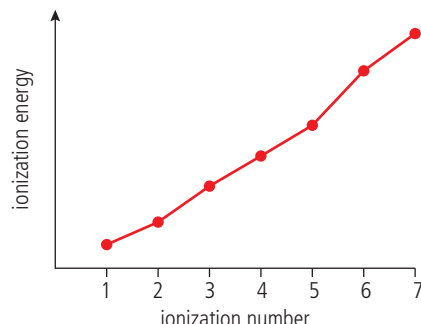
Q35 (a) There is a general increase from left to right across a period, as the nuclear charge increases. As the electrons are removed from the same main energy level, there is increase in the force of electrostatic attraction between the nucleus and outer electrons.

(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] $3s^23p^1_x3p^1_y3p^1_z$, S has the configuration [Ne] $3s^23p^2_x3p^1_y3p^1_z$. 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.

Challenge yourself

1 D

$$E_{photon} = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{588 \times 10^{-9}} = 3.38 \times 10^{-19}\,J$$

$\Delta E_{atom} = 3.38 \times 10^{-19}\,J$

This corresponds to IV → II:
$-2.42 \times 10^{-19} - (-5.80 \times 10^{-19}) = 3.38 \times 10^{-19}\,J$

2 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.

3 A

4 $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^64f^{14}5d^{10}6s^26p^66d^27s^2$

or [Rn] $6d^27s^2$

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

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

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

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

(b) 4 groups in the p and d block.

7
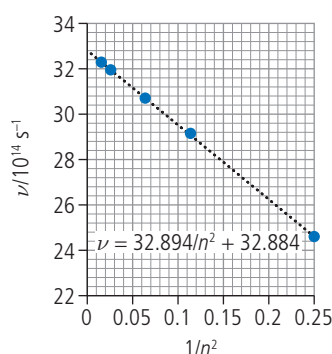
The frequency corresponding to $n = \infty$ can be read as the intercept on the y-axis and equals $32.884 \times 10^{-14}\,s^{-1}$.

We can use the frequency obtained to calculate the ionization energy.

Using the equation $E = h\nu$ we have the ionization energy for one atom:

$E = 32.884 \times 10^{-14}\,s^{-1} \times 6.63 \times 10^{-34}\,J\,s$

So for one mole the ionization energy is given by:

I.E.
$= 32.884 \times 10^{-14}\,s^{-1} \times 6.63 \times 10^{-34}\,J\,s \times 6.02 \times 10^{23}\,mol^{-1}$
$= 1312\,kJ\,mol^{-1}$

This agrees with the value given in Section 8 of the IB data booklet.

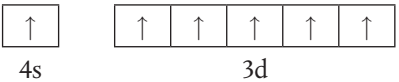The second method gives a more accurate value as the points better fit a straight line.

Practice questions

1. D

2 A

3 B

4 B

5 **(a)** the electron configuration of argon, which is
$1s^2 2s^2 2p^6 3s^2 3p^6$ [1]

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

(c)

4s   3d [1]

Accept all six arrows pointing down rather than up.

6 **(a)** IV < I < II < III *or* ultraviolet radiation < yellow light < red light < infrared radiation [1]

(b) A continuous spectrum has all colours / wavelengths / frequencies whereas a line spectrum has only lines of sharp / discrete / specific colours / wavelengths / frequencies. [1]

7 B

8 B

9 B

10 $1s^2 2s^2 2p^6 3s^1$ [1]

Do not accept [Ne]3s¹

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]

11 **(a)** Evidence for main levels:

highest values for noble gases / lowest values for alkali metals / *OWTTE* [1]

general increase across a period [1]

Evidence for sublevels:

drop in I.E. from Be to B/Mg to Al/group 2 to group 13 [1]

drop in I.E. from N to O/P to S/group 15 to group 16 [1]

(b) $M^+(g) \rightarrow M^{2+}(g) + e^-$ *OWTTE* [1]

Accept e instead of e⁻

12 From the graph $\lambda = 294$ nm

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{294 \times 10^{-9}}$$ [1]

For one mole:

$$E = 6.02 \times 10^{23} \times \frac{6.63 \times 10^{-34} \times 3.0 \times 10^8}{294 \times 10^{-9}}$$

$$= 410 \text{ kJ mol}^{-1}$$ [1]

S1.4 Counting particles by mass: The mole

Exercises

Q1 Note: these calculations have used $L = 6 \times 10^{23}$

(a) 7.2×10^{22}

(b) 3×10^{24}

(c) 1.2×10^{23}

Q2 0.53 mol H

Q3 0.250 mol

Q4 As the value for A_r is closer to 35 than 37, the ^{35}Cl must be the most abundant isotope. A 50 : 50 mixture would have A_r of 36.

Q5 **(a)** 262.87

(b) 176.14

(c) 164.10

(d) 248.22

Q6 189.1 g

Q7 1.5 mol

Q8 0.0074 mol Cl⁻

Q9 1.83×10^{24} C atoms

Q10 171 g (integer values used)

Q11 10.0 g H_2O

Q12 2.0 mol N_2 > 3.0 mol NH_3 > 25.0 mol H_2 > 1.0 mol N_2H_4

Q13 (a) CH

  (b) CH_2O

  (c) $C_{12}H_{22}O_{11}$

  (d) C_4H_9

  (e) C_4H_7

  (f) CH_2O

Q14 $Na_2S_2O_3$

Q15 $CoSO_4.7H_2O$

Q16 $C_{17}H_{25}N$

Q17 NH_3

Q18 6.94 Li

Q19 Atomic masses: S = 32, Se = 79, Te = 128, so the highest % by mass of Cd is in CdS.

Q20 empirical formula CH; molecular formula C_6H_6

Q21 empirical formula H_2PO_3; molecular formula $H_4P_2O_6$

Q22 $C_{10}H_{16}N_5P_3O_{13}$ for both empirical and molecular formulas

Q23 C_3H_8O

Q24 Let change in mass on using the chalk = y g $CaCO_3$

mass C in chalk = $\dfrac{12}{M(CaCO_3)} \times y$

number of C atoms = $6.02 \times 10^{23} \times \dfrac{12}{M(CaCO_3)} \times y$

Q25 2.81 g

Q26 4.93 g

Q27 0.0100 mol

Q28 0.40 mol dm^{-3}

Q29 3.1 cm^3

Q30 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

Q31 Ar

Q32 B

Q33 45 dm^3

Q34 10 dm^3, assuming the H atoms are present as a gas

Challenge yourself

1 Group 1: H has one electron in outer energy level, forms H$^+$ ion.

Group 17: H needs one electron to fill its outer energy level, can form H$^-$ ion, is a gaseous element (H_2) not a metal.

Not in a group: H is anomalous, and is not a group 1 metal or a group 17 halogen.

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

3 % N in fertilizer = 18%

P_2O_5 = 44% P by mass, so %P in fertilizer = 51% × 44% = 22%

K_2O = 83% K by mass, so %K in fertilizer = 20% × 83% = 17%

4 As NaOH dissolves, the separated ions Na$^+$ and OH$^-$ ions become hydrated, i.e. 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.

5 The relationship between concentration and absorbance becomes non-linear at higher concentrations, so interpretation of data to deduce the unknown concentration will be less accurate in this region. It is therefore important that the absorbance of the unknown sample falls within the lower linear part of the graph where it will give a more accurate reading of the unknown concentration.

6 The key reaction in the expansion of the bag is the release of nitrogen gas from the decomposition of sodium azide:

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

The reactions to remove the dangerously reactive sodium metal can take several forms, resulting in silicates such as K_2SiO_3 and Na_2SiO_3. For example:

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

$K_2O(s) + Na_2O(s) + 2SiO_2(s) \rightarrow K_2SiO_3(s) + Na_2SiO_3(s)$
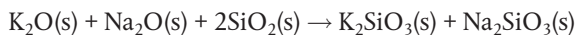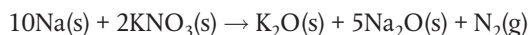
S1.4 Practice questions

1 D

2 B

3 A

9

4 B

5 D

6 D

7 C

8 D

9 C

10 D

11 A

12 (a) 0.115 mol H_2O [1]

(b) 0.0574 mol K_2CO_3 [1]

(c) $K_2CO_3.2H_2O$ [1]

(d) Heat to constant mass; when further heating does not lead to further decrease in mass. [1]

13 % O = 100 − (62.02 + 10.43) = 27.55% [1]

	C	H	O
% by mass	62.02	10.43	27.55
divide % by mass by A_r	$\frac{62.02}{12.01} = 5.164$	$\frac{10.43}{1.01} = 10.33$	$\frac{27.55}{16.00} = 1.722$
divide by smallest	3.00	6.00	1

[1]

empirical formula = C_3H_6O [1]

14 (a) % O = 100 − 43.6 = 56.4% [1]

	P	O
% by mass	43.6%	56.4%
divide % by mass by A_r	$\frac{43.6}{30.97} = 1.4078$	$\frac{56.4}{16.00} = 3.525$
divide by smallest	1	2.50

[1]

empirical formula = P_2O_5 [1]

(b) molecular formula = (empirical formula) × n

$285\,g\,mol^{-1} = [(30.97 \times 2) + (16.00 \times 5)] \times n = 141.94 \times n$

$n = \frac{285}{142} = 2$

molecular formula = P_4O_{10} [1]

15 (a) $M_r(NaHCO_3)$ = 22.99 + 1.01 + 12.01 + (16.00 × 3)
= 84.01 g mol⁻¹ [1]

$n(NaHCO_3)$ = conc. × volume

= $0.500\,mol\,dm^{-3} \times \frac{250.00}{1000.00}\,dm^3$

= 0.125 mol [1]

$mass(NaHCO_3)$ = 0.125 mol × 84.01 g mol⁻¹ = 10.5 g [1]

Measure a mass of 10.5 g $NaHCO_3$ using a balance and transfer to a 250 cm³ volumetric flask. [1]

Add distilled water to the flask, with frequent shaking, up to the mark. [1]

(b) To prepare dilutions of stock solution:

Using a 10 cm³ pipette transfer 10.00 cm³ of the stock solution from (**a**) into a 100 cm³ volumetric flask. Make up to the mark with distilled water → 0.0500 mol dm⁻³ solution. [2]

Using a clean 10 cm³ pipette transfer 10.00 cm³ of the 0.0500 mol dm⁻³ solution into a 100 cm³ volumetric flask. Make up to the mark with distilled water → 0.00500 mol dm⁻³ solution. [2]

S1.5 Ideal gases

Exercises

Q1 A

Q2 C

Q3 A

Q4 D

Q5 D

Q6 3 and 4

Q7 B

Q8 (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 intermolecular 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 intermolecular forces and reduces gas pressure.

Q9 The assumptions are most valid when the gas particles are widely separated and the intermolecular forces weakest. These occur at conditions of high temperature and low pressure.

Q10 D

Q11 C

Q12 D

Q13 B

Q14 D

Q15 **(a)** It is is a linear relationship.

(b) The equation of the best fit line is:
$P = 0.3338T + 95.625$

When $P = 0$, $0.3338T + 95.625 = 0$

$T = \dfrac{-95.625}{0.3338} = -286.5\,°C$

(c) The temperature is lower than expected. The literature value is absolute zero $= -273\,°C$

(d) Proportional; a straight line which passes through/close to the origin.

(e) In the ideal gas model, as the temeprature decreases, the particles decrease their movement until at 0 K there is no movement and the particles are attracted together in a minimal volume. With the experimental results, the volume of the gas will not be precisely zero as the molecules have some volume.

Q16 For a given volume, Curve 1 has the higher pressure. It therefore has the higher temperature.

Q17 **(a)** $P_1V_1 = P_2V_2$

$V_2 = \dfrac{P_1V_1}{P_2} = \dfrac{2.02 \times 10^6 \times 0.0400}{1.01 \times 10^5} = 0.800\,m^3$

volume of balloon is $0.800 - 0.0400 = 0.760\,m^3$

(b) The atoms will decrease their speed.

Q18 B

Q19 C

Q20 90 kPa

Q21 16 °C

Q22 3.0 dm³

Q23 2.8 dm³

Q24 $M = 131\,g\,mol^{-1}$ so gas is Xe

Q25 90.4 g mol⁻¹

Q26 helium (a greater mass in the same volume; density is mass/volume)

Q27 At higher altitude the external air pressure is less. As the air in the tyre expands on heating (due to friction with the road surface), the internal pressure increases.

Q28 NH_3 shows greater deviation than CH_4 due to stronger intermolecular attractions, especially at low temperature.

Q29 **(a)** II as $\dfrac{PV}{RT} < 1$ at high pressure

The pressure is reduced by intermolecular forces.

(b) III as $\dfrac{PV}{RT} > 1$ as the pressure increases

The pressure is greater than an ideal gas due to the space occupied by the molecules.

Challenge yourself

1 If the molecular collisions are not perfectly elastic, then the kinetic energy of the molecules would be gradually lost. The molecules would slow down and the pressure would gradually reduce to zero.

2 **(a)** $PV = $ constant: $P_1V_1 = P_0V_2$

(b) $\dfrac{P}{T} = $ constant: $\dfrac{P_0}{T_1} = \dfrac{P_2}{T_2}$

(c) From **(b)**, $P_0 = \dfrac{P_2T_1}{T_2}$

Substitution in **(a)**, $\dfrac{P_1V_1}{V_2} = \dfrac{P_2T_1}{T_2}$, $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

3 The atmospheric pressure decreases with altitude. When the pressure inside the balloon is larger than the external pressure the volume of the balloon increases.

4 **(a)** $PV = nRT$; 18.0 g = 1 mol; $n = 1$

$V = \dfrac{RT}{P}$

$= \dfrac{8.31 \times 500}{1.00 \times 10^5} = 0.04155\,m^3 = 41\,550\,cm^3$

An approximate value for the volume of the particles can be obtained by considering 18.0 g of water, which has a volume of 18 cm³

% volume occupied by particles

$$= \frac{18}{41550} \times 100 = 0.04\%$$

(b) $V = \frac{RT}{P}$

$$= \frac{8.31 \times 400}{5.00 \times 10^7} = 6.65 \times 10^{-5}\,\text{m}^3 = 66.5\,\text{cm}^3$$

% volume occupied by particles = 27%

In Challenges 5 and 6, we are considering 1 mol of gas, so $n = 1$.

5 $\left(P + \dfrac{a}{V^2}\right)(V - b) = RT$

At high pressure, $\dfrac{a}{V^2}$ can be neglected.

$PV - Pb = RT$

$\dfrac{PV}{RT} = 1 + \dfrac{Pb}{RT}$

Note the deviation, which depends on b, increases as the pressure is increased and the temperature is decreased, in agreement with S1.5 Figure 12.

6 $\left(P + \dfrac{a}{V^2}\right)(V - b) = RT$

At low pressure, the parameter b can be neglected.

$\left(P + \dfrac{a}{V^2}\right)V = RT$

$PV + \dfrac{a}{V} = RT$

$\dfrac{PV}{RT} = 1 - \dfrac{a}{VRT}$

Note the deviation, which depends on a, increases as the temperature is decreased, in agreement with S1.5 Figure 12.

Practice questions

1 C

2 C

3 D

4 A

5 B

6 C

7 C

8 A

9 C

10 D

11 (a) two from:

weak intermolecular / dispersion forces

small atomic volume

smaller number of electrons [2]

(b) $n = \dfrac{pV}{RT}$

$$= \frac{2.0 \times 10^6 \times 3.0 \times 10^{-2}}{8.31 \times 300}$$ [1]

$= 24.1$ (mol) [1]

(c) $N = 24.1 \times 6.02 \times 10^{23} = 1.45 \times 10^{25}$ [1]

volume of 1 atom $= \dfrac{3.00 \times 10^{-2}\,\text{m}^3}{1.45 \times 10^{25}}$

$= 2.07 \times 10^{-27}\,\text{m}^3$ [1]

Accept value from 1×10^{-27} to 6×10^{-27} m

(d) assuming the atoms each occupy a cube;
distance $= \sqrt[3]{(2.07 \times 10^{-27})} = 1.27 \times 10^{-9}\,\text{m}$

assuming the atoms each occupy a sphere;
distance $= 7.9 \times 10^{-10}\,\text{m}$ [1]

12 (a) temperature: 4
mass: 3
pressure: 3 [1]

(b) $0.0650\,\text{kg} = 65.0\,\text{g}$

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

No penalty for using whole number atomic masses.

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

$T = 25.00 + 273.15 = 298.15\,\text{K}$ *or* $25.00 + 273 = 298\,\text{K}$

$P = 1.08 \times 1.01 \times 10^5\,\text{Pa}$ *or* $1.08 \times 1.01 \times 10^2\,\text{kPa}$ *or* $1.09 \times 10^5\,\text{Pa}$ *or* $1.09 \times 10^2\,\text{kPa}$

$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$ (from the data booklet)

Use $PV = nRT$ (from the data booklet)

$V = \dfrac{nRT}{P} = \dfrac{1.50 \times 8.31 \times 298.15}{1.08 \times 1.01 \times 10^5} = 0.034.1\,\text{m}^3$

$= 34.1\,\text{dm}^3$ [4]

Award [4] for correct final answer.

Award (3 max) for 0.0341 dm³ or 22.7 dm³.

Award (3 max) for 34.4 dm³.

Award (2 max) for 22.9 dm³.

Award (2 max) for 0.0227 dm³.

*Award (**2 max**) for 0.034 dm³.*

13 (a) Gas behaves ideally; as $p \propto T$ (in K) «at constant V» [1]

P = 0 gives 0.400T = −109.2

$T = \dfrac{-109.2}{0.400} = -273\,°C$ [1]

(b) From a point on the graph, find the temperature in K and the pressure, e.g. $T = 0\,°C = 273\,K$, $P = 109.2\,kPa$

$PV = nRT$

$n = \dfrac{PV}{RT} = \dfrac{109.2 \times 10^3 \times 1.0 \times 10^{-3}}{8.31 \times 273} = 0.048135\,mol$ [1]

$M = \dfrac{m}{n} = \dfrac{0.193}{0.048135} = 4.01\,g\,mol^{-1}$

The gas is helium. [1]

14 molar volume at STP = $22.4\,dm^3\,mol^{-1}$

density = $1.94\,g\,dm^{-3}$

molar mass = molar volume × density

$= 22.4 \times 1.94 = 43.456\,g\,mol^{-1}$ [1]

or

$PV = nRT$; $n = \dfrac{PV}{RT} = \dfrac{1 \times 10^5 \times 1 \times 10^{-3}}{8.31 \times 273} = 0.044\,mol$,

which have mass of 1.94 g

1 mol has mass of 44.01 g [1]

the alkane is C_3H_8 [1]

15 (a) The reaction stops after 25 m³ of O_2 is added. [1]

(b) $n(NO) = \dfrac{PV}{RT} = \dfrac{1 \times 10^5 \times 50 \times 10^{-6}}{8.31 \times 273} = 0.0022\,mol$ [1]

$n(O_2) = \dfrac{PV}{RT} = \dfrac{1 \times 10^5 \times 25 \times 10^{-6}}{8.31 \times 273} = 0.0011\,mol$ [1]

(c) volume = 75 cm³ − 25 cm³ = 50 cm³ [1]
$n(X) = 0.0022$

(d) $2NO(g) + O_2(g) \rightarrow 2X(g)$ therefore X = NO_2 [1]
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ [1]
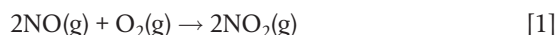
S2.1 Models of bonding and structure

Exercises

Q1 D

Q2 D

Q3 C

Q4 A

Q5 (a) KBr

(b) ZnO

(c) Na_2SO_4

(d) $CuBr_2$

(e) $Cr_2(SO_4)_3$

(f) AlH_3

Q6 (a) tin(II) phosphate

(b) titanium(IV) sulfate

(c) manganese(II) hydrogencarbonate

(d) barium sulfate

(e) mercury(I) sulfide

(f) vanadium(III) oxide

(g) chromium(III) oxide

(h) lead (IV) oxide

Q7 X_3Y_2

Q8 Mg: Z = 12: electron configuration [Ne] $3s^2$

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

The magnesium atom loses its two electrons from the 3s orbital to form Mg^{2+}, with electron configuration [Ne].

Two bromine atoms each gain one electron into their 4p sub-shell to form Br^-, with electron configuration [Kr].

The ions attract each other by electrostatic forces and form a lattice with the formula $MgBr_2$.

Q9 Ionic bonding between NH_4^+ ions and NO_3^- ions. Covalent bonding within NH_4^+ ions and NO_3^- ions.

Q10 B

Q11 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.

Q12 **(a)** D

(b) A

(c) C

Q13 B

Challenge yourself

1 Our calculation does not include the shielding effect of electrons in a lower sublevel. The two 3s electrons in aluminium, for example, partially shield the 3p electron so it (the 3p electron) experiences a smaller effective nuclear charge then the +3 calculated using the simple model. The reduced effective nuclear charge makes it easier to remove the 3p electron from aluminium than to remove one of the 3s electrons in magnesium.

2 For example, the production of chlorine during the electrolysis of sodium chloride provides indirect evidence for the existence of ions. The negative chloride ion is attracted to the positive electrode and is discharged with the production of gaseous chlorine.

3

Identity of ion	Location of atoms	Number of locations	Contribution	Total atoms
Cl^-	centre of face	6	$6 \times \frac{1}{2}$	3
Cl^-	corner	8	$8 \times \frac{1}{8}$	1
Na^+	centre of edge	12	$12 \times \frac{1}{4}$	3
Na^+	centre of cube	1	1×1	1

4NaCl

This confirms the formula unit as NaCl.

4 The ionic radius of Mg^{2+} is smaller than Na^+. The smaller radius would also lead to increased attraction between the ions.

Our analysis has also assumed that the compounds have similar structures. This may not be so, in which case, the structures may also affect the melting point.

5 Aluminium fluoride (1564 K) has a higher melting point than magnesium fluoride (1534 K), due to the increased charge of the aluminium cation.

The melting point of aluminium oxide (2345 K) is less than magnesium oxide (3125 K), which is not expected from the ionic model. This suggests that aluminium oxide has some covalent character.

6 Some things to consider:

- Model shows cubic structure very clearly.
- Model shows ionic bonds with grey connections as directional. Ionic bonds are due to electrostatic attraction of ions. They are not physical connections.
- Model shows ions as separated. Ions in real structure fill most of the volume, as illustrated in other models shown earlier in the chapter.

Practice questions

1 C

2 C

3 B

4 D

5 B

6 C

7 D

8 A

9 Electrostatic attraction increases with charge and decreases with distance. [1]

Mg^{2+} has smaller radius than Ba^{2+}, O^{2-} has smaller radius than S^{2-} [1]

so ionic radius of MgO is smaller than BaS. [1]

10 (a) electrostatic attraction [1]

between Fe^{3+} and O^{2-} ions [1]

(b) Fe^{3+}: $1s^22s^22p^63s^23p^63d^54s^2$ [1]

O^{2-}: $1s^22s^22p^6$ [1]

(c) iron(III) oxide [1]

(d) Applied force moves layers so ions of the same charge are forced to be closer [1]

repulsion between layers makes the compound brittle. [1]

(e) $Fe_3O_4 - Fe_2O_3 = FeO$, so the additional ion of iron is Fe^{2+} [1]

11 (a) Structure: lattice of ions [1]

Bonding: electrostatic attraction between K^+ ions and S^{2-} ions [1]

(b) K^+: $1s^2 2s^2 2p^6 3s^2 3p^6$ [1]

S^{2-}: $1s^2 2s^2 2p^6 3s^2 3p^6$ [1]

(c) S^{2-} is larger than K^+ [1]

Both have same electron configuration but K has larger nuclear charge so attracts electrons more strongly. [1]

(d) Solid: doesn't conduct because no mobile ions [1]

Molten: conducts because of free moving / mobile ions in molten state [1]

12 (a) +5 [1]

Ionization energies increase in a linear pattern and then there is a large jump when 6th electron removed / removal of 6th electron is unfavourable. [1]

(b) X_2O_5 [1]

Ion would have large charge density and so would polarise the anion; compound would show covalent character. [1]

(c) X^{2+} and X^{3+} [1]

13 Ionic bonding / electrostatic attraction between Na^+ and NO_3^- ions [1]

Covalent bonding between nitrogen and oxygen atoms within the nitrate ion. [1]
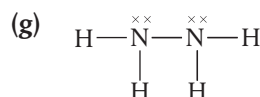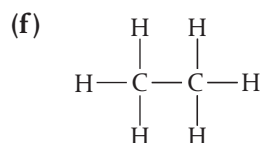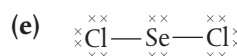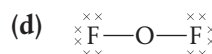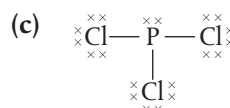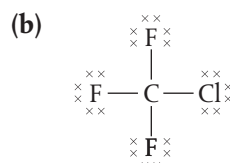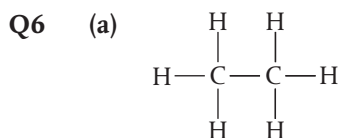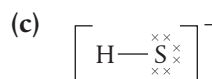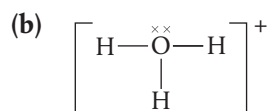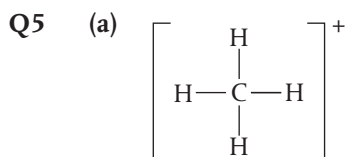
S2.2 The covalent model

Exercises

Q1 C

Q2 A

Q3 **(a)**

(b)

(c)

(d)

(e)

(f)

(g)

Q4 **(a)** 16
(b) 24
(c) 32
(d) 8
(e) 20
(f) 26

Q5 **(a)**

(b)

(c)

Q6 **(a)**

(b)

(c)   H—C≡C—H

Q7   C

Q8   **(a)**

(b)
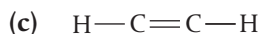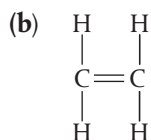
(c)
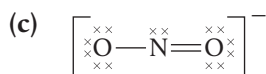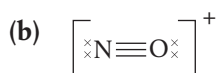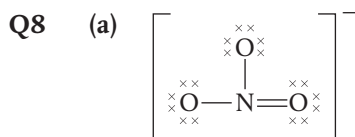
Q9   C

Q10   A

Q11   D

Q12   A

Q13   B

Q14   D

Q15
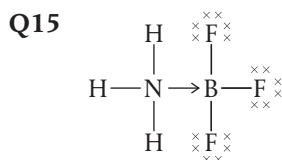
Q16   **(a)**   Bent / V-shaped, 105° / less than 109.5°

(b)   Tetrahedral, 109.5°

(c)   Linear, 180°

(d)   Trigonal pyramidal, 107° / less than 109.5°

(e)   Triangular planar, 120°

(f)   Trigonal pyramidal, 107° / less than 109.5°

(g)   Bent / V-shaped, 105° / less than 109.5°

Q17   **(a)**   Linear, 180°

(b)   Bent / V-shaped, less than 120° / in the range 100–119°

(c)   Bent / V-shaped, less than 109.5° / in the range 100–108°

(d)   Trigonal pyramidal, less than 109.5° / in the range 100–108°

Q18   **(a)**   4

(b)   3 or 4

(c)   2 or 5

(d)   4

(e)   3

Q19   D

Q20   **(a)**

(b)

(c)

(d)   O=O

(e)
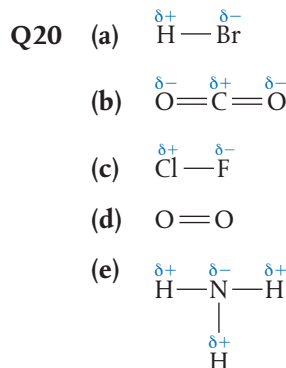
Q21   **(a)**   C 2.6, H 2.2, difference = 0.4
C 2.6, Cl 3.2, difference = 0.6, more polar

(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

Q22   **(a)**   polar

(b)   non-polar

(c)   polar

(d)   non-polar

(e)   non-polar

(f)   polar

(g)   non-polar

(h)   non-polar

Q23   *cis* isomer has a net dipole moment

Q24   Similarities: composed of carbon atoms only, both are covalent network structures.

Differences: each carbon is bonded to four other carbon atoms in diamond and three other carbon atoms in graphite; geometry around carbon atoms is tetrahedral in diamond and trigonal planar in graphite; diamond is a continuous C–C structure whereas graphite is distinct layers of carbon atoms (layers are held together by weak intermolecular forces); graphite has delocalized electrons but diamond does not.

Q25 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.

Q26 Graphite and graphene have delocalized electrons that are mobile and so conduct electrical charge. In diamond all electrons are held in covalent bonds and so none are mobile.

Q27 A metal
B covalent network
C polar molecular
D non-polar molecular
E ionic compound

Q28 A

Q29 **(a)** London dispersion forces
(b) London dispersion, dipole–dipole, hydrogen bonding
(c) London dispersion forces
(d) London dispersion, dipole–dipole
(e) London dispersion, dipole–dipole, dipole–induced dipole

Q30 **(a)** C_2H_6
(b) H_2S
(c) Cl_2
(d) HCl

Q31 C

Q32 R_F spot 1 = $\frac{9.0}{12.0}$ = 0.75; R_F spot 2 = $\frac{6.0}{12.0}$ = 0.50

Q33 **(a)** R_F spot X = $\frac{24}{80}$ = 0.30; R_F spot Y = $\frac{72}{80}$ = 0.90
(b) Compound Y is more soluble in the non-polar solvent (mobile phase) so must be less polar than compound X.

Q34
$$\left[\overset{\times\times}{\underset{\times\times}{\times}}O - N = \overset{\times\times}{\underset{\times\times}{O}} \right]^{-} \longleftrightarrow \left[\overset{\times\times}{\underset{\times\times}{O}} = N - \overset{\times\times}{\underset{\times\times}{O}}\overset{\times}{\times} \right]^{-}$$
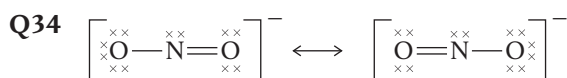
Q35 $CH_3OH < CO_3^{2-} < CO_2 < CO$

Q36 NO_3^- has three resonance structures so a N−O bond order of 1.33 (the average number of bonds found in a given bonding position when all possibilities are considered). HNO_3 has two resonance structures so

the N−O bond order of the bonds that resonate is 1.5; there is also a single bond (bond order of 1) not involved in resonance. So the N−O bonds that resonate in HNO_3 are shortest (and strongest) followed by the N−O bonds in NO_3^- and then the N−O single bond in in HNO_3.

Q37
$$\left[H - C \overset{\displaystyle O}{\underset{\displaystyle O}{\Big\langle}} \right]^{-}$$

Q38
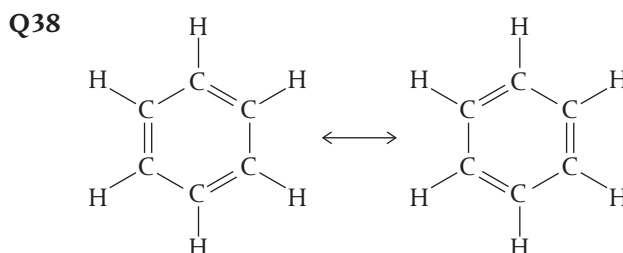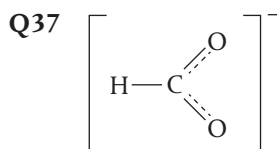
Q39 As the delocalised pi electrons in benzene are shared across all bonding positions in the carbon ring, we find the bond lengths are identical and of an intermediate value instead of alternating single and double bond lengths. (See structure 2.2.16 for more detail on 'pi' bonds.)

Q40 Benzene contains six carbon atoms arranged in a hexagonal ring, each also with a single bond to a hydrogen atom. The bonds between the carbon atoms are identical and have a length and strength that lies in between that of a single bond and a double bond. This is due to the delocalisation of pi electrons that are shared equally across the carbon ring, increasing its energetic stability. (See structure 2.2.16 for more detail on 'pi' bonds.)

Q41 D

Q42 **(a)** Linear, 180°
(b) Trigonal pyramidal, 107° / less than 109.5°
(c) Bent / V-shaped, 105° / less than 109.5°
(d) Tetrahedral, 109.5°
(e) Octahedral, 90°
(f) See-saw, 117° / less than 120°

Q43 **(a)** 6
(b) 6
(c) 6

(d) 5

(e) 2 or 5

Q44 **(a)** 90°

(b) 107° / less than 109°

(c) 90°

Q45 **(a)** Tetrahedral, 109.5°

(b) Square planar, 90°

(c) Tetrahedral, 109.5°

(d) Bent / V-shaped, 105° / less than 109.5°

Q46 **(a)** Linear, 180°, non-polar

(b) Bent / V-shaped, less than 109.5° / in range 100–108°, polar

(c) Tetrahedral, 109.5°, non-polar

(d) T-shaped, approximately 90 / less than 90°, polar

(e) Octahedral, 90°, non-polar

Q47 Xe = 8 − (4 + 4) = 0
each F = 7 − (1 + 6) = 0

Q48 Left-hand structure: P = 5 − 4 = +1;
each O = 6 − (1 + 6) = −1

Right-hand structure: P = 5 − 5 = 0;
top O = 6 − (2 + 4) = 0;
left / right / bottom O = 6 − (1+6) = −1

Right-hand structure has formal charges closest to 0 so is the preferred structure.

Q49 Assigning formal charges to Lewis formulas of BF_3 with and without a complete octet:

BF_3 with an incomplete octet is the preferred structure as all the atoms have formal charge of 0.

Q50 Complete octet
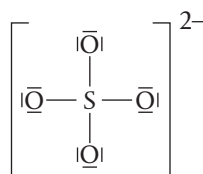
Formal charges:
S = +2
0 = −1

Two possibilities for an expanded octet:
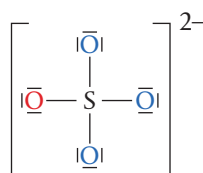
Formal charges:
S = +1
0 = −1
0 = 0
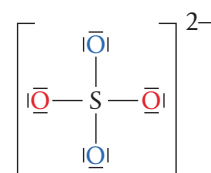
Formal charges:
S = 0
0 = −1
0 = 0

The expanded octet is the preferred structure in either case as it has formal charges closest to zero.

Q51 A sigma bond is formed by the head-on combination of atomic orbitals where the electron density is concentrated along the bond axis. A pi bond is formed by the lateral combination of p-orbitals where the electron density is concentrated on opposite sides of the bond axis.

Q52 B

Q53 A carbon–carbon sigma bond is stronger than a pi bond as there is greater overlap of the atomic orbitals so the shared electron density is located closer to the two nuclei.

Q54 **(a)** H–H in H_2

(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 CH_2CHCl

Q55 **(a)** sp^2

(b) sp^3

(c) sp^2

(d) sp

(e) sp^2

Q56 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°.

Challenge yourself

1 F_2 has a 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.

2 The definition of electronegativity relates to the attraction of an atom to electrons in a covalent bond. As group 18 elements tend not to bond with other atoms, we do not assign them a Pauling electronegativity value.

3 When bonded to a more electronegative element. Only F is more electronegative than O. For example, in OF_2.

4 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, thermal energy can be readily transferred through the network from one bond to the next. Silicon is similarly a good thermal conductor (but not a good electrical conductor), which is why computer chips need to be cooled to prevent overheating.

5 Diamonds are kinetically stable with respect to graphite, as the conversion has a very high activation energy (see Reactivity 2.2.4). So the reaction generally occurs too slowly to be observed.

6 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 solvents. The polar solvent will be a better solvent for polar / ionic solutes; the non-polar solvent better for covalent / non-polar solutes.

7

Possible arrangements	see-saw, preferred	
LP–LP 90° angles	none	none
LP–BP 90° angles	2	3

Possible arrangements	T-shaped, preferred		
LP–LP 90° angles	0	1	0
LP–BP 90° angles	4	3	6

Possible arrangements	linear, preferred		
LP–LP 90° angles	0	2	2
LP–BP 90° angles	6	3	4

8 Central oxygen has 2 bonding domains and 1 non-bonding domain so geometry is bent or V-shaped. The resonance structures and formal charges on each atom are follows:
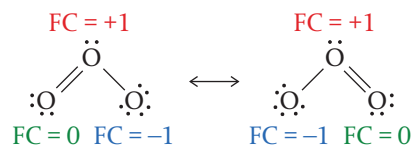
The central oxygen (at the top of the Lewis formula) has a formal charge of +1 and an outer oxygen (pointing down) has a formal charge of −1 in both structures. So the actual structure, the resonance hybrid, has a permanent dipole moment:

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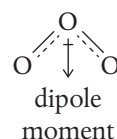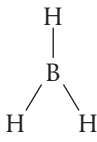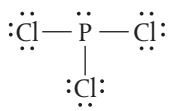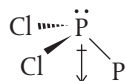
9 It is difficult to know the number of valence electrons a transition metal has. Treating bonds from covalent molecules results in transition metals in complex ions with large negative formal charges. The formal charge model may not be as useful for complex ions, as the values obtained do not make much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

10 Phosphorus in PCl_5 would require sp^3d hybrid orbitals.

Sulfur in SF_6 would require sp^3d^2 hybrid orbitals.

Practice questions

1 C

2 A

3 A

4 A

5 B

6 C

7 D

8 B

9 B

10 hydrogen bonding in butan-1-ol stronger; [1]

than dipole–dipole attractions in butanal. [1]

Accept converse argument. Do not penalize 'dipole–dipole bonding' instead of 'dipole–dipole attractions'.

11 (a)

BH₃	PCl₃

(i) *Lewis formula:*
 	
H
|
B
H   H
 	
Allow x's, dots or lines to represent electrons.
	(ii) *Lewis formula:*
	
	:Cl — P — Cl:
	    |
	   :Cl:
	
	Allow x's, dots or lines to represent electrons.
	Lone pairs must be included for mark.

(ii) *Shape:* Triangular / trigonal planar; *Bond angle:* 120°	**(ii)** *Shape:* Triangular / trigonal pyramidal; *Bond angle:* Less than 109.5° / in range 100–108°
(iii) *Polarity:* non-polar **and** *Explanation:* no net dipole moment / B and H very similar electronegativity values / «small» bond dipole but molecule symmetrical / «small» bond dipoles cancel out / *OWTTE*;	**(iii)** *Polarity:* polar **and** *Explanation:* net dipole moment / polar P–Cl bonds **and** asymmetrical molecule / bond dipoles do not cancel / Cl ⤙ P Cl ↓ P / *OWTTE*;

[8]

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

*Allow (**1 max**) for stating that PCl_3 is polar and BH_3 is non-polar without giving a reason or if explanations are incorrect.*

Allow polar bonds cancel for BH_3 and polar bonds do not cancel for PCl_3.

Do not allow asymmetric molecule as reason for PCl_3 or symmetric molecule for BH_3 as reason alone.

(b) (i) *σ bond:*
head-on / end-on / axial combination / overlap of atomic orbitals **and** electron density concentrated along bond axis / between the two carbon atoms / nuclei / *OWTTE*; [1]

π bond:
lateral / sideways / parallel combination / overlap of p orbitals **and** electron density concentrated on opposite sides of bond axis / *OWTTE*; [1]

Marks can be scored from a suitable diagram. Award (1 max) for stating head-on / end-on / axial combination for σ and lateral / sideways / parallel combination for π only i.e. without mentioning electron density OR stating electron density between two atoms / nuclei for σ and above and below bond axis for π.
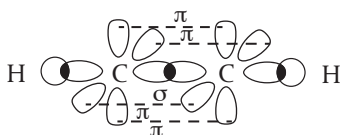
(ii) $11 \times \sigma$ **and** $3 \times \pi$. [1]

(iii) (strong) intermolecular hydrogen bonding in *trans* but (strong) intramolecular hydrogen bonding in *cis* so attraction between different molecules is less in *cis* (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 is sp^3 and O of C=O is sp^2 [1]

Oxygens must be identified.

12 (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° and 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) / coordination 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; [1]
equal bond order / strength / length / spreading charge (equally) over all three oxygens; [1]
gives carbonate ion a greater stability / lower potential energy; [1]
M3 can be scored independently.

Accept suitable labelled diagrams for M1 and M2 e.g.
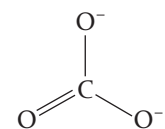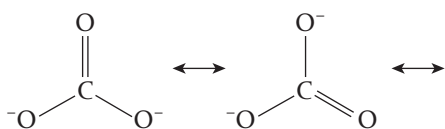
or
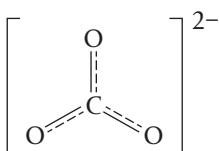
(e) mixing / combining / merging of (atomic) orbitals to form new orbitals (for bonding)   [1]

Allow molecular or hybrid instead of new.

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

Carbon dioxide: sp;   [1]

Diamond: sp³;   [1]

Graphite: sp²;   [1]

Carbonate ion: sp²;   [1]

**13** Methoxymethane is very weakly polar / weak dipole–dipole forces exist between methoxymethane molecules;   [1]

Accept London dispersion forces / weak van der Waals' 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;   [1]

the forces of attraction between molecules are stronger in ethanol than in methoxymethane / hydrogen bonding stronger than van der Waals' / dipole–dipole attractions.   [1]

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

Penalise only once if no reference given to intermolecular nature of hydrogen bonding or London dispersion / dipole–dipole / van der Waals' forces.

14 (a) (i)   ;
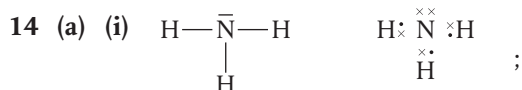
trigonal pyramidal;

less than 109° / in the range of 100–108°;   [3]

(ii)   ;

Must include negative charge for the mark.

bent / V-shaped;

less than 109° / in the range of 100–106°;   [3]

(iii)   ;
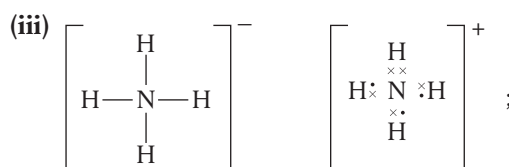
tetrahedral;

109.5°;   [3]

Penalise once only if electron pairs are missed off outer atoms

(b) (i) sigma bonds are formed by head-on / end on / axial combination / overlap of atomic orbitals with electron density concentrated along the bond axis / between the two atoms / nuclei;   [1]

pi bonds are formed by lateral / sideways combination / overlap of parallel p orbitals with electron density concentrated on opposite sides / above and below bond axis;   [1]

Accept suitably annotated diagrams

(ii) 8 × sigma / σ;   [1]

1 × pi / π;   [1]

(iii) 109° / 109.5°;   [1]

120°;   [1]

(iv) sp hybridization;   [1]

1 sigma and 2 pi;   [1]

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   [1]

15 (a) (i)

$$|\overline{O}-\overline{C}l| \qquad \underset{\times\times}{\overset{\times\times}{O}}\times \,:\overset{..}{\underset{..}{C}}l:$$
$$\underset{|}{\,\,|\underline{C}l|} \qquad\qquad :\overset{..}{\underset{..}{C}}:$$

bent / v-shaped;

less than 109° / in the range of 100–106°; [3]

(ii)

$$\left[\overset{..}{O}=N=\overset{..}{O} \right]^{+} \qquad \left[:\overset{..}{\underset{..}{O}}\times N\times\overset{..}{\underset{..}{O}}: \right]^{+} \qquad ;$$

linear;

180°; [3]

Allow dots, crosses or lines in Lewis formula.

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

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

(b) NO_2:

$$\underset{O}{\overset{N}{\diagup}}\underset{O}{\overset{\downarrow}{\diagdown}}$$
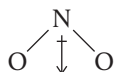
Award [1] for correct representation of the bent shape and [1] for showing the net dipole moment, or explaining it in words (unsymmetrical distribution of charge).

CO_2:

$$\overset{\longleftarrow\,+\,\longrightarrow}{O=C=O}$$
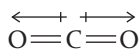
Award [1] for correct representation of the linear shape and for showing the two equal but opposite dipoles or explaining it in words (symmetrical distribution of charge). [3]

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; [1]

Bonding:

(single) covalent (bonds). [1]

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

(d) (i) [1]

$$|\overset{\textstyle |\overline{O}|}{\underset{|}{H-C-\overline{N}-H}}$$
$$\underset{H}{|}$$

(ii) sigma bonds are formed by head-on / end on / axial combination / overlap of atomic orbitals with electron density concentrated along the bond axis / between the two atoms / nuclei; [1]

pi bonds are formed by lateral / sideways combination / overlap of parallel p orbitals with electron density concentrated on opposite sides / above and below bond axis; [1]

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 bond axis for π i.e. without mentioning overlap of orbitals.

(iii) C is sp^2; [1]

N is sp^2 / sp^3; [1]

Correct answer is actually sp^2 for nitrogen because of delocalization of lone pair / overlap of carbon p orbital and nitrogen hybrid orbital / planar geometry.

Accept sp^3.

16 (a) $H-C\equiv C-H$; [1]

$$\underset{H}{\overset{H}{\diagdown}}C=C\underset{H}{\overset{H}{\diagup}} \qquad [1]$$

(b) ethyne bond is shorter because of the greater number of shared electrons so stronger electrostatic attraction to (bonded) nuclei; [1]

(c) London (dispersion) forces; [1]

17 (a) measure of how far a component spot has travelled in comparison to the solvent front / mobile phase; [1]

Accept formula

$$R_f = \frac{\text{distance travelled by spot}}{\text{distance travelled by solvent front}}$$

(b) $(R_f = \frac{32}{96} =) \, 0.33$; [1]

(c) R_f value compared with literature values «that used the same stationary phase and solvent / mobile phase». [1]

(d) component will have a different degree of solubility in a different solvent; [1]

R_f value is dependent on solubility of component in the mobile phase «and stationary phase»; [1]

(e) thin layer chromatography / TLC;

Accept GLC or HPLC [1]

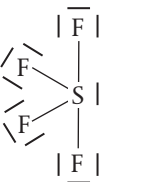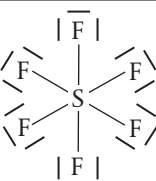**18** A

19 B

20 D

21 B
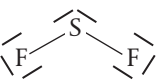
22 C

23 D

24 A

25 (a) (bond formed by) lateral / sideways combination / overlap; [1]

of p orbitals; [1]

Accept electron density on opposite sides of bond axis for M1

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

26

	Lewis formula	Name of shape
SF_2	*2 lone pairs on S required for the mark*	bent / V-shaped
SF_4	*1 lone pair on S required for the mark*	see-saw
SF_6		octahedral *Accept square bipyramidal*

[6]

27 (a) (i) both H = 0, C = 0, left N = +1, right N = −1 [1]

(ii) both H = 0, C = +1, left N = 0, right N = −1 [1]

formal charges show same differences but structure (i) will be more important because carbon / all atoms have a stable octet [1]

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

(ii) from left O = −1, Cl = 0, O = 0 [1]

structure (ii) is preferred as formal charges closer to zero [1]

28 (a) $\overline{\text{O}}{=}\overline{\text{O}}$; [1]

$\overline{\text{O}}{=}\overline{\text{O}}{-}\overline{\text{O}}|$ $|\overline{\text{O}}{-}\overline{\text{O}}{=}\overline{\text{O}}$; [1]

(b) delocalized electrons are shared equally across both bonding positions / molecule is combination of two possible resonance structures; [1]

bond length in range 121–148 «× 10^{-12} m / pm» [1]

Do not accept 121 or 148 «× 10^{-12} m / pm»

(c) electron domain geometry is triangular planar / trigonal planar; [1]

molecular geometry is bent / V-shaped; [1]

less than 109° / in range of 100–119°; [1]

29 (a) Physical evidence:

equal C–C bond «lengths / strengths»

or

regular hexagonal shape

or

«all» C–C have bond order of 1.5

or

«all» C–C intermediate between single and double bonds [1]

Chemical evidence:

undergoes substitution reaction «more readily than addition»

or

does not discolour / react with bromine water

or

only three isomers exist of dibromobenzene

or

more stable than expected «compared to hypothetical cyclohexa-1,3,5-triene»

or

enthalpy change of hydrogenation / combustion is less exothermic than predicted «for cyclohexa-1,3,5-triene» [1]

S2.3 The metallic model

Exercises

Q1 B

Q2 **(a)** Delocalized electrons are able to move freely so can move across a metallic structure in response to an applied voltage.

(b) Delocalized electrons and closely packed cations enable efficient transfer of thermal energy.

(c) The metallic bond is non-directional due to the random movement of delocalised electrons. This allows the metallic bond to remain intact when the lattice of cations undergoes conformation changes under pressure.

Q3 **(a)** malleability, thermal conductivity, high melting point, chemically unreactive due to oxide layer

(b) light, strong, forms alloys

(c) thermal conductivity, high melting point, non-corrosive, chemically unreactive due to oxide layer

(d) light, strong, non-corrosive, chemically unreactive due to oxide layer

Q4 Beryllium has stronger electrostatic attraction in its metallic bonding as it forms a structure of smaller cations with greater magnitudes of charge (Be^{2+}) and delocalizes two electrons for each cation formed. Lithium has larger cations with only one positive charge (Li^+) and delocalizes only one electron for each cation formed.

Q5 C

Q6 The strength of metallic bonding decreases down a group as the size of the cation increases, reducing the attraction between the delocalized electrons and the positively charged nuclei. Weaker bonds require less energy to break, so melting points are lower.

Q7 A

Q8 Transition elements are able to delocalize d-electrons in addition to their valence s-electrons to form ions with higher magnitudes of charge than s and p block metals. This leads to stronger electrostatic attraction in the metallic bond and so higher melting points.

Q9 Transition elements form a metallic structure with a large number of delocalized electrons leading to high electrical conductivity.

Challenge yourself

1 Silver is used in small amounts due to its high cost. It is mostly used on the interior of electronic devices as it can tarnish when exposed to sulfur-containing gases in the air. This tarnish can occur even with low concentrations of gases such as sulfur dioxide and hydrogen sulfide.

Practice questions

1 C

2 D

3 A

4 B

5 **(a)** the electrostatic attraction; [1]

between lattice of cations AND delocalized electrons; [1]

mobile electrons are able to carry charge across a metallic structure. [1]

(b) calcium has smaller ionic radius; [1]

greater attraction between delocalized electrons and «nuclei of» cations; [1]

or

strontium has a larger ionic radius; [1]

weaker attraction between delocalized electrons and «nuclei of» cations. [1]

6 metallic bond / electrostatic attraction / movement of delocalized electrons is non-directional; [1]

metallic bond remains intact when structure undergoes conformation changes; [1]

closely packed cations AND delocalized electrons; [1]

allow for efficient transfer of thermal energy «across metallic structure». [1]

7 able to delocalize d-electrons (in addition to valence s and / or p-electrons); [1]

larger number of delocalised electrons «leading to better electrical conductivity». [1]

S2.4 From models to materials

Exercises

Q1

	Substance	$\chi_{average}$	$\Delta\chi$	% ionic character	Bonding
(a)	Cl_2O	3.3	0.2	6	(Polar) covalent
(b)	$PbCl_2$	2.5	1.4	44	Polar covalent
(c)	Al_2O_3	2.5	1.8	56	Ionic
(d)	HBr	2.6	0.8	25	Polar covalent
(e)	NaBr	1.95	2.1	66	Ionic

The % ionic character is taken from the bonding triangle (S2.4 Figure 2).

Q2

Substance	$\chi_{average}$	$\Delta\chi$	% ionic character	Bonding
CuO	2.65	1.5	47	Polar covalent
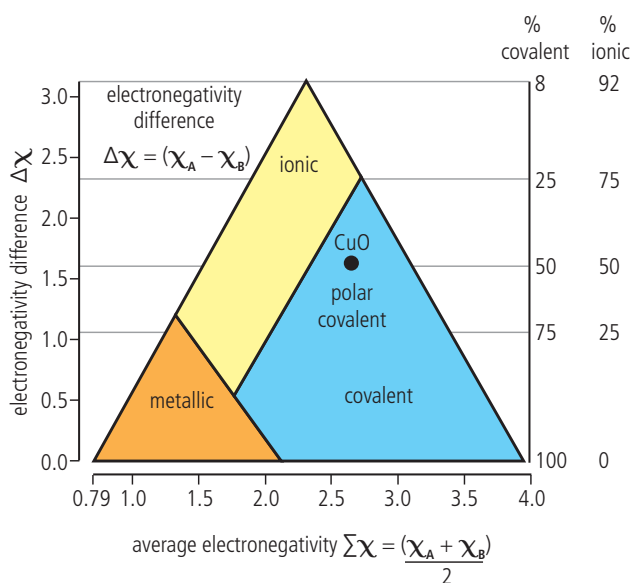
Q3

Substance	$\chi_{average}$	$\Delta\chi$	Bonding
SiO_2	2.65	1.5	Polar covalent
Al_2O_3	2.5	1.8	Polar covalent/ionic

Applying these data, we can position these compounds in the bonding triangle. SiO_2 is positioned lower and to the right of Al_2O_3 and therefore has the greater covalent character.
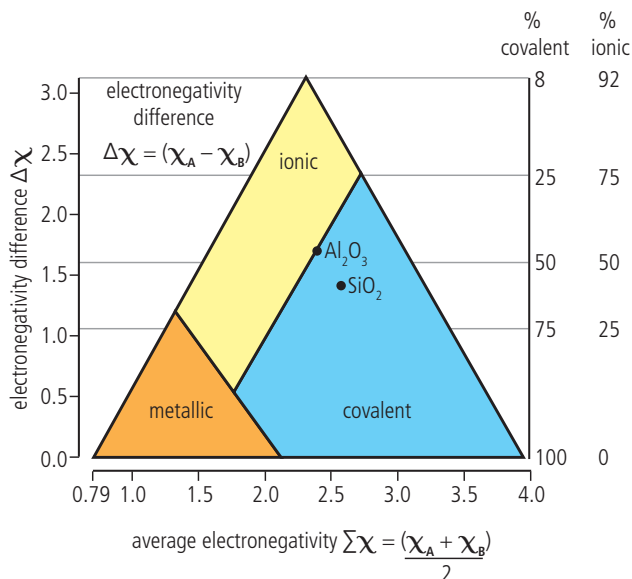
Q4 A

Q5 B

Q6 Alloying element(s) disrupts regular / repeating (metal) lattice. It is 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 the metal harder / stronger / more corrosion resistant / brittle.

Q7 An alloy is a mixture of one or more metals with other elements. Composites may not contain a metal. Alloys are generally homogeneous mixtures whereas a composite is always a heterogeneous mixture with the components present as separate phases.

Q8 B

Q9 C

Q10 A

Q11 *Recyclable* means a substance can be processed by chemical means into new products.

Biodegradable means a substance will be broken down in the natural environment into harmless end products.

Reusable means a substance can be reused without being changed physically or chemically.

Reusable plastics potentially have a low impact on the environment, as they can remain in circulation rather than accumulating in land-fill or oceans, and there are no side-products of processing. This depends though on individual responsibility for reusing rather than disposing.

Biodegradable plastics also reduce the environmental impact of plastics as they break down into harmless products. This depends though on time and on the conditions during the breakdown process. In some cases, biodegradable plastics may not break down fully.

Recyclable plastics enable parts or all of the substance to be reused rather than discarded, which reduces their environmental impact. But the sorting, processing and manufacturing stages in the recycling process have side-products, energy costs and waste products that may themselves have an environmental impact.

The best way to reduce the amount of plastic waste is to reduce consumption. For example, limiting the use of single-use plastics and packaging, and encouraging more reusable plastics. Individuals also must be mindful of responsible disposal of plastics according to their chemical nature and ability to be recycled, biodegraded or composted.

Q12 $-(-NH-(CH_2)_6-NH-CO-(CH_2)_8-CO-)_n-$

Q13

Q14 **(a)**

$$\left[-O-CH_2-CH_2-CH_2-O-CO-CH_2-CH_2-CO- \right]_n + H_2O$$

(b)

$$\left[HN-CH_2-(CH_2)_4-CH_2-NH-CO-CH_2-CH_2-CO- \right]_n + HCl$$
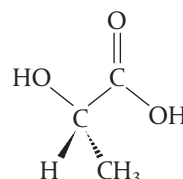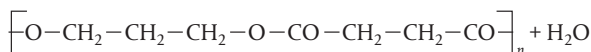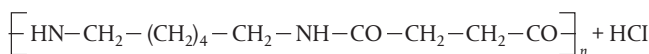
Q15 **(a)** The primary amine and carboxylic acid groups.

(b) H_2O

(c)
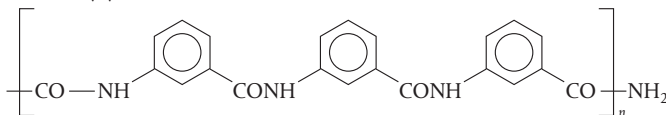
(d) The 1 and 4 positions are opposite each other, so the functional groups are arranged in a straight line. Each polymer will form a linear molecule.

The condensation reactions occur between functional groups that are 180° apart, forming molecular chains which are fully extended. Hydrogen bonds can form between the chains when they are correctly aligned.

(e) Kevlar contains lighter elements (H, C, O and N) than steel, which is mostly the heavier element, iron, Fe.

Challenge yourself

1   Alloys are a mixture of metals in which the components are held together by metallic bonding. These bonds are able to form between atoms of the same metals and atoms of different metals due to their non-directional nature. In order to separate a metal from an alloy, the bonds between the different metals have to be broken. This can be done by heating until the metal with the lower melting point forms a liquid and can be separated by filtration from the remaining solid. This is not an economically efficient process. Alloys can also be separated into their component metals by chemical means, such as selectively dissolving with acids.

2
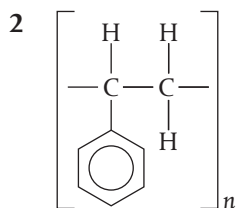
Practice questions

1   A

2   A

3   A

4   **(a)** Y: [1]

    bottom left position is metallic bonding.   [1]

    (b) X (ionic compound), Y (metal)   [1]

    generally have high melting points.   [1]

    (c) X; ionic compounds are brittle.   [1]

    When the regular structure of the lattice is displaced, the ionic bonds can no longer hold the oppositely charged ions in position.   [1]

    (d) Z (covalent substance)   [1]

    has low boiling point due to relatively weak intermolecular forces.   [1]

5

Substance	$\chi_{average}$	$\Delta\chi$	Position in triangle and type of bonding	Predicted properties	
Sn	2.0	0.0	metallic	high mp and bp, electrical and thermal conductor	[2]
P_4O_{10}	2.8	1.2	polar covalent	soluble in water, high mp	[2]
Cd_3Mg	1.5	0.4	metallic	high mp and bp, electrical and thermal conductor	[2]
MgO	2.35	2.1	ionic	high mp and bp, conductor of electricity when molten or in aqueous solution	[2]
NCl_3	3.1	0.2	covalent	low mp and bp, non-conductor of electricity, not soluble in water	[2]

6   Polymerization reactions of polypropylene are addition reactions with only one product, the polymer. So all the atoms of reactant are found in the product and the atom economy is 100%. In this sense, the reactions are "green chemistry", as there is no waste or by-product. However, factors such as energy usage, catalysts and yield less than 100% may all have environmental impact.   [2]

7   The alloy is stronger than the pure metal.   [1]

    Adding atoms of a different size disrupts the regular metal lattice so that it is difficult for one layer to slide over another.   [1]

    Alloying can make the metal harder, stronger and more resistant to corrosion.   [1]

8   **(a)** average electronegativity = $\frac{3.0 + 2.0}{2}$ = 2.5

    electronegativity difference = 3.0 − 2.0 = 1.0   [1]

    bonding in $SbBr_3$ is polar covalent   [1]

    (b) bonding in $LaBr_3$ is ionic bonding *or* electrostatic forces between ions   [1]

slight movement brings ions of same charge adjacent to each other, causing the crystal to break *or* slight movement results in repulsion between layers, causing the crystal to break [1]

9 (a)

H   CH₃
| |
— C — C —
| |
H   CH₃

or
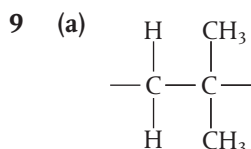
$-CH_2C(CH_3)_2-$ [1]

Continuation bonds needed for mark.

No penalty if brackets present or 'n' appears after the bracket / formula.

(b) same mass of product as reactant, thus 100% [1]

accept "less than 100%" only if a reason is given, e.g. the catalyst is not converted into the product, or other reasonable answer.

(c) due to stability of plastics / strong covalent bonds

or

low volatility preventing good mixing with oxygen gas

or

lack of / insufficient oxygen

or

plastics are often parts of devices with non-combustible components, which mechanically prevent the combustion of plastic components

or

PVC already partly oxidized (because some C−H bonds are replaced with C−Cl bonds), so it cannot produce enough heat for complete combustion

or

many industrial / household materials contain additives that reduce their flammability / act as flame retardants [1]

10 (a) metallic bonding [1]

(b) In MgB_2, difference in EN = 0.7, average EN = 1.65 [1]

bonding is on the boundary between ionic and metallic

or

not just one type of bonding [1]

11 C

12 D

S3.1 Classification of matter

Exercises

Q1 D

Q2 C

Q3 B

Q4

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

Q5 (a) Periods are rows and groups are columns.

(b) $1s^2 2s^2 2p^6 3s^2 3p^3$

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.

Q6 Element 51 is antimony (Sb), which is in Group 15. Its valence electrons are $5s^2 5p^3$, and so it has 5 valence electrons.

Q7 C

Q8 A

Q9
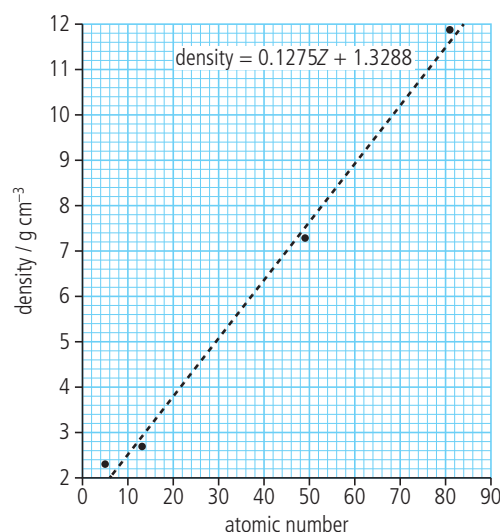
Predicted density 5.3 g cm⁻³. This agrees with the measured value of 5.1 g cm⁻³.

Q10 C

Q11 A

Q12 B

Q13 C

Q14 D

Q15 D

Q16 B

Q17 **(a)** Half the distance between the nuclei of neighbouring atoms of the same element bonded together by a covalent bond.

(b) **(i)** The noble gases do not form bonds so the distance between neighbouring atoms is not defined.

(ii) The atomic radii decrease across a period. The nuclear charge increases as the number of protons increases. Electrons are added to the same main energy level. The electrostatic attraction between the outer electrons and the nucleus increases.

Q18 Si^{4+} has two occupied energy levels (isoelectronic with Ne) and Si^{4-} has three (isoelectronic with Ar) and so Si^{4-} is larger.

Q19 **(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 one more principal energy level than Si^{4+}. Positive ions are smaller than their parent ions while negative ions are larger than their parent ions.

(c) The ions have the same electron configuration: both have two complete shells; the two extra protons in Na^+ attract the electrons more strongly.

Q20 $Cl^- > Cl > Cl^+$

Q21 D

Q22 D

Q23 B

Q24 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.

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

Q25 Down the group, the reactivities of the alkali metals increase but those of the halogens decrease.

Q26 They all have valence electron configuration ns^1. They react by losing this electron. The electron is easier to remove as the atomic radii increase due to decreased attraction between the electron and the nucleus.

Q27 They all have valence electron configuration $ns^{2n}p^5$. They react by gaining an electron. An electron is easier to add as the atomic radii decrease due to increased attraction between the electron and the nucleus.

Q28 A

Q29 D

Q30 C

Q31 **(a)** $MgO(s)$, $SiO_2(s)$, $P_4O_{10}(s)$, $SO_2(g)$

(b) MgO: giant structure with ionic bonding; strong attraction between oppositely charged ions.

SiO_2 (quartz): giant structure covalent bonding; strong covalent bonds throughout structure.

$P_4O_{10}(s)$ molecular, covalent bonding; weak van der Waals' forces between molecules; P_4O_{10} is larger molecule and so has stronger intermolecular bonding.

SO_2: molecular, covalent bonding; weak van der Waals' forces between molecules; SO_2 is smaller molecule and so has weaker intermolecular bonding.

(c) MgO: alkaline solution

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$

SiO_2 (quartz): oxide is insoluble

P_4O_{10}: acidic solution

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

SO_2: acidic solution

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

(ii) $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow$
$2NaAl(OH)_4(aq)$
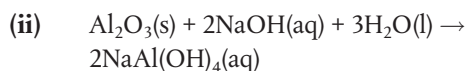
Q32 The oxides of Na and Mg are basic; the oxide of Al is amphoteric; the oxides of Si to Cl are acidic. Ar forms no oxide.

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
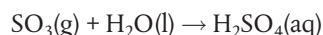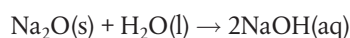
Q33 **(a)** Natural rain contains dissolved carbon dioxide, which reacts with water to form carbonic acid:

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

(b) sulfuric acid

$S(s) + O_2(g) \rightarrow SO_2(g)$

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$
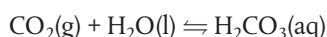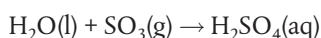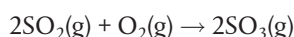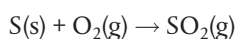
(c) nitric acid

production reduced by use of lean burn engines, catalytic converters, recirculation of exhaust gases

Q34 C

Q35 C

Q36 **(a)** N = −3, H = +1

(b) Sn = +2, Cl = −1

(c) H = +1, O = −2

(d) N = +5, O = −2

(e) Pb = +4, O = −2

(f) P = +5, O = −2

(g) Cl = +7, O = −2

(h) H = +1, O = −2, Cl = +1

Q37 **(a)** nitric(V) acid

(b) nitric(III) acid

(c) phosphoric(V) acid

(d) lead(IV) oxide

(e) lead(II) sulfate(VI)

Q38 **(a)** Cu_2O

(b) Fe_2O_3

(c) SnO_2

(d) $NaBrO_3$

Q39 **(a)** I is oxidized (−1 to 0), Cl is reduced (0 to −1)

(b) O is oxidized (−2 to 0), F is reduced (0 to −1)

(c) P is oxidized (0 to +5), F is reduced (0 to −1)

(d) Na is oxidized (0 to +1), H is reduced (0 to −1)

Q40 C

Q41 A

Q42 A

Q43 **(a)** $M(g) \rightarrow M^+(g) + e−$

(b) repeating pattern

(c) In B, an electron removed from a 2p sublevel. In Be, electron removed from 2s sublevel

2p higher energy (as more shielded from nucleus).

(d) Electron removed from nitrogen is from a doubly occupied p orbital, electron repulsion makes it easier to remove.

Q44 D

Q45 D

Q46 **(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.

Q47

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

Q48 Chromium has the electron configuration [Ar] $3d^54s^1$; it has six unpaired electrons, which is the maximum number for the series. Zn has the [Ar] $3d^{10}$ configuration, with no unpaired electrons.

Q49 The sample near the electromagnet would go down and so appear to have more mass. It is pulled into magnetic field as it has lone pairs of electrons.

Q50 B

Q51 D

Q52 Al only shows the +3 state, which corresponds to the loss of the two outer 3s electrons and one 3p electron. The other electrons are in lower energy levels and so are not available for bonding. Cr shows oxidation states ranging from +2 to +6. The 3d and 4s orbitals are of similar energy and so are available for bonding.

Q53 Fe^{2+} has configuration [Ar] 3d^6 and Zn^{2+} is [Ar] 3d^{10}. Colour is due to splitting of partially filled d orbitals at different energy levels; colour absorbed as electrons are excited from lower sublevel to higher sublevel and the complementary colour transmitted. Fe^{2+} has partially filled d orbitals and Zn^{2+} does not so Zn^{2+} is not coloured.

Q54 any value or range between 400 and 424 nm

Q55 **(a)** difference in nuclear charge of metal (ion)

(b) difference in oxidation number

(c) difference in ligand

Q56 λ_{max} = 525 nm. The colour absorbed is green; the colour transmitted is red / violet. (Note: [Ti(H$_2$O)$_6$]$^{3+}$ is violet; answers depend on the colour wheel used.)

Q57 For an ion [Ar]3d^6 in the field of the complex the d sublevel splits, to give

↑	↑	
↑↓	↑	↑

Challenge yourself

1 ytterbium, yttrium, terbium, erbium

2 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

3 Two liquids, ten gases

4 'Metalloid' refers to the properties of certain elements in relation to the periodic table. 'Semiconductor' refers to the physical properties of materials (including alloys and compounds). There is a partial overlap between the two sets.

5 Coal and oil are fossilized decayed plants or animals; the plants and animals would have contained amino acids. The amino acids methionine and cysteine contain sulfur. Coal and oil with a higher percentage of sulfur are considered 'dirty' because of the sulfur dioxide pollution that is produced on combustion. Sulfur dioxide results in acid rain.

6 $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$; $CaSO_4(s)$ has low solubility

$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

7 The d sublevel splits due to the presence of the ligand's lone pair of electrons. Electron transitions between d orbitals is the result of the absorption of energy from the visible region of the EM spectrum. The energy difference between the two sets of d orbitals depends on the coordination number, which changes from six to four, and the ligand, which changes from H$_2$O to Cl$^-$.

8 The broad absorption spectrum of the complex ions should be contrasted with the sharp lines of atomic spectra (discussed in Structure 1.3). Both phenomena are due to electronic transitions, but the spectrum of a complex ion is affected by surrounding ligands which can possess both vibrational and rotational energy. This allows the central ion to accept a wider range of frequencies, as any excess energy can be taken up by the ligands in the form of increased vibrational and rotational energy. The isolated gaseous ions which are excited in atomic absorption spectra do not have this option so will only absorb energy of the exact wavelength required to move an electron from a lower energy to an higher energy atomic orbital.

Practice questions

1 C

2 A

3 B

4 B

5 B

6 D

7 A

8 D

9 D

10 A

11 C

12 D

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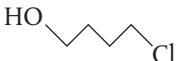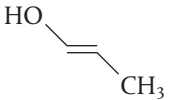
$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ [1]

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 two electron shells / energy levels, Na has three / *OWTTE* [1]

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

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

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

or

Si^{4+} has two energy levels whereas P^{3-} has three / 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) ions are in fixed positions in the solid state / 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 ⇌

19 (a) 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 shell electrons more than 11 p in Na nucleus / greater nuclear charge attracts outer shell electrons 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 changes the amount the d orbitals are split / energy difference between the d orbitals / *OWTTE* [1]

21 (a) $Fe^{2+}(aq)$ absorbs any value or range between 647 and 700 nm [1]

$Fe^{3+}(aq)$ absorbs any value or range between 400 and 491 nm [1]

(b) both are attracted into magnetic field as both have unpaired electrons [1]

Fe^{3+} is more magnetic as it contains more unpaired electrons [1]

S3.2 Functional groups: Classification of organic compounds

Exercises

Q1 **(a)** $CH_3C(CH_3)(OH)CH_3$

(b) $CH_3CH(CH_3)CH_2CH_3$

(c) $CH_3CHCHCH_3$

(d) $CH_3C(CH_3)_2CH_2CH_3$

Q2 **(a)**

(b)

(c)

(d)

Q3 **(a)** $CH_3CH(CH_3)CH(CH_3)CH_3$

(b) $CH_3CHClCHBrCH_3$

(c) $CH_3CH_2C(CH_3)CHCH_3$

(d) $CH_3CHCClCHClCH_3$

Q4 **(a)** class: carboxylic acid; functional group: carboxyl (acid)

(b) class: alkene; functional group: alkenyl

(c) class: alcohol; functional group: hydroxyl

(d) class: ester; functional group: carboxyl (ester)

(e) class: aldehyde; functional group: carbonyl (aldehyde)

(f) class: amine; functional group: amino

Q5 B

Q6 D

Q7 D

Q8 A

Q9 B

Q10 Order of increasing volatility: CH_3CH_2COOH $< CH_3CH_2CH_2Br < CH_3CH_2CH_3$

Reasoning: strength of intermolecular forces goes in order: alkane (London dispersion forces) < halogenoalkane (dipole–dipole) < carboxylic acid (H-bonding); volatility is reverse to this order.

Q11 The solubility of the alcohols in water will decrease as the chain length increases. The alcohols contain a highly polar −OH group and a non-polar carbon chain. As the carbon chain increases in length the alcohol will become less polar overall and therefore less soluble in water which is a polar solvent.

Q12 **(a)** class: alkane; name: 2-methylbutane

(b) class: carboxylic acid; name: 2-methylpropanoic acid

(c) class: ketone; name: butanone

(d) class: ester; name: propyl ethanoate

(e) class: alcohol; name: propan-1-ol

(f) class: aldehyde; name: pentanal

Q13 **(a)** HCOOH

(b) $CH_3CH_2CCCH_2CH_3$

(c) $CH_3CH_2CH_2CH_2CHO$

(d) $CH_3COCH_2CH_3$

(e) $CH_3CH_2OCH_2CH_2CH_3$

(f) $CH_3CHBrCH_2OH$

Q14
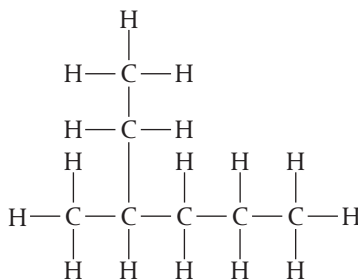
The longest chain contains six carbons. The correct name is 3-methylhexane.

Q15 D

Q16 (a)

H—C(H)(H)—C(H)(H)—C(H)(H)—C≡CH

H—C(H)(H)—C(H)(H)—C≡C—C(H)(H)—H

(b)

H—C(H)(H)(H) attached; H—C(H)(H)—C(H)—C≡CH
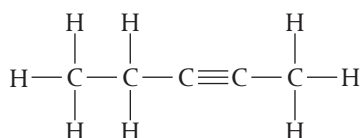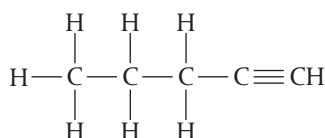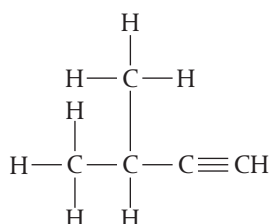
Q17 D

Q18 1-bromobutane, primary

Br—C(H)(H)—C(H)(H)—C(H)(H)—C(H)(H)—H
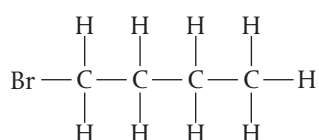
2-bromobutane, secondary

H—C(H)(H)—C(H)(Br)—C(H)(H)—C(H)(H)—H
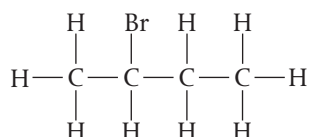
1-bromo-2-methylpropane, primary

Br—C(H)(H)—C(CH3)(H)—C(H)(H)—H
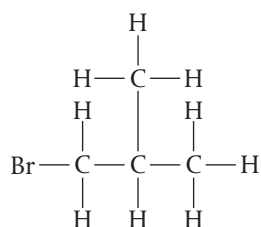
2-bromo-2-methylpropane, tertiary

H—C(H)(H)—C(CH3)(Br)—C(H)(H)—H
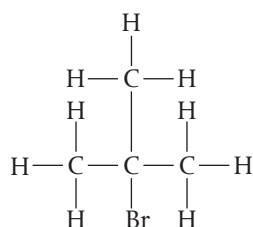
Q19 (a) $CH_3OCH_2CH_3$ (methoxyethane) and either $CH_3CH_2CH_2OH$ (propan-1-ol) or $CH_3CH(OH)CH_3$ (propan-2-ol)

(b) CH_3COCH_3 (propanone) and CH_3CH_2CHO (propanal)

(c) CH_3CH_2COOH, (propanoic acid) and CH_3COOCH_3 (methyl ethanoate)

Q20 (a)

H, CH_3 / $C=C$ / H_3C, H

(b)

Cl, Cl / $C=C$ / H, CH_3

(c)

cyclopentane with H_3C and CH_3

(d)

cyclohexane with Br, H substituents
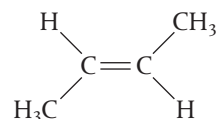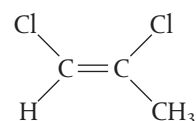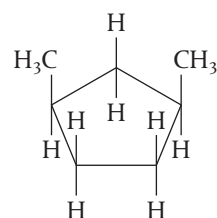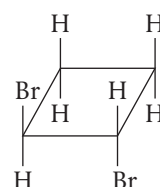
Q21 (a) cis-1,3-dibromocyclobutane

(b) trans-but-2-ene-2,3-diol

(c) cis-3,4-dimethylhex-3-ene

(d) trans-1,3-dichlorocyclopentane

Q22

Cl / H⸱⸱⸱C / Br, CH3   Cl / C⸱⸱⸱H / H3C, Br
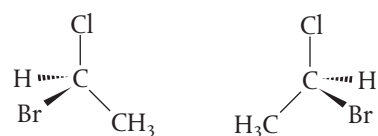
Q23 D

Q24 (a) CH_3CH_2*$CH(CH_3)CH_2CH_2CH_3$

(b)

OH / H_3C⸱⸱⸱C / H, CH_2CH_3
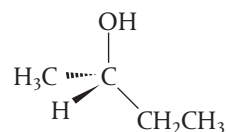
butan-2-ol

Q25 C

Q26 B

Q27 Spectrum A corresponds to propanal (CH_3CH_2CHO). Spectrum B corresponds to propanone (CH_3COCH_3).

Similarities: both spectra have a molecular ion with $\frac{m}{z} = 58$

Differences: A has peaks at $\frac{m}{z} = 29$ ($CH_3CH_2^+$) and $\frac{m}{z} = 57$ ($CH_3CH_2CO^+$). B has a peak at $\frac{m}{z} = 43$ (CH_3CO^+) and $\frac{m}{z} = 15$ (CH_3^+).

Q28 **(a)**

Mass charge	Mass charge
15	CH_3^+
29	$C_2H_5^+$
43	$C_3H_7^+$
58	$C_4H_{10}^+$

(b) The mass of the parent ion is 58. The molecular formula is C_4H_{10} as this is a multiple of the empirical formula, C_2H_5, with mass 58. The masses of the fragments show a pattern consistent with a straight-chain alkane, so the molecular structure is $CH_3CH_2CH_2CH_3$.

Q29 B

Q30 IR radiation of the shortest wavelength corresponds to the highest frequency.

(a) C=O is a stronger bond than C−O so will vibrate at the higher frequency and absorb radiation of a shorter wavelength.

(b) Cl is lighter than Br so C−Cl will vibrate at a higher frequency and absorb radiation of a shorter wavelength.

Q31 The molecular formula of the two compounds is consistent with the formula for a carboxylic acid and for an ester and also for an alcohol with a C=C double bond. However, neither compound has an absorption frequency in the range 1620−1680 cm⁻¹, so neither contains a C=C double bond.

(a) The bonds corresponding to the absorption frequencies are O−H (3000 cm⁻¹), C=O (1730 cm⁻¹) and C−O (1230 cm⁻¹). This indicates the compound is a carboxylic acid.

Compound A is propanoic acid.

(b) Compound B does not have an O−H bond present as there is no absorption in the 2500−3000 cm⁻¹ region. The bonds that are present are C=O (1730 cm⁻¹) and C−O (1230 cm⁻¹). This indicates the compound is an ester.

There are two possible esters: CH_3COOCH_3 (methyl ethanoate) and $HCOOCH_2CH_3$ (ethyl methanoate).

Q32 Molecules can only absorb IR radiation if it results in a change in the overall dipole. For diatomic molecules this can only happen if they are polar molecules. N_2 and O_2 are both non-polar diatomic molecules so they cannot absorb IR radiation and so cannot contribute to the greenhouse effect.

Q33 SO_2 is V-shaped (bent) so it has three modes of vibration.

| symmetric stretch | asymmetric stretch | symmetric bend |
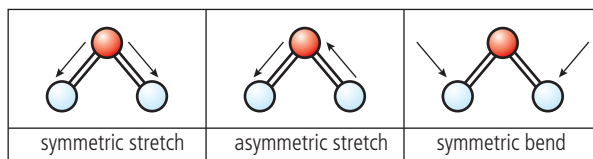
All three modes are IR active as each results in a change in the overall dipole.

Q34 Because it contains a C=C double bond, hex-1-ene will have an IR absorption in the range 1620−1680 cm⁻¹. Hexane only contains C−C single bonds so will not have an absorption in this range.

Q35 Ethanol contains C−H, C−C, C−O and O−H bonds. Of these, the only bonds that absorb at 2900 cm⁻¹ are C−H bonds. (The O−H bond in alcohols absorbs in the 3200−3600 cm⁻¹ range.)

Q36 **(a)** Two signals. The two −CH_3 groups are in different chemical environments.

(b) One signal. The molecule is symmetrical so the two −CH_3 groups have the same chemical environment.

(c) One signal. All four −CH_3 groups are equivalent so the protons have the same chemical environment.

(d) Two signals. The two −CH_3 groups are equivalent so their protons have the same chemical environment. The H on the central carbon will have a different chemical environment.

Q37

Signal	Generated by	Chemical shift (ppm)
1	$(\mathbf{CH_3})_2$CHCOOH	0.9–1.0
2	$(CH_3)_2\mathbf{CH}$COOH	2.0–2.5
3	$(CH_3)_2$CHCOO$\mathbf{H}$	9.0–13.0

Q38 C

Q39 (a)
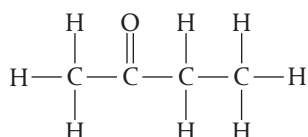
(b)

Hydrogen atom	Chemical shift / ppm	No. of H atoms (area of signal)	Splitting pattern ($n+1$ rule)
$\mathbf{CH_3}$COCH$_2$CH$_3$	2.2–2.7	3	singlet
CH$_3$CO$\mathbf{CH_2}$CH$_3$	2.2–2.7	2	quartet, 1:3:3:1
CH$_3$COCH$_2$$\mathbf{CH_3}$	0.9–1.0	3	triplet, 1:2:1

Q39

Compound	Hydrogen atom	Chemical shift / ppm	No. of H atoms	Splitting pattern
ethanal, CH$_3$CHO	$\mathbf{CH_3}$CHO	2.2–2.7	3	doublet, 1:1
	CH$_3$$\mathbf{C}$HO	9.4–10.0	1	quartet, 1:3:3:1
propanone, CH$_3$COCH$_3$	$\mathbf{CH_3}$CO$\mathbf{CH_3}$	2.2–2.7	6	singlet

Q41 The formula $C_3H_6O_2$ is consistent with a carboxylic acid or an ester. However, the singlet at 10.0 ppm is only consistent with the –COOH of a carboxylic acid.

The compound is propanoic acid, CH_3CH_2COOH

Chemical shift / ppm	Number of H atoms	Splitting pattern	Hydrogen atom
1.3	3	3	$\mathbf{CH_3}$CH$_2$COOH
4.3	2	4	CH$_3$$\mathbf{CH_2}$COOH
10.0	1	1	CH$_3$CH$_2$COO$\mathbf{H}$

Challenge yourself

1 Using the experimental data, the ratio of the carbon–carbon bond length to the radius of a carbon nucleus can be calculated;

$$\text{Ratio} = \frac{154 \times 10^{-12}\,\text{m}}{2.7 \times 10^{-15}\,\text{m}} = 57\,000$$

Therefore, the plastic stick used in a model would need to be 57 000 times longer than the radius of the plastic ball used to represent a carbon nucleus.

$57\,000 \times 0.5\,\text{cm} = 28\,500\,\text{cm} = 285\,\text{m}$

heptane

2-methylhexane

3-methylhexane

2,3-dimethylpentane

2,4-dimethylpentane

2,2-dimethylpentane

3,3-dimethylpentane

3-ethylpentane

2,2,3-trimethylbutane

3

1,2-dimethylbenzene   1,3-dimethylbenzene

1,4-dimethylbenzene

There are no highly polar atoms in dimethylbenzene so the strongest intermolecular forces will be London dispersion forces. As discussed on page 362, these forces are strongest when molecules can stack together easily as this results in a greater surface contact. 1,4-Dimethylbenzene has the most symmetrical structure of the three isomers and this allows the individual molecules to more easily stack together, giving it the highest melting point. (1,2-dimethyl benzene; m.p. −25 °C, 1,3-dimethyl benzene; m.p. −48 °C, 1,4-dimethylbenzene; m.p. 13 °C.)

4 In both square planar and octahedral compounds, geometric isomers can arise due to groups having the possibility of being in adjacent (*cis*) and across (*trans*) positions. In tetrahedral compounds, all positions are adjacent to each other, so these isomers are not possible.

cis-platin (left) and *trans*-platin (right) are examples of *cis-trans* isomerism in square planar complexes.

The *cis*-tetraaminedichlorochromium(III) ion (left) and *trans*-tetraaminedichlorochromium(III) ion (right) are examples of *cis-trans* isomerism in octahedral complexes.

5 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.

6 Red asterisks mark the position of chiral carbon atoms.

* the eleven chiral carbon centres

7. Energy of a single photon = hf

$$= 6.63 \times 10^{-34} \text{J s} \times 3.0 \times 10^{14} \text{s}^{-1}$$

$$= 2.0 \times 10^{-19} \text{J}$$

Energy of one mole of photons = $2.0 \times 10^{-19} \text{J} \times 6.02 \times 10^{23} \text{mol}^{-1}$

$$= 120\,000 \text{J mol}^{-1}$$

$$= 120 \text{kJ mol}^{-1}$$

8 The frequency of the absorption is given in wavenumbers (cm^{-1})

Wavelength (λ) = 1/wavenumber

$$\lambda = \frac{1}{2100\,\text{cm}^{-1}} = 4.76 \times 10^{-4}\,\text{cm} = 4.76 \times 10^{-6}\,\text{m}$$

Natural frequency (s^{-1}) can be calculated using $c = f\lambda$

$$f = \frac{c}{\lambda} = \frac{3.00 \times 10^8\,\text{ms}^{-1}}{4.76 \times 10^{-6}\,\text{m}} = 6.30 \times 10^{13}\,\text{s}^{-1}$$

Practice questions

1 B

2 D

3 A

4 D

5 **(a)** A 1-bromobutane [1]

B 2-bromobutane [1]

C 2-bromo-2-methylpropane [1]

D 1-bromo-2-methylpropane [1]

(b) Optical isomers (enantiomers) are a type of stereoisomer that exist in compounds that contain chiral carbons.

A chiral carbon is a carbon atom with four different groups attached.

Isomer B, 2-bromobutane, has a chiral carbon, shown in the diagram below with *, and can exist as two optical isomers.

[1]

A polarimeter measures the angle that plane-polarized light is rotated through due to its interactions with an optical isomer. [1]

One optical isomer will rotate the plane of plane-polarized light in a clockwise direction whereas the other optical isomer will rotate the plane of plane-polarized light by the same amount in the anti-clockwise direction. [1]

The physical properties of optical isomers are identical except for their rotation of plane-polarized light. [1]

The chemical properties of optical isomers are also identical except for their reactions with other chiral compounds. [1]

6 **(a)** The compound contains the −COO− group, so it is an ester. [1]

(b) ethyl butanoate [1]

(c) belonging to same class: propyl propanoate (other ester isomers are possible)

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3-CH_2-C}}-O-CH_2-CH_2-CH_3$$ [1]

belonging to different class: hexanoic acid (other branched carboxylic acid isomers are possible)

$$CH_3-CH_2-CH_2-CH_2-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-OH$$ [1]

7 **(a)** A: 1-chlorobutane; it is a primary compound

B: 2-chloro-2-methylpropane; it is a tertiary compound

1 mark for correct name for A.

1 mark for correct name for B.

1 mark for primary for A **and** tertiary for B. [3]

(b) 1-chlorobutane will have four signals as there are four different proton chemical environments.

2-chloro-2-methylpropane will only have one signal as the $-CH_3$ protons all have the same chemical environment. [1]

(c) [2]

8 (a) (i) ethyl methanoate and methyl ethanoate are both esters [1]

(ii) the three compounds are structural isomers [1]

(iii) propanoic acid

[1]

ethyl methanoate

[1]

methyl ethanoate

[1]

(b)

Compound	Number of signals	Chemical shift range / ppm	Integrated area	Splitting pattern
propanoic acid	3	0.9–1.0	3	triplet
		2.0–2.5	2	quartet
		9.0–13.0	1	singlet
methyl ethanoate	2	3.7–4.8	3	singlet
		2.0–2.5	3	singlet

(1 mark for each) [5]

9 D

10 D

11 D

12 A

13 C

14 B

15 D

16 A

17 B

18 C

19 (a) $\frac{m}{z} = 60$ corresponds to the molecular ion, $C_3H_8O^+$ [1]

(b) $\frac{m}{z} = 31$ corresponds to the fragment ion, CH_3O^+ (CH_2OH^+) [1]

(c) A has fragment peaks corresponding to CH_3CH_2+ at $\frac{m}{z} = 29$ and CH_2OH+ at $\frac{m}{z} = 31$ (loss of CH_2CH_3). The structure that can give these fragments is

$$\overset{29}{CH_3} - CH_2 \mid \overset{31}{CH_2} - OH$$

[1]

B has fragment peaks corresponding to at $\frac{m}{z} = 45$ that corresponds to loss of $-CH_3$. There are no peaks at $\frac{m}{z} = 29$, corresponding to a $CH_3CH_2^+$, or at $\frac{m}{z} = 31$, corresponding to a loss of CH_3CH_2. The structure that can give these fragments is

$$\overset{15}{CH_3} \mid \overset{45}{\underset{H}{\overset{OH}{C}}} - CH_3$$
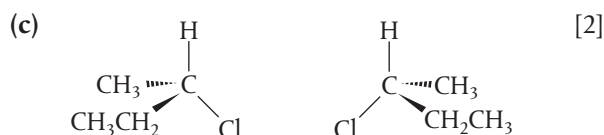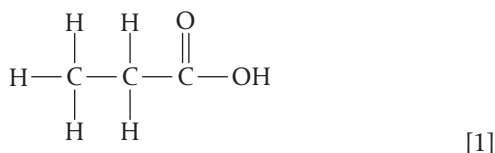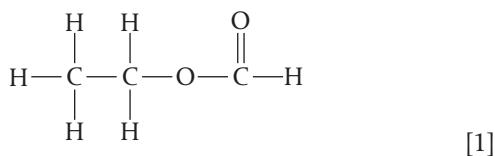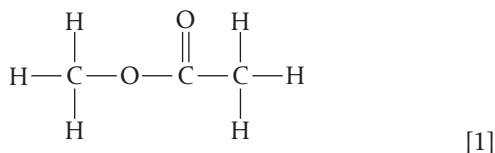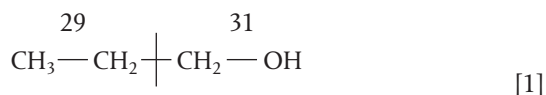
[1]
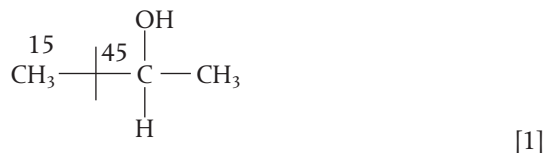
20 When IR radiation is absorbed by CO_2 this excites molecular vibrations and results in a change in the molecular dipole. [1]

The C=O bond lengths change (symmetric stretch). [1]

The OCO bond angle changes (symmetric bend). [1]

21 (a) B [1]

A is a symmetrical compound and would only have one signal in its spectrum. C has four different chemical environments and would have

four signals in its spectrum. B has three different chemical environments so would have three signals in its spectrum and the integrated areas of these signals would have the 1:2:3 ratio observed. [1]

(b) The signal at 2.5 ppm is due to hydrogen atoms adjacent to a carbonyl group ($R-CO-CH_2$). [1]

This would also occur for compound A, where the CH_3 hydrogens are adjacent to a C=O group. [1]

(c) (i) CH_3-CH_2-CHO would have an absorption at $1700-1750$ cm^{-1} due to the C=O bond. [1]

(ii) The infrared spectrum of compound C would have absorptions at $1620-1680$ cm^{-1} due to the C=C bond and at $3200-3600$ cm^{-1} due to the O-H bond. [1]

(d) The mass spectrum of compound X will show peaks at $\frac{m}{z}$ values of:

two from:

58, due to the molecular ion $CH_3CH_2CHO^+$

29, which could be due to the fragments CHO^+ or $CH_3CH_2^+$

15 due to the fragment CH_3^+ [2]

22 (a) To be IR active the absorption of IR energy by the bond must involve a change in the bond dipole. As H−Br is a polar bond the absorption of IR radiation by the bond stretch will result in a longer bond and a change in the bond dipole − so it is IR active. As Br−Br is non-polar there will be no dipole change if it absorbs IR radiation and stretches the bond − so it is IR inactive. [1]

(b) (i) I is a strong, very broad absorption at 3000 cm^{-1}. The bond responsible is O−H ($2500-3000$ cm^{-1} for acids). [1]

II is a strong absorption at 2750 cm^{-1}. The bond responsible is C−H ($2850-3090$ cm^{-1}). Although this absorption is outside the range in the data booklet it is most likely to be responsible. [1]

III is a strong absorption at 1700 cm^{-1}. The bond responsible is C=O ($1700-1750$ cm^{-1}). [1]

(ii) The peak at $\frac{m}{z}$ = 102 is due to the molecular ion $C_5H_{10}O_2^+$. [1]

The peak at $\frac{m}{z}$ = 57 is due to the fragment ion $C_4H_9^+$. [1]

The peak at $\frac{m}{z}$ = 45 is due to the fragment ion COOH$^+$. [1]

(iii) The signal in the ^{1}H NMR spectrum at 11.5 ppm is due to the proton in the acid group −COO**H**. (Acid protons occur in the range 9.0−13.0 ppm.) [1]

(iv) Using a ruler to measure the heights of the integrated signals it is found that the signal at 1.2 ppm has an integrated area of 9 times the integrated area of the signal at 11.5 ppm. This tells us that 9 protons share the same chemical environment. This is consistent with a −C(CH$_3$)$_3$ group. [1]

(v) From **(iii)** and **(iv)** we have deduced that X contains a −C(CH$_3$)$_3$ group and an acid functional group −COOH. The structure must be:

[1]
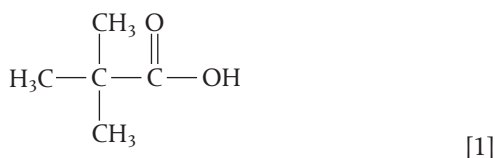
(vi) CH$_3$COOCH$_2$CH$_2$CH$_3$ has four different proton chemical environments so it will have four signals with integration 3 : 2 : 2 : 3. [1]

Because it is an ester it will not have a signal due to an acid proton in the 9.0−13.0 ppm region. [1]

23 (a) A is a strong, very broad absorption at 2900 cm^{-1}. The bond responsible is O−H (2500−3000 cm^{-1} for acids).

B is a strong absorption at 1700 cm^{-1}. The bond responsible is C=O (1700−1750cm^{-1}).

C is a strong absorption at 1200 cm^{-1}. The bond responsible is C−O (1050−1410 cm^{-1}).

All three correctly assigned = 2 marks

Any two correctly assigned = 1 mark [2]

(b) The peak at m/z = 74 is due to the molecular ion $C_3H_6O_2^+$. [1]

The peak at $\frac{m}{z}$ = 45 is due to the fragment ion COOH$^+$. [1]

The peak at $\frac{m}{z}$ = 29 is due to the fragment ion $C_2H_5^+$. [1]

(c) The signal in the 1H NMR spectrum at 11.73 ppm is due to the proton in the acid group −COO**H**. (Acid protons occur in the range 9.0−13.0 ppm.) [1]

(d) IR peaks at 2900 cm^{-1}, 1700 cm^{-1} and 1200 cm^{-1} along with a mass spectrometer peak at $\frac{m}{z}$ = 45 and a 1H NMR signal at 11.73 ppm are all consistent with an acid group (−COOH) being present.

A mass spectrometer peak at $\frac{m}{z}$ = 29 along with ^{1}H NMR signals at 1.2 ppm (3H triplet) and 2.4 ppm (2H quartet) are consistent with CH$_3$−CH$_2$− being present.

The structure is:

[1]
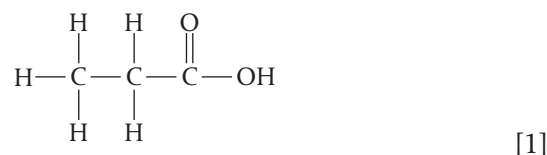
24 (a) Two from:

The structure provided contains an O−H bond. The IR spectrum is not of this structure as a strong, very broad peak would be observed in the 3200−3600 cm^{-1} region if an O−H bond of an alcohol was present.

The structure provided is an alkene and contains a C=C bond. The IR spectrum is not of this structure as a strong peak would be observed in the 1620−1680 cm^{-1} region if a C=C bond was present.

The IR spectrum of X shows a strong absorption at 1750 cm^{-1}, which indicates that a C=O bond is present. The structure provided does not contain a C=O bond so it is not consistent with the IR spectrum. [2]

(b) The molecular formula of C_3H_6O is consistent with either a ketone or an aldehyde. Possible structures are:
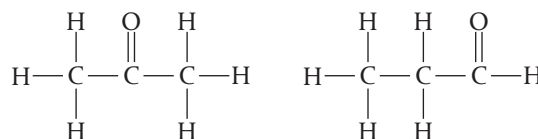
Structure I is not the correct structure as it is a symmetrical molecule and only has one proton chemical environment. The ^{1}H NMR spectrum of I would only contain one signal.

Structure II is the correct structure.   [1]

This would give a ^{1}H NMR spectrum with three signals as it has three different proton chemical environments. CH_3-, $-CH_2-$ and $-CHO$ and the integrated areas of these signals would be $3:2:1$.   [1]

25 (a) The structures of the four alcohols are given below:

OH
|
H — C — CH$_2$ — CH$_2$ — CH$_3$
|
H

   butan-1-ol

OH   H
| |
H — C — C — CH$_3$
| |
H   CH$_3$

2-methylpropan-1-ol

OH
|
CH$_3$ — C — CH$_2$ — CH$_3$
|
H

   butan-2-ol

OH
|
CH$_3$ — C — CH$_3$
|
CH$_3$

2-methylpropan-2-ol
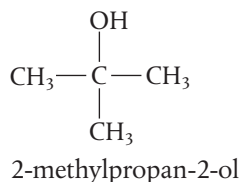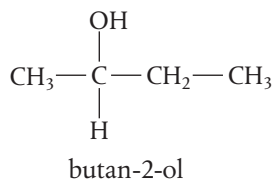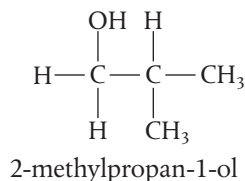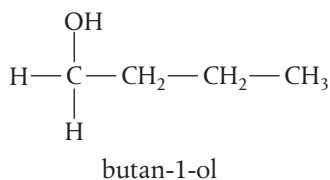
(i) Spectrum 1 has two signals in the ^{1}H NMR spectrum so the alcohol responsible must contain two different proton chemical environments. From the structures above we can see that the only alcohol with two chemical environments is 2-methylpropan-2-ol.

(Butan-1-ol and butan-2-ol have five different proton chemical environments and 2-methylpropan-1-ol has four chemical environments.)   [1]

The signal at 1.3 ppm with an integration trace of nine units is due to the nine protons on the three chemically equivalent $-CH_3$ groups.   [1]

The signal at 2.0 ppm with an integration trace of one unit is due to the alcohol proton, $-OH$.   [1]

(ii) Spectrum 2 has four signals in the ^{1}H NMR spectrum so the alcohol responsible must contain four different proton chemical environments. From the structures above we can see that the only alcohol with four chemical environments is 2-methylpropan-1-ol.   [1]

The signal at 0.9 ppm with an integration trace of six units is due to the six protons on the two chemically equivalent $-CH_3$ groups.   [1]

The signal at 3.4 ppm with an integration trace of two units is due to the two protons on the carbon attached to the hydroxyl group $-CH_2OH$.   [1]

(b) (i) The peak at $\frac{m}{z}$ = 74 is due to the molecular ion $C_4H_{10}O^+$.   [1]

The peak at $\frac{m}{z}$ = 59 is due to the fragment ion $C_3H_7O^+$ (loss of CH_3).   [1]

The peak at $\frac{m}{z}$ = 45 is due to the fragment ion $C_2H_5O^+$ (loss of CH_2CH_3).   [1]

From the structures we can see that the loss of CH_3 and CH_2CH_3 to give $C_3H_7O^+$ and $C_2H_5O^+$ can occur for two of the alcohols; butan-1-ol and butan-2-ol.   [1]

(ii) The peak at $\frac{m}{z}$ = 31 is due to the fragment ion CH_3O^+ (loss of $CH_2CH_2CH_3$).   [1]

From the structures we can see that the loss of $CH_2CH_2CH_3$ can only occur for butan-1-ol.   [1]

(c) The IR spectra for the four alcohols will be similar as they contain the same bonds; $C-H$, $C-C$, $C-O$ and $O-H$ [1]

and will absorb IR energy of the same frequencies.   [1]

26 With the molecular formula $C_4H_8O_2$ the compound could be a carboxylic acid or an ester. The ^{1}H NMR spectrum does not have a signal in the region expected for an acid proton, 9.0–13.0 ppm, so the compound is more likely to be an ester.   [1]

The signal at 3.7 ppm is a singlet with an integrated area of three units, which indicates a methyl group $-CH_3$. Because it is a singlet the $n+1$ rule tells us there are no protons on the neighbouring atoms. Because it is at a higher chemical shift this indicates it is adjacent to the oxygen atom of the carboxy group, $CH_3-O-CO-$. (From the data booklet $R-CO-OCH_2-$ occurs at 3.7–4.8 ppm.)   [1]

The signal at 2.3 ppm is a quartet with an integrated area of two units, which indicates a methylene group $-CH_2-$. Because it is a quartet the $n + 1$ rule tells us there are three protons on the neighbouring atoms: CH_3-CH_2-. Because it is at a moderately high chemical shift this indicates it is adjacent to the carbon atom of the carboxy group, $-CH_2-CO-O-$. (From the data booklet $RO-CO-CH_2-$ occurs at 2.0–2.5 ppm.) [1]

The signal at 1.0 ppm is a triplet with an integrated area of three units, which indicates a methyl group $-CH_3$. Because it is a triplet the $n + 1$ rule tells us there are two protons on the neighbouring atoms: CH_3-CH_2-. Because it is at a low chemical shift this indicates it is reasonably distant from the carboxy group, $CH_3-CH_2-CO-O-$. (From the data booklet $-CH_3$ occurs at 0.9–1.0 ppm.)

The structure is:

[1]
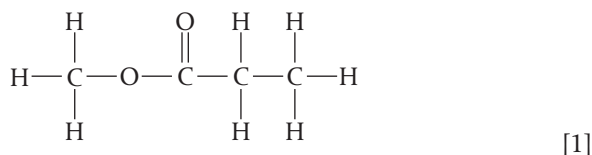
27 (a) (i) The peak with the highest $\frac{m}{z}$ occurs at 88. This is likely to be caused by the molecular ion so the relative molecular mass is 88. [1]

The empirical formula provided is C_2H_4O which has a relative formula mass of 44. As the molecular mass obtained from the mass spectrum is twice that of the formula mass the molecular formula is $2 \times C_2H_4O$, which is $C_4H_8O_2$. The molecular ion is therefore $C_4H_8O_2^+$. [1]

(ii) The peak at $\frac{m}{z} = 29$ could be due to fragment ions $C_2H_5^+$ or CHO^+ (only one needed). [1]

(iii) 29 + 59 = 88. A peak is shown at $\frac{m}{z} = 29$ but not at $\frac{m}{z} = 59$. If a fragment is not charged it cannot be deflected and observed in a mass spectrum. Therefore, neither fragment $C_2H_3O_2^+$ nor $C_3H_7O^+$ are formed. [1]

(b) (i) A is a strong absorption at 1750 cm^{-1}. The bond responsible is C=O (1700–1750 cm^{-1}).

B is a strong absorption at 1250 cm^{-1}. The bond responsible is C−O (1050–1410 cm^{-1}). [1]

(ii) The IR spectrum shows that both C=O and C−O bonds are present, which is consistent with either an ester or a carboxylic acid. The strong broad peak observed for acid −OH

bonds at 2500–3000 cm^{-1} is not observed, so X must contain an **ester** functional group. [1]

(c) (i) a possible structure is

[1]
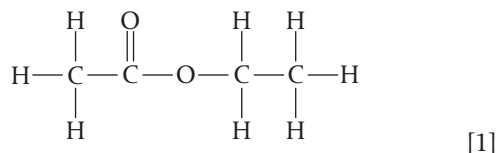
Reasoning:

From the IR spectrum it was determined that the compound was an ester.

From the ^{1}H NMR spectrum:

- the signal at 2.0 ppm is a singlet with an integrated area of three units which indicates a methyl group $-CH_3$. Because it is a singlet the $n + 1$ rule tells us there are no protons on adjacent atoms. The moderately high chemical shift indicates it is adjacent to the carbon of the carboxy group, $CH_3-CO-O-$. (From the data booklet, $RO-COCH_2-$ occurs at 2.0–2.5 ppm.)

- the signal at 4.1 ppm is a quartet with an integrated area of two units which indicates a methylene group $-CH_2-$. Because it is a quartet the $n + 1$ rule tells us there are three protons on adjacent atoms; $-CH_2-CH_3$. The high chemical shift indicates it is adjacent to the oxygen of the carboxy group, $CH_3-CH_2-O-CO-$. (From the data booklet, $R-CO-CH_2-$ occurs at 3.7–4.8 ppm.)

- because the signal at 4.1 ppm is a quartet we can conclude that third signal must be generated by three protons in the same environment. The $-CH_2-$ generating the quartet must be adjacent to a methyl group, $-CH_3$.

(ii)

Signal	Chemical shift / ppm	Relative area	Splitting pattern
first	2.0	3	singlet
second	4.1	2	quartet
third	0.9–1.0	3	triplet

The third signal is due to the methyl group at the end of the carbon chain, $CH_3-CO-O-CH_2-CH_3$.

The relative area will be 3. [1]

The $n + 1$ rule tells us this signal will be a triplet due to the two protons on the neighbouring carbon. [1]

From the data booklet we see that $-CH_3$ occurs at 0.9–1.0 ppm. [1]

(iii) The signal at 4.1 ppm is due to the methylene protons in the carbon chain, $CH_3-CO-O-CH_2-CH_3$. [1]

It is a quartet as there are three protons on the neighbouring atoms. [1]

R1.1 Measuring enthalpy changes

Exercises

Q1 Heat is transferred from the object with a high temperature T_H to the object at temperature T_C.

The two objects will have the same final temperature. The final temperature is closer to T_H than T_C.

Q2 $\Delta T = 310 - 300 = 10$ K

$\Delta T = (310 - 273) - (300 - 273) = 10\,°C$

Q3 B

Q4 B

Q5 B

Q6 C

Q7 A

Q8 B

Q9 A

Q10 A

Q11 D

Q12 C

Q13 A

Q14 A

Q15 C

Q16 C

Q17 **(a)** B

(b) C

Q18 B

Q19 $q = mc\Delta T$, so $\Delta T = \dfrac{q}{mc}$

$\dfrac{q}{mc} = \dfrac{100}{100 \times 0.138} = 7.2\,°C$

$T = 25.0 + 7.2 = 32.2\,°C$

Q20 **(a)** $\Delta T = 36.50 - 25.85 = 10.65\,°C$ (or K)

$q = mc\Delta T$

$q = [m(H_2O) \times c(H_2O) \times \Delta T(H_2O)] + [m(Cu) \times c(Cu) \times \Delta T(Cu)]$

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

$= 8903.4 + 492.0$ J

$= 9395.4$ J

$n(C_6H_{12}O_6) = \dfrac{1.10\,g}{180.18\,g\,mol^{-1}}$

$= 6.11 \times 10^{-3}$ mol

$\Delta H_c = \dfrac{9395.4\,J}{6.11 \times 10^{-3}\,mol}$

$= -1539 \times 10^3\,J\,mol^{-1}$

$= -1539\,kJ\,mol^{-1}$

(b)
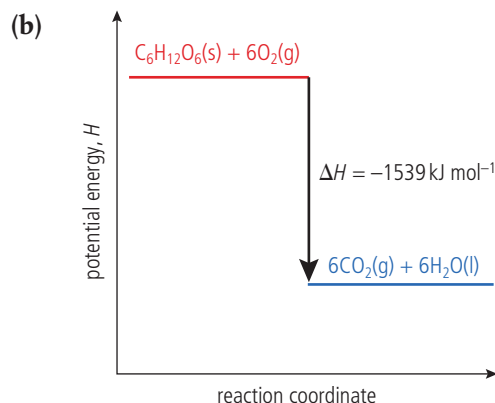
Q21 $q = mc\Delta T$

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

$= 4075.5$ J

$n(P) = \dfrac{0.0500\,g}{30.97\,g\,mol^{-1}}$

$= 1.614 \times 10^{-3}$ mol

$\Delta H_c = \dfrac{4075.5\,J}{1.614 \times 10^{-3}\,mol}$

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

$\approx 2500\,kJ\,mol^{-1}$

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.

Q22 **(a)** m(propan-1-ol) = 45.65 − 45.05 = 0.60 (g)

n(propan-1-ol) = 0.60 / 60.11 = 0.00998 mol

(b) ΔT = 41.5 − 23.7 = 17.8 (K)

$q = mc\Delta T$

= 210 × 4.18 × 17.8

= 15.62 kJ

(c) enthalpy change (kJ mol^{-1}) = $\dfrac{15.62 \text{ kJ}}{0.00998 \text{ mol}}$

= −1565 kJ mol^{-1}

(d) Not all heat produced transferred to water as heat is lost to surroundings. Incomplete combustion, with carbon and carbon monoxide being formed instead of carbon dioxide also leads to a less exothermic reaction.

Challenge yourself

1 When heat energy is added to water some of the energy is needed to break hydrogen bonds and so less energy is available to increase the kinetic energy. The presence of hydrogen bonds reduces the temperature increase and so increases the specific heat capacity.

2 $Q = m \times c \times \Delta T$

temperature change (water and aluminium)
= 77.5 − 24.5 = 53.0 ± 0.2 K

energy lost by brass = energy gained by water and calorimeter

energy gained by water and calorimeter
= (200.00 × 4.18 × 53.0) + (80.00 × 0.900 × 53.0) J

= 44 308 + 3 816 = 48 124 J

energy lost by brass = 48 124 J

212.10 × 0.400 × (T_{Bunsen} − 77.5) = 48 124 J

$T_{\text{Bunsen}} - 77.5 = \dfrac{48\ 124}{212.10 \times 0.400}$

= 567.2 °C

temperature of brass in Bunsen flame = 567.2 + 77.5 °C

= 644.7 » 645 °C

Practice questions

1 A

2 D

3 B

4 C

5 D

6 **(a)** **(i)** m(methanol) = 80.557 − 80.034 = 0.523 (g) [1]

n(methanol) = $\dfrac{0.523 \text{ g}}{32.05 \text{ g mol}^{-1}}$ = 0.0163 (mol) [1]

Award [2] for correct final answer.

(ii) ΔT = 26.4 − 21.5 = 4.9 (K) [1]

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

= 410 J *or* 0.41 kJ [1]

Award [3] for correct final answer.

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

= −25 103 J mol^{-1} *or* −25 kJ mol^{-1} [1]

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

(b) 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'*] [2]

7 **(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_{final} = 73.0 (°C) [1]

Allow in the range 72 to 74 (°C).

ΔT = 73.0 − 24.8 = 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) $-201\,\text{kJ mol}^{-1}$ [1]

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

8 (a) $\Delta T = 30.3 - 24.5 = 5.8\,\text{K}$ [1]

$q = m(\text{H}_2\text{O}) \times c(\text{H}_2\text{O}) \times \Delta T(\text{H}_2\text{O})$

$= 100.0\,\text{g} \times 4.18\,\text{J g}^{-1}\,\text{K}^{-1} \times 5.8\,\text{K}$

$= 2424.4\,\text{J}$ [1]

KOH is the limiting reagent.

$n(\text{KOH}) = \dfrac{50 \times 0.950}{1000} = 0.0475\,\text{mol}$ [1]

$\Delta H = -\dfrac{2424.4}{0.0475} = -68.64 \times 10^3\,\text{J mol}^{-1}$

$= -51.04\,\text{kJ mol}^{-1}$ [1]

(b) Assumptions: no heat loss, $c(\text{solution}) = c(\text{water})$, $m(\text{solution}) = m(\text{H}_2\text{O})$, density$(\text{H}_2\text{O}) = 1.00$ [1]

9 $\Delta H_{\text{reaction}} = -\Delta H_{\text{water}}$

$q = mc\Delta T$

$\Delta H_{\text{water}} = 100.00\,\text{g} \times 4.18\,\text{J g}^{-1}\,\text{K}^{-1} \times (21.79 - 25.55)\,\text{K}$
$= -1571.68\,\text{J}$ [1]

$n(\text{NH}_4\text{Cl}) = \dfrac{5.35\,\text{g}}{53.50\,\text{g mol}^{-1}} = 0.100\,\text{mol}$ [1]

$\Delta H = \dfrac{-\Delta H_{\text{water}}}{n(\text{NH}_4\text{Cl})} = \dfrac{-(-1571.68\,\text{J})}{0.100\,\text{mol}} = +15\,716.8\,\text{J mol}^{-1}$

$= +15.7\,\text{kJ mol}^{-1}$ [1]

R1.2 Energy cycles in reactions

Exercises

Q1 B

Q2 A

Q3 $1 \times \text{C–C} + 6 \times \text{C–H}$

Q4 B

Q5 B

Q6 B

Q7 D

Q8 $-482\,\text{kJ mol}^{-1}$

$\text{C}_2\text{H}_5\text{OH(l)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 3\text{H}_2\text{O(g)}$
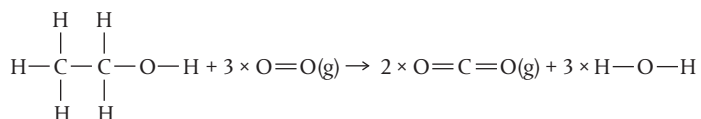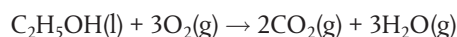
Bonds broken	$\Delta H^{\ominus}$ / kJ mol^{-1}	Bonds formed	$\Delta H^{\ominus}$ / kJ mol^{-1}
C–C	+346	4 C=O	4 × (−804)
3 × O=O	3 × (+498)	6 H–O	6 × (−463)
O–H	+463		
C–O	+358		
5 × C–H	5 × (+414)		
Total	+4731		−5994

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

The calculated value is less exothermic than the enthalpy of combustion in Table 14 of the data booklet ($-1367\,\text{kJ mol}^{-1}$) because the bond enthalpy calculation assumes all species are in the gaseous state: water and ethanol are liquids.

Q10 B

Q11 B

Q12 $\Delta H^{\ominus} = -394 - (-283)\,\text{kJ} = -111\,\text{kJ mol}^{-1}$

Q13 $\Delta H^{\ominus} = -180.5 + (+66.4) = -114.1\,\text{kJ mol}^{-1}$

Q14 $\Delta H^{\ominus} = 2 \times (-33.2) + (+9.16) = -57.24\,\text{kJ mol}^{-1}$

Q15 C

Q16 B

Q17 D

Q18

	H$_2$(g)	CH$_4$(g)
$\Delta H_c^{\ominus}$ / kJ mol^{-1}	−286	−891
M / g mol^{-1}	2.02	16.05
Heat / kJ g^{-1}	142	55.5

Q19 (a) $\text{C}_3\text{H}_8\text{(g)} + 5\text{O}_2\text{(g)} \rightarrow 3\text{CO}_2\text{(g)} + 4\text{H}_2\text{O(l)}$

$\text{C}_4\text{H}_{10}\text{(g)} + 6\frac{1}{2}\text{O}_2\text{(g)} \rightarrow 4\text{CO}_2\text{(g)} + 5\text{H}_2\text{O(l)}$
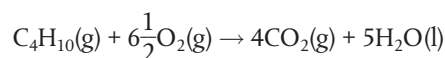
(b) 1 mol of $C_3H_8(g)$ releases 2219 kJ mol^{-1}

$\dfrac{\text{heat}}{\text{mass}} = \dfrac{2219}{44.11} = 50.3$ kJ g^{-1}

1 mol of $C_4H_{10}(g)$ releases 2878 kJ mol^{-1}

$\dfrac{\text{heat}}{\text{mass}} = \dfrac{2878}{58.14} = 49.5$ kJ g^{-1}

$C_3H_8(g)$ releases the most energy per gram.

Q20 (a) $3C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow$

$CH_3COCH_3(l)$ $\Delta H_f^{\ominus} = -248$ kJ mol^{-1}

(b) Under standard conditions of 298 K (25 °C) and 1.00×10^5 Pa

Q21 C

Q22 B

Q23 D

Q24 The value for the enthalpy of combustion of benzene is -3268 kJ mol^{-1}.

(a) $6C(\text{graphite}) + 3H_2(g) \rightarrow C_6H_6(l)$

(b) $\Delta H_{\text{reaction}}^{\ominus} = \Sigma\Delta H_c^{\ominus}(\text{reactants}) - \Sigma\Delta H_c^{\ominus}(\text{products})$

$= [6 \times (-394) + 3 \times (-286)] - (-3268)$

$= +46$ kJ mol^{-1}

(c) $\Delta H_f^{\ominus}(C_6H_6(l))$ in Section 12 of the data booklet is $+49$ kJ mol^{-1}. The values are in approximate agreement. Experimental error accounts for the disparity between the values.

Q25 $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

$\Delta H_{\text{reaction}}^{\ominus} = \Sigma\Delta H_c^{\ominus}(\text{reactants}) - \Sigma\Delta H_c^{\ominus}(\text{products})$

$= [-1411 + -286] - (-1561)$

$= -136$ kJ mol^{-1}

Q26 $+330$ kJ mol^{-1}

Q27 $2MgO(s) + C(s) \rightarrow CO_2(g) + 2Mg(s)$

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

Such an endothermic reaction is unlikely to be spontaneous over a wide range of temperatures. Carbon is not a suitable reducing agent.

(As discussed in Reactivity 1.4, there is an increase in entropy of the system as $CO_2(g)$ is produced so the reaction could become feasible at very high temperatures.)

Q28 A

Q29 C

Q30 D

Q31 C

Q32 B

Q33 A

Q34 (a) $K_2O(s) \rightarrow 2K^+(g) + O^{2-}(g)$

(b) $W = \frac{1}{2}E(O=O)$

$X = 2\Delta H_i^{\ominus}(K)$

$Y = \Delta H_{e1}^{\ominus}(O) + \Delta H_{e2}^{\ominus}(O)$; the sum of the first and second electron affinities

$Z = \Delta H_f^{\ominus}(K_2O)$

(c) $\Delta H_{\text{latt}}^{\ominus}(K_2O) = +361 + 2(89.2) + \frac{1}{2}(498) +$

$2(419) + (-141) + 753 = +2238.4$ kJ mol^{-1}

Q35 (a) They decrease down Group 17 as the ionic radius of the halide ion increases.

(b)

Halide	$\Delta H_{\text{latt}}^{\ominus}$/ kJ mol^{-1}		Difference between ionic model and experimental values/ kJ mol^{-1}	% Difference between ionic model and experimental values
	Ionic model	Experimental		
NaF	+912	+930	−18	−1.94
NaCl	+770	+790	−20	−2.53
NaBr	+735	+754	−19	−2.52
NaI	+687	+705	−18	−−2.55

The agreement between the model generally decreases down Group 17. Halides with larger ionic radius have more covalent character as they are more easily polarized.

Q36 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 smaller ionic radius of the oxide ion as it has only two energy levels occupied compared to chlorine with three.

Q37 (a) M_C^+

(b) Theoretical values are based on an ionic model. It does not take into account any additional covalent contributions to the bonding.

(c)

	% Agreement between ionic model and experimental values
M_ABr	0.94
M_BBr	0.46
M_CBr	0.50

(d) The largest difference in values occurs for M_ABr, indicating this has the most covalent character. M_A has the lowest electronegativity.

Challenge yourself

1 (a) The bond enthalpies generally decrease down the halogen group but the bond enthalpy in F_2 is weaker than Cl_2 and Br_2. This is due to repulsion between the non-bonding pairs in the two fluorine atoms.

(b)

Average of $E(H-H)$ and $E(F-F)$ / kJ mol^{-1}	$E(H-F)$ / kJ mol^{-1}	$E(H-F) - (\frac{E(H-H) + E(F-F)}{2})$ / kJ mol^{-1}
$\frac{436 + 159}{2}$ = +297.5	+567	+269.5

The difference shows that the H−F bond is very polar and F is very electronegative.

2 The difference in the values is largely due to the assumption that H_2O is gaseous in the bond enthalpy calculation.

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

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
$\Delta H^{\ominus} = -808$ kJ mol^{-1}
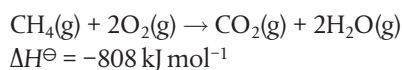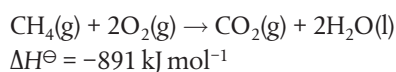
The difference is due to formation of H_2O in different states:

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

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

There are (on average) 2 hydrogen bonds between each water molecule so the strength of a hydrogen bond is approximately 20 kJ mol^{-1}.

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

3 (a) $E(O-O) = +144$ kJ mol^{-1}, $E(O=O) = +498$ kJ mol^{-1}. The average value = 321 kJ mol^{-1}.

This suggests that the oxygen−oxygen bond in ozone is intermediate between a single bond and double bond, as discussed in Structure 2.2.

(b) The O=O bond in O_2 is stronger than the bond in O_3. Less energy / longer wavelength radiation is required to dissociate O_3 than O_2.

4 The compounds must be heated for reaction to occur. It is difficult to distinguish any energy changes due to the reaction from the heat input.

5 Within the sheets of graphite, the bond order is 1.5, 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. The total bonding is slightly stronger in graphite.

Practice questions

1 C

2 B

3 C

4 D

5 B

6 A

7 bonds broken: $4 \times N-H$, $1 \times N-N$, $1 \times O=O$ = +2220 (kJ mol^{-1})   [1]

bonds formed: $1 \times N\equiv N$, $4 \times O-H$ = −2797 (kJ mol^{-1})   [1]

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

Award [3] for correct final answer.

8 A

9 A

10 (a) bonds broken are C=C and H−H

energy required = 614 + 436 = 1050

bonds formed are C−C and 2(C−H)

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

overall: ΔH = 1050 − 1174 = −124 kJ mol^{-1} [1]

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

bonds broken are C=C + H−H + 4(C−H)

energy required = 614 + 436 + 4(414) = 2706

bonds formed are C−C + 6(C−H)

energy released = 346 + 6(414) = 2830 [1]

overall: ΔH = 2706 − 2830 = −124 kJ mol^{-1} [1]

(b) ΔH = −1411 + (−286) − (−1561) = −136 kJ mol^{-1} [1]

(c) The actual values for bond energies 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*. [1]

11 (a) I is atomization/sublimation (of Mg) / $\Delta H_{atomization}^{\ominus}$(Mg) / $\Delta H_{sublimation}^{\ominus}$(Mg) [1]

V is enthalpy change of formation of (MgCl$_2$) / $\Delta H_{formation}^{\ominus}$(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) = −698 [1]

$\Delta H_{lat}^{\ominus}$(MgCl$_2$) = 642 + 148 + 242 + 2189 + −698 = (+)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.

12 (a) $\frac{1}{2}O_2(g) \rightarrow O^{2-}(g)$

«$\Delta H_{atomization}$(O) + 1st EA + 2nd EA = 249 kJ mol^{-1} − 141 kJ mol^{-1} + 753 kJ mol^{-1} =» «+»861 «kJ mol^{-1}» [1]

Na(s) → Na$^+$(g)

«$\Delta H_{atomization}$(Na) + 1st IE = 107 kJ mol^{-1} + 496 kJ mol^{-1} =» «+»603 «kJ mol^{-1}» [1]

(b) lattice enthalpy = 861 «kJ mol^{-1}» + 2 × 603 «kJ mol^{-1}» −(−414 «kJ mol^{-1}») [1]

«= +» 2481 «kJ mol^{-1}» [1]

Note: Award [2] for correct final answer.

If given values are used:

M1: lattice enthalpy = 850 «kJ mol^{-1}» +2 × 600 «kJ mol^{-1}» −(−414 «kJ mol^{-1}»)

M2: «= +» 2464 «kJ mol^{-1}»

(c) K$^+$ ion is larger than Na$^+$

or

smaller attractive force because of greater distance between ion «centres» [1]

(d) $\sum\Delta H_f$(products) = 2 × (−1130.7) = −2261.4 «kJ» [1]

$\sum\Delta H_f$(reactants) = 2 × (−510.9) + 2 × (−394) = −1809.8 «kJ» [1]

ΔH = «$\sum\Delta H_f$(products) − $\sum\Delta H_f$(reactants) = −2261.4 − (−1809.8) =» −451.6 «kJ» [1]

Note: Award [3] for correct final answer.

Award (2 max) for "+ 451.6 «kJ»

(e)

only valid for covalent bonds

or

only valid in gaseous state [1]

R1.3 Energy from fuels

Exercises

Q1 C

Q2 A

Q3 C

Q4 8.78 g

Q5 The compound contains C and H and possibly O

$n(CO_2) = \frac{0.88}{44.01} = 0.0200 = n(C)$

0.60 g contains 0.0200 × 12.01 = 0.24 g of C

$n(H_2O) = \frac{0.36}{18.02} = 0.0200$; $n(H) = 0.0400$

0.60 g contains 0.0200 × 2 × 1.01 = 0.0404 g of H

Mass of O = 0.60 − (0.24 + 0.04) = 0.32 g; $n(O)$

$= \frac{0.32}{16.00} = 0.02$

Empirical formula = CH$_2$O

Q6 $C_xH_y + (x + \frac{y}{4})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$

Q7 $C_xH_y + (\frac{x}{2} + \frac{y}{4})O_2(g) \rightarrow xCO(g) + \frac{y}{2}H_2O(l)$

Q8 $C_6H_{14} + 8O_2(g) \rightarrow 3CO(g) + 3CO_2(g) + 7H_2O(l)$

Q9 **(a)** $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

(b) 1 mol of C_8H_{18} reacts with $12\frac{1}{2}$ mol of O_2
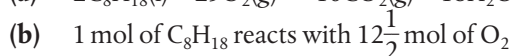
114.26 g of C_8H_{18} reacts with 400 g of O_2

1.00 g of C_8H_{18} reacts with 3.50 g of O_2

(c) mass of air $= \frac{100}{20} \times 3.50$ g $= 17.5$ g

(d) CO affects oxygen uptake in the blood. It is absorbed by the lungs and binds to haemoglobin in red blood cells more effectively than oxygen and is bound permanently. This prevents oxygen from being transported around the body.

(e) catalytic converters

Q10 **(a)** Carbon has a higher enthalpy of combustion than hydrogen (per mol) but the atomic mass of hydrogen is much less than the atomic mass of carbon. As the percentage carbon content decreases and the percentage hydrogen content increases, the specific energy increases.

(b) Carbon dioxide is a greenhouse gas and causes global warming.

(c)

Fuel	Specific energy / kJ g^{-1}	Carbon content by mass / %	Carbon dioxide produced / g
Coal	32	94	108
Oil	42	83	72
Natural gas	55	75	50
Wood	15	70	171
Hydrogen	142	0	0

Hydrogen is the best fuel and wood is the worst fuel on this basis. But, the carbon dioxide in the wood was taken out of the atmosphere when the wood was growing and more wood can be grown. Taking this into account, coal is the worst fuel.

Q11 **(a)** Empirical formula: $C_{135}H_{96}O_9NS$ or $C_{136}H_{97}O_9NS$. (It typically also contains trace amounts of silicon, sodium, calcium, aluminium, nickel, copper, zinc, arsenic, lead and mercury.)

(b) Some elements burn to give acidic oxides that dissolve / react with water to give acid rain.

$S(s) + O_2(g) \rightarrow SO_2(g); 2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$H_2O(aq) + SO_2(g) \rightarrow H_2SO_3(aq);$

$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$

$2N(g) + O_2(g) \rightarrow 2NO(g);$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g);$

$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$
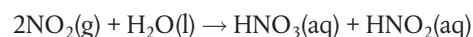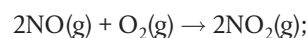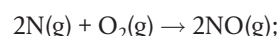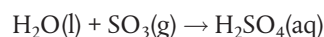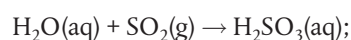
Q12 **(a)** $\frac{\text{useful output energy}}{\text{total input energy}} = \frac{\text{useful electrical energy}}{\text{total input heat energy}} = 0.38$

heat energy produced by combustion per

second $= \frac{5.00 \times 10^5 \text{ kJ s}^{-1}}{0.38}$

mass per second $= \frac{5.00 \times 10^5 \text{ kJ s}^{-1}}{0.38 \times 33.0 \text{ kJ g}^{-1}}$

$= 39\,872$ g s^{-1} » 39.9 kg s^{-1}

(b) We have the balanced equation:

$4CH(s) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$
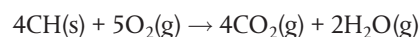
no. of moles of CO_2 = no. of moles of CH

no. of moles of CH burnt per second

$= \frac{39872}{12.01 + 1.01} = 3062$ mol

mass of CO_2 per second $= 3062 \times 44.01$
$= 134\,775$ g » 135 kg

Q13 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.

Q14 **(a)** High specific energy / energy density. As a liquid it is convenient to handle and deliver. Easy to vaporize, which assists combustion.

(b) It was formed by the partial decomposition of marine plants millions of years ago.

Q15 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.

Q16 **(a)** Fossil fuels and biomass are derived from the sun through photosynthesis.

(b) Advantages: renewable and has little environmental impact.

Disadvantages: photosynthesis is not very efficient, so relatively little of the available solar

energy is trapped. Land used to grow plants for biomass could be used to grow plants for food.

Q17 **(a)** $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(b) chlorophyll

(c) 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.

Q18 **(a)** methane

(b) particulates (soot), hydrocarbons, carbon monoxide

(c) Fossil fuels are being phased out due to carbon dioxide production and limited resources. Biomass is a renewable source.

Q19 **(a)** $H_2(g)$ is oxidized at the anode:
$2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

$O_2(g)$ is reduced at the cathode:
$4H^+(aq) + O_2(g) + 4e^- \rightarrow 2H_2O(l)$

(b) Less waste heat produced and more chemical energy converted to useful energy. They can use a renewable energy source to form the hydrogen, which is more efficient.

Challenge yourself

1 The compound contains C, H and N.

$n(CO_2) = \dfrac{0.456}{44.01} = 0.010361 = n(C)$

0.20 g contains 0.010361×12.01 g of C

$= 0.124439$ g of C

$n(H_2O) = \dfrac{0.248}{18.02} = 0.013762$

$n(H) = 2 \times 0.013762 = 0.027525$

0.20 g contains 0.027525×1.01 g of H

$= 0.0278$ g of H

mass of N $= 0.20 - 0.124439 - 0.0278 = 0.047761$ g

$n(N) = \dfrac{0.047761}{14.01} = 0.003409$

	C	**H**	**N**
Mol	0.010361	0.027525	0.003409
Ratio	3	8	1

Empirical formula $= C_3H_8N$

2 combination of nitrogen and oxygen at high temperatures: $N_2(g) + O_2(g) \rightarrow 2NO(g)$

acid rain and (photochemical) smog

3 **(a)** % mass of C in coal:

$\dfrac{12.01}{13.02} \times 100 = 92.24\%$

% mass of C in wood:

$\dfrac{5 \times 12.01}{5 \times 12.01 + 9 \times 1.01 + 4 \times 16.00} \times 100 = 45.10\%$

(b) Carbon footprint of coal:

mass of coal needed:
$\dfrac{1.33 \times 10^6 \text{kJ}}{31 \text{ kJ g}^{-1}} \times \dfrac{100}{65} = 66\,005 \text{ g} = 66.0 \text{ kg}$

mass of carbon dioxide produced:
$66.0 \text{ kg} \times \dfrac{92.24\%}{100} \times \dfrac{44.01}{12.01} = 223.1 \text{ kg}$

Carbon footprint of wood:

mass of wood needed:
$\dfrac{1.33 \times 10^6 \text{kJ}}{22 \text{ kJ g}^{-1}} \times \dfrac{100}{70} = 86\,364 \text{ g} = 86.4 \text{ kg}$

mass of carbon dioxide produced:
$86.4 \text{ kg} \times \dfrac{45.10\%}{100} \times \dfrac{44.01}{12.01} = 142.7 \text{ kg}$

(c) Carbon footprint for wood doesn't account for the carbon dioxide taken in while the wood was growing or that more wood can be grown relatively quickly, taking carbon dioxide out of the atmosphere,

4 **(a)** Distant from localized areas of pollution; data present an accurate measure of global levels of CO_2.

(b) The annual variation is due to CO_2 uptake by growing plants. Over a year, the uptake is highest in the northern hemisphere springtime. Considerably more of the northern hemisphere is land (for plants) compared with the southern hemisphere.

(c) Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

CO_2 dissolves in water: $CO_2 + H_2O \rightarrow H_2CO_3(aq)$

(d) Decreased level of photosynthesis: less CO_2 taken in by plants.

5 **(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's surface.

6 **(a)** $2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow xH_2 + yCO + zCO_2$

	$-\dfrac{1}{16}$			$+2$	$+4$	C
	$+1$	$+1$	0			H
	-2	-2	0	-2	-2	O
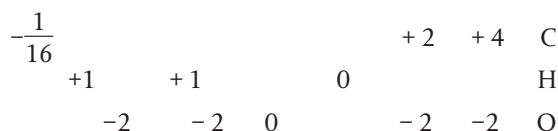
(b) C is oxidized

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 = -4

Total increase in oxidation number of C = $+88$

Balancing the change in oxidation numbers for C:
$+88 - 2 = 2y + 4z$

Balancing the C atoms: $y + z = 32$

Solving the equations: $2z = 86 - 64 = 22$

$z = 11$ and $y = 21$

$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow 42H_2 + 21CO + 11CO_2$

(e) $2H_2 + CO \rightarrow CH_3OH$

$42H_2 + 21CO \rightarrow 21CH_3OH$

2 molecules of wood produce 21 molecules of methanol

1 molecule of wood produces 10.5 molecules of methanol

7 The entropy decrease is smaller for the reaction which produces one mole of gaseous water, which leads to a larger efficiency.

Practice questions

1 **(a)** long wavelength / infrared / IR radiation from Earth's surface

(some of this radiation) is absorbed (by gas) [1]

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 [1]

Accept 're-transmits'

Do not accept 'reflects/bounces'

(b) no change in polarity/dipole (moment) when molecule vibrates; [1]

(c) two from:

CO: prevents haemoglobin from transporting oxygen

Particulate / Soot: respiratory problems, lung diseases, carcinogenic

Nitrogen oxides: photochemical smog / acid deposition/rain [2]

2 **(a)** two from:

wide availability

produce energy at appropriate rate

ease of transportation

current technology is based on fossil fuels

high energy density / specific energy [2]

(b) hydrogen [1]

3 **(a)** coal 92.2%, petrol 84.1% and natural gas 74.8% [3]

(b) two from:

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]

(c) two from:

hydrogen has a very high specific energy / energy density

it is clean burning, producing only H_2O when it is burned

can be generated by electrolysis, electricity can come from renewable sources [2]

4 **(a)**

Formula	M /g mol^{-1}	ΔH_c /kJ mol^{-1}	Specific enthalpy /kJ g^{-1}
C_3H_8	44.11	-2219	$\dfrac{2219}{44.11} = 50.31$
C_4H_{10}	58.14	-2878	$\dfrac{2878}{58.14} = 49.50$

[2]

(b) $pV = nRT$

$\rho = \dfrac{m}{V}; M = \dfrac{m}{n}$

$\rho = \dfrac{PM}{RT}$

C_3H_8

$\rho = \dfrac{1.00 \times 10^5 \times 44.11}{8.13 \times 273} = 1987$ g m^{-3}

= 1.987 × 10^{-3} g cm^{-3} heat produced per cm^3

= 50.31 kJ g^{-1} × 1.987 × 10^{-3} g cm^{-3}

= 0.09999 kJ g^{-1}

» 0.10 kJ g^{-1}

C_4H_{10}

$\rho = \dfrac{1.00 \times 10^5 \times 58.14}{8.13 \times 273} = 2620$ g m^{-3}

= 2.620 × 10^{-3} g cm^{-3}

heat produced per cm^3

= 49.50 kJ g^{-1} × 2.620 × 10^{-3} g cm^{-3}

= 0.1297 kJ g^{-1}

» 0.13 kJ g^{-1} [3]

5 **(a)** photosynthesis [1]

(b) $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ [1]

(c) fermentation [1]
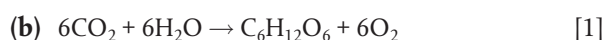
$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ [1]

6 **(a)**

Fuel	Formula	Standard enthalpy of combustion ΔH / kJ mol^{-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:

4 × H is +4, so ox. no. (C) = −4

CH_3OH:

4 × H is +4 and O is −2, so ox. no. (C) = −2 [1]

(c) the more oxidized the C the lower the specific energy [1]

(d) for $C_6H_{12}O_6$, specific energy = $\dfrac{2803}{180.18}$ = 15.56 kJ g^{-1}

for $C_6H_{12}O_6$: 12 × H is +12, 6 × O is −12, so ox. no. C = 0

the result supports the hypothesis [3]

7 **(a)** Cathode: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Award [1] if both equations given but at wrong electrodes. [2]

8 **(a)** $M_r(C_8H_{18})$ = 114.26 and $\Delta Hc^{\ominus}$ = −5470 «kJ mol^{-1}»;

«specific energy = $\dfrac{5470 \text{ kJ}}{0.11426 \text{ kg}}$ =» 4.79 × 10^4 / 47873

| 47900 «kJ kg^{-1}»;

Award [2] for correct final answer.

Accept "48 x 10^3 «kJ kg^{-1}»" OR "47.9 x 10^3 «kJ kg^{-1}»".

(b) Wood is less useful because it requires «about three times» more mass for same energy. [1]

Accept "octane is more useful because it has higher specific energy".

9 **(a)** specific energy = $\dfrac{\text{energy released}}{\text{molecular mass}}$

$= \dfrac{5470 \text{ kJ mol}^{-1}}{114.26 \text{ g mol}^{-1}}$ = 47.9 «kJ g^{-1}»

energy density = specific energy × density

= 47.9 kJ g^{-1} × 0.703 g cm^{-3}» = 33.7 «kJ cm^{-3} »

*Do **not** accept "−47.9 «kJ g^{-1}»".*

*Do **not** accept "−33.7 «kJ cm^{-3}»" unless "−47.9 «kJ g^{-1}»" already penalized.* [2]

(b) energy is lost «to the surroundings» as heat/sound/friction

or

energy is lost to the surroundings «as heat/sound/friction»

or

incomplete combustion

*Do **not** accept just "energy is lost".* [1]

10 **(a)** Methane is the major component of natural gas. It has the formula CH_4. [1]

$CH_4(g) + 2O_2 (g) \rightarrow CO_2(g) + 2H_2O(g)$ [1]
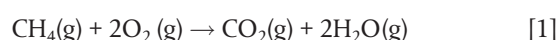
(b) Natural gas is the cleanest of the fossil fuels to burn as it has a high H:C ratio. [1]

The combustion of natural gas produces minimal amounts of carbon monoxide, hydrocarbons and particulates. [1]

It does contribute to global warming but does not contribute to acid rain, unlike coal and oil. [1]

(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. Coal, which is distributed more evenly around the world, is expected to last longer still. [1]

R1.4 Entropy and spontaneity (HL)

Exercises

Q1 B

Q2 C

Q3 A

Q4 D

Q5 **(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 changes into one mole of solid and four moles of gas. There is a small decrease in disorder.

(c) ΔS is positive. The number of moles of aqueous ions increases from reactants to products.

Q6
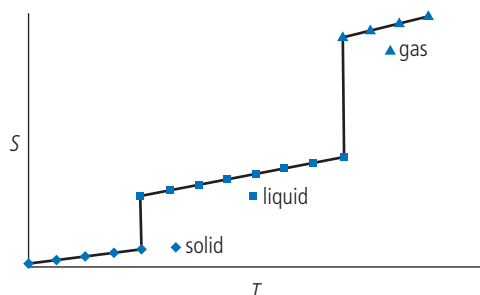
Q7 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

191   3 × 131   2 × 193 $S^{\ominus}/$ J K^{-1} mol^{-1}

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

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

Q8 $C(graphite) + 2H_2(g) \rightarrow CH_4(g)$

5.7   2 × 131   186 $S^{\ominus}/$ J K^{-1} mol^{-1}

$\Delta S_{reaction}{}^{\ominus} = (186) - (5.7 + 2 \times 131)$

$= -81.7$ J K^{-1} mol$^{-1} = -82$ J K^{-1} mol^{-1}

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

Q9 $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

131    $\frac{1}{2}$ × 205   +70 $S^{\ominus}/$ J K^{-1} mol^{-1}

$\Delta S_{reaction}{}^{\ominus} = (70) - (131 + \frac{1}{2} \times 205)$

$= -163.5$ J K^{-1} mol$^{-1} = -164$ J K^{-1} mol^{-1}

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

Q10 D

Q11 C

Q12 D

Q13 $\Delta G_{reaction} = (-604 + -394) - (-1129) = +131$ 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.

Q14 **(a)** $\Delta G = \Delta H - T\Delta S$

$$\Delta S_{reaction} = \frac{\Delta H_{reaction} - \Delta G_{reaction}}{T}$$

$$= \frac{(-217 - -212) \times 10^3}{298} = -16.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

It is a small entropy change as there no changes in the number of moles of solid, liquid or gas during the reaction.

(b) 212 kJ mol^{-1} of free energy is available to produce electrical energy.

Q15 B

Q16 A

Q17 D

Q18 B

Q19 C

Q20 $\Delta G = \Delta H - T\Delta S$

$\Delta H = +178$ kJ mol^{-1}; $\Delta S = +161$ J K^{-1} mol^{-1}; $T = 2000$ K

$\Delta G = +178 - (2000 \times +161 \times 10^{-3})$

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

Q21 **(a)** $2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$

(b) $\Delta S_{reaction}{}^{\ominus} = +161 - (2 \times 5.7) - (3 \times 130.6)$

$- (\frac{1}{2} \times 205)$

$= -344.7$ J K^{-1} mol^{-1}

(c) $\Delta G_{reaction} = -278 - (500 \times -344.7 \times 10^{-3})$

$= -105.65$ 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.

Q22 (a) $H_2O(s) \rightarrow H_2O(l)$

$\Delta H_{reaction}^{\ominus} = -286 - (-292) = +6.0\,\text{kJ mol}^{-1}$

(b) If ice is melting, then $\Delta G = 0$

$\Delta G = \Delta H - T\Delta S; \Delta H = T\Delta S$

$T = \dfrac{\Delta H^{\ominus}(\text{reaction})}{\Delta S^{\ominus}(\text{reaction})} = \dfrac{6000}{22.0} = 273\,\text{K}$

Q23 C

Q24 C

Q25 A

Q26 B

Q27 D

Q28 (a) 0

(b) negative

(c) positive

Q29 $\Delta G = \Delta G^{\ominus} + RT\ln Q = 0$

$\Delta G^{\ominus} = -RT\ln K$

$\Delta G = RT\ln Q - RT\ln K = RT\ln\dfrac{Q}{K}$

At equilibrium $\Delta G = 0$

$\ln\dfrac{Q}{K} = 0$

$Q = K$

Q30 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 $\Delta G = +30\,\text{kJ mol}^{-1}$

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

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

$T_2 = 1195\,\text{K}$

Q31 $\Delta G^{\ominus}_{reaction} = -RT\ln K_c$

$= -(8.31\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K}) \times \ln 160$

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

Q32 (a) $\Delta G^{\ominus} = 0$

(b) $\Delta G^{\ominus}_{reaction} = -RT\ln K_c$

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

$= -70\,\text{kJ mol}^{-1}$

Challenge yourself

1 The outcome is identical. Neither reaction is favoured so an equilibrium mixture with equal amounts of reactant and product is likely to be produced.

2 The entropy is due to mixing. The entropy of both pure states will be the same.

Consider the simple case of 6 Reactants → 6 Products

S (5 Reactants, 1 Product) = S (1 Reactant, 5 Products)

The entropy increases to a maximum at S (3 Reactants, 3 Products)

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

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

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

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

Practice questions

1 C

2 D

3 B

4 B

5 B

6 A

7 B

8 B

9 (a) «$-398.9\,\text{kJ mol}^{-1} - (-306.4\,\text{kJ mol}^{-1})$ =» -92.5 «kJ mol^{-1}» [1]

(b) «$\Delta S = 364.5\,\text{J K}^{-1}\,\text{mol}^{-1} - (311.7\,\text{J K}^{-1}\,\text{mol}^{-1} + 223.0\,\text{J K}^{-1}\,\text{mol}^{-1})$=» -170.2 «J K^{-1} mol^{-1}» [1]

(c) «$\Delta G = -92.5\,\text{kJ mol}^{-1} - (298\,\text{K} \times -0.1702\,\text{kJ mol}^{-1}\text{K}^{-1})$ =» -41.8 «kJ mol^{-1}» [2]

If -87.6 and -150.5 are used then -42.8.

(d) «$\Delta G = -41.8\,\text{kJ mol}^{-1} = -\dfrac{8.31\,\text{J mol}^{-1}\,\text{K}^{-1}}{1000} \times 298\,\text{K} \times \ln K$»

or

«$\Delta G = -41800\,\text{J mol}^{-1} = -8.31\,\text{J mol}^{-1}\text{K}^{-1} \times 298\,\text{K} \times \ln K$»

«$\ln K =$ =» 16.9 [1]

«$K = e^{16.9} =$» 2.14×10^7 [1]

Award [2] for correct final answer.

Accept range of 1.80×10^6–2.60×10^7.

If -43.5 is used then 4.25×10^7

10 **(a)** «$\Delta H =$» $(-635 \text{«kJ»} + -393.5 \text{«kJ»}) - (-1207 \text{«kJ»})$ ✓

«$\Delta H = + $» $+179$ «kJ» [2]

Award (1 max) for -179 kJ.

(b) «$\Delta S = (40 \text{ J K}^{-1} + 214 \text{ J K}^{-1}) - (93 \text{ J K}^{-1}) =$» $+161$ «J K^{-1}» [1]

(c) «spontaneous» if $\Delta G = \Delta H - T\Delta S < 0$

or

$\Delta H < T\Delta S$ [1]

«$T > \dfrac{179 \text{ kJ}}{0.161 \text{ kJ K}^{-1}}$» 1112 «K» [2]

Accept 1056 K if both of the incorrect values are used to solve the problem.

*Do **not** award M2 for any negative T value.*

R2.1 How much? The amount of chemical change

Exercises

Q1 **(a)** $CuCO_3(s) \rightarrow CuO(s) + CO_2(g)$

(b) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

(c) $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

(d) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(e) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Q2 **(a)** $2K + 2H_2O \rightarrow 2KOH + H_2$

(b) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

(c) $Cl_2 + 2KI \rightarrow 2KCl + I_2$

(d) $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$

(e) $Fe_2O_3 + 3C \rightarrow 3CO + 2Fe$

Q3 **(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) $4C_2H_7N + 15O_2 \rightarrow 8CO_2 + 14H_2O + 2N_2$

Q4 **(a)** 2.50 mol

(b) 5.63 mol

(c) 665.4 g

Q5 **(a)** $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

(b) 1.59 g

Q6 4.355 kg

Q7 **(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.

Q8 **(a)** 2.40 mol

(b) 0.01101 mol

(c) 44 mol

Q9 **(a)** 35.64 dm^3

(b) 5.7 dm^3

Q10 $0.6524\,dm^3$

Q11 $0.138\,mol\,Br_2$ and $0.1561\,mol\,Cl_2$, so more molecules of Cl_2

Q12 $0.113\,dm^3$

Q13 $0.28\,dm^3$

Q14 $0.178\,mol\,dm^{-3}$

Q15 $0.0220\,mol\,dm^{-3}$, 0.0802% HCl

Q16 $0.106\,mol\,dm^{-3}$ Na_2SO_4 and $0.115\,mol\,dm^{-3}$ $Pb(NO_3)_2$; assume no side reactions, all $PbSO_4$ precipitates, $PbSO_4$ is completely dry and none is lost in the drying process.

Q17   C

Q18   B

Q19   **(a)** $10\,cm^3$

        (b) $5\,cm^3$

Q20   **(a)** $85.2\,g$

        (b) $1.25\,g\,H_2$

Q21 $5.22\,g\,C_2H_4Cl_2$

Q22 $253\,g$ theoretical $CaSO_3$; 78.2%

Q23 $3.16\,g$ of ester

Q24 $107\,g$ of C_6H_6 needed

Q25 72.0%

Q26 63.2%

Q27   Method 2

Challenge yourself

1 52% NH_3 by mass; assuming no side reactions occur and gases behave as ideal gases.

2   Many reactions with 'useless' by-products could have high stoichiometric yield under optimum conditions but have a low atom economy.

    For example, methanoic acid production:

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

    For 100% yield, the atom economy is

    $\dfrac{2 \times 46.03}{(2 \times 68.01) + 98.09} \times 100\,\% = 39.32\%$

3 1217 tonnes (There is an error in the formula of tri-ammonium phosphate in the first print run of the book. The correct formula for tri-ammonium is $(NH_4)_3PO_4$, Using the corrected formula gives an answer of 1242 tonnes.)

4 320 tonnes / $3.20 \times 10^5\,kg$

5 $0.225\,mol\,dm^{-3}$ (or round to $0.23\,mol\,dm^{-3}$)

6 $[Na_2CO_3] = \dfrac{YP}{X}\,mol\,dm^{-3}$

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

7 $100\,mol\,O_2$; $3.2\,kg$

Practice questions

1   D

2   D

3   B

4   C

5   C

6   D

7   D

8   D

9   D

10 A

11 **(a)** $n(N_2) = \dfrac{80.0}{22.7} = 3.52\,mol$;   [1]

         $n(NaN_3) = \dfrac{2}{3} \times 3.52 = 2.35\,mol$;   [1]

         $m(NaN_3) = 2.35 \times (22.99 + 3 \times 14.01) = 153\,g$ [1]

    (b) $n(Na) = n(NaN_3) = 2.35\,mol$;   [1]

         $m(Na) = 2.35 \times 22.99 = 54.0\,g$ [1]

12 NH_3/ammonia in excess AND by $10\,dm^3$ [1]

    $25.0\,dm^3\,N_2$ produced   [1]

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

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

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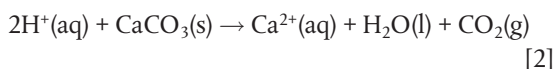
Award [1] for correct reactants and products.

Award [1] if the equation is correctly balanced.

Award (1 max) for the following equations:

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

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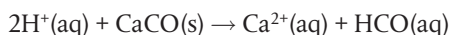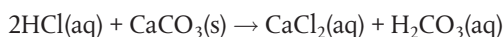
Ignore state symbols.

(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 $\times 100.09$ 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 / impurities are inert / non-basic / impurities do not react with the acid / nothing else in the eggshell reacts with acid / no other carbonates. [1]

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

14 (a) M(desired product) $= 3(12.01$ g mol$^{-1}) + 6(1.01$ g mol$^{-1}) + 6(14.01$ g mol$^{-1}) = 126.15$ g mol^{-1} AND M(all reactants) $= 24(1.01$ g mol$^{-1}) + 12(14.01$ g mol$^{-1}) + 6(12.01$ g mol$^{-1}) + 6(16.00$ g mol$^{-1}) = 360.42$ g mol^{-1} [1]

atom economy $= \frac{126.15 \text{ g mol}^{-1}}{360.42 \text{ g mol}^{-1}} \times 100\% = 35.0\%$ [1]

(b) $n((NH_2)_2CO) = \frac{14.0}{60.07} = 0.233$ mol; [1]

$n(C_3H_6N_6) = \frac{0.233 \times 1}{6} = 0.0388$ mol AND

«theoretical yield» $m(C_3H_6N_6) = 0.0388 \times 126.15 = 4.89$ g [1]

(c) % yield $= \frac{4.12}{4.89} \times 100 = 84.3\%$ [1]

Using alternative answer % yield $= \frac{4.12}{5.00} \times 100 = 82.4\%$

Allow ECF from part (b).

R2.2 How fast? The rate of chemical change

Exercises

Q1 Reaction gives off a gas, so change in volume of gas or mass of flask and contents could be measured.

Reaction involves purple MnO_4^- ions being reduced to colourless Mn^{2+} ions, so colorimetry could be used.

Reaction involves a change in the concentration of ions (23 on the reactants side and 2 on the products sides), so conductivity could be used.

Q2 C

Q3 (a) Measure the decrease in the mass of flask and contents.

Measure the increase in pH of the reaction mixture.

Measure the increase in volume of gas collected.

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

Q4
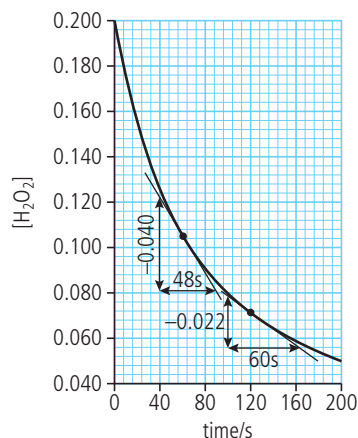
At 60 s, rate $= 8.3 \times 10^{-4}$ mol dm^{-3} s^{-1}

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

Q5 D

Q6 A

Q7 The reaction requiring the simultaneous collision of two particles is faster. The simultaneous collision of three particles is statistically less likely.

Q8 B

Q9 B

Q10 B

Q11 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.)

Q12 (a) $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$

(b Carbon monoxide and nitrogen monoxide are toxic gases.

(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.

Q13 B

Q14 C

Q15 F is an intermediate.

Overall reaction equation: $2NO_2 + F_2 \rightarrow 2NO_2F$

Q16 Zero order reaction: rate = $k\,[A]^0$ / rate = k

First order reaction: rate = $k\,[A]$

Second order reaction: rate = $k\,[A]^2$

Q17 NO: 1st order

O_3: 1st order

Overall order of reaction: 2nd order

Q18 rate = $k\,[CH_3Cl]\,[OH^-]$

rate = $k\,[CH_3Cl]^2$

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

Q19 rate = $k\,[NO_2]\,[CO]$

Q20 Yes, it fits the kinetic data and overall stoichiometry.

Q21 C

Q22 (a) $2AB_2 \rightarrow A_2 + 2B_2$

(b) Rate = $k[AB2]^2$

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

Q23 C

Q24 NO: 2nd order

O_2: 1st order

rate = $k\,[NO_2]^2\,[O_2]$

Q25 Experiment 2: rate = $1.5 \times 10^{-2}\,mol\,dm^{-3}\,s^{-1}$

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

Q26 (a) $mol^{-1}\,dm^3\,s^{-1}$

(b) s^{-1}

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

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

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

Q27 From the units of k, it must be 1st order.

Rate = $k[N_2O_5]$

Q28 $k = \dfrac{\text{rate}}{[B]^2}$

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

$= 1.1 \times 10^2\,mol^{-3}\,m^3\,min^{-1}$

Q29 C

Q30 D

Q31 B

Q32 $134\,kJ\,mol^{-1}$

Challenge yourself

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

2 A homogeneous catalyst is likely to be more difficult to recover as it is in the same phase as the reactants and products. Possible approaches might include a solvent extraction or distillation.

3 0.0850 g

Practice questions

1 B

2 A

3 A

4 C

5 (a) $ZnCO_3(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + CO_2(g) + H_2O(l)$ [2]

Award [1] for correct formulas and balancing; [1] for correct state symbols.

(b) CO_2 is produced and escapes in an open system. [1]

(c) the rate of reaction is greatest at the start and decreases with time;

the concentration of acid decreases as it reacts and so collisions between reactants become less frequent;

the rate approaches zero as the limiting reactant is used up. [3]

(d) draw a tangent to curve A and curve B at $t = 0$;

measure the gradient of each tangent;

tangent on curve A has higher gradient than tangent on curve B [3]

(e) A at a higher temperature than B;

catalyst used in A but not in B;

the $ZnCO_3(s)$ in A was in smaller pieces than in B [3]

Accept $ZnCO_3$ had larger surface area in A (or converse argument).

(f) «Higher temperature» increases the frequency of collisions;

«and» increase proportion of particles with kinetic energy greater than activation energy / more particles with KE > E_a;

«A catalyst» provides an alternate reaction route with a lower E_a / decreases activation energy;

«therefore» proportion of particles with kinetic energy greater than activation energy increases / more particles have KE > E_a;

«Smaller particle size/greater surface area» leads to higher frequency of collisions between reactants;

«therefore» higher frequency of successful collisions. [6]

(g) The change in mass would be much less as $H_2(g)$ has a much lower molar mass than $CO_2(g)$;

Not satisfactory as the change in mass as the reaction proceeds is too small to measure accurately / very small changes in mass would have large experimental uncertainty / *OWTTE*. [2]

6 (a) T2 is greater than T1. [1]

(b) Higher temperature leads to higher average kinetic energy of particles;
graph shifts to the right «and area under curve remains constant». [2]

(c)

[4]
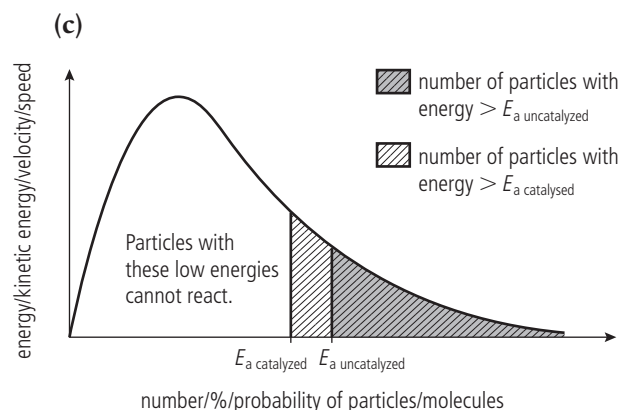
(d) (i) and (ii) «Catalysts» do not change energy/potential energy of reactants and products;

«so» enthalpy change/difference between PEreactants and PEproducts «at constant pressure» does not change;

«catalysts» decrease Ea for forward and backward reaction equally;

reaction occurs faster but yield remains constant. **[4]**

7 B

8 C

9 C

10 A

11 B

12 D

13 (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 = $-E_a/R$;

$-30\,000$ (K) $= -E_a/R$;

Allow value in range $-28\,800$ to $-31\,300$ (K).

$E_a = (30000 \times 8.31 =) \, 2.49 \times 10^5 \, \text{J mol}^{-1}/$
$249 \, \text{kJ mol}^{-1}$ [3]

Allow value in range $240–260 \, \text{kJ mol}^{-1}$.

Allow [3] for correct final answer.

(c) y-intercept $= \ln A \, / \, A = e^{y-\text{intercept}}$;

$A = e^{28.1} = 1.60 \times 10^{12}$ «$\text{mol dm}^{-3} \, \text{s}^{-1}$» [2]

Ignore units.

Allow [2] for correct final answer.

(d) $0.9 \times 0.200 = 0.180 \, (\text{mol dm}^{-3})$;

rate $= (0.244 \times (0.180)^2 =) \, 7.91 \times 10^{-3} \, \text{mol dm}^{-3} \, \text{s}^{-1}$

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

*Award (**1 max**) for either $9.76 \times 10^{-3} \, \text{mol dm}^{-3} \, \text{s}^{-1}$ or $9.76 \times 10^{-5} \, \text{mol dm}^{-3} \, \text{s}^{-1}$.*

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 / Andy was right about propanone and wrong about iodine / Suhailah was right about propanone and hydrogen ions but wrong about iodine / *OWTTE* [1]

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

$k = \dfrac{4.96 \times 10^{-6}}{0.100 \times 0.100} = 4.96 \times 10^{-4}$;

$\text{mol}^{-1} \, \text{dm}^{-3} \, \text{s}^{-1}$ [3]

Ignore calculation of $[I_2]$.

No ECF here for incorrect units.

(d) (i)
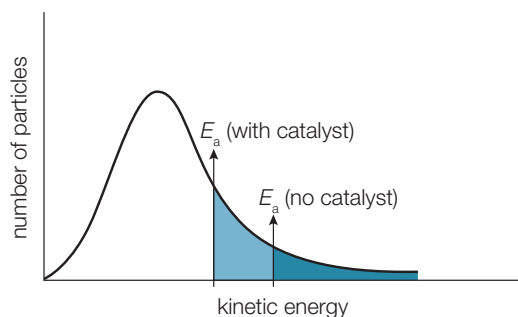
axes correctly labelled x = kinetic energy/ velocity/speed, y = number/% of molecules/ particles/probability;

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) $XY + Z \rightarrow X + YZ$ [1]

(b)
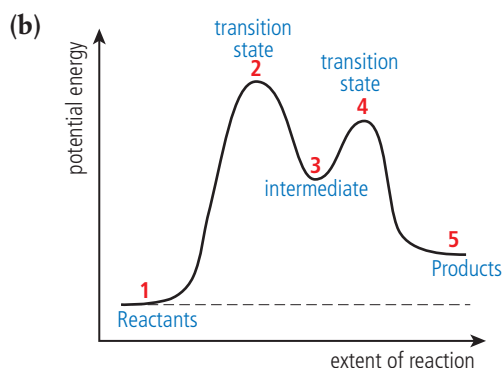
Award [3] for all 5 correct, [2] for 4 correct, [1] for 3 correct.

(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. [1]

(f)

[2]
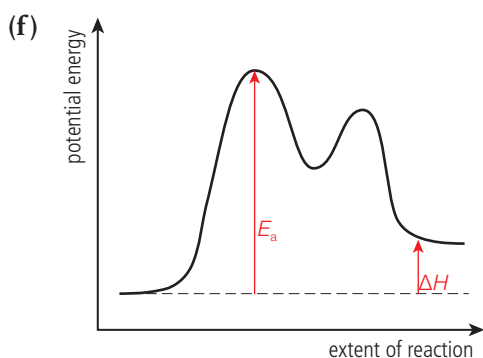
R2.3 How far? The extent of chemical change

Exercises

Q1 A

Q2 C

Q3 B

Q4 (a) $K = \dfrac{[NO_2]^2}{[NO]^2 \, [O_2]}$

(b) $K = \dfrac{[NO_2]^4 \, [H_2O]^6}{[NH_3]^4 \, [O_2]^7}$

(c) $K = \dfrac{[CH_3OH] \, [Cl^-]}{[CH_3Cl] \, [OH^-]}$

Q5 (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

Q6 (a) $3F_2(g) + Cl_2(g) \rightleftharpoons 2ClF_3(g)$

$K = \dfrac{[ClF_3]^2}{[F_2]^3 [Cl_2]}$

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

$K = \dfrac{[N_2] \, [O_2]}{[NO]^2}$

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

$K = \dfrac{[CO] \, [H_2]^3}{[CH_4] \, [H_2O]}$

Q7 (a) Mostly reactants

(b) Mostly reactants

(c) Mostly products

Q8 2.00

Q9 3.60×10^{-3}

Q10 B

Q11 D

Q12 C

Q13 (a) Shift to the left

(b) Shift to the right

(c) No shift in equilibrium

Q14 (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

Q15 (a) amount of CO will decrease

(b) amount of CO will decrease

(c) amount of CO will increase

(d) no change in amount of CO

Q16 C

Q17 B

Q18 The Haber process is exothermic in the forward direction. Therefore, increasing the temperature will decrease the value of K. This represents a decrease in the reaction yield.

Q19 (a) $\dfrac{[HOCl]^2}{[H_2O][Cl_2O]} . > K$ not at equilibrium; reaction proceeds to the left

(b) At equilibrium

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

Q20 $Q = 4.00$

Reaction will proceed to the left to reach equilibrium.

Q21 (a)

	$2HI(g) \rightleftharpoons$	$H_2(g) +$	$I_2(g)$
Initial:	1.00	0.00	0.00
Change:	−0.22	+0.11	+0.11
Equilibrium:	0.78	0.11	0.11

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

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

Q22
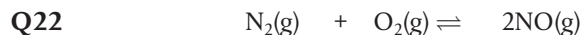
	$N_2(g)$	+	$O_2(g) \rightleftharpoons$	$2NO(g)$
Initial:	1.6		1.6	0.0
Change:	$-x$		$-x$	$2x$
Equilibrium:	$1.6 - x$		$1.6 - x$	$2x$

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

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

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

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

Q23 **(a)**

	$CO(g) +$	$H_2O(g) \rightleftharpoons$	$H_2(g) +$	$CO_2(g)$
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

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

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

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

This is not equal to the value of K so the reaction is not at equilibrium. As the Q value of this mixture is lower than K, the reaction will move to the right in order that equilibrium can be established.

Q24 C

Q25 **(a)** 0

(b) Negative

(c) Positive

Q26 **(a)** 79.8 kJ

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

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 indicate different stabilities of the hydrogen halides. The bonding is the strongest in HCl and the weakest in HI.

This is largely because of the size of the atoms. As I has a larger atomic radius that Cl, the bonding pair in HI is further from the nucleus than the bonding pair in HCl. This means that the bonding pair in HI experiences a weaker pull. The HI bond breaks more easily and so the dissociation reaction to form H_2 and I_2 is favoured.

3 **(a)** $K' = K^2 = 77\,300$

(b) $K' = \dfrac{1}{\sqrt{K}} = 0.0600$

(c) $K' = \dfrac{1}{K^3} = 4.65 \times 10^{-8}$

4 The value for K 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 oxidised 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 economy of the Haber process is 100% as there is only one product. In other words, there is no waste. But, due to the reversible nature of this reaction, this does not mean that all reactants are converted into 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.

Practice questions

1 C

2 A

3 D

4 A

5 C

6 D

7 A

8 D

9 **(a)** **(i)** $K = \dfrac{[SO_3]^2}{[O_2][SO_2]^2}$ [1]

Ignore state symbols.

Square brackets required.

(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 [3]

(b) $[H_2]$ 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});

«$K = \dfrac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \dfrac{(0.019)(0.138)^2}{(0.062)^2(0.013)^2} =$» 5.6×10^2 [4]

Award [4] for final correct answer.

Accept any value in range 557–560.

Do not penalize significant figures.

10 **(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» $= \dfrac{[NH_3]^2}{[N_2][H_2]^3}$ [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}»;

«$K = \dfrac{(0.062)^2}{(0.969)(2.91)^3}$» $= 1.6 \times 10^{-4}$ [3]

Ignore units.

Award [1] for K = 1.4 × 10⁻⁴.

(e) no effect [1]

11 **(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) $K = \dfrac{[HI]^2}{[H_2][I_2]}$ [1]

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

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

(e) $K' = \dfrac{1}{K} = \dfrac{1}{160} = 6.25 \times 10^{-3}$ [1]

(f) $n(H_2)$ at equilibrium «= 1.60 − $\dfrac{1.80}{2}$» = 0.70 mol;

$n(I_2)$ at equilibrium «= 1.00 − $\dfrac{1.80}{2}$» = 0.10 mol;

$K = \dfrac{\left(\dfrac{1.80}{4.00}\right)^2}{\left(\dfrac{0.70}{4.00}\right) \times \left(\dfrac{0.10}{4.00}\right)} / \dfrac{1.80^2}{0.70 \ \times \ 0.10}$;

$K = 46.3$ [4]

Accept 46.

Award [4] for correct final answer.

(g) 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]

12 D

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

Ignore state symbols.

Square brackets required.

(b) 7.835×10^{-3} mol «dm^{-3}» of SO_2 **and**
7.835×10^{-3} mol «dm^{-3}» of Cl_2;

7.835×10^{-3} mol «dm^{-3}» of SO_2 **and**
7.835×10^{-3} mol «dm^{-3}» of Cl_2 **and** 7.65×10^{-4} mol «dm^{-3}» of SO_2Cl_2;

«$K =$» 12.5 [3]

Award [1] for 10.34.

Award [3] for the correct final answer.

(c) value of K 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 / 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]

14 (a) «$\Delta G^{\ominus} = -RT \ln K$ and $\ln[1] = 0$ so» $\Delta G^{\ominus} = 0$ «$kJ\,mol^{-1}$» [1]

(b) «$\Delta G^{\ominus} = -RT \ln K$
$= -(8.31\ J\,K^{-1}\,mol^{-1})(298\ K)(\ln(1.7 \times 10^{12}))$
$=$» $-7.0 \times 10^4\ J\,mol^{-1}$;

«$\Delta G^{\ominus} =$» -70 «$kJ\,mol^{-1}$»;

Award [2] for −70 kJ mol⁻¹

«Very high value of K/large negative value for $\Delta G^{\ominus}$ so» equilibrium position lies far to the product side / reaction goes «essentially» to completion. [3]

15 $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$;

«$Q = \dfrac{(3.00)^2}{(0.500)(0.400)^3} =$» 281;

Q is greater than K so must decrease to reach equilibrium / *OWTTE* **and** equilibrium will shift to the left/reactant side. [3]

R3.1 Proton transfer reactions

Exercises

Q1 **(a)** HSO_3^-

(b) $CH_3NH_3^+$

(c) C_2H_5COOH

(d) HNO_3

(e) HF

(f) H_2CO_4

Q2 **(a)** $H_2PO_4^-$

(b) CH_3COO^-

(c) HSO_3^-

(d) SO_4^{2-}

(e) O_2^-

(f) Br^-

Q3 **(a)** CH_3COOH (acid) / CH_3COO^- (base)
BH_3 (base) / NH_4^+ (acid)

(b) CO_3^{2-} (base) / HCO_3^- (acid)
H_3O^+ (acid) / H_2O (base)

(c) NO_2^- (base)/NHO_2 (acid)

Q4 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)

Q5 **(a)** Dissolved carbon dioxide forms the weak acid carbonic acid, which ionises partially in solution to release H^+ ions.

H_2O(l) $+ CO_2$(g) $\rightleftharpoons H_2CO_3$(aq)

H_2CO_3(aq) $\rightleftharpoons H^+$(aq) $+ HCO_3^-$(aq)

(b) $2SO_2$(g) $+ O_2$(g) $\rightarrow 2SO_3$(g)

SO_3(g) $+ H_2O$(l) $\rightarrow H_2SO_4$(aq)

(c) Lime, CaO, is basic and so can help to neutralise acidity.

CaO(s) $+ H_2SO_4$(aq) $\rightarrow CaSO_4$(s) $+ H_2O$(l)

Q6 Burning coal releases non-metal oxides, such as SO_2 and nitrogen oxides, NO_x, which contribute to acid rain. Burning coal also contributes to climate change from the release of greenhouse gases, and to respiratory diseases from release of particulates

and some heavy metals. Coal mining also has large impacts on the environment and health.

Q7 pH increases by 1 unit

Q8 pH = 4.72

Q9 pH = 2.0

Q10 pH = 4.49, acidic

Q11 $[H^+] = 5.0 \times 10^{-9}\,mol\,dm^{-3}$

Q12 The pH scale converts $[H^+]$ values with a wide range of concentrations, and most often with negative exponents, into a simpler numeric scale. pH numbers are usually positive and have no exponents. The pH scale is a smaller range of numbers than $[H^+]$ values in $mol\,dm^{-3}$.

Q13 temperature < 298 K

Q14 $[H^+] = 1.3 \times 10^{-9}\,mol\,dm^{-3}$

Q15 $[H^+] = 1.5 \times 10^{-7}$, pH = 6.8

Q16 $[H^+] = 1.0 \times 10^{-9}\,mol\,dm^{-3}$, $[OH^-] = 1.0 \times 10^{-5}\,mol\,dm^{-3}$

Q17 **(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

Q18 $[OH^-] = 2.2 \times 10^{-7}$, basic

Q19 **(a)** pH = 6.9

 (b) pH = 2

 (c) pH = 4.8

Q20 NH_3 acts as a weak Brønsted–Lowry base because it ionizes only partially in solution to accept a proton.

$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
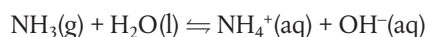
The equilibrium position of this reaction lies to the left, in favour of reactants.

Q21 B

Q22 A

Q23 **(a)** H_2CO_3

 (b) HCOOH

Q24 **(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) $HCl(aq) + CH_3NH_2(l) \rightarrow CH_3NH_3^+Cl^-$

Q25 B

Q26 **(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

$HCOOH(aq) + KOH(aq) \rightarrow KCOOH(aq) + H_2O(l)$

Q27 pH 7.0; equivalence point

Q28 $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$

pH = 2.0

Q29 $0.0083\,mol\,dm^{-3}$

Q30 pH = 13.17

Q31 $[H^+] = [OH^-] = 1.55 \times 10^{-7}\,mol\,dm^{-3}$

pH = pOH = 6.81

pH + pOH = pK_w = 13.62

neutral

Q32 pOH = 7.23

$[H^+] = 1.7 \times 10^{-7}\,mol\,dm^{-3}$

$[OH^-] = 5.9 \times 10^{-8}\,mol\,dm^{-3}$

acidic

Q33 **(a)** 0.40

 (b) 10.57

 (c) 10.00

Q34 **(a)** $K_b = \dfrac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]}$

 (b) $K_b = \dfrac{[H_2SO_4][OH^-]}{[HSO_4^-]}$

 (c) $K_b = \dfrac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$

Q35 $HNO_2 < H_3PO_4 < H_2SO_3$

Q36 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.

Q37 B

Q38 $K_b = 5.66 \times 10^{-4}$

Q39 $[H^+] = 1.0 \times 10^{-4}\,\text{mol dm}^{-3}$;
$[OH^-] = 1.0 \times 10^{-10}\,\text{mol dm}^{-3}$

Q40 $[H^+] = 6.0 \times 10^{-4}\,\text{mol dm}^{-3}$; pH = 3.22

Q41 A

Q42 HF is the stronger acid

Q43 pK_b, $CN^- = 4.79$; pK_b, $F^- = 10.83$

CN$^-$ is the stronger base

Q44 **(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.

Q45 **(a)** equal to 7
(b) less than 7
(c) less than 7
(d) greater than 7

Q46 B

salt of strong base and weak acid

Q47 **(a)** less than 7
(b) greater than 7
(c) equal to 7

Q48 $NaHCO_3(aq) \rightarrow Na^+(aq) + HCO_3^-(aq)$
$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$
HCO_3^- hydrolyzes to release hydroxide ions, which raise the pH

Q49 D

Q50

buffer region

pH

<7 ---- equivalence point

25 cm^3
volume of HCl added
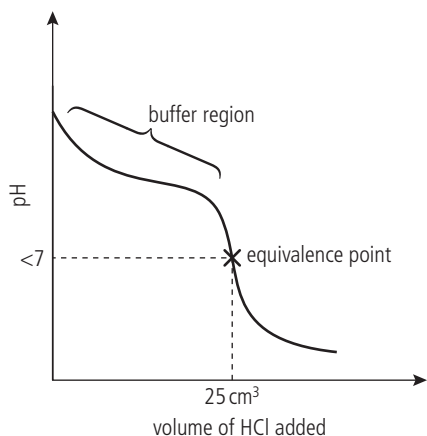
Q51 Initial pH of acid $\Rightarrow K_a$ of acid $\Rightarrow pK_a$ of acid.

At half equivalence, pH = pK_a, so this can be read directly off the curve.

Q52 D

Q53 **(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

Q54 B

Q55 B

Q56 **(i)** because it has a higher concentration of the acid and its conjugate base

Q57 75 cm^3 of 0.05 mol dm^{-3} NaOH

Challenge yourself

1 The product NH_4Cl forms smoke which is a solid, from gaseous reactants and so can be classified as sublimation or deposition.

2 $2OH^- \rightarrow O^{2-} + H_2O$

This shows the transfer of a proton from one hydroxide ion to another. So OH$^-$ is both accepting H$^+$ to form H_2O (basic behaviour) and losing H$^+$ to form O^{2-} (acidic behaviour).

The two equations showing amphiprotic behaviour are:

$OH^- + H^+ \rightarrow H_2O$ and $OH^- \rightarrow O^{2-} + H^+$

3 $Al_2(SO_4)_3(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s) + 3H_2SO_4(aq)$

Aluminium sulfate dissolves to form aluminium hydroxide, which is insoluble and so is responsible for the cloudy appearance, and a dilute solution of sulfuric acid, which causes the low pH.

A more detailed explanation is that $Al_2(SO_4)_3(s)$ ionizes in water to form Al^{3+} and SO_4^{2-} ions. As Al^{3+} is small with a high charge density, it hydrolyzes water that is bound to it in the hydrated complex, releasing H$^+$ and lowering the pH.

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$

Aluminium sulfate is the salt of a strong acid and a weak base, and forms an acidic solution.

4 Vinegar is ethanoic acid, CH_3COOH. When added to soil this will lower the pH and cause hydrangea flowers to turn blue, as explained in the text.

5 In weak acids and weak bases, the majority of the acid or base is not ionized at the start of the reaction, so energy is used to break bonds in ionizing the reactants. This endothermic process reduces the net energy released when water forms. For example, the neutralization reaction between NaOH and CH_3COOH is less exothermic than the neutralization reaction between NaOH and HCl.

6 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.

7 $HNO_3(aq) + NH_4OH(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$

Ammonium nitrate is formed from a strong acid and a weak base. The solution will be acidic.

Solid ammonium nitrate decomposes on heating.

$2NH_4NO_3(s) \rightarrow 2N_2(g) + O_2(g) + 4H_2O(g)$
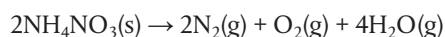
Every 2 moles of solid release 7 moles of gas, which causes a rapid expansion and increase in pressure leading to explosion. Also, O_2 ignites easily.

8 Conductivity decreases during the neutralization as the concentration of the most mobile ions, H^+ and OH^-, falls. After equivalence, the conductivity increases again with the increasing concentration of free ions from the excess acid or base. The minimum level of conductivity therefore can be used to determine the equivalence point.

9 Indicators contain conjugated delocalized electrons, as a result of alternating double bonds. The structure of the indicator changes with the addition/removal of H^+ and the change to the delocalized system changes the energy of light absorbed by the indicator molecule.

10 (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.

Practice questions

1 C

2 A

3 C

4 A

5 D

6 (a) (i) use a pH meter, use a suitable indicator

(ii)

HCOOH(aq)	5	weak acid
KCl(aq)	7	neutral salt
$HNO_3(aq)$	1	strong acid
Na(OH)(aq)	13	strong base
$NH_3(aq)$	10	weak base

(b) (i) $2NaHCO_3(s) + 2HCl(aq) \rightarrow Na_2CO_3(aq) + CO_2(g) + H_2O(l)$

effervescence

solid being used up

increase in temperature/exothermic reaction [5]

(ii) HCO_3^- can act as a Brønsted–Lowry acid and base by giving and accepting protons:

as acid: $HCO_3^- \rightarrow H^+ + CO_3^{2-}$

as base: $HCO_3^- \rightarrow H^+ + H_2CO_3$ [4]

(c) Conductivity can be quantified, so more objective. [1]

The method described in (a) is qualitative only. [1]

7 (a) *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.

(b) 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).

Do not accept just corrodes or damages.

8 **(a)** $(K_w) = [H^+][OH^-]$ / $(K_w) = [H_3O^+][OH^-]$

Do not award mark if [] omitted or other brackets are used. [1]

(b) $[H^+]$ increases, $[OH^-]$ decreases but still some present (K_w constant) / $[OH^-]$ cannot go to zero

as equilibrium present / $[OH^-] = \dfrac{K_w}{[H^+]}$, thus $[OH^-]$ cannot be zero *OWTTE*; [1]

(c) (changing T disturbs equilibrium) endothermic reaction / forward reaction favoured / equilibrium shifts to the right;

to use up (some of the) heat supplied;

K_w increases (as both $[H^+]$ and $[OH^-]$ increase); [3]

(d) (as $[H^+]$ increases) pH decreases / pH < 7;

No mark for more acidic.

inverse relationship between pH and $[H^+]$ /

$pH = -\log[H^+]$ / $pH = \log_{10}\dfrac{1}{[H^+]}$; [2]

Accept $[H_3O^+]$ in place of $[H^+]$.

9 D

10 C

11 C

12 B

13 C

14 A

15 A

16 C

17 **(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$)$

$K_b = (10^{-6.48}) = 3.3 \times 10^{-7}$ [1]

Do not award mark if answer just left as $10^{-6.48}$.

(ii) $K_b = \dfrac{[HOCl][OH^-]}{[OCl^-]} = \dfrac{x^2}{0.705} = 3.3 \times 10^{-7}$

$[OH^-] = 4.8 \times 10^{-4}$ (mol dm^{-3})

Award (2) for correct value of $[OH^-]$.

OCl^- only partially hydrolysed / x negligible (compared to $[OCl^-]$) / *OWTTE* [3]

Accept $[HOCl] = [OH^-]$.

(iii) $[H_3O^+]/[H^+] = K_w$

$[OH^-] =$

$\dfrac{1.00 \times 10^{-14}}{4.8 \times 10^{-4}} = 2.1 \times 10^{-11}$

$pH = (-\log_{10}[H_3O^+]/-\log_{10}[H^+] =$

$-\log_{10}(2.1 \times 10^{-11}) =)10.68$ [2]

Award (2) for correct final answer.

18 **(a)** **(i)** 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]

(ii) 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).

(iii)
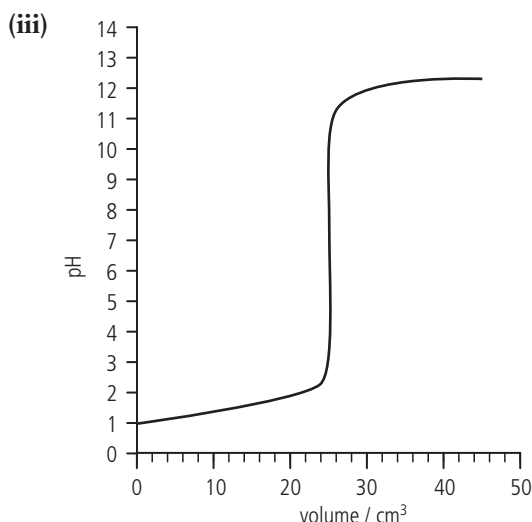
Starting pH: 1

Equivalence point: pH = 7 **and** 25 cm

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

$$HIn \quad\rightleftharpoons H^+ + \quad In^-$$
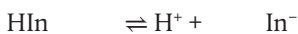
colour 1   colour 2

$\rightleftharpoons$ *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.

19 (a) strong acid completely dissociated/ionized **and** weak acid partially dissociated/ionized;

$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$;
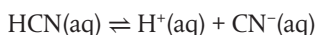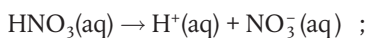
$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ [3]

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^+.

$K_a = 10^{-9.21} = 6.17 \times 10^{-10}$ [2]

(c) $[H^+] = \sqrt{K_a[HCN]}$ / $\sqrt{(\sqrt{6.17 \times 10^{-10} \times 0.108}}$

$= 8.16 \times 10^{-6}$

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 answers correct, award (3), if one answer correct, award (2).

assume $[H^+] << 0.108$ / negligible dissociation [4]

20 (a) (i) *Acid*: $H_2PO_4^-$

(Conjugate) base: HPO_4^{2-}

No mark for NaH_2PO_4 or Na_2HPO_4

$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$
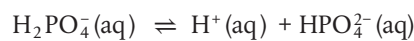
Accept reverse equation or reaction with water.

Ignore state symbols, but equilibrium sign is required.

Accept OH^- (ions) react with H^+ (ions) to form H_2O. [3]

(ii) strong base / OH^- replaced by weak base (HPO_4^{2-}, and effect minimized) / strong base / OH^- reacts with acid of buffer / equilibrium in **(i)** shifts in forward direction;
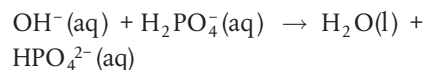
$OH^-(aq) + H_2PO_4^-(aq) \rightarrow H_2O(l) + HPO_4^{2-}(aq)$ [2]

Ignore state symbols, accept equilibrium sign.

Accept OH^- added reacts with H^+ to form H_2O.

(iii) strong acid/H^+ replaced by weak acid ($H_2PO_4^-$, and effect minimized) / strong acid reacts with base of buffer / equilibrium in **(i)** shifts in reverse direction;

$H^+(aq) + HPO_4^{2-}(aq) \rightarrow H_2PO_4^-(aq)$;
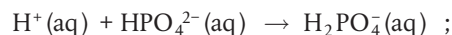
Accept reaction with H_2O^+.

Ignore state symbols.

(b) (i) NH_3 weak(er) base/partial dissociation; [2]

$[OH^-] < 0.1(0)$ / pOH > 1 (thus pH < 13 / pH + pOH = 14);

(ii) around pH = 5;

Accept a value between 4 and 6.

strong acid–weak base titration, (thus acidic) at equivalence point, NH_4^+ present is acidic / $NH_4^+ \rightleftharpoons NH_3 + H^+$ [2]

(iii) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+ + OH^-(aq)$

Ignore state symbols, but equilibrium sign required.

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$ [2]

(iv) $[NH_3] = [NH_4^+]$; [1]

(v) pOH = 14.00 − 9.25 = 4.75;

pK_b (= pOH) = 4.75;

$K_b = 1.78 \times 10^{-5}$;

Ignore units.

Award (3) for correct final answer.

(vi) optimum / most effective / highest buffer capacity / 50%–50% buffer / equally effective as an acidic buffer and a basic buffer / *OWTTE* [1]

21 (a) $K_b = 10^{-5.77} / 1.698 \times 10^{-6}$

$or\ K_b = \dfrac{[N_2H_5^+][OH^-]}{[N_2H_4]}$

$[OH^-]^2$ «$= 1.698 \times 10^{-6} \times 0.0100$» $= 1.698 \times 10^{-8}$

$or\ [OH^-] =$ «$= \sqrt{1.698 \times 10^{-8}}$» $= 1.303 \times 10^{-4}$ «$mol\,dm^{-3}$»

pH «$= -\log_{10}\dfrac{1 \times 10^{-14}}{1.3 \times 10^{-4}}$» $= 10.1$

Award (3) for correct final answer.

Give appropriate credit for other methods containing answers that do not yield correct final answer.

(b) methyl red / bromocresol green / bromophenol blue / methyl orange [1]

22 (a) weak acid – only partially / slightly ionized

strong acid – fully ionized [1]

(b) pH scale simpler numbers / avoids use of negative exponents [1]

(c) (i) phenolphthalein or phenol red [1]

(ii) 0.00140 mol NaOH [1]

(iii) 0.00070 mol $(COOH)_2 \cdot 2H_2O$ [1]

(iv) 70.6% [3]

23 (a) $[OH^-] = \sqrt{1.50 \times 1.78 \times 10^{-5}} = 5.17 \times 10^{-3}$ $(mol\,dm^{-3})$;

pH = (14 − pOH = 14 − 2.29 =) 11.71;

Award (2) for correct final answer.

Accept correct answer with more than 2 decimal places.

(b) (i) solution which resists change in pH / changes pH slightly / *OWTTE*;

when <u>small</u> amounts of acid or base are added; [2]

(ii) $[NH_3] = \left(\dfrac{(1.50 \times 0.0200) - (0.500 \times 0.0250)}{0.0450}\right)$ 0.389 $(mol\,dm^{-3})$;

$[NH_4^+] = \left(\dfrac{0.500 \times 0.0250}{0.0450}\right)$ 0.278 $(mol\,dm^{-3})$;

$[OH^-] = \left(\dfrac{K_b[NH_3]}{[NH_4^+]} = \right)\dfrac{1.78 \times 10^{-5} \times 0.389}{0.278} = $ 2.49 × 10⁻⁵ $(mol\,dm^{-3})$;

pH = (14.0 − pOH = 14.0 − 4.60 =) 9.40;

or

$pOH = pK_b + \log\dfrac{[NH_4^+]}{[NH_3]} = pK_b$

$+\log\dfrac{(12.5/1000)}{(17.5/1000)}$;

$pOH = 4.75 + \log\dfrac{12.5}{17.5} = 4.75 - 0.146 = 4.604$;

pH = 14.0 − 4.604 = 9.40;

Award (4) for the correct final answer.

(c) (i) $\left(V(NH_3) = \dfrac{25.0 \times 0.500}{1.50} = 8.33\,cm^3\right)$

V = V(NH₃) + V(HCl) = 8.33 + 25.0 = 33.3 cm³ / 0.0333 dm³; [1]

(ii) (NH_4^+ ions are present at equivalence point $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$ at equivalence $n(NH_4^+$ produced) = $n(NH_3$ added) = $n(HCl)$)

$[NH_4^+] = \dfrac{0.500 \times 0.0250}{0.0333} = 0.375\,(mol\,dm^{-3})$;

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) / NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
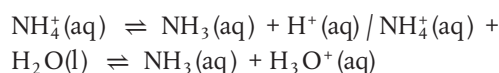
$pK_a(NH_4^+) = 14 - pK_b(NH_3) = 14.00 - 4.75 = 9.25$

$K_a = \dfrac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]} = 5.62 \times 10^{-10}$;

$[H^+(aq)] = \sqrt{5.62 \times 10^{-10} \times 0.375} = 1.45 \times 10^{-5}$ $(mol\,dm^{-3})$;

pH = 4.84;

Award (4) for the correct final answer.

(iii) bromocresol green / methyl red;

ECF for answer in 23(c)(ii) if pH given is below 7. [1]

R3.2 Electron transfer reactions

Exercises

Q1 B

Q2 C

Q3 C

Q4 **(a)** CH_4: C = −4, H = +1

(b) $CuSO_4$: Cu = +2, S = +6, O = −2

(c) C_2H_4: H = +1, O = −2

(d) CO: C = +2, O = −2

(e) $K_2Cr_2O_7$: K = +1, Cr = +6, O = −2

(f) K_2CrO_4: K = +1, Cr = +6, O = −2

(g) H_2O_2: H = +1, O = −1

(h) C_4H_{10}: C = −2.5, H = +1

Q5 **(a)** $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

  +2   +3   +4   +2

oxidation: Sn +2 → +4, so $Sn^{2+}(aq)$ is oxidized

reduction: Fe +3 → +2, so $Fe^{3+}(aq)$ is reduced

(b) $2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

  +2 −1   0   +3 −1

oxidation: Fe +2 → +3, so $2FeCl_2(aq)$ is oxidized

reduction: Cl 0 → −1, so $Cl_2(aq)$ is reduced

(c) $2H^+(aq) + S_2O_3^{2-}(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$

  +1   +2 −2   0   +4 −2   +1 −2

oxidation: S +2 → +4, so $S_2O_3^{2-}(aq)$ is oxidized

reduction: S +2 → 0, so $S_2O_3^{2-}(aq)$ is also reduced

(d) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

  +1 −1   +1 −2   0

oxidation: O −1 → 0, so $H_2O_2(aq)$ is oxidized

reduction: O −1 → −2, so $H_2O_2(aq)$ is also reduced

(e) $I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) +$

  0   +4 −2   +1 −2   −1

$SO_4^{2-}(aq) + 2H^+(aq)$

  +6 −2   +1

oxidation: S +4 → +6, so $SO_3^{2-}(aq)$ is oxidized

reduction: I 0 → −1, so $I_2(aq)$ is reduced

Q6 **(a)** assign H = +1, O = −2

Therefore, in ethanol,
(6 × +1) + −2 + (2 × C) = 0, so C = −2

This is an average value as the two carbon atoms are not equivalent.
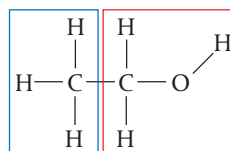
We can divide the molecule into two regions, each with a zero charge.

For the carbon atom in the red region (CH_2OH),
C + (3 × +1) + −2 = 0, so C = −1

For the carbon atom in the blue region (CH_3),
C + (3 × +1) = 0, so C = −3

The average oxidation state = $\dfrac{-3 + -1}{2}$ = −2 as expected.

(b) In CO_2, the oxidation state of C is +4

Ethanol is oxidized:

• the elements have combined with oxygen

• hydrogen has been removed

• the oxidation state of carbon has increased from −2 to +4

• the electron density of the carbon atom has reduced but no electron loss has led to production of positive ions.

Q7 **(a)** reducing agent = $H_2(g)$;
oxidizing agent = $Cl_2(g)$

(b) reducing agent = Al(s);
oxidizing agent = $PbCl_2(s)$

(c) reducing agent = KI(aq);
oxidizing agent = $Cl_2(aq)$

(d) reducing agent = $CH_4(g)$;
oxidizing agent = $O_2(g)$

Q8 A

Q9 C

Q10 **(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: $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

Q11 **(a)** $2I^-(aq) + HSO_4^-(aq) + 3H^+(aq) \rightarrow I_2(aq) + SO_2(g) + 2H_2O(l)$

(b) $I_2(aq) + 5OCl^-(aq) + H_2O(l) \rightarrow 2IO_3^-(aq) + 5Cl^-(aq) + 2H^+(aq)$

(c) $2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 3H_2O(l) + 4H^+(aq)$

Q12 **(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%

Q13 **(a)** 0.117%

(b) solution changes from orange to green

Q14 D

Q15 B

Q16 **(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

Q17 **(a)** $W > X > Y > Z$

(b) **(i)** no reaction

(ii) no reaction

Q18 C

Q19 B

Q20 **(a)** $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

(b) $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

(c) $Zn(s) + 2CH_3CO_2H(aq) \rightarrow Zn(CH_3CO_2)_2 + H_2(g)$

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Q21 **(a)** $Zn(s) + SO_4^{2-}(conc.) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + SO_2(g) + 2H_2O(l)$

(b) $NO_3^-(conc.) + 4Zn(s) + 10H^+(aq) \rightarrow NH_4^+(aq) + 4Zn^{2+}(aq) + 3H_2O(l)$

(c) $2NO_3^-(aq) + 3Cu(s) + 8H^+(aq) \rightarrow 2NO(aq) + 3Cu^{2+}(aq) + 4H_2O(l)$

(d) $2NO_3^-(conc.) + Cu(s) + 4H^+(aq) \rightarrow 2NO_2(g) + Cu^{2+}(aq) + 2H_2O(l)$

Q22 A

Q23 A

Q24 **(a)** Zn is a more reactive metal than Fe, so is oxidized

$Zn \,/\, Zn^{2+}$ is anode; $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$Fe \,/\, Fe^{2+}$ is cathode; $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

(b) Mg is a more reactive metal than Fe, so is oxidized

$Mg \,/\, Mg^{2+}$ is the anode; $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

$Fe \,/\, Fe^{2+}$ is the cathode; $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

(c) Mg is a more reactive metal than Cu, so is oxidized

$Mg \,/\, Mg^{2+}$ is the anode; $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

$Cu \,/\, Cu^{2+}$ is the cathode; $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Q25 **(a)** Mg is a more reactive metal than Zn so will be oxidized in the voltaic cell.

oxidation — Mg(s) → Mg²⁺(aq) + 2e⁻
reduction — Zn²⁺(aq) + 2e⁻ → Zn(s)
e⁻ flow
anions
salt bridge
cations
magnesium electrode
zinc electrode
solution of magnesium nitrate
solution of zinc nitrate
Anode −
Cathode +

(b) $Mg(s) \mid Mg^{2+}(aq) \parallel Zn^{2+}(aq) \mid Zn(s)$
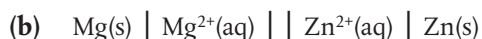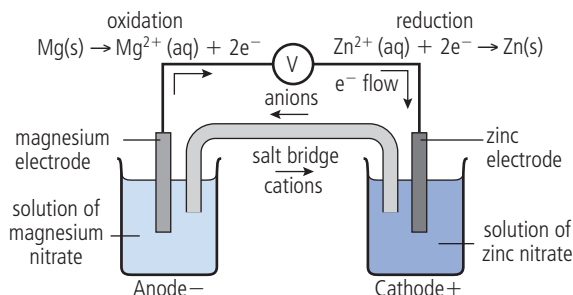
Q26 Fe is more reactive than Cu and so will reduce Cu^{2+} ions in solution.

The iron spatula would slowly dissolve as it is oxidized to Fe^{2+} ions. Copper metal (red/brown) would precipitate as Cu^{2+} ions are reduced. The blue colour of the solution would fade, as Cu^{2+} ions are removed.

Q27 **(a)** Oxidation number increases from 0 to +2. Pb(s) is oxidized.

(b) $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

(c) $PbSO_4$ is insoluble: the Pb^{2+} ions do not disperse into solution.

(d) Advantage: delivers large amounts of energy over short periods; rechargeable.

Disadvantage: heavy mass; lead and sulfuric acid could cause pollution.

Q28 **(a)** $CH_3OH(aq) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

(b) $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

(c) Advantage: does not need to be recharged, less hazardous if broken/exposed to the environment, weighs less for same energy output

Disadvantage: more expensive, needs constant supply of fuel, methanol fuel cells produce carbon dioxide, does not produce high current

Q29 **(a)** $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

(b) Fuel cells (and an electric motor) are more efficient as less waste heat produced and more chemical energy converted to useful electrical energy. They may also use a renewable energy source, which is more efficient.

(c) All convert chemical energy **directly** into electrical energy.

Q30 D

Q31 B

Q32 D

Q33 **(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: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$

(d) at anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
at cathode: $Ca^{2+}(l) + 2e^- \rightarrow Ca(l)$

Q34 **(a)**

e⁻
anode + oxidation
− cathode reduction
inert electrodes
Cl^- Mg^{2+} $MgCl_2(l)$
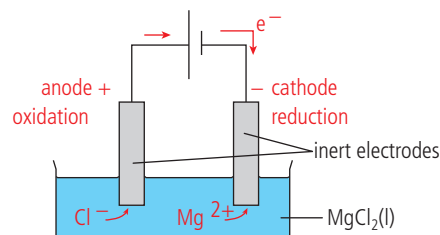
(b) anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
cathode: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$
overall: $Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(s) + Cl_2(g)$

Q35 C

Q36 C

Q37 B

Q38 $C_4H_9OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$
$C_5H_{11}OH(l) + 7.5O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$

Q39 **(a)** butanone; orange → green

(b) methanal; orange → green

(c) no reaction; no colour change

Q40 B

Q41 C

Q42 **(a)** Use $LiAlH_4$ in dry ether and heat. The acid is reduced first to the aldehyde and then to the alcohol.
$CH_3CH_2COOH \xrightarrow{+H} CH_3CH_2CH_2OH$
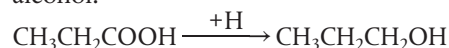
(b) Ethanal is heated with $NaBH_4(aq)$.
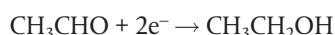$CH_3CHO \xrightarrow{+H} CH_3CH_2OH$

Q43 $CH_3CHO \rightarrow CH_3CH_2OH$
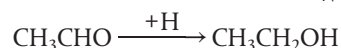
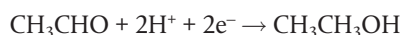Average oxidation state of C in ethanal $= \dfrac{(-4+2)}{2}$

$= \dfrac{-2}{2} = -1$

Average oxidation state of C in ethanol $= \dfrac{(-6+2)}{2}$

$= \dfrac{-4}{2} = -2$

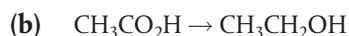The carbon atoms decrease their average oxidation state by 1, so 2 electrons are needed:

$CH_3CHO + 2e^- \rightarrow CH_3CH_2OH$

Add $2H^+$ to balance the charges:

$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_3OH$

Q44 Hydrogenation (of vegetable oils) with nickel catalyst.

Oils are liquid as they contain unsaturated fatty acid chains with C=C.

Margarines are solids as they contain saturated fatty acid chains with C–C.

Double bond has restricted rotation which gives molecule kinks which restricts packing of molecules and reduces intermolecular forces.

Saturated compounds can pack more effectively and have stronger intermolecular forces.

Q45 (a) $CH_3COCH_3 \rightarrow CH_3CH(OH)CH_3$

(b) $CH_3CO_2H \rightarrow CH_3CH_2OH$

(c) $CH_2CHCl \rightarrow CH_3CH_2Cl$

(d) $C_3H_4 \rightarrow C_3H_8$

Q46 B

Q47 A

Q48 B

Q49 C

Q50 $E^{\ominus}_{cell} = E^{\ominus}$ half-cell where Cd^{2+} reduced $- E^{\ominus}$ half-cell where Cr oxidized

$= -0.40 - (-0.75)$ V $= +0.35$ V

Q51 A

Q52 BrO_3^- will be reduced (higher $E°$ value); I^- will be oxidized.

Cell reaction:

$BrO_3^-(aq) + 6H^+(aq) + 6I^-(aq) \rightarrow Br^-(aq) + 3H_2O(l) + 3I_2(s)$
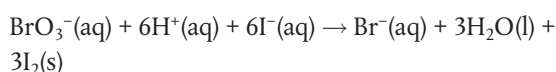
$E^{\ominus}_{cell} = E^{\ominus}_{BrO^{3-}} - E^{\ominus}_{I^2} = +1.44 - (+0.54) = +0.90$ V

Q53 strongest oxidizing agent Cu^{2+}; strongest reducing agent Mg

Q54 (a) no reaction

(b) reaction occurs: $BrO_3^-(aq) + 6H^+(aq) + 3Cd(s) \rightarrow Br^-(aq) + 3H_2O(l) + 3Cd^{2+}(aq)$

$\dfrac{E^{\ominus}}{cell} = E^{\ominus}$ half-cell where BrO_3^- reduced $- E^{\ominus}$ half-cell where

Cd oxidized

$= 1.44 - (-0.40) = 1.84$ V

(c) no reaction

Q55 B

Q56 -270 kJ

Q57 C

Q58 B

Q59

	Cathode	**Anode**
Ions present	$K^+(aq)$	$F^-(aq)$
Relevant half reactions	H^+ has a higher $E°$ than K^+ H_2O gains electrons most readily as has higher $E^{\ominus}$ and so is preferentially reduced: $H_2(g)$ is produced	$H_2O(l)$ has a lower $E°$ than F^- $H_2O(l)$ loses electrons most readily as it has lower $E^{\ominus}$ and so is preferentially oxidized: $O_2(g)$ is produced.
Reaction at electrode	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$
Products	$H_2(g)$	$O_2(g)$

The overall balanced equation is:

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Q60 (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.

Equations at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ or $4OH^- \rightarrow 2H_2O(l) + O_2(g) + 4e^-$
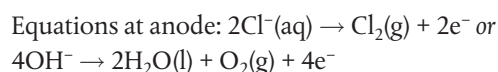
Depending on the concentration of the solution.

Equations at 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. Reaction at the anode would be different: 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.

**Q61** During electrolysis of NaCl(aq) at the cathode. $H_2O(l)$ is reduced:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
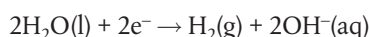
Q62 D

Q63 The metal spoon is the cathode and this will increase in mass as it is plated with silver. The impure silver anode will decrease in mass and impurities will form in the solution.

Challenge yourself

1 assign H = +1 and O = −2, with C variable

For $C_6H_{12}O_6$, $6 \times C + (12 \times +1) + (6 \times -2) = 0$, so C = 0

$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

+4 −2   +1 −2   0 +1 −2   0
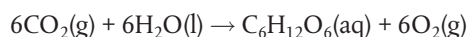
oxidation: O −2 → 0, so $6H_2O(l)$ is oxidized

reduction: C +4 → 0, so $CO_2(g)$ is reduced

2 H_2O_2: H = +1, O = −1

The oxidation state for oxygen is −1, which is halfway between 0 (element) and −2 (usual oxidation state in compounds). The oxygen 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.

3 $3I_2(aq) + 6KOH(aq) \rightarrow 5KI(aq) + KIO_3(aq) + 3H_2O(l)$

I changes from 0 (in I_2) to −1 (in KI), which is reduction.

I changes from 0 (in I_2) to +5 (in KIO_3), which is oxidation.

These changes occur simultaneously.

4

Most active								Least active
Mg	Al	C	Zn	Fe	Pb	H_2	Cu	Ag

Carbon is more reactive than zinc and iron as it can remove oxygen from their oxides.

Carbon is less reactive than aluminium as electricity is needed for the extraction of aluminium.

Hydrogen is more reactive than copper, as copper metal does not react with dilute acids, but less reactive than lead.

5 At the negative electrode (anode); $H_2(g)$ is oxidized:

$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$
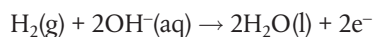
At the positive electrode (cathode) $O_2(g)$ is reduced:

$2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-$
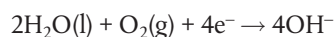
6 **(a)** efficiency $= \dfrac{237}{286} \times 100\% = 82.9\%$

(b) $H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(g)$
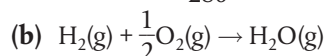
$\Delta H_f^\ominus$ (kJ mol^{-1}) =

−242 kJ mol^{-1}

$\Delta G_f^\ominus$ (kJ mol^{-1}) = −229 kJ mol^{-1}

efficiency $\dfrac{229}{242} \times 100\% = 94.6\%$

(c) Efficiency $= \dfrac{-\Delta G_{sys}}{-\Delta H_{sys}} \times 100\%$

$= \dfrac{-\Delta H_{sys} + T\Delta S_{sys}}{-\Delta H_{sys}} \times$

$100 = 1 + \dfrac{T\Delta S_{sys}}{-\Delta H_{sys}}$

The entropy decrease is smaller for the reaction which produces one mole of gaseous water, which leads to a larger efficiency.

7 At the anode, oxide ions are oxidized:

$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$
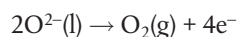
The oxygen is produced at the carbon anode at the operating temperature of around 800 °C, so the carbon reacts.

8 Aluminium oxide has some covalent character, as aluminium has quite a high electronegativity (1.6).

9 Oxidation state of hydrogen in both compounds = +1

In propane (8 hydrogens) the average oxidation state of $C = \dfrac{-8}{3}$

In propene (6 hydrogens) the average oxidation state of $C = \dfrac{-6}{3} = -2$

Combustion of propane involves a bigger change of oxidation state and more oxygen is needed.

10 Consider first the oxidation reaction:

ethanol → ethanal

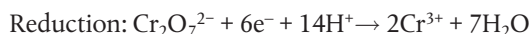The average oxidation state of C in ethanol (C_2H_6O)

$$= \frac{(-6 + 2)}{2} = -2$$

The average oxidation state of C in ethanal (C_2H_4O)

$$= \frac{(-4 + 2)}{2} = -1$$

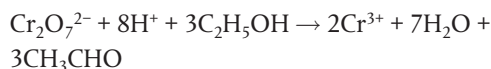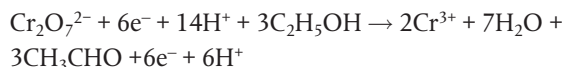As both carbon atoms increase their oxidation state by +1 (from −2 to −1), two electrons are released:

$C_2H_5OH \rightarrow CH_3CHO + 2e^-$

Add $2H^+$ to balance the charges:

$C_2H_5OH \rightarrow CH_3CHO + 2e^- + 2H^+$

Reduction: $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

To deduce the overall reaction, balance the number of electrons in the half reactions, so need 3× the ethanol/ethanal equation:

$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

$3C_2H_5OH \rightarrow 3CH_3CHO + 6e^- + 6H^+$

add and simplify:

$Cr_2O_7^{2-} + 6e^- + 14H^+ + 3C_2H_5OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO + 6e^- + 6H^+$

$Cr_2O_7^{2-} + 8H^+ + 3C_2H_5OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$

11 $HCHO \rightarrow CH_3OH$

The oxidation state of C in methanal = $-2 + 2 = 0$

The oxidation state of C in methanol = $-4 + 2 = -2$

The carbon atom decreases its oxidation state by 2, so 2 electrons are needed:

$HCHO + 2e^- \rightarrow CH_3OH$

Add $2H^+$ to balance the charges:

$HCHO + 2H^+ + 2e^- \rightarrow CH_3OH$
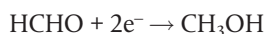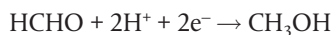
12 $n_{H_2} = \frac{1}{2} \times [2n + 2 - p - s + t]$

Saturated hydrocarbons have the general formula C_nH_{2n+2}

For C_nH_p:

H atoms needed = $2n + 2 - p$

H_2 molecules needed = $\frac{1}{2}(2n + 2 - p)$

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:

H_2 molecules needed = $\frac{1}{2}(2n + 2 - p)$

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 H_2 molecules needed by 1:

H_2 molecules needed = $\frac{1}{2}(2n + 2 - p + r)$

For $C_nH_pO_qN_rX_s$:

A halogen, X, forms one bond, like hydrogen, so can be treated in the same way:

H_2 molecules needed = $\frac{1}{2}(2n + 2 - p + r - s)$

13 Charge per e^- = 1.602177×10^{-19} C

Electrons per mole = 6.02×10^{23} mol^{-1}

Therefore, charge per mole

= 1.602177×10^{-19} C × 6.02×10^{23} mol^{-1}

= 96451.06 C mol^{-1}

14 $\Delta DG = -RT \ln K_c$ and $\Delta G = -nFE_{cell}$

Therefore $E_{cell} = \dfrac{RT \ln K_c}{nF}$

15 Lithium has the lowest (most negative) electrode potential but is not observed to the most reactive metal in the list. The lower reactivity is possibly due the slower rate of reaction. This may be linked to the relatively high melting point. As it remains as a solid when it reacts, only lithium atoms on the surface are available for reaction. The other Group 1 metals melt, which increases the surface area available for reaction.

Practice questions

1 A

2 B

3 A

4 A

5 A

6 A

7 **(a)** An electrolytic cell converts electrical energy to chemical energy and a voltaic cell converts chemical energy to electrical energy / an electrolytic cell uses electricity to carry out a (redox) chemical reaction and a voltaic cell uses a (redox) chemical reaction to produce electricity / an electrolytic cell requires a power supply and a voltaic cell does not.

An electrolytic cell involves a non-spontaneous (redox) reaction and a voltaic cell involves a spontaneous (redox) reaction.

In an electrolytic cell, the cathode is negative and the anode is positive and vice versa for a voltaic cell.

A voltaic cell has two separate solutions and an electrolytic cell has one solution / a voltaic cell has salt bridge and an electrolytic cell has no salt bridge.

In an electrolytic cell, oxidation occurs at the positive electrode/anode and in a 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:

$Na^+(l) + Cl^-(l) \rightarrow Na(l) + \frac{1}{2}Cl_2(g)$ [5]
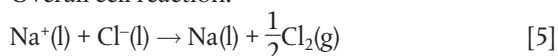
Award (1) for correct equation and (1) for correct state symbols.

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.

8 **(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]
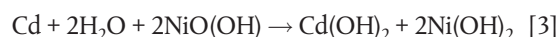
9 **(a)** contains no lithium / metal / uses lithium salt in an organic solvent (as electrolyte)

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
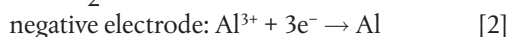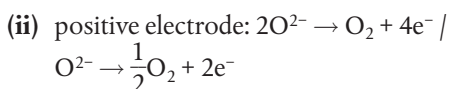
Difference:

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]

10 **(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]

11 (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) $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

(ii) $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$ [2]
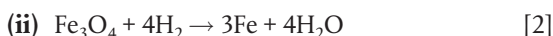
12 (a) Positive electrode: graphite/carbon

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]

13 (a) (i) copper: 0 to +2 / increases by 2 / +2 / 2+

Allow zero/nought for 0.

nitrogen: +5 to +4 / decreases by 1 / −1 / 1− [2]

Penalize missing + sign or incorrect notation such as 2+, 2^+ or II, once only.

(ii) nitric acid / HNO_3 / NO_3^- / nitrate [1]

(b) (i) 0.100×0.0285

2.85×10^{-3} (mol) [2]

Award (2) for correct final answer.

(ii) 2.85×10^{-3} (mol) [1]

(iii) $(63.55 \times 2.85 \times 10^{-3}) = 0.181$ g [1]

Allow use of 63.5.

(iv) $\left(\frac{0.181}{0.456} \times 100 =\right)$ 39.7% [1]

(v) $\left(\frac{44.2 - 39.7}{44.2} \times 100 =\right)$ 10% / 10.1% [1]

Allow 11.3%, i.e. percentage obtained in (iv) is used to divide instead of 44.2%.

14 D

15 (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.
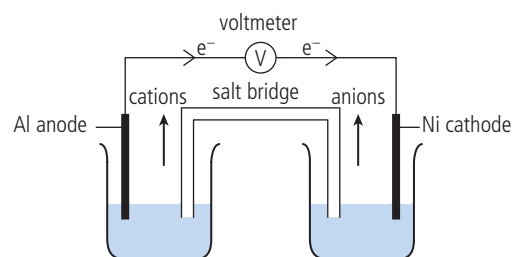
16 C

17 C

18 B

19 C

20 (a) (i) The voltage obtained when the half-cell is connected to the standard hydrogen electrode;

under standard conditions of 298 K 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]

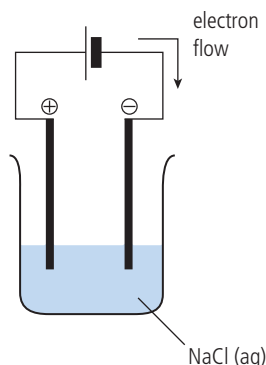**(b) (i)** +2

(ii) +3

(iii) +2　　　　　　　　　　　　　　　　[3]

Only penalise once if roman numerals are used or if written as 2+ or 3+.

(c) (i) diagram to show

NaCl (aq)

battery / source of electricity connected to two electrodes in the solution with positive and negative electrodes correctly labelled;
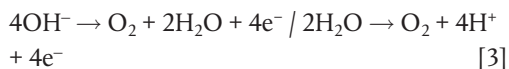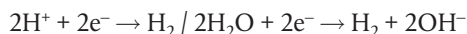
electrons / current flowing from the cell to the negative electrode;

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).

R3.3 Electron sharing reactions

Exercises

Q1　A

Q2　B

Q3　D

Q4　D

Q5　D

Q6

Q7　Thermolytic fission occurs when a bond breaks due to the addition of heat. Photolytic fission occurs when a bond breaks after the absorption of light energy (a photon).

Q8　The three stages of a radical reaction are initiation, propagation and termination.

Initiation: Br–Br $\xrightarrow{UV}$ Br• + Br•

Propagation: $CH_4 + Br• \rightarrow CH_3• + HBr$

Termination: $CH_3• + Br• \rightarrow CH_3Br$

Q9 (a)　The reaction proceeds through a radical mechanism.

Initiation: Br–Br $\xrightarrow{UV}$ Br• + Br•

Propagation: $C_2H_6 + Br• \rightarrow C_2H_5• + HBr$

Termination: $C_2H_5• + Br• \rightarrow C_2H_5Br$

(b)　Butane can be formed if two ethyl radicals formed in the propagation steps combine:

$C_2H_5• + C_2H_5• \rightarrow C_4H_{10}$

(c)
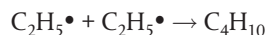
1,2-dibromoethane　　　　1,1-dibromoethane

Q10 (a)　The bromine water would be decolourized as radical substitution reactions require UV light to initiate the reaction.

(b) The bromine water would not be decolourized as there is no UV light to initiate the reaction.

Q11 **(a)** The absorption of UV light causes homolytic fission of a C–Cl bond and the formation of $CCl_2F\bullet$ and $Cl\bullet$ radicals
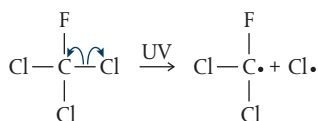
(b) $Cl\bullet(g) + O_3(g) \rightarrow O_2(g) + ClO\bullet(g)$

$ClO\bullet(g) + O_3(g) \rightarrow O_2(g) + Cl\bullet(g)$
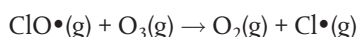
A chlorine radical reacts in the first step but another is formed in the second step, which makes the chlorine radical a catalyst.

Challenge yourself

1 For the C–F bond:

bond energy per molecule $= \dfrac{492 \times 10^3\,\mathrm{J\,mol^{-1}}}{6.02 \times 10^{23}\,\mathrm{mol^{-1}}}$

$= 8.17^{28} \times 10^{-19}\,\mathrm{J}$

Need to use the equation

$\lambda = \dfrac{hc}{E} =$

$\dfrac{6.63 \times 10^{-34}\,\mathrm{J\,s^{-1}} \times 3.00 \times 10^8\,\mathrm{m\,s^{-1}}}{8.17^{28} \times 10^{-19}}\mathrm{J} = 2.43 \times 10^{-7}\,\mathrm{m}$

$= 243\,\mathrm{nm}$

For the C–Cl bond:

bond energy per molecule $= \dfrac{324 \times 10^3\,\mathrm{J\,mol^{-1}}}{6.02 \times 10^{23}\,\mathrm{mol^{-1}}}$

$= 5.38206 \times 10^{-19}\,\mathrm{J}$

$\lambda = \dfrac{hc}{E} = \dfrac{6.63 \times 10^{-34}\,\mathrm{J\,s} \times 3.00 \times 10^8\,\mathrm{m\,s^{-1}}}{5.3821 \times 10^{-19}\,\mathrm{J}}$

$= 3.70 \times 10^{-7}\,\mathrm{m}$

$= 370\,\mathrm{nm}$

Practice questions

1 A

2 D

3 **(a)** HBr [1]

(b) The reaction requires UV light to break the Br–Br bond and initiate the reaction. [1]

(c) Initiation: Br–Br $\xrightarrow{\text{UV}}$ Br• + Br• [1]

Propagation: $C_5H_{12} + Br\bullet \rightarrow C_5H_{11}\bullet + HBr$ [1]

Termination: $C_5H_{11}\bullet + Br\bullet \rightarrow C_5H_{11}Br$ [1]

(d) **(i)** The three products are structural isomers. [1]

(ii) $CH_2BrCH_2CH_2CH_2CH_3$, 1-bromopentane [1]

$CH_3CHBrCH_2CH_2CH_3$, 2-bromopentane [1]

$CH_3CH_2CHBrCH_2CH_3$, 3-bromopentane [1]
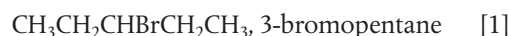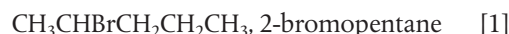
4 **(a)** Radical substitution [1]

(b) A radical substitution mechanism has three stages:

Initiation: Cl–Cl $\xrightarrow{\text{UV}}$ Cl• + Cl• [1]

Propagation: $C_3H_8 + Cl\bullet \rightarrow C_3H_7\bullet + HCl$ [1]

Termination: $C_3H_7\bullet + Cl\bullet \rightarrow C_3H_7Cl$ [1]
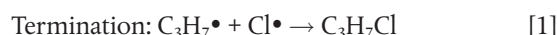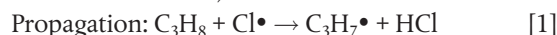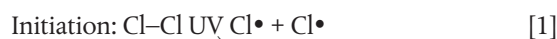
(c) $CH_2ClCH_2CH_3$, 1-chloropropane [1]

$CH_3CHClCH_3$, 2-chloropropane [1]

(d) Propane is regarded as kinetically stable as most of its reactions have high activation reactions and it won't react at regular temperatures. The products of these reactions have a lower enthalpy than propane so it is thermodynamically unstable compared to these products. [2]

5 **(a)** The reaction occurs through a radical mechanism which has three stages;

Initiation: Cl–Cl $\xrightarrow{\text{UV}}$ Cl• + Cl•

Propagation: $C_2H_6 + Cl\bullet \rightarrow C_2H_5\bullet + HCl$

Termination: $C_2H_5\bullet + Cl\bullet \rightarrow C_2H_5Cl$
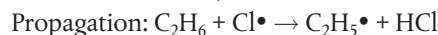
(b) Small amounts of butane could be formed in the reaction if two ethyl radicals, formed in the propagation steps, combine in a termination step:

$C_2H_5\bullet + C_2H_5\bullet \rightarrow C_4H_{10}$ [1]
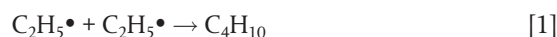
## R3.4 Electron-pair sharing reactions
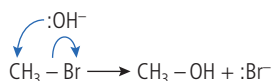
Exercises

Q1 A

Q2 C

Q3 D

Q4 Nucleophilic substitution reactions occur when a nucleophile replaces a substituent, such as a halogen, in an organic compound.

In the reaction between NaOH and chloroethane, OH⁻ acts as the nucleophile and it substitutes the

chlorine atom in chloroethane. (:Cl⁻ is the leaving group.)

$CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$
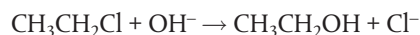
Q5

Q6 Section 12 in the data booklet lists the strengths of covalent bonds. From this table the bond strengths for the carbon halogen bonds can be compared.

Bond	C–F	C–Cl	C–Br	C–I
Bond enthalpy / kJ mol⁻¹	492	324	285	228

The bond that is the easiest to break will generate the best leaving group. The weakest bond is C–I so I⁻ will be the best leaving group.

Q7 B

Q8 Homolytic fission:

The one-headed arrows (fish hooks) show that the bond breaks with one electron going to each atom, to form two radicals.

Heterolytic fission:
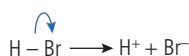
The two-headed arrow show that the bond breaks with the pair of electrons going to the more electronegative atom, to form a positive ion and a negative ion.

Q9 B

Q10 D

Q11 D

Q12 **(a)** This is an addition reaction with HBr: an alkene is converted to a halogenoalkane.

$CH_3CH_2CHBrCH_3$, 2-bromobutane

(b) With conc. H_2SO_4 followed by dilution with water, –H and –OH add across the alkene double bond, forming the alcohol.

CH_3CH_2OH, ethanol

(c) This is an addition reaction with bromine: an alkene is converted to an dibromoalkane.

$CH_3CHBrCH_2Br$, 1,2-dibromopropane

Q13 Bromine water readily reacts with alkenes but will only react with alkanes in the presence of UV light. If no UV light sources are present then:

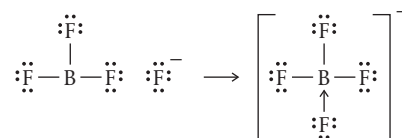adding bromine water to an alkene results in an instantaneous colour change (brown to colourless)

adding bromine water to an alkane results in no colour change.

Q14 D

Q15 A

Q16 C

Q17 **(a)** **(i)**

In Lewis acid–base reactions the Lewis base donates an electron pair and the Lewis acid accepts the electron pair. The boron atom in trifluoroborate does not have a complete octet and can accept an electron pair from the fluoride ion.

(ii) Because the fluoride ion donates both electrons in forming the covalent bond to boron it is a coordination bond.

(b) Brønsted–Lowry acid–base reactions involve the transfer of a proton (H^+). The reaction of BF_3 with F^- does not include any protons so this is not a Brønsted–Lowry reaction.

Q18 C

Q19 B

Q20 The overall charge on a complex ion is equal to sum of the charge on the transition metal ion and the charge on the ligands.

(a) Cyanide ligands, CN^-, have a 1– charge. Charge on complex ion = +3 + (6 × –1) = –3

Formula of complex ion: $[Fe(CN)_6]^{3-}$

(b) Bromide ligands, Br^-, have a 1– charge. Charge on complex ion = +2 + (6 × –1) = –4

Formula of complex ion: $[Cu(Br)_6]^{2-}$

(c) Chloride ligands, Cl^-, have a 1– charge and water ligands are neutral. Charge on complex ion = +3 + (4 × 0) + (2 × –1) = +1

Formula of complex ion: $[Cr(H_2O)_4Cl_2]^+$

**Q21** C

Q22 D

Q23 B

Q24 The iodo- and bromo- compounds are more useful because they are more reactive than the chloro-compounds. Br$^-$ and I$^-$ are better leaving groups because C–Br and C–I bonds are easier to break than C–Cl bonds. This means that they can react with a wider range of compounds and give rise to a range of intermediates and products.
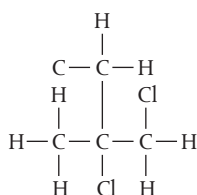
Q25 **(a)** **(i)**
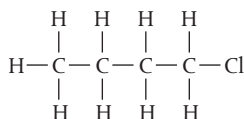
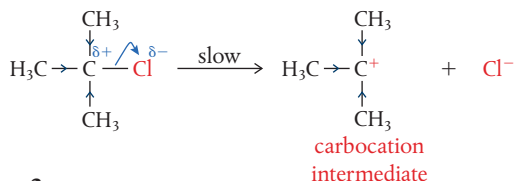1-chlorobutane (1-chloro-2-methylpropane is also possible)

(ii)
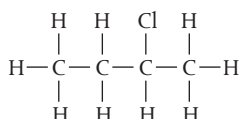
2-chlorobutane

(iii)

2-chloro-2-methylpropane

(b) **(i)** S$_N$1 is characteristic of tertiary halogenoalkanes so 2-chloro-2-methylpropane will react almost exclusively by S$_N$1.

S$_N$1 stands for substitution, nucleophilic, 1st order (unimolecular).

(ii)

Step 1

carbocation intermediate

Step 2
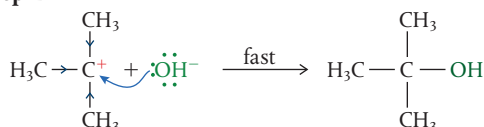
(c) **(i)** S$_N$2 is characteristic of primary halogenoalkanes so 1-chlorobutane will react almost exclusively by S$_N$2.
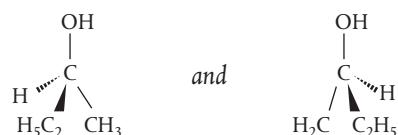
(ii)


unstable transition state
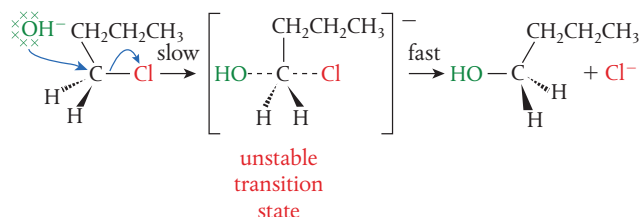
Q26 **(a)**
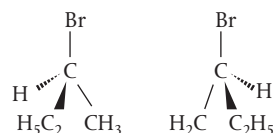
(b) For the S$_N$1 mechanism an optically pure reactant will give a product mixture that contains equal amounts of the two optical isomers (a racemic mixture).

The –Br is substituted by –OH to give

(c) For the S$_N$2 mechanism an optically pure reactant will give a product mixture that is also optically pure and only contains one optical isomer.

The –Br is substituted by –OH to give
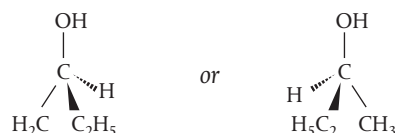
if optical isomer of 2-bromobutane on left reacts

if optical isomer of 2-bromobutane on right reacts

(d) A polarimeter measures the angle that plane-polarized light is rotated through due to its interactions with optical isomers. One isomer of 2-bromobutane will rotate the plane clockwise and the other rotates the plane an equal amount in the anti-clockwise direction.

If the optical isomer of 2-bromobutane reacts via a S$_N$1 mechanism the products are a racemic mixture. Racemic mixtures do not rotate

polarized light so no rotation would be observed for the product mixture using a polarimeter.

If the optical isomer of 2-bromobutane reacts via a S_N2 mechanism, then only one optically pure product will be formed. This product will rotate polarized light and this would be observed using a polarimeter.

Q27 **(a)** **(i)** S_N1 reactions are first order so the reaction rate only depends on the concentration of the halogenoalkane: rate = k[R–X]

(ii) S_N2 reactions are second order so the reaction rate depends on the concentration of both the halogenoalkane and hydroxide ion: rate = k[R–X][OH$^-$]

**(b)** S_N2:
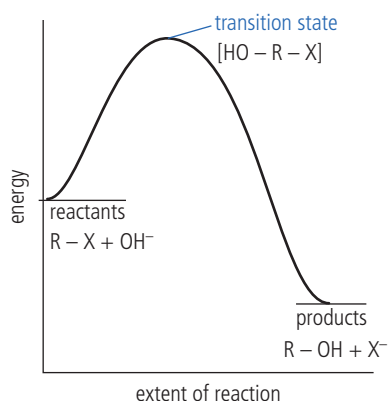
S_N1:
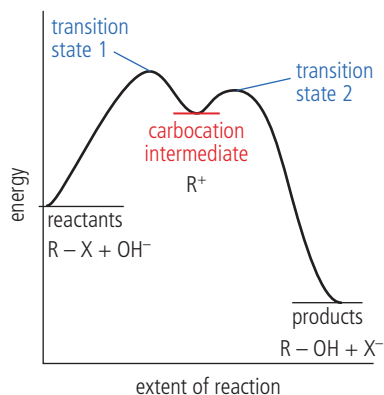
Q28 C

Q29 A

Q30 C

Q31 D

Q32 Alkenes have a double bond which is an electron-dense region and so is susceptible to attack by electrophiles, which are themselves electron deficient. Alkenes 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, the bromine 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 double bond opens. This produces an unstable carbocation which then rapidly reacts with the Br$^-$ ion. The product is 2,3-dibromobutane.

Step 1:

Step 2:
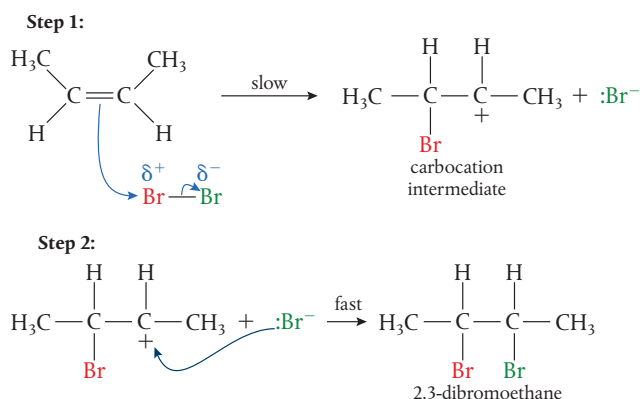
Q33 Product is butan-2-ol. Catalyst of solid silicon dioxide coated with phosphoric(V) acid, at a temperature of 300 °C and a high pressure (60 atmospheres).

Q34 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.

Q35 ICl is polarized as 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. (See worked example on pages 859–60). The product is therefore 1-iodo-2-chloropropane, $CH_3CHClCH_2I$.
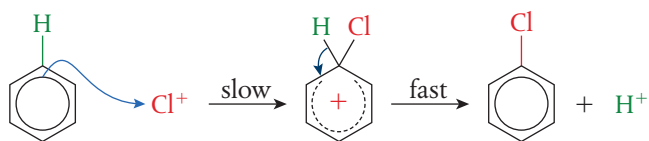
Q36 B

Q37 D

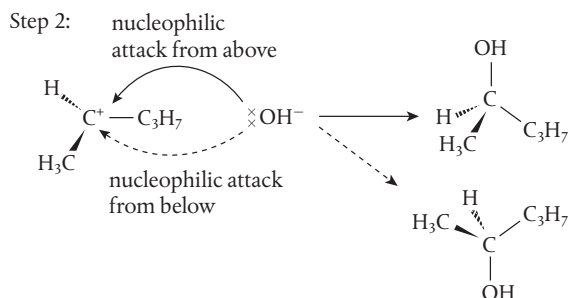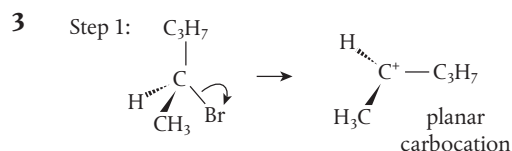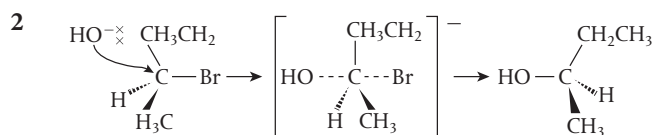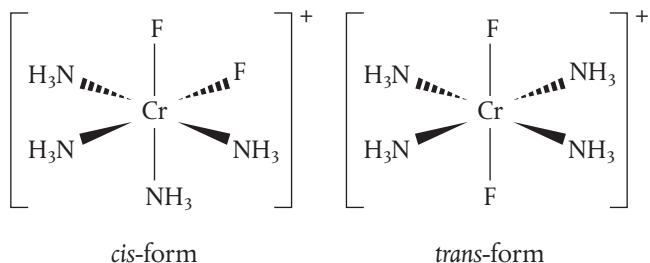**Q38** Reactants are concentrated H_2SO_4 and concentrated HNO_3.

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 pi electrons of the benzene ring and NO_2^+ substitutes an H^+ to form nitrobenzene.
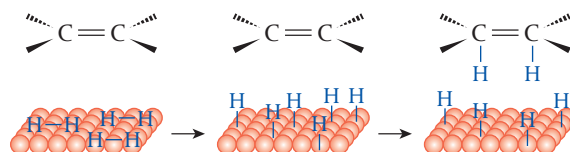
Q39 **(a)** Electrophilic substitution

(b)

Challenge yourself

1

cis-form   *trans*-form

2

3 Step 1:

planar carbocation

Step 2: nucleophilic attack from above

nucleophilic attack from below

4 The S_N1 reaction is not stereospecific, so will produce 15% of each optical isomer. The S_N2 reaction is stereospecific, so will produce 70% of one optical isomer. Overall, the reactions will produce 15% of one optical isomer and 85% of the other.

5 Due to their small size, the hydrogen atoms in H_2 are not polarizable and this means that the H2 will not readily form instantaneous dipoles. It is therefore a very weak electrophile.

When metal catalysts such as Pt are used, the alkene and H2 are both absorbed onto the surface of the metal. This breaks the H–H bond and weakens the pi bond of the alkene. The H atoms now present on the metal surface can add to the alkene forming the hydrogenated product.


A typical electrophilic substitution mechanism does not require a catalyst and the pi bond in the alkene breaks due to electrophilic attack. (The pi electrons are strongly attracted to the electrophile and form a sigma bond with the electrophilic atom.)

6 Vegetable oils contain long carbon chains with one or more C=C double bonds.

Hydrogenation of vegetable oils results in the formation of saturated products due to the C=C pi bonds breaking and the addition of C–H sigma bonds.

The flexible alkyl chains of the saturated products are able to stack together more readily than the chains in the oils which are more rigid due to the C=C double bonds. This results in the saturated products having stronger intermolecular forces and higher melting points so the saturated products are typically solids (or soft semi-solids) rather than liquids at room temperature.

7 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 nitrovenzene is electron withdrawing due to the electronegativity of the nitrogen and oxygen atoms.
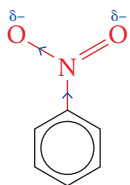
Also, the electrons in its double bond conjugate with the π electrons in the ring, causing the electron density of the ring to be decreased, making it less susceptible to electrophilic attack.

Practice questions

1 C

2 B

3 B

4 D

5 A

6 B

7 D

8 B

9 The overall charge on the complex ions is equal to sum of the charge on the transition metal ion and the charge on the ligands.

   (a) Thiocyanate ligands, SCN^-, have a 1– charge.
Charge on complex ion = $+3 + (6 \times -1) = -3$.
Formula of complex ion: $[Fe(SCN)_6]^{3-}$ [1]

   (b) Chloride ligands, Cl^-, have a 1– charge and water ligands are neutral.
Charge on complex ion = $+2 + (5 \times 0) + -1 = +1$.
Formula of complex ion: $[Co(H_2O)_5Cl]^+$ [1]

   (c) Fluoride ligands, F^-, have a 1– charge and ammonia ligands are neutral.
Charge on complex ion = $+3 + (2 \times 0) + (4 \times -1) = -1$.
Formula of complex ion: $[Cr(NH_3)_2F_4]^-$ [1]

10 C

11 A

12 A

13 A

14 (a) Lewis bases are electron-pair donors. Brønsted–Lowry bases are proton (H^+) acceptors.

In reaction **(i)** the OH^- donates a lone pair to CO_2 to form HCO_3^-, so it is acting as a Lewis base.   [1]

In reaction **(ii)** the OH^- accepts a proton from H_2CO_3 to form H_2O, so it is acting as a Brønsted–Lowry base.   [1]

   (b) In the $[Fe(OH_2)_6]^{3+}$ complex ion, each water ligand has donated a lone pair of electrons to form a coordination bond with the central Fe^{3+} ion. Because they have donated electron pairs, the water ligands have behaved as Lewis bases. Because it has accepted electron pairs, the Fe^{3+} ion has behaved as a Lewis acid.   [2]

15 (a) A: 1-bromobutane   [1]
       B: 2-bromobutane   [1]
       C: 2-bromo-2-methylpropane   [1]
       D: 1-bromo-2-methylpropane   [1]

   (b) (i) S_N1 means substitution, nucleophilic, 1st order (unimolecular); i.e. a 1st order nucleophilic substitution reaction.
S_N1 reactions are favoured by tertiary halogenoalkanes.   [1]

C is a tertiary bromoalkane so it will react almost exclusively via a S_N1 mechanism.   [1]

(A and D are primary bromoalkanes which react via S_N2 and B is a secondary bromoalkane that reacts via both S_N1 and S_N2.)

      (ii) S_N1 reactions occur via a two-step mechanism. The first step, which involves the breaking of a C–Br bond in the bromoalkane to form a carbocation, is rate determining.
$RBr \rightarrow R^+ + Br^-$ [1]

     (iii) S_N2 reactions are favoured by primary halogenoalkanes.

A and D are both primary bromoalkanes so will react almost exclusively via a S_N2 mechanism.

Drawing a mechanism for either of these two isomers is acceptable. Here it is drawn for isomer A, 1-bromobutane.
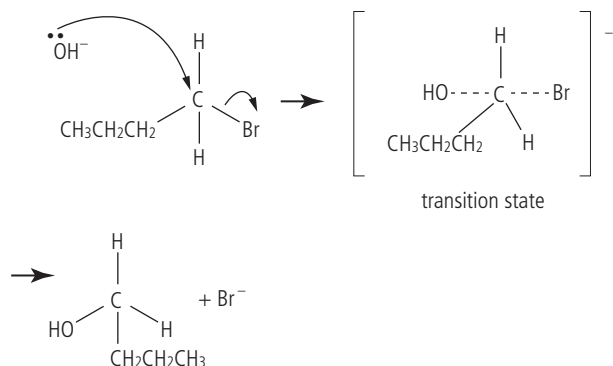
1 mark for double headed curly arrow from lone pair on OH- to C.

1 mark for double headed curly arrow from C-Br bond to Br.

1 mark for transition state showing partial bonds AND negative charge.

1 mark for correct products.

(c) Part (b)(i) refers to a S_N1 mechanism which has the rate expression rate = k[RBr]. The reaction is zero order with respect to OH⁻; so doubling the concentration of OH⁻ will have no effect on the rate. [1]

Part (b)(iii) refers to a S_N2 mechanism which has the rate expression rate = k[RBr][OH⁻]. The reaction is first order with respect to OH⁻; so doubling the concentration of OH⁻ will double the rate. [1]

(d) The C–Br bond is weaker than the C–Cl bond [1]

so the C–Br bond breaks more easily and Br⁻ is a better leaving group than Cl⁻. 1-bromobutane will react faster than 1-chorobutane. [1]

16 (a) C_3H_6 is an alkene and it reacts with HBr via an electrophilic addition reaction. [1]

(b) [4]

Step: 1

Step: 2

2-bromopropane
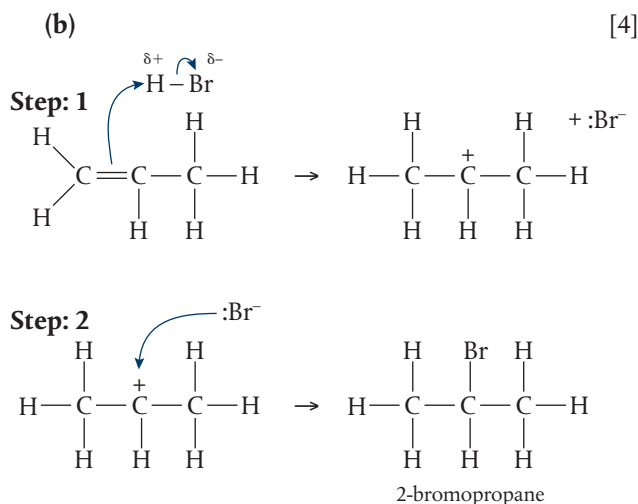
(c) The reaction involves an asymmetrical alkene so it follows Markovnikov's rule: the hydrogen atom in HBr bonds to the less substituted carbon atom in the alkene. [1]

The electrophilic attack by HBr causes the pi bond to selectively open so that the more stabilized secondary carbocation is formed. Nucleophilic addition of Br⁻ to the secondary carbocation gives **2-bromopropane** as the product. [1]

17 (a) Comparing trials 1 and 2: [C_4H_9Br] is constant and [OH⁻] has been doubled. The initial rate does not change so the reaction is zero order with respect to OH⁻. [1]

Comparing trials 1 and 3: [OH⁻] is constant and [C_4H_9Br] has been doubled. The initial rate also doubles so the reaction is first order with respect to C_4H_9Br.
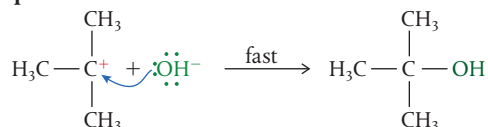
The rate expression is: rate = k[C_4H_9Br] [1]

(b) From (i) we see that the reaction is 1st order overall so it must occur via an S_N1 mechanism. [1]

Tertiary halogenoalkanes react almost exclusively by the S_N1 mechanism. There is one isomer of C_4H_9Br that is a tertiary halogenoalkane: 2-bromo-2-methylpropane. [1]
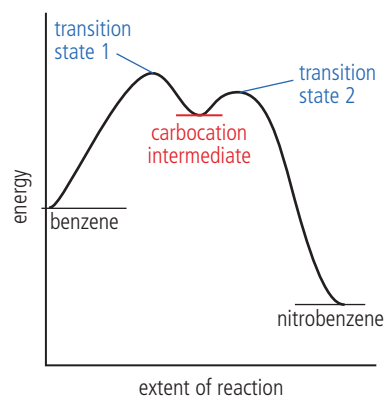
(c) **Step 1**

Step 2

[4]
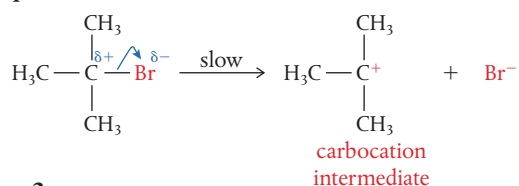
18 (a) The other two reactants required are concentrated sulfuric acid, H_2SO_4, and concentrated nitric acid, HNO_3. The electrophile is the nitronium ion, NO_2^+

[2]

(b) [4]

(c) [3]