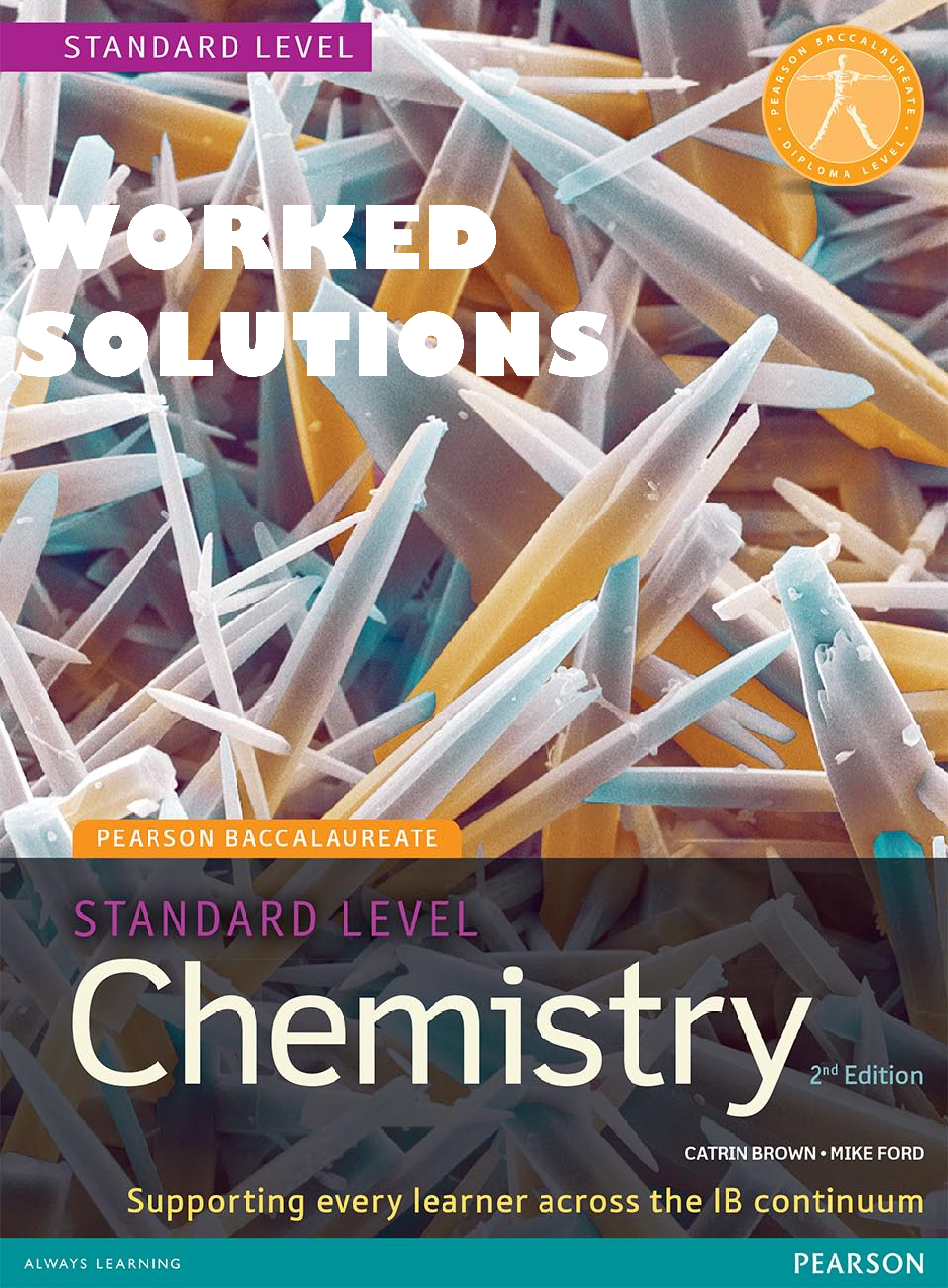
STANDARD LEVEL

WORKED SOLUTIONS



PEARSON BACCALAUREATE

STANDARD LEVEL

Chemistry

2nd Edition

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Supporting every learner across the IB continuum

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PEARSON

Worked solutions

Chapter 1

Exercises

1 For each of these questions (a) to (e):

- write the information from the question in the form of an equation
- check the number of atoms on each side of the equation
- introduce coefficients in front of the formulae in order to ensure that there are equal numbers of atoms on each side of the equation.

(a) $CuCO_3 \rightarrow CuO + CO_2$

(b) $2Mg + O_2 \rightarrow 2MgO$

(c) $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

(d) $N_2 + 3H_2 \rightarrow 2NH_3$

(e) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

2 For each of these questions (a) to (e):

- introduce coefficients in front of each formula to ensure that there are equal numbers of atoms on each side of the equation.

(a) $2K + 2H_2O \rightarrow 2KOH + H_2$

(b) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(c) $Cl_2 + 2KI \rightarrow 2KCl + I_2$

(d) $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$

(e) $Fe_2O_3 + 3C \rightarrow 3CO + 2Fe$

3 For each of these questions (a) to (e):

- introduce coefficients in front of each formula to ensure that there are equal numbers of atoms on each side of the equation.

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

(b) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

(c) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(d) $6H_2O_2 + 2N_2H_4 \rightarrow 2N_2 + 10H_2O + O_2$

(e) $4C_2H_7N + 15O_2 \rightarrow 8CO_2 + 14H_2O + 2N_2$

4 **(a)** Sand is an insoluble solid and water a liquid – heterogeneous.

(b) Smoke is made up of solid particles dispersed in air (a gas) – heterogeneous.

(c) Sugar dissolves in water to give a clear solution – homogeneous. (If it is a saturated solution with excess sugar that cannot dissolve, the overall mixture is then heterogeneous.)

(d) Salt and iron filings mix but don't interact with each other – heterogeneous.

(e) Ethanol dissolves in water to give a clear solution – homogeneous.

(f) Steel consists of an alloy of iron and carbon, it has the same properties throughout – homogeneous.

5 For each of questions (a) to (e):

- introduce coefficients in front of each formula to ensure that there are equal numbers of atoms on each side of the equation
- remember when assigning state symbols that if there is water present and one of the products is soluble, then the symbol aq (aqueous) must be used (water itself as a liquid is always (l), never (aq)).

(a) $2KNO_3(s) \rightarrow 2KNO_2(s) + O_2(g)$

(b) $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

(c) $2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$

(d) $Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$

(e) $2C_3H_6(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

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

7 From the kinetic molecular theory we would expect a solid to be more dense than its liquid. We would expect that ice would sink in water. That ice floats is an indication that something

else is involved in the structure of ice (see page 152).

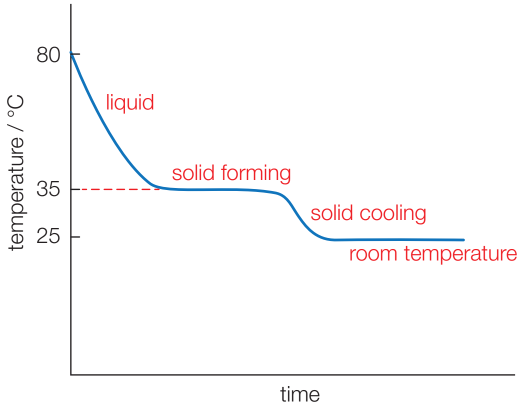
8 Bubbles will be present through the volume of the liquid. A brown gas is visible above the brown liquid. As the two states are at the same temperature, the particles have the same average kinetic energy and are moving at the same speed. The inter-particle distances in the gas are significantly larger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

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

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

11 B, as a change of state is taking place.

12



13 Use $L = 6.02 \times 10^{23}$ mol^{-1}.

(a) 1 mole of C_2H_5OH contains 6 moles of hydrogen atoms

1 mole of C_2H_5OH contains $6 \times (6.02 \times 10^{23})$ hydrogen atoms

1 mole of C_2H_5OH contains 3.61×10^{24} hydrogen atoms

0.020 moles therefore contains $(3.61 \times 10^{24}) \times 0.020$ hydrogen atoms

$= 7.2 \times 10^{22}$ hydrogen atoms

(b) 1 mole of H_2O contains 2 moles of hydrogen atoms

1 mole of H_2O contains $2 \times (6.02 \times 10^{23})$ hydrogen atoms

1 mole of H_2O contains 1.20×10^{24} hydrogen atoms

2.50 moles therefore contains $(1.20 \times 10^{24}) \times 2.50$ hydrogen atoms

$= 3.01 \times 10^{22}$ hydrogen atoms

(c) 1 mole of $Ca(HCO_3)_2$ contains 2 moles of hydrogen atoms

1 mole of $Ca(HCO_3)_2$ contains $2 \times (6.02 \times 10^{23})$ hydrogen atoms

1 mole of $Ca(HCO_3)_2$ contains 1.20×10^{24} hydrogen atoms

0.10 moles therefore contains $(1.20 \times 10^{24}) \times 0.10$ hydrogen atoms

$= 1.2 \times 10^{23}$ hydrogen atoms

14 Propane contains three carbon atoms and eight hydrogen atoms. If the three carbon atoms are equivalent to 0.20 moles of carbon then one carbon atom would be equivalent to 0.20/3 moles of carbon. So eight atoms of hydrogen would be equivalent to (0.20/3) × 8 moles of hydrogen, i.e. 0.53 moles of H.

15 Sulfuric acid contains four oxygen atoms. If there are 6.02×10^{23} atoms of oxygen in total then there must be $(6.02 \times 10^{23})/4$ molecules of sulfuric acid, i.e. 1.51×10^{23} molecules of sulfuric acid (= 0.250 mol of sulfuric acid).

16 **(a)** Magnesium phosphate, $Mg_3(PO_4)_2$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
Mg	24.31	3	72.93
P	30.97	2	61.94
O	16.00	8	128.00
Molar mass			262.87 g mol^{-1}

(b) Ascorbic acid, $C_6H_8O_6$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
C	12.01	6	72.06
H	1.01	8	8.08
O	16.00	6	96.00
Molar mass			176.14 g mol^{-1}

(c) Calcium nitrate, $Ca(NO_3)_2$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
Ca	40.08	1	40.08
N	14.01	2	28.02
O	16.00	6	96.00
Molar mass			164.10 g mol^{-1}

(d) Hydrated sodium thiosulfate, $Na_2S_2O_3.5H_2O$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
Na	22.99	2	45.98
S	32.07	2	64.14
O	16.00	8	128.00
H	1.01	10	10.10
Molar mass			248.22 g mol^{-1}

17 Calculate the molar mass of calcium arsenate, $Ca_3(AsO_4)_2$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
Ca	40.08	3	120.24
As	74.92	2	149.84
O	16.00	8	128.00
Molar mass			398.08 g mol^{-1}

$$\text{Mass} = nM = 0.475 \text{ mol} \times 398.08 \text{ g mol}^{-1} = 189.1 \text{ g}$$

18 (If not using a calculator, use rounded values for A_r.)

M of CO_2 = (12 + (16 × 2)) g mol^{-1} = 44 g mol^{-1}

$$\text{moles} = \frac{m}{M} = \frac{66 \text{ g}}{44 \text{ g mol}^{-1}} = 1.5 \text{ mol}$$

19 Copper(II) chloride, $CuCl_2$, has M of (63.55 + (35.45 × 2)) g mol^{-1} = 134.45 g mol^{-1}

0.50 g is equivalent to (0.50 g/134.45 g mol^{-1}) mol of copper chloride, i.e. 3.7×10^{-3} mol

There are two chloride ions in copper chloride, $CuCl_2$

There must be 2 × (3.7×10^{-3}) mol of chloride ions present, i.e. 7.4×10^{-3} mol (= 0.0074 mol)

20 36.55 g of carbon = 36.55 g/12.01 g mol^{-1}
= 3.043 mol of carbon

1 mole of carbon contains 6.02×10^{23} atoms of carbon

Therefore 3.043 moles of carbon contain 3.043 × (6.02×10^{23}) atoms of carbon, i.e. 1.83×10^{24} atoms

21 (If not using a calculator, use rounded values for A_r.)

Calculate the M_r of sucrose, $C_{12}H_{22}O_{11}$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
carbon	12	12	144
hydrogen	1	22	22
oxygen	16	11	176
M			342 g mol^{-1}

Mass = nM = 0.500 mol × 342 g mol^{-1} = 171 g

22 (If not using a calculator, use rounded values for A_r.)

Water: the M_r of H_2O is 18 (= 16 + 2 × 1)

Therefore 10.0 g of water is equivalent to (10 g/18 g mol^{-1}) mol of water (= 0.55 mol)

Mercury: the relative atomic mass of mercury is 201

Therefore 10.0 g is equivalent to (10 g/201 g mol^{-1}) mol of mercury (≈ 0.05 mol)

10.0 g of water contains more particles than 10.0 g of mercury.

23 (If not using a calculator, use rounded values for A_r.)

M_r of N_2H_4 is (2 × 14) + (4 × 1) = 32, therefore 1.0 mol has a mass of 32 g

M_r of N_2 is (2 × 14) = 28, therefore 2.0 mol has a mass of 56 g

M_r of NH_3 is 14 + (3 × 1) = 17, therefore 3.0 mol has a mass of 51 g

M_r of H_2 is (2 × 1) = 2, therefore 25.0 mol has a mass of 50 g

So in order of decreasing order of mass:

2.0 mol nitrogen > 3.0 mol ammonia > 25.0 mol hydrogen > 1.0 mol hydrazine

24 **(a)** C_2H_2: the ratio of carbon to hydrogen atoms can be simplified to CH

(b) $C_6H_{12}O_6$: the ratio of atoms can be simplified to CH_2O

(c) $C_{12}H_{22}O_{11}$: the ratio of atoms cannot be simplified – the empirical and molecular formula are the same.

(d) C_8H_{18}: the ratio of atoms can be simplified to C_4H_9

(e) C_8H_{14}: the ratio of atoms can be simplified to C_4H_7

(f) CH_3COOH, i.e. $C_2H_4O_2$: the ratio of atoms can be simplified to CH_2O

25

	Sodium	Sulfur	Oxygen
mass / g	0.979	1.365	1.021
moles	$\frac{0.979}{22.99}$ = 0.0426	$\frac{1.365}{32.07}$ = 0.0426	$\frac{1.021}{16.00}$ = 0.06381
divide by smallest	1.00	1.00	1.50
nearest whole number ratio	2	2	3

The empirical formula is $Na_2S_2O_3$

26

	Cobalt	Sulfur	Oxygen	Water (H_2O)
mass / g	2.10	1.14	2.28	4.50
moles	$\frac{2.10}{58.93}$ = 0.0356	$\frac{1.14}{32.07}$ = 0.0355	$\frac{2.28}{16.00}$ = 0.143	$\frac{4.50}{18.02}$ = 0.250
divide by smallest	1.00	1.00	4.03	7.04
nearest whole number ratio	1	1	4	7

The empirical formula is $CoSO_4.7H_2O$

27

	Carbon	Hydrogen	Nitrogen
% by mass	83.89	10.35	5.76
moles	$\frac{83.89}{12.01}$ = 6.985	$\frac{10.35}{1.01}$ = 10.2	$\frac{5.76}{14.01}$ = 0.411
divide by smallest	17.0	24.8	1.00
nearest whole number ratio	17	25	1

The empirical formula is $C_{17}H_{25}N$

28 M_r of NH_3 = 14.01 + (3 × 1.01) = 17.04

% by mass of N is $\frac{14.01}{17.04} \times 100 = 82.22\%$

M_r of $CO(NH_2)_2$ = 12.01 + 16.00 + 2 × [14.01 + (2 × 1.01)] = 62.07

% by mass of N is $\frac{28.02}{62.07} \times 100 = 45.14\%$

(Note: 28.02 since there are two nitrogen atoms in the molecule)

M_r of $(NH_4)_2SO_4$ = (2 × 14.01) + (8 × 1.01) + 32.07 + (4 × 16.00) = 132.17

% by mass of N is $\frac{28.02}{132.17} \times 100 = 21.20\%$

(Note: 28.02 since there are two nitrogen atoms in the molecule)

So overall, ammonia, NH_3, has the highest % by mass of nitrogen.

29 moles of nitrogen = 0.673 g/14.01 g mol^{-1}
= 0.0480 mol

In the formula there are 3 moles of nitrogen associated with each mole of metal. Therefore moles of metal in the compound = 3 × 0.0480 = 0.144

$$\text{atomic mass} = \frac{\text{mass}}{\text{moles}} = \frac{1.00\ \text{g}}{0.144\ \text{g mol}^{-1}} = 6.94\ \text{g mol}^{-1}$$

The relative atomic mass of the element is 6.94. By looking at the periodic table (section 6 of the IB data booklet), it can be seen that the element is lithium.

30 $\text{percentage by mass} = \dfrac{\text{relative atomic mass of cadmium}}{M_r} \times 100$

- For CdS, percentage by mass = $\dfrac{112.41}{112.41 + 32.07} \times 100 = 77.80\%$
- For CdSe, percentage by mass = $\dfrac{112.41}{112.41 + 78.96} \times 100 = 58.74\%$
- For CdTe, percentage by mass = $\dfrac{112.41}{112.41 + 127.60} \times 100 = 46.84\%$

Overall, CdS has the highest percentage by mass of cadmium.

You could also approach this question by considering the A_r of the other element in the compound. Sulfur has the lowest A_r and so CdS will have the highest percentage by mass of cadmium.

31

	Carbon	Hydrogen
% by mass	100 – 7.74 = 92.26	7.74
moles	$\frac{92.26}{12.01} = 7.681$	$\frac{7.74}{1.01} = 7.66$
divide by smallest	1.00	1.00
nearest whole number ratio	1	1

Empirical formula is therefore CH. This has a mass of 13.02 g mol^{-1}. This number divides into the molar mass of the whole compound six times (i.e. $\frac{78.10\ \text{g mol}^{-1}}{13.02\ \text{g mol}^{-1}} = 6$).

The molecular formula is therefore six times the empirical formula, i.e. C_6H_6

32

	Hydrogen	Phosphorus	Oxygen
mass / g	0.0220	0.3374	0.8821 – (0.0220 + 0.3374) = 0.5227
moles	$\frac{0.0220}{1.01} =$ 0.0218	$\frac{0.3374}{30.97} =$ 0.01089	$\frac{0.5227}{16.00} =$ 0.03267
divide by smallest	2.00	1.00	3.00
nearest whole number ratio	2	1	3

Empirical formula is therefore H_2PO_3. This has a mass of 80.99 g mol^{-1}. This number divides into the molar mass of the whole compound twice (i.e. $\frac{162\ \text{g mol}^{-1}}{80.99\ \text{g mol}^{-1}} = 2$).

The molecular formula is therefore twice the empirical formula, i.e. $H_4P_2O_6$

33

	Carbon	Hydrogen	Nitrogen
mass / g	0.1927	0.02590	0.1124
moles	$\frac{0.1927}{12.01} =$ 0.01604	$\frac{0.02590}{1.01} =$ 0.0256	$\frac{0.1124}{14.01} =$ 0.008022
divide by smallest	3.332	5.32	1.666
nearest whole number ratio	10	16	5

	Phosphorus	Oxygen
mass / g	0.1491	0.3337
moles	$\frac{0.1491}{30.97} =$ 0.004814	$\frac{0.3337}{16.00} =$ 0.02086
divide by smallest	1.000	4.333
nearest whole number ratio	3	13

Note:

- the mass for oxygen is obtained by subtracting all the masses of the other elements from 0.8138 g
- the nearest whole number ratio is obtained by multiplying by 3 to round everything up (numbers ending in '.33' and '.66' are the clue here).

The empirical formula is $C_{10}H_{16}N_5O_{13}P_3$. The formula mass of this is 507 g mol^{-1} so the empirical and molecular formulae are the same.

34 Moles of CO_2 $= \dfrac{0.66 \text{ g}}{(12.01 + (2 \times 16.00)) \text{ g mol}^{-1}}$
$= 0.015$ mol

- This is the same as the number of moles of carbon atoms present.

Moles of water $= \dfrac{0.36 \text{ g}}{(1.01 \times (2 + 16.00)) \text{ g mol}^{-1}}$
$= 0.020$ mol

- Twice this number is the number of moles of hydrogen atoms present, i.e. 0.040 mol.

Convert these into masses in order to find the mass of oxygen in the original sample:

mass of carbon = 0.015 mol × 12.01g mol^{-1}
= 0.18 g

mass of hydrogen = 0.040 mol × 1.01 g mol^{-1}
= 0.040 g

therefore mass of oxygen = 0.30 g – 0.18 g – 0.040 g = 0.08 g

Now the calculation can proceed as usual.

	Carbon	Hydrogen	Oxygen
mass / g	0.18	0.040	0.08
moles	$\frac{0.18}{12.01} =$ 0.015	$\frac{0.040}{1.01} =$ 0.040	$\frac{0.08}{16.00} =$ 0.005
divide by smallest	3	8	1
nearest whole number ratio	3	8	1

Empirical formula is C_3H_8O

35
- Weigh the chalk before and after the name has been written.
- Subtract the values to obtain the mass of chalk used.
- Calculate the number of moles of chalk used.

Let *y* = the mass of chalk used in g

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

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

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

Therefore the number of carbon atoms used =

moles of chalk × (6.02 × 10^{23} mol^{-1}) $\dfrac{6.20 \times 10^{23}\, y}{100.09}$

36 **(a)** From the stoichiometric equation 2 moles of iron can be made from 1 mole of iron oxide.

Hence 2 × 1.25 mol = 2.50 mol of iron can be made from 1.25 mol of iron oxide.

(b) From the stoichiometric equation 2 moles of iron need 3 moles of hydrogen.

Hence 3.75 mol of iron need $\frac{3}{2} \times 3.75$ mol = 5.63 mol of hydrogen.

(c) From the stoichiometric equation 3 moles of water are produced from 1 mole of iron oxide.

Hence 12.50 moles of water are produced from $\frac{1}{3} \times 12.50$ mol = 4.167 moles of iron oxide.

4.167 moles of iron oxide have a mass of 4.167 × $M_r(Fe_2O_3)$ = 4.167 mol × 159.70 g mol^{-1} = 665.5 g (= 665 g)

37 **(a)** Write the chemical equation:

$C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

Then balance the equation by deducing the appropriate numbers in front of the formulae:

$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

(b) From the equation 2 moles of butane produce 10 moles of water.

$\frac{2.46\text{ g}}{18.02\text{ g mol}^{-1}}$ = 0.137 moles of water were produced.

0.137 moles of water must have been made from $\frac{2}{10}$ × 0.137 = 0.0274 moles of butane.

0.0274 moles of butane has a mass of 0.0274 × $M_r(C_4H_{10})$ = 0.0274 mol × 58.14 g mol^{-1} = 1.59 g

38 From the equation, 1 mole of Al reacts with 1 mole of NH_4ClO_4

26.98 g of Al react with 14.01 + (4 × 1.01) + 35.45 + (4 × 16.00) = 117.50 g of NH_4ClO_4

Therefore 1000 g of Al react with $\frac{117.50}{26.98}$ × 1000 = 4355 g = 4.355 kg of NH_4ClO_4

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

(b) 0.657 g of CO_2 = $\frac{n}{M}$ = $\frac{0.657\text{ g}}{44.01\text{ g mol}^{-1}}$ = 0.0149 moles of CO_2

This was produced from 0.0149 moles of $CaCO_3$.

0.0149 moles of $CaCO_3$ has a mass of 0.0149 × $M_r(CaCO_3)$ = 0.0149 mol × 100.09 g mol^{-1}= 1.49 g

Therefore % of $CaCO_3$ in the impure limestone = $\frac{1.49\text{ g}}{1.605\text{ g}}$ × 100 = 92.8%

(c) Assumptions are:

- $CaCO_3$ is the only source of carbon dioxide
- all the $CaCO_3$ undergoes complete decomposition
- all CO_2 released is captured
- heating does not cause any change in mass of any of the other minerals present.

40 **(a)** moles of H_2 = $\frac{12.0\text{ g}}{2.02\text{ g mol}^{-1}}$ = 5.94 mol

moles of CO = $\frac{74.5\text{ g}}{28.01\text{ g mol}^{-1}}$ = 2.66 mol

As the CO reacts with H_2 in a 1 : 2 ratio, this means that the H_2 is in excess (2 × 2.66 mol = 5.32 mol).

2.66 mol of CO therefore produce 2.66 mol of CH_3OH.

This has a mass of 2.66 × $M_r(CH_3OH)$ = 2.66 mol × 32.05 g mol^{-1} = 85.2 g

(b) moles of H_2 in excess = 5.94 mol – (2 × 2.66) mol = 0.62 mol

This is equivalent to a mass of 0.62 mol × 2.02 g mol^{-1} = 1.3 g

41 moles of C_2H_4 = $\frac{15.40\text{ g}}{(2 \times 12.01) + (4 \times 1.01)\text{ g mol}^{-1}}$ = 0.5488 mol

moles of Cl_2 = $\frac{3.74\text{ g}}{(2 \times 35.45)\text{ g mol}^{-1}}$ = 0.0528 mol

As the reactants react in the ratio of 1 : 1, C_2H_4 is in excess.

moles of product formed = 0.0528 mol

mass of product formed = 0.0528 × $M_r(C_2H_4Cl_2)$ = 0.0528 mol × 98.96 g mol^{-1} = 5.23 g

42 moles of $CaCO_3$ = $\frac{255\text{ g}}{(40.08+12.01+(4\times16.00))\text{ g mol}^{-1}}$ = 2.55 mol

moles of SO_2 = $\frac{135\text{ g}}{(32.07 + (2 \times 16.00))\text{ g mol}^{-1}}$ = 2.11 mol

Therefore as they react in a 1 : 1 ratio, the number of moles of $CaSO_3$ produced = 2.11 mol

mass of $CaSO_3$ = 2.11 mol × (40.08 + 32.07 + (3 × 16.00)) g mol^{-1} = 254 g

Therefore percentage yield = $\frac{198\text{ g}}{254\text{ g mol}^{-1}}$ × 100 = 77.9%

43 moles of CH_3COOH used = $\frac{3.58\text{ g}}{((2 \times 12.01) + (4 \times 1.01) + (2 \times 16.00))\text{ g mol}^{-1}}$ = 0.0596 mol

moles of $C_5H_{11}OH$ = $\frac{4.75\text{ g}}{((5 \times 12.01) + (12 \times 1.01) + 16.00)\text{ g mol}^{-1}}$ = 0.0539 mol

Therefore $C_5H_{11}OH$ is the limiting reagent, so 0.0539 mol of $CH_3COOC_5H_{11}$ is the maximum that can form.

This will have a mass of 0.0539 × [(7 × 12.01) + (14 × 1.01) + (2 × 16.00)] g mol^{-1} = 7.01 g

This is the 100% yield, therefore 45% yield has a mass of 0.45 × 7.01 g = 3.16 g

44 100 g of C_6H_5Cl is equivalent to

$$\frac{100\ \text{g}}{((6 \times 12.01) + (5 \times 1.01) + 35.45)\ \text{g mol}^{-1}} =$$

0.888 mol

If this is 65% yield then 100% yield would be

$$0.888\ \text{mol} \times \frac{100}{65} = 1.37\ \text{mol}$$

1.37 moles of benzene has a mass of 1.37 mol × [(6 × 12.01) + (6 × 1.01)] g mol^{-1} = 107 g

45 **(a)** 1 mole of gas has a volume of 22.7 dm^3 at STP.

Therefore 54.5 dm^3 is equivalent to $\frac{54.5}{22.7}$ mol = 2.40 mol

(b) 1 mole of gas has a volume of 22.7 dm^3 at STP.

This is equivalent to 22.7 × 1000 cm^3 = 227 000 cm^3

Therefore 250.0 cm^3 of gas contains

$$\frac{250.0}{227\,000}\ \text{mol} = 1.10 \times 10^{-3}\ \text{mol}$$

(= 0.0110 mol)

(c) 1 mole of gas has a volume of 22.7 dm^3 at STP.

This is equivalent to 0.0227 m^3

1.0 m^3 of gas therefore contains $\frac{1.0}{0.0227}$ mol = 44 mol

46 **(a)** 44.00 g of N_2 is equivalent to

$$\frac{44.00\ \text{g}}{(2 \times 14.01)\ \text{g mol}^{-1}}\ \text{of } N_2 \text{ gas} = 1.57\ \text{mol}$$

1 mole of gas has a volume of 22.7 dm^3 at STP.

Therefore 1.57 mol has a volume of 35.6 dm^3

(b) 1 mole of gas has a volume of 22.7 dm^3 at STP.

Therefore 0.25 mol of ammonia has a volume of 5.7 dm^3

47 moles HgO = $\frac{12.45\ \text{g}}{(200.59 + 16.00)\ \text{g mol}^{-1}}$ = 0.0575 mol

On decomposition this would produce 0.0287 mol of oxygen (since 2 mol of HgO produces 1 mol of O_2).

1 mole of gas has a volume of 22.7 dm^3 at STP.

Therefore 0.0287 mol have a volume of 0.652 dm^3

48 Assume all measurements are made at STP.

3.14 dm^3 of bromine is equivalent to

$$\frac{3.14\ \text{dm}^3}{22.7\ \text{mol dm}^3} = 0.138\ \text{mol}\ Br_2$$

11.07 g of chlorine is equivalent to

$$\frac{11.07\ \text{g}}{(2 \times 35.45)\ \text{g mol}^{-1}} = 0.1561\ \text{mol}\ Cl_2$$

Therefore the sample of chlorine contains more molecules.

49 0.200 g calcium is $\frac{0.200\ \text{g}}{40.08\ \text{g mol}^{-1}}$ =

4.99×10^{-3} mol

4.99×10^{-3} mol of Ca will make 4.99×10^{-3} mol of hydrogen

4.99×10^{-3} mol of hydrogen will occupy 4.99×10^{-3} mol × 22.7 dm^3 mol^{-1} = 0.113 dm^3 (or 113 cm^3) at STP.

50 The first step, as usual, is to calculate how many moles of reactant we have.

1.0 g of ammonium nitrate is $\frac{1.0\ \text{g}}{80.06\ \text{g mol}^{-1}}$ = 0.012 mol

According to the balanced chemical equation, 0.012 mol of ammonium nitrate will produce 0.012 mol of dinitrogen oxide.

At STP, 1 mole of gas occupies 22.7 dm^3, so 0.012 mol will occupy 22.7 dm^3 mol^{-1} × 0.012 mol = 0.28 dm^3

51 Using $\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$

List all the data that is given in the question:

- P_1 = 85 kPa

- P_2 = ???
- $V_1 = 2.50\ \text{dm}^3$
- $V_2 = 2.75\ \text{dm}^3$
- $T_1 = 25\ °\text{C}\ (= 298\ \text{K})$
- $T_2 = 75\ °\text{C}\ (= 348\ \text{K})$

$$\frac{85\ \text{kPa} \times 2.50\ \text{dm}^3}{298\ \text{K}} = \frac{P_2 \times 2.75\ \text{dm}^3}{348\ \text{K}}$$

Rearranging and solving for P_2 gives the final pressure = 90 kPa

52 Using $\dfrac{P_1 \times V_1}{T_1} = \dfrac{P_2 \times V_2}{T_2}$

List all the data that is given in the question:

- $P_1 = 1.00 \times 10^5\ \text{Pa}$
- $V_1 = 675\ \text{cm}^3$
- T_1 = ???
- $P_2 = 2.00 \times 10^5\ \text{Pa}$
- $V_2 = 350\ \text{cm}^3$
- $T_2 = 27.0\ °\text{C}\ (= 300\ \text{K})$

$$\frac{(1.00 \times 10^5)\ \text{Pa} \times 675\ \text{cm}^3}{T_1} = \frac{(2.00 \times 10^5)\ \text{Pa} \times 350\ \text{cm}^3}{300\ \text{K}}$$

Rearranging and solving for T_1 gives initial temperature = 289 K = 16 °C

53 Using $\dfrac{P_1 \times V_1}{T_1} = \dfrac{P_2 \times V_2}{T_2}$

$$\frac{P_1 \times 4.0\ \text{dm}^3}{T_1} = \frac{4P_1 \times V_2}{3T_1}$$

Rearranging and solving for V_2 gives

$$V_2 = \frac{3 \times T_1 \times P_1 \times 4.0\ \text{dm}^3}{4 \times P_1 \times T_1} = 3.0\ \text{dm}^3$$

54 Using $M = \dfrac{mRT}{PV}$

List all the data that is given in the question:

- m = mass = 4.40 g
- $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
- T = temperature in K = (273 + 27) = 300 K
- P = pressure = 90 kPa = 90×10^3 kPa
- M = molar mass = (12.01 + (2 × 16.00)) g mol^{-1} = 44.01 g mol^{-1}

Rearranging for V gives

$$V = \frac{mRT}{PM}$$

$$V = \frac{4.40\ \text{g} \times 8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{90 \times 10^3\ \text{Pa} \times 44.01\ \text{g mol}^{-1}}$$

$$V = 2.8 \times 10^{-3}\ \text{m}^3\ (= 2.8\ \text{dm}^3)$$

55 At STP, 1 mole of the gas would occupy 22.7 dm^3

1 mole would have a molar mass of $5.84\ \text{g dm}^{-3} \times 22.7\ \text{dm}^3\ \text{mol}^{-1} = 133\ \text{g mol}^{-1}$

From section 6 of the IB data booklet, xenon is the noble gas with the closest molar mass, 131.29 g mol^{-1}

56 Using $M = \dfrac{mRT}{PV}$

List all the data that is given in the question:

- m = 12.1 mg = 0.0121 g
- $R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
- T = 25 °C = 298 K
- P = 1300 Pa
- $V = 255\ \text{cm}^3 = 255 \times 10^{-6}\ \text{m}^3$

$$M = \frac{0.0121\ \text{g} \times 8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{1300\ \text{Pa} \times 255 \times 10^{-6}\ \text{m}^3}$$

$$= 90.4\ \text{g mol}^{-1}$$

57 As density = $\dfrac{\text{mass}}{\text{volume}}$ for a fixed volume of gas, the density will depend on the formula mass of the element. Hydrogen has a formula mass of 2.02 g mol^{-1} and helium of 4.00 g mol^{-1}. Hence helium has the greater density.

58 The equation for the complete combustion of octane is:

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

1 mole of octane reacts with 12.5 moles of oxygen.

$M(C_8H_{18})$ = ((8 × 12.01) + (18 × 1.01)) g mol^{-1} = 114.26 g mol^{-1}

$$\text{moles of octane} = \frac{n}{M} = \frac{125\ \text{g}}{114.26\ \text{g mol}^{-1}} = 1.09\ \text{mol}$$

Therefore 1.09 mol of octane react with $1.09 \times \dfrac{25}{2}$ = 13.7 mol of oxygen

1 mol of gas occupies 22.7 dm^3, hence 13.7 mol occupy $13.7\ \text{mol} \times 22.7\ \text{dm}^3\ \text{mol}^{-1} = 311\ \text{dm}^3$

59 Using $M = \dfrac{mRT}{PV}$

List all the data that is given in the question:

- $m = 3.620$ g
- $R = 8.31$ J K^{-1} mol^{-1}
- $T = 25$ °C $= 298$ K
- $P = 99$ kPa $= 99 \times 103$ Pa
- $V = 1120$ $cm^3 = 1120 \times 10^{-6}$ m^3

$$M = \frac{3.620 \text{ g} \times 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{99 \times 10^3 \text{ Pa} \times 1120 \times 10^{-6} \text{ m}^3}$$

$= 80.8$ g mol^{-1}

	Oxygen	Sulfur
mass / g	2.172	1.448
moles	$\frac{2.172}{16.00} = 0.1357$	$\frac{1.448}{32.07} = 0.04515$
divide by smallest	3.01	1.00
nearest whole number ratio	3	1

Empirical formula = SO_3

Since this has an M_r of 80.07, the empirical and molecular formulae must be the same.

60 At higher altitude the external pressure is less. As the air in the tyre expands on heating, due to friction with the road surface, the internal pressure increases. (This can be a much greater problem during a descent when friction from the brakes on the wheel rim causes the tyre to heat up further.)

61 **(a)**

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

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

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

63 **B** Ideal gases are assumed to have no attractive forces between the particles; however, gases are not ideal.

64 number of moles required = concentration × volume

$= 0.200$ mol $dm^{-3} \times 0.250$ dm^3 (1 $dm^3 = 1000$ cm^3)

$= 0.0500$ mol

Formula of potassium hydroxide is KOH. (You should know that the ions are K^+ and OH^-.)

Molar mass of KOH = (39.10 + 16.00 + 1.01) g mol^{-1} = 56.11 g mol^{-1}

Mass of 0.0500 mol of KOH = 0.0500 mol × 56.11 g mol^{-1} = 2.81 g

65 $MgSO_4.7H_2O$ has a molar mass of (24.31 + 32.07 + 11 × 16.00 + 14 × 1.01) g mol^{-1} = 246.52 g mol^{-1}

0.100 dm^3 of a 0.200 mol dm^{-3} solution contains 0.100 × 0.200 g mol^{-1} = 0.0200 mol of solute

0.0200 mol of $MgSO_4.7H_2O$ has a mass of 0.0200 mol × 246.52 g mol^{-1} = 4.93 g

66 In 0.250 dm^3 of 0.0200 mol dm^{-3} of solution there are 0.250 × 0.0200 = 0.00500 mol of solute

For every mole of $ZnCl_2$, two moles of chloride ions are released in solutions:

$ZnCl_2(s) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq)$

so, 0.00500 mol of $ZnCl_2$ will give 0.0100 mol of chloride ions in solution

67 250 cm^3 of solution contain 5.85 g of sodium chloride

1 dm^3 of solution contains 5.85 g = $\dfrac{1000 \text{ cm}^3}{250 \text{ cm}^3}$ = 23.40 g of sodium chloride

23.40 g of NaCl is equivalent to $\dfrac{23.40 \text{ g}}{(22.99 + 35.45) \text{ g mol}^{-1}} = 0.400$ mol

Hence concentration is 0.400 mol dm^{-3}

68 100 cm^3 of 0.50 mol dm^{-3} nitric acid contains 0.050 moles of acid volume of 16.0 mol dm^{-3} acid to contain this number of moles $= \frac{n}{c} = \frac{0.050 \text{ mol}}{16.0 \text{ mol dm}} = 3.1 \times 10^{-3}$ dm^3 = 3.1 cm^3

69 $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

moles of NaOH = cV = 0.147 mol dm^{-3} × $\frac{36.42}{1000}$ dm^3 = 5.35 × 10^{-3} mol

As this reacts with the sulfuric acid in a 2 : 1 ratio, the number of moles of sulfuric acid present = 2.68 × 10^{-3} mol

Hence concentration of sulfuric acid $= \frac{n}{V} = \frac{2.68 \times 10^{3} \text{ mol}}{\left(\frac{15.00}{1000}\right) \text{dm}^3} = 0.178 \text{ mol dm}^{-3}$

70 moles of KOH used in titration = cV = 0.0100 mol dm^{-3} × $\frac{11.00}{1000}$ dm^3 = 1.10 × 10^{-4} mol

Since KOH reacts with HCl in a 1:1 ratio, moles of HCl = 1.10 × 10^{-4} mol

$$\text{Concentration of HCl} = \frac{n}{V} = \frac{1.10 \times 10^{-4} \text{ mol}}{\left(\frac{5.00}{1000}\right) \text{dm}^3}$$
$$= 0.0220 \text{ mol dm}^{-3}$$

$$\text{Molar mass of HCl} = (1.01 + 35.45) \text{ g mol}^{-1}$$
$$= 36.46 \text{ g mol}^{-1}$$

Quantity of HCl is equivalent to 36.46 × 0.0220 = 0.802 g dissolved in 1 dm^3

Concentration of HCl in g dm^{-3} = 0.0220 mol dm^{-3} × 36.46 g mol^{-1} = 0.802 g dm^{-3}

Therefore in 1.00 cm^3 there would be 0.000802 g of HCl

Assuming a density of 1.00 g cm^{-3} a 1.00 cm^3 sample of solution has a mass of 1.00 g

$$\%\text{HCl} = \frac{\text{mass HCl}}{\text{mass solution}} \times 100$$
$$= \frac{0.000802 \text{ g}}{1.00 \text{ g}} \times 100 = 0.0802\%$$

71 $Na_2SO_4(aq) + Pb(NO_3)_2(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$

First determine the moles of $PbSO_4$ formed in the reaction:

$$n(PbSO_4) = m/M(PbSO_4) = \frac{1.13 \text{ g}}{303.25 \text{ g mol}^{-1}}$$
$$= 3.73 \times 10^{-3} \text{ mol}$$

From the balanced equation:

$n(PbSO_4)$ formed = $n(Pb(NO_3)_2)$ reacted = $n(Na_2SO_4)$ reacted = 3.73 × 10^{-3} mol

$$[Pb(NO_3)_2] = \frac{n}{V} = \frac{3.73 \times 10^{-2} \text{ mol}}{(32.50/1000) \text{ dm}^3}$$
$$= 0.115 \text{ mol dm}^{-3}$$

$$[Na_2SO_4] = \frac{n}{V} = \frac{3.73 \times 10^{-3} \text{ mol}}{(35.30/1000) \text{ dm}^3}$$
$$= 0.106 \text{ mol dm}^{-3}$$

Two assumptions are:

(i) No side reactions occur that generate other products.

(ii) All of the $PbSO_4$ formed precipitates out as a solid and can be weighed.

Practice questions

Questions 1–17 are multiple-choice questions similar to those in Paper 1 of the IB examinations. As calculators are not allowed in Paper 1 it is appropriate for whole-number values to be used for molar masses. Any relevant constants can also be rounded where appropriate to make the calculations simpler.

1 One mole of $CuSO_4.5H_2O$ will contain 9 moles of oxygen atoms.

0.100 moles of $CuSO_4.5H_2O$ will contain 0.900 moles of oxygen atoms.

0.900 moles = 0.900 × N_A atoms = 0.900 × 6.02 × 10^{23} atoms = 5.42 × 10^{23} atoms.

Correct answer is D.

2 The balanced equation is $Fe_2O_3(s) + \underline{\mathbf{3}}CO(g) \rightarrow \underline{\mathbf{2}}Fe(s) + \underline{\mathbf{3}}CO_2(g)$.

Sum of coefficients = 1 + 3 + 2 + 3 = 9.

Correct answer is D.

3 We can assume that the gases are all ideal gases. This means that under the same conditions of pressure, volume and temperature, they all contain the same amount of gas molecules.

The heaviest container will therefore contain the gas with the largest molar mass.

Nitrogen: $M(N_2) = 2 \times 14\ \text{g mol}^{-1} = 28\ \text{g mol}^{-1}$

Oxygen: $M(O_2) = 2 \times 16\ \text{g mol}^{-1} = 32\ \text{g mol}^{-1}$

Ethane: $M(C_2H_6) = (2 \times 12) + (6 \times 1)\ \text{g mol}^{-1}$
$= 30\ \text{g mol}^{-1}$

Neon: $M(Ne) = 20\ \text{g mol}^{-1}$

Oxygen has the largest molar mass so the heaviest container will be B.

Correct answer is B.

4 This can be solved by converting temperatures from degrees Celsius to Kelvin and applying Charles' Law, $\frac{V}{T}$ = constant:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{1.0\ \text{dm}^3 \times 323\ \text{K}}{298\ \text{K}} = 1.1\ \text{dm}^3$$

Correct answer is C.

5 $n(FeSO_4) = cV = 0.020\ \text{mol dm}^{-3} \times \frac{100}{1000}\ \text{dm}^3$

$= 0.0020\ \text{mol} = 2.0 \times 10^{-3}\ \text{mol}$

$n(SO_4^{2-}) = n(FeSO_4) = 2.0 \times 10^{-3}\ \text{mol}$

Correct answer is A.

6 To calculate a concentration we first need to convert the mass of $NaNO_3$ to moles using the M_r of 85 provided for $NaNO_3$:

$$n(NaNO_3) = \frac{1.7\ \text{g}}{85\ \text{g mol}^{-1}} = 0.020\ \text{mol}$$

$$[NaNO_3] = \frac{n}{V} = \frac{0.020\ \text{mol}}{0.20\ \text{dm}^3} = 0.10\ \text{mol dm}^{-3}$$

Correct answer is B.

7 From the balanced equation provided in the question:

$n(H_2)$ produced $= \frac{3}{2}n(Al)$ reacted

If 3 mol of Al reacts, the amount of H_2 produced $= \frac{3}{2} \times 3\ \text{mol} = 4.5\ \text{mol}$.

$m(H_2) = nM(H_2) = 4.5\ \text{mol} \times 2\ \text{g mol}^{-1} = 9.0\ \text{g}$

Correct answer is D.

8 Based on the empirical formula of the gas, CH_2, the relative formula mass can be calculated:

relative formula mass $(CH_2) = 12 + (2 \times 1) = 14$

Dividing the relative molar mass by the relative formula mass gives us the multiplier, x, that must be applied to the empirical formula to give the molecular formula:

$$x = \frac{\text{relative molecular mass}}{\text{relative formula mass}} = \frac{56}{14} = 4$$

Molecular formula = '$4 \times CH_2$' = C_4H_8

Correct answer is D.

9 The balanced equation is $\underline{\mathbf{2}}C_2H_2 + \underline{\mathbf{5}}O_2(g) \rightarrow \underline{\mathbf{4}}CO_2(g) + \underline{\mathbf{2}}H_2O$.

Sum of coefficients = 2 + 5 + 4 + 2 = 13

Correct answer is D.

10 1 mole of benzamide, $C_6H_5CONH_2$, will contain 7 moles of hydrogen atoms.

1.0 moles of $C_6H_5CONH_2$ will contain 7.0 moles of hydrogen atoms.

7.0 moles $= 7.0 \times (6.02 \times 10^{23})$ atoms
$= 4.2 \times 10^{24}$ atoms

Correct answer is D.

11 O_2 is the limiting reagent as 10.0 mol of C_2H_3Cl would require 25.0 mol of O_2.

From the balanced equation, $n(H_2O) = \frac{2}{5}n(O_2)$.

If 10.0 mol of O_2 reacts the amount of H_2O produced $= \frac{2}{5} \times 10.0\ \text{mol} = 4.00\ \text{mol}$.

Correct answer is A.

12 We first calculate the total number of moles of NaCl present in the two solutions:

$n(\text{total}) = n(\text{solution 1}) + n(\text{solution 2})$

$= c_1V_1 + c_2V_2$

$= (0.200\ \text{mol dm}^{-3} \times \frac{10.0}{1000}\ \text{dm}^3) + (0.600\ \text{mol dm}^{-3} \times \frac{30.0}{1000}\ \text{dm}^3)$

$= 0.00200\ \text{mol} + 0.0180\ \text{mol}$

$= 0.0200\ \text{mol}$

$$[NaCl] = \frac{n}{(V_1 + V_2)} = \frac{0.0200\ \text{mol}}{\frac{(10.0 + 30.0)}{1000}\ \text{dm}^3}$$

$$= \frac{0.0200\ \text{mol}}{0.0400\ \text{dm}^3} = 0.500\ \text{mol dm}^{-3}$$

Correct answer is C.

13 Determine the empirical formula of the compound.

	C	H	O
Mass (g)	12	2	16
Moles	$\frac{12\text{ g}}{12\text{ g mol}^{-1}}$	$\frac{2\text{ g}}{1\text{ g mol}^{-1}}$	$\frac{16\text{ g}}{16\text{ g mol}^{-1}}$
	= 1.0	= 2.0	= 1.0

Empirical formula = CH_2O

$$\text{Formula mass }(CH_2O) = (12 + (2 \times 1) + 16)\text{ g mol}^{-1} = 30\text{ g mol}^{-1}$$

Dividing the molar mass by the formula mass gives us the multiplier, *x*, that must be applied to the empirical formula to give the molecular formula:

$$x = \frac{\text{relative molecular mass}}{\text{relative formula mass}} = \frac{60\text{ g mol}^{-1}}{30\text{ g mol}^{-1}} = 2$$

Molecular formula = ‘2 × CH_2O’ = $C_2H_4O_2$

Correct answer is D.

14 We can calculate the final concentration, c_2, using the dilution formula $c_1V_1 = c_2V_2$.

$$c_2 = \frac{c_1\,V_1}{V_2} = \frac{0.5\text{ mol dm}^{-3} \times 200\text{ cm}^3}{(200 + 300)\text{ cm}^3}$$
$$= \frac{0.5\text{ mol dm}^{-3} \times 200\text{ cm}^3}{500\text{ cm}^3} = 0.2\text{ mol dm}^{-3}$$

Correct answer is C.

15 The question asks for an approximate value so we can use whole numbers for the atomic masses of the constituent elements of $MgSO_4.7H_2O$:

$M(MgSO_4.7H_2O) = (24 + 32 + (4 \times 16) + (14 \times 1) + (7 \times 16))\text{ g mol}^{-1} = 246\text{ g mol}^{-1}$

Correct answer is D.

16 For a molecular formula to also be an empirical formula it cannot be converted to a simpler ratio. With the exception of C_5H_{12} all of the formulas provided can be simplified.

$C_5H_{10} \rightarrow CH_2$ $\quad C_4H_8 \rightarrow CH_2$ $\quad C_4H_{10} \rightarrow C_2H_5$

Correct answer is A.

17 **(a)** Temperature is 25.00 °C. This has **four** significant figures.

Mass is 0.0650 kg. This has **three** significant figures.

Pressure is 1.08 atm. This has **three** significant figures.

(b) $n(NaN_3) = \frac{m}{M(NaN_3)} = \frac{65.0\text{ g}}{65.02\text{ g mol}^{-1}} = 1.00\text{ mol}$

(c) From the balanced equation, $n(N_2) = \frac{3}{2}n(NaN_3) = \frac{3}{2} \times 1.00\text{ mol} = 1.50\text{ mol}$.

We can calculate the volume of $N_2(g)$ produced using the ideal gas equation, $PV = nRT$, recognizing that temperature must be converted to K and pressure to Pa:

25.00 °C = (25.00 + 273.15) K = 298.15 K

$$1.08\text{ atm} = 1.08 \times (1.01 \times 10^5)\text{ Pa} = 1.09 \times 10^5\text{ Pa}$$

$$V = \frac{nRT}{P} = \frac{1.50\text{ mol} \times 8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 298.15\text{ K}}{1.09 \times 10^5\text{ Pa}} =$$

$0.0341\text{ m}^3 = (0.0341 \times 1000)\text{ dm}^3 = 34.1\text{ dm}^3$

18 **(a)** The amount of C present in **J** can be found from the mass of CO_2 formed in the combustion reaction:

$$n(CO_2) = \frac{m}{M(CO_2)} = \frac{0.872\text{ g}}{44.01\text{ g mol}^{-1}} = 0.0198\text{ mol}$$

$n(C) = n(CO_2) = 0.0198\text{ mol}$

$$\text{mass of C} = nM = 0.0198\text{ mol} \times 12.01\text{ g mol}^{-1} = 0.238\text{ g}$$

$$\%\text{ mass of C in } \mathbf{J} = \frac{0.238\text{ g}}{1.30\text{ g}} \times 100\% = 18.3\%$$

The amount of H present in **J** can be found from the mass of H_2O formed in the combustion reaction:

$$n(H_2O) = \frac{m}{M(H_2O)} = \frac{0.089\text{ g}}{18.02\text{ g mol}^{-1}} = 0.0049\text{ mol}$$

$$n(H) = 2 \times n(H_2O) = 2 \times 0.0049\text{ mol} = 0.0098\text{ mol}$$

$$\text{mass of H} = nM = 0.0098\text{ mol} \times 1.01\text{ g mol}^{-1} = 0.0099\text{ g}$$

$$\%\text{ mass of H in } \mathbf{J} = \frac{0.0099\text{ g}}{1.30\text{ g}} \times 100\%$$
$$= 0.76\%$$

(An answer of 0.77% is also acceptable. This value is obtained if the calculation is performed in a single step and no rounding error is introduced.)

(b) The amount of Cl present in **J** can be found from the mass of AgCl formed in the precipitation reaction:

$$n(\text{AgCl}) = \frac{m}{M(\text{AgCl})} = \frac{1.75\text{ g}}{143.32\text{ g mol}^{-1}}$$
$$= 0.0122\text{ mol}$$

$n(\text{Cl}) = n(\text{AgCl}) = 0.0122\text{ mol}$

$$\text{mass of Cl} = nM = 0.0122\text{ mol} \times 35.45\text{ g mol}^{-1}$$
$$= 0.432\text{ g}$$

$$\%\text{ mass of Cl in } \mathbf{J} = \frac{0.432\text{ g}}{0.535\text{ g}} \times 100\%$$
$$= 80.7\%$$

(An answer of 80.9% is also acceptable. This value is obtained if the calculation is performed in a single step and no rounding error is introduced.)

(c) We can determine the empirical formula using the % compositions obtained in part (b) and the mass that would be in a 100 g sample of **J**.

	C	H	O
Mass/g	18.3	0.76	80.7
M/g mol^{-1}	12.01	1.01	16.00
Number of moles/mol	1.52	0.75	2.28
Divide by smallest	2.03	1.0	3.04
Nearest whole number ratio	2	1	3

Empirical formula of **J** = C_2HCl_3

The formula mass of C_2HCl_3 = (2 × 12.01) + 1.01 + (3 × 35.45) g mol^{-1} = 131.38 g mol^{-1}.

As the formula mass calculated for the empirical formula is the same as the molar mass given in the question the molecular formula of J is confirmed as C_2HCl_3.

19 We can determine which gas is in excess based on the assumption that they are ideal gases and therefore the volumetric ratios are the same as the molar ratios.

From the balanced equation, $n(\text{NO}) = 1.5n(\text{NH}_3)$

Therefore assuming ideal gases, $V(\text{NO}) = 1.5V(\text{NH}_3)$

30.0 dm^3 of NH_3 would require 1.5 × 30 cm^3 of NO = 45.0 dm^3 of NO

As there are only 30.0 dm^3 of NO it is the limiting reactant and NH_3 is in excess.

We can determine how much NH_3 reacts with 30.0 dm^3 of NO:

$$V(\text{NH}_3) = \frac{V(\text{NO})}{1.5} = \frac{30.0\text{ dm}^3}{1.5} = 20.0\text{ dm}^3$$

$$\text{The volume of excess NH}_3 = 30.0\text{ dm}^3 - 20.0\text{ dm}^3$$
$$= 10.0\text{ dm}^3$$

Using the balanced equation, the volume of N_2 produced can be determined from the volume of NO reacted:

$$V(\text{N}_2) = \frac{5}{6}V(\text{NO}) = \frac{5}{6} \times 30.0\text{ dm}^3 = 25.0\text{ dm}^3$$

20 **(a)** $n(\text{HCl}) = c \times V = 0.200\text{ mol dm}^{-3} \times \frac{27.20}{1000}\text{ dm}^3$

$$= 0.00544\text{ mol}$$

(b) We need to write the balanced equation for the neutralization of HCl(aq) with NaOH(aq):

$$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$

From the balanced equation, $n(\text{HCl}) = n(\text{NaOH})$:

$$n(\text{NaOH}) = cV = 0.100\text{ mol dm}^{-3} \times \frac{23.80}{1000}\text{ dm}^3$$
$$= 0.00238\text{ mol}$$

$n(\text{HCl})$ in excess = 0.00238 mol

(c) The amount of HCl that reacted with the calcium carbonate in the eggshell is found from the difference between the original HCl added and the excess HCl that then reacted with the NaOH:

$$n(\text{HCl reacted}) = 0.00544\text{ mol} - 0.00238\text{ mol}$$
$$= 0.00306\text{ mol}$$

(d) $2\text{HCl(aq)} + \text{CaCO}_3\text{(s)} \rightarrow \text{CaCl}_2\text{(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$

An acceptable alternative that omits spectator ions is:

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

(e) From the balanced equation in (d) the amount of $CaCO_3$ can be determined based on the amount of HCl that reacts:

$$n(CaCO_3) = \frac{1}{2}\, n(\text{HCl reacted})$$
$$= \frac{1}{2} \times 0.00306 \text{ mol} = 0.00153 \text{ mol}$$

(f) $m(CaCO_3) = nM(CaCO_3) = 0.00153 \text{ mol} \times 100.09 \text{ g mol}^{-1} = 0.153 \text{ g}$

$$\% \; CaCO_3 \text{ in eggshell} = \frac{\text{mass of } CaCO_2}{\text{mass of eggshell}} \times 100\% = \frac{0.153 \text{ g}}{0.188 \text{ g}} \times 100\% = 81.4\%$$

(g) The main assumption is that $CaCO_3$ is the only component of the eggshell that reacts with HCl, i.e. there are no basic impurities present in the eggshell that would also react with HCl.

21 We first need to determine the number of moles of AgCl solid that were precipitated:

$$n(AgCl) = \frac{m}{M(AgCl)} = \frac{6.127 \text{ g}}{143.32 \text{ g mol}^{-1}}$$
$$= 0.04275 \text{ mol}$$

$n(Cl^-) = n(AgCl) = 0.04275$ mol

We can now solve this problem using simultaneous equations:

Let x = mass of NaCl in g

Let y = mass of $CaCl_2$ in g

$x + y = 2.450$ (1)

We can determine a second equation based on the number of moles of Cl^- in the two solids along with the total number of moles of Cl^- in the precipitate:

$n(Cl^- \text{ from NaCl}) + n(Cl^- \text{ from } CaCl_2) = 0.04275$

$$\frac{x}{M(NaCl)} + 2\left(\frac{y}{M(CaCl_2)}\right) = 0.04275$$

$$\frac{x}{58.44} + 2\left(\frac{y}{110.98}\right) = 0.04275 \qquad (2)$$

Applying simultaneous equations:

$x + y = 2.450$ (1)

$$\frac{x}{58.44} + 2\left(\frac{y}{110.98}\right) = 0.04275 \qquad (2)$$

(2) × 58.44 $\quad x + 1.053y = 2.498$ (2′)

(2′) – (1) $\quad 0.053y = 0.048$

$$y = \frac{0.048}{0.053}$$
$$= 0.91$$

Subbing y into (1) $\quad x + 0.91 = 2.450$

$x = 1.54$

The sample contains 1.54 g of NaCl and 0.91 g of $CaCl_2$.

$$\% \text{ NaCl} = \frac{\text{mass NaCl}}{\text{total mass}} \times 100\% = \frac{1.54 \text{ g}}{2.450 \text{ g}} \times 100\% = 62.9\%$$

$$\% \; CaCl_2 = \frac{\text{mass } CaCl_2}{\text{total mass}} \times 100\% = \frac{0.91 \text{ g}}{2.450 \text{ g}} \times 100\% = 37.1\%$$

22 **(a)** We first find the mass of water that was removed in drying the potassium carbonate:

$m(H_2O) = m(\text{hydrated } K_2CO_3) - m(\text{dry } K_2CO_3)$

$= 10.00 \text{ g} - 7.93 \text{ g}$

$= 2.07 \text{ g}$

$$n(H_2O) = \frac{m}{M(H_2O)} = \frac{2.07 \text{ g}}{18.02 \text{ g mol}^{-1}}$$
$$= 0.115 \text{ mol}$$

(b) $$n(K_2CO_3) = \frac{m}{M(K_2CO_2)} = \frac{7.93 \text{ g}}{138.21 \text{ g mol}^{-1}}$$
$$= 0.0574 \text{ mol}$$

(c) We can determine the value of x in the hydrated potassium carbonate:

$$x = \frac{n(H_2O \text{ removed})}{n(\text{dry } K_2CO_2)} = \frac{0.115 \text{ mol}}{0.0574 \text{ mol}} = 2.00$$

Therefore the formula of the hydrate is $K_2CO_3.2H_2O$

(d) By repeating the process of heating and weighing until a constant mass is obtained. (To ensure accurate results it will be necessary to cool the sample to room temperature before each weighing.)

23 **(a)** We can determine the moles of each reactant using the ideal gas law, $PV = nRT$, recognizing that temperature must be converted to K, pressure to Pa and volume to m^3.

For ammonia gas:

$T = (42 + 273)\ \text{K} = 315\ \text{K},\ P = 160 \times 10^3\ \text{Pa},$

$$V = \frac{625}{1 \times 10^6}\ \text{m}^3 = 6.25 \times 10^{-4}\ \text{m}^3$$

$$n(\text{NH}_3) = \frac{PV}{RT} = \frac{160\ 000\ \text{Pa} \times 6.25 \times 10^4\ \text{m}^3}{8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 315\ \text{K}}$$

$$= 0.0382\ \text{mol}$$

For hydrogen chloride gas:

$T = (57 + 273)\ \text{K} = 330\ \text{K},\ P = 113.3 \times 10^3$ Pa, $V = \frac{740}{1 \times 10^6}\ \text{m}^3 = 7.40 \times 10^{-4}\ \text{m}^3$

$$n(\text{HCl}) = \frac{PV}{RT} = \frac{113\ 300\ \text{Pa} \times 7.40 \times 10^4\ \text{m}^3}{8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 330\ \text{K}}$$

$$= 0.0306\ \text{mol}$$

Therefore ammonia gas (NH_3) is in excess.

(b) If ammonia gas is in excess then the hydrogen chloride gas (HCl) is limiting.

(c) The balanced equation for the reaction is $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$.

From this equation, $n(NH_4Cl) = n(HCl) =$ 0.0306 mol.

$$m(\text{NH}_4\text{Cl}) = nM(\text{NH}_4\text{Cl})$$
$$= 0.0306\ \text{mol} \times 53.50\ \text{g mol}^{-1}$$
$$= 1.64\ \text{g}$$

24 **(a)** $2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$

(b) $2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$

The terms in red indicate those of interest to the question.

Mole ratio $2PbS:2SO_2 = 1:1$

$$M(\text{PbS}) = 207.19 + 32.06$$
$$= 239.25\ \text{g mol}^{-1}$$

$$M(\text{SO}_2) = 32.06 + (16.00 \times 2)$$
$$= 64.06\ \text{g mol}^{-1}$$

Therefore 239.25 g PbS → 64.06 g SO_2

$$\text{So 1 tonne PbS} \rightarrow \frac{1\ \text{tonne} \times 64.06\ \text{g}}{239.25\ \text{g}}$$

$$= 0.268\ \text{tonne} = 0.268 \times 10^3\ \text{kg} = 268\ \text{kg}$$

(c) The calculation assumes that PbS is the limiting reactant and so is fully reacted in the presence of excess oxygen. It also assumes that the only reaction occurring is the production of PbO and SO_2.

25 **(a)** $2Al(s) + 3CuSO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3Cu(s)$

(b) $2Al(s) + 3CuSO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3Cu(s)$

The question is about the reacting ratio of the terms in red.

Mole ratio $2Al:3CuSO_4$ so $\frac{x}{2} = \frac{10.38}{3}$

x mol:10.38 mol

$x = 6.920$ mol Al

(c) $2Al(s) + 3CuSO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3Cu(s)$

Mole ratio $3CuSO_4:3Cu = 1:1$

Therefore 3.95 mol Cu is produced from 3.95 mol $CuSO_4$.

Note this question only asks for amounts in moles so it is not necessary to calculate the molar masses of the reactants and products.

(d) The colour changes that occur when metals react with solutions of other metal ions will become familiar after you have studied redox reactions in Chapter 9.

Challenge yourself

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

2 We can determine which compounds are hydrated by comparing the molar masses provided in the photograph with the calculated molar masses for the unhydrated compounds.

Compound	Mass shown in photograph	Calculated molar mass	Hydrated or unhydrated
potassium iodide (KI)	166.0 g mol^{-1}	166.0 g mol^{-1}	unhydrated
sodium chloride (NaCl)	58.5 g mol^{-1}	58.5 g mol^{-1}	unhydrated

Compound	Mass shown in photograph	Calculated molar mass	Hydrated or unhydrated
potassium manganate(VII) ($KMnO_4$)	158.0 g mol^{-1}	158.0 g mol^{-1}	unhydrated
iron(III) chloride ($FeCl_3$)	270.3 g mol^{-1}	162.2 g mol^{-1}	hydrated
copper(II) sulfate ($CuSO_4$)	249.7 g mol^{-1}	159.6 g mol^{-1}	hydrated
cobalt(II) nitrate ($Co(NO_3)_2$)	291.0 g mol^{-1}	183.0 g mol^{-1}	hydrated

Iron(III) chloride, copper(II) sulfate and cobalt(II) nitrate are hydrated.

Formulas of hydrated compounds

Mass of H_2O in one mole of hydrated $FeCl_3$ = 270.3 g – 162.2 g = 108.1 g

$$n(H_2O) = \frac{m}{M(H_2O)} = \frac{108.1 \text{ g}}{18.02 \text{ g mol}^{-1}} \approx 6$$

In 1 mole of hydrated iron(III) chloride there are 6 moles of water, therefore the formula of hydrated iron(III) chloride is $FeCl_3.6H_2O$.

Applying the same working to the hydrated copper(II) sulfate and cobalt(II) nitrate gives the formulas $CuSO_4.5H_2O$ and $Co(NO_3)_2.6H_2O$.

3 From the information box on page 24 we can see that a N-P-K rating of 18-51-20 means the fertilizer is 18% N, 51% P_2O_5 and 20% K_2O.

$$\% \text{ P} = \frac{2 \times M_r(\text{P})}{M_r(\text{P}_2\text{O}_5)} \times \% \text{ P}_2\text{O}_5$$

$$= \frac{2 \times 30.07}{(2 \times 30.07 + 5 \times 16.00} \times 51 = 0.436 \times 51$$

$$= 22\%$$

$$\% \text{ K} = \frac{2 \times M_r(\text{K})}{M_r(\text{K}_2\text{O})} \times \% \text{ K}_2\text{O}$$

$$= \frac{2 \times 39.10}{(2 \times 39.10 \text{ g} + 16.00} \times 20 = 0.830 \times 20$$

$$= 17\%$$

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

4 Many reactions with ‘useless’ by-products could have a high stoichiometric yield under optimum conditions, but low atom economy, for example the production of methanoic acid from the reaction of sodium methanoate and sulfuric acid:

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

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

$$\% \text{ atom economy} = \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100\%$$

$$= \frac{2 \times M(\text{HCOOH})}{2 \times M(\text{NaHCOO}) + M(\text{H}_2\text{SO}_4)} \times 100\%$$

$$= \frac{2 \times 46.03}{2 \times 68.01 + 98.08} \times 100\%$$

$$= 39.33\%$$

5 From the information on page 33, the main reaction in an airbag is the conversion of sodium azide, NaN_3, to nitrogen gas, N_2. Recognizing that solid sodium must be the other product gives the balanced equation:

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

Sodium metal is hazardous so it is converted to sodium oxide, Na_2O, through reaction with potassium nitrate, KNO_3:

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

The oxides formed in the above reaction are then reacted with silicon dioxide to form the harmless silicate $Na_2K_2SiO_4$ (alkaline silicate glass):

$$K_2O(s) + Na_2O(s) + SiO_2(s) \rightarrow Na_2K_2SiO_4$$

6 As NaOH dissolves, the separated Na^+ and OH^- ions become hydrated due to the polar H_2O molecules being attracted to the charge on the ions and surrounding them. This attraction to the ions disrupts the hydrogen bonding between the H_2O molecules and allows for closer packing of the H_2O molecules in the NaOH solution, which reduces the volume of the solution.

Worked solutions

Chapter 2

Exercises

1
- density (mass per unit volume)
- rate of diffusion (the lighter isotope would diffuse slightly faster)

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

3
- The number of protons is the same as the atomic number and is found from the Periodic Table.
- The number of neutrons is the mass number (as given in the question) minus the number of protons.
- The number of electrons is the number of protons minus the charge (as given in the question). For $^{19}F^{-}$, for example, this is 9 – (–1) = –10.

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

4
- Use the number of protons to identify the element, via the atomic number in the Periodic Table.
- Add the number of neutrons to the number of protons to give the mass number.
- The charge is the difference between the number of protons and the number of electrons.

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

5 **C** Organizing your answer in a table will help with a question like this:

	Species	No. of protons*	No. of neutrons**	No. of electrons***
A	$^{2}_{1}H$	1	2 – 1 = 1	1 – 0 = 1
B	$^{11}_{5}B$	5	11 – 5 = 6	5 – 0 = 5
C	$^{16}_{8}O^{2-}$	8	16 – 8 = 8	8 – (–2) = 10
D	$^{19}_{9}F^{-}$	9	19 – 9 = 10	9 – (–1) = 10

*Taken from the question (but also in the Periodic Table).

**The mass number minus the atomic (proton) number.

***Subtract the charge from the proton number.

Only **C** has more electrons (10) than neutrons (8).

6 **B** $^{71}Ga^{+}$ must have 31 protons (information from the Periodic Table) and 40 neutrons (since these add up to 71, the atomic mass). A neutral gallium atom would have 31 electrons, so therefore Ga^{+} must have 30 electrons.

7 **B** These are isotopes, so the mass numbers (26 and 27) and therefore the neutron numbers (11 and 12) differ. It is the atomic number that is the same, meaning that the number of protons and number of electrons are the same.

8 The relative atomic mass of neon is 20.18, according to the Periodic Table in the IB data booklet.

If the percentage of neon-20 is x then in 100 moles of neon there will be x moles of neon-20 and $(100 - x)$ moles of neon-22.

x moles of neon-20 have a mass of $20x$ g

$(100 - x)$ moles of neon-22 have a mass of $22 \times (100 - x)$ g

The mass of 100 moles of neon is $20x + (22 \times (100 - x))$ g

$= 20x + 2200 - 22x$

$= 2200 - 2x$

The molar mass of neon is $20.18 = \dfrac{\text{mass}}{\text{number of moles}}$

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

multiply both sides by 100 and rearrange …

$2018 = 2200 - 2x$

$2x = 2200 - 2018$

$x = 91\%$

The abundance of ^{20}Ne is 91%.

9 Chlorine has two isotopes: ^{35}Cl, which has an approximate relative abundance of 0.75 (75%), and ^{37}Cl, which has an approximate percentage abundance of 0.25 (25%).

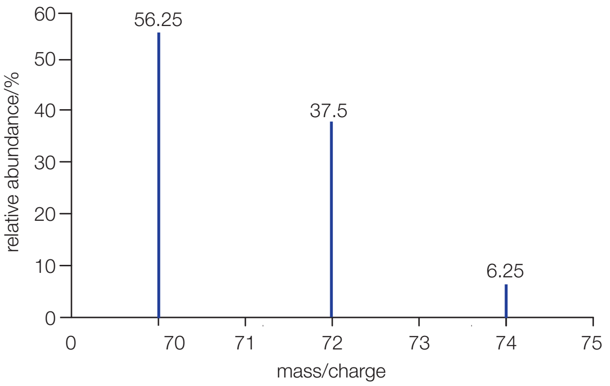
There are therefore four combinations of these isotopes that can occur in a Cl_2 molecule: ^{35}Cl/^{35}Cl (relative mass = 70), ^{35}Cl/^{37}Cl (relative mass = 72), ^{37}Cl/^{35}Cl (relative mass = 72) and ^{37}Cl/^{37}Cl (relative mass = 74).

The mass spectrum of Cl_2 will show three peaks at *m*/*z* values of 70, 72 and 74. The intensities of these peaks will be related to the percentage abundancies of the combinations.

Relative abundance of ^{35}Cl/^{35}Cl = 0.75 × 0.75 = 0.5625 (56.25%)

Relative abundance of ^{35}Cl/^{37}Cl and ^{37}Cl/^{35}Cl = 0.75 × 0.25 + 0.25 × 0.75 = 0.375 (37.5%)

Relative abundance of ^{37}Cl/^{37}Cl and ^{37}Cl/^{35}Cl = 0.25 × 0.25 = 0.0625 (6.25%)



10 The abundance of ^{24}Mg is given as 78.90%.

Let the abundance of ^{25}Mg be *x*.

Consider 100 atoms. The abundance of ^{26}Mg will be 100 – 78.9 – *x* (i.e. 100 minus the abundance of the other isotopes).

The relative atomic mass of Mg is 24.31 (from the IB data booklet) so overall:

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

$2431 = 1893.6 + 25x + 2600 - 2051.4 - 26x$

$= 2442.2 - x$

$x = 11.20$

Therefore, ^{25}Mg has an abundance of 11.20% and ^{26}Mg has an abundance of 9.90% (i.e. 100 – 78.90 – 11.20)

11 **B** Deflection of the alpha particles results from repulsion between the positive charges of the alpha particle and the nucleus, so the nucleus also had to be positively charged. The nucleus has to be dense. Most of the gold foil is empty space, as most alpha particles pass straight through. If the mass of the gold is concentrated in a small part of the foil, the nucleus must be dense.

12 **C** The lines in the spectra are produced by the transition of electrons between atomic energy levels (see page 73).

13 **A** Visible transitions result from the Balmer series of transitions, which involve emissions that end at the *n* = 2 level. There are three possible transitions using the energy levels shown in the diagram: *n* = 5 to *n* = 2, *n* = 4 to *n* = 2 and *n* = 3 to *n* = 2. Any other emissions would involve electromagnetic radiation outside of the visible region of the spectrum.

14 **A** The energy of the lines in the emission spectra of atomic hydrogen have fixed values resulting from specific transitions between energy levels within the atom, thus supporting the Bohr model of the hydrogen atom.

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

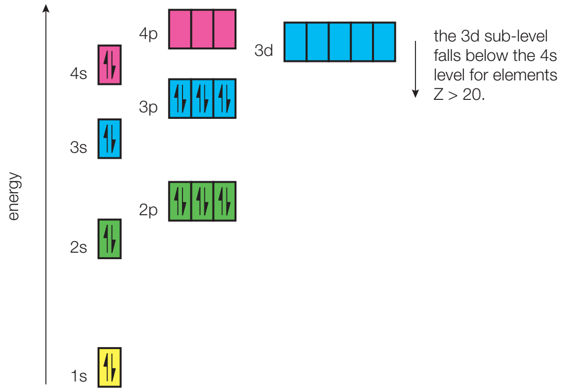
(You need to learn that the energy ordering for the orbitals is s < p < d < f.)

16

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

You need to learn this: one s orbital, three p orbitals, five d orbitals and seven f orbitals (a total of 16 orbitals for an energy level containing all four types). (16 orbitals means 32 elements, which can be counted on the Periodic Table between K and Kr plus Ce to Lu.)

17 Fill the atomic orbitals with electrons from the lowest energy level.



Calcium has an atomic number of 20 and so has 20 electrons. These will fill the 1s, 2s, 2p, 3s, 3p, and 4s energy levels. The electron configuration for calcium is $1s^22s^22p^63s^23p^64s^2$, which totals 20 electrons.

18 The atomic number of phosphorus is 15. Fill up the sub-orbitals with electrons. When the 3p orbital is reached there are three electrons, but according to Hund's rule they have to occupy separate p orbitals. Hence the overall arrangement will be: $1s^22s^22p_x^{\,2}2p_y^{\,2}2p_z^{\,2}3s^23p_x^{\,1}3p_y^{\,1}3p_z^{\,1}$, so there are three unpaired electrons.

19 **C** Shell 1 is the first shell and only contains an s orbital, shell 2 is the first shell that contains s and p orbitals, shell 3 is the first shell that contains s, p and d orbitals, shell 4 is the first shell that contains s, p, d and f orbitals. Therefore 3f is the non-existent sub-level.

20 **A** is wrong: 3d is after 4s

B is wrong: 5s is after 4p

C is correct

D is wrong: 5p is after 4d and 5s is before 4d

21
- Use the Periodic Table to find out the atomic numbers.
- You also need to recall that the orbitals are filled in the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s. (For transition metals the final electron configuration is often written with 3d before 4s as it is the 4s electrons that are lost first when forming transition metal ions.)

(a) V: $1s^22s^22p^63s^23p^63d^34s^2$

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

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

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

22 **D** Iodine is near the end of Period 5, so it has full 3d and 4d sub-shells. As there are five d orbitals in each of these sub-shells this requires a total of 20 d electrons.

This can also be determined by adding up the total number of d electrons in the electronic configuration, I: $1s^22s^22p^63s^23p^63\mathbf{d}^{\mathbf{10}}4s^24p^64\mathbf{d}^{\mathbf{10}}5s^25p^5$.

23 **B** It is unusual to have more than one unfilled sub-shell in the ground state of an atom. As $[\text{Ne}]3s^23p^34s^1$ has two unfilled sub-shells it is an excited state configuration (and $[\text{Ne}]3s^23p^44s^0$ would be the ground state.)

(Chromium ($[\text{Ar}]3d^54s^1$) and similar elements have two unfilled sub-shells in their ground state, but these are exceptional and show the stability of the half-filled d sub-shell.)

24 **B** Titanium is element 22, so its electron configuration is the same as argon (element 18) plus four electrons: $[\text{Ar}]4s^23d^2$. The 4s electrons are paired (as the orbital is full) but the two electrons in the 3d orbitals will be unpaired in separate orbitals (Hund's rule).

25 The first two are relatively easy. From the atomic number and the charge we can deduce the number of electrons. We then arrange the electrons as usual.

(a) O^{2-} has 10 electrons: $1s^22s^22p^6$

(b) Cl^- has 18 electrons: $1s^22s^22p^63s^23p^6$

The d-block elements are trickier because the ions form by losing 4s electrons before any 3d electrons. Ti is $1s^22s^22p^63s^23p^63d^24s^2$.

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

With copper it is more complex still, as we need to remember the $4s^1$ configuration for the atom, although this isn't relevant when looking at Cu^{2+}. Cu is $1s^22s^22p^63s^23p^63d^{10}4s^1$.

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

26 Before determining the electron configurations of the transition metal ions it is useful to first determine the electron configuations of the relevant elements.

	Atom	3d					4s
(a)	Ti	↑	↑				↑↓
(b)	Fe	↑↓	↑	↑	↑	↑	↑↓
(c)	Ni	↑↓	↑↓	↑↓	↑	↑	↑↓
(d)	Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Remember that d electrons will only pair up if all five d orbitals have a single electron in them. When the ions form, it is the 4s electrons which are lost first:

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

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

(b) Possible negatively charged ions are F^-, O^{2-}, or N^{3-}; possible positively charged ions are Na^+, Mg^{2+}, or Al^{3+} as these all have the same electron configuration as neon.

28 The Periodic Table is useful in two ways.

(i) It gives the atomic number of the element.

(ii) From the group and block, we know the configuration of the unfilled orbitals.

(a) Cl: $1s^22s^22p^63s^23p^5$

(Cl has the typical Group 17 configuration of ns^2np^5)

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

(Nb is comparable to V: $1s^22s^22p^63s^23p^63d^34s^2$)

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

(Ge has the typical Group 14 configuration of ns^2np^2)

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

(Sb has the typical Group 15 configuration of ns^2np^3)

29 You simply need to add up the numbers of electrons in the electron configuration to determine the atomic number (Z) and the identity of the element.

(a) Si [Ne]$3s^23p^2$, 10 + 2 + 2 = 14, i.e. $Z = 14$ is Si

(b) Mn [Ar]$3d^54s^2$, 18 + 5 + 2 = 25, i.e. $Z = 25$ is Mn

(c) Sr [Kr]$5s^2$, 36 + 2 = 38, i.e. $Z = 38$ is Sr

(d) Sc $1s^22s^22p^63s^23p^63d^14s^2$, 2 + 2 + 6 + 2 + 6 + 1 + 2 = 21, i.e. $Z = 21$ is Sc

30 11 Tin (Sn) has an electronic configuration of $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^2$. Each p sub-shell contains three p orbitals. In total there are 3 occupied orbitals for the 2p sub-shell, 3 for the 3p sub-shell, 3 for the 4p sub-shell and only 2 occupied 5p orbitals.

3 + 3 + 3 + 2 gives 11 occupied p orbitals in tin.

31 20 Barium has an electronic configuration of $1s^22s^22p^63s^23p^64s^23\mathbf{d}^{10}4p^65s^24\mathbf{d}^{10}5p^66s^2$. Therefore there are 20 electrons in d orbitals.

32 $1s^22s^22p^63s^23p^64s^23d^{10}4p^64d^{10}$, which can also be given as $[Kr]4d^{10}$

Neutral cadmium has an electronic configuration of $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}$. When it forms the Cd^{2+} ion it loses its two 5s electrons.

Practice questions

1 The electron configuration of Cr is $[Ar]\ 3d^54s^1$.

First row transition metal ions lose 4s electrons first then 3d electrons. As Cr^{2+} has lost two electrons the electron configuration is $[Ar]\ 3d^44s^0$ (this can also be written as $[Ar]\ 3d^4$).

Correct answer is D.

2 $A_r = \sum$ isotopic mass × relative abundance

$$= \left(23 \times \frac{80}{100}\right) + \left(28 \times \frac{20}{100}\right) = 24$$

Correct answer is A.

3 Ultraviolet radiation is higher in energy than infrared radiation.

$E = hc/\lambda = h\nu$. Electromagnetic energy (E) increases with decreasing wavelength (λ) and increasing frequency (ν). Ultraviolet radiation has a short wavelength and high frequency so therefore has a high energy. Infrared radiation has a long wavelength and a low frequency so therefore has a low energy.

Correct answer is A.

4 The electron configurations of the ions given as possible answers are:

A Ni^{2+}: $1s^22s^22p^63s^23p^63d^8$

B Cu^{+}: $1s^22s^22p^63s^23p^63d^{10}$

C Cu^{2+}: $1s^22s^22p^63s^23p^63d^9$

D Co^{3+}: $1s^22s^22p^63s^23p^63d^6$

Correct answer is B.

5 The visible spectrum of hydrogen is observed as discrete lines that converge at higher energy/higher frequency/shorter wavelength.

Correct answer is D.

6 As isotopes are different forms of the same element they must have the same atomic number.

They have the same chemical properties as they have the same number of electrons but different physical properties as they have different masses due to different numbers of neutrons.

Correct answer is A.

7 All atoms of an element, including isotopes, must always have the same number of electrons and protons but can have different numbers of neutrons.

Correct answer is C.

8 All atoms of chlorine, including isotopes, must always have the same number of electrons and protons but can have different numbers of neutrons.

Correct answer is B.

9 The visible spectrum of hydrogen is observed for emissions that occur from a higher energy level to the second energy level: $n > 2 \rightarrow n = 2$.

Correct answer is B.

10 $^{31}_{15}P$ has 15 protons and 15 electrons therefore $^{31}_{15}P^{3-}$ has gained three electrons to form the 3^- ion. The total number of electrons in $^{31}_{15}P^{3-}$ is $15 + 3 = 18$ electrons.

Correct answer is D.

11 A neutral atom of aluminium contains 13 protons and 13 electrons, but to form the 3+ ion three electrons have to be lost. The numbers of neutrons and electrons remain unchanged.

Correct answer is C.

12 $A_r = \sum$ isotopic mass × relative abundance

$$= \left(54 \times \frac{5.95}{100}\right) + \left(56 \times \frac{91.88}{100}\right) + \left(57 \times \frac{2.17}{100}\right)$$

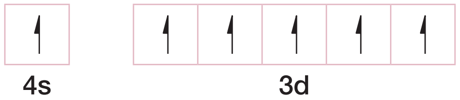
$= 55.90$ (to 2 decimal places).

13 **(a)** $[Ar]$ represents the electron configuration of the argon atom: $1s^22s^22p^63s^23p^6$.

(b) $x = 1$, $y = 5$

(Cr is an exception to the usual electronic configuration of first row transition metals, which is [Ar] $4s^2 3d^n$.)

(c)



14 The neutral copper atom contains one 4s electron and a full complement of 3d electrons. On becoming ionized two electrons are lost: the 4s electron and one of the 3d electrons.

15 **(a)** Nickel has more protons than cobalt therefore it has a higher atomic number. The higher atomic mass of cobalt is a result of it having a higher abundance of heavier isotopes that contain more neutrons than the isotopes of nickel do.

(b) Co has atomic number 27 which means a Co atom has 27 electrons and 27 protons. Co^{2+} has lost two electrons so it has 25 electrons and 27 protons.

(c) The electron configuration of Co^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ (or [Ar] $3d^7$).

Challenge yourself

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

2 Potash, soda, magnesia and barytes are compounds of Group 1 and 2 elements. As Group 1 and 2 elements are very reactive it is very difficult to separate these compounds into their constituent elements using chemical means and this would have been impossible using the equipment and techniques available at that time. These compounds were later broken down into their component elements by electrolysis.

3 The Schrödinger model:

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

4 **(a)** $[Rn]7s^2 5f^{14} 6d^7$

(b) The first g-block element would have the electronic configuration $[Rn]7s^2 5f^{14} 6d^{10} 7p^6 8s^2 8g^1$.

The atomic number of the element can be determined from the number of electrons in the electronic configuration, recognizing that Rn has 86 electrons:

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

5 Based on the National Institute of Standards and Technology database the electron configuration of uranium is:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$$
$$4f^{14} 5d^{10} 6p^6 5f^3 6d^1 7s^2$$

Actinide ions will lose their 6d and 7s electrons and the 4f orbitals will be preferentially occupied so the electron configuration of U^{2+} will be:

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

(Note: It is very difficult to find a definitive answer for this as the behaviour of actinide elements is very complicated.)

6 **(a)** There would be two types of p orbital, p_x and p_y, and two types of d orbitals, d_{xy} and $d_{x^2-y^2}$

(b) As there is a maximum of two electrons that can occupy each orbital there would be four groups in the p block if there were only two types of p orbitals, and four groups in the d block if there were only two types of d orbitals.

Worked solutions

Chapter 3

Exercises

1

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

This question is really just checking that you know what ‘group’ and ‘period’ mean – the answers can then be taken from the Periodic Table (Section 6 of the IB data booklet).

2 **(a)** Periods are the horizontal rows in the Periodic Table. Periods are numbered according to the number of energy levels (shells) in the atoms in that period that have electrons.

Groups are the vertical columns in the Periodic Table. Groups are numbered according to the number of electrons in the outer energy level of the atoms in that group, although this is complicated for transition elements.

(b) Phosphorus is element 15 and its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^3$. The final electron went into a p orbital, which places phosphorus in the p block of the Periodic Table. As it has an np^3 configuration phosphorous is a member of Group 15.

In an older numbering scheme for the groups in the Periodic Table phosphorus was given as being in Group 5 (or Group V), which corresponded to it having five valence electrons in its outer shell (in the 3s and 3p sub-shells). This connection between outer shell occupation and group number is now lost; in the modern group numbering phosphorus is in Group 15. Phosphorus has three shells of electrons, so it is in period 3.

3 Element 51 is antimony, Sb. It is in Group 15. It has the configuration $[Kr]4d^{10}5s^2 5p^3$. Its valence electrons are $5s^2 5p^3$ so it has 5 valence electrons.

4 **C** Germanium, it has properties of both a metal (e.g. forms alloys with other metals) and a non-metal (e.g. brittle). Calcium, manganese and magnesium are all metals.

5 **B** Graphite, as it has a network of delocalized electrons throughout its structure.

6 **C** Elements are arranged in the Periodic Table in order of increasing atomic number.

7 **(a)** It is difficult to define the ‘edge’ of an atom, but when two or more atoms of the same element are bonded together we can define the atomic radius as half the distance between neighbouring nuclei.

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

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

8 Si^{4+} has an electronic configuration of $1s^2 2s^2 2p^6$ whereas Si^{4-} has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. Si^{4+} has two occupied energy levels and Si^{4-} has three and so Si^{4-} is larger.

9 **A** Both ionization energy (I) and electron affinity (II) are properties of gaseous atoms, whereas electronegativity (III) is a property of an atom in a molecule.

10 **B** Removing an electron from the Ca atom and adding an electron to the O^- ion both require energy. Adding an electron to an iodine atom is an exothermic process (see Section 8 in the IB data booklet).

11 **C** Electronegativity decreases down the Periodic Table and increases from left to right across the Periodic Table. Elements that are diagonally next to each other (on a top left to bottom right diagonal) tend to have similar electronegativities.

12 **D** Ionization energy decreases down the group as the valence electrons are further from the nucleus and so become easier to remove.

Ionic radius (**A**) and atomic radius (**B**) increase down a group as more electron shells are added. Neutron/proton ratio (**C**) also increases down a group; it is 1 : 1 for Mg and Ca but 1.4 : 1 for Ba.

13 **(a)** The electron in the outer electron energy level (level 4) is removed from the K atom to form K^+. The valence electrons of K^+ are in the third energy level. They experience a greater attractive force and are held much closer to the nucleus.

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

(c) The ions have the same electron configuration, $1s^22s^22p^6$, but Na^+ has two more protons than F^-. The extra protons in Na^+ attract the electrons more strongly and hold them closer to the nucleus so it has a smaller ionic radius.

14 Usually, sulfur exists as large S_8 molecules whereas phosphorus exists as P_4 molecules. The larger S_8 molecules have stronger London dispersion forces (resulting from S being a larger molecule), which explains the higher melting point.

15 **D** Atomic radius increases down a group but decreases across a period. Down a group further electron shells are added, increasing the atomic radius. Across a period further electrons are added into the same electron shell, and the attraction between the nucleus and the outer electrons increases as the nuclear charge increases.

Melting point does decrease down some groups (e.g. Group 1) but increases down others (e.g. Group 17). The trend across a period is complicated (answer **A**).

Electronegativity decreases down groups and increases across a period (answer **B**).

Ionization energy decreases down groups but generally increases across periods (answer **C**).

16 **C** Nuclear charge (always positive) is another way of expressing atomic number; the nuclear charge comes from the protons.

Relative atomic mass is how the elements were arranged, despite anomalies such as iodine and tellurium being out of sequence (**A**). Ionic radii (**B**) and ionization energy (**D**) show periodic properties, but are not used to arrange the elements.

17 As these species all have the same number of protons the largest species will be one with the most electrons, so the order of decreasing size is $Cl^- > Cl > Cl^+$.

18 **B** Cl is nearest F, which is the most electronegative element in the Periodic Table, so it should have the largest electronegativity of the elements listed. This is confirmed by checking Section 8 in the IB data booklet.

19 **C** Across the period from sodium to argon the number of protons increases (so the nuclear charge increases). Electronegativity also increases as the period is traversed from left to right.

Atomic radius decreases across a period (**A**, **B**, **D**).

20 **D** The peak occurs at element 6 (carbon) and is followed by very low values. The troughs in the graph correspond with elements on the right-hand side of the Periodic Table, where the elements are gases and so have very low melting points.

Atomic radius falls across each period (**A**). First ionization energy peaks with the noble gases, which are elements 10 and 18 (**B**). Ionic radius peaks with elements 7 and 16 (**C**).

21 **B** The three ions are isoelectronic as they all have 18 electrons and the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6$. The ionic radius will therefore depend on the nuclear charges of these species. The ion with the most protons in the nucleus will be the one with the smallest ionic radius as its valence electrons will experience the greatest attraction to the nucleus and be held closest. Ca^{2+} has 20 protons, K^+ has 19 protons and Cl^- has 17 protons so the order of size is $Ca^{2+} < K^+ < Cl^-$.

22 The equation for the reaction of sodium with water is $2Na(l) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$. The heat of the reaction will melt the sodium, which forms a small ball that moves around on the surface of the water.

As hydrogen gas is produced in the reaction bubbles are observed in the water around the sodium. Smoke can be observed and popping/fizzing can be heard.

The gas may ignite and burn with a yellow flame, which is due to emission from excited sodium ions.

The temperature of the solution increases due to the heat released by the reaction.

23 **D** Reactivity increases on descending the group. As the atom becomes larger, so the valence electron experiences a weaker nuclear attraction and is more available to take part in chemical reactions.

All the other properties mentioned in the question decrease down Group 1, for the reason given above.

24 Alkali metals become more reactive down the group, but halogens become less reactive down the group.

25 **C** The melting point increases from fluorine (gas) to iodine (solid) as the London dispersion forces increase due to the increase in the size of the molecules.

The charge on the halide ion is the same for all members of the group (**A**). Electronegativity decreases down the group (**B**). The reactivity with metals also decreases down the group (**D**).

26 **D** The most reactive element in Group 1 (i.e. the lowest in the group) reacts most readily with the most reactive in Group 17 (i.e. the highest in the group).

27 **D** The halogens exist as diatomic molecules: Cl_2, Br_2 and I_2. As we go down the group the number of electrons in the molecule increases and this results in stronger London dispersion forces and a lower volatility. (Volatility refers to how easily a compound can be converted into a gas.) Cl_2 has the fewest electrons, the weakest London dispersion forces and a high volatility, existing as a gas at room temperature. Br_2 has more electrons, stronger London dispersion forces and a lower volatility, existing as a liquid at room temperature. I_2 has the most electrons, the strongest London dispersion forces and the lowest volatility, existing as a solid at room temperature.

28 **A** Uus has an atomic number of 117. This means that the nucleus contains 117 protons, which each have a positive charge, giving a total relative (atomic) charge of 117.

29 **A** Only Mg forms a basic oxide.

Al_2O_3 is amphoteric, P_4O_6, P_4O_{10}, SO_2, and SO_3 are acidic. The oxides of sulfur are gases or liquids, but the other oxides are solids.

30 **B** N and P are both in Group 15 and so will have similar chemical properties.

31 **D** SO_3 is the only small covalent oxide, therefore it forms an acidic aqueous solution.

Na_2O and MgO are ionic, but the oxide ion reacts with water to form alkaline hydroxide ions. SiO_2 is a giant covalent lattice which does not dissolve or react with water.

32 Standard temperature is 273 K (0 °C).

(a) MgO, SiO_2, and P_4O_{10} have melting points above standard temperature, so they are solids. SO_2 has a boiling point below standard temperature, so it is a gas.

(b) MgO is an ionic lattice and has a high melting point due to the strong attraction between the oppositely charged ions. SiO_2 is a covalent lattice and has a high melting point due to all atoms being held together by strong covalent bonds. SO_2 and P_4O_{10} have much lower melting and boiling points because they are simple molecules, held together by weaker intramolecular forces. P_4O_{10} has higher melting and boiling points than SO_2 because it is a larger molecule, which strengthens its London dispersion forces. SO_2 has dipole–dipole interactions which are usually stronger than London dispersion forces for compounds with small atoms but not in this case as P is a large atom.

(c) The oxide ion of MgO reacts with water to form an alkaline solution:

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

SiO_2 does not react or dissolve in water.

SO_2 and P_4O_{10} both react with water to form acidic solutions:

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

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

(d) **(i)** This is essentially a reaction between the acidic H^+ ions and the basic O^{2-} ions:

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

(ii) Aluminium shows its amphoteric nature by reacting with bases as well as acids:

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

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

$Na_2O + H_2O \rightarrow 2NaOH$

$SO_3 + H_2O \rightarrow H_2SO_4$

Practice questions

1 Atomic radius decreases across a period due to the increasing effective nuclear charge. Atomic number, electronegativity and first ionization energy all increase across a period.

Correct answer is C.

2 The only incorrect statement is III as oxides of elements on the left of a period are ionic and therefore basic. Oxides of elements on the right of a period are covalent and therefore acidic.

Correct answer is A.

3 Electronegativity decreases down Group 17 due to the valence electrons being in shells that are further removed from the nucleus. Melting point, atomic radius and ionic radius all increase down Group 17.

Correct answer is B.

4 ‘Covalent oxides are acidic oxides’. P_4O_{10} and SO_3 are covalent oxides so will produce acidic solutions when added to water. (MgO is an ionic oxide and will produce a basic solution.)

Correct answer is B.

5 Electronegativity increases across Period 3. The ionic radius and the atomic radius decrease across Period 3. Melting point increases for the metallic and metalloid elements Li, Be and B until a maximum is reached for carbon (which is a network solid), then decreases for N, O and F, which exist as diatomic molecules, and Ne, a noble gas, all with weak intermolecular forces.

Correct answer is A.

6 The best definition for electronegativity is the attraction of an atom for a bonding pair of electrons.

Correct answer is B.

7 The equation for the reaction of chlorine with water is $Cl_2(g) + H_2O(l) \rightarrow HOCl(aq) + HCl(aq)$.

Correct answer is C.

8 **(a)** The first ionization energy is the energy required to remove one mole of electrons from one mole of atoms in the gaseous state.

(b) Magnesium has more protons and therefore a greater effective nuclear charge than sodium so its valence electrons experience a greater electrostatic attraction to the nucleus. More energy is therefore required to ionize magnesium and remove a valence electron.

9 Sodium oxide:

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

Na_2O is a basic oxide as basic NaOH formed.

Sulfur trioxide:

$$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$$

SO_3 is an acidic oxide as acidic H_2SO_4 formed.

10 **(a)** **(i)** The sodium ion has a greater effective nuclear charge than the sodium atom as they both have 11 protons but the ion has 10 electrons compared to the atom, which has 11. The greater effective nuclear charge on the sodium ion attracts the electrons closer to the nucleus than in the atom.

(ii) The electron configuration of Na is $1s^22s^22p^63s^1$.

The electron configuration of Na^+ is $1s^22s^22p^6$.

Because the valence electrons of the sodium ion are in the second level it will have a smaller radius than the sodium atom, where the valence electron is in the third energy level and further from the nucleus.

(b) P^{3-} has electron configuration $1s^22s^22p^63s^22p^6$.

Si^{4+} has electron configuration $1s^22s^22p^6$.

Because the valence electrons of P^{3-} are in the third energy level and the valence electrons of Si^{4+} are in the second energy level, P^{3-} will have the greater ionic radius.

11 **(a)** Although it contains charged ions, Na_2O is unable to conduct electricity in the solid state as the ions are not able to move.

(b) $2O^{2-}(l) \rightarrow O_2(g) + 4e^-$ (or $O^{2-}(l) \rightarrow \frac{1}{2}O_2(g) + 2e^-$) (see Chapter 9 for more details on the electrolysis of molten salts)

(c) **(i)** Sodium oxide is a basic oxide. (Sodium oxide is ionic and ionic oxides are basic oxides.)

(ii) $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ (or $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$)

Challenge yourself

1 Ytterbium, yttrium, terbium, erbium.

2 Two elements are liquids: Br and Hg.

Eleven elements are gases: H, He, N, O, F, Ne, Cl, Ar, Kr, Xe and Rn.

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

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

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

4 $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64f^76s^2$ (or [Xe] $4f^76s^2$)

Worked solutions

Chapter 4

Exercises

1 Write the ions with their charges:

lead nitrate; ions present: Pb^{2+} NO_3^-, so forms $Pb(NO_3)_2$

barium hydroxide; ions present: Ba^{2+} OH^-, so forms $Ba(OH)_2$

potassium hydrogencarbonate; ions present: K^+ HCO_3^-, so forms $KHCO_3$

magnesium carbonate; ions present: Mg^{2+} CO_3^{2-}, so forms $MgCO_3$

copper sulfate; ions present: Cu^{2+} SO_4^{2-}, so forms $CuSO_4$

calcium phosphate; ions present: Ca^{2+} PO_4^{3-}, so forms $Ca_3(PO_4)_2$

ammonium chloride; ions present: NH_4^+ Cl^-, so forms NH_4Cl

2 **(a)** potassium bromide; ions present: K^+ Br^-, so forms KBr

(b) zinc oxide; ions present: Zn^{2+} O^{2-}, so forms ZnO

(c) sodium sulfate; ions present: Na^+ SO_4^{2-}, 2 × 1+ with 1 × 2–, so forms Na_2SO_4

Note: Na does not need to be put in brackets because it contains a single atom

(d) copper(II) bromide; ions present: Cu^{2+} Br^-, 1 × 2+ with 2 × 1–, so forms $CuBr_2$

(e) chromium(III) sulfate; ions present: Cr^{3+} SO_4^{2-}, 2 × 3+ with 3 × 2–, so forms $Cr_2(SO_4)_3$

(f) aluminium hydride; ions present: Al^{3+} H^-, 1 × 3+ with 3 × 1–, so forms AlH_3

3 The names are deduced directly from the formulas, referring to the table of ions on page 116 if needed. Note that where a Roman numeral is given in brackets after the name of the cation, it refers to the oxidation number, which is explained in Chapter 9. This is used where an element may form different ions with different oxidation states.

(a) tin(II) phosphate

(b) titanium(IV) sulfate

(c) manganese(II) hydrogencarbonate

(d) barium sulfate

(e) mercury(I) sulfide

4 The charges on the positive ions are deduced from the formulas, again using the information on page 116. The guiding principle is that the overall charge must be zero.

(a) Sn^{2+} **(b)** Ti^{4+}

(c) Mn^{2+} **(d)** Ba^{2+}

(e) Hg^+

5 A will have a charge of 2+ (Group 2) and B will have a charge of 3– (Group 15). Cross multiplying we get the formula: A_3B_2.

6 Mg, atomic number = 12: electron configuration $[Ne]3s^2$

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

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

7 **B** The most ionic fluoride will contain elements with the largest difference in electronegativity – i.e. will contain the metal with the lowest electronegativity. From the Periodic Table, we know this will be the metal the furthest to the left and the lowest, which is Cs. The fluoride will be CsF.

Note that in multiple-choice questions on Paper I you will not have access to the IB data booklet, but you do have a Periodic Table. You do not need specific electronegativity values to answer this question, but you do need to know the trends.

8 **D** The elements which react most readily will be those with the largest difference in electronegativity, i.e. between those on the bottom left and those on the top right. From the Periodic Table we can see that K is below Li and Cl is above Br.

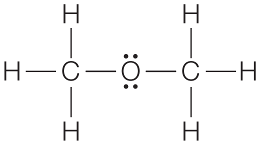
9
- Test the melting point: ionic solids have high melting points.
- Test the solubility: ionic compounds usually dissolve in water but not in hexane.
- Test the conductivity: ionic compounds in aqueous solution are good conductors, as are ionic compounds when they are molten.

10 **D** All the other substances contain polyatomic ions that contain covalent bonds.

11 **C**

$O=C=O$

A

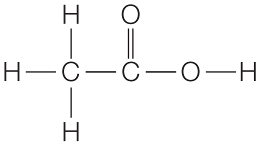


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\ddot{\underset{\cdot\cdot}{O}}{-}\overset{H}{\underset{H}{C}}{-}H}$$

B

$C\equiv O$

C



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}H}$$

D

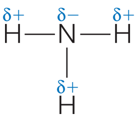
Substances A and D contain carbon–oxygen double bonds and substance B contains carbon–oxygen single bonds. Compound C (carbon monoxide) contains a triple bond. Triple bonds are shorter than both single and double bonds.

12 Any bonds between two different atoms will be polar: the element which is further to the left and/or lower will be δ+ and the element which is further to the right and/or higher will be δ+. These can be predicted from the Periodic Table without the need to consult electronegativity values.

(a) $\overset{\delta+}{H}-\overset{\delta-}{Br}$ **(b)** $\overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$

(c) $\overset{\delta+}{Cl}-\overset{\delta-}{F}$ **(d)** $O=O$

(e)



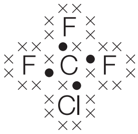
$$\overset{\delta+}{H}-\underset{\underset{\overset{\delta+}{H}}{|}}{\overset{\delta-}{N}}-\overset{\delta+}{H}$$

13

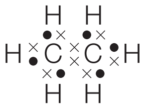
(a)	C 2.6	H 2.2	difference = 0.4
	C 2.6	Cl 3.2	difference = 0.6, more polar
(b)	Si 1.9	Li 1.0	difference = 0.9
	Si 1.9	Cl 3.2	difference = 1.3, more polar
(c)	N 3.0	Cl 3.2	difference = 0.2
	N 3.0	Mg 1.3	difference = 1.7, more polar

14 **(a)**

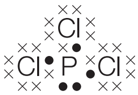
(b)



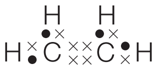
(c)



(d)



(e)



(f)

15 The number of valence electrons in a molecule is the sum of the valence electrons of all the atoms present.

(a) $BeCl_2$: Be has 2 valence electrons and each Cl has 7; 2 + (2 × 7) = 16

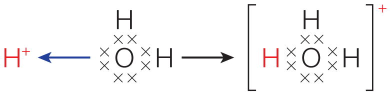
(b) BCl_3: Be has 3 valence electrons and each Cl has 7; 3 + (3 × 7) = 24

(c) CCl_4: C has 4 valence electrons and each Cl has 7; 4 + (4 × 7) = 32

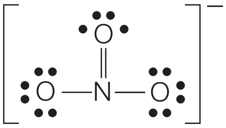
(d) PH_3: P has 5 valence electrons and each H has 1; 5 + (3 × 1) = 8

(e) NCl_3: N has 5 valence electrons and each Cl has 7; 5 + (3 × 7) = 26

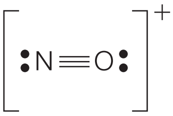
16



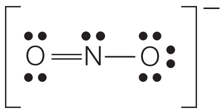
17



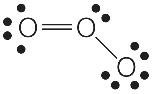
(a)



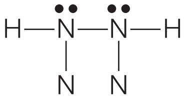
(b)



(c)



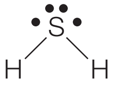
(d)



(e)

18 The steps to follow:

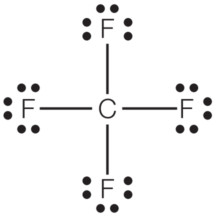
- work out the Lewis structure (as in question 4)
- count the number of electron domains around the central atom, which gives the geometric arrangement of the electron domains
- determine the number and positions of the bonded atoms within this geometric arrangement to give the shape of the molecule
- adjust bond angles in the case of the presence of non-bonded pairs (lone pairs).

(a) H_2S: Lewis structure is 

Four domains of electrons around the sulfur atom, electron domain geometry is tetrahedral.

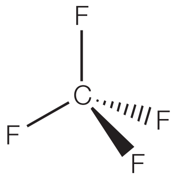
Two lone pairs and two bonded pairs so shape is bent (as drawn in Lewis structure).

As lone pairs repel more than bonded pairs the bond angles are less than 109.5°. Observed bond angle is 105°.

(b) CF_4: Lewis structure is 

Four domains of electrons around the carbon atom, electron domain geometry is tetrahedral.

All electron pairs are bonded so shape is tetrahedral.

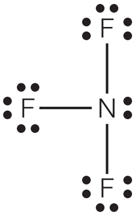


Bond angles are 109.5°.

(c) HCN: Lewis structure is $H-C\equiv N:$

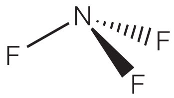
Two domains of electrons around the carbon atom, electron domain geometry is linear.

All electron pairs are bonded so shape is linear (as drawn in Lewis structure). Bond angle is 180°.

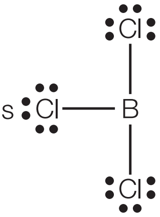
(d) NF_3: Lewis structure is 

Four domains of electrons around the nitrogen atom, electron domain geometry is tetrahedral.

One lone pair and three bonded pairs so shape is trigonal pyramidal.



As lone pairs repel more than bonded pairs the bond angles are less than 109.5°. Observed bond angle is 107°.

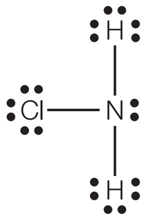
(e) BCl_3: Lewis structure is 

Three domains of electrons around the boron atom, electron domain geometry is trigonal planar.

All electron pairs are bonded so shape is trigonal planar. Bond angles are 120°.

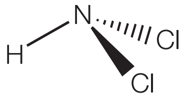
120° bond angle, triangular planar, three domains of electrons around the boron atom.

(f) NH_2Cl: Lewis structure is



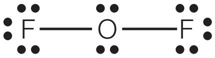
Four domains of electrons around the nitrogen atom, electron domain geometry is tetrahedral.

One lone pair and three bonded electron pairs so shape is trigonal pyramidal.



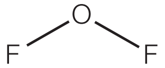
As lone pairs repel more than bonded pairs the bond angles are less than 109.5°. Observed bond angle is 107°.

(g) OF_2: Lewis structure is



Four domains of electrons around the oxygen atom, electron domain geometry is tetrahedral.

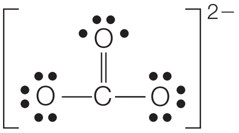
Two lone pairs and two bonded pairs so shape is bent.



As lone pairs repel more than bonded pairs the bond angles are less than 109.5°. Observed bond angle is 105°.

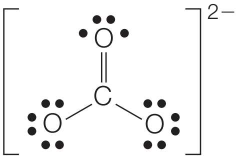
19 Drawing the Lewis structure of these ions will help you to sort out their structure.

(a) CO_3^{2-}: Lewis structure is



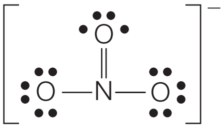
Three domains of electrons around the carbon atom, electron domain geometry is trigonal planar.

All electron domains are bonded so shape is trigonal planar.



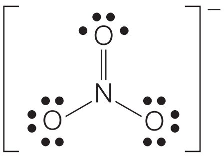
Bond angles are 120°.

(b) NO_3^-: Lewis structure is



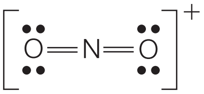
Three domains of electrons around the nitrogen atom, electron domain geometry is trigonal planar.

All electron domains are bonded so shape is trigonal planar.



Bond angles are 120°.

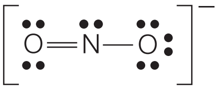
(c) NO_2^+: Lewis structure is



Two domains of electrons around the nitrogen atom, electron domain geometry is linear.

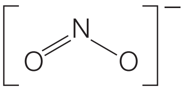
All electron domains are bonded so shape is linear (as drawn in Lewis structure). Bond angle is 180°.

(d) NO_2^-: Lewis structure is



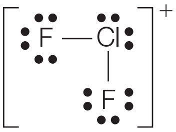
Three domains of electrons around the nitrogen atom, electron domain geometry is trigonal planar.

One lone pair and two bonded electron domains so shape is bent.



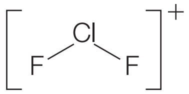
Lone pairs repel more so bond angle will be slightly less than 120°.

(e) ClF_2^+: Lewis structure is



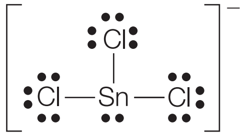
Four domains of electrons around the chlorine atom, electron domain geometry is tetrahedral.

Two lone pairs and two bonded pairs so shape is bent.



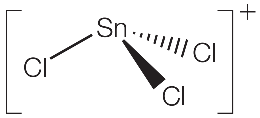
Lone pairs repel more so bond angle will be less than 109.5°. Observed angle is 105°.

(f) $SnCl_3^-$: Lewis structure is



Four domains of electrons around the tin atom, electron domain geometry is tetrahedral.

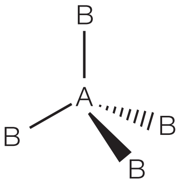
One lone pair and three bonded pairs so shape is trigonal pyramidal.



Lone pairs repel more so bond angle will be less than 109.5°. Observed angle is 107°.

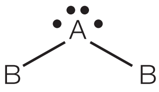
20 Drawing the shapes will help you to visualize them.

(a)

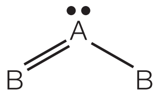


A tetrahedral shape can only be obtained from a tetrahedral electron domain geometry with **four** electron domains and with all domains bonded.

(b)



A bent shape can be formed from a tetrahedral electron domain geometry with **four** electron domains if two domains are bonded and there are two lone pairs.

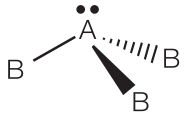


A bent shape can also be obtained from a trigonal planar electron domain geometry with **three** electron domains if one domain is a lone pair. A bent shape can also be obtained from a trigonal planar electron domain with three electron domains if two domains are bonded and there is one lone pair.

(c) B—A—B

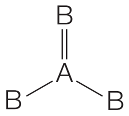
A linear shape can be obtained from a linear electron domain geometry with **two** electron domains if both domains are bonded.

(d)



A trigonal pyramidal shape can be obtained from a tetrahedral electron domain geometry with **four** electron domains if three domains are bonded and there is one lone pair.

(e)



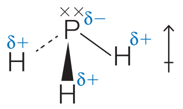
A trigonal planar shape can only be obtained from a trigonal planar electron domain geometry with **three** electron domains and with all domains bonded.

21 The polarity of a molecule depends on the presence of polar bonds and whether or not those bonds are symmetrically arranged.

The steps to follow are:

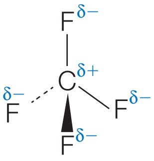
- work out the shape of the molecule (as in question 18)
- from the relative position of the polar bonds, determine whether or not there is a net dipole.

(a) PH_3



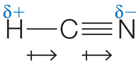
This is a pyramidal molecule, it is polar.

(b) CF_4



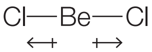
This is a tetrahedral molecule, all bond dipoles cancel, so it is non-polar.

(c) HCN



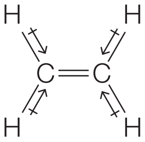
This is a linear molecule, the two dipoles (from the H–C bond and the C–N bond) do not cancel (in fact, they add together), so it is polar.

(d) $BeCl_2$



This is a linear molecule, the two dipoles cancel, so it is non-polar.

(e) C_2H_4



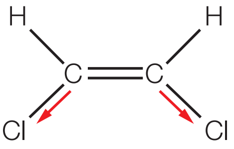
Each C is trigonal planar, each C—H bond is slightly polar, the C=C is non-polar, the structure is symmetrical, so non-polar.

(f) Polar, due to uneven distribution of electrons as fluorine is more electronegative than chlorine.

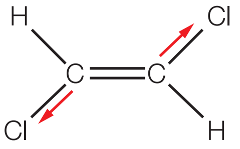
(g) Non-polar; F_2 is a symmetrical molecule so the bonding electrons are shared equally between atoms.

(h) Non-polar; although F is more electronegative than B, the shape of the molecule is trigonal planar, and so all the dipoles cancel out.

22



cis-dichloroethene



trans-dichloroethene

The *cis* isomer has a net dipole moment as both the electronegative atoms are on the same side of the molecule and so there is an overall dipole moment for the molecule. In the *trans* isomer the dipoles cancel out.

23 The C–O bond order for each species can be determined from their Lewis structures.

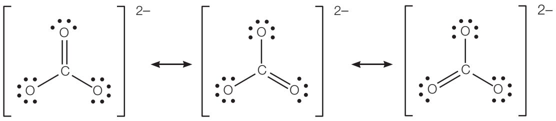
CO: Lewis structure is $:C\equiv O:$

It contains a C≡O triple bond, bond order = 3.

CO_2: Lewis structure is $:\ddot{O}=C=\ddot{O}:$

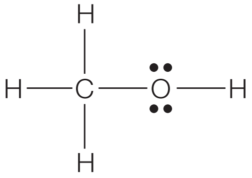
It contains two C=O double bonds, bond order = 2.

CO_3^{2-}: Three resonance structures:



The C–O bonds are delocalized and have a bond order of 1.33.

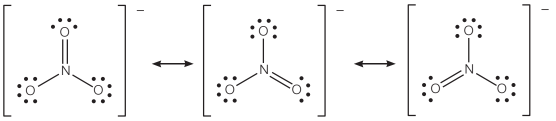
CH_3OH: Lewis structure is



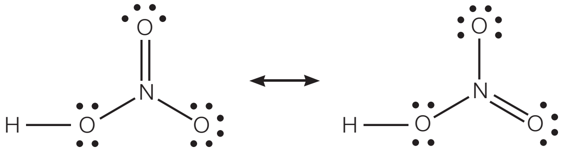
It contains a C–O single bond, bond order = 1.

To rank in order of increasing CO bond length we need to put the species with the shortest bond (highest CO bond order) first: CO < CO_2 < CO_3^{2-} < CH_3OH.

24 NO_3^- has three resonance structures and the N–O bond order is 1.33:



HNO_3 has two resonance structures and there are two distinct N–O bonds. The N–O(H) bond is always a single bond and has a bond order of 1. The N–O bond that resonates has a bond order of 1.5.



Bond lengths decrease as bond order (and bond strength) increases, therefore the N–O bonds in the nitrate(V) ion that all have a bond order of 1.33 will be longer than the two bonds in nitric(V) acid with a bond order of 1.5 and shorter than the N–O bond with a bond order of 1.

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

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

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

27 **A** is a metal; it conducts electricity when solid.

B is giant molecular substance; it doesn't dissolve in water (so isn't an ionic solid), it doesn't conduct electricity when solid (so isn't a metal) and it has the highest melting point.

C is a polar molecular solid; it is soluble in water but doesn't conduct (so isn't an ionic solid); its melting point is low (but not the lowest), so it isn't the non-polar molecular solid.

D is a non-polar molecular solid; it isn't soluble in water (so isn't an ionic solid), it doesn't conduct electricity when solid (so isn't a metal) and it has the lowest melting point.

E is an ionic compound; it is soluble in water, the aqueous solution conducts electricity while the solid doesn't and it has the next to highest melting point.

28 **A** Both methanol and ethanol (D) are soluble in water due to hydrogen bonding between the alcohol and water; however, methanol will be the more soluble as it has the smaller non-polar part of the molecule. Neither methane (B) nor ethane (C) will dissolve in water as neither have any polar bonds.

29 **(a)** London dispersion forces, as it is a non-polar molecule.

(b) H bonds, dipole–dipole, London dispersion forces, as it is a polar molecule due to its tetrahedral shape and lone pair of electrons. Nitrogen is sufficiently electronegative to allow hydrogen bonding to occur.

(c) London dispersion forces, as it is a non-polar molecule.

(d) Dipole–dipole, London dispersion forces, as the molecule is bent about the oxygen atom due to its two lone pairs of electrons and so has a dipole.

30 **(a)** C_2H_6, it is the smaller molecule and so has fewer London (dispersion) forces between adjacent molecules.

(b) H_2S, sulfur is less electronegative than oxygen (in water) and so the dipole–dipole forces are weaker.

(c) Cl_2, it has the smallest molecule and so London dispersion forces are weaker between molecules. (At room temperature, chlorine is a gas but bromine is a liquid.)

(d) HCl, chlorine is less electronegative than fluorine and so the dipole–dipole forces are weaker.

31 **B** Metallic bonding is the attraction between cations and delocalized electrons. See page 157 for more detail.

32 **(a)** Malleability, thermal conductivity, thermal stability, insolubility (so no danger of toxicity).

(b) Light, strong, forms alloys, thermal stability (both high temperatures due to friction and low temperatures high in the atmosphere).

(c) Thermal conductivity, thermal stability, non-corrosive, insolubility.

(d) Light, strong, non-corrosive.

33 **(i)** Anodizing: increasing the thickness of the surface oxide layer helps resist corrosion, also adds colour and enables designs to be added to the surface.

(ii) Alloying: mixing Al with other metals such as Mg and Cu increases hardness and strength while retaining lightness.

Practice questions

1 The larger the electronegativity difference between the two atoms involved in a covalent bond the more polar that bond will be.

	H–I	H–Br	H–Cl	H–F
Electronegativity difference	0.4	0.7	0.9	1.9

Correct answer is C.

2 Carbon forms a covalent network solid where the atoms are all linked to each other by strong covalent bonds. It has a high melting point as the melting of carbon involves breaking these strong bonds.

Carbon dioxide, CO_2, is a covalently bonded molecule. Weak intermolecular forces exist between the molecules and these are easily overcome, giving CO_2 a very low melting point.

Correct answer is A.

3 As these are non-polar or weakly polar compounds the boiling points will depend on the strength of the London dispersion forces between the molecules. These increase with the size of the atoms in the molecules so the order is $CH_3CH_3 < CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_2I$.

Correct answer is A.

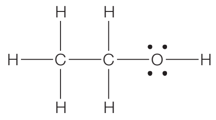
4 Compounds can form hydrogen bonds when:

(i) they contain a hydrogen atom covalently bonded to a highly electronegative atom, N, O or F

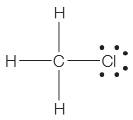
(ii) they have a lone pair on a highly electronegative atom, N, O or F.

The structures of the compounds are (see Chapter 10 for structures of organic compounds):

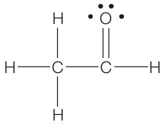
A



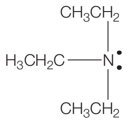
B



C



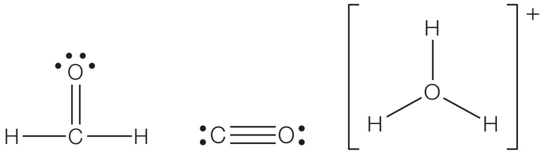
D



Only C_2H_5OH meets both requirements.

Correct answer is A.

5 A dative coordinate bond is a coordination bond. It occurs when one atom donates both of the electrons required to form a covalent bond. Consider the Lewis structures of the compounds:



An oxygen atom has two unbonded electrons that can pair with an electron donated from another atom to form two covalent bonds.

For oxygen to form a third bond this must be a coordination bond where it donates both the electrons in one of the lone pairs. H_3O^+ and CO both contain oxygen atoms that have three bonds.

Correct answer is C.

6 Group 2 elements are metals that form A^{2+} ions, Group 17 elements are non-metals that form B^- ions. They react to form an ionic compound in which the charges are balanced.

Correct answer is B.

7 N_2 contains a triple bond, O_2 a double bond and CO_2 two double bonds.

Correct answer is C.

8 H_2O angle 105°, PH_3 angle 107°, CCl_4 angle 109.5°, H_2CO angle 120°

Correct answer is A.

9 Group 1 and Group 17 elements have the largest difference in their electronegativities so are the most ionic. KF is more ionic than LiF as K is less electronegative than Li.

Correct answer is B.

10 Cl_2 is non-polar because the atoms are the same; BCl_3 is non-polar because the bond dipoles cancel in the planar triangular shape; NCl_3 is polar because the bond dipoles do not cancel in the triangular pyramidal shape; CCl_4 is non-polar because the bond dipoles cancel in the tetrahedral shape.

Correct answer is C.

11 The carbonate ion, CO_3^{2-}, has three electron domains, with one double C=O bond and two single C–O bonds in the Lewis structure. VSEPR theory predicts that the three domains occupy planar triangular positions in the molecule with bond angles of 120°.

Correct answer is C.

12 O_3 has no polar bonds; CCl_4 has polar bonds that are symmetrically arranged; NH_3 has polar bonds that are non-symmetrically arranged; N_2 has no polar bonds.

Correct answer is B.

13 HCl(g) is a covalent molecule with no mobile ions or delocalized electrons to conduct electricity.

Correct answer is D.

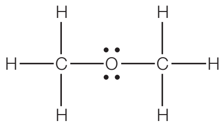
14 Compounds can form hydrogen bonds when:

(i) they contain a hydrogen atom covalently bonded to a highly electronegative atom, N, O or F

(ii) they have a lone pair on a highly electronegative atom, N, O or F.

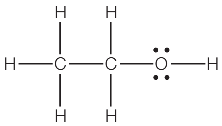
Structures of compounds (see Chapter 10 for structures of organic compounds):

A



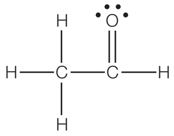
CH_3OCH_3

B



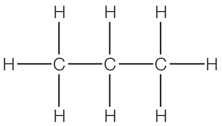
CH_3CH_2OH

C



CH_3CHO

D

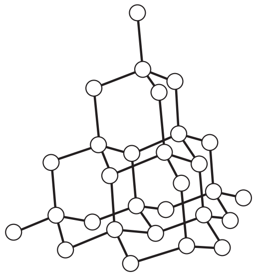


$CH_3CH_2CH_3$

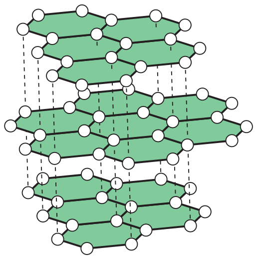
Only CH_3CH_2OH meets both requirements.

Correct answer is B.

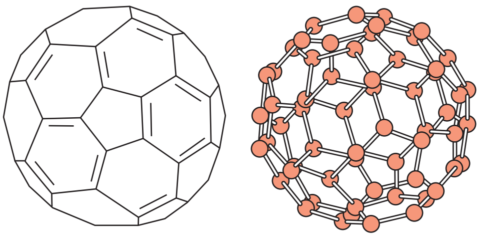
15 **(a)** Diamond is a covalent network structure where the carbon atoms are sp^3 hybridized and every carbon atom is covalently bonded to four others, forming a repeating tetrahedral arrangement with 109.5° bond angles. Diamond does not have delocalized electrons so it is not able to conduct electricity.



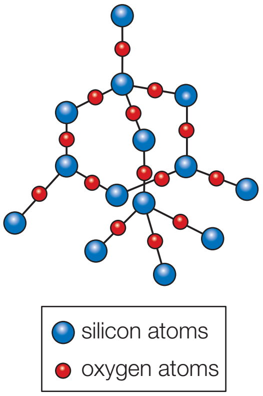
Graphite is a covalent network structure where the carbon atoms are sp^2 hybridized and each atom is covalently bonded to three other atoms, with bond angles of 120°, forming sheets of interlinked hexagons. London dispersion forces exist between the sheets. Electrons are delocalized over each sheet so graphite is able to conduct electricity.



C_{60} fullerene contains carbon atoms that are sp^2 hybridized and each atom is covalently bonded to three other atoms to form interlinked hexagons and pentagons with bond angles between 109.5° and 120°, resulting in a cage-like structure. London dispersion forces exist between the C_{60} fullerenes. Electrons are delocalized on each fullerene but limited contact between the individual fullerenes makes fullerene a semi-conductor at room temperature.



(b) **(i)** SiO_2 is a covalent network solid with each silicon bonded to four oxygen atoms and each oxygen atom bonded to two silicon atoms, giving the empirical formula SiO_2.



(ii) Because SiO_2 is a covalent network solid it is necessary to break strong covalent bonds for it to melt. This requires a large amount of energy and SiO_2 has a high melting point so it is a solid at room temperature.

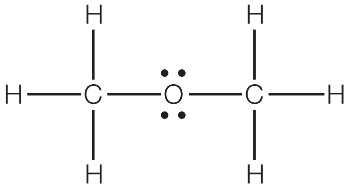
CO_2 is a discrete molecule with weak London dispersion forces between the molecules. These intermolecular forces are weak and easy to overcome so CO_2 has a low boiling point and is a gas at room temperature.

(c) The Lewis structure of carbon monoxide is:

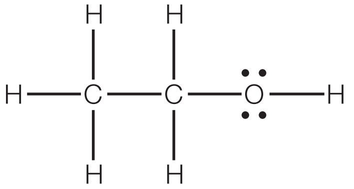
$$:C\equiv O:$$

The carbon and oxygen atoms are both sp hybridized and they form a covalent triple bond. One of these bonds is a coordination bond where the oxygen atom has donated both electrons.

16 Consider the Lewis structures (see Chapter 10 for structures of organic compounds):



2-methoxymethane



ethanol

In methoxymethane the intermolecular forces present are London dispersion forces and dipole–dipole interactions due to the polar C–O bond. These are relatively weak intermolecular forces so methoxymethane will have a low boiling point (–24 °C).

In ethanol hydrogen-bonding intermolecular forces can occur as there is a hydrogen atom bonded to a highly electronegative oxygen atom and a lone pair of electrons on a highly electronegative oxygen atom. As hydrogen bonding is significantly stronger than London dispersion forces and dipole–dipole interactions, ethanol will have a much higher boiling point (78 °C) than methoxymethane.

17 **(a)** CCl_2F_2: number of valence electrons = $4 + (7 \times 2) + (7 \times 2) = 32$.

Lewis structure shows each atom with an octet.

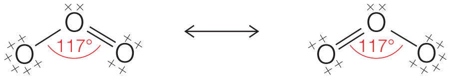
(b) Four electron domains = tetrahedral.

All four are bonding, with bond angle = 109.5°.

(c) Polar

C–F bond is more polar than C–Cl bond/F more electronegative than Cl and the bond dipoles do not cancel.

(d) In O_3 there is more than one possible position for the double bond.



The true structure is a resonance hybrid in which the oxygen–oxygen bonds are intermediate in length and strength between single and double bonds.

(e) The bonds in O_3 are weaker than the bonds in O_2 so are easier to break. The wavelength of light is indirectly proportional to its energy so longer wavelength represents lower energy and this is sufficient to break the bonds in O_3 but not in O_2.

18 **(a)** **(i)** PH_3 has four electron domains, three bonding and one non-bonding.

(ii) H_2O has four electron domains, two bonding and two non-bonding.

(iii) C_2H_6 has four electron domains, all bonding, around each C atom.

(iv) CH_3CHO has four electron domains around one C atom and three electron domains around the other.

(b) H_2O can form hydrogen bonds with other H_2O molecules.

It is the only one of (i) to (iv) that contains an H atom directly bonded to O, N, or F.

19 **(a)** **(i)** Potassium consists of a lattice of cations/K^+ ions surrounded by a sea of delocalized electrons/mobile electrons.

The bonding is non-directional.

(ii)

conducts electricity	delocalized electrons are mobile and can carry charge
conducts heat	delocalized electrons and close-packed ions enable transfer of heat energy
malleable/ ductile	non-directional nature of metallic bond means that it remains intact while conformation changes with applied pressure
high melting point	delocalized electrons cause metallic bonds to be strong
lustrous/shiny	delocalized electrons in crystal structure reflect light

(b) F_2 is a non-polar molecule so the only inter-molecular forces are London dispersion forces.

(c) Potassium fluoride = K^+F^-, with one electron transferred from K to F.

(d) Ions held tightly (by electrostatic forces)/non-mobile in solid state.

Ions can move (and carry charge) when molten or in solution.

20 **(a)** **(i)** SiH_4 has four electron domains, all bonding, so it is a symmetrical tetrahedral shape.

(ii) PH_3 has four electron domains, three bonding and one non-bonding so is a trigonal pyramidal shape with greater repulsion from the lone pair reducing the H–P–H bond angles.

(b) 109.5°

Four electron domains in both SiH_4 and PH_3, but lone pair in PH_3 causes greater repulsion and decreases the angles between the H atoms.

21 The differences between the shapes of NH_3 and NH_4^+ are due to the number of bonding pairs/lone pairs in the molecule. NH_4^+, with four bonding electron domains, is a symmetrical tetrahedron that is non-polar; NH_3 also has four electron domains but one is non-bonding so it is non-symmetrical and has a net dipole.

22 Lewis structures must show all electron pairs, bonding and non-bonding, for the central and surrounding atoms in a molecule. Double bonds are shorter and stronger than single bonds between the same atoms. Resonance structures arise whenever there is more than one possible position for a double bond in a molecule; the true form is a resonance hybrid, which cannot be represented by a single Lewis structure.

Challenge yourself

1 Aluminium oxide, Al_2O_3, is less ionic than MgO due to the smaller difference in electronegativity between Al and O. Al_2O_3 has some partially covalent character, which means the comparison with more ionic oxides is not fully valid.

2 F_2 has lower bond enthalpy (158 kJ mol^{-1}) than expected based on its atomic radius due to repulsion between the non-bonding lone pairs on the two F atoms. The F–F bond length is so short (0.142 nm) that the lone pairs on the two atoms are close enough to repel each other and weaken the bond.

3 Oxygen will have a partial positive charge when it is covalently bonded to the more electronegative element fluorine, e.g. in the compound OF_2.

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

Test the solubility of ionic and covalent solutes in the two solutions. The polar solution will be a better solvent (more solute will dissolve) for polar and ionic solutes; the non-polar solution for non-polar covalent solutes.

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

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

Worked solutions

Chapter 5

Exercises

1 **B** If the temperature drops, the process must be endothermic. ΔH for endothermic reactions is always positive.

2 **B** All exothermic reactions give out heat. While there are examples of exothermic reactions that produce gases, occur quickly and involve combustion the only statement that is always true is B: all exothermic reactions give out heat.

3 **A** The equation you need is $q = mc\Delta T$.

Rearranging gives $\Delta T = \frac{q}{mc}$. From the rearranged equation we can see that the largest temperature increase will occur for the metal with the smallest specific heat capacity.

4 **D** Again use $q = mc\Delta T$, recognizing that a temperature change, ΔT, of 2 °C is the same as a temperature change of 2 K.

$q = 5.0\ \text{g} \times 0.385\ \text{J g}^{-1}\ \text{K}^{-1} \times 2\ \text{K} = 3.85\ \text{J}$

(As there is only 1 significant figure in the value for ΔT (2 K), the answer should also be expressed to 1 significant figure (4 J). However, this is not one of the possible answers so the best answer is D.)

5 **C** Since the mass of each is the same and the heat change is the same, the temperature change is inversely proportional to the heat capacity, $\Delta T = \frac{q}{mc}$. The substance with the lowest heat capacity must therefore have the highest temperature change and, as they all started at room temperature, will have the highest final temperature. Cadmium must have the highest final temperature as it has the lowest heat capacity.

6 $q = mc\Delta T$ rearranges to give $\Delta T = \frac{q}{mc}$.

$$\Delta T = \frac{100.0\ \text{J}}{100.0\ \text{g} \times 0.138\ \text{J g}^{-1}\ {}^\circ\text{C}^{-1}} = 7.2\ {}^\circ\text{C}$$

$$\Delta T = \frac{q}{mc} = \frac{100.0\ \text{J}}{100.0\ \text{g} \times 0.138\ \text{J g}^{-1}\ \text{K}^{-1}} = 7.25\ \text{K}$$

$$= 7.25\ {}^\circ\text{C}$$

$$\Delta T = T_f - T_i$$

$$T_f = T_i + \Delta T = 25.0\ {}^\circ\text{C} + 7.25\ {}^\circ\text{C} = 32.3\ {}^\circ\text{C}$$

7 **A** The mass of the burner will decrease as its contents are burned. The temperature recorded by the thermometer will increase as the heat from combustion warms the water.

8 **A** An accurate result requires that all the heat produced by loss of alcohol is used to heat the water in the calorimeter. It should be clear that heat loss reduces the rise in temperature of the water (I). Loss of fuel by evaporation suggests that more fuel had been burned (II). If the thermometer touched the bottom of the container then this would give a higher temperature reading and the calculated enthalpy of combustion would be higher than predicted (III).

9 **C** Incomplete combustion and heat loss would both result in a lower observed ΔT and a calculated experimental enthalpy of combustion value lower than expected compared to the literature value. The effect of random errors is accounted for in the uncertainty calculated for the experimental value (±200 kJ mol^{-1}). If only random errors were present the literature value would be within the range determined for the experimental value.

10 **(a)** Note that incorrect units are given for the heat capacities in the question. These should both have units of J g^{-1} K^{-1}.

Temperature change: $\Delta T = 36.50 - 25.85 = 10.65\ {}^\circ\text{C}$ (or K)

Heat change, $q = mc\Delta T$

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

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

$= 8900\ J + 492\ J$

$q = 9392\ J$

Moles of glucose burnt: $n(C_6H_{12}O_6)$

$= \dfrac{m}{M\ (C_6H_{12}O_6)} = \dfrac{1.10\ g}{180.18\ g\ mol^{-1}} = 6.11 \times 10^{-3}\ mol$

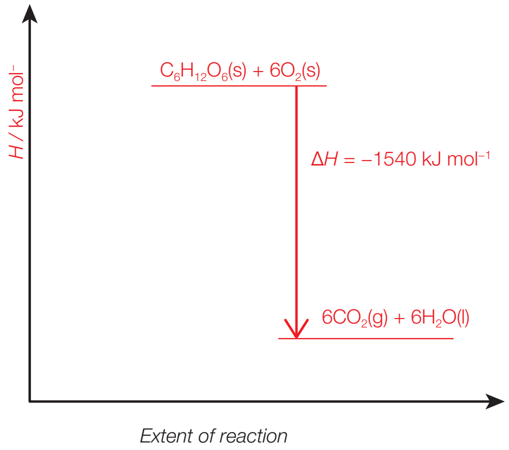
In calculating the enthalpy change of combustion ΔH_c we have to recognize that this is an exothermic reaction and that ΔH_c will therefore be a negative value.

Enthalpy of combustion per mole, $\Delta H_c = \dfrac{-9392\ J}{6.11 \times 10^{-3}\ mol}$

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

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

(b)



11 $q = mc\Delta T$

- Temperature increase, $\Delta T = 6.5\ °C = 6.5\ K$
- Specific heat capacity of water (from Section 2 in the IB data booklet) $= 4.18\ J\ g^{-1}\ K^{-1}$
- Mass of water = 150.00 g

$q = 150.0\ g \times 4.18\ J\ g^{-1}\ K^{-1} \times 6.5\ K = 4100\ J$

0.0500 g is $\dfrac{0.0500\ g}{30.97\ g\ mol^{-1}} = 1.61 \times 10^{-3}$ mol of phosphorus atoms

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

$\Delta H^{\ominus}_c = \dfrac{-q}{n} = \dfrac{-4100\ J}{1.61 \times 10^{-3}\ mol}$

$= -2.5 \times 10^{6}\ J\ mol^{-1} = -2500\ kJ\ mol^{-1}$

(If we take the question as referring to white phosphorus molecules, P_4, instead of phosphorus atoms, the molar mass is 123.88 g mol^{-1} and the final answer is 10000 kJ mol^{-1}.)

The major source of error in such experiments is heat being transferred to anything other than the water. Such errors will reduce the value of the calculated enthalpy. Heat can be lost to the container holding the water (by conduction), to the atmosphere surrounding the apparatus (by convection) or to the surroundings in general (by radiation).

Other sources of error include incomplete combustion, the measurement of the quantities of phosphorus and water, impurities in the chemicals used, the heat used to ignite the phosphorus and variation in water's heat capacity as its temperature changes.

12 $q = mc\Delta T$

- Temperature increase, $\Delta T = 50.0\ °C = 50.0\ K$
- Specific heat capacity of water (from Section 2 in the IB data booklet), $c = 4.18\ J\ g^{-1}\ K^{-1}$
- Volume = 1.00 dm^3 = 1000 cm^3 and will have a mass of 1000 g (if assume density is the same as that of water, 1.00 g cm^{-3})

$q = 1000\ g \times 4.18\ J\ g^{-1}\ K^{-1} \times 50.0\ K = 209\ kJ$

1000 cm^3 of 1.00 mol dm^{-3} solution contains 1.00 mole of copper sulfate, so the standard enthalpy change for this reaction is –209 kJ mol^{-1}.

As the zinc powder was in excess the molar enthalpy must be based on the moles of $CuSO_4$ initially present.

$n(CuSO_4) = cV = 1.00\ mol\ dm^{-3} \times 1.00\ dm^3 = 1.00\ mol$

In calculating the molar enthalpy change ΔH we have to recognize that this is an exothermic reaction and that ΔH will therefore be a negative value.

$$\Delta H = \frac{-q}{n} = \frac{-209\ \text{kJ}}{1.00\ \text{mol}} = -209\ \text{kJ mol}^{-1}$$

13 Temperature change $\Delta T = 32.3\ °\text{C} - 24.5\ °\text{C} = 7.8\ °\text{C} = 7.8\ \text{K}$

In the experiment the mass that is being heated is the combined mass of the NaOH and HCl solutions. If we assume that these solutions have the same density as water, $1.000\ \text{g cm}^{-1}$, then $50.00\ \text{cm}^3$ of the solutions has a mass of 50.00 g. Total mass = 50.00 g + 50.00 g = 100.00 g.

$q = mc\Delta T = 100.00\ \text{g} \times 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times 7.8\ \text{K}$

$= 3300\ \text{J}$

Moles of sodium hydroxide, $n(\text{NaOH}) = cV =$

$0.950\ \text{mol dm}^{-3} \times \frac{50.00}{1000}\ \text{dm}^3 = 0.0475\ \text{mol}$.

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

$$\Delta H = \frac{-q}{n} = \frac{-3300\ \text{J}}{0.0475\ \text{mol}} = -6.9 \times 10^5\ \text{J mol}^{-1} =$$

$-69\ \text{kJ mol}^{-1}$

Assumptions:

- There is no heat loss to the surroundings during the reaction.
- The density of the solution is the same as the density of water, $1.00\ \text{g cm}^{-3}$.
- The heat capacity of the solution is the same as the heat capacity of water, $4.18\ \text{J g}^{-1}\ \text{K}^{-1}$.

14 heat change, $q = mc\Delta T$

In this question the mass that is undergoing a temperature change is the mass of the solution resulting from 5.035 g of NH_4Cl being added to $100.00\ \text{cm}^3$ of water.

As the density of water is $1.00\ \text{g cm}^{-3}$ the $100.00\ \text{cm}^3$ has a mass of 100.00 g.

Mass of solution = 100.00 g + 5.035 g = 105.04 g

$q = mc\Delta T = 105.04\ \text{g} \times 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times (21.79 - 25.55)\ \text{K} = -1650\ \text{J}$

$$n(\text{NH}_4\text{Cl}) = \frac{m}{M}\ \frac{5.350\ \text{g}}{53.50\ \text{g mol}^{-1}} = 0.1000\ \text{mol}$$

In calculating the molar enthalpy change ΔH for this reaction (enthalpy change when 1 mole of NH_4Cl is dissolved) we have to recognize that this is an endothermic reaction and that ΔH will therefore have a positive value.

$$\Delta H^{\ominus} = \frac{+q}{n} = \frac{+1650\ \text{J}}{0.1000\ \text{mol}} = +16\,500\ \text{J mol}^{-1}$$

$$= +16.5\ \text{kJ mol}^{-1}$$

(A different answer is obtained if the mass of the solution is assumed to be the same as the mass of the water only, i.e. 100.00 g. In this case $\Delta H = +15.7\ \text{kJ mol}^{-1}$.)

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

16 **A** Applying Hess's law the appropriate enthalpy changes can be calculated:

$\Delta H\ (\text{P} \rightarrow \text{S}) = \Delta H\ (\text{P} \rightarrow \text{Q}) + \Delta H\ (\text{Q} \rightarrow \text{S}) = +50\ \text{kJ} + -60\ \text{kJ} = -10\ \text{kJ}$

$\Delta H\ (\text{R} \rightarrow \text{Q}) = \Delta H\ (\text{R} \rightarrow \text{S}) - \Delta H\ (\text{S} \rightarrow \text{Q}) = +30\ \text{kJ} - (-60\ \text{kJ}) = +90\ \text{kJ}$

$\Delta H\ (\text{P} \rightarrow \text{R}) = \Delta H\ (\text{P} \rightarrow \text{Q}) + \Delta H\ (\text{Q} \rightarrow \text{S}) - \Delta H\ (\text{S} \rightarrow \text{R}) = +50\ \text{kJ} + -60\ \text{kJ} - 30\ \text{kJ} = -40\ \text{kJ}$

The correct values are I and II. $\Delta H\ (\text{P} \rightarrow \text{S}) = -10\ \text{kJ}$ and $\Delta H\ (\text{R} \rightarrow \text{Q}) = +90\ \text{kJ}$.

17 Applying Hess' law the enthalpy change for the overall equation can be obtained from the first equation and the reverse of the second equation:

$\text{C(graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	$\Delta H^{\ominus} = -394\ \text{kJ}$
$\text{CO}_2\text{(g)} \rightarrow \text{CO(g)} + \tfrac{1}{2}\text{O}_2\text{(g)}$	$\Delta H^{\ominus} = +283\ \text{kJ}$
$\text{C(graphite)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$	$\Delta H^{\ominus} = (-394 + 283)\ \text{kJ} = -111\ \text{kJ}$

18 Applying Hess' law the enthalpy change for the overall equation can be obtained from the reverse of the first equation and the second equation:

$2NO(g) \rightarrow N_2(g) + O_2(g)$	$\Delta H^\ominus = -180.5$ kJ
$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$	$\Delta H^\ominus = +66.4$ kJ mol^{-1}
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$\Delta H^\ominus = (-180.5 + 66.4)$ kJ $= -114.1$ kJ

19 Applying Hess' law the enthalpy change for the overall equation can be obtained from doubling the reverse of the first equation and the second equation:

$2NO_2(g) \rightarrow N_2(g) + 2O_2(g)$	$\Delta H^\ominus = 2 \times -33.2$ kJmol^{-1}
$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g)$	$\Delta H^\ominus = +9.16$ kJ mol^{-1}
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$\Delta H^\ominus = (-66.4 + 9.16)$ kJ $mol^{-1} = -57.2$ kJ mol^{-1}

20 **B** Applying Hess' law ΔH_3 can be obtained from reversing the first equation and halving the second equation:

$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$	$\Delta H_1 = +283$ kJ mol^{-1}
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	$\Delta H_2 = \frac{1}{2} \times -572$ kJ mol^{-1}
$CO_2(g) + H_2(g) \rightarrow H_2O(l)$	$\Delta H_3 = (+283 + -286)$ kJ $mol^{-1} = -3$ kJ mol^{-1}

21 **C** The enthalpy of formation is defined as the formation of 1 mole of substance from its constituent elements in their standard states.

If the elemental substances listed correspond to the standard states of the elements then the standard heat of formation will be zero at 25.0 °C and 1.00 × 10^5 Pa.

$Cl_2(g)$, $I_2(g)$ and Na(s) are the standard states of Cl, I and Na so these substances will have a standard heat of formation of zero.

The standard state of Br is Br_2(**l**) not $Br_2(g)$, therefore $Br_2(g)$ will not have a standard heat of formation of zero.

22 **D** The enthalpy of formation is defined as the formation of 1 mole of substance from its constituent elements in their standard states.

If the elemental substances listed correspond to the standard states of the elements then the standard heat of formation will be zero at 25.0 °C and 1.00 × 10^5 Pa.

The standard state of H is $H_2(g)$ not H(g). The standard state of Hg is Hg(**l**) not Hg(s).

The standard state of C is C(graphite) not C(diamond). The standard state of Si is Si(s).

The only substance listed that **does** have a standard heat of formation of zero at 25.0 °C and 1.00 × 10^5 Pa is Si(s).

23 **D** The enthalpy of formation is defined as the formation of 1 mole of substance from its constituent elements in their standard states.

The enthalpy change for any equation that starts with compounds, not pure elements in their standard states, cannot correspond to an enthalpy change of formation, therefore A and C are incorrect.

If the product of the equation is not a pure substance then the enthalpy change of that equation cannot correspond to an enthalpy change of formation. $CuSO_4(aq)$ is a homogeneous mixture and not a pure substance so B is incorrect.

Only equation D describes one mole of a pure substance being formed from its constituent elements in their standard states so D is correct.

24 **(a)** The enthalpy of formation is defined as the formation of 1 mole of substance from its constituent elements in their standard states. The constituent elements of $CH_3COCH_3(l)$ are C, H and O and their standard states are C(graphite), $H_2(g)$ and $O_2(g)$.

$3C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3COCH_3(l)$, $\Delta H^\ominus_f = -248$ kJ mol^{-1}

(The $\Delta H^\ominus_f$ value can be found in Section 12 of the IB data booklet.)

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

25 $Fe_3O_4(s) + 2C(\text{graphite}) \rightarrow 3Fe(s) + 2CO_2(g)$

$\Delta H_{\text{reaction}} = \Sigma\Delta H^\ominus_f(\text{products}) - \Sigma\Delta H^\ominus_f(\text{reactants})$

Recognizing that C(graphite) and Fe(s) are already in their standard states ($\Delta H^\ominus_f = 0$):

$\Delta H_{\text{reaction}} = 2\Delta H^\ominus_f(CO_2(g)) - \Delta H^\ominus_f(Fe_3O_4(s))$

$= (2 \times -394) - (-1118\ )$ kJ mol^{-1}

$= +330$ kJ mol^{-1}

26 $2NO_2(g) \rightarrow N_2O_4(g)$

$\Delta H_{\text{reaction}} = \Sigma\Delta H^\ominus_f(\text{products}) - \Sigma\Delta H^\ominus_f(\text{reactants})$

$= \Delta H^\ominus_f(N_2O_4(g)) - 2\Delta H^\ominus_f(2NO_2(g))$

$= +9.2 - (2 \times +33.2)$ kJ mol^{-1}

$= -57.2$ kJ mol^{-1}

27 **D** $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

$\Delta H_{\text{reaction}} = \Sigma\Delta H^\ominus_f(\text{products}) - \Sigma\Delta H^\ominus_f(\text{reactants})$

Recognizing that $O_2(g)$ is already in its standard state ($\Delta H^\ominus_f = 0$):

$\Delta H_{\text{reaction}} = 2\Delta H^\ominus_f(H_2O(l)) - 2\Delta H^\ominus_f(H_2O_2(g))$

$= (2 \times -286) - (2 \times -188)$ kJ mol^{-1}

$= -196$ kJ mol^{-1}

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

$\Delta H_{\text{reaction}} = \Sigma\Delta H^\ominus_f(\text{products}) - \Sigma\Delta H^\ominus_f(\text{reactants})$

Recognizing that C(s) and Mg(s) are already in their standard states ($\Delta H^\ominus_f = 0$), this assumes that C(s) is C(graphite), which is the standard for carbon.

$\Delta H_{\text{reaction}} = \Delta H^\ominus_f(CO_2(g)) - 2\Delta H^\ominus_f(MgO(s))$

$= -394 - (2 \times -602)$ kJ mol^{-1}

$= +810$ kJ mol^{-1}

Such a highly endothermic reaction is unlikely to be feasible. (Instead, magnesium is produced by electrolysis of its ores.)

29 **B** Reaction I is the sublimation of water, which is an endothermic process. (It takes energy to convert a solid to a gas.)

Reaction II is the deposition of carbon dioxide, which is an exothermic process. (If it takes energy to convert a solid to gas then the opposite process will release energy.)

Reaction III represents the bond dissociation of O_2, which is an endothermic process. (It takes energy to break an O=O bond.)

I and III only are endothermic.

30 **A** The bond enthalpy is the energy required to homolytically break 1 mole of bonds in gaseous molecules under standard conditions. The bond enthalpy of the H–Cl bond is therefore represented by A, HCl(g) H(g) + Cl(g).

B is wrong because it also involves formation of H–H and Cl–Cl bonds. C is wrong because ions form (the bond has been broken heterolytically with both electrons going to the chlorine atom). All the products and reactants must be in the gas phase, so D is wrong.

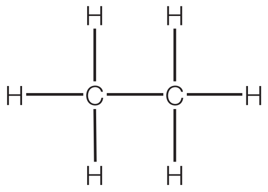
31 **C** Reaction I is the deposition of carbon dioxide, which is an exothermic process. (If it takes energy to convert a solid to gas then the opposite process will release energy.)

Reaction II is the sublimation of water, which is an endothermic process. (It takes energy to convert a solid to a gas.)

Reaction III represents the bond dissociation of O_2, which is an endothermic process. (It takes energy to break an O=O bond.)

II and III only are endothermic.

32 This question needs you to know the structure of C_2H_6 (ethane) as this is the reactant whose bonds are being broken:



From this structure we can see that the bonds broken are six C–H bonds and one C–C bond.

33 **B** The bond enthalpy is the energy required to homolytically break 1 mole of bonds in gaseous molecules under standard conditions. The bond enthalpy of the C≡O bond is therefore represented by B, $CO(g) \rightarrow C(g) + O(g)$.

A and C are wrong because the products formed must also be in the gaseous state and C(s) is present. C and D are wrong because the equations also represent the formation of O=O bonds with $O_2(g)$ as a product.

34 $H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3$

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$

Bonds broken	ΔH / kJ mol^{-1} (endothermic)	Bonds formed	H / kJ mol^{-1} (exothermic)
C=C	+612	C–C	–(–347)
4C–H	4 × (+413)	6 × C–H	6 × (–413)
H–H	+436		
Total	= +2700		= –2825

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed}) = (+2700 + (-2825))$ kJ mol^{-1} = –125 kJ mol^{-1}

This is the full method, and is totally correct. However, it is simpler to 'cancel out' the four unchanged C–H bonds:

Bonds broken	ΔH / kJ mol^{-1} (endothermic)	Bonds formed	H / kJ mol^{-1} (exothermic)
C=C	+612	C–C	–(–347)
		2 × C–H	2 × (–413)
H–H	+436		
Total	= +1048		= –1173

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed}) = (+1048 + (-1173))$ kJ mol^{-1} = –125 kJ mol^{-1}

(Answers will vary slightly depending on the values used! The bond enthalpies given with the question differ from those in Section 11 of the IB data booklet.)

35 $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

Bonds broken	ΔH / kJ mol^{-1} (endothermic)	Bonds formed	H / kJ mol^{-1} (exothermic)
O=O	+498		
2H–H	2 × (+ 436)	4 × O–H	4 × (–464)
Total	= +1370		= –1856

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed}) = (+1370 + (-1856))$ kJ mol^{-1} = –486 kJ mol^{-1}

(Answers will vary slightly depending on the values used! The bond enthalpy for the O–H bond given with the question differs from that in Section 11 of the IB data booklet.)

36 **B** The reaction for the hydrogenation of a double bond is

$-CH{=}CH- + H_2 \rightarrow -CH_2{-}CH_2-$

Bonds broken	ΔH / kJ mol^{-1} (endothermic)	Bonds formed	ΔH / kJ mol^{-1} (exothermic)
C=C	+612	C–C	347
H–H	+436	2 × C–H	2 × (–412)
Total	= +1048		= –1171

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed}) = (+1048 + (-1171))$ kJ mol^{-1} = –123 kJ mol^{-1}

(Note that the bond enthalpies given in the question differ from those in Section 11 of the IB data booklet.)

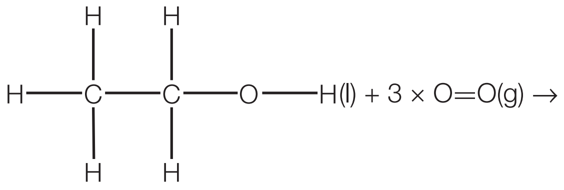
37 **C** $C_2H_4(g) + F_2(g) \rightarrow CH_2FCH_2F(g)$

Bonds broken	ΔH / kJ mol^{-1} (endothermic)	Bonds formed	ΔH / kJ mol^{-1} (exothermic)
C=C	+612	C–C	–347
4C–H	4 × (+436)	4 × C–H	4 × (–436)
F–F	158	2 × C–F	2 × (–467)
Total	= +2514		= –3025

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed}) = (+2514 + (-3025))$ kJ mol^{-1} = –511 kJ mol^{-1}

(Note that the bond enthalpies given in the question on page 189 differ from those in Section 11 of the IB data booklet, particularly for the C–F bond!)

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



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

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

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

$\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed) = (+4731 + (–5994)) kJ mol^{-1} = –1263 kJ mol^{-1}

The calculated value is less exothermic than the enthalpy of combustion given for ethanol in Table 13 in the IB data booklet, which is –1367 kJ mol^{-1}. This is because the bond enthalpy calculation assumes all species are in the gaseous state, but water and ethanol are liquids in this reaction. The calculated value is less exothermic as it does not account for the energy changes associated with changing ethanol and water liquids to gases.

Another reason is that the tabulated bond enthalpies are average values obtained from a range of compounds and are not specific to the compounds in this reaction.

39 **(a)** Step II, as bonds are formed; the other steps involve breaking bonds, which is an endothermic process.

(b) O_2 has a double bond so the bond order is 2. O_3 has resonance structures/delocalization with bonding intermediate between double and single bonds; the bond order is 1.5. As it has a higher bond order the bonding in O_2 is stronger therefore step I needs more energy than step III.

40 From Table 11 in the IB data booklet the O=O bond enthalpy is 498 kJ mol^{-1} (the energy required to break one mole of O=O bonds).

The energy required to break a single O=O bond

$$= \frac{498 \text{ kJ mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 8.27 \times 10^{-22} \text{ kJ} = 8.27$$

$\times 10^{-19}$J. A light photon will therefore need a minimum energy of 8.27×10^{-19}J to break the O=O bond in an O_2 molecule.

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

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{6.63 \times 10^{34} \text{ J s} \times 3 \times 10^{8} \text{ m s}^{-1}}{8.27 \times 10^{-19} \text{ J}}$$

$$= 2.41 \times 10^{-7} \text{ m} = 241 \text{ nm}$$

Any radiation with a wavelength shorter than 241 nm has sufficient energy to break the O=O bond in oxygen.

41 The oxygen double bond with a bond order of 2 is stronger than the 1.5 bond in ozone. Thus, less energy is required to dissociate O_3 than O_2. Longer wavelength radiation of lower energy is needed to dissociate O_3.

Practice questions

1 Using the values provided, heat change = $mc\Delta T$ = (10 g × 8.99 × 10^{-1} J K^{-1} g^{-1}) × (50 – 20) K. This gives the answer in joules: (10 × 8.99 × 10^{-1} × 30) J.

However, the question requires the answer in kJ so it needs to be divided by 1000: heat change

$$= \frac{10 \times 8.99 \times 10^{-1} \times 30}{1000} \text{ kJ}$$

Correct answer is D.

2 Negative enthalpy changes occur for exothermic reactions and processes.

I is the combustion reaction of methanol so is exothermic.

II is an acid–base neutralization reaction so is exothermic.

III is the condensation of water so is exothermic.

Correct answer is D.

3 Both beakers have sufficient acid (0.10 mol) present to react with all of the Mg so both reactions will release the same amount of heat. However, this heat is being absorbed by a smaller mass of solution in beaker A so it will experience a greater temperature increase as both solutions will have the same heat capacity.

$q = mc\Delta T$ or $\Delta T = \dfrac{q}{mc}$

Correct answer is A.

4 Applying Hess' Law the enthalpy change for the overall equation can be obtained from the first equation and the reverse of the second equation:

$$\begin{array}{ll} Cu_2O(s) + \frac{1}{2}O_2(g) \rightarrow 2CuO(s) & \Delta H^\ominus = -144\ \text{kJ mol}^{-1} \\ Cu(s) + Cu_2O(s) \rightarrow Cu_2O(s) & \Delta H^\ominus = -11\ \text{kJ mol}^{-1} \\ \hline Cu(s) + \frac{1}{2}O_2(g) \rightarrow CuO(s) & \Delta H^\ominus = (-144 - 11)\ \text{kJ mol}^{-1} \end{array}$$

Correct answer is C.

5 Bond enthalpy is the energy required to break 1 mole of a bond in a gaseous molecule averaged over similar compounds. The bond breaks homolytically, with each atom taking one of the bonded electrons, and no charged species are formed. B is the only equation that shows the H–Cl bond being broken homolytically to give H(g) and Cl(g).

Correct answer is B.

6 Applying Hess' Law the enthalpy change of the overall equation can be obtained from doubling the first and second equations and combining with the third equation:

$$\begin{array}{ll} \mathbf{2}CH_4(g) + \mathbf{2}O_2(g) \rightarrow \mathbf{2}HCHO(l) + \mathbf{2}H_2O(l) & \Delta H^\ominus = \mathbf{2}x \\ \mathbf{2}HCHO(l) + O_2(g) \rightarrow \mathbf{2}HCOOH(l) & \Delta H^\ominus = \mathbf{2}y \\ 2HCOOH(l) + \frac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + H_2O(l) & \\ & \Delta H^\ominus = \boldsymbol{z} \\ \hline 2CH_4(g) + 3\frac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + 3H_2O(l) & \\ & \Delta H^\ominus = 2x + 2y + z \end{array}$$

Correct answer is C.

7 Bond enthalpy is the energy required to homolytically break 1 mole of a bond in a gaseous molecule averaged over similar compounds, therefore the equation representing the bond enthalpy of the C–Cl bond should only involve the breaking of one C–Cl bond. Only equation B meets this requirement.

Correct answer is B.

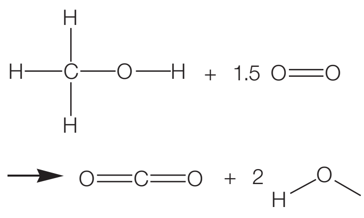
8 The equation provided involves the burning of 2 moles of CO(g). The enthalpy for the burning of 1.00 mole will be half of the enthalpy associated with this equation:

–564 kJ × 0.5 = –282 kJ

The question asks for the *energy released* when 1.00 mol of CO is burned, not the enthalpy change, so the answer is 282 kJ.

Correct answer is B.

9 **(a)** $\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$



$\Sigma E(\text{bonds broken}) = (3 \times E(\text{C–H})) + E(\text{C–O}) + E(\text{O–H}) + (1.5 \times E(\text{O=O}))$

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

$= 2810\ \text{kJ mol}^{-1}$

$\Sigma E(\text{bonds formed}) = 2 \times E(\text{C=O}) + 4 \times E(\text{O–H})$

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

$= 3460\ \text{kJ mol}^{-1}$

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed}) = 2810 - 3460\ \text{kJ mol}^{-1} = -650\ \text{kJ mol}^{-1}$

(b) **(i)** $n(CH_3OH) = \dfrac{m}{M(CH_3OH)}$

$= \dfrac{(80.557 - 80.034)\ \text{g}}{32.05\ \text{g mol}^{-1}} = \dfrac{0.523\ \text{g}}{32.05\ \text{g mol}^{-1}}$

$= 0.0163$ mol

(ii) $q = mc\Delta T = 20.000\ \text{g} \times 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times (26.4 - 21.5)\ \text{K} = 410\ \text{J (2 s.f.)} = 0.41\ \text{kJ}$

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

$$\Delta H^{\ominus}_{c} = \frac{\text{heat change}}{n(\text{CH}_3\text{OH})}$$

$$= \frac{-410\ \text{J}}{0.0163\ \text{mol}} = -25\ \text{kJ mol}^{-1}$$

(c) (i) The enthalpy change calculated from bond enthalpies can only be an estimate as the tabulated bond enthalpies are average values obtained from similar compounds and are not specific to the compounds in the reaction.

The tabulated bond enthalpies are also obtained from gaseous compounds but the combustion reaction conducted in the experiment uses liquid methanol.

(ii) Heat released from the reaction is lost to the surrounding air as well as going into heating the glass test-tube and is not all going into heating the water.

Complete combustion may not be occurring, which would decrease the amount of heat released by the reaction.

10 (a) Possible assumptions:

- All of the heat released by the reaction is transferred to the solution and there is no heat loss to the surroundings.
- The specific heat capacity of the solution is equal to the specific heat capacity of water.
- The density of the solution is 1.00 g cm^3 (i.e. 50.0 cm^3 of solution has a mass of 50.0 g).
- The temperature changes occur uniformly through the solution.
- The polystyrene cup does not absorb any of the heat (i.e. it has negligible heat capacity).
- The excess zinc powder does not absorb any heat (i.e. it has negligible heat capacity).

(b) (i) The final temperature, T_{final}, that would have occurred for an instantaneous reaction can be calculated from the equation provided using the time of mixing, t = 100 s.

$T_{\text{final}} = -0.050(100) + 78.0 = 73.0\ °\text{C}$

From the data table provided we can see that the initial temperature, T_{initial}, was 24.8 °C.

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 73.0 - 24.8\ °\text{C}$$
$$= 48.2\ °\text{C}\ (= 48.2\ \text{K})$$

(ii) That the temperature decreases at a uniform rate (i.e. the linear fit is appropriate).

(iii) Heat change (q) = $mc\Delta T$ = 50.0 g × 4.18 J g^{-1} K^{-1} × 48.2 K = 1.01 × 10^4 J = 10.1 kJ

(c) If the solution became colourless then all of the Cu^{2+} ions have reacted with the zinc powder.

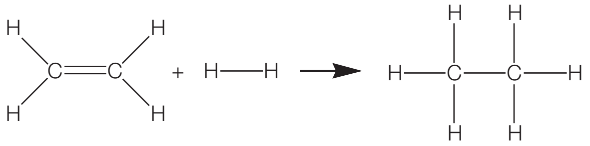
$n(\text{Cu}^{2+}) = cV = 1.00\ \text{mol dm}^{-3} \times \frac{50.0}{1000}\ \text{dm}^3 =$ 0.0500 mol

From the balanced equation, $n(\text{Zn}) = n(\text{Cu}^{2+})$ = 0.0500 mol.

(d) $$\Delta H = \frac{\text{heat change}}{n(\text{Cu}^{2+})} = \frac{-10.1\ \text{kJ}}{0.0500\ \text{mol}}$$
$$= -202\ \text{kJ mol}^{-1}$$

(The enthalpy change is negative as this is an exothermic reaction and heat is released by the reaction.)

11 (a) $\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$



$\Sigma E(\text{bonds broken}) = (4 \times E(\text{C–H})) + E(\text{C=C}) + E(\text{H–H})$

$= (4 \times 414) + 614 + 436\ \text{kJ mol}^{-1}$

$= 2706\ \text{kJ mol}^{-1}$

$\Sigma E(\text{bonds formed}) = (6 \times E(\text{C–H})) + E(\text{C–C})$

$= (6 \times 414) + 346\ \text{kJ mol}^{-1}$

$= 2830\ \text{kJ mol}^{-1}$

$\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed)
= 2706 – 2830 kJ mol^{-1} = –124 kJ mol^{-1}

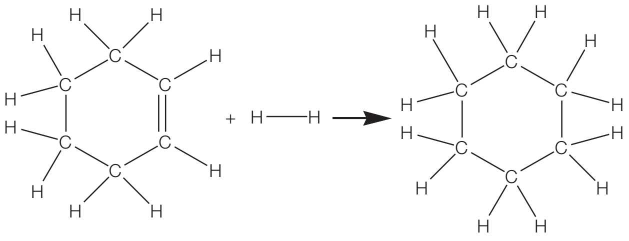
(The same value can be obtained by excluding bonds common to both reactants and products, and focusing on the bonds unique to both reactants and products:

$\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed) = (E(C=C) + E(H–H)) – (E(C–C) + (2 × E(C–H))))

(b) $\Delta H_{\text{reaction}} = \Sigma H^{\ominus}_{c}$ (reactants) – $\Sigma H^{\ominus}_{c}$ (products)
= $\Delta H^{\ominus}_{c}$ (C_2H_4(g)) + $\Delta H^{\ominus}_{c}$ (H_2(g)) – $\Delta H^{\ominus}_{c}$ (C_2H_6(g))
= (–1411 – 286) kJ mol^{-1} – (–1560) kJ mol^{-1}
= –137 kJ mol^{-1}

(c) The values John used for bond enthalpies were average values obtained for various compounds whereas Marit used enthalpies of combustion values that were specific to the compounds used in the reaction.

(d) **(i)** $\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed)



ΣE(bonds broken) = (10 × E(C–H)) + E(C=C) + (5 × E(C–C)) + E(H–H)
= (10 × 414) + 614 + (5 × 346) + 436 kJ mol^{-1}
= 6920 kJ mol^{-1}

ΣE(bonds formed) = (12 × E(C–H)) + (6 × E(C–C))
= (12 × 414) + (6 × 346) kJ mol^{-1}
= 7044 kJ mol^{-1}

$\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed) = (6920 – 7044) kJ mol^{-1} = –124 kJ mol^{-1}

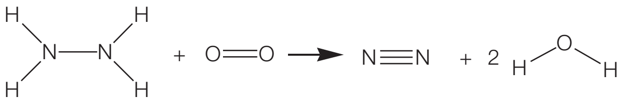
(The same value can be obtained by excluding bonds common to both reactants and products, and focusing on the bonds unique to both reactants and products:

$\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed) = (E(C=C) + E(H–H)) – (E(C–C) + (2 × E(C–H))))

(ii) Both cyclohexene and cyclohexane are liquids so it is not appropriate to calculate reaction enthalpies for these complexes using bond enthalpies as these are determined for compounds in the gaseous state.

It would be necessary to determine the energy required to convert these liquids to gases, i.e. the enthalpies of vapourization and incorporate these values into the calculations.

12 $\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed)

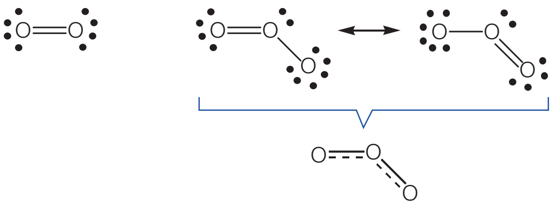


ΣE(bonds broken) = (4 × E(N–H)) + E(N–N) + E(O=O)
= (4 × 391) + 158 + 498 kJ mol^{-1}
= 2220 kJ mol^{-1}

ΣE(bonds formed) = E(N≡N) + (4 × E(O–H))
= 945 + (4 × 463) kJ mol^{-1}
= 2797 kJ mol^{-1}

$\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed)
= 2220 – 2797 kJ mol^{-1} = –577 kJ mol^{-1}

13 Consider the Lewis structures of O_2 and O_3:



Bond order in O_2 = 2. Because it has two resonance structures the bond order in O_3 = 1.5.

Reaction II will require shorter wavelength as the bond in O_2 has a higher bond order and is stronger than the bonds in O_3. Ultraviolet light of a higher energy (i.e. shorter wavelength) will be required to break the stronger bond in O_2.

Challenge yourself

1 Nitrogen is an element with a positive enthalpy of combustion:

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

It takes more energy to break the strong N≡N triple bond and the O=O bond than is released in the formation of the N≡O triple bond.

2 The specific heat capacity of a metal increases with the number of atoms in the sample. For 1-g samples the metal with the lowest molar mass will have the largest number of atoms present and the highest specific heat capacity. Specific heat capacity is approximately inversely proportional to the relative atomic mass.

3 After being placed into the calorimeter the heat energy lost by the piece of brass is transferred into the water as well as the aluminium walls of the calorimeter, which are in contact with the water. We therefore need to calculate the heat transferred to the water and to the aluminium calorimeter using the appropriate specific heat capacities.

Temperature change for water and aluminium calorimeter (ΔT) = (77.50 – 24.50) °C = 53.00 °C = 53.00 K

Heat change (water) = $mc\Delta T$

= 200.00 g × 4.18 J g^{-1} K^{-1} × 53.00 K

= 4.43×10^4 J

Heat change (aluminium) = $mc\Delta T$

= 80.00 g × 0.900 J g^{-1} K^{-1} × 53.00 K

= 3.82×10^3 J

Total heat energy gained by water and aluminium = (4.43×10^4 J) + (3.82×10^3 J) = 4.81×10^4 J

Therefore heat energy lost by the brass = 4.81×10^4 J

Heat change (brass) = $mc\Delta T$

4.81×10^4 J = 21.20 g × 0.400 J g^{-1} K^{-1} × ΔT

ΔT = 5670 K (5670 °C)

Initial temperature = $T_f + \Delta T$ = 77.50 °C + 5670 °C = 5748 °C

The temperature of the flame is 5748 °C.

Assumptions are:

- The brass was the same temperature as the flame before it was removed and transferred to the calorimeter.
- No heat is lost by the brass to the air while it is being transferred to the calorimeter.
- The aluminium walls of the calorimeter and the water are in thermal equilibrium (have the same temperature).
- No heat loss occurs from the calorimeter to the surrounding air.

4 The worked example gives $\Delta H^{\ominus}_c = -808$ kJ mol^{-1} and the value for $\Delta H^{\ominus}_c$ provided in Table 13 of the IB data booklet is –891 kJ mol^{-1}. The difference in the values is largely to due to the assumption in the bond enthalpy calculation that all the bonds being broken and formed belong to molecules in the gaseous state:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$.

In reality the combustion reaction forms water in the liquid state:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

The difference between the two values for $\Delta H^{\ominus}_c$ is therefore due to the energy required to vapourize water:

$H_2O(l) \rightarrow H_2O(g)$

Applying Hess's Law we can obtain a value for the enthalpy change associated with the water vapourization using the relevant equations for the two processes. This value can then be used to estimate the strength of the hydrogen bonding in water.

(1) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
$\Delta H = -890$ kJ mol^{-1}

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

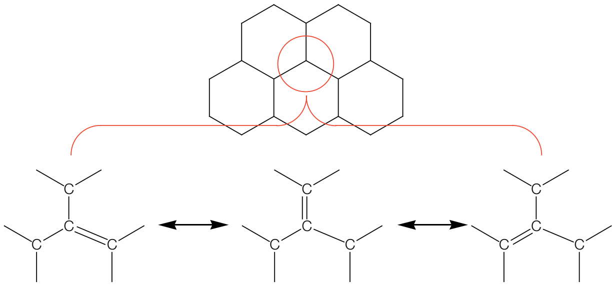
(2.1) $2H_2O(l) \rightarrow 2H_2O(g)$
$\Delta H = -808 - (-891) = +83$ kJ mol^{-1}

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

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

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

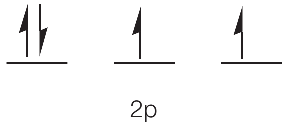
5 Based on the bonding discussions in Chapter 4 we can assign a bond order of 1 to each of the C–C single bonds in diamond as each carbon atom is sp^3 hybridized and bonded to four other carbons via single bonds so there are no possible resonance structures. In graphite the C–C bond order is 1.33 as each carbon atom is sp^2 hybridized and has three possible resonance forms – each with one C=C double bond and two C–C single bonds.



The C–C bonds in graphite are therefore intermediate between single and double bonds. As the C–C bonds in graphite have a higher bond order (stronger bonds), they are harder to break and graphite is more stable than diamond.

6 Free radicals are species that have unpaired electrons.

The electron configuration of O is $1s^22s^22p^4$ and the occupancy of the p orbitals can be shown using a box diagram:



As the box diagram shows, oxygen has unpaired electrons and will therefore behave as a free radical.

Worked solutions

Chapter 6

Exercises

1 The information given on pages 201–203 is very comprehensive. Suitable methods follow from an analysis of the equation given, including a consideration of state symbols and ions.

- Reaction gives off CO_2 gas: change in volume of CO_2 gas released could be measured using a gas syringe. (It cannot be measured using the water displacement method as CO_2 gas dissolves in water.)
- Reaction gives off CO_2 gas: loss of mass could be measured by conducting the reaction in an open flask on a digital balance.
- Reaction involves purple MnO_4^- ions being reduced to colourless Mn^{2+} ions: colorimetry could be used to measure the change in solution absorbance.
- Reaction involves a change in the concentration of ions (23 on the reactants side and 2 on the products side): a conductivity meter could be used to measure the change in solution conductivity.
- Reaction involves a change in pH as H^+ ions are used up: a pH meter could be used to measure the change in solution pH.

2 **C** Here it is best to answer the question yourself without looking at the answers (remember they are designed to trick you). Rate is expressed as the change in concentration with time.

$$\text{Rate} = \frac{\Delta[\text{A}]}{\Delta t}$$

$$\text{Units of rate} = \frac{\text{units of concentration}}{\text{units of time}} = \frac{\text{mol dm}^{-3}}{\text{time}}$$
$$= \text{mol dm}^{-3}\ \text{time}^{-1}$$

(time^{-1} could represent any unit of time, e.g. s^{-1}, min^{-1}, hr^{-1} etc.)

3 **(a)** **(i)** As CO_2 gas is produced in the reaction we could measure the decrease in the mass of flask + contents.

(ii) As H^+ (HCl) is consumed in the reaction we could measure the increase in pH of the reaction mixture.

(iii) As CO_2 gas is produced in the reaction we could measure the increase in volume of gas collected using a gas syringe. (It cannot be measured using the water displacement method as CO_2 gas dissolves in water.)

(b) The rate of the reaction decreases with time because the concentration of the acid decreases (rate $\propto$ [HCl]).

4 Note that 'time' here is the independent variable so it goes on the *x*-axis. 'Concentration' is the dependent variable and goes on the *y*-axis. A graph is plotted using all the data given and a smooth curve is drawn through the points.

The rate of the reaction at a particular interval of time = gradient of the tangent to the curve at that time. Tangents to the curve are drawn at time = 60 s and at time = 120 s.

Gradients are calculated from $\Delta y/\Delta x$

At 60 s, a tangent line passes through the points (0, 0.155) and (185, 0).

$$\text{gradient} = \frac{(0 - 0.155)\ \text{mol dm}^{3}}{(185 - 0)\ \text{s}}$$
$$= -8.4 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

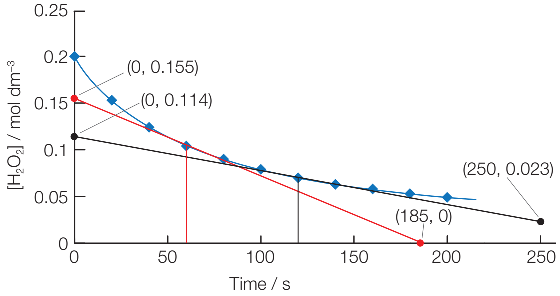
rate of reaction = 8.4×10^{-4} mol dm^{-3} s^{-1}

At 120 s, a tangent line passes through the points (0, 0.114) and (250, 0.023).

$$\text{gradient} = \frac{(0.023 - 0.114)\ \text{mol dm}^{3}}{(250 - 0)\ \text{s}}$$
$$= -3.6 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Note that the gradient to the tangent can be derived from any values of $\Delta y/\Delta x$ so long as they are measured from a right-angled triangle. Negative values are obtained for the gradients at t = 60 s and t = 120 s as the experiment is measuring the decrease in concentration of the

H_2O_2 reactant. However, rates of reaction are expressed as positive values.



5 **D** Colliding particles must have a kinetic energy that is greater than the activation energy in order that the reaction might take place (they must also have the correct geometry).

6 **A** Both the orientation and energy of the molecules are factors in determining whether a reaction will occur.

7 The reaction requiring the simultaneous collision of two particles is likely to be faster. The simultaneous collision of three particles is statistically less likely (i.e. the probability of three particles simultaneously colliding is much lower than the probability of two particles colliding).

8 **B** Catalysts increase the rate of *both* the forward and the backward reactions by lowering the activation energy of the reaction in both directions. The use of a catalyst does not necessarily increase the yield of products.

9 **B** Catalysts increase the rate of both the forward and the backward reactions by lowering the activation energy of the reaction. By increasing the temperature the collision frequency increases and so leads to a greater rate of reaction.

10 **B** A higher rate of a reaction involving a solid will occur if it is present as a powder as it has a larger surface area. For two concentrations of acid the rate will be faster for the higher concentration as there are more acid (H^+) particles available to collide with the $CaCO_3(s)$.

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

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

(b) CO is a toxic gas: it combines with haemoglobin in the blood and prevents it from carrying oxygen. NO is a primary air pollutant: it is oxidized in the air to form acidic oxides, $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$, leading to acid rain: $NO_2(g) + H_2O(l) \rightarrow HNO_3(aq)$. It also reacts with other pollutants in the atmosphere forming smog.

(c) Coating beads with the catalyst increases the surface area of the catalyst in contact with exhaust gases and increases the efficiency of the catalytic converter.

(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 as well as the rate at which the reaction occurs on the surface and the rate at which the products desorb from the surface.

(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.

Note that in part (e) where the command verb is ‘Discuss’, you are expected to try and think of arguments on both sides of the question.

Practice questions

1 Curve Y shows a greater volume of O_2 being produced after it reaches completion than in the initial reaction therefore the change being made must involve a greater amount of reactants than in the initial reaction. The only possible change that will do this is B, where additional hydrogen peroxide solution is added.

Correct answer is B.

2 Any change that increases the frequency of collisions between reactants will increase the rate of a reaction.

Increasing pressure of gaseous reactants increases the number of molecules per unit volume so will increase the frequency of collisions.

Increasing temperature results in molecules moving faster and will increase the frequency of collisions (as well as the proportion of successful collisions).

Removing the product will not affect the frequency of collisions between the reactants.

Correct answer is A.

3 Because there are no acids or bases present the reaction cannot be monitored using pH changes. No gases are released so no change in mass will occur during the reaction and the volume of the solutions will also not change during the reaction.

As discussed in Chapter 3 transition metal complexes are coloured and the colour of the complexes of any metal ion will change for different ligands. $Co(H_2O)_6^{2+}$ will therefore have a different colour to $CoCl_4^{2-}$ and the rate of reaction can be monitored by the change in colour that occurs as the reaction proceeds.

Correct answer is C.

4 The information provided indicates that powdered MnO_2 is a heterogenous catalyst for the decomposition of H_2O_2. Catalysts speed up reactions by providing an alternative reaction pathway with a lower activation energy and are not used up in the reaction so statements II and III are correct. Statement I is incorrect as increasing the surface area of a solid catalyst speeds up the rate of reaction.

Correct answer is C.

5 Rate and time are *indirectly* proportional.

Correct answer is B.

6 Increasing the time means reducing the rate; diluting a solution lowers the concentration and so decreases the frequency of collisions between reactant particles.

Correct answer is C.

7 The combination of highest concentration of acid and smallest particle size of solid will have the greatest rate.

Correct answer is C.

8 There will be a decrease not an increase in mass during the reaction. All the other changes (**B–D**) will occur and can be used to measure rate of reaction.

Correct answer is A.

9 The curve shows the highest gradient at the start, representing the highest rate. This decreases as the reaction continues due to the decrease in concentration of the acid as it reacts.

Correct answer is C.

10 Collisions will only be successful (lead to reaction) when the reacting particles possess kinetic energy greater than the activation energy.

Correct answer is D.

11 It is the proportion of particles with KE > E_a that most influences the increase in the rate of the reaction. Note that **A** and **C** are true statements, but are not the main reason for the increase in rate.

Correct answer is B.

12 Rate of reaction is increased by increasing reactant concentration, decreasing particle size and increasing temperature.

Correct answer is D.

13 Rate of reaction must be expressed as change in concentration per time, i.e. divided by time.

Correct answer is A.

14 The higher the activation energy the lower the rate of a reaction.

Correct answer is B.

15 **(a)** The reaction is typical of a dilute acid:

acid + metal carbonate $\rightarrow$ salt + H_2O + CO_2

(b) CO_2 is produced and escapes in an open system.

(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.

(d) The gradient of the graph at any value of time indicates the rate at that time. As the curves get less steep as the reaction proceeds, this indicates that the rate of the reaction decreases. The fastest rate of the reaction is at $t = 0$.

(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.

(f) Higher temperature increases the frequency of collisions involving particles with KE > E_a.

A catalyst provides an alternate reaction route with lower E_a.

Smaller particle size/greater surface area leads to higher frequency of collisions between reactants.

(g) Measuring mass change due to loss of hydrogen is generally not a suitable method to measure rate of reaction, although measuring change in volume as hydrogen is evolved could be used.

16 **(a), (b)** Maxwell–Boltzmann distributions shift to the right with increasing temperature as the average kinetic energy of the particles increases. At higher temperature the particles therefore have a larger spread of values for kinetic energy, although the area under the two curves remains the same when the number of particles in the sample is constant.

(c) The catalyst provides an alternative route for the reaction that has a lower activation energy, E_a. This means that without increasing the temperature, a higher proportion of particles in the presence of the catalyst have sufficient energy (KE > E_a) to react and so the rate is increased.

(d) The effect of catalysts on the rate of reaction does not change the energy difference between reactants and products, ΔH, nor does it change the equilibrium position or value of K_c (discussed in Chapter 7).

Challenge yourself

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

Worked solutions

Chapter 7

Exercises

1 **A** Statement I is correct: equilibrium is dynamic, meaning that both the forward and reverse reactions continue. Statement II is correct, as this is what defines the equilibrium state. Statement III is not correct: equilibrium can be established with a mixture containing mostly reactant, mostly products, or anything in between.

2 **C** **A** is not always true; equilibrium is often established with a product yield of <50%. **B** is emphatically not true: at equilibrium the rates of forward and reverse reactions must be equal. **C** true: because the rates of forward and reverse reactions are equal, the amounts of reactants and products do not change (no change in macroscopic properties). **D** is not true: both reactions continue as equilibrium is dynamic.

3 **B** If the system is in equilibrium the rate at which ice melts to water and the rate at which water freezes to ice will be equal so **A** is true. The amounts of ice and water need not be the same at equilibrium, the amounts present will depend on the position of equilibrium so **B** is *not true* and **B** is the correct answer. (Note the word 'not' in the question!) Equilibrium can be achieved from either the forward or reverse direction so statement **C** is true. While equilibrium is dynamic at the microscopic level at the macroscopic level no observable changes will occur so **D** is also true.

4 In each case the equilibrium constant is equal to the concentrations of the products, each raised to the power of the coefficient of each product in the original equation, divided by the concentrations of the reactants, each raised to the power of the coefficient of each product in the original equation.

(a) $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$

(b) $K_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

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

5 Note the following points, which sometimes get missed in this work:

- The products of the reaction are found in the numerator (top line of the fraction) of the equilibrium expression, K_c, and the reactants of the reaction are found in the denominator (bottom line of the fraction).
- The stoichiometric coefficient for each reactant or product is equal to the power it is raised to in the equilibrium expression.

(a) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$ $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(b) $K_c = \frac{[CO][H_2]^2}{[CH_4][H_2O]}$ $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

6 In this question it is essential that you first write the chemical equation from the information given. You need to check that it is correctly balanced with respect to each element. Then apply the equilibrium law, using the coefficients from the equation as the powers to which the concentration of each species is raised.

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

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

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

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

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

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

7 **(a)** $K_c = 7.4 \times 10^{-26}$. As $K_c << 1$ this means the denominator in the equilibrium expression

must be much larger than the numerator, which occurs when the concentration of reactants is much larger than the concentration of products. The equilibrium mixture must therefore contain mostly reactants.

(b) $K_c = 2.7 \times 10^{-18}$. As $K_c << 1$ this means the denominator in the equilibrium expression must be much larger than the numerator, which occurs when the concentration of reactants is much larger than the concentration of products. The equilibrium mixture must therefore contain mostly reactants.

(c) $K_c = 6.0 \times 10^{13}$. As $K_c >> 1$ this means the numerator in the equilibrium expression must be much larger than the denominator, which occurs when the concentration of products is much larger than the concentration of reactants. The equilibrium mixture must therefore contain mostly products.

8 **(a)** Calculate Q (the reaction quotient)

$$\frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{1.00^2}{0.100 \times 0.100} = 100$$

Not at equilibrium. As $Q > K_c$ the reaction proceeds to the left.

(b) Calculate Q (reaction quotient)

$$\frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{0.042^2}{0.49 \times 0.04} = 0.090$$

At equilibrium since $Q = K_c$

(c) Calculate Q (reaction quotient)

$$\frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{0.083^2}{0.19 \times 0.00033} = 1.3 \times 10^2$$

$$= 1300$$

Not at equilibrium. As $Q > K_c$ the reaction proceeds to the left.

9 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_\mathbf{c} = \dfrac{[SO_3]^2}{[SO_2]^4[O_2]^2} = 278$

(a) $4SO_2(g) + 2O_2(g) \rightleftharpoons 4SO_3(g)$

$$K_c' = \frac{[SO_3]^4}{[SO_2]^4[O_2]^2} = K_c^2 = (278)^2 = 7.73 \times 10^4$$

As the stoichiometry of the reaction has been doubled so K_c is squared.

(b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

$$K_c' = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{1}{K_c} = \frac{1}{278} = 3.60 \times 10^{-3}$$

As the equation has been reversed so the value of K_c is inversed.

(c) $SO_3(g) \rightleftharpoons SO_2(g) + ½O_2(g)$

$$K_c' = \frac{[SO_2][O]_2^{½}}{[SO_3]^2} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{278}}$$

$$= 6.00 \times 10^{-2}$$

It is also possible to reach the correct answer for (c) by recognizing that the reaction coefficients from (b) have been halved, so the value of K_c is the square root of the value of K_c in (b). $K_c = \sqrt{3.60 \times 10^{-3}} = 6.00 \times 10^{-2}$

10 **B** Stop and think carefully about what a catalyst does before looking at the answers. A catalyst lowers the activation energy of a reaction and so increases the rate of both forward and reverse reactions. **A** is incorrect – the rate of both reactions increases. **C** is incorrect – the enthalpy change is not altered by the catalyst. **D** is incorrect – a catalyst has no effect on the yield, only on the rate of production.

11 **D** Here it is best to consider each column separately and then see which answer has two correct responses. Note that the reaction is endothermic. Position of equilibrium: **C** and **D** are correct – increasing temperature favours the forward endothermic reaction. Value of equilibrium constant: **B** and **D** are correct – equilibrium shifting to the right increases the value of K here.

12 **C** Statement I: no – adding a catalyst does not shift the equilibrium in either direction as it has an equal effect on both forward and reverse reactions. Statement II: yes – decreasing the oxygen (product) concentration shifts the equilibrium to the right, by Le Chatelier's principle. Statement III: yes – increasing the volume will reduce the pressure and so favour the side with the

larger number of gas molecules. Here there are 2 moles of gas on the left and 3 on the right, so it will shift to the right.

13 By Le Chatelier's principle to reactions involving gases, an increase in pressure will favour the side of the reaction with the smaller number of molecules. Applying this enables us to predict the directional change in each of the given reactions.

(a) 2 molecules on the left, 3 on the right so equilibrium will shift left.

(b) 3 molecules on the left, 1 on the right so equilibrium will shift right.

(c) 2 molecules on each side, so there will be no shift in the equilibrium position.

14 By studying the given equation we can deduce:

- 3 molecules of gas on the left, 5 molecules of gas on the right
- forward reaction is endothermic

(a) $H_2(g)$ is a product of the reaction: when its concentration is increased the equilibrium will shift to the left.

(b) $CH_4(g)$ is a reactant: when its concentration is increased the equilibrium will shift to the right.

(c) A decrease in volume is equivalent to an increase in pressure. So the equilibrium shifts in the direction of the smaller number of molecules, which is to the left.

(d) $CS_2(g)$ is a product of the reaction. As its concentration is decreased the equilibrium will shift to the right.

(e) An increase in temperature will favour the endothermic (forward) reaction. The equilibrium will shift to the right.

15 From the information given we note:

- there are 3 molecules of gas on the left and 2 on the right
- the forward reaction is exothermic
- CO is a reactant

(a) Higher pressure will favour the side with the smaller number of molecules – the products. So the equilibrium will shift to the right and [CO] will decrease.

(b) Increasing $[O_2]$ – a reactant – will shift the equilibrium to the right and so [CO] will decrease.

(c) Increasing the temperature will favour the endothermic – backward – reaction. So [CO] will increase.

(d) Adding a catalyst has no effect on the equilibrium position and so [CO] will be unchanged.

16 **C** The question is asking you to distinguish between the effect of a catalyst on the rate of a reaction and on the yield. Deal with each column in the answer options separately. Remember that a catalyst increases the rate, but has no effect on the yield. When considering the rate of formation of NH_3, answers **A**, **B**, and **C** are correct. When considering the amount of NH_3 formed only **C** is correct.

17 **B** Analyse the information given in the equation to determine the effects of temperature and pressure on the equilibrium reaction. Temperature: the reaction is exothermic, so product yield is favoured by a low temperature. Pressure: the reaction has 3 moles of gas on the left and 2 moles of gas on the right, so product yield is favoured by a high pressure.

18 In order to answer this question, you need to know that the Haber process reaction is exothermic in the forward reaction.

An increase in temperature will favour the endothermic – backward – reaction – so the equilibrium will shift to the left. This will cause:

- the value of K_c to be decreased
- the yield of the reaction to be decreased

Practice questions

1 When a reaction is at equilibrium the concentrations of the reactants and products do not change and the equilibrium position remains constant. The reactants and products do continue to react, but as the forward and backward reactions are occurring at the same rate, no observable changes in concentration occur.

Correct answer is C.

2 Because the reaction is exothermic ($\Delta H^{\ominus}$ is negative), heat can be regarded as a product. Increasing temperature would therefore shift the equilibrium to the left as well as increasing the rate of both the forward and reverse reactions. As there are 4 moles of gaseous reactants and 2 moles of gaseous products, increasing pressure will shift the equilibrium to the right. However, conducting reactions at high pressure increases the costs.

Correct answer is D.

3 Because the reaction is exothermic ($\Delta H^{\ominus}$ is negative), increasing temperature will shift the equilibrium to the left, decreasing the yield of products and decreasing the equilibrium constant.

Correct answer is D.

4 The equilibrium being considered involves the vapourization of methanol, which is an endothermic process, therefore decreasing temperature will move the equilibrium to the left, decreasing the amount of products and decreasing the value of K_c.

Correct answer is A.

5 Increasing temperature will increase the rate of both the forward and reverse reactions. For the amount of chlorine product to increase the rate of the forward reaction must have increased more than the rate of the reverse reaction.

Correct answer is C.

6 As H^+ is a product, adding more H^+ will shift the position of the equilibrium to the left. However, the value of K_c will remain unchanged as the temperature remains constant. (The value of K_c only changes when the temperature is changed.)

Correct answer is D.

7 The equilibrium being considered involves the condensation of water, which is an exothermic process, therefore increasing temperature will move the equilibrium to the left and increase the amount of gas present. As the system will establish a new equilibrium at the new temperature the rate of condensation will be equal to the rate of vapourization at this equilibrium.

Correct answer is A.

8 Because the system is at equilibrium the rates of the forward and reverse reactions are equal and the amount of $H_2O(g)$ will not change. The pressure exerted by $H_2O(g)$ will therefore remain constant.

Correct answer is D.

9 **(a)** $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

(b) There are 3 moles of gaseous reactants and 2 moles of gaseous products therefore increasing pressure will move the equilibrium position to the right and increase the yield of $SO_3(g)$.

(c) Because the reaction is exothermic ($\Delta H^{\ominus}$ is negative) increasing temperature will move the equilibrium position to the left and decrease the yield of $SO_3(g)$.

(d) A catalyst will increase the rate of both the forward and reverse reactions. However, the forward and reverse rates of reaction increase equally so a catalyst has no effect on the position of equilibrium or the value of K_c.

10 **(a)** If the system is homogeneous all of the reactants and products are in the same phase. If it is in equilibrium the concentrations of the reactants and products remain constant as the rates of the forward and reverse reactions are the same.

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

(c) There are 2 moles of gaseous reactants and 2 moles of gaseous products so increasing the pressure will have no effect on the position of equilibrium.

(d) If K_c decreases as temperature increases then less product is formed at the higher temperature. A decreased yield of product at higher temperature occurs when the forward reaction is exothermic.

(e) A catalyst will increase the rate of both the forward and reverse reactions equally so the platinum has no effect on the position of equilibrium or the value of K_c.

Challenge yourself

1 Earth receives energy from the Sun and disperses energy, largely as heat. Exchange of matter is minimal – the only exceptions to Earth being a closed system are matter received from space such as asteroids and space dust, and matter lost to space such as spacecraft.

2 The different values of K_c indicate the different stabilities of the hydrogen halides. The bonding is strongest in HCl and weakest in HI. This is largely because of the size of the atoms. As I has a larger atomic radius than Cl, in HI the bonding pair is further from the nucleus than the bonding pair in HCl, and so experiences a weaker pull. The HI bond breaks more easily and the reverse dissociation reaction is favoured, giving a small K_c value. As the HCl bond is strong the reverse dissociation reaction is much less favoured, giving this reaction a large K_c value.

3 The concentration of a pure solid or pure liquid is a constant, effectively its density, which is independent of its amount. These constant values therefore do not form part of the equilibrium expression.

4 The value for K_c at 298 K for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is extremely low, so the equilibrium mixture lies to the left, with almost no production of NO. At higher temperatures, such as in vehicle exhaust fumes, the reaction shifts to the right (as it is an endothermic reaction) and a higher concentration of NO is produced. This gas is easily oxidized in the air, producing the brown gas NO_2 that is responsible for the brownish haze: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$.

5 The atom economies of the Haber process and Contact process reaction described in this chapter are both 100% as there is only one product. In other words, there is no waste if the reaction goes to completion. However, this does not mean that all reactants are converted to product, so the stoichiometric yield is less than 100%. It is the goal of these industries to maximize yield and efficiency by choosing the optimum conditions, taking equilibrium and kinetic considerations into account.

Worked solutions

Chapter 8

Exercises

Significant figures and logarithms

Many of the calculations for this chapter involve the use of logarithms. Determining the correct significant figures for logarithm calculations does not involve the same rules as calculations involving addition, subtraction, multiplication or division. When taking a log the answer will have the same number of decimal places as the number of significant figures in the value that the log is being applied to, for example:

$\log(5) = 0.7$	$\log(2.3 \times 10^4) = 4.36$	$\log(1.00 \times 10^{-7}) = 7.000$
1 s.f. 1 d.p.	2 s.f. 2 d.p.	3 s.f. 3 d.p.

Doing the inverse function (the anti-log) involves the opposite reasoning. Here the number of significant figures in the answer will be the same as the number of decimal places in the value the anti-log is being applied to, for example:

$10^{5.2} = 2 \times 10^5$	$10^{-4.20} = 6.3 \times 10^{-5}$	$10^{0.100} = 1.26$
1 d.p. 1 s.f.	2 d.p. 2 s.f.	3 d.p. 3 s.f.

1 The conjugate acids of the given bases are deduced by adding H^+ to each species. Remember to adjust the charge by +1 in each case.

(a) HSO_3^- **(b)** $CH_3NH_3^+$

(c) C_2H_5COOH **(d)** HNO_3

(e) HF **(f)** H_2SO_4

2 The conjugate bases of the given acids are deduced by removing H^+ from each species. Remember to subtract 1+ from the net charge in each case.

(a) $H_2PO_4^-$ **(b)** CH_3COO^-

(c) HSO_3^- **(d)** SO_4^{2-}

(e) O^{2-} **(f)** Br^-

3 Note that conjugate acid–base pairs follow from Brønsted–Lowry theory. They differ by just one proton – the acid has the extra H^+ and the base has lost it. There are two such pairs in each of the equations in this question; there is an acid and a base on both sides of each equation.

(a) CH_3COOH (acid)/CH_3COO^- (base)

NH_3 (base)/NH_4^+ (acid)

(b) CO_3^{2-} (base)/HCO_3^- (acid)

H_3O^+ (acid)/H_2O (base)

(c) NH_4^+ (acid)/NH_3 (base)

NO_2^- (base)/HNO_2 (acid)

4 To be amphiprotic the substance must be able to both accept and release protons:

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$ (acid behaviour as protons are released)

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$ (base behaviour as protons are accepted)

5 acid + metal → salt + hydrogen

acid + base → salt + water

acid + carbonate → salt + water + carbon dioxide

Then be sure that each equation is balanced and has the correct state symbols.

(a) $H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$

(b) $HNO_3(aq) + NaHCO_3(s) \rightarrow NaNO_3(aq) + H_2O(l) + CO_2(g)$

(c) $H_3PO_4(aq) + 3KOH(aq) \rightarrow K_3PO_4(aq) + 3H_2O(l)$

(d) $6CH_3COOH(aq) + 2Al(s) \rightarrow 2Al(CH_3COO)_3(aq) + 3H_2(g)$

6 **B** Calcium metal will react with an acid. All the other compounds in the question are bases.

7 **B** metal oxide (base) + acid → salt + water

8 **(a)** nitric acid + sodium carbonate (or sodium hydrogencarbonate or sodium hydroxide)

e.g. $2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$

(b) hydrochloric acid + ammonia solution

$HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$

(c) copper(II) oxide + sulfuric acid

$H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$

(d) methanoic acid + potassium hydroxide

$HCOOH(aq) + KOH(aq) \rightarrow KCOOH(aq) + H_2O(l)$

9 The pH increases by 1 unit, as the concentration of H^+ ions has been decreased tenfold, and pH is a logarithmic scale, $pH = -\log[H^+]$.

10 $[H^+] = 1.9 \times 10^{-5}$

$pH = -\log (1.9 \times 10^{-5}) = 4.72$

11 At pH 9, $[H^+] = 10^{-pH} = 10^{-9}$ mol dm^{-3}

At 25 °C, $K_w = [H^+]\,[OH^-] = 1.00 \times 10^{-14}$

$\therefore [OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{10^{-9}} = 1.0 \times 10^{-5}$ mol dm^{-3}

12 $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

At 298 K: solutions are acidic if $[H^+] > 1 \times 10^{-7}$ mol dm^{-3}, $[OH^-] < 1 \times 10^{-7}$ mol dm^{-3}

solutions are basic if $[H^+] < 1 \times 10^{-7}$ mol dm^{-3}, $[OH^-] > 1 \times 10^{-7}$ mol dm^{-3}

(a) $1.00 \times 10^{-14} = [3.4 \times 10^{-9}][OH^-]$, hence $[OH^-] = 2.9 \times 10^{-6}$ mol dm^{-3}; solution is basic as $[OH^-] > 1 \times 10^{-7}$ mol dm^{-3}

(b) $1.00 \times 10^{-14} = [H^+][0.010]$, hence $[H^+] = 1.0 \times 10^{-12}$ mol dm^{-3}; solution is basic as $[H^+] < 1 \times 10^{-7}$ mol dm^{-3}

(c) $1.00 \times 10^{-14} = [H^+][1.0 \times 10^{-10}]$, hence $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}; solution is acidic as $[H^+] > 1 \times 10^{-7}$ mol dm^{-3}

(d) $1.00 \times 10^{-14} = [8.6 \times 10^{-5}][OH^-]$, hence $[OH^-] = 1.2 \times 10^{-10}$ mol dm^{-3}; solution is acidic as $[OH^-] < 1 \times 10^{-7}$ mol dm^{-3}

13 $pH = -\log [H^+] = -\log [0.01] = 2.0$

14 **(a)** $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

Hence $[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{8 \times 10^{-8}} = 1.25 \times 10^{-7}$, so $pH = -\log[1.25] = 6.9$

(b) $pH = -\log [H^+] = -\log [10^{-2}] = 2$

(c) $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

Hence $[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{6 \times 10^{-10}} = 1.7 \times 10^{-5}$, so pH = 4.8

15 Formula mass of NaOH = 40.00 g mol^{-1}

$n(NaOH) = \frac{6.0 \text{ g}}{40.0 \text{ g mol}^{-1}} = 0.15$ mol

One mole of dissolved NaOH gives one mole of OH^- ions.

$[OH^-] = \frac{n}{V} = \frac{0.15 \text{ mol}}{1.0 \text{ dm}^3} = 0.15$ mol dm^{-3}

$K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

Hence $[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.15} = 6.7 \times 10^{-14}$, so pH = 13.17

16 **B** The solution with the lowest conductivity will be the one with the fewest dissociated ions. The solution of ethanoic acid (CH_3COOH) will be the poorest conductor of electricity as ethanoic acid is a weak acid and only partially dissociates into its ions in solution. All the other examples are strong acids (HCl), strong bases (NaOH) or salts (NaCl) and so will dissociate into ions completely in solution. As the solutions are all 1 mol dm^{-3} the total number of ions in the HCl, NaOH and NaCl solutions will be much higher than the number of ions in the CH_3COOH solution.

17 **A** Magnesium will react with the acid and not the base (statement I). Sodium hydroxide will react with the acid (liberating heat); there will be no change when added to the base (statement II). As both are equimolar and either a strong acid or a strong alkali that dissociates completely into its ions to create an electrically conductive solution, the bulb will light brightly in both solutions (statement III).

18 **(a)** H_2CO_3 is a weak acid and H_2SO_4 is a strong acid. H_2CO_3 has the stronger conjugate base, as the conjugate base is formed from the weaker of the two acids.

(b) HCOOH is a weak acid and HCl is a strong acid. HCOOH has the stronger conjugate base, as the conjugate base is formed from the weaker of the two acids.

19 **(a)** Natural rain contains dissolved carbon dioxide, which reacts with water to form carbonic acid, which then dissociates to give H^+, making the rain acidic:

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

$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

(b) Sulfuric acid

Sulfur present in coal combusts with oxygen when the coal is burnt:

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

The $SO_2(g)$ generated can then react further with oxygen in the atmosphere to form $SO_3(g)$:

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

$SO_3(g)$ can dissolve in water to form H_2SO_4, sulfuric acid:

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

As sulfuric acid is a strong acid this results in acid rain being much more acidic than natural rain.

(c) Nitric acid

This is produced when the combustion of fossil fuels takes place in air and the high temperatures present catalyse the reaction between $N_2(g)$ and $O_2(g)$: $N_2(g) + O_2(g) \rightarrow 2NO(g)$.

The $N_2(g)$ generated can then react further with oxygen in the atmosphere to form $NO_2(g)$:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

$NO_2(g)$ can dissolve in water to form HNO_3, nitric acid:

$H_2O(l) + NO_2(g) \rightarrow HNO_3(aq)$

The formation of HNO_3 can be reduced by the use of catalytic converters which convert NO and NO_2 back to N_2, and the recirculation of exhaust gases, which reduce the temperature in the combustion chamber and thus decreases the amount of NO forming.

(d) $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$

(e) Acid rain can have many adverse effects.

Plant life can be impacted by leaching due to acid rain. The acid rain causes minerals in the soil to become more soluble and they are washed away and become unavailable to the plant, hindering growth. This may also result in the release of ions and minerals in soil that are toxic to plants.

Marble and limestone are affected by acid rain as they both contain calcium carbonate, $CaCO_3$, which reacts with acids to form soluble salts, resulting in the erosion of buildings, statues and other structures containing these materials.

Acid rain can have serious impacts on lakes and aquatic life. If lakes become too acidic ($pH < 5$) then many species of fish and other aquatic life cannot survive.

Sulfuric acid and nitric acid in acid rain can react to form sulfate and nitrate particulates that can cause respiratory complaints and other health issues.

(f) Use alternative energy sources to fossil fuels such as solar, wind, hydro, geothermal or nuclear energy. While not as desirable it is also possible to only use coal with a low sulfur content.

20 **(a)** The pollutants that contribute to acid rain are SO_2 and NO. SO_2 reacts with O_2 to give SO_3, which then dissolves in water to give sulfuric acid, H_2SO_4. NO reacts with O_2 to give NO_2, which then dissolves in water to give nitric acid, HNO_3.

(b) Power stations that burn coal produce SO_2 and particulates. The SO_2 is a product of the combustion of sulfur, which is present in coal. Particulates can be nitrates and sulfates that are formed from the nitric and sulfuric acids that result from the NO and SO_2 produced in a coal-burning power station. They can also include unburnt hydrocarbons and carbon soot that is released from the power station.

(c) Particulates act as catalysts in the production of secondary pollutants. They absorb other pollutants such as SO_2 and NO onto their surface, where reactions involving these primary pollutants can be catalysed.

(d) SO_2 can be reacted with CaO before it exits the exhaust system and forms $CaSO_4$:
$CaO(s) + SO_2(g) \rightarrow CaSO_3(g)$

(e) NO comes primarily from motor vehicles. It is formed in the combustion chamber of the engine where the nitrogen and oxygen that are present in the air can react due to the high temperatures present: $N_2(g) + O_2(g) \rightarrow 2NO(g)$

21 **(a)** Dry acid deposition typically occurs close to the source of emission before the gases involved have had the opportunity to encounter water moisture and become dissolved acids. Wet acid deposition can occur any time after the gases have dissolved to become acids and is therefore dispersed over a much larger area and distance from the emission source.

(b) The acid is formed in the air from sulfur dioxide (SO_2) and nitrogen oxide (NO) which are emitted by thermal power stations, industry and motor vehicles. A major source is the burning of fossil fuels, particularly in coal-fired power stations. Pollutants are carried by prevailing winds and converted (oxidized) into sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These are then dissolved in cloud droplets (rain, snow, mist, hail) and this precipitation may fall to the ground as dilute forms of sulfuric acid and nitric acid. The dissolved acids consist of sulfate ions, nitrate ions and hydrogen ions.

22 The hydroxyl free radical $^{\bullet}OH$ is involved in the formation of sulfuric acid and nitric acid.

$^{\bullet}OH + SO_2 \rightarrow {}^{\bullet}HOSO_2$ $^{\bullet}OH + NO_2 \rightarrow HNO_2$
$^{\bullet}HOSO_2 + O_2 \rightarrow {}^{\bullet}HO_2 + SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$

$^{\bullet}OH$ is formed by the reaction between water and either ozone or atomic oxygen:

$H_2O + O^{\bullet} \rightarrow 2{}^{\bullet}OH$
$O_2 + O^{\bullet} \rightarrow O_3$
$O_3 + H_2O \rightarrow 2{}^{\bullet}OH + O_2$

Practice questions

Significant figures and logarithms

Many of the calculations for this chapter involve the use of logarithms. Determining the correct significant figures for logarithm calculations does not involve the same rules as calculations involving addition, subtraction, multiplication or division. When taking a log the answer will have the same number of decimal places as the number of significant figures in the value that the log is being applied to, for example:

$\log(5) = 0.7$		$\log(2.3 \times 10^4) = 4.36$		$\log(1.00 \times 10^{-7}) = 7.000$	
1 s.f.	1 d.p.	2 s.f.	2 d.p.	3 s.f.	3 d.p.

Doing the inverse function (the anti-log) involves the opposite reasoning. Here the number of significant figures in the answer wil be the same as the number of decimal places in the value the anti-log is being applied to, for example:

$10^{5.2} = 2 \times 10^5$		$10^{-4.20} = 6.3 \times 10^{-5}$		$10^{0.100} = 1.26$	
1 d.p.	1 s.f.	2 d.p.	2 s.f.	3 d.p.	3 s.f.

1 Barium hydroxide is a strong base and therefore has the highest pH value.

Correct answer is C.

2 Alkalis, not acids, have a soapy feel.

Correct answer is D.

3 The conjugate base forms from the acid by loss of H^+.

Correct answer is B.

4 The hydroxide ion can gain H^+ to form H_2O and lose H^+ to form O^{2-}.

Correct answer is A.

5 The volume of base will be the same to neutralize equal volumes of the two acids. Both the electrical conductivity and the rate of reaction with calcium carbonate will be higher with the strong acid.

Correct answer is A.

6 The conjugate base of a weak acid is a relatively strong base.

Correct answer is C.

7 These are the two species that donate a proton in the forward and backward reactions respectively.

Correct answer is D.

8 Neutralizing acidified lakes with lime reduces the effects of acid rain, but does not decrease its production.

Both answers I and III involve removing the sources of acid rain by decreasing the release (in I) or the production (in III) of acidic gases into the atmosphere.

Correct answer is B.

9 Acid rain causes leaching of Ca^{2+} from the soil and releases toxic Al^{3+} ions from rocks into bodies of water.

Correct answer is B.

10 HNO_3/NO_3^- and H_2O/OH^- differ by one proton only.

Correct answer is B.

11 The two acids are of the same concentration so differences in pH must be due to differences in acid strength/extent of dissociation.

Correct answer is A.

12 Bronsted–Lowry bases are proton/H^+ acceptors.

Correct answer is D.

13 **(a)** Use a pH meter.

Use a suitable indicator.

(b)

$HCOOH(aq)$	5	weak acid
$KCl(aq)$	7	neutral salt
$HNO_3(aq)$	1	strong acid
$Ba(OH)_2(aq)$	13	strong base
$NH_3(aq)$	10	weak base

(c) **(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

Acid + carbonate/hydrogencarbonate → salt + H_2O + CO_2

(ii) HCO_3^- can act as a Bronsted–Lowry acid and base by giving and accepting protons:

as acid: $HCO_3^- \rightarrow H^+ + CO_3^{2-}$

as base: $HCO_3^- + H^+ \rightarrow H_2CO_3$

(d) Acids release $H_2(g)$ when reacted with reactive metal Mg.

Reaction with strong acid more vigorous than reaction with weak acid.

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

$Mg(s) + 2CH_3COOH(aq) \rightarrow Mg(CH_3COO)_2 + H_2(g)$

(e) Conductivity can be quantified so more objective.

The method described in (c) is qualitative only.

14 **(a)** According to the Brønsted–Lowry theory an acid is a proton (H^+) donor and a base is a proton (H^+) acceptor.

A weak base is a base that will only be partially protonated in aqueous solution:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

A strong base is a base that will be completely protonated in aqueous solution:

$$B(aq) + H_2O(l) \rightarrow BH^+(aq) + OH^-(aq)$$

Ammonia (NH_3) is an example of a weak base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

(b) Many weak acids can cause damage in the environment. Three common ones are sulfurous acid (H_2SO_3), nitrous acid (HNO_3) and carbonic acid (H_2CO_3).

All of these weak acids can corrode marble and limestone buildings, and cause leaching in soils. Sulfurous and nitrous acid are harmful to plant life as leaching removes minerals from the soil that are essential for plant growth. Because of increased concentrations of CO_2 in the atmosphere, its absorption by oceans and lakes generates carbonic acid and the increased acidity of the lakes and oceans can impact on aquatic life. Many aquatic species cannot survive at pH < 5, e.g. the calcium carbonate shells of shellfish dissolve in acidic conditions.

Challenge yourself

1 Sulfur is present in proteins in living cells (a component of two out of the twenty amino acids). Decomposition of plant material to peat and then coal conserves this sulfur. Additional sources are the depositional environment such as sea water, where sulfates are reduced by bacteria to form H_2S, which can react further to form organic sulfur structures.

2 The combustion reaction of nitrogen is $N_2(g) + O_2(g) \rightarrow 2NO(g)$. Combustion of nitrogen involves the highly endothermic step of breaking the extremely strong triple N≡N bond (+942 kJ mol^{-1}), as well as the O=O bond (+498 kJ mol^{-1}). The exothermic step of forming the triple N≡O bond releases less energy – approximately 630 kJ mol^{-1}, therefore the enthalpy change of the reaction (bonds broken minus bonds formed) is endothermic. The stability and strength of the nitrogen triple bond therefore creates an unusual situation where the products of combustion are less stable than the reactants.

3 As the oxidation number of H is +1 and O is –2 we can determine the oxidation numbers of nitrogen, realizing that the sum of the oxidation numbers must equal zero as all the acids are neutral molecules.

HNO_2: $+1 + x + 2(-2) = 0; x = +3$

Oxidation number of nitrogen is +3. Name is nitric(III) acid.

HNO_3: $+1 + x + 3(-2) = 0; x = +5$

Oxidation number of nitrogen is +5. Name is nitric(V) acid.

H_2SO_3: $2(+1) + x + 3(-2) = 0; x = +4$

Oxidation number of sulfur is +4. Name is sulfuric(IV) acid.

H_2SO_4: $2(+1) + x + 4(-2) = 0; x = +6$

Oxidation number of sulfur is +6. Name is sulfuric(VI) acid.

Worked solutions

Chapter 9

Exercises

1 The numbers are assigned following the strategy on page 270. In most of these it is best to assign the values for O [–2] and H [+1] first, and then assign values to the remaining elements so that the sum of the oxidation states of each element in the species is equal to the charge on the species (or zero in the case of neutral species), e.g.

for NH_4^+:

charge on species = oxidation state of N + 4 × oxidation state of H

$+1$ = oxidation state of N + 4 × (+1)

Oxidation state of N = +1 – (+4) = –3

Oxidation states of elements: N = –3, H = +1

Remember that the elements P, S and N, as well as the transition metals, can take different oxidation states, depending on the compound.

(a) NH_4^+ = N –3, H +1

(b) $CuCl_2$: As no other information is available we can assume that Cl will be present in the –1 oxidation state, which is the preferred oxidation state for Group 17 elements that typically form 1^- ions.

0 = oxidation state of Cu + 2 × (–1)

Oxidation state of Cu = 0 – (–2) = +2

Oxidation states of elements: Cu = +2, Cl = –1

(c) H_2O: See if the oxidations states balance by assuming both H and O are present in their preferred oxidation states.

0 = 2 × (+1) + –2

Oxidation states of elements: H = +1, O = –2

(d) SO_2^-

0 = oxidation state of S + 2 × (–2)

Oxidation state of S = 0 – (–4) = +4

Oxidation states of elements: S = +4, O = –2

(e) Fe_2O_3:

0 = 2 × (oxidation state of Fe) + 3 × (–2)

Oxidation state of Fe = $\frac{(0 - -6)}{2}$ = +3

Oxidation states of elements: Fe = +3, O = –2

(f) NO_3^-:

–1 = oxidation state of N + 3 × (–2)

Oxidation state of N = –1 – (–6) = +5

Oxidation states of elements: N = +5, O = –2

(g) MnO_2:

0 = oxidation state of Mn + 2 × (–2)

Oxidation state of Mn = 0 – (–4) = +4

Oxidation states of elements: Mn = +4, O = –2

(h) PO_4^{3-}:

–3 = oxidation state of P + 4 × (–2)

Oxidation state of P = –3 – (–8) = +5

Oxidation states of elements: P = +5, O = –2

(i) $K_2Cr_2O_7$: We need to assume that O will be present with an oxidation state of –2 and, as it is a Group 1 element that can only lose one electron, K will be present with an oxidation state of +1.

0 = 2 × (+1) + 2 × (oxidation state of Cr) + 7 × (–2)

2 × (oxidation state of Cr) = 0 – (–14) = +14

Oxidation state of Cr = +7

Oxidation states of elements: K = +1, Cr = +7, O = –2

(j) MnO_4^-:

–1 = oxidation state of Mn + 4 × (–2)

Oxidation state of Mn = –1 – (–8) = +7

Oxidation states of elements: Mn = +7, O = –2

2 The best strategy here is to pick out one element at a time and work out its oxidation state on both sides of the equation. If it has increased, it has been oxidized; if it has decreased it has been reduced. If there is no change in oxidation state that atom has neither been oxidized nor reduced. Check that you have one element being oxidized and one being reduced on each side of the equation.

(a)

reduction

$Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

+2 +3 +4 +2

oxidation

(b)

reduction

$Cl_2(aq) + 2NaBr(aq) \rightarrow Br_2(aq) + 2NaCl(aq)$

0 +1 −1 0 +1 −1

oxidation

(c)

reduction

$2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

+2 −1 0 +3 −1

oxidation

(d)

reduction

$2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$

+1 −2 0 +1 −1 0

oxidation

(e)

reduction

$I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

0 +4 −2 +1 −2 −1 +6 −2 +1

oxidation

3 Follow the same steps as in Q2, assigning oxidation states to the atoms on both sides of the equation and using these to deduce what is being oxidized and what is reduced. Then separate these into half-equations as described on pages 274–275. Remember to balance the charge of each half-equation by adding electrons – to the reactants side in reduction half-reactions and to the products side in oxidation half-reactions.

(a) $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$

0 +1 +2 0

oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$

reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

(b) $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

+2 0 +3 −1

oxidation: $2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2e^-$

reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

(c) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

+2 +3 +4 +2

oxidation: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

reduction: $2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$

(d) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

0 −1 −1 0

oxidation: $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

reduction: $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

4 The steps for writing the redox equations are given on page 275. The interim steps for each of these examples are given below.

(a) 1 Assign oxidation states and determine what is being oxidized and reduced:

$Zn(s) + SO_4^{2-}(aq) \rightarrow Zn^{2+}(aq) + SO_2(g)$

0 +6 −2 +2 + 4 −2

Zn is being oxidized and S is being reduced.

2 **(i)** Identify species being oxidized and reduced in the half-equations:

oxidation: $Zn \rightarrow Zn^{2+}$

reduction: $SO_4^{2-} \rightarrow SO_2$

(ii) Balance the reduction equation for O by adding H_2O:

reduction: $SO_4^{2-} \rightarrow SO_2 + 2H_2O$

(iii) Balance the reduction equation for H by adding H^+:

reduction: $SO_4^{2-} + 4H^+ \rightarrow SO_2 + 2H_2O$

(iv) Balance each equation for charge by adding electrons:

oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

reduction: $SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

3 Electrons are equal (2) in the two half-equations.

4 Add half-equations together:

$Zn(s) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + SO_2(g) + 2H_2O(l)$

(b) **1** Assign oxidation states:

$I^-(aq) + HSO_4^-(aq) \rightarrow I_2(aq) + SO_2(g)$

-1 $+1$ $+6$ -2 0 $+4$ -2

I^- is being oxidized and S is being reduced.

2 **(i)** Identify species being oxidized and reduced in the half-equations:

oxidation: $2I^- \rightarrow I_2$

reduction: $HSO_4^- \rightarrow SO_2$

(ii) Balance the reduction equation for O by adding H_2O:

reduction: $HSO_4^- \rightarrow SO_2 + 2H_2O$

(iii) Balance the reduction equation for H by adding H^+:

reduction: $HSO_4^- + 3H^+ \rightarrow SO_2 + 2H_2O$

(iv) Balance each equation for charge by adding electrons:

oxidation: $2I^- \rightarrow I_2 + 2e^-$

reduction: $HSO_4^- + 3H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

3 Electrons are equal (2) in the two half-equations.

4 Add half-equations together:

$2I^-(aq) + HSO_4^-(aq) + 3H^+(aq) \rightarrow I_2(aq) + SO_2(g) + 2H_2O(l)$

(c) **1** Assign oxidation states:

$NO_3^-(aq) + Zn(s) \rightarrow NH_4^+(aq) + Zn^{2+}(aq)$

$+5$ -2 0 -3 $+1$ $+2$

N is being reduced and Zn is being oxidized.

2 **(i)** Identify species being oxidized and reduced in the half-equations:

reduction: $NO_3^- \rightarrow NH_4^+$

oxidation: $Zn \rightarrow Zn^{2+}$

(ii) Balance the reduction equation for O by adding H_2O:

reduction: $NO_3^- \rightarrow NH_4^+ + 3H_2O$

(iii) Balance the reduction equation for H by adding H^+:

reduction: $NO_3^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$

(iv) Balance each equation for charge by adding electrons:

reduction: $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$

oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

3 Multiply oxidation half-equation by 4 to equalize electrons in the two half-equations:

oxidation: $4Zn \rightarrow 4Zn^{2+} + 8e^-$

4 Add half-equations together:

$4Zn(s) + NO_3^-(aq) + 10H^+(aq) \rightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(l)$

(d) **1** Assign oxidation states:

$I_2(aq) + OCl^-(aq) \rightarrow IO_3^-(aq) + Cl^-(aq)$

0 -2 $+1$ $+5$ -2 -1

(Note: OCl^- is unusual in that it contains Cl with an oxidation state of +1. This is because it is in the presence of the more electronegative oxygen.)

I_2 is being oxidized and Cl^- is being reduced.

2 **(i)** Identify species being oxidized and reduced in the half-equations:

oxidation: $I_2 \rightarrow 2IO_3^-$

reduction: $OCl^- \rightarrow Cl^-$

(ii) Balance both equations for O by adding H_2O:

oxidation: $I_2 + 6H_2O \rightarrow 2IO_3^-$

reduction: $OCl^- \rightarrow Cl^- + H_2O$

(iii) Balance reduction equation for H by adding H^+:

oxidation: $I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+$

reduction: $OCl^- + 2H^+ \rightarrow Cl^- + H_2O$

(iv) Balance each equation for charge by adding electrons:

oxidation: $I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$

reduction: $OCl^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$

3 Multiply reduction half-equation by 5 to equalize electrons:

reduction: $5OCl^- + 10H^+ + 10e^- \rightarrow 5Cl^- + 5H_2O$

4 Add half-equations together, noting that much of the H^+ and H_2O cancel here:
$I_2(aq) + H_2O(l) + 5OCl^-(aq) \rightarrow 2IO_3^-(aq) + 2H^+(aq) + 5Cl^-(aq)$

(e) 1 Assign oxidation states:

$MnO_4^-(aq) + H_2SO_3(aq) \rightarrow$
+7 −2   +1 +4 −2

$Mn^{2+}(aq) + SO_4^{2-}(aq)$
+2   +6 −2

Mn is being reduced and S is being oxidized.

2 **(i)** Identify species being oxidized and reduced in the half-equations:
oxidation: $H_2SO_3 \rightarrow SO_4^{2-}$
reduction: $MnO_4^- \rightarrow Mn^{2+}$

(ii) Balance both equations for O by adding H_2O:
oxidation: $H_2SO_3 + H_2O \rightarrow SO_4^{2-}$
reduction: $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

(iii) Balance the reduction equation for H by adding H^+:
oxidation: $H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+$
reduction: $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

(iv) Balance each equation for charge by adding electrons:
oxidation: $H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$
reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

3 Multiply oxidation half-equation by 5 and reduction half-equation by 2 to equalize electrons:
oxidation: $5H_2SO_3 + 5H_2O \rightarrow 5SO_4^{2-} + 20H^+ + 10e^-$
reduction: $2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$

4 Add half-equations together, noting that much of the H^+ and H_2O cancel here:
$5H_2SO_3(aq) + 2MnO_4^-(aq) \rightarrow 5SO_4^{2-}(aq) + 4H^+(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$

5 B This is the only equation where any elements in the reactants change oxidation state during the course of the reaction. In all the other reactions the oxidation states of the elements are the same on both the reactants side and products side as no electrons are being exchanged and therefore no redox occurs.

A: Na = +1, O = −2, H = +1, N = +5 for both sides

B: Reactants Zn = 0, H = +1, Cl = −1; products Zn = +2, Cl = −1, H = 0

C: Cu = +2, O = −2, H = +1, Cl = −1 for both sides

D: Mg = +2, C = +4, O = −2, H = +1, N = +5 for both sides

6 D We can assume that O is present in oxidation state −2 and Cl is present in oxidation state −1, the preferred oxidation state for Group 17 elements. We can also take a shortcut for $Cr_2(CO_3)_3$ by assigning an oxidation state of −2 to the CO_3^{2-} ion rather than to the component elements.

A $CrCl_3$
+3 −1

B Cr_2O_3
+3 −2

C $Cr_2(CO_3)_3$
+3 (−2)

D CrO_3
+6 −2

Oxidation state of chromium in CrO_3 = +6, but in $CrCl_3$, Cr_2O_3 and $Cr_2(CO_3)_3$ it is +3.

7 In each case, calculate the oxidation state of the metal (or nitrogen) and use this to help name the compound. Remember that the sum of the oxidation states has to equal zero. The oxidation states of the other elements under consideration are O = −2, H = +1 and Cl = −1.

(a) Cr_2O_3

0 = 2 × (oxidation state of Cr) + 3 × (−2)

$$\text{Oxidation state of Cr} = \frac{0-(-6)}{2} = +3$$

The name of the compound is chromium(III) oxide.

(b) CuCl

0 = oxidation state of Cu + −1
Oxidation state of Cu = 0 − (−1) = +1
The name of the compound is copper(I) chloride.

(c) HNO_3

0 = +1 + oxidation state of N + 3 × (–2)

Oxidation state of N = 0 – (+1) – (–6) = +5

The name of the compound is nitric(V) acid. (From Chapter 8 we can recognize that this is an acidic compound.)

(d) HNO_2

0 = +1 + oxidation state of N + 2 × (–2)

Oxidation state of N = 0 – (+1) – (–4) = +3

The name of the compound is nitric(III) acid. (From Chapter 8 we can recognize that this is an acidic compound.)

(e) PbO_2

0 = oxidation state of Pb + 2 × (–2)

Oxidation state of Pb = 0 – (–4) = +4

The name of the compound is lead(IV) oxide.

8 Again the first thing to do here is to assign oxidation states to each element on both sides of the equation. The species that contains the element that is oxidized acts as the reducing agent, the one that contains the element that is reduced acts as the oxidizing agent.

(a) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

0 0 +1 –1

oxidizing agent: Cl_2

reducing agent: H_2

(b) $2Al(s) + 3PbCl_2(s) \rightarrow 2AlCl_3(s) + 3Pb(s)$

0 +2 –1 +1 –1 0

oxidizing agent: Pb^{2+}

reducing agent: Al

(c) $Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$

0 +1 –1 +1 –1 0

oxidizing agent: Cl_2

reducing agent: I^-

(d) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

–4 +1 0 +4 –2 +1 –2

oxidizing agent: O_2

reducing agent: CH_4

9 Note the following:

- the more reactive metal always gets oxidized (acts as reducing agent)
- the more reactive non-metal always gets reduced (acts as oxidizing agent).

(a) $CuCl_2(aq) + Ag(s)$

No reaction, Cu is a more reactive metal than Ag.

(b) $Fe(NO_3)_2(aq) + Al(s)$

Al is a more reactive metal than Fe, so is able to reduce Fe^{3+} to Fe(s). (Al(s) will be oxidized to Al^{3+} ions.)

The balanced equation is $3Fe(NO_3)_2(aq) + 2Al(s) \rightarrow 2Al(NO_3)_3(aq) + 3Fe(s)$.

(c) $NaI(aq) + Br_2(aq)$

Br is a more reactive non-metal than I, so is able to oxidize I^- to I_2. (Br_2 will be reduced to Br^- ions.)

The balanced equation is $2NaI(aq) + Br_2(aq) \rightarrow 2NaBr(aq) + I_2(aq)$.

(d) $KCl(aq) + I_2(aq)$

No reaction, Cl is a more reactive non-metal than I.

10 **(a)** A more reactive metal will displace a less reactive metal from its salt in solution.

From the reactions given:

$W + X^+ \rightarrow W^+ + X$

therefore W is more reactive than X

$X + Z^+ \rightarrow X^+ + Z$

therefore X is more reactive than Z

$Y^+ + Z \rightarrow$ no reaction

therefore Z is less reactive than Y

$X + Y^+ \rightarrow X^+ + Y$

therefore X is more reactive than Y

So the overall order of reactivity is W > X > Y > Z

(b) **(i)** No reaction as Y is less reactive than W

(ii) No reaction as Z is less reactive than W

11 **(a)** The solution changes from purple to colourless (since $MnO_4^-(aq)$ is purple and $Mn^{2+}(aq)$ ions are very pale pink).

(b) Oxidation reaction involves oxalate ions being oxidized to $CO_2(g)$: $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g)$

All elements are balanced so only need to balance charge by adding electrons:

$C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$

(c) Reduction reaction involves permanganate ions being reduced to manganese (II) ions: $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

Balance O by adding water:

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Balance H by adding H⁺:

$MnO_4^-(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Balance charge by adding electrons:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

(d) Multiply equation (b) by 5 and equation (c) by 2 so that both reactions involve 10 electrons and when they are added together the electrons cancel out.

5 × (b) $5C_2O_4^{2-}(aq) \rightarrow 10CO_2(g) + 10e^-$

2 × (c) $2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$

Combined: $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

(e) Moles of $KMnO_4$ ions = cV = 0.100 mol $dm^{-3} \times \left(\frac{24.65}{1000}\right) dm^3 = 2.465 \times 10^{-3}$ mol

Hence moles of oxalate ions = 2.465×10^{-3} mol $\times \frac{5}{2} = 6.16 \times 10^{-3}$ mol (since oxalate reacts with permanganate in the ratio of 5 to 2).

(f) Moles of Ca^{2+} in original sample = 6.16×10^{-3} (since the ratio of calcium ions to carboxylate ions is 1 to 1).

(g) Mass of calcium chloride = $nM(CaCl_2)$ = $(6.16 \times 10^{-3}$ mol$) \times 110.98$ g mol^{-1} = 0.684 g

Hence percentage of calcium chloride in original mixture = $\frac{0.684 \text{ g}}{2.765 \text{ g}} \times 100\% = 24.7\%$

12 **(a)** Moles of $K_2Cr_2O_7$ = cV = 0.0550 mol $dm^{-3} \times \left(\frac{9.25}{1000}\right) dm^3 = 5.09 \times 10^{-4}$ mol

This reacts with 2.54×10^{-4} moles of C_2H_5OH (as $K_2Cr_2O_7$ and C_2H_5OH react in the ratio 2 : 1).

Mass of $C_2H_5OH = nM(C_2H_5OH)$ = $(2.54 \times 10^{-4}$ mol$) \times 46.08$ g mol^{-1} = 0.0117 g

Therefore percentage by mass = $\frac{0.0117 \text{ g}}{10.000 \text{ g}} \times 100\% = 0.117\%$

(b) $K_2Cr_2O_7(aq)$ is orange, $Cr^{3+}(aq)$ is dark green so the solution changes from orange to green.

13 **(a)** Zn is a more reactive metal than Fe, so is oxidized.

Zn/Zn^{2+} is the anode, where oxidation occurs

Fe/Fe^{2+} is the cathode, where reduction occurs

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

(b) Mg is a more reactive metal than Fe, so is oxidized.

Fe/Fe^{2+} is the cathode, where reduction occurs

Mg/Mg^{2+} is the anode, where oxidation occurs

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

(c) Mg is a more reactive metal than Cu, so is oxidized.

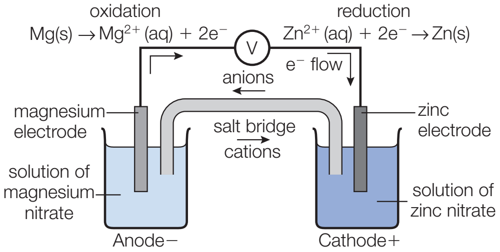
Mg/Mg^{2+} is the anode, where oxidation occurs

Cu/Cu^{2+} is the cathode, where reduction occurs

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

14 **(a)** Mg is a more reactive metal than Zn so will be oxidized in the voltaic cell.



(b) $Mg(s) \mid Mg^{2+}(aq) \parallel Zn^{2+}(aq) \mid Zn(s)$

15 First establish from the reactivity series that Fe is a more reactive metal than Cu and so will reduce Cu^{2+} ions in solution (and form Fe^{2+} ions). The observations depend on knowledge that Cu^{2+} ions are blue in solution and that copper metal is red/brown. Overall equation will be:

$$\underset{\text{(blue)}}{Fe(s) + Cu^{2+}(aq)} \rightarrow \underset{\text{(red/brown)}}{Fe^{2+}(aq) + Cu(s)}$$

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.

16 The question is best tackled by:

- writing out the formula for the ions present in each compound
- stating that negative ions are oxidized at the anode
- stating that positive ions are reduced at the cathode
- writing the equations by adding (reduction) or losing (oxidation) the appropriate number of electrons to form the neutral element.

(a) KBr: Ions present are K^+ and Br^-. K^+ will be reduced at cathode and Br^- will be oxidized at anode.

Oxidation occurs at the anode:
$2Br^-(l) \rightarrow Br_2(l) + 2e^-$

Reduction occurs at the cathode:
$2K^+(l) + 2e^- \rightarrow 2K(l)$

(b) MgF_2: Ions present are Mg^{2+} and F^-. Mg^{2+} will be reduced at the cathode and F^- will be oxidized at the anode.

Oxidation occurs at the anode:
$2F^-(l) \rightarrow F_2(g) + 2e^-$

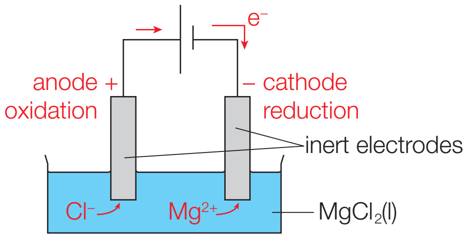
Reduction occurs at the cathode:
$Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$

(c) ZnS: Ions present are Zn^{2+} and S^{2-}. Zn^{2+} will be reduced at the cathode and S^{2-} will be oxidized at the anode.

Oxidation occurs at the anode:
$S^{2-}(l) \rightarrow S(l) + 2e^-$

Reduction occurs at the cathode:
$Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$

17 **(a)**



(b) anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

cathode: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$

overall: $Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(s) + Cl_2(g)$

18 **D** $MgCl_2$ contains Mg^{2+} and Cl^- ions. In the molten state the Mg^{2+} and Cl^- ions can migrate to the electrodes (**A** is correct). Mg^{2+} will be reduced at the cathode and Cl^- (chloride ions) will be oxidized at the anode (**B** is correct). During electrolysis the electrons being transferred travel through the external circuit (**C** is correct). Chlorine (Cl_2) is not present in the reactants so it cannot be oxidized at the cathode so **D** is incorrect. **D** is also incorrect as reduction takes place at the cathode, not oxidation.

Practice questions

1 As the oxidation state of oxygen is –2 we can determine that the oxidation state of nitrogen in NO_2 is +4. The species being reduced to form NO_2 must contain nitrogen in an oxidation state greater than +4.

A N_2O	**B** NO_3^-	**C** HNO_2	**D** NO
+1	+5	+3	+2

Correct answer is B.

2 $\underset{+7}{MnO_4^-}(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow \underset{+2}{Mn^{2+}}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

The oxidation state of Mn changes from +7 in $MnO_4^-(aq)$ to +2 in $Mn^{2+}(aq)$. This means that

Mn has been reduced, therefore it has gained electrons and MnO_4^- is the oxidizing agent.

Correct answer is C.

3 $2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow$
+7 −1

$2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$
+4 +5

The reducing agent is the species that gets oxidized. In the reaction the oxidation state for Br has changed from −1 in $Br^-(aq)$ to +5 in $BrO_3^-(aq)$, therefore Br has been oxidized and $Br^-(aq)$ is the reducing agent.

Correct answer is A.

4 In a voltaic cell reduction occurs at the positive electrode.

I. Change in oxidation state for Zn is +2 → 0, reduction occurs.
II. Change in oxidation state for Cl is 0 → −1, reduction occurs.
III. Change in oxidation state for Mg is 0 → +2, oxidation occurs.

Correct answer is A.

5 In a voltaic cell the negative electrode is the anode and oxidation occurs. In an electrolytic cell the negative electrode is the cathode and reduction occurs.

Correct answer is A.

6 Oxidation state changes from −3 to +3.

Correct answer is C.

7 The half-equation is $16H_2O + P_4 \rightarrow 4H_2PO_4^- + 24H^+ + 20e^-$.

Correct answer is A.

8 The ions are free to move in the molten state, even when no current flows.

Correct answer is D.

9 Electrons will flow from zinc (the anode) to silver (the cathode).

Correct answer is A.

10 Oxidation is an increase in oxidation number. It occurs in I (0 → +1) and III (+1 → +5).

Correct answer is D.

11 Negative ions (anions) flow from cathode to anode, which helps maintain electrical neutrality.

Correct answer is C.

12 The oxidation number of Mn changes from +2 to +7 so 5 moles of electrons are needed per mole, therefore 5 × 0.20 moles needed.

Correct answer is D.

13 Cl^- is oxidized at the anode, releasing $Cl_2(g)$.

$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Correct answer is C.

14 Oxidizing agents are reduced by the reaction. In **A** nitrogen is reduced from +5 → +4.

Correct answer is A.

15 **(a)** As water is a neutral ligand the overall charge is due to the oxidation state of the central cobalt ion. The oxidation state of cobalt is +2.

(b) The charge on the sulfate ion is −2. This gives a total negative charge due to the three sulfate ions of −6. To be neutral overall a +6 charge must be shared by the two cobalt centres. The oxidation state of cobalt is +3.

(c) The charge on the chloride ion is −1. This gives a total negative charge due to the four chloride ions of −4. For an overall charge of −2 on the complex ion the charge on the cobalt centre must be +2. The oxidation state of cobalt is +2.

16 **(a)** A voltaic cell involves a spontaneous reaction and converts chemical energy to electrical energy whereas an electrolytic cell involves a non-spontaneous reaction with electrical energy being converted to chemical energy.

In a voltaic cell the cathode is negative and the anode is positive whereas in an electrolytic cell the anode is negative and the cathode is positive. (In both types of cell oxidation occurs at the anode and reduction at the cathode.)

A voltaic cell requires two separate solutions joined by a salt bridge whereas an electrolytic cell involves a single solution and does not require a salt bridge.

(b) For a substance to conduct electricity it must have charged species that are mobile. In solid NaCl the ions are unable to move and it cannot conduct electricity. In molten (liquid) NaCl the ions are able to move and it is able to conduct electricity.

(c) Molten NaCl contains Na^+ and Cl^- ions.

Reduction occurs at the cathode:

$Na^+(l) + e^- \rightarrow Na(s)$

Oxidation occurs at the anode:

$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

reduction: $2Na^+(l) + 2e^- \rightarrow 2Na(s)$

oxidation: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

---

overall: $2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(s) + Cl_2(g)$

(d) Aluminium is less dense and more malleable than iron as well as being more resistant to corrosion, all of which makes aluminium preferable to iron in many applications, such as aircraft and car construction. Aluminium is also a better heat conductor, which makes it more suitable for uses such as saucepans, and a better electrical conductor than iron, which makes it more suitable for electronics.

17 **(a)** The oxidizing agent is itself reduced, so HNO_3 is identified because of the reduction in oxidation state of N.

(b) **(i)** $n = cV$

$n = 0.100 \text{ mol dm}^{-3} \times 28.50/1000 \text{ dm}^3$
$= 2.85 \times 10^{-3}$ mol (answer to 3 s.f.)

(ii) From the stoichiometric ratios in steps 1–3, we can deduce that:

2 mol $S_2O_3^{2-}$: 1 I_2

1 I_2 : 2 Cu^{2+}

1 Cu^{2+} : 1 Cu

Therefore 1 Cu in brass : 1 $S_2O_3^{2-}$ so $n(Cu) = n(S_2O_3^{2-}) = 2.85 \times 10^{-3}$ mol.

(iii) mass $= n \times M = 2.85 \times 10^{-3} \text{ mol} \times 63.55 \text{ g mol}^{-1} = 0.181$ g

(iv) % by mass of copper = mass of copper/total mass × 100
= 0.181 g/0.456 g × 100 = 39.7%

(v) % error = theoretical – experimental/theoretical × 100
= (44.2% – 39.7%)/44.2% × 100
= 10.2%

18 **(a)** Oxidized: S –2 → 0

Reduced: O 0 → –2

(b) Reducing agent is H_2S

Reduces $SO_2(g)$ to S(s)/is oxidized from $H_2S(g)$ to S(s)

(c) pH increases

SO_2 and H_2S are both acids that are used up in the reaction.

(d) Release of $SO_2(g)$ can lead to acid rain.

$SO_2(g)$ dissolves in water to form weakly acid solutions.

19 **(a)** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

(b) Oxidation of zinc occurs preferentially.

Protects the iron from oxidation.

(c) Iron rusts/corrodes/flakes off.

Colour changes, forming dark red/black patches.

20 **(a)** The equation is balanced for atoms/elements.

The equation is not balanced for charge.

(b) Balance the equation using the half-equation method, using H_2O to balance for O and H^+ to balance for H.

oxidation: $Sn^{2+}(aq) + 2H_2O(l) \rightarrow$
$SnO_2(s) + 4H^+(aq) + 2e^-$

reduction: $MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow$
$MnO_2(s) + 2H_2O(l)$

Balance electrons in the two half-equations: the oxidation reaction must be multiplied by 3 and the reduction equation by 2. Add the two half-equations together and cancel terms on both sides.

$$3Sn^{2+}(aq) + 2H_2O(l) + 2MnO_4^-(aq) \rightarrow$$
$$3SnO_2(s) + 4H^+(aq) + 2MnO_2(s)$$

Challenge yourself

1 Oxidation state of elements in H_2O_2: H = +1, O = −1.

The oxidation state of the oxygen atom in H_2O_2 is halfway between 0 (element) and −2 (usual oxidation state of oxygen in compounds), so it can be oxidized (to 0) or reduced (to −2) and H_2O_2 will act as a reducing agent or oxidizing agent, respectively. As oxygen is a very electronegative element it will more easily be reduced from −1 to −2 and hydrogen peroxide is more likely to act as an oxidizing agent.

2 $$\underset{0}{Cl_2}(aq) + 2NaOH(aq) \rightarrow$$

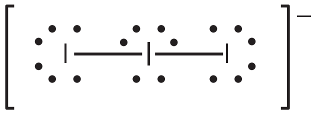
$$\underset{-1}{NaCl}(aq) + \underset{+1}{NaClO}(aq) + H_2O(l)$$

Consider the changes that occur in the oxidation state for Cl in the reaction above:

- In forming NaCl from Cl_2 the oxidation state changes from 0 to −1 and reduction occurs.
- In forming NaClO from Cl_2 the oxidation state changes from 0 to +1 and oxidation occurs.

As the oxidation and reduction of Cl_2 occur simultaneously this is a disproportionation reaction.

3 The Lewis structure of I_3^- is:



As the central atom has five electron domains with two bonding electron pairs this gives a linear shape. The negative charge is spread out over the linear ion and due to the large size of the iodine atoms there is a low charge density. This low charge density enables I_3^- to form a stable complex in the hydrophobic interior of the amylose helix.

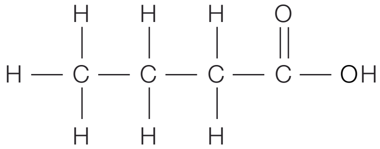
4 As the temperature of water increases the amount of dissolved oxygen decreases as more gas molecules will have sufficient kinetic energy to escape the water surface. The discharge of hot water will cause a decrease in the dissolved oxygen in the lake (with possible negative consequences for aquatic life).

Chapter 10

Exercises

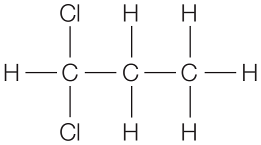
1 Remember to count the carbon of the functional group when naming an organic compound.

(a) $CH_3CH_2CH_2COOH$



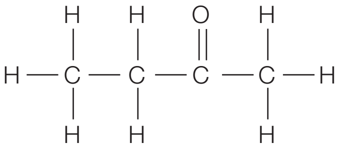
The compound contains the –COOH functional group so it is a **carboxylic acid**. Because it is a carboxylic acid its name will ends in -oic acid. The carbon chain is an alkane that contains four carbons so the compound's name has the stem but-. The compound's name is **butanoic acid**.

(b) $CHCl_2CH_2CH_3$



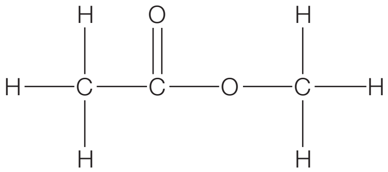
The compound contains two chlorine substituents so it is a **halogenoalkane** (more specifically a **chloroalkane**). Because it is a chloroalkane, its name will have the prefix chloro-. The carbon chain is an alkane that contains three carbons so the compound's name has the stem prop-. There are two chlorine atoms, both on the first carbon so the prefix becomes 1,1-dichloro-. The compound's name is 1,1-dichloropropane.

(c) $CH_3CH_2COCH_3$



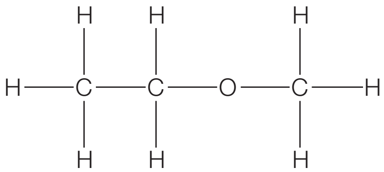
The compound contains a carbonyl functional group (–C=O). Because the carbonyl group is attached to two carbons the compound is a **ketone**. Because it is a ketone its name will end in -one. The carbon chain is an alkane that contains four carbons so the compound's name has the stem but-. The compound's name is **butanone**. (We do not need to specify the position of the ketone group for this compound – if it is on either of the two middle carbons it is the same compound.)

(d) CH_3COOCH_3



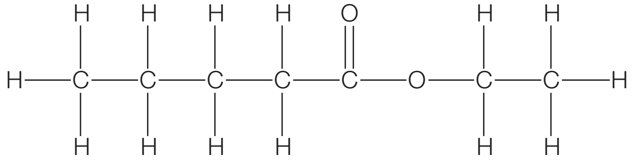
The compound contains an ester functional group (R–COO–R) so it is an **ester**. Because the carbonyl component of the ester contains two carbons the compound's name ends in ethanoate. Because the oxygen component of the ester is attached to a one-carbon chain the name starts with methyl. The compound's name is **methyl ethanoate**.

(e) $CH_3CH_2OCH_3$



The compound contains an ether functional group (R–O–R) so it is an **ether**. Because the smallest carbon chain has one carbon the compound's name starts with methoxy-. Because the longest carbon chain contains two carbons the compound's name ends in -ethane. The compound's name is **methoxyethane**.

(f) $CH_3CH_2CH_2CH_2COOCH_2CH_3$

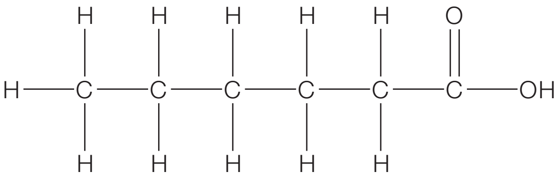


The compound contains an ester functional group (R–COO–R) so it is an **ester**. Because the carbonyl component of the ester contains five carbons the compound's name ends in pentanoate. Because the oxygen component of the ester is attached to a two-carbon chain the name starts with ethyl. The compound's name is **ethyl pentanoate**.

2 For each compound the condensed structural formula is given first and the full structural formula is given second. Either type of structural formula is an acceptable answer.

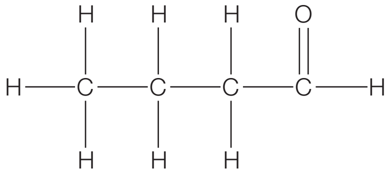
(a) Hexanoic acid: The compound has a six-carbon chain and the –COOH carboxylic acid functional group.

$CH_3(CH_2)_4COOH$



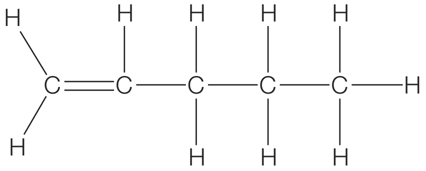
(b) Butanal: The compound has a four-carbon chain and the –CHO aldehyde functional group.

$CH_3CH_2CH_2CHO$



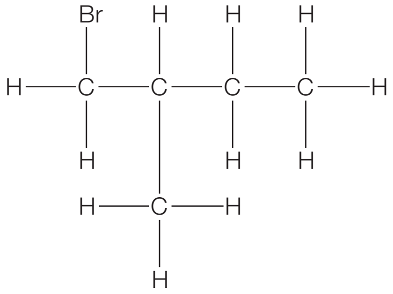
(c) Pent-1-ene: The compound has a five-carbon chain with a C=C double bond after the first carbon.

$CH_2CHCH_2CH_2CH_3$ or $CH_2CH(CH_2)_2CH_3$



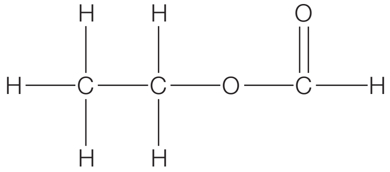
(d) 1-bromo-2-methylbutane: The longest chain has four carbons with a bromine on the first carbon and a methyl (one-carbon branch) on the second carbon.

$CH_2BrCH(CH_3)CH_2CH_3$



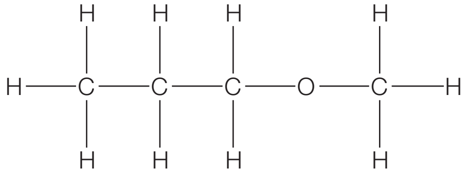
(e) Ethyl methanoate: The compound is an ester with a two-carbon chain attached to the O in the ester and the carbonyl group is part of a one-carbon chain.

$HCOOCH_2CH_3$



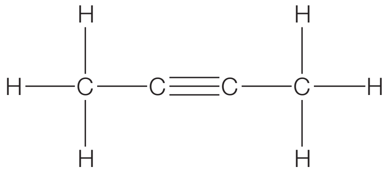
(f) Methoxypropane: The compound is an ether with a one-carbon chain on one side of the ether linkage and a three-carbon chain on the other side.

$CH_3OCH_2CH_2CH_3$



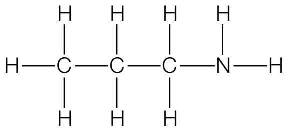
(g) But-2-yne: The compound has a four-carbon chain with a C≡C triple bond after the second carbon.

$CH_3C{\equiv}CCH_3$

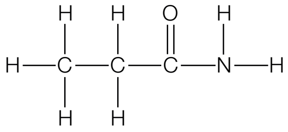


3 **A** Amines contain at least one carbon–nitrogen single bond (it is an analogue of ammonia).

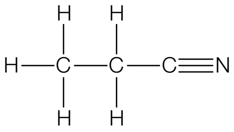
B is not an amine but a primary amide as it contains the $CONH_2$ group. **C** is a nitrile (C≡N group). **D** is a substituted amide as it contains CONH–R (it is a secondary amide).



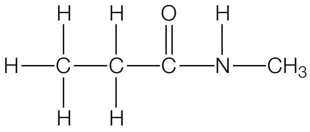
A is an amine



B is an amide

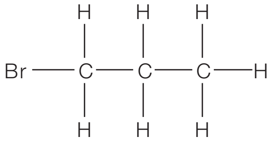


C is a nitrile

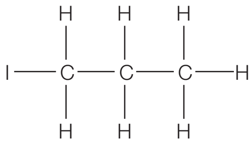


D is a secondary amide

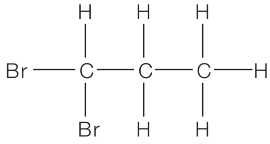
4 **D** Members of homologous series have the same functional group but differ by the number of $–CH_2–$ units present (different chain length). Because 1-bromopropane is a bromoalkane the correct answer will be another 1-bromoalkane with a different chain length.



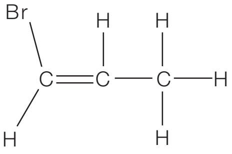
1-bromopropane



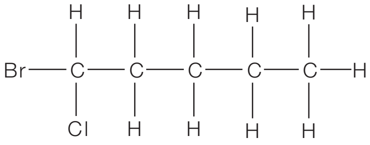
A: 1-iodopropane



B: 1,1-dibromopropane



C: 1-bromopropene

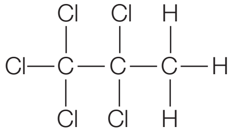


D: 1-bromopentane

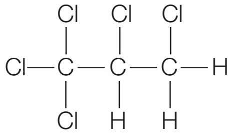
A is an iodo compound, **B** is a dibromo compound and **C** is a bromoalk**ene** so these cannot be members of the same homologous series as 1-bromopropane.

The correct answer is **D**, 1-bromopentane as it has two more $–CH_2–$ units than 1-bromopropane.

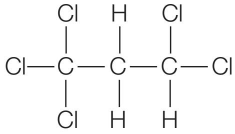
5 The three carbon chain can only exist in a straight chain, so there are no branched isomers. You need to be careful about recognizing when compounds that you have drawn are identical. Remember that there is free rotation about all the C–C bonds. All the compounds are pentachloropropanes. Perhaps the easiest way to approach this question is to work out the different ways of numbering the five chloro substituents.



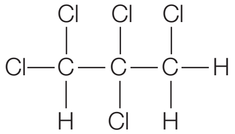
1,1,1,2,2-pentachloropropane



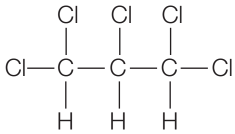
1,1,1,2,3-pentachloropropane



1,1,1,3,3-pentachloropropane

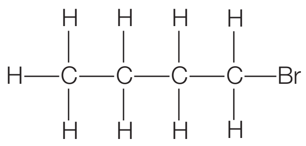


1,1,2,2,3-pentachloropropane

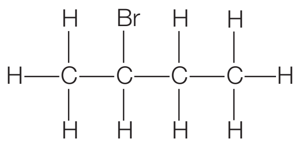


1,1,2,3,3-pentachloropropane

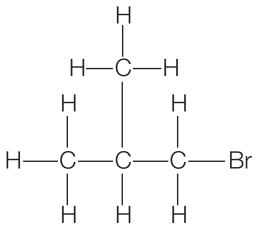
6 **B** A secondary halogenoalkane (bromoalkane in this case) must have a halogen atom bonded to a carbon atom that is also attached to one hydrogen atom and two alkyl groups. **A** is a primary halogenoalkane, **C** is a primary halogenoalkane, and **D** is a tertiary halogenoalkane.



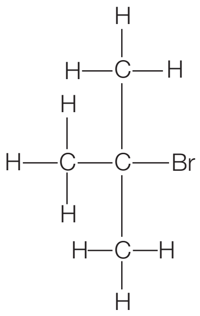
A is a primary bromoalkane



B is a secondary bromoalkane

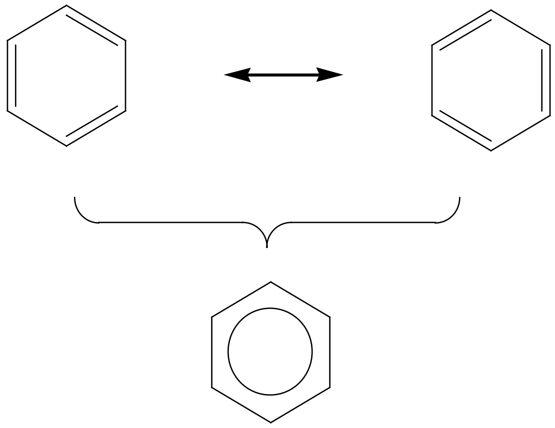


C is a primary bromoalkane



D is a tertiary bromoalkane

7 Benzene is a cyclic molecule with a planar framework of single bonds between the six carbon atoms and six hydrogen atoms. There are three double bonds present and two resonance structures can be drawn for benzene. The pi electrons of the double bond become a delocalized cloud of electrons which is shared equally over the six carbons in the ring with the electron density being above and below the ring. The delocalized pi electrons result in a very stable arrangement, so benzene is much more energetically stable than would be expected based on other compounds containing double bonds.



8 **(a)** Similar molar mass will mean molecules have approximately equal London (dispersion) forces and so differences in boiling point can be attributed to differences in dipole–dipole or hydrogen bonding intermolecular forces associated with the functional groups present in different classes of compounds.

(b) As hexane is a non-polar solvent it will most readily dissolve other compounds that are non-polar. As alcohols contain a polar –OH group their solubility in hexane will increase as the carbon chain increases and the molecule contains a larger non-polar component.

$$\underbrace{H_3C}_{\text{non-polar}}\text{—}\underbrace{OH}_{\text{polar}}$$

lower solubility in hexane

$$\underbrace{CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2}_{\text{non-polar}}\text{—}\underbrace{OH}_{\text{polar}}$$

higher solubility in hexane

9 When trying to balance organic combustion reactions do so in the order C, then H, then O.

(a) $C_5H_{14}(l) + 6O_2(g) \rightarrow 5CO(g) + 7H_2O(l)$

(b) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

(c) $C_3H_4(g) + O_2(g) \rightarrow 3C(s) + 2H_2O(l)$

10
- initiation

  $Br_2 \xrightarrow{\text{UV light}} 2Br^{\bullet}$ bromine radicals
- propagation

  $Br^{\bullet} + C_2H_6 \rightarrow C_2H_5^{\bullet} + HBr$

  $C_2H_5^{\bullet} + Br_2 \rightarrow C_2H_5Br + Br^{\bullet}$

  $C_2H_5Br + Br^{\bullet} \rightarrow C_2H_4Br^{\bullet} + HBr$

  $C_2H_4Br^{\bullet} + Br_2 \rightarrow C_2H_4Br_2 + Br^{\bullet}$
- termination

  $Br^{\bullet} + Br^{\bullet} \rightarrow Br_2$

  $C_2H_5^{\bullet} + Br^{\bullet} \rightarrow C_2H_5Br$

  $C_2H_5^{\bullet} + C_2H_5^{\bullet} \rightarrow C_4H_{10}$

Overall, these reactions show how a mixture of products is formed.

11 **(a)** This is an addition reaction with hydrogen: an alkene is converted to an alkane.

$CH_3CH_2CH_2CH_3$, butane

(b) With conc. H_2SO_4 —H and —OH adds across the alkene double bond, forming the alcohol.

$CH_3CH_2CH(OH)CH_3$, butan-2-ol

(c) This is an addition reaction with HBr: an alkene is converted to a halogenoalkane.

$CH_3CH_2CHBrCH_3$, 2-bromobutane

12 **(a)** No observable change, as there isn't enough energy/UV light to start the free radical reaction (the test tube is covered in foil). Also, the organic compound doesn't contain a carbon–carbon multiple bond so the bromine water will not decolorize.

(b) Burns with very smoky flame, as incomplete combustion occurs due to the large amount of oxygen needed for complete combustion to occur.

(c) The bromine water changes from brown to colourless, as the UV light provides enough energy for a free radical substitution reaction to occur.

13 When trying to balance organic combustion reactions do so in the order C, then H, then O.

(a) $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$2C_3H_7OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)$

(b) $C_2H_5COOH(aq) + C_4H_9OH(aq) \rightarrow C_2H_5COOC_4H_9(aq) + H_2O(l)$

14 **(a)** butanone; orange → green (as butan-2-ol is a secondary alcohol and so oxidizes to a ketone)

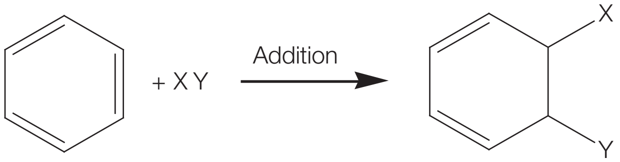
(b) methanal; orange → green (by distilling the reaction mixture the methanal is distilled off before it has time to be oxidized further to methanoic acid)

(c) no reaction; no colour change (as 2-methylbutan-2-ol is a tertiary alcohol and so cannot easily be oxidized into other products)

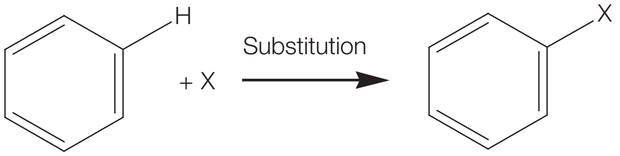
15 Nucleophilic substitution involves an electron-rich species (e.g. OH^-) which acts as a nucleophile attacking an electron-deficient carbon atom attached to an electronegative element (e.g. in chloroethane), leading to substitution of the halogen functional group by the nucleophile.

$C_2H_5Cl + OH^- \rightarrow C_2H_5OH + Cl^-$

16 Benzene has a very stable structure as a result of its symmetrical ring of delocalized pi electrons from its three double bonds (the aromatic ring). Addition reactions would involve breaking the aromatic ring and therefore decreasing its stability.



Substitution reactions in which one or more hydrogen atoms of the ring are replaced by other atoms or groups preserves the aromatic ring structure and therefore its stability.



Practice questions

1 Halogenoalkanes engage in nucleophilic substitution reactions.

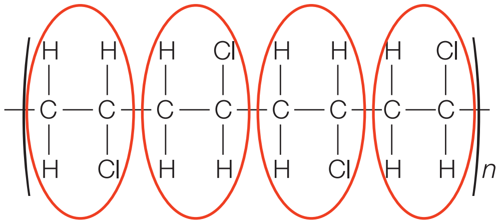
Electrophilic addition reactions occur with alkenes.

Nucleophilic substitution reactions occur for aromatic compounds containing benzene rings.

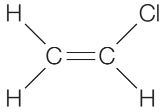
Nucleophilic addition reactions occur for aldehydes and ketones.

Correct answer is C.

2 As there are no ester or amide linkages this is an addition polymer and the monomer must be an alkene. From the structure provided for the polymer we can identify the repeating unit. (The fact that the Cl substituents alternate up and down can be ignored.)



The alkene that would create this addition polymer is therefore:



Correct answer is A.

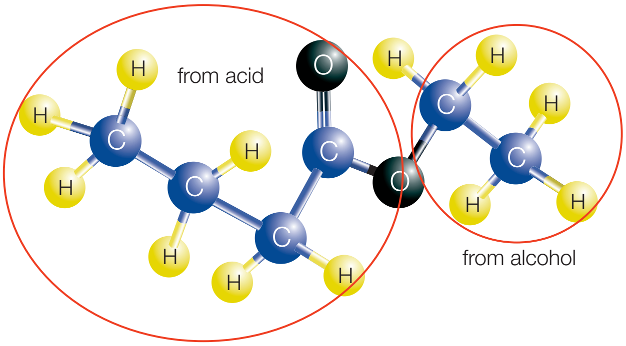
3 Step I converts a halogenoalkane into an alcohol so is a substitution reaction.

Step II converts an alcohol into a carboxylic acid so is an oxidation reaction.

Step III converts a carboxylic acid into an ester so is a condensation reaction.

Correct answer is A.

4 The compound shown is an ester, which is formed from the reaction of a carboxylic acid and an alcohol. The alkanoate component of an ester comes from the acid and the alkyl component comes from the alcohol.



The alkanoate component has four carbons so the acid is butanoic acid.

The alkyl component has two carbons so the alcohol is ethanol.

Correct answer is A.

5 With complete combustion of hydrocarbons the products are carbon dioxide and water, so A is incorrect.

With incomplete combustion of hydrocarbons the products are carbon monoxide and water (in cases where oxygen is extremely limited carbon particles, soot, can be formed), so B is correct.

Hydrogen gas is not a product of combustion reactions of hydrocarbons, so C and D are incorrect.

Correct answer is B.

6 The substitution reactions of alkanes occur via a free-radical mechanism.

A Converting alkane to halogenoalkane: substitution of Br via free-radical mechanism.

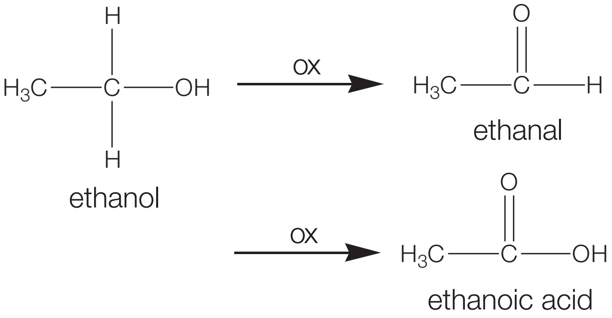
B Converting alkene to dibromoalkane: addition reaction.

C Converting iodoalkane to alcohol: nucleophilic substitution.

D Converting iodoalkane to alcohol: nucleophilic substitution.

Correct answer is A.

7 The oxidation of ethanol to ethanoic acid with potassium dichromate requires an acid catalyst. The oxidation of ethanol first produces ethanal, which is subsequently oxidized to ethanoic acid.



Heating under reflux ensures that the reaction goes through to ethanoic acid as the final product. If the reaction is conducted at a temperature above the boiling point of ethanal then ethanal can be distilled off and ethanoic acid will not be formed.

Correct answer is A.

8 Hexane (and other alkanes) is unable to react with bromine in the absence of UV light.

Correct answer is A.

9 Propan-1-ol is fully oxidized to propanoic acid.

Correct answer is C.

10 It is an ester with methanoic acid as the parent acid.

Correct answer is B.

11 Propanone and propanal both possess the carbonyl group C=O.

Correct answer is C.

12 The four compounds have a similar molar mass. Ethanoic acid, A, is the most extensively hydrogen bonded and so has the strongest intermolecular forces.

Correct answer is A.

13 The three isomers are pentane, 2-methylbutane and 2,2-dimethylpropane.

Correct answer is B.

14 **A** 1-bromobutane

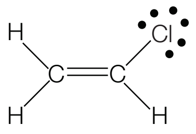
B 2-bromobutane

C 2-bromo-2-methylpropane

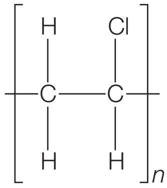
D 1-bromo-2-methylpropane

15 **(a)** When bromine water is added to any alkene it changes colour from orange/brown to colourless as the colourless dibromoalkane products are formed.

(b) *Remember that a Lewis structure is different to a regular organic structure so the Lewis structure of chloroethene must show all valence electrons!*



chloroethene



repeating unit of polychloroethene

(c) Important commercial uses of alkenes include:

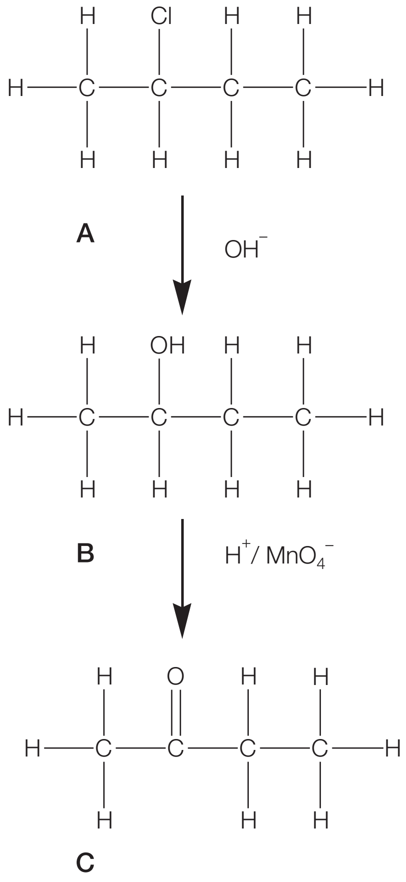
- production of ethanol from ethene (and subsequent production of ethanoic acid)
- synthesis of ethylene glycol (ethane-1,2-diol)
- use as reagents or precursors in synthesis of drugs and pesticides
- manufacture of margarine from unsaturated oils.

16 **(a)** We can deduce the structural formulas for A–C by working backwards.

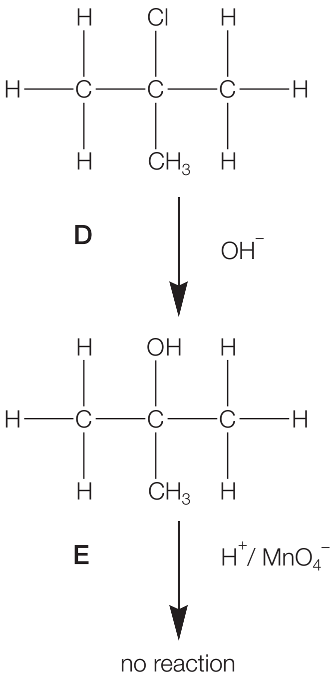
If C has the formula C_4H_8O and was formed from an oxidation reaction with acidified manganite(VII) it must be an aldehyde or a ketone. If it resists further oxidation it is a ketone.

Ketones are formed from the oxidation of secondary alcohols so B is a secondary alcohol.

If B is a secondary alcohol then it must have been formed from the nucleophilic substitution reaction of hydroxide with a secondary halogenoalkane so A is a secondary chloroalkane.



D will react with hydroxide via a nucleophilic substitution reaction to form an alcohol.
If E is resistant to oxidation by acidified dichromate then it must be a tertiary alcohol and D must be a tertiary chloroalkane.



(b) Reaction is $CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$.

This is an esterification reaction and requires concentrated sulfuric acid as a catalyst.

Ester names have the format 'alkyl alkanoate' where the alkyl component comes from the alcohol and the alkanoate component comes from the carboxylic acid. As the alcohol and carboxylic acid used in the reaction were methanol and propanoic acid the name of the ester formed is methyl propanoate.

17 **(a)** The colour change associated with reduction of Cr(VI) to Cr(III) should be known as orange to green.

(b) Using x for oxidation state of Cr and inserting –2 for oxidation state of O:

$2x + 7(x - 2) = -2$ so $x = +6$

(c) First write out the reactants and products and balance for the species that is reduced:

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$

Then balance for O by adding H_2O:

$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Then balance for H by adding H^+:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

Finally balance for charge by adding electrons:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

(d) Follow the same steps as in (c) for the oxidation half-equation:

$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^-$

The overall equation must balance the number of electrons in the two half-equations, so multiply the oxidation half-equation by three and then add the two half-equations together. Check that the electrons cancel.

$Cr_2O_7^{2-} + 3CH_3CH_2OH + 8H^+ \rightarrow 2Cr^{3+} + 3CH_3CHO + 7H_2O$

(e) Acidic conditions supply H^+ ions for the reaction.

(f) Under reflux the oxidation reaction is prolonged and the aldehyde ethanal is oxidized further to ethanoic acid.

Challenge yourself

1 Consider the combustion reactions of ethane, C_2H_6:

complete combustion

$$2\overset{-3}{C}_2H_6\,(g) + 7O_2(g) \rightarrow 4\overset{+4}{C}O_2(g) + 6H_2O(l)$$

incomplete combustion

$$2\overset{-3}{C}_2H_6\,(g) + 5O_2(g) \rightarrow 4\overset{+2}{C}O(g) + 6H_2O(l)$$

Because it has a more positive oxidation number the carbon is oxidized to a greater extent with complete combustion than it is when incomplete combustion occurs.

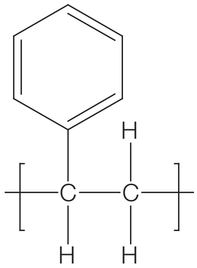
2 Heterolytic fission involves the breaking of the bond with one atom taking both of the bonded electrons, resulting in the formation of a positive and negative ion:

3 The monomer in polystyrene, showing the double bond, is $C_6H_5CH{=}CH_2$.

In polymerization the addition reaction opens the double bond and the repeating unit will be:

$$-\!\!\left[\, CH(C_6H_5) — CH_2 \,\right]\!\!-$$

An alternative representation, showing the benzene ring, is



Chapter 11

Exercises

1 The scale on the measuring cylinder is marked in 1 cm^3 divisions, so we should be able to estimate the value to ±0.5 cm^3.

2 9.92 ± 0.05 g gives a range of 9.87–9.97 g. 10.1 ± 0.2 g gives a range of 9.9–10.3 g. As the two ranges overlap, they could be measuring the same mass.

3 **(a)** 4×10^{-2} g

(b) 2.22×10^{2} cm^3

(c) 3.0×10^{-2} g. Note how the number of significant figures is retained, and compare with answer (a).

(d) 3 × 10 °C or 3.0 × 10 °C as we do not know if the 0 is significant or not. (In practice, '× 10' and '$\times 10^{-1}$' are very rarely used).

4 **(a)** Four

(b) Two or three. Is the zero significant? Or is it just there to show where the decimal point is? This question shows the value of using standard notation.

(c) Three. The zeroes just show where the significant figures are relative to the decimal point.

(d) Four

5 A Random errors will eventually average out if multiple measurements are made. However, systematic errors will always be present, no matter how many measurements are made.

6 A The absolute uncertainty = $\frac{2\%}{100\%} \times 57.536 \text{ kJ mol}^{-1} = 1.15072$.
As the % uncertainty lies in the range of 2% or greater, the absolute uncertainty should only have 1 s.f.; absolute uncertainty = 1 (see page 354).

The value must have the same number of decimal places as the absolute uncertainty so the value can only be expressed as 59 kJ mol^{-1}.

7 B The volume reading will be higher than the true value so the accuracy will be affected.

8 A Wet burettes and pipettes would affect the concentration of the solution delivered from them (making the solution more dilute); however, a wet conical flask would not lead to a systematic error as the total number of moles of reactants in the conical flask would remain unchanged.

9 B Systematic errors only can cancel when differences in quantities are calculated. This wouldn't have any effect on random errors.

10 D All three of the statements are true.

11 C The volumes are not accurate as they fall outside ±0.1 cm^3 of 38.5 cm^3. However, they are precise as they all fall within ±0.1 cm^3 of each other.

12 The average value = 49.0 s. The uncertainty in the measurements is given as ±0.1 s but the results show that there is additional uncertainty, suggesting that the value could be anywhere between 48.8 s and 49.2 s. The value should be quoted as 49.0 s ± 0.2 s.

13 *Note that the correct solution to this question is not one of the possible answers listed.*

The thermometer has a smallest division of 0.05 °C. The uncertainty of an analogue scale is half the smallest division so the readings will have an uncertainty of ±0.025 °C. (As the uncertainty has 3 d.p. the thermometer can be read to 3 d.p.)

Initial temperature = –0.650 ± 0.025 °C

Final temperature = 1.400 ± 0.025 °C

Temperature change = final temperature – initial temperature = 1.400 °C – (–0.650 °C) = 2.050 °C = 2.050 K

Uncertainty in temperature difference = 0.025 + 0.025 = 0.05

Temperature change = 2.05 K ± 0.05

Uncertainty = uncertainty in final temperature + uncertainty in initial temperature = 0.025 °C + 0.025 °C = 0.050 °C = 0.050 K

The temperature change expressed to the appropriate precision is 2.05 ± 0.05 K.

14 **D** Since the precision is ±0.5 °C the percentage uncertainty is $\frac{0.5 + 0.5}{\text{temperature difference}} \times 100\%$

i.e. $\frac{1}{20} \times 100\% = 5\%$

15 **B** 'Heat exchange' includes heat loss in exothermic reactions and heat gain in endothermic reactions.

16 **B** The overall number of significant figures depends on the measurement with the smallest number of significant figures in the calculation.

17 **C** Because this is a subtraction of two values with four decimal places the answer should also have four decimal places. 11.6235 g – 10.5805 g = 1.0430 g. This answer has five significant figures.

18 **A** Mass lost = 0.266g – 0.186 g = 0.080 g

$\%$ mass lost $= \frac{0.080\text{ g}}{0.266\text{ g}} \times 100\% = 30\%$ (as 0.080 g has 2 s.f. the answer can only have 2 s.f.)

19 **C** The answer has to be quoted to 2 significant figures and the error associated is 5% + 5% = 10% = ±0.0001.

20 number of moles = volume × concentration

$= 1.00\text{ mol dm}^{-3} \times 10.0 \times 10^{-3}\text{ dm}^3$

$= 10.0 \times 10^{-3}\text{ mol} = 1.00 \times 10^{-2}\text{ mol}$

% uncertainty in concentration is 0.05 mol dm^{-3}/1.00 mol dm^{-3} × 100% = 5%

% uncertainty in volume is 0.1 cm^3/10.0 cm^3 × 100% = 1%

The overall uncertainty in the number of moles = 5% + 1% = 6%

6% of 1.00×10^{-2} mol is 0.06×10^{-2} mol

Final answer is $(1.00 \pm 0.06) \times 10^{-2}$ mol

21 **(a)** $\Delta T = 43.2 - 21.2\text{ °C} = 22.0\text{ °C}$

absolute uncertainty = (±)0.2 °C

(b) % uncertainty $= \frac{0.2}{22.0} \times 100\% \approx 1\%$

(c) $\Delta H = \frac{-4.18 \times 22.0}{0.500} = -184\text{ kJ mol}^{-1}$

(d) 1%

(e) absolute uncertainty $= \frac{1}{100} \times 184$

$= \pm 2\text{ kJ mol}^{-1}$

(f) experimental value for $\Delta H = -184 \pm 2\text{ kJ mol}^{-1}$

The literature value is outside this range. The random errors involved in reading the thermometer do not account for this difference.

There are systematic errors. The assumptions on which the calculation is based are not strictly valid. Some of the heat of reaction passes into the surroundings and the other uncertainties in the measurements cannot be ignored. It should also be noted that the standard value for ΔH refers to standard conditions of 298 K and 100 kPa.

22 **B** If $PV = nRT$ is rearranged to obtain a general equation of a straight line ($y = mx$) then $P = \text{constant} \times \frac{1}{V}$

23 The scale of the graph does not allow for an accurate determination of the two coordinates for two points on the line.

Estimates for two points on the line are (16, 50) and (73, 200).

Density of object = mass/volume, which corresponds to the slope of the line.

Slope $= (y_2 - y_1)(x_2 - x_1) = (200 - 50)\text{ g}/(73 - 16)\text{ cm}^3 = 150\text{ g}/57\text{ cm}^3 = 2.6\text{ g cm}^{-3}$

The density of 2.6 g cm^{-3} that we obtain from the slope indicates that the objects are made of aluminium as it is the only metal listed that has a similar density, 2.70 g cm^{-3}.

The fact that the best-fit line passes through all of the points, and their associated error bars, indicates that there were no significant random errors in the experiment.

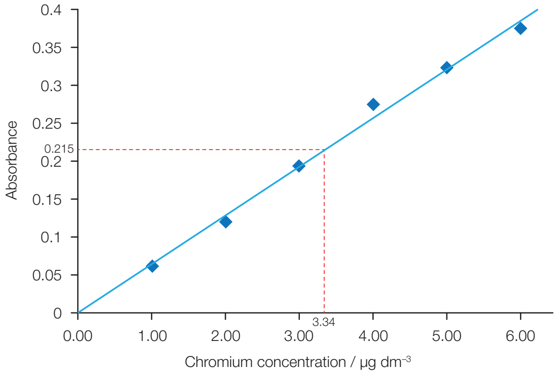
The scale of the graph does not allow us to determine a reliable uncertainty for the slope. Because of this we are unable to determine if the experimental value obtained agrees within uncertainty with the literature values and this prevents us from concluding if significant systematic errors were present.

The fact that the extrapolated straight line does not pass through the origin suggests that there are some systematic errors.

Answers A and B are therefore both acceptable without the extra detail required to determine a reliable uncertainty for the density obtained from the slope of the line.

24 **B** The results are inaccurate as distilled water (at 25 °C) should have a pH of 7.00; however, they are precise as they are all within 0.02 of a pH unit of each other.

25 Concentration of chromium = 3.34 μg dm^{-3}. Plot a graph of absorbance against chromium concentration using the values given. Then use the graph to find the chromium concentration of the sample.



26 **C** $C_2H_3O^+$ will produce a peak at 43, $C_3H_5O^+$ at 57 and $C_4H_8O^+$ at 72. Ion peaks are present at 57 and 72.

27 **C** The formula masses of the compounds are **A** = 44, **B** = 88, **C** = 88, **D** = 88. **A** cannot be correct as the spectrum has a peak at 88. The peaks at 29 ($C_2H_5^+$) and 73 ($C_2H_5CO_2^+$) suggest that the spectrum corresponds to $C_2H_5CO_2CH_3$.

28 A (the spectrum on the left) corresponds to CH_3CH_2CHO

B (the spectrum on the right) corresponds to CH_3COCH_3

Similarities

Both have a molecular ion corresponding to 58.

Differences

A has peaks corresponding to 29 ($CH_3CH_2^+$), 28 (loss of CH_3CH_2) and 57 ($CH_3CH_2CO^+$).

B has a peak corresponding to 43 (loss of CH_3).

29 **(a)**

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

(b) $CH_3CH_2CH_2CH_3$ – this can be deduced from the peaks or from the molecular ion peak corresponding to the molecular mass of 58. The empirical formula is C_2H_5 and the molecular formula is C_4H_{10}.

30

Molecule	Corresponding saturated non-cyclic molecule	IHD
C_6H_6	C_6H_{14}	4
CH_3COCH_3	C_3H_8O	1
$C_7H_6O_2$	$C_7H_{16}O$	5
C_2H_3Cl	C_2H_5Cl	1
C_4H_9N	$C_4H_9NH_2$	1
$C_6H_{12}O_6$	$C_6H_{14}O_6$	1

31 **B** With single bonds between large atoms, the molecules will vibrate the lowest frequency and so will have the longest wavelength absorption.

32 **D** The absorptions given in the question correspond to carbon–carbon triple bonds (2100 cm^{-1}), carbonyl groups (1700 cm^{-1}) and carbon–oxygen bonds (1200 cm^{-1}) (see table on page 372).

33 **B** Both aldehydes and esters contain carbonyl groups, which absorb at 1720 cm^{-1} (see table on page 372).

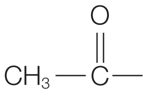
34 **(a)**

	C	H	O
% composition	40.0	6.7	53.3
Moles	$\frac{40.0}{12.01}$	$\frac{6.7}{1.01}$	$\frac{53.3}{16.00}$
Ratio	3.33	6.6	3.33
Simplest ratio	1	2	1

Empirical formula CH_2O. This has a relative formula mass of 30. The relative molecular mass is 60 so the molecular formula is $C_2H_4O_2$.

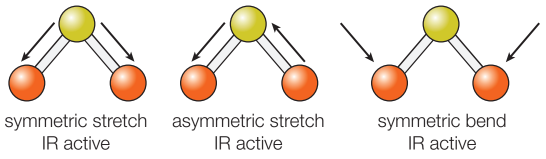
(b) IHD = 1

(c) The absorptions correspond to a carbonyl group and hydrogen-bonded hydroxyl group. Molecular structure is



$CH_3-\overset{\overset{O}{\|}}{C}-OH$, ethanoic acid.

35



36 **B** C—O and C=O bonds absorb strongly whereas C=C only has a medium-weak absorption (see table on page 372).

37 IR radiation can only be absorbed if it results in a change in the dipole moment of a bond or molecule therefore whenever it is absorbed by a bond or molecule the polarity (of bond or molecule) changes due to the change in dipole moment as the bonds are bent or stretched.

38 Hex-1-ene shows an absorption in the range 1610–1680 cm^{-1} due to the presence of the C=C bond. Cyclohexane won't show an absorption in this range as it only has C—C bonds.

39 C—H bond (see table on page 372).

40 The structure is CH_3OCH_3 (methoxymethane / dimethyl ether). The IHD is 0, so there are no double bonds (neither C=O nor C=C). The absorption at 1000–1300 cm^{-1} is due to a C–O single bond so the molecule must be an ether or an alcohol. It cannot be an alcohol as there are no absorbances above 3000 cm^{-1}.

41 **C** The peak area corresponds to the relative numbers of hydrogen atoms in that particular environment. The unknown compound has two different CH_3 groups and a CH_2 group. The only molecule that satisfies this is molecule **C**. **A** would have two peaks, in a 2 : 6 ratio, **B** would have three peaks, in a 3 : 2 : 1 ratio (and the CHO group would have chemical shift of 9.4–10), while **D** would have three peaks, but in a 2 : 4 : 6 ratio.

42 **A** This is the only molecule with two different hydrogen environments. Molecules **B** and **D** have one environment and molecule **C** has three different environments.

43 **(a)** 2, the two CH_3 groups are in different environments

(b) 1, the molecule is symmetrical so the CH_3 groups are in the same environment

(c) 1, the molecule is symmetrical so the CH_3 groups are in the same environment

(d) 2, the two CH_3 groups are in a different environment to the H atom bonded to the central carbon atom

44 The H atoms are in three different environments so there are three peaks in the ^1H NMR spectrum, in the ratio of peak area of 3 : 2 : 1 corresponding to the CH_3, CH_2, and H atom. Chemical shifts will be around 1.0 for the $-CH_3$, around 3.5 for $-CH_2-O$, and between 1.0 and 6.0 for the O—H (see Section 27 of the IB data booklet and the table on pages 376–377).

Practice questions

1 If the burette reading is recorded as 27.70 ± 0.05 cm^3 the actual value could be any value between 27.65 cm^3 and 27.75 cm^3.

Correct answer is B.

2 The mass is 10.044 g, which is precise to five significant figures.

The volume is 3.70 cm^3, which is precise to three significant figures.

Because the final value is calculated through a division the answer can only be presented to the same precision as the least precise piece of data.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{10.044\ \text{g}}{3.70\ \text{cm}^3} = 2.71\ \text{g cm}^{-3}$$

Correct answer is C.

3 The procedures in A, B and D are all conducted with specialized and highly precise pieces of equipment: burette, pipette and gas syringe. The piece of equipment used in procedure C is a lab beaker, which is not precise for measuring volume or a suitable reaction vessel for measuring temperature changes that occur with neutralization reactions.

Correct answer is C.

4 Random uncertainties can only be decreased through the conduction of repeat measurements. The methods suggested in B, C and D are all associated with the reduction of systematic errors.

Correct answer is A.

5 **(a)** The low-resolution ^{1}H NMR spectrum shows three peaks so the compound contains three different chemical environments.

A CH_3–CO–CH_3 has one chemical environment (the CH_3 hydrogens are all equivalent).

B CH_3–CH_2–CHO has three chemical environments. (These environments will give an integration of 3:2:1, consistent with the spectrum observed. The spectrum also gives a peak at 9.8 ppm due to one hydrogen that is consistent with an aldehyde.)

C CH_2=CH–CH_2OH has four chemical environments.

X is compound B, CH_3–CH_2–CHO.

(b) The peak at 2.5 ppm is due to hydrogen atoms that are on a carbon adjacent to a carbonyl group (–C=O). This would also occur for compound A, where the CH_3 hydrogens are adjacent to a C=O group.

(c) **(i)** The infrared spectrum of compound X, CH_3–CH_2–CHO, would have an absorption at 1700–1750 cm^{-1} due to the C=O bond.

(ii) Comparing X to compound A: The infrared spectrum of compound A, CH_3–CO–CH_3, would have an absorption at 1700–1750 cm^{-1} due to the C=O bond. This peak would be absent in the spectrum of X.

Comparing X to compound C: The infrared spectrum of compound C, CH_2=CH–CH_2OH, would have absorptions at 1620–1680 cm^{-1} due to the C=C bond and 3200–3600 cm^{-1} due to the O–H bond. These two peaks would be absent in the spectrum of X.

(d) The mass spectrum of compound X will show peaks at *m/z* values of:

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

* 29, which could be due to the fragment CHO^+ or the fragment $C_2H_5^+$

* 15 due to the fragment CH_3^+.

6 **(a)** To be IR active the absorption of energy by the vibration 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 a non-polar bond there will be no dipole change by the bond stretch if it absorbs IR radiation, so it is IR inactive.

(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).

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 this bond is most likely to be responsible.

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

(ii) The peak at *m/z* = 102 is due to the molecular ion $C_5H_{10}O_2^+$.

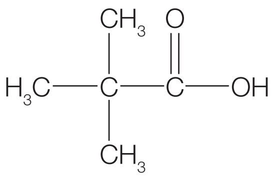
The peak at *m/z* = 57 is due to fragment $C_4H_9^+$.

The peak at *m/z* = 45 is due to fragment COOH$^+$.

(iii) The peak in the ^{1}H NMR spectrum at 11.5 ppm is due to the hydrogen in the acid group, –COO<u>H</u>. (Acid hydrogens occur in the region 89.0–13.0 ppm.)

(iv) The peak at 1.2 ppm has an integrated area of 9. This tells us that nine hydrogen atoms share this chemical environment, which is consistent with a $-C(CH_3)_3$ group.

(v) From (ii) and (iii) we have deduced that X contains a $-C(CH_3)_3$ group and an acid group, –COOH. The structure must be:



$H_3C-C(CH_3)_2-C(=O)-OH$

(vi) $CH_3COOCH_2CH_2CH_3$ has four chemical environments so its ^{1}H NMR spectrum will have four peaks with integration traces 3:2:2:3. $CH_3COOCH_2CH_2CH_3$ is an ester so it will not have a peak in the 9.0–13.0 ppm region due to an acid hydrogen.

7 The absorption of IR radiation by a molecule must result in a change in the molecular dipole. For CO_2 this can only happen with absorption of the asymmetric stretch and the bending vibrations. The symmetric stretch is IR inactive as it results in no dipole change.

The absorption of IR energy due to the asymmetric stretch of CO_2 will result in a change in the C=O bond lengths.

The absorption of IR energy due to the bends of CO_2 will result in a change in the O=C=O bond angles.

8 **(a)** $C_3H_8O^+$

(3 × 12) + (8 × 1) + (16 × 1) = 60

More detailed formula also acceptable, e.g. $CH_3CH_2CH_2OH^+$.

(b) CH_3O^+/CH_2OH^+

(1 × 12) + (3 × 1) + (16 × 1) = 31

(c) A $CH_3CH_2CH_2OH$

Add the fragments: 29 + 31 = $CH_3CH_2^+$ + CH_2OH^+

More detailed formula also acceptable.

B $CH_3CH(OH)CH_3$

45 = $CH(OH)CH_3^+$, CH_3 fragment broken off

More detailed formula also acceptable.

9 **(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 (1700–1750 cm^{-1}).

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

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

The peak at *m/z* = 45 is due to fragment CO_2H^+.

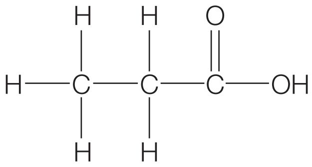
The peak at *m/z* = 29 is due to fragment $C_2H_5^+$.

(c) The peak in the ^{1}H NMR spectrum at 11.73 ppm is due to the hydrogen in the acid group, –COO<u>H</u>. (Acid hydrogens occur in the region 89.0–13.0 ppm.)

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

A mass spectrometer peak at *m/z* = 29 along with ^{1}H NMR peaks at 1.2 ppm (3H triplet) and 2.4 ppm (2H quartet) is consistent with $CH_3–CH_2–$ being present.

Structure is:

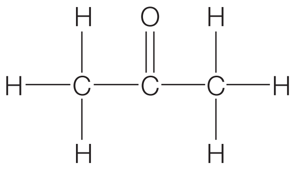


10 **(a)** The structure given contains an alcohol group. The spectrum is not of this structure as a strong, very broad peak would be observed in the 3200–3600 cm^{-1} region if an O–H bond was present.

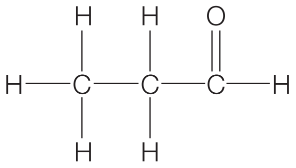
The structure given contains an alkene. The spectrum is not of this structure as a strong peak would be observed in the 1620–1680 cm^{-1} region if a C=C bond was present.

The spectrum has a strong peak at 1750 cm^{-1}, which indicates that a C=O bond is present in the compound. As the structure provided does not contain a C=O bond it is not consistent with the IR spectrum.

(b) The molecular formula of C_3H_6O indicates that the compound contains one double bond. As the C=C peak is not observed in the IR spectrum the compound must be a ketone or an aldehyde. Possible structures are therefore:



I

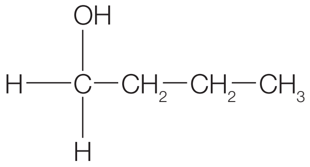


II

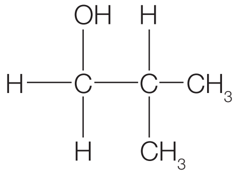
Structure I is not the correct structure as it would give an ^{1}H NMR spectrum with only one peak as all the $C\underline{H}_3$ hydrogens have the same chemical environment.

Structure II is the correct structure as this would give an ^{1}H NMR spectrum with three peaks as there are three chemical environments: $C\underline{H}_3$–, –$C\underline{H}_2$– and –C(O)–$\underline{H}$. The integrated areas of these peaks would be 3:2:1.

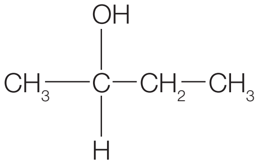
11 The structures of the four alcohols are given below.



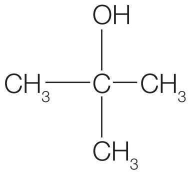
butan-1-ol



2-methylpropan-1-ol



butan-2-ol



2-methylpropan-1-ol

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

(Butan-1-ol and butan-2-ol each have five chemical environments and 2-methylpropan-1-ol has four chemical environments.)

The peak at 1.3 ppm, with an integration trace of nine units, is due to the nine hydrogens on the three chemically equivalent –C$\mathbf{H}_3$ groups.

The peak at 2.0 ppm, with an integration trace of one unit, is due to the alcohol hydrogen, –O**H**.

(ii) Spectrum 2 has four peaks in the ^1H NMR spectrum so the alcohol responsible must contain four chemical environments. From the structures we can see that the only alcohol with four chemical environments is 2-methylpropan-1-ol.

The peak at 0.9 ppm, with an integration trace of six units, is due to the six hydrogens on the two chemically equivalent $–C\mathbf{H}_3$ groups.

The peak at 3.4 ppm, with an integration trace of two units, is due to the two hydrogens on the carbon attached to the alcohol, $–C\mathbf{H}_2OH$.

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

The peak at $m/z = 59$ is due to fragment $C_3H_7O^+$ (loss of CH_3).

The peak at $m/z = 45$ is due to fragment $C_2H_5O^+$ (loss of CH_2CH_3).

From the structures we can see that the loss of both 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.

(ii) The peak at $m/z = 31$ is due to fragment CH_3O^+ (loss of $CH_2CH_2CH_3$).

From the structures we can see that loss of $CH_2CH_2CH_3$ to give CH_3O^+ (CH_2OH^+) can only occur for butan-1-ol.

(c) The IR spectra will be similar for the four alcohols as they contain the same bonds: C–H, C–C, C–O and O–H.

Challenge yourself

1 $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2\times(-2)) + (-1\times(-1)) + 0 + (1\times1) + (2\times2)}{(-2)^2 + (-1)^2 + 0^2 + 1^2 + 2^2} = 1$$

2 $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2\times2) + (-1\times1) + 0 + (1\times(-1)) + (2\times(-2))}{(-2)^2 + (-1)^2 + 0^2 + 1^2 + 2^2} = -1$$

3 $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2\times(-2)) + (-1\times2) + 0 + (1\times1) + (2\times(-1))}{2^2 + 1^2 + 0^2 + 1^2 + 2^2} = 0.10$$

4 The index of hydrogen deficiency (IHD) can be determined for a molecule with the formula $C_nH_pO_qN_rX_s$ by seeing how it changes from that of an alkane, C_nH_{2n+2}, where IHD = 0, by successively adding functional groups containing each element of interest and seeing how it affects the IHD.

For C_nH_p:

H atoms needed = number required for saturated hydrocarbon – number present

$= 2n + 2 - p$

H_2 molecules needed $= ½(2n + 2 - p)$

For $C_nH_pO_q$:

O is typically present with two single bonds (ether or alcohol) or a double bond (ketone, aldehydes, esters)

Consider ethanol, CH_3CH_2OH, which is saturated (IHD = 0):

H atoms needed $= 2n + 2 - p$

$= 2(2) + 2 - 6 = 0$

H_2 molecules needed = 0

Consider propanal, CH_3CH_2CHO, which is unsaturated due to the C=O bond (IHD = 1):

H atoms needed $= 2n + 2 - p$

$= 2(3) + 2 - 6 = 2$

H_2 molecules needed $= ½(2n + 2 - p) = 1$

In both cases, CH_2CH_2OH and CH_3CH_2CHO, we find that the correct IHD is obtained even though the equation does not include the number of oxygen atoms, q.

(This answers the second part of the question.)

For $C_nH_pO_qN_r$:

N is typically present with three single bonds (amine) or a triple bond (nitrile).

Consider ethylamine, $CH_3CH_2NH_2$, which is saturated (IHD = 0):

If we use $2n + 2 - p$ then:

H atoms needed = $2n + 2 - p = 2(2) + 2 - 7 = -1$

This answer is incorrect so the equation needs to be modified to $2n + 2 - p + r$.

H atoms needed = $2n + 2 - p + r$
$= 2(2) + 2 - 6 + 1 = 0$

H_2 molecules needed = $\frac{1}{2}(2n + 2 - p + r) = 0$

Consider propanenitrile, CH_3CH_2CN, which is unsaturated due to the C≡N bond (IHD = 2):

H atoms needed = $2n + 2 - p + r$
$= 2(3) + 2 - 5 + 1 = 4$

H_2 molecules needed = $\frac{1}{2}(2n + 2 - p + r) = 2$

For $C_nH_pO_qN_rX_s$:

X represents a halogen atom, which is typically present with one single bond.

Consider chloroethane, CH_3CH_2Cl, which is saturated:

If we use $2n + 2 - p + r$ then:

H atoms needed = $2n + 2 - p + r$
$= 2(2) + 2 - 5 = 1$

This answer is incorrect so the equation needs to be modified to $2n + 2 - p - s + r$.

H atoms needed = $2n + 2 - p - s + r$
$= 2(2) + 2 - 5 - 1 = 0$

H_2 molecules needed = $\frac{1}{2}(2n + 2 - p - s + r) = 0$

Therefore we find that the IHD for a general formula $C_nH_pO_qN_rX_s$ can be calculated using:

$$\text{IHD} = \tfrac{1}{2}(2n + 2 - p - s + r)$$

5 As we are given the frequency, ν, of the photon of light we can calculate the energy of a single photon using the equation $E = h\nu$:

$E = h\nu$
$= 6.63 \times 10^{-34}\ \text{J s} \times 3.0 \times 10^{14}\ \text{s}^{-1}$
$= 2.0 \times 10^{-19}\ \text{J}$

We can calculate the energy in kJ mol^{-1} by multiplying the energy of one photon by Avogadro's number:

$E = 6.02 \times 10^{23}\ \text{mol}^{-1} \times 2.0 \times 10^{-19}\ \text{J}$
$= 1.2 \times 10^{5}\ \text{J mol}^{-1} = 120\ \text{kJ mol}^{-1}$

6 The IR absorption is given as 2100 cm^{-1}, which is in wavenumber units.

Wavenumber = $1/\lambda$, where λ is the wavelength of the light absorbed.

$$\lambda = \frac{1}{\text{wavenumber}} = \frac{1}{2100\ \text{cm}^{-1}}$$
$$= 4.762 \times 10^{-4}\ \text{cm} = 4.762 \times 10^{-6}\ \text{m}$$

Frequency is related to wavelength by the equation $\nu = c/\lambda$

$$\nu = \frac{3.00 \times 10^{8}\ \text{m s}^{-1}}{4.762 \times 10^{-6}\ \text{m}} = 6.30 \times 10^{13}\ \text{s}^{-1}$$

Worked solutions

Chapter 12

Exercises

1 **A** A composite is a mixture where one material acts as a matrix (e.g. fibreglass).

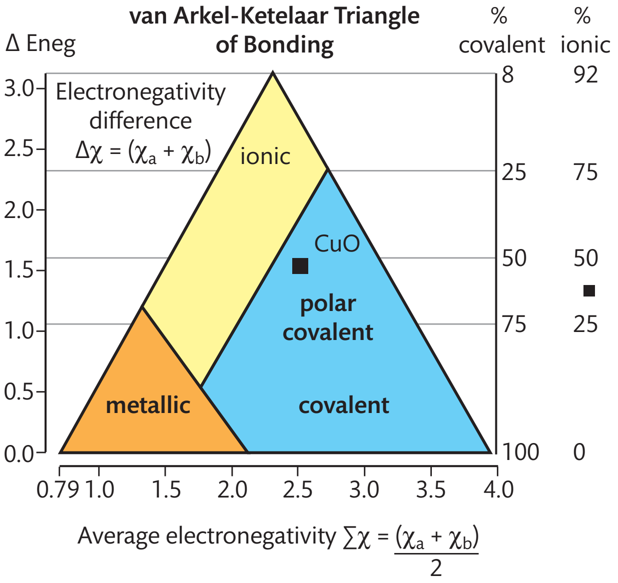
2

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

The % ionic character is taken from the bonding triangle (Figure 12.1).

3

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



4 Metal atoms can slide across each other with the metallic bonding not breaking as the delocalized electrons can move to accommodate the changes in the lattice.

In ceramics the ionic and covalent bonds are directional and more rigid. They resist changes in the atomic arrangement but will break if the applied forces are too strong.

5 Concrete can contain iron (as a reinforcing material) or carbon fibres. If these are connected into a network within the concrete the material will conduct electricity along the network.

6 **(a)** Bauxite (aluminium ore containing aluminium oxide).

(b) Aluminium is more reactive than carbon so cannot be reduced from its ore using carbon.

(c) Aluminium ions are attracted towards the negative electrode where they are reduced to aluminium atoms:

$Al^{3+}(l) + 3e^- \rightarrow Al(l)$

(d) Aluminium is more reactive than hydrogen. Hydrogen gas would be produced as the hydrogen from the water is reduced in preference to the aluminium.

(e) Aluminium oxide is only 56% ionic, based on electronegativity values and Figure 12.1. The ions are not completely free in the molten compound.

(f) Oxygen is produced at the anode from the oxide ions:

$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$

The oxygen reacts with the carbon of the anode to produce carbon dioxide and this causes the anodes to disintegrate:

$C(s) + O_2(g) \rightarrow CO_2(g)$

7 At the cathode: 2 moles of electrons are required to reduce 1 mole of Cu^{2+} ions

0.100 F is equivalent to 0.100 mol of electrons, hence this will reduce 0.050 mol of Cu^{2+} ions.

0.050 moles of Cu^{2+} ions = 0.050 × 63.55g of copper = 3.2 g

At the anode: to oxidize 2 moles of chloride ions to make 1 mole of chlorine molecules requires the loss of 2 moles of electrons. 0.100 F is equivalent to 0.100 mol of electrons so 0.050 mol of chlorine gas will be formed. 1 mole of gas occupies 22.4 dm^3, so 0.050 mol will be equivalent to 0.050 × 22.4 = 1.1 dm^3 of chlorine gas

8 $n(e^-) = \frac{I \times t}{F} = \frac{0.0965 \text{ A} \times 1000 \text{ s}}{96\,500 \text{ C mol}^{-1}} = \frac{96.5}{96\,500}$

$= 0.001\,00$ mol

$n(\text{Ti}) = \frac{0.011\,975}{47.9} = 0.000\,250$ mol

$\frac{n(e^-)}{n(\text{Ti})} = 4$

Ti is in the +4 oxidation state. Formula is $TiCl_4$.

9 $Fe_2O_3(s) + CH_4(g) + O_2 \rightarrow 2Fe(l) + CO_2(g) + H_2O(l)$; unbalanced

- Balance the elements that are only present in a combined state.
- First balance the C and H:

  $Fe_2O_3(s) + CH_4(g) + O_2 \rightarrow 2Fe(l) + CO_2(g) + 2H_2O(l)$; unbalanced
- Now balance the Fe and O:

  $Fe_2O_3(s) + CH_4(g) + \frac{1}{2}O_2 \rightarrow 2Fe(l) + CO_2(g) + 2H_2O(l)$; balanced but involves a fraction

  $2Fe_2O_3(s) + 2CH_4(g) + O_2 \rightarrow 4Fe(l) + 2CO_2(g) + 4H_2O(l)$; balanced

10 **(a)** $TiO_2 + 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO$

(b) $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

11 The alloy is stronger than the pure metal.

Adding atoms of different size disrupts the regular metal lattice so that it is difficult for one layer to slide over another. Alloying can make the metal harder, stronger, and more resistant to corrosion.

12 All of the electron spins are paired in diamagnetic elements.

Atoms are paramagnetic if they have unpaired electrons. So, to determine whether the elements are paramagnetic or diamagnetic, we need to consider the electron configuration for each element.

Element	Electron configuration	Number of unpaired electrons	Magnetic behaviour
Na	$[Ne]3s^1$	1	paramagnetic
Mg	$[Ne]3s^2$	0	diamagnetic
Al	$[Ne]3s^23p^1$	1	paramagnetic
Si	$[Ne]3s^23p^2$	2	paramagnetic
P	$[Ne]3s^23p^3$	3	paramagnetic
S	$[Ne]3s^23p^4$	2	paramagnetic
Cl	$[Ne]3s^23p^5$	1	paramagnetic
Ar	$[Ne]3s^23p^6$	0	diamagnetic

Phosphorus has the most unpaired electrons and so is the most paramagnetic.

13

Atom	Electron configuration	No. of unpaired electrons
K	$[Ar]4s^1$	1
Sc	$[Ar]3d^14s^2$	1
V	$[Ar]3d^34s^2$	3
Mn	$[Ar]3d^54s^2$	5
Ga	$[Ar]3d^{10}4s^24p^1$	1
As	$[Ar]3d^{10}4s^24p^3$	3

Order is therefore: K, Sc, Ga < V, As < Mn

14 **(a)** Positive argon ions and (free) electrons.

(b) Argon, as it is present in the plasma.

(c) ICP-MS

(d) ICP-OES, as the non-metals do not form positive ions so readily in ICP-MS.

15 **(a)** Different calibrations are produced for each electron transition so three transitions are analysed.

(b) It produced 3.00×10^7 counts in one minute $= 0.0500 \times 10^7$ c s^{-1} $= 5.00 \times 10^5$ c s^{-1} $= 500$ kc s^{-1}. From the graph and line II, [Hg] is between 1.9 and 2.0 μg dm^{-3}

(c) approx. 800 kc s^{-1}. Find the concentration from your answer to part (b) and extrapolate up to the blue line and then read intensity on the *y*-axis.

(d) Series I, as it has the steepest gradient; small differences in concentration can be detected with large differences in count rate.

16 Read the answer directly off the graph to obtain the manganese content: 0.37% by mass.

17 Transition metals are effective heterogeneous catalysts as they form weak bonds to small reactant molecules which allow them to come together with the correct orientation.

The ability of transition metals to show variable oxidation states allows them to be particularly effective homogeneous catalysts.

18 **(a)** Lower temperatures needed so reduced energy costs. Catalysts act selectively, increasing the yield of the desired product. They are not used up and so can be reused over long periods of time.

(b) Sulfur impurities block the active sites of the catalyst; the impurities are adsorbed on the catalyst surface more strongly than reactant molecules.

19 **(a)** An activated complex is an unstable combination of reactant molecules that can go on to form products or fall apart to form reactants. A reaction intermediate is a species that is produced and consumed during a reaction but does not occur in the overall equation.

An activated complex corresponds to a maximum in the energy and a reaction intermediate corresponds to a local minimum in energy. Reaction intermediates can in theory be isolated.

(b) Heterogeneous catalysts are in a different phase from the reactants; they can be easily removed by filtration.

(c) They have a large surface area per unit mass for reactants to be adsorbed and their surface structure can be modified to improve effectiveness.

(d) Toxicity of the nanoparticles is dependent on their size, so there is a need to regulate for type of material *and* size of particles.

20 **(a)**

	Liquid	Liquid crystal
Molecular arrangement	disordered	disordered
Molecular orientation	disordered	ordered

(b) The phase transitions of thermotropic liquid crystals depend on temperature. The phase transitions of lyotropic liquid crystals depend on both temperature and concentration.

(c) The molecules/ions group together to form a spherical arrangement; the hydrophilic heads are exposed to water, shielding the non-polar tails within the micelle.

21 Thermotropic liquid crystal materials are pure substances that show liquid crystal behaviour over a temperature range between the solid and liquid states. Example: biphenyl nitriles.

Lyotropic liquid crystals are solutions that show the liquid crystal state at certain concentrations and temperatures. Examples: soap and water, Kevlar® in solution.

22 **(a)** Low reactivity of C–H bond in the hydrocarbon chain due to high bond energy and low polarity.

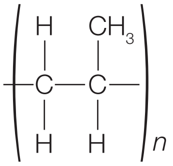
(b) Increases polarity and there are greater intermolecular forces between the molecules that cause them to align their orientation. The more polar molecule is also more responsive to changing orientation when an electric field is applied.

23 **(a)** $C_{24}H_{23}N$

(b) The addition of a benzene ring makes the molecule more rigid and rod-shaped. This increases the London dispersion forces between the molecules, which results in a higher temperature being required to disrupt their alignment and change from the liquid crystal phase to the liquid phase.

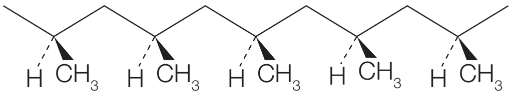
24 **A** There are strong C–C covalent bonds within the chains and relatively strong intermolecular forces between the large polymer chains.

25 **(a)**



$$\left[-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\right]_n$$

(b)



isotactic poly(propene)

(c) Isotactic polypropene has a stereoregular structure with the methyl groups pointing in the same direction and so is crystalline and tough.

(d) M_r (C_3H_6 monomer) = (3 × 12.01) + (6 × 1.01) = 42.09

No. of monomer units $= \dfrac{2.1 \times 10^6}{42.09} = 50\,000$

(e) The chains in a polymer are not all the same length.

26 **(a)** The pure form, which has strong diplole–dipole interactions between the chains, is hard and brittle. The addition of plasticizers allows the chains to slip across each other and makes the plastic more flexible.

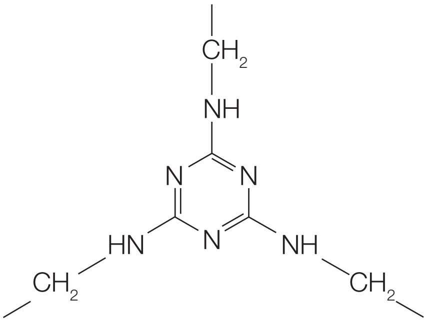
(b) The non-expanded form of polystyrene is a colourless, transparent, brittle plastic. The expanded form is opaque with a lower density. It is a better insulator and shock absorber. The expanded form is produced by heating polystyrene beads with a volatile hydrocarbon such as pentane. The pentane evaporates and causes bubbles to form in the plastic.

27 **(a)** Relative molar mass of reactant = (6 × 12.01) + (24 × 1.01) + (12 × 14.01) + (6 × 16.00) = 360.42

Relative molar mass of desired product = (3 × 12.01) + (6 × 1.01) + (6 × 14.01) = 126.15

Atom economy $= \dfrac{126.15}{360.42} \times 100\% = 35.0\%$

(b)



(c) There are relatively weak intermolecular forces between the chains in poly(ethene). These forces are broken when the solid melts but are reformed when the liquid is cooled. The cross-links between the chains in the thermosetting resin are made from strong covalent bonds. When heated to high temperature the resin does not melt but burns.

(d) There is extensive cross-linking in thermosetting plastics which means they cannot be reshaped and do not melt when heated. Elastomers have very limited cross-links which knot some chains together and prevent molecules slipping across each other without restricting the freedom of the molecules to coil and uncoil.

28 **(a)** Expanded polystyrene can act as a good shock absorber. Its low density will reduce transport costs and make it easier to handle. It is also a good thermal insulator and will protect package contents from extreme temperatures.

(b) A volatile hydrocarbon, such as pentane, is added during the polymerization process. The volatile hydrocarbon turns into a gas, forming bubbles that force the surrounding polymer to expand and take the shape of the mould.

29 **(a)** number of diameters $= \dfrac{10 \times 10^{-6}\text{ m}}{1 \times 10^{-9}\text{ m}} = \dfrac{10^{-5}}{10^{-9}}$

$= 10^4 = 10\,000$

(b) Strong covalent C—C bonds must be broken.

(c) Range of tube lengths with different structures leads to a less regular structure in the solid, which reduces strength. As properties are sensitive to tube length, it is difficult to produce tubes with required properties.

(d) Large surface area for reactants to be adsorbed; the shape and size of the tubes make them shape-selective catalysts, only reactants of the appropriate geometry being able to interact effectively with the active sites.

(e) Quantum effects predominate and the electrons behave like waves; the length of the tube affects the behaviour of electrons; the tubes are conductors or semiconductors depending on the length.

30 **(a)** The size of the nanoparticles is similar to the wavelength of harmful UV radiation. UV is scattered and not absorbed.

(b) Toxicity of the nanoparticles is dependent on their size, so need to regulate for type of material *and* size of particles.

31 **(a)** Approximately 25 atoms high; each C atom has a diameter of $2 \times 75 \times 10^{-12}$ m and each O atom has a diameter of $2 \times 64 \times 10^{-12}$ m. Approximate length = $25 \times 2 \times 70 \times 10^{-12}$ m = 3.5×10^{-9} m

(b) Scanning tunnelling microscope (STM) or atomic force microscope (AFM).

32 **(a)** Plastics are easily moulded; they are non-biodegradable; and they have low density.

(b)

Method	Advantages	Disadvantages
landfill	simple method to deal with large volumes	plastics are not biodegradable; limited sites
incineration	reduces volume; plastics are concentrated energy source	CO_2 is a greenhouse gas; CO is poisonous; HCl produced from combustion of PVC causes acid rain; other toxic chemicals such as dioxins can be released
recycling	conserves natural resources	plastics need to be sorted

(c) Bacteria do not have the enzymes needed to break the C—C bonds present.

(d) Natural polymers (e.g. starch, cellulose, or protein) can be added. Bacteria can break down the natural polymers and so the bag is broken down into smaller pieces.

33

Method	Advantages	Disadvantages
landfill	efficient method to deal with large volumes	not popular with locals; needs to be maintained and monitored after use
incineration	reduces volume; energy source	can cause pollutants, such as greenhouse gases and dioxins

34 *Advantages:* saves natural resources; saves energy; reduces pollution.

Disadvantages: materials need to be sorted.

35 **(a)** 1–5

(b) 1–4

36 Both molecules have C—H bonds, so they have strong absorptions between 2850 and 3090 cm^{-1}. The monomer has a C=C bond not found in the polymer so it will have a weak absorption at 1620–1680 cm^{-1}.

Practice questions

1 **(a)** **(i)** By using molten cryolite the melting point of the mixture is much lower than that of pure alumina so the electrolysis can be conducted at a lower temperature.

(ii) Reduction happens at the cathode (negative electrode): $Al^{3+}(l) + 3e^{-} \rightarrow Al(s)$

Oxidation happens at the anode (positive electrode): $2O^{2-}(l) \rightarrow O_2(g) + 4e^{-}$

(b) CO_2 can be produced as a product of the electrolysis reaction through the reaction of the $O_2(g)$ formed with the carbon (graphite) anode itself: $C(s) + O_2(g) \rightarrow CO_2(g)$

CO_2 can also be formed indirectly if a power plant burns fossil fuels to provide the heat and electricity necessary for the electrolysis reaction.

2 **(a)** From standard electrode potentials we see that Al^{3+} is much harder to reduce than Fe^{2+}:

$Al^{3+}(aq) + 3e^{-} \rightleftharpoons Al(s)$ $E^{\ominus} = -1.66\ V$

$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$ $E^{\ominus} = -0.45\ V$

Al^{3+} is so difficult to reduce that it cannot be done using chemical reducing agents so electrolysis is necessary to obtain aluminium metal from its ores. Fe^{2+} is easier to reduce so iron metal can be obtained from its ores using chemical reducing agents.

(b) **(i)** $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

(ii) $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$

3 **(a)** Alloys are homogenous mixtures of metals with other metals or non-metals.

(b) The added metal or element fits between the metal cations and disrupts the regular repeating lattice of the metal. This can prevent the metal cation layers within the lattice from sliding past one another, resulting in the alloy being harder and less malleable. However, this may also make the metal brittle.

The added metal or element can also alter the chemical properties of the metal and make it more resistant to corrosion.

4 Homogeneous catalysts are in the same state of matter as the reactants. They chemically combine with the reactants in one step to form an activated complex (or intermediate) with a lower activation energy, which is why the rate of the reaction is accelerated. The catalyst is then regenerated in a subsequent step.

One example of homogenous catalysis was encountered in Chapter 10, where we saw that the reaction of carboxylic acids with alcohols to form esters is acid catalysed:

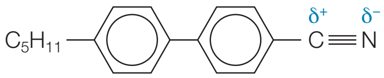
$$CH_3COOH + CH_3CH_2OH \overset{H^+}{\rightleftharpoons} CH_3COOCH_2CH_3 + H_2O$$

Heterogeneous catalysts are in a different state of matter to the reactants, usually they are solids and the reactants are solutions, liquids or gases. The reactants adsorb onto active sites on the surface of the catalyst where the reaction occurs. After being formed the products then desorb from the surface and regenerate the catalyst.

An example of heterogenous catalysis was also encountered in Chapter 10, where we saw that the reduction of alkenes by hydrogen requires a nickel catalyst:

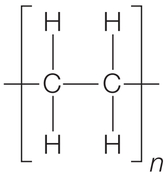
$$H_2C{=}CH_2 + H_2 \overset{Ni(s)}{\rightleftharpoons} CH_3CH_3$$

5 **(a)** Biphenyl nitriles are an example of thermotropic liquid crystals. The diagram below is 4-pentyl-4-cyanobiphenyl.



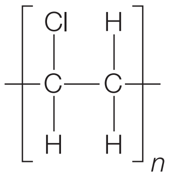
(b) The nitrile group (–CN) makes the molecule polar and the biphenyl group makes the molecule rigid. The strong intermolecular forces between molecules cause them to align in a common direction but the long flexible alkyl chain prevents the molecules from packing too closely and forming a solid.

6 **(a)** Poly(ethene) only contains non-polar C—H and C—C bonds whereas poly(vinylchloride) contains polar C—Cl bonds.



$\left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- \right]_n$

poly(ethene)



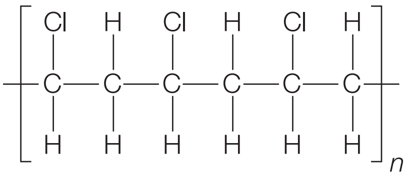
$\left[-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- \right]_n$

poly(vinylchloride)

The polar C—Cl bonds create stronger dipole–dipole interactions between the poly(vinylchloride) polymer chains than in poly(ethene), where London dispersion forces exist between the polymer chains. The greater intermolecular attractions between the polymer chains make poly(vinylchloride) more rigid and less flexible than poly(ethene).

(b) Poly(vinylchloride) can be made more flexible by the addition of plasticizers. Plasticizers are molecules that can fit in between the polymer chains and decrease the intermolecular forces between them. This allows the polymer chains to move more freely past each other and increases flexibility.

(c) In isotactic polymers the substituent groups are arranged on the same side of the chain whereas in atactic polymers the substituent groups are randomly arranged on both sides. The isotactic form of PVC will have all the chlorine atoms on the same side of the chain:



$\left[-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- \right]_n$

7 Adding a volatile hydrocarbon gives the polymer certain properties: low density, good thermal insulator, expanded, softer, better shock absorber.

The product can be used in packaging and insulation.

8 **(a)** 1 nm to 100 nm

(b) Physical techniques move atoms to a specific position.

Chemical techniques involve chemical reactions to position atoms (in molecules).

(c) Nanotechnology has implications for human health (e.g. unknown effects, immune system may not cope, unsatisfactory toxicity regulations), employment (e.g. increased/decreased job opportunities, adverse effect on traditional industries), quality of life (e.g. medical advances, faster computers, improved performance of electronic equipment), public opinion (e.g. need to improve information, encourage discussion, seek approval).

Nanotechnology is being developed in wealthier nations, which may increase the divide between different nations.

9 Advantages: reduce volume, stable odour-free residue, source of energy.

Disadvantages: expensive to build and operate, can form dioxins/toxic gases, requires energy, adds to greenhouse effect.

10 **(a)** Advantages for using landfills are that they can cope with a large volume of waste, they are relatively cheap to operate and filled ground can be re-used.

Advantages for using incinerators are that they reduce the volume of waste, they do not require much space for their operation and the heat produced can be used to produce electricity.

(b) The environment under the surface of a landfill can become anaerobic, which means that there will be limited oxygen available for the bacteria to use in breaking down the plastic.

11 **(a)** As Figure 12.5 on page 400 shows, the commercial production of aluminium by electrolysis involves graphite anodes and graphite cathodes.

(b) Producing aluminium from its ores by electrolysis is a very energy intensive and expensive process so recycling consumes less energy than producing new aluminium.

As the electrolysis of aluminium produces significant amounts of CO_2, recycling will also reduce the greenhouse gas emissions associated with aluminium production.

Recycling aluminium will also reduce the amount of unnecessary waste material accumulating in landfill sites.

12 **(a)** The wall of the nanotube is a rolled sheet of graphite that contains carbons bonded in linked repeating hexagons. The cap at the end is similar to half a Buckminster fullerene, which is an allotrope of carbon where the atoms are bonded in interlinked pentagon and hexagon rings. The presence of the pentagon rings causes the structure to curve back on itself, forming the cap (see Figure 12.35 on page 435 of a nanotube capped at both ends).

(b) Nanotubes are very strong as all the carbon atoms are linked together by very strong C–C covalent bonds that require a lot of energy to break.

(c) **(i)** Nanotubes are effective as heterogeneous catalysts as they have a large surface area and they can also demonstrate a high degree of selectivity for different reactants based on the dimensions of the nanotubes.

(ii) Nanotubes are relatively new materials and their possible effects on human health have not been fully determined. There is some concern that they may prove harmful as their extremely small size may result in the body's regular defences against foreign bodies and toxins being ineffective against nanotubes (and other nanomaterials) if they are ingested or inhaled.

13 **(a)** **(i)** The CN group on 4-pentyl-4-cyanobiphenyl is polar and it is the intermolecular forces resulting from this polar group that cause the molecules to align themselves.

(ii) The long alkyl chain, C_5H_{11}, makes it difficult for the molecules to close pack and form a solid.

(iii) The biphenyl group provides the rigid rod shape that makes it easy for the molecules to align themselves.

(b) See Figures 12.21 and 12.22 on page 421. In twisted nematic liquid crystal displays the liquid crystalline material is placed between two glass plates that have parallel scratches. The two plates are orientated so that the scratches on the two plates are at 90° to each other. Liquid crystal molecules align themselves with the scratches as well as each other due to intermolecular forces. This results in the formation of twisted columns of molecules between the two plates to accommodate the 90° offset between the plates.

If polarizing filters are aligned with the scratches on the glass plates polarized light can pass through both as the plane of polarization twists with the orientation of the molecules as it passes through the liquid crystals.

When a voltage is applied this changes the alignment of the liquid crystal molecules and the polarized light is no longer deflected 90° so that it can pass through the second polarizing filter and the pixel appears dark.

14 Liquid crystals tend to be rigid rod-shaped molecules that contain a polar group and a long alkyl chain. Strong intermolecular forces due to the polar group, along with the rigid rod shape, cause the molecules to align themselves but the long alkane chain prevents close packing. When temperature is increased the molecules have sufficient kinetic energy to overcome the attractions between them and they stop being aligned, creating a regular liquid where all the molecules are randomly arranged.

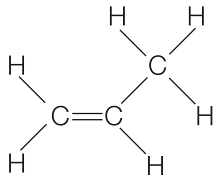
15 The difference between high-density poly(ethene) and low-density poly(ethene) is the amount of branching in the polymer chains. High-density poly(ethene) has very little branching and this allows stronger intermolecular forces and closer packing of the polymer chains. The stronger intermolecular forces also result in high-density poly(ethene) having a higher melting point.

16 **(a)** The main method of modifying PVC is the addition of plasticizers, which are molecules that can fit in between the polymer chains and decrease the intermolecular forces between them. This allows the polymer chains to move more freely past each other and increases flexibility.

(b) Two disadvantages of (addition) polymers such as poly(ethene) and PVC is that they are difficult to dispose of and not biodegradable. As a result they contribute to litter and as they do not break down they start to fill up landfills.

One disadvantage of PVC is that when it is burned it produces HCl, which contributes to acid rain. Incomplete combustion of PVC can also result in the production of toxic polychlorinated dioxins.

17 **(a)** The polymer shown is isotactic poly(ethene) and the monomer it is produced from is propene:



(b) Because it has shorter polymer chains polymer B will have weaker intermolecular forces between its polymer chains so it will have a lower melting point than polymer A. Polymer B is also likely to be softer and more flexible than polymer A due to the weaker intermolecular forces.

(c) Polymer C is an atactic polymer and the methyl groups will be randomly arranged along the polymer chain. This differs from polymers A and B, which are isotactic polymers with the methyl groups on the same side of the chain.

Challenge yourself

1 **(a)** One molecular feature of cholesteryl benzoate that allows it to form liquid crystals is that the system of linked hydrocarbon rings gives it a rigid rod shape. Other features are the long alkane chain that prevents close packing of the molecules and the polar ester group that generates the dipole–dipole intermolecular forces that encourage alignment.

(b) As cholesteryl benzoate does not contain a polar head and non-polar tail it is does not have the features of a lyotropic liquid crystal. Cholesteryl benzoate is a thermoropic liquid crystal that shows liquid crystal behaviour over a certain temperature range.

2 **(a)** If there were no liquid crystal present the observer would not observe any light passing through and being reflected back by the mirror so the whole region would appear dark. As the polarizer and the analyser are crossed (at 90° to each other) the polarized light will not pass through the analyser.

(b) As the liquid crystal is able to rotate the plane of polarized light the polarized light would be able to pass through the analyser and be reflected back by the mirror so the whole region would appear light.

(c) In answering this question we need to assume that the application of the potential difference causes the liquid crystals within the electric field to align themselves in a manner that will not rotate the polarized light. Therefore polarized light travelling outside the electric field created by the circular electrodes will pass through and polarized light travelling through the electric field created by the circular electrodes will not. The observer will see a dark circle surrounded by a light region.

3 One way of describing chemical bonds is to view them as tiny springs whose behaviour can be modelled using Hooke's Law and the associated equations for simple harmonic motion:

$$f = 1/2(\sqrt{(k/m)})$$

As the equation shows the frequency of the oscillation, f, is inversely proportional to the mass of the object, m, therefore bonds containing heavy atoms such as halogens, C—X bonds, will vibrate at a lower frequency than C—H bonds, and occur at lower wavenumbers.

Worked solutions

Chapter 13

Exercises

1 Glucose has the formula $C_6H_{12}O_6$. The trisaccharide contains 18 carbon atoms so there must be three glucose isomers formed as product. Water molecules are added to the equation in order that it balances.

$C_{18}H_{32}O_{16} + 2H_2O \rightarrow 3C_6H_{12}O_6$

The addition of two water molecules would also agree with the hydrolysis of two –O– linkages to form three monomers

2 Monomers must each have two functional groups, such as hydroxyl and carboxylic acid functional groups. A molecule of water is given off for each bond that forms between the monomers.

3 **(a)** Anabolic (as this is a synthesis reaction)

(b) Catabolic (as the fatty acids are broken down)

(c) Catabolic (as glucose is broken down into carbon dioxide and water)

(d) Anabolic (as DNA molecules are synthesized from their precursors)

4 Conditions needed are: sunlight, photosynthetic pigments to absorb light energy, water, and carbon dioxide.

Carbon dioxide is reduced by the hydrogen from water forming carbohydrate. The oxidation state of carbon decreases from +4 in CO_2 to 0 in $C_6H_{12}O_6$. Oxygen is oxidized from –2 in H_2O to 0 in O_2.

5 Aerobic respiration yields a great deal more energy than anaerobic respiration, as in the presence of oxygen the oxidation of glucose to CO_2 and H_2O is complete. In anaerobic respiration, oxidation is incomplete, and much of the energy remains in the end products such as ethanol.

6 **C** Glucose is oxidized in both processes, but only partially in anaerobic respiration whereas it is fully oxidized in aerobic respiration.

7 **(a)** There are six possibilities because the sequence of amino acids is different in each case. These are:

His—Tyr—Val

His—Val—Tyr

Tyr—His—Val

Tyr—Val—His

Val—His—Tyr

Val—Tyr—His

Note that His—Tyr—Val is different to Val—Tyr—His.

(b) 24 different tetrapeptides exist based on the number of possible positions for each amino acid: 4 × 3 × 2 × 1 = 24

8 **(a)** Leucine, as it is very compact and its R group is non-polar

(b) Threonine

(c) Glutamic acid, as a pH of 5 is above its isoelectronic point of 3.2

(d) Lysine, as a pH of 7 is below its isoelectronic pH of 9.7

9 Fibrous proteins are usually elongated molecules with a well-defined secondary structure. They are structural materials and are insoluble in water. Globular proteins have a well-defined tertiary structure and are compact spherical molecules, soluble in water. They are functional as enzymes, carriers, hormones, and receptors.

10 Hydrogen bonds in the secondary structure are between groups that are part of the peptide bonds of amino acids four residues apart in a polypeptide chain. Hydrogen bonds in the tertiary structure are between groups such as –OH in the side chains of amino acids.

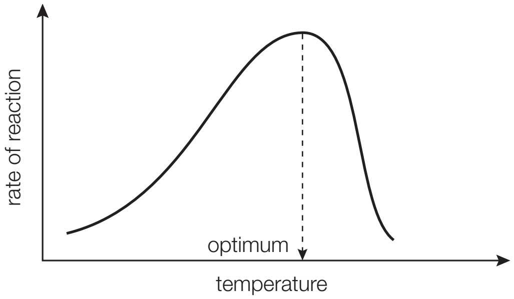
11 **(a)** Note the question asks you to ‘state’ not to ‘describe’ or ‘explain’, so a bulleted list of features would be a good approach here. Make sure your answer includes four

different characteristics, not just different words for the same thing.

Enzymes are:

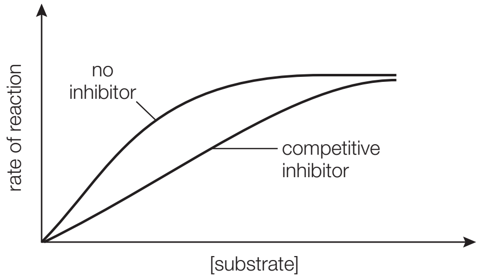
- biological catalysts
- made of proteins
- very specific in their action
- affected by changes in temperature and pH
- able to form an enzyme–substrate complex in which the reaction occurs.

(b) In a sketch graph it is essential to label the axes (but without units) and give the shape clearly. Use a ruler when drawing the axes. The graph given here shows how the explanation must make reference to the structure of the protein in reference to the enzyme activity.



The shape shows increasing rate with increasing temperature as a result of the increase in average kinetic energy leading to more successful collisions between enzyme and substrate. This continues to a maximum point (close to 40 °C in humans), known as the optimum. At temperatures higher than this, the rate of the reaction falls dramatically as the enzyme is denatured. This means that it loses its specific tertiary structure and can no longer bind the substrate at the active site.

12 This type of question seems to be quite common, so it is a good idea to be familiar with it.



13 *Similarities:* both increase rate of reaction by providing pathway of lower E_a; both have no effect on K_c or yield.

Differences: enzymes are proteins, inorganic catalysts have a varied structure; enzymes show saturation kinetics, inorganic catalysts usually do not; enzymes are regulated by inhibitors, inorganic catalysts are usually not; enzymes are sensitive to pH and temperature, inorganic catalysts usually work well at a wide range of temperature and pressure.

14 **(a)** Hands are likely to contain free amino acids that could be deposited on the paper and interfere with the chromatogram.

(b) Isoleucine has an isoelectric point = 6.0. Therefore, at pH < 6.0 it will be positively charged and so attracted to the cathode; at pH > 6.0 it will be negatively charged and so attracted to the anode.

(c) Glutamic acid has an isoelectric point = 3.2; histidine has an isoelectric point = 7.6. Therefore, pH between 3.2 and 7.6 would achieve separation, e.g. pH 5.0. Glutamic acid will be negatively charged and attracted to the anode. Histidine will be positively charged and attracted to the cathode.

15 Moles of $I_2 = \frac{n}{M(I_2)}$

$$= \frac{10.16\ \text{g}}{253.8\ \text{g mol}^{-1}} = 0.04003 \text{ moles } I_2$$

Therefore, 0.02 moles of fat react with 0.04 moles of I_2 so there are two double bonds in the fat.

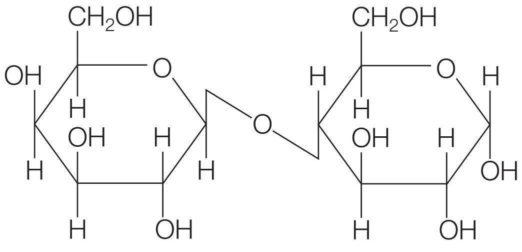
16 **B** The essential fatty acids cannot be made in the body so must be present in the diet.

17 Hydrolytic rancidity occurs when the fat is broken down by ester hydrolysis. This occurs more rapidly if heat is involved. Oxidative rancidity occurs when double bonds in the fat react with oxygen in the air via a free-radical reaction. It occurs most often between fats and oils that contain a high proportion of double bonds.

18 **(a)** Monosaccharides all have the molecular formula $C_6H_{12}O_6$ and so their empirical formula is CH_2O.

(b) Monosaccharides are water soluble as they are small molecules with many free —OH groups which can form hydrogen bonds with water. Polysaccharides are insoluble as they are much larger molecules.

19



Lactose

molecular formula = $C_{12}H_{22}O_{11}$. The bond between the sugars is a glycosidic bond.

20 **(a)** Carbon–carbon double bonds and hydroxyl groups.

(b) Water-soluble: vitamin C; fat-soluble vitamin A/vitamin D. Vitamin C has many —OH and polar groups able to form hydrogen bonds with water. Vitamins A and D are predominantly non-polar/have hydrophobic groups and so cannot form hydrogen bonds with water. Instead they dissolve more readily in non-polar fats.

21 Fortification of certain staple foods such as rice and flour with micronutrients; supply of nutritional supplements, particularly in places where certain deficiencies are known (e.g. iodine); possible changes and improvements in nutrient content through genetic modification.

22 Ionic bonds, hydrogen bonds, London dispersion forces, hydrophobic interactions.

23 Biomagnification refers to the increasing concentration of a xenobiotic substance at different levels in a food web. It is often associated with toxic effects for organisms that feed at a high trophic level, as their cells contain the highest concentrations.

24 Break down oil spills, help break down some plastics, in biological detergents that improve energy efficiency, in Green Chemistry involving less toxic chemical pathways and solvents.

Practice questions

1 **(a)** Melting point above 25 °C: lauric, myristic, palmitic and stearic acids are solids at room temperature.

(b) Melting point increases as van der Waals forces increase with size of the R group, due to an increase in number of electrons.

(c) An increase in the number of the C=C double bonds adds kinks to the structure, which reduces the ability of the molecules to pack together. The intermolecular forces are weaker and the melting points decrease.

2 The peptide bond is an amide link, the glycosidic bond is an ether C–O–C link and the bond between fatty acids and glycerol is an ester link.

Correct answer is B.

3 Peptide groups form hydrogen bonds and so fold the polypeptide chain in a regular pattern.

Correct answer is D.

4 Denaturation involves loss of the tertiary structure through breakage of the bonds between the R groups.

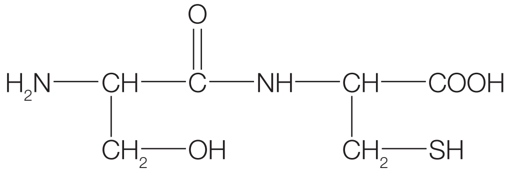
Correct answer is C.

5 Enzymes, like all catalysts, increase the rate of the reaction but not the yield.

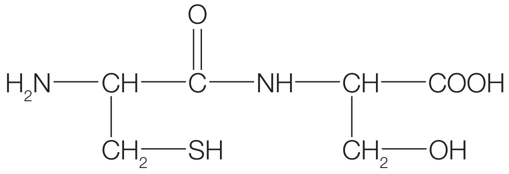
Correct answer is D.

6 **(a)** When two amino acids such as cysteine and serine react to form a dipeptide the reaction that takes place is a condensation reaction. As it is a condensation reaction water is also produced.

(b) The two amino acids can combine in two ways: through the amine on cysteine and the acid on serine or through the amine on serine and the acid on cysteine.



Ser-Cys



Cys-Ser

(c) We saw in part (b) that there are two ways that two amino acids can combine. When there are *n* amino acids there are *n*! possible ways they can combine, therefore for three amino acids there are 3! possible combinations, i.e. six possible combinations.

The symbols for the amino acids are Arg (arginine), Leu (leucine) and His (histidine).

The six possible combinations are:

Arg-Leu-His, Arg-His-Leu, Leu-His-Arg, Leu-Arg-His, His-Arg-Leu, His-Leu-Arg

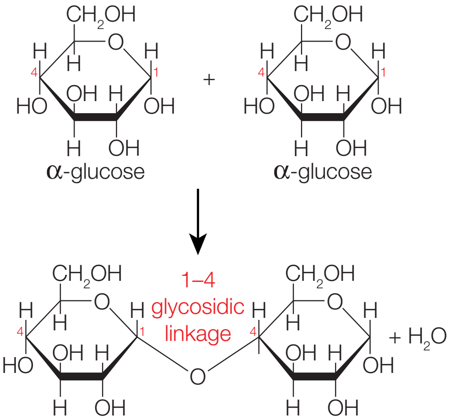
(d) **(i)** The secondary structure of proteins is maintained by hydrogen bonding that occurs between peptide bonds along the length of the protein chain.

(ii) The tertiary structure is due to interactions between the side chains of the protein. These can be:

- hydrophobic interactions (London dispersion forces) between non-polar side chains
- ionic bonding between charged side chains
- covalent bonding between sulfur-containing side chains.

(Hydrogen bonding between side chains can occur but is not an allowable answer due to the context of the question.)

7 **(a)** **(i)** Maltose is a disaccharide formed from the condensation reaction between the –OH on carbon 1 of one α-glucose and the –OH on carbon 4 of another α-glucose to form a 1–4 glycosidic linkage.



maltose

(ii) $C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6$

(iii) The metabolic processes that result in the breakdown of anabolic products such as maltose to release energy are known as catabolism.

8 **(a)** The graph shows the rate of reaction increasing from 0 °C to 35 °C. This is consistent with the average kinetic energy of both the enzyme and substrate increasing, which then increases the probability of a successful collision forming an enzyme–substrate complex.

The reaction is catalysed as the formation of the enzyme–substrate complex provides an alternative reaction pathway with a lower activation energy.

Approaching 40 °C the rate of reaction plateaus and then decreases as the enzyme becomes denatured as the increased kinetic energy overcomes the interactions responsible for the tertiary structure. Less enzyme–substrate complex is formed and the reaction rate decreases.

Above 40 °C the rate of reaction decreases rapidly as denaturation has occurred to such an extent that the enzyme can no longer bind the substrate and catalyse the reaction.

(b) The maximum reaction rate for an enzyme in a plant adapted to a cold climate would occur at a lower temperature, reflecting the ambient conditions within which it operates.

The graph also shows a faster increase in the rate of reaction at the lower temperatures.

9 **(a)** **(i)** Linoleic acid has the formula $CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$, which shows it contains two double bonds. The iodine number is the mass of iodine, I_2, that will react with 100 g of a fat.

$M(\text{linoleic acid}) = (18 \times 12.01) + (32 \times 1.01) + (2 \times 16.00)\,\text{g mol}^{-1} = 280.50\ \text{g mol}^{-1}$

In exactly 100 g, $n(\text{linoleic acid})$

$$= \frac{m(\text{linoleic acid})}{M(\text{linoleic acid})} = \frac{100\ \text{g}}{280.50\ \text{g mol}^{-1}}$$

$= 0.357\ \text{mol}$

Linoleic acid contains two double bonds so 1 mole of linoleic acid reacts with 2 moles of I_2.

$n(I_2) = 2 \times 0.357\ \text{mol} = 0.714\ \text{mol}$

$m(I_2) = nM = 0.714\ \text{mol} \times (2 \times 126.9)\ \text{g mol}^{-1} = 181\ \text{g}$

The iodine number of linoleic acid is 181.

(ii) If the unknown fatty acid X has a lower iodine number than linoleic acid this means that 100 g of this fatty acid (of similar molar mass) will react with less iodine and must therefore contain fewer double bonds.

(iii) The melting points of fatty acids depend on the strength of the intermolecular forces between the long chains. The fewer double bonds in the chain then the fewer kinks that occur in the chain and the more linear it is. The more linear the chain the closer the packing that can occur between the fatty acid chains and this results in stronger London dispersion forces between the fatty acid chains and a higher melting point. As X has fewer double bonds than linoleic acid it will have a higher melting point.

(b) The two types of rancidity that can occur in fats are hydrolytic rancidity and oxidative rancidity.

Hydrolytic rancidity occurs when the fat is hydrolysed and breaks down into glycerol and the three constituent fatty acids. (This is the opposite of the condensation reaction that forms the fat.) Hydrolytic rancidity is favoured by high temperatures and it is also catalysed by the enzyme lipase.

Oxidative rancidity occurs when unsaturated fats react with oxygen. The reaction occurs at the C=C double bonds to form aldehydes and ketones. Oxidative rancidity can be catalysed by light, enzymes and metal ions so is favoured under conditions where these factors are present.

(c) Lipids release more energy per unit mass on oxidation than carbohydrates, as they are more reduced. Lipids are insoluble and difficult to transport so their breakdown is more difficult and slower than that of carbohydrates. Hence carbohydrates, especially simple carbohydrates, are a good short-term source of energy and lipids are a good long-term source of energy.

10 **(a)** Xenobiotics are foreign substances that are found in an organism but are not normally present in that organism.

(b) Plastics that have a high starch content can absorb water and swell, causing the plastic to break into small pieces that can be broken down by bacteria.

(c) PVC cannot be broken down through microbial action as it contains C–Cl bonds and there are no enzymes capable of breaking this bond.

11 This is a descriptive question worth 4 marks, so be sure your answer includes four separate facts, as shown in the IB markscheme answer.

'Specificity' refers to the ability of an enzyme to recognize/bind to only one or a small number of different substrate molecules.

The answer could include mention of an active site/induced-fit mechanism based on complementary chemical groups in the enzyme and substrate. As the substrate reacts to form product, the complementarity is no longer there and the product detaches.

Summary equation: $E + S \rightleftharpoons ES \rightleftharpoons EP \rightleftharpoons E + P$

Challenge yourself

1 The entropy of the environment increases. Energy is returned as less useful forms such as heat and other forms which quickly become randomized. Order is created at the expense of the environment, which becomes more disordered.

2 To solve for the oxidation state of carbon in $C_6H_{12}O_6$ and CO_2 we need to make the assumption that H will have an oxidation state of +1 and O will have an oxidation state of –2 as a highly electronegative Group 16 element.

As the overall charge on the $C_6H_{12}O_6$ is 0:

6(oxidation state of C) + 12(oxidation state of H) + 6(oxidation state of O) = 0

6(oxidation state of C) + 12(+1) +6(–2) = 0

6(oxidation state of C) = –12 – 12 = 0

oxidation state of C = 0 in $C_6H_{12}O_6$

As the overall charge on the CO_2 is 0:

oxidation state of C + 2(oxidation state of O) = 0

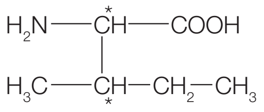
oxidation state of C +2(–2)= 0

oxidation state of C – 4 = 0

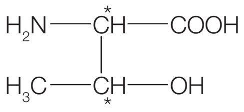
oxidation state of C = +4 in CO_2

During respiration $C_6H_{12}O_6$ is converted to CO_2. As the oxidation state of carbon changes from 0 in $C_6H_{12}O_6$ to +4 in CO_2 the carbon is oxidized during respiration.

3 The two amino acids that each contain two chiral carbon atoms are threonine and isoleucine:



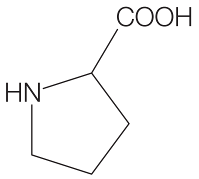
isoleucine



threonine

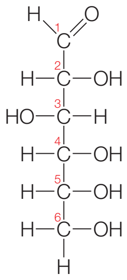
* = chiral carbon

4 Proline is the amino acid that contains a secondary amine (a secondary amine has a nitrogen atom bonded to two carbons and one hydrogen):

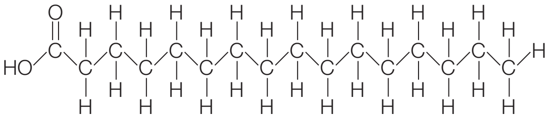


When it forms peptide linkages the nitrogen in proline becomes a tertiary nitrogen with no hydrogens bonded to it so it cannot be a hydrogen bond donor, but it retains a lone pair of electrons so it can be a hydrogen bond acceptor. Because of this the presence of proline leads to a bend or kink in the polypeptide chain.

5 In general carbon atoms in carbohydrates have higher oxidation states than carbon atoms in lipids. Consider glucose and palmitic acid:



glucose



palmitic acid

In glucose the oxidation states of the carbon atoms are all +1 except for C_6, which has an oxidation state of 0.

In palmitic acid the oxidation states of the carbon atoms range from –3 in the terminal $–CH_3$ to +4 in –COOH. The majority of carbon atoms are present as $–CH_2–$ units where the oxidation state of the carbon atom is –2.

Chapter 14

Exercises

1 **(a)** Recent solar radiation: solar heating, solar electricity, hydroelectricity, wind power, biomass.

(b) Ancient solar radiation: fossil fuels.

(c) Forces from the formation of the Earth: tidal is due to the presence of the moon, nuclear fission due to the presence of radioactive elements found in the Earth, geothermal (heat from below the crust from nuclear fission due to the presence of radioactive elements found in the Earth).

(d) Renewable sources are derived from recent solar energy with some also from forces from the formation of the Earth (e.g. tidal, geothermal).

Note: Nuclear fusion doesn't feature in any of (a) to (c) as it is not yet used on Earth. It is, however, the source of solar radiation (both recent and ancient).

2 **(a)** $\frac{\text{useful output energy}}{\text{total input energy}} = \frac{\text{useful heat energy}}{\text{total input heat energy}} = 0.85$

Heat energy produced by combustion

$= \frac{4.00 \times 10^7\ \text{kJ}}{0.85}$

$= 4.71 \times 10^7$ kJ

$\Delta H_{\text{combustion}}$ for $CH_4 = -891\ \text{kJ mol}^{-1}$ (from Section 13 of IB data booklet)

Moles of $CH_4 = \frac{4.71 \times 10^7\ \text{kJ}}{891\ \text{kJ mol}^{-1}} = 5.28 \times 10^4$ mol

Mass of $CH_4 = 5.28 \times 10^4\ \text{mol} \times 16.05\ \text{g mol}^{-1}$

$= 8.48 \times 10^5\ \text{g} = 8.48 \times 10^2$ kg

(b) Energy produced by combustion

$= \frac{4.00 \times 10^7\ \text{kJ}}{0.50}$

$= 8.00 \times 10^7$ kJ

Moles of $CH_4 = \frac{8.00 \times 10^7\ \text{kJ}}{891\ \text{kJ mol}^{-1}} = 8.98 \times 10^4$ mol

Mass $= 8.98 \times 10^4\ \text{mol} \times 16.05\ \text{g mol}^{-1}$

$= 1.44 \times 10^6\ \text{g} = 1.44 \times 10^3$ kg

3 **(a)**

Formula	M /g mol^{-1}	ΔH_c / kJ mol^{-1}	Specific energy / kJ g^{-1}
H_2	$= 2 \times 1.01 = 2.02$	-286	$= \frac{286}{2.02} = 142$
CH_4	$= 12.01 + (4 \times 1.01)$ $= 16.05$	-891	$= \frac{891}{16.05} = 55.5$

(b) Assuming ideal behaviour: $PV = nRT$

$PV = \frac{m}{M}RT$

density (ρ) $= \frac{\text{mass}}{\text{volume}} = \frac{m}{V} = \frac{PM}{RT}$

With everything in SI units, the units of density are kg m^{-3}

With the molar mass in g mol^{-1}, the units of density are g m^{-3}

STP conditions: $T = 273$ K and $P = 100$ kPa

Energy density = specific energy × density

3 **(b) contd**

Formula	Specific energy / kJ g^{-1}	Density / g m^{-3}	Energy / kJ m^{-3}
H_2	$= \frac{286}{2.02} = 142$	$= \frac{1.00 \times 10^5 \times 2.02}{8.13 \times 273} = 91.0$	$= \frac{286}{2.02} \times \frac{1.00 \times 10^5 \times 2.02}{8.13 \times 273} = 12\,900$
CH_4	$= \frac{891}{16.05} = 55.5$	$= \frac{1.00 \times 10^5 \times 16.05}{8.13 \times 273} = 723$	$= \frac{891}{16.05} \times \frac{1.00 \times 10^5 \times 16.05}{8.13 \times 273} = 40\,100$

Note: The energy density of a gas is not determined by the molar mass

(c) Hydrogen is the best fuel, based on the specific energy. However, it is dangerous to store (as it can't be liquefied) and it may explode on combustion if the conditions are not right.

4 **(a)**

	C	H	O
Mass / g	84.96	5.08	7.55
Moles	$\frac{84.96}{12.01}$ = 7.07	$\frac{5.08}{1.01}$ = 5.03	$\frac{7.55}{16.00}$ = 0.47
Divide by smallest	136	96.73	9.04
Nearest whole number ratio	136	97	9

	N	S
Mass / g	0.73	1.68
Moles	$\frac{0.73}{14.01} = 5.2 \times 10^{-2}$	$\frac{1.68}{32.07} = 5.2 \times 10^{-2}$
Divide by smallest	1	1
Nearest whole number ratio	1	1

Empirical formula: $C_{136}H_{97}O_9NS$. (It typically also contains traces of silicon, sodium, calcium, aluminium, nickel, copper, zinc, arsenic, lead, and mercury.)

(b) Combustion causes the oxidation of sulfur and nitrogen in the coal, oxidizing them to the appropriate acids:

$S + O_2 \rightarrow SO_2$ and $2SO_2 + O_2 \rightarrow 2SO_3$ and $H_2O + SO_2 \rightarrow H_2SO_3$ and $H_2O + SO_3 \rightarrow H_2SO_4$

$2N + O_2 \rightarrow 2NO$ and $2NO + O_2 \rightarrow 2NO_2$ and $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$

5 **(a)** $\frac{\text{useful output energy}}{\text{total input energy}} = \frac{\text{useful electrical energy}}{\text{total input heat energy}} = 0.38$

Heat energy produced by combustion

$= \frac{5.00 \times 10^5\ \text{kJ s}^{-1}}{0.38}$

$\text{Mass} = \frac{5.00 \times 10^5\ \text{kJ s}^{-1}}{0.38} \times \frac{1}{33.0\ \text{kJ g}^{-1}}$

$= 39\,900\ \text{g s}^{-1} = 39.9\ \text{kg s}^{-1}$

(b) The unbalanced equation is $CH + O_2 \rightarrow CO_2 + H_2O$

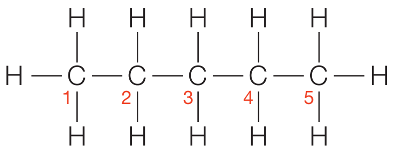
Balanced equation is $CH + \frac{5}{4}O_2 \rightarrow CO_2 + \frac{1}{2}H_2O$

No. of moles of CO_2 = no. of moles of CH

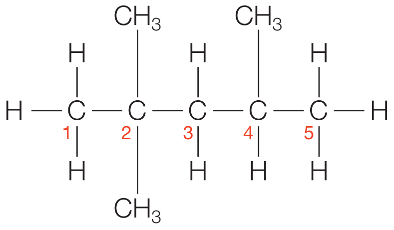
No. of moles of CH per second = $\frac{39\,900}{12.01 + 1.01} = 3062\ \text{mol s}^{-1}$

Mass of CO_2 per second = 3062 × 44.01 $= 135\,000\ \text{g} = 135\ \text{kg s}^{-1}$

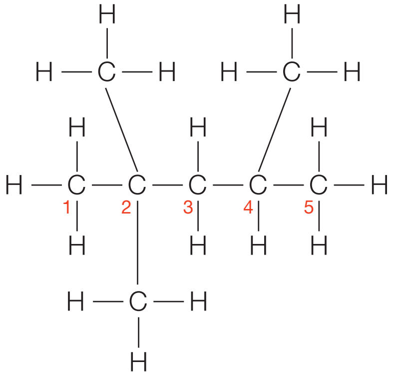
6 The structure is based on pentane:



Then add methyl groups at positions 2, 2, and 4:



or



7 **(a)** Cracking an alkane always produces one (smaller) alkane and at least one alkene. The question seems to ask for three molecules of the same alkene, which could only be propene or ethane:

$C_{11}H_{24} \rightarrow 3C_3H_6 + C_2H_6$

or

$C_{11}H_{24} \rightarrow 3C_2H_4 + C_5H_{12}$

(More realistically, a variety of alkenes would be produced.)

(b) Cracking is a useful process for two reasons. Long-chain alkanes are not sought-after chemicals but the products of cracking are valuable. Shorter-chain alkanes are valuable for fuel and alkenes are important chemical precursors in many industrial reactions including plastics production.

(c) Using a catalyst reduces the cost of generating the high temperatures required for thermal cracking. The catalytic method allows greater control over the products of the reaction, whereas thermal cracking tends to produce a wide range of products.

8 **(a)** Octane (C_8H_{18}) is one of the main components of petroleum, but pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), nonane (C_9H_{20}), and decane ($C_{10}H_{22}$) are also present.

(b) They are isolated from crude oil by fractional distillation.

- The mixture of hydrocarbons is heated, causing them to vaporize.
- As the vapour travels up the fractionating column the hydrocarbons condense at different heights, resulting in their separation.
- The different compounds have different boiling points: the lowest boiling point compounds condense at the top and the highest boiling point compounds condense at the bottom.
- As the relative molar mass increases, the attractive London dispersion forces between the molecules increase, leading to an increase in the boiling point.

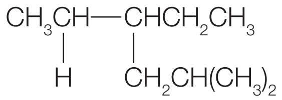
(c) The components of gasoline have boiling points above normal temperatures. They are volatile liquids. They can be easily vaporized in the car cylinder for reaction with oxygen. Lower molar mass compounds are gases which occupy too much volume, while higher molar mass compounds do not vaporize or burn easily.

(d) Higher fractions can be cracked into smaller molecules; the larger molecules are heated with a catalyst and broken into smaller molecules. Alkenes formed in the cracking process can undergo alkylation reactions with lower molecular mass alkanes to further increase the yield of gasoline.

(e) *Cracking*: $C_{16}H_{34} \rightarrow C_6H_{12} + C_{10}H_{22}$

$C_6H_{10} + C_{10}H_{24}$

Alkylation: $(CH_3)_3CH + CH_3CH{=}CHCH_2CH_3$

→ 

$$\rightarrow CH_3\underset{\underset{H}{|}}{CH}-\underset{\underset{CH_2CH(CH_3)_2}{|}}{CH}CH_2CH_3$$

9 The general pattern is:

straight-chain alkanes < cycloalkanes < alkenes < aromatics

pentane < cyclopentane < pentene < benzene

10 The general pattern is that the octane number of straight-chain alkanes decreases with an increase in chain length. Alcohols have very high octane numbers.

heptane < hexane < pentane < ethanol

11 **(a)** High specific energy/energy density. As a liquid it is convenient to handle and deliver. Easy to vaporize, which assists combustion.

(b) It is formed by the anaerobic partial decomposition of marine plants millions of years ago.

(c) Compounds are separated by fractional distillation. Increase of petrol fraction by cracking. Further refining: reforming, alkylation, or isomerization to increase octane number.

12 *Coal gasification*

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(l)$

Coal liquefaction

Direct: $5C(s) + 6H_2(g) \rightarrow C_5H_{12}(l)$

$11H_2(g) + 5CO(g) \rightarrow C_5H_{12}(l) + 5H_2O(l)$

13 Carbon-containing fossil fuels are non-renewable. They are needed as chemical feedstocks. Their combustion adds carbon dioxide to the atmosphere, which contributes to global warming. Carbon-containing renewable fuels displace food production; the food is needed to feed a growing population.

14 **(a)** $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$: $\Delta H_c^{\ominus} = -283$ kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$: $\Delta H_c^{\ominus} = -286$ kJ mol^{-1}

$CO(g) + H_2(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$:

$\Delta H_c^{\ominus} = -283 + (-286)$ kJ mol^{-1} = -569 kJ mol^{-1}

(b) 1 mole of carbon monoxide would be converted to 1 mole of methane.

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

(This part of the question ignores the energy involved in the conversion of carbon monoxide to methane. Using Hess's law would suggest that converting carbon monoxide to methane and then burning the methane should have no net effect.)

(c) One mole of synthesis gas has the same volume as two moles of methane. One mole of synthesis gas produces 569 kJ and two moles of methane produces 2 × 891 kJ = 1782 kJ.

15 **(a)** Methane is the major component of natural gas. It has the formula CH_4.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

(b) Natural gas is the cleanest of the fossil fuels to burn as it has a high H : C ratio.

The combustion of natural gas produces minimal amounts of carbon monoxide, hydrocarbons, and particulates. It does contribute to global warming but does not contribute to acid rain (unlike coal and oil).

(c) Natural gas is the fossil fuel in the shortest supply and it is unevenly distributed around the world. Oil is expected to last a little longer and coal, which is distributed more evenly around the world, longer still.

(d) Supplies of methane can be increased as a result of the cracking of larger hydrocarbons from oil or by coal gasification.

Cracking

$C_4H_{10}(g) \rightarrow CH_4(g) + C_3H_6(g)$

Coal gasification

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$

16 **(a)** Wide availability, relatively cheap compared to other sources, ease of transportation, power stations can be built close to the source, high energy density, can be used with existing technology, concern over nuclear fuel as a source of energy, limited productivity of other sources, not possible to generate sufficient electrical energy without it, many transport systems rely on fossil fuels.

(b) Oil, as when it is distilled, cracked, etc., it is used to power internal combustion engines.

17 It is more efficient; it produces more thermal energy per unit of mass / has a higher specific energy / energy density; it produces less CO_2 per unit of output energy.

18 **(a)** Note that the question doesn't specify which oxygenate to consider. Ethanol is the obvious compound, but other alcohols or a range of ethers could also be considered.

Fuel	ΔH_c / kJ mol^{-1}	Moles needed to produce 10 000 kJ	Molar mass / g mol^{-1}	Mass needed to produce 10 000 kJ / g
Methylbenzene	–3910	$\frac{10\,000}{3910} = 2.56$	(12.01 × 7) + (8 × 1.01) = 92.15	2.56 × 92.15 = 236
Ethanol	–1367	$\frac{10\,000}{1367} = 7.31$	(12.01 × 2) + (6 × 1.01) + 16.00 = 46.08	7.31 × 46.08 = 337

(b)

Fuel	Moles of CO_2 produced / mol	Mass of CO_2 produced / g
Methylbenzene	7 × 2.56 = 17.92	17.92 × 44.01 = 789
Ethanol	2 × 7.31 = 14.62	14.62 × 44.01 = 643

(c) Oxygenates produce less carbon dioxide / have a smaller carbon footprint.

19 **(a)** ${}^{1}_{0}$n – the sum of the superscripts to the left of the arrow have to equal the sum of the superscripts to the right of the arrow, and the same for the subscripts.

(b) ${}^{17}_{8}$O – the sum of the superscripts to the left of the arrow have to equal the sum of the superscripts to the right of the arrow, and the same for the subscripts. The subscript '8' defines the species as oxygen.

20 **(a)** $\Delta E = \dfrac{hc}{\lambda}$

$$= \frac{6.63 \times 10^{-34} \times 3.00 \times 10^{8}}{\lambda}\ \text{J}$$

$$= \frac{6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3.00 \times 10^{8}}{\lambda}\ \text{J mol}^{-1}$$

$$= \frac{6.02 \times 10^{20} \times 6.63 \times 10^{-34} \times 3.00 \times 10^{8}}{\lambda}\ \text{kJ mol}^{-1}$$

$$= \frac{0.000\,120}{\lambda}\ \text{kJ mol}^{-1}$$

λ / m	ΔE/ kJ mol^{-1}	
656 × 10^{-9}	$\frac{0.000\,120}{656 \times 10^{-9}} = 183$	red
486 × 10^{-9}	$\frac{0.000\,120}{486 \times 10^{-9}} = 247$	blue
434 × 10^{-9}	$\frac{0.000\,120}{434 \times 10^{-9}} = 276$	violet

(b) By inspection, we can see that transitions from $n = 2$ fall into this range.

ΔE / kJ mol^{-1}	Transition
183	$n = 2 \rightarrow n = 3$
247	$n = 2 \rightarrow n = 4$
276	$n = 2 \rightarrow n = 5$

(c) At higher energy, energy levels become closer together; the energy differences between higher energy levels and the lower level (n = 2) become closer together and the difference in wavelength decreases.

21 **(a)** W: atomic number = 92 – 2 = 90, mass number = 233 – 4 = 229: ${}^{229}_{90}$Th

X: atomic number = (92 + 0) – 56 + 36 = 0, mass number = (235 + 1) – (141 + 92) = 3: 3${}^{1}_{0}$n

Y: atomic number = 92 – (–1) = 93, mass number = 239: ${}^{239}_{93}$Np

Z: atomic number = 92 – 58 = 34, mass number (233 + 1) – (140 + 2) = 92: ${}^{92}_{34}$Se

(b) Process II (fission) is used to produce electricity in nuclear power plants. (Process IV is also a fission reaction and is another potential reaction.) This process can be initiated as required by controlling the input of neutrons, whereas the other processes are natural ones and occur randomly. Process II is self-sustaining if the critical mass is available. It produces more neutrons than are needed initially and so a chain reaction occurs which can lead to the fission of more nuclei.

(c) The mass of the products is less than the mass of the reactants. The difference is converted to energy according to the equation: $\Delta E = \Delta mc^2$.

22 Less than 1% of natural uranium is the fissionable isotope: $^{235}_{92}U$. There is less than the critical mass present. There is insufficient $^{235}_{92}U$ to sustain the chain reaction.

23 **(a)** 0.5 of original remains after each half-life, so 0.5^{10} remains after 10 half-lives ≈ 0.001 (= 0.1%)

(b) 100.0% – 0.1% = 99.9%

24 First notice that $\frac{96.0}{19.2} = 5$, so 96.0 s = 5 half-lives

Either use the information in the question to compile a table or carry out a calculation.

Time / half-lives	Time / s	Activity / s^{-1}
0	0	1200
1	19.2	600
2	38.4	300
3	57.6	150
4	76.8	75
5	96.0	37.5

5 half-lives corresponds $(0.5)^5$ remaining = $1200 \times (0.5)^5 = 37.5$

The count rate would be 37 or 38 disintegrations per second. (Can't have half a count so 37.5 means either 37 or 38 counts are likely to be observed.)

25 $^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U \rightarrow ^{90}_{38}Sr + ^{144}_{54}Xe + 2^{1}_{0}n$

This is worked out from the sum of the superscripts to the left of the arrow having to equal the sum of the superscripts to the right of the arrow, and the same for the subscripts.

26 High-level waste: contains fission products.

Low-level waste: clothing / fuel cans / other.

High-level waste is initially stored under water. It can then be encased in steel/concrete or vitrified / made into glass and buried underground.

Low-level waste is also initially stored under water as the activity falls to safe levels. The waste can then be stored in steel containers inside concrete-lined vaults.

27 Use the information in the question to compile a table:

Time / years	Activity / $hr^{-1}\,g^{-1}$
0	60.0
5730	30.0
5730 × 2	15.0
5730 × 3	7.5
5730 × 4	3.75

The shell is approximately 5730 × 4 years = 22 920 years old.

More precisely, $(0.5)^x = \frac{4}{60}$, where x is the number of half-lives.
Taking logs of both sides: $x \log 0.5 = \log 0.067$
$x = 3.9$
3.9 half-lives = 22350 years

28 **(a)** $CH_2{=}CH{-}CH{=}CH_2$ is a conjugated system with two double bonds separated by a single bond which extends along the full length of the molecule.

(b) The double bonds disappear as the molecules undergo an addition reaction with bromine.

(c) Benzene absorbs radiation in the UV region. In nitrobenzene, conjugation between the benzene ring and the nitro group allows radiation of longer wavelength to be absorbed. This radiation occurs in the visible region of the spectrum and so the compound is coloured.

29 **(a)** Increased conjugation (increased n) moves the absorption band λ_{max} towards longer wavelength.

(b) The first members of the series are colourless as they absorb in the UV region, but the later members ($n > 2$) are coloured as they absorb in the visible region.

(c) $C_6H_5{-}(CH{=}CH)_5{-}C_6H_5$ absorbs in the purple region and is probably yellow.

$C_6H_5—(CH=CH)_6—C_6H_5$ absorbs in the purple/blue region and is probably orange.

(d) Only λ_{max} and not the full spectrum is given so it not possible to give a precise answer. There may be more than one transition occurring and the overall colour observed will be a composite of the individual colours associated with each transition.

30 The conjugated system includes eleven C=C bonds and so absorbs in the visible region. The molecule absorbs blue light and so appears orange.

31 **(a)** Fossil fuels and biomass are derived from the Sun through photosynthesis. Other sources are wind and hydroelectricity.

(b) Advantage: renewable and has little environmental impact. Disadvantage: photosynthesis is not very efficient so relatively little of the available solar energy is trapped.

32 **(a)** $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(b) Chlorophyll

(c) Conjugated system of double and single bonds

(d) Process: fermentation

Equation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

Conditions: acidity / absence of oxygen / below 40 °C, yeast provides enzyme

33 **(a)** Methane.

(b) Carbon monoxide and hydrogen.

(c) Particulates (soot), hydrocarbons, carbon monoxide.

(d) Fossil fuels are running out. Biomass is a renewable source.

34 **(a)** Percentage of light absorbed by plants

$$= \frac{1.25 \times 10^4}{1.25 \times 10^6} = 1.00\%$$

(b) Wavelength of radiation not absorbed by chlorophyll. Some radiation is reflected or heats the surface of the Earth. Plants do not cover all the Earth.

(c) Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(d) Production of biogas, production of ethanol / fermentation

35
- Biodiesel is renewable.
- Biodiesel is carbon neutral. Plants use the same amount of CO_2 to make the oil that is released when the fuel is burned.
- Biodiesel is rapidly biodegradable and completely non-toxic, meaning spillages represent far less risk than petroleum diesel spillages.
- Biodiesel has a higher flash point than petroleum diesel, making it safer in the event of a crash.
- Blends of 20% biodiesel with 80% petroleum diesel can be used in unmodified diesel engines.
- Biodiesel can be used in its pure form but engines may require certain modifications to avoid maintenance and performance problems.
- Biodiesel can be made from recycled vegetable and animal oils or fats.

36 **(a)** Distant from localized areas of pollution; data present an accurate measure of global levels of CO_2.

(b) $$\% \text{ increase} = \frac{\text{increase}}{\text{initial value}} \times 100\%$$

$$= \frac{384 - 316}{316} \times 100\% = 21.5\%$$

(c) Combustion of fossil fuels.

(d) The annual variation is due to CO_2 uptake by growing plants. The uptake is highest in the northern hemisphere springtime.

(e) Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

CO_2 dissolves in water: $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

(f) Decreased level of photosynthesis: less CO_2 taken in by plants.

(g) CO_2 absorbs infrared radiation, which leads to increased vibrations and bending and stretching of the bonds.

37 **(a)** Carbon dioxide has polar C=O bonds and the oxygen atoms have lone pairs. It can form hydrogen bonds with water molecules.

(b) Relatively strong hydrogen bonds are formed: ΔH is negative. The solubility decreases with increasing temperature because the equilibrium shifts to the endothermic (reverse) direction as the temperature increases.

(c) Increased temperatures due to increased atmospheric carbon dioxide concentrations could result in reduced solubility of carbon dioxide. More carbon dioxide is then released, which amplifies the initial change.

(d) Increased carbon dioxide increases the rate of photosynthesis, producing more phytoplankton, which further reduce levels of carbon dioxide.

38 If carbonate ions are removed from solution the

$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

equilibrium will shift to the right. A reduction in hydrogencarbonate ions also affects the following equation, also shifting this equilibrium to the right, reducing the amount of dissolved carbon dioxide:

$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

This equilibrium is linked to the amount of carbon dioxide in the air and so a decrease in the amount of carbonic acid will also reduce the amount of carbon dioxide in the atmosphere.

39 pH = 8.2: $[H^+] = 10^{-8.2}$

pH = 8.1: $[H^+] = 10^{-8.1}$

$$\% \text{ increase} = \frac{10^{-8.1} - 10^{-8.2}}{10^{-8.2}} \times 100\%$$

$$= (10^{0.1} - 1) \times 100\%$$

$10^{01} = 1.26$, so change is 26% (≈ 25%)

40 **(a)** Sources of carbon dioxide: respiration, volcanic eruption, complete aerobic decomposition of organic matter, forest fires

(b) Methane produced from anaerobic decomposition

(c) Smoke particulates: block out sunlight

(d) High-energy short-wavelength radiation passes through the atmosphere; lower energy / longer wavelength radiation from the Earth's surface is absorbed by vibrating bonds in CO_2 molecules

(e) Melting of polar ice caps; thermal expansion of oceans will lead to rise in sea levels which can cause coastal flooding; crop yields reduced; changes in flora and fauna distribution; drought; increased rainfall; alteration in annual weather patterns; desertification

41 **(a)** Incoming radiation from the Sun is of short wavelength; long-wavelength infrared radiation leaves the Earth's surface and some is absorbed by gases in the atmosphere; results in increased vibration of bonds in molecules which then re-radiate heat back to the Earth.

(b) *Natural:* (evaporation from) oceans, evaporation from plants in transpiration. *Artificial:* the burning of fossil fuels.

(c) CO_2 is more abundant but CH_4 absorbs the radiation more effectively / has a larger greenhouse factor. Taking both factors into consideration, overall CO_2 contributes to 50% of global warming and CH_4 to 18% (see page 553).

42 **(a)** coal / diesel (fuel) / wood

(b) $CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(l)$ (although particulate production isn't a problem with the burning of natural gas)

Practice questions

1 **(a)** High-energy visible and UV light from the sun that passes through the atmosphere is absorbed by the earth, which then emits some of this energy as infrared radiation. Greenhouse gases in the atmosphere can absorb this infrared irradiation and then re-radiate the energy as heat to the surface of the planet, causing warming.

(b) Increasing amounts of greenhouse gases in the atmosphere result in increased surface temperatures and the effects of this include:

- melting of polar ice caps and glaciers, and an increase in sea levels
- thermal expansion of the oceans and an increase in sea levels
- an increase in extreme weather events such as droughts, increased rainfall and flooding
- reduced crop yields as a result of extreme weather events
- changes in the distribution of plants, animals and insects.

2 High-level waste is radioactive waste such as spent fuel rods, which are highly radioactive and have a long lifetime. Because it is extremely hazardous very strict precautions need to be taken in the disposal of high-level waste. It is typically encased in glass (vitrified) or ceramics and then buried deep underground in granite rock or deep mine shafts, or under water. Disposal sites must be geologically stable to prevent the risk of earthquakes or landslides that would allow the waste to escape into water sources or the surrounding environment.

Low-level waste includes clothing and materials used where radioactive materials are handled, as well as containers used for radioactive fuels. It typically has a low level of radioactivity and a short lifetime. It is stored in cooling ponds until the radioactivity has fallen to safe levels and the water is run through ion-exchange resins to remove the radioactive isotopes, which can then be diluted and released into the sea. Solid low-level waste can also be kept in steel containers inside concrete lined vaults.

3 Catalytic cracking is used to reduce long-chain alkanes to moderate hydrocarbons that can be used as fuels. The use of catalysts allows the process to be conducted at lower temperatures and the process requires less energy. It also results in branched hydrocarbon products and/or hydrocarbons that contain benzene rings, which are desirable as they burn more evenly in engines.

4 Nuclear fission involves the splitting of heavy nuclei into lighter nuclei.

Nuclear fusion involves the combination of two light nuclei to form a heavier nucleus.

5 If the half-life of ${}^{234}_{92}\text{Ra}$ is 1600 years the amount present after t years, A(t), can be determined using the equation $\ln\frac{[\text{A}]_t}{[\text{A}]_\text{o}} = -\lambda t$.

The decay constant, λ, can be found from the value of the half-life, $t_{½}$:

$$\lambda = \frac{\ln 2}{t_{½}} = \frac{\ln 2}{1600\text{ yr}} = 4.33 \times 10^{-4}\text{ yr}^{-1}$$

If 93.75% of the ${}^{234}_{92}\text{Ra}$ decays then $\frac{[\text{A}]_t}{[\text{A}]_\text{o}} = \frac{(1 - 0.9375)}{1} = 0.0625$

$$\ln\frac{[\text{A}]_t}{[\text{A}]_\text{o}} = -\lambda t$$

$$\ln(0.0625) = -4.33 \times 10^{-4}\text{ yr}^{-1} \times t$$

$$t = \frac{\ln(0.0625)}{-4.33 \times 10^{-4}\text{ yr}^{-1}} = 6400\text{ years}$$

It takes 6400 years for 93.75% of ${}^{234}_{92}\text{Ra}$ to decay.

6 **(a)** Degraded energy is energy that is no longer available to do useful work as it has been transferred from the system to the surroundings and cannot be used again.

(b) The absorption of a neutron by ${}^{235}_{92}\text{U}$ results in a fission reaction occurring:

$${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3{}^{1}_{0}\text{n} + \text{energy}$$

The three neutrons released in the reaction can trigger three more fission reactions if they are each absorbed by ${}^{235}_{92}\text{U}$ atoms. However, fuel rods are designed so that only one neutron is absorbed to ensure that the chain reaction that occurs can be kept under control. Because the mass of the products is slightly less than the mass of the reactants a large amount of energy is released by the reaction, the amount being determined by $E = \Delta mc^2$.

(c) The critical mass of a fissile material is the mass that is needed for a reaction to be self-sustaining.

7 **(a)** Much of the world's energy comes from fossil fuels because they are widely available and readily accessible. The fact that fossil fuels have a high energy density, so that small amounts can produce a significant amount of energy, also makes their use very attractive. Fossil fuels are also easily transportable and their overall ease of use has resulted in much of our current technology being developed around them. Fossil fuels are also highly suitable as fuels because the rate at which they are combusted can be readily controlled and the rate of energy production can therefore be matched to the immediate demand.

(b) Specific energy is the amount of energy produced per unit mass, measured in kJ kg^{-1}.

(c) Uranium and hydrogen are two fuels that have higher specific energies than fossil fuels.

(d) *Note: The question in the book has an incorrect value. The specific energy of natural gas (methane) should be 60 × 10³* ***J*** *g^{-1} not 60 × 10³* ***kJ*** *g^{-1}.*

The rate at which energy is being generated by the combustion of the natural gas can be determined from the energy output of the power station and its efficiency:

$$\text{efficiency} = \frac{\text{energy output}}{\text{energy generated}} \times 100\%$$

$$\text{energy generated} = \frac{\text{energy output}}{\text{efficiency}} \times 100$$

$$= \frac{600 \times 10^{6}\ \text{J s}^{-1}}{30} \times 100 = 2.0 \times 10^{9}\ \text{J s}^{-1}$$

The rate at which methane is combusted can be determined from the energy generated and the specific energy of methane:

energy generated = mass combusted × specific energy

$$\text{mass combusted} = \frac{\text{energy generated}}{\text{specific energy}}$$

$$= \frac{2.0 \times 10^{9}\ \text{J s}^{-1}}{60 \times 10^{3}\ \text{J g}^{-1}} = 33 \times 10^{3}\ \text{g s}^{-1}$$

8 **(a)** Relative formula mass of coal (CH) = 12.01 + 1.01 = 13.02.

$$\text{carbon in coal} = \frac{12.01}{13.02} \times 100\% = 92.24\%$$

Relative formula mass of gasoline (C_8H_{18}) = (8 × 12.01) + (18 × 1.01) = 114.26.

$$\text{carbon in gasoline (petroleum)} = \frac{8 \times 12.01}{114.26} \times 100\% = 84.09\%$$

Relative formula mass of natural gas (CH_4) = 12.01 + (4 × 1.01) = 16.05

$$\text{carbon in natural gas} = \frac{12.01}{16.05} \times 100\%$$

$$= 74.83\%$$

(b) There are many reasons why coal has been replaced by natural gas and gasoline as an energy source. A very practical reason is that natural gas and gasoline have higher specific energies and produce more energy for the same mass. They are also easier to transport and use, being in the gaseous and liquid states whereas coal is a solid. There are also environmental reasons for not burning coal as it produces more greenhouse gases for the same energy output and it often contains sulfur, which generates SO_2 when it is burnt and is a major contributor to acid rain.

(c) Two advantages of using hydrogen as a fuel are that it has a higher specific energy than fossil fuels and its only combustion product is water rather than CO_2, which is a greenhouse gas and contributes to climate change.

9 **(a)** The specific energies for propane and butane can be calculated from their molar masses and enthalpies of combustion:

$M(C_3H_8) = (3 \times 12.01) + (8 \times 1.01)$ g mol^{-1} = 44.11 g mol^{-1}

$\Delta H_c(C_3H_8) = -2219$ kJ mol^{-1}

$$\text{Specific energy of propane} = \frac{|\Delta H_c|}{M(C_3H_8)}$$

$$= \frac{2219\text{ kJ mol}^{-1}}{44.11\text{ g mol}^{-1}} = 50.31\text{ kJ g}^{-1}$$

$M(C_4H_{10}) = (4 \times 12.01) + (10 \times 1.01)$ g mol^{-1} =58.14 g mol^{-1}

$\Delta H_c\ (C_4H_{10}) = -2878\text{ kJ mol}^{-1}$

$$\text{Specific energy of butane} = \frac{|\Delta H_c|}{M(C_4H_{10})}$$

$$= \frac{2878\text{ kJ mol}^{-1}}{58.14\text{ g mol}^{-1}} = 49.50\text{ kJ g}^{-1}$$

(b) The ideal gas equation is $pV = nRT$

Substituting for $n = \frac{m}{M}$ gives:

$$pV = \frac{m}{M}RT$$

Rearranging to give $\frac{m}{V}$ and recognizing that this is equal to the density, ρ, gives:

$\rho = \frac{pM}{RT}$, units will be g m^{-3}.

$$\rho(C_3H_8) = \frac{1.00 \times 10^5\text{ Pa} \times 44.11\text{ g mol}^{-1}}{8.31\text{ J K}^{-1}\text{ mol}^{-1} \times 273.15\text{ K}}$$

$$= 1.94 \times 10^3\text{ g m}^{-3}$$

$$= 1.94 \times 10^{-3}\text{ g cm}^{-3}$$

Energy density of propane = specific energy × density

$$= 50.31\text{ kJ g}^{-1} \times 1.94 \times 10^{-3}\text{ g cm}^{-3}$$

$$= 0.0976\text{ kJ cm}^{-3}$$

(Rounding errors will give answers in the range 0.0950–0.103 kJ mol^{-1})

$$\rho(C_4H_{10}) = \frac{1.00 \times 10^5\text{ Pa} \times 58.14\text{ g mol}^{-1}}{8.31\text{ J K}^{-1}\text{ mol}^{-1} \times 273.15\text{ K}}$$

$$= 2.56 \times 10^3\text{ g m}^{-3}$$

$$= 2.56 \times 10^{-3}\text{ g cm}^{-3}$$

Energy density of butane = specific energy × density

$$= 49.50\text{ kJ g}^{-1} \times 2.56 \times 10^{-3}\text{ g cm}^{-3}$$

$$= 0.127\text{ kJ cm}^{-3}$$

(Rounding errors will give answers in the range 0.125–0.132 kJ mol^{-1})

10 **(a)** Photosynthesis is the process which plants use to create glucose from carbon dioxide and water using light energy from the sun.

(b) Chlorophyll is a molecule in plants that absorbs sunlight. It is highly conjugated, with π electrons delocalized through interconnected π bonds. The energy gap between the molecular energy levels that results from this conjugation corresponds to the energy of visible light so chlorophyll can absorb visible light and an electron is excited from a low-energy orbital to a higher energy orbital.

(c) $6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$

(d) $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(e) **(i)** The conversion of glucose into ethanol is known as fermentation.

The chemical equation for fermentation is:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

(ii) Thermodynamic efficiency $= \frac{-\Delta G_{sys}}{-\Delta H_{sys}} \times$ 100%

The combustion reaction of ethanol is:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta G_c = \sum\Delta G_f(\text{products}) - \sum\Delta G_f(\text{reactants})$$

$$= (2 \times \Delta G_f(CO_2(g))) + (3 \times \Delta G_f(H_2O(l))) - \Delta G_f(C_2H_5OH(l))$$

$$= (2 \times -394.4) + (3 \times -237.1) - (-175)\text{ kJ mol}^{-1}$$

$$= -1325.1\text{ kJ mol}^{-1}$$

$$\text{Thermodynamic efficiency} = \frac{\Delta G_c}{\Delta H_c} \times 100\%$$

$$= \frac{-1325.1\text{ kJ mol}^{-1}}{-1367\text{ kJ mol}^{-1}} \times 100\% = 96.93\%$$

= 97% to nearest whole number

11 **(a)** The octane number indicates the resistance of a motor fuel to premature ignition (knocking) in the combustion chamber of an engine. It is based on a scale where isooctane (2,2,4-trimethylheptane) is assigned a value of 100 and heptane is assigned a value of 0. The higher the octane number the greater the resistance to premature ignition.

(b) For the compounds shown the octane numbers will increase in the order:

hexane < pentane < benzene < ethanol

Reasoning:

For straight-chain alkanes the octane number decreases as chain length increases: hexane < pentane.

Aromatic compounds have higher octane numbers than alkanes: pentane < benzene.

Alcohols have very high octane numbers: benzene < ethanol.

12 **(a)** The nuclear formula for an alpha particle is ${}^{4}_{2}\mathrm{He}$ so the decay of ${}^{235}_{92}\mathrm{U}$ can be expressed as:

$${}^{235}_{92}\mathrm{U} \rightarrow {}^{x}_{y}\mathrm{Z} + {}^{4}_{2}\mathrm{He}$$

Using this equation we can determine the values of x and y as well as the identity of Z:

$$235 = x + 4 \qquad x = 231$$

$$92 = y + 2 \qquad y = 90$$

y represents the atomic number so if y is 90 the element is thorium (Th) and the decay product is ${}^{231}_{90}\mathrm{Th}$.

(b) *Note: This question needs extra information in order to be answered. It can only be answered if we know the half-life of* ${}^{235}_{92}\mathrm{U}$*, which is 704 million years.*

After one half-life the amount of ${}^{235}_{92}\mathrm{U}$ will have decayed to 50% of its original amount.

After two half-lives the amount of ${}^{235}_{92}\mathrm{U}$ will have decayed to 25% of its original amount, i.e. 75% will have decayed.

$$2 \times 704 \text{ million years} = 1408 \text{ million years}$$

It will take 1408 million years for 75% of the${}^{235}_{92}\mathrm{U}$ to decay.

13 **(a)** The use of fossil fuels is leading to increased atmospheric concentrations of CO_2 and climate change due to global warming. Some fossil fuels, particularly coal, contain sulfur and nitrogen, which when burned release sulfur oxides and nitrogen oxides, causing acid rain. Incomplete combustion of fossil fuels can release carbon monoxide, unburnt hydrocarbons or particulate carbon (soot), all of which have impacts on human health.

(b) Strategies to reduce these effects could include:

- Reduce consumption of fossil fuels by improving the efficiency of vehicle fleets and limiting air flights. In regions where household heating is through fossil fuel burning better insulation of houses will reduce demand. In regions where electricity is generated through fossil fuels more efficient appliances should be used and appliances should be turned off when not in use.
- Alternative energy sources should be developed for energy production, e.g. wind, solar, geothermal, hydro, tidal and wave power. Vehicle fleets should also be converted to alternative power, i.e. electricity (not generated from fossil fuels) or hydrogen fuel cells. A greater use of hybrid vehicles should be an interim step towards this goal.
- If fossil fuels continue to be burned then the carbon dioxide generated should be captured at the site of generation and stored or converted into other compounds.

(c) The cost of gasoline affects a country's average carbon footprint as countries with cheap gasoline tend to use more gasoline, have less public transport infrastructure, use fewer fuel-efficient vehicles and overall tend to produce more carbon dioxide.

14 **(a)** Gasoline contains a mixture of hydrocarbons in the C_5–C_{10} range. Two compounds in gasoline are octane and isooctane (2,2,4-trimethylpentane). *Note: While the answer should include octane as one of the answers, any other compound within the* C_5–C_{10} *range is acceptable for the second answer.*

(b) The crude oil is fractionally distilled so that the components of different sizes can be separated. Heating the mixture will cause the components to vapourize and the gases will rise up the distillation column. While the column is very hot at the bottom, where it is being heated, it becomes gradually cooler as the distance from the bottom increases. The smaller compounds in the crude oil mixture will have the weakest intermolecular forces (London dispersion forces) and the lowest boiling points, so these will not condense until their vapour reaches the highest part of the distillation column. Successively larger compounds condense lower on the distillation column.

(c) Larger hydrocarbons can be broken into smaller ones through a process called cracking. This involves heating the hydrocarbon to a high temperature (500 °C) with a zeolite catalyst. The cracking of long-chain alkanes produces an alkane and an alkene, e.g. for $C_{14}H_{30}$ the cracking equation is:

$$C_{14}H_{30} \rightarrow C_7H_{16} + C_7H_{14}$$

15 **(a)** The specific energies for methane and methanol can be calculated from their molar masses and enthalpies of combustion:

$$M(CH_4) = 12.01 + (4 \times 1.01)\ \text{g mol}^{-1} = 16.05\ \text{g mol}^{-1}$$

$$\Delta H_c\,(C_3H_8) = -891\ \text{kJ mol}^{-1}$$

$$\text{specific energy of methane} = \frac{|\Delta H_c|}{M(CH_4)}$$

$$= \frac{891\ \text{kJ mol}^{-1}}{16.05\ \text{g mol}^{-1}} = 55.5\ \text{kJ g}^{-1}$$

$$M(CH_3OH) = 12.01 + (4 \times 1.01) + 16.00\ \text{g mol}^{-1} = 32.05\ \text{g mol}^{-1}$$

$$\Delta H_c\,(CH_3OH) = -726\ \text{kJ mol}^{-1}$$

$$\text{specific energy of methanol} = \frac{|\Delta H_c|}{M(CH_3OH)}$$

$$= \frac{726\ \text{kJ mol}^{-1}}{32.05\ \text{g mol}^{-1}} = 22.7\ \text{kJ g}^{-1}$$

(b) The oxidation state of carbon in the two compounds can be determined by assuming that hydrogen will be in the +1 oxidation state and oxygen in the –2 oxidation state and that the sum of the oxidation states must equal zero for neutral molecules:

Oxidation state of carbon in methane, CH_4:

oxidation state of C + (4 × oxidation state of H) = 0

oxidation state of C + (4 × (+1)) = 0

oxidation state of C = –4

Oxidation state of carbon in methanol, CH_3OH:

oxidation state of C + (4 × oxidation state of H) + oxidation state of O = 0

oxidation state of C + (4 × (+1)) + (–2) = 0

oxidation state of C = –2

(c) The relationship between the oxidation state of carbon and specific energy, based on methane and methanol, is that specific energy decreases as the carbon becomes more oxidized and has a higher oxidation state.

(d) $M(C_6H_{12}O_6) = (6 \times 12.01) + (12 \times 1.01) + (6 \times 16.00)\ \text{g mol}^{-1} = 180.18\ \text{g mol}^{-1}$

$\Delta H_c(C_6H_{12}O_6) = -2803\ \text{kJ mol}^{-1}$

$$\text{specific energy of methanol} = \frac{|\Delta H_c|}{M(CH_3OH)}$$

$$= \frac{2803\ \text{kJ mol}^{-1}}{180.18\ \text{g mol}^{-1}} = 15.56\ \text{kJ g}^{-1}$$

Oxidation state of carbon in glucose, $C_6H_{12}O_6$:

(6 × oxidation state of C) + (12 × oxidation state of H) + (6 × oxidation state of O) = 0

(6 × oxidation state of C) + (12 × (+1)) + (6 × (–2)) = 0

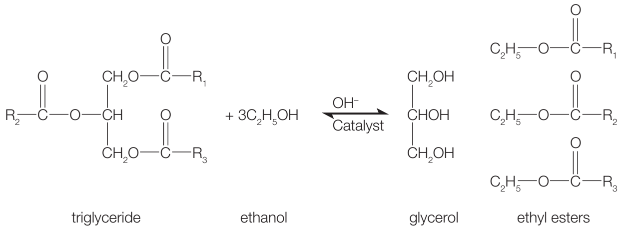
6 × oxidation state of C = 0

oxidation state of C = 0

The result supports the hypothesis as the carbon atoms are more oxidized in glucose, having a higher oxidation number, than in methane or methanol, and glucose has a lower specific energy than methanol and methane.

16 **(a)** Vegetable oils are very viscous because of the strong intermolecular forces between the triglyceride molecules. As a result they do not flow well so are not suitable for internal combustion engines.

(b) The process by which vegetable oils are converted to more useful fuels is called transesterification. The triglycerides in vegetable oil are reacted with strong acid or base catalysts in ethanol or methanol to form the methyl or ethyl esters of the fatty acids present in the triglyceride. These esters can then be used as fuels and are often referred to as biodiesels.



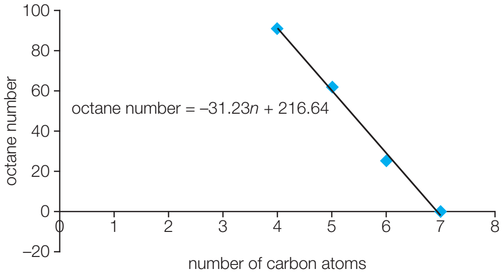
Challenge yourself

1 The remaining energy is given off as heat. This means that 320 kJ is used for the purpose of the TV, which is to provide images (light) and sound, and 680 kJ is lost as heat:

$$\text{energy efficiency} = \frac{\text{energy utilised for purpose}}{\text{total energy}} \times 100\% = \frac{320\text{ kJ}}{1000\text{ kJ}} \times 100\% = 32.0\%$$

2 Coal and crude oil are formed from the decomposition of plants or animals in the absence of air. Biological compounds that contain sulfur are therefore the source of sulfur in coal and crude oil, e.g. any polypeptides that contain the amino acids cysteine and methionine, both of which contain sulfur. Coal and oil with a higher percentage of sulfur are considered ‘dirty’ because of the sulfur dioxide pollution that they produce on combustion: $S + O_2 \rightarrow SO_2$. Sulfur dioxide can react with oxygen in the atmosphere to form SO_3, which dissolves in water vapour to form sulfuric acid and create acid rain: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$.

3 **(a)** From the table on page 519 we can obtain the average octane numbers for the straight-chain alkanes butane, pentane, hexane and heptane. If these average octane numbers are plotted against the number of carbons we get the following graph:



Fitting this data to a line gives the best-fit equation:

$$\text{octane number} = -31.23n + 216.64.$$

For octane, $n = 8$, the octane number (which is expressed as the nearest whole number) can be calculated from the best-fit equation:

$$\text{octane number} = -31.23(8) + 216.64$$
$$= -33$$

(In practice, and with more data points, we find that the graph is actually a curve rather than a straight line and octane has an octane number of −19.)

(b) Assuming the same straight line trend then we can find what straight-chain carbons have an octane number greater than 100 by solving for n when the octane number is 100:

$$\text{octane number} = -31.23n + 216.64$$

$$100 = -31.23n + 216.64$$

$$n = 3.73$$

Alkane chains with three or fewer carbons will have octane numbers greater than 100, i.e. propane, ethane and methane.

4 The compounds octane, 2,4-dimethylhexane and 2,2,4-trimethylpentane are structural isomers therefore they contain the same number of C–C and C–H bonds. If the octane number was dependent on bond enthalpies then these three compounds would have the same octane number. The numbers vary dramatically so this indicates that bond enthalpies are not a key factor in determining octane number.

5 The energies of the different energy levels of the hydrogen atom and helium ion were provided in the table on page 532, which is reproduced below.

As the table below shows there is a factor of four between the energy levels of the hydrogen atom and the helium ion.

Energy level	Energy H atom/ kJ mol^{-1}	Energy He atom/ kJ mol^{-1}	$\frac{\text{Energy H atom}}{\text{Energy He atom}}$
1	–1312.0	–5250	4.00
2	–327.5	–1310.0	4.00
3	–145.4	–581.8	4.00
4	–81.9	–327.5	4.00
5	–52.0	–209.6	4.03
∞	0	0	–

A factor of four is consistent with the general formula for the energy for any level, n, in a one-electron species:

$$E_n = -k\frac{Z^2}{n^2}, \text{ where } Z \text{ is the atomic number}$$

Because the atomic number of the helium ion is 2, $Z = 2$ and the energy levels of this species will be a factor of 2^2 higher, i.e. four times higher, than the energy levels of hydrogen, where $Z = 1$.

The energy levels for any one-electron species are proportional to the square of the atomic number.

6 The molecular formula for α-carotene and β-carotene is $C_{40}H_{56}$. From the structures provided we can see that the only difference between the two isomers is the position of the double bond within the cyclohexene ring on the right-hand side of the molecule.

7 **(a)**

$$2\overset{+\frac{1}{16}}{C}_{16}\overset{+1}{H}_{23}\overset{-2}{O}_{11} + 19\overset{+1}{H}_2\overset{-2}{O} + \overset{0}{O}_2 \rightarrow x\overset{0}{H}_2 + y\overset{+2}{C}\overset{-2}{O} + z\overset{+4}{C}\overset{-2}{O}_2$$

(b) The oxidation number of carbon changes from $+\frac{1}{16}$ to +2 and +4 so it is oxidized.

The oxidation number of hydrogen changes from +1 to 0 so it is reduced.

The oxidation number of oxygen changes from to 0 to –2 so it is reduced.

(c) As there are 84 hydrogen atoms on the left x must be 42.

$$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow xH_2 + yCO + zCO_2$$

$$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow 42H_2 + yCO + zCO_2$$

(d) The total increase in oxidation state for the species being reduced must match the total decrease in oxidation state for the species being reduced.

Total change in oxidation state for hydrogen atoms $= 0 - (84 \times -1) = +84$

Total change in oxidation state for carbon atoms $= 2y + 4z - \left(32 \times \frac{1}{16}\right)$

$= 2y + 4z + 2$

Total change in oxidation state for oxygen atoms $= -2(y + z) - (-2(y + z - 2)) + 0$

$= -2y - 2z + 2y + 2z - 4$

$= -4$

Total change in oxidation must equal total change in reduction:

$2y + 4z + 2 - 4 = 84$

$2y + 4z = 86$ (i)

A second equation in y and z can be obtained from the fact that the sum of the carbon atoms must equal 32:

$y + z = 32$ (ii)

Applying simultaneous equations:

(i) – 2(ii) $2z = 22$

$z = 11$

$y = 32 - z = 32 - 11 = 21$

Balanced equation is

$$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow 42H_2 + 21CO + 11CO_2$$

(e) Methanol can be formed from the reaction between H_2 and CO. Consider the reaction that would occur between the amounts of H_2 and CO formed in the combustion of two molecules of wood, as determined in the answer to (d).

$$42H_2 + 21CO \rightarrow 21CH_3OH$$

Twenty-one molecules of methanol can be formed from the products that result from the combustion of *two* molecules of wood, therefore one wood molecule could produce 10.5 molecules of methanol.

8 The solubility of carbon dioxide increases at lower temperatures and higher pressures, therefore at lower depths, where temperature is low and pressure is high, there will be a higher concentration of dissolved CO_2 that can react with calcium carbonate to form calcium bicarbonate, which is more soluble, and prevent shell formation.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

Worked solutions

Chapter 15

Exercises

1 In a question like this, you can either give the technical term, e.g. intravenous, or give a description, e.g. into the blood. If you are not sure of the correct term it is best to play safe and describe it.

- intramuscular (into muscle)
- intravenous (into the blood), this is the fastest route as no time is spent in travelling from the point of injection to the bloodstream
- subcutaneous (under the skin)

2 Tolerance occurs when repeated doses of a drug result in smaller physiological effects. As a result, higher doses are needed to produce the same effect, and this increases the chances of toxic side-effects.

3 **(a)** The therapeutic index (TI) is the ratio of the dose that produces toxicity to the dose that produces a clinically effective response in a population. The upper dose is defined differently in animals (the dose that is *lethal* to 50% of the population) and humans (the dose that is *toxic* to 50% of the population). Lethal doses can be determined for animals but not humans.

(b) Bioavailability, side-effects, possibility of tolerance and addiction of the drug; age, sex, diet, and weight of patient.

(c) Low therapeutic index means a low margin of safety, so small changes in dosage may produce adverse side-effects.

4 Method of administration of drug, solubility (in water and lipid), and functional group activity.

5 **(a)** 1 mole of salicylic acid produces 1 mole of aspirin.

Formula for salicylic acid is $C_7H_6O_3$, M_r = 138.13

Formula of aspirin is $C_9H_8O_4$, M_r = 180.17

50.05 g of salicylic acid is $\frac{50.05}{138.13}$ moles = 0.3623 moles

With 100% yield 0.3623 moles of aspirin would be obtained. This is 0.3623 × 180.17 g mol^{-1} of aspirin = 65.28 g

Overall yield therefore = $\frac{\text{actual yield}}{\text{predicted yield}} \times 100\% = \frac{55.45}{65.28} \times 100\% = 84.94\%$

(b) Melting point determination. The melting point of aspirin is between 138 and 140 °C. The narrower the melting range observed the purer the product.

6 The bioavailability of aspirin can be increased by increasing its solubility in water by converting it to its sodium salt.

7 **(a)** Mild analgesic blocks transmission of impulses at site of injury, not in the brain; anticoagulant acts to prevent coagulation / thickening of the blood and so reduces risk of coronary disease.

(b) Alcohol has synergistic effect with other drugs; can cause stomach bleeding with aspirin.

8 **(a)** $R{-}C_9H_{11}N_2O_4S$

(b) At the R group. Modification prevents the binding of the penicillinase enzyme and so maintains the action of the drug / prevents resistant bacteria rendering it inactive.

(c) Beta-lactam ring undergoes cleavage and binds irreversibly to the transpeptidase enzyme in bacteria. This inactivates the enzyme, which interrupts the synthesis of bacterial cell walls.

9 Overuse of antibiotics in animal stocks / food chain; over-prescription; failure of patients to complete treatment regimen.

It is a good idea to bullet-point your answer here to ensure that you give several different types of activities. Note that the question is 'Discuss' so you can include comments on the relative extent to which the activities have caused an increase in resistant strains.

10 **(a)** It is expected that you will refer to their structures as given in Section 37 of the IB data booklet – you are not expected to know these molecules. The functional groups in common are ether linkage (–C–O–C–), tertiary amine linkage (R–N(R′)–R″), alkenyl (–C=C–) and arene (see page 583).

(b) Main effect is as a strong analgesic. Side-effects include constipation, suppression of cough reflex, constriction of the eye pupil, narcotic effects.

11 Diamorphine (heroin) has two ester groups in place of two —OH groups in morphine. The less polar diamorphine is more soluble in lipids and so crosses the blood–brain barrier more easily and enters the brain where it blocks the perception of pain.

12 In favour: strongest pain killer known; the only effective analgesic against extreme pain. Against: addictive drug; leads to dependence and serious side-effects, large market in some countries as an illegal drug.

13 H_2-receptor antagonists: block the binding of histamine, which prevents the reactions leading to stomach acid secretion.

Proton-pump inhibitors: directly prevent the release of acid into the stomach lumen.

14 **(a)** $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$

(b) $Al(OH)_3$ reacts with H^+ in a mole ratio of 1:3

$Mg(OH)_2$ reacts with H^+ in a mole ratio of 1:2

So 0.1 mol $Al(OH)_3$ will neutralize the greater amount.

(c) KOH is a strong alkali so would be dangerous for body cells; it is corrosive and would upset the stomach pH.

15 **(a)** pH of buffer solution:

$$pH = pK_a + \log_{10}\frac{[salt]}{[acid]}$$

$$pH = 4.82 + \log_{10}\frac{0.020}{0.010}$$

$$pH = 4.82 + 0.30 = 5.12$$

(b) The pH of a buffer solution depends on the pK_a of the acid and the *ratio* of its acid and salt concentrations. Neither the pK_a nor the acid/salt ratio changes with dilution, so the pH of the buffer remains constant. (The buffering capacity, however, which is the amount of acid and base that can be added before the pH changes, is reduced when a buffer is diluted.)

16 Viruses lack a cellular structure and so are difficult to target. Antibiotics specifically interfere with bacterial cell walls or internal structures. Viruses replicate inside host cells and so treatment may involve killing host cells.

17 Subunits in hemagglutinin (H) and neuraminidase (N) can mutate and mix and match so forming different strains. These change the specific nature of the glycoprotein–host interactions, and alter the body's immune response. This is why it is possible to suffer from flu several times during a lifetime.

18 Tamiflu and Relenza do not prevent the flu virus from entering cells, but act to stop it from being released from the host cells. So if the infection is not stopped early, too many new viral particles may have already been released.

19 Challenges: antiretroviral costs, distribution and availability; patient compliance with regimen and multiple drug treatments; sociocultural issues.

Successes: new and more effective antivirals that can be used in combination; better screening of HIV-positive; controlling infection through drugs.

20 Solvents cause problems of disposal. Organic solvents can be incinerated, causing release of pollutants, greenhouse gases, and toxins (although power can be generated). Solvents can contaminate ground water and soil. Some solvents can be hazardous to the health of workers.

21 Protective shoe-covers, clothing, gloves, paper towels, and contaminated implements. Interim storage in sealed containers for radioactivity to decay before conventional disposal.

22 The success of antibiotics in treating disease has led to their widespread use, and in some cases over-use. Exposure of bacteria to antibiotics increases the spread of resistant strains. Antibiotic resistance renders some antibiotics ineffective, especially with multiply resistant strains, e.g. MRSA.

23 Patient compliance refers to the importance of patients following medical instructions, in particular to completing the course of an antibiotic treatment. This helps prevent the spread of antibiotic-resistant bacteria.

24 Green Chemistry principles seek to reduce toxic emissions and waste substances in the manufacture of drugs. This includes reduction in the amount of solvent used, the adoption of synthesis pathways with shorter routes, the replacement of inorganic catalysts with enzymes, and the recycling of waste.

Practice questions

1 The solubility in non-polar solvents is not significant when a drug is destined to enter the bloodstream.

Correct answer is C.

2 Aluminium hydroxide is $Al(OH)_3$ and therefore has a 1 : 3 molar ratio reaction with HCl.

Correct answer is B.

3 Strong analgesics bind to opioid receptors and so alter the perception of pain.

Correct answer is D.

4 Ethanol consumption should be limited as the synergistic effects can lead to very serious or fatal results.

Correct answer is B.

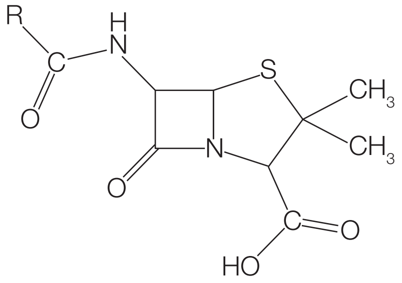
5 Resistant bacteria produce the enzyme beta-lactamase, which destroys the beta-lactam ring in the penicillin before it can deactivate the transpeptidase enzyme.

Correct answer is C.

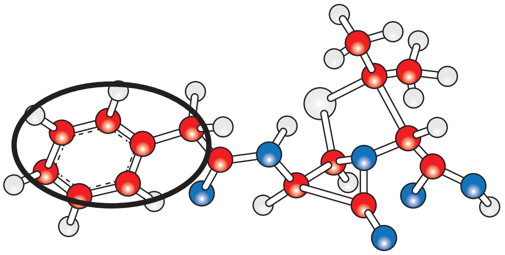
6 Heroin has two ester groups relative to two hydroxyl groups in morphine, so is more non-polar. This is important in its ability to cross the blood–brain barrier and enter the brain.

Correct answer is C.

7 **(a)** The side chain can be identified in benzylpenicillin compared to general penicillin as it is attached to the amide functional group.



penicillin (from data booklet)



benzylpenicillin

(b) Over-prescription of penicillin can result in beneficial bacteria also being destroyed along with the harmful bacteria being targeted.

Over-prescription of penicillin can also result in penicillin-resistant strains of bacteria developing as the bacteria that survive over-exposure to penicillin can multiply and pass on this resistance.

Over-prescription of penicillin can result in allergic reactions in patients taking it.

All these problems can possibly be addressed by changing the side chain to produce new forms of penicillin. Depending on the side chains introduced these new penicillins may be:

- more specific in which bacteria they target
- more effective against bacteria that have become resistant to other penicillins
- less likely to generate allergic reactions in patients.

8 **(a)** The neutralization reactions for the two antacids are:

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

(b) 0.1 mol of magnesium hydroxide contains 0.2 mol of hydroxide ions whereas 0.1 mol of aluminium hydroxide contains 0.3 mol of hydroxide ions so magnesium hydroxide will be less effective than aluminium hydroxide in neutralizing the hydrochloric acid.

9 **(a)** Viruses are different from bacteria in that they:

- do not have a cellular structure
- do not have a nucleus
- do not have a cell wall
- do not have cytoplasm.

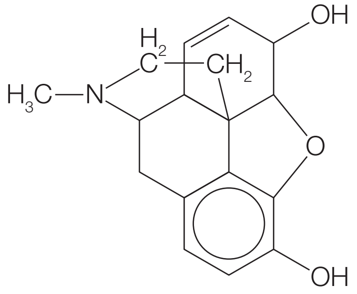
These are all found in bacteria.

(b) Antiviral drugs work by stopping virus replication. One way they act is to become part of the virus DNA and block the polymerase that builds the DNA. They can also change cell membranes and prevent viruses entering the cell and/or prevent them from leaving the cell after reproducing.

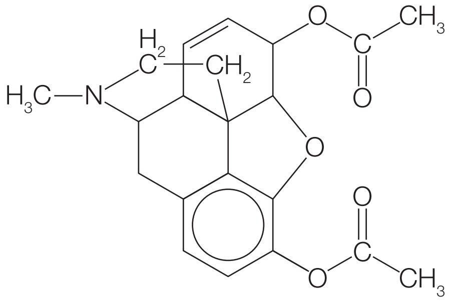
(c) The human immunodeficiency virus (HIV) that causes AIDs mutates very quickly, which makes it difficult to develop an effective long-lasting treatment. As HIV uses the host cells, drugs that target HIV may also harm the host cells so it is difficult to target HIV without causing harm to the host.

10 **(a)** Morphine is injected intravenously to ensure fast delivery.

(b) Diamorphine has two ester groups where morphine has two alcohol groups. This makes diamorphine less polar than morphine and it is therefore more easily absorbed into non-polar fatty tissue.



morphine

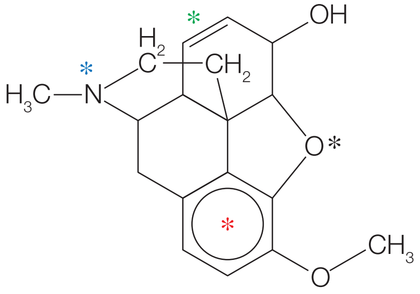


diamorphine (heroin)

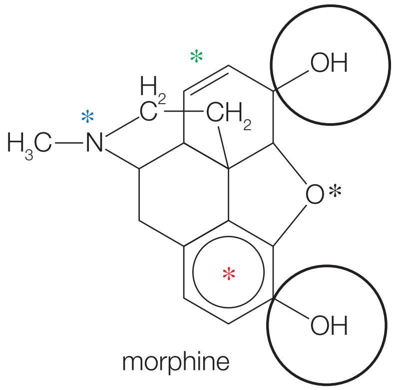
11 The therapeutic window is the range of dosages between the minimal amount necessary to produce a therapeutic effect and the amount that produces medically unacceptable adverse effects. It is determined from the ratio between ED_{50} and LD_{50}, the dosage where 50% of the population experiences noticeable therapeutic effect (ED_{50}) and the dosage that is lethal to 50% of the population (LD_{50}, estimated for humans based on rats.)

The size of the therapeutic window will vary according to the drug and the age, sex and weight of the patient. A large therapeutic window allows for dosages to be increased until the desired therapeutic effect is obtained without significant risk of serious health complications. A small therapeutic window means that dosages have to be carefully monitored and administered because of the serious risk of overdose and the development of serious health complications associated with the use of the drug. A drug with a small therapeutic window is only likely to be administered for serious conditions where the risk of death or serious complications due to the ailment outweighs the risks associated with administering the drug.

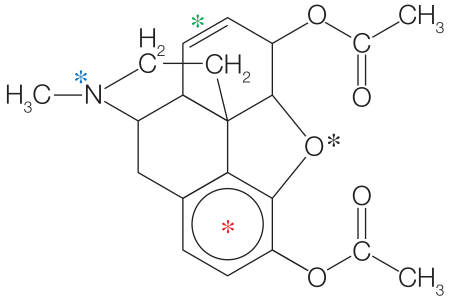
12 **(a)** The structures of codeine, morphine and diamorphine are shown below, with groups present in all three compounds (tertiary amine, alkenyl, arene and ether) highlighted with asterisks.



codeine



morphine



diamorphine (heroin)

The functional groups present in these compounds are:

* = alkenyl

* = arene

* = amine

* = ether

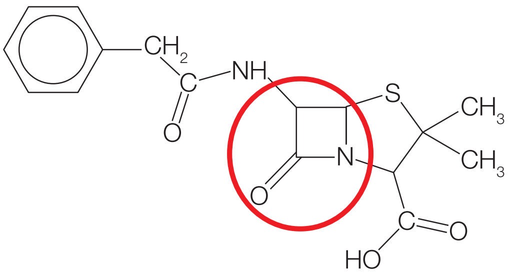
(b) The functional group present in morphine but not diamorphine is the alcohol group. The alcohol groups in morphine are circled in the diagram in part (a) above.

(c) Diamorphine differs from morphine in that it contains two ester groups rather than two alcohol groups. It can be synthesized from morphine through an esterification reaction. (Esterification is a specific type of condensation reaction. This esterification reaction is known as a diacetylation reaction as two acetyl groups are used to make the ester.)

13 **(a)** The beta-lactam groups of penicillins allow them to interfere with the enzymes responsible for creating bacterial cell walls. This interference by the penicillin causes osmotic pressure to build up within the bacteria cell, which eventually ruptures, killing the bacteria.

(b) Modifying the side-chain allows for the creation of new penicillins that are effective against bacteria that have become resistant to penicillin G. Modifications can also create penicillins that are resistant to being broken down by bacterial enzymes that degrade penicillin. Another benefit to modifying the side-chain is creating penicillins that are acid-resistant and can be taken orally rather than by injection.

(c) The beta-lactam ring in penicillin is circled in the diagram below.



The functional group contained within the beta-lactam group is an amide group (–N–CO–).

The bond angles within the beta-lactam ring are 90° and this makes it very strained so the ring is easily broken. When it breaks open it can irreversibly bind to the bacterial enzyme and prevent it from fulfilling its function.

14 **(a)** Because drug C has low physiological effects with minimal side-effects and a large therapeutic window this makes it suitable for patients to take without supervision.

(b) Because drug A has high physiological effects with severe side-effects it should only be administered by qualified staff even though it has a medium therapeutic window.

Drug B has moderate physiological effects with moderate side-effects but it has a narrow therapeutic window, which means it should only be administered by qualified staff.

Drugs A and B should both be administered by qualified staff.

(c) Because of its severe side-effects drug A should only be used in a medical emergency.

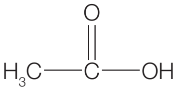
15 **(a)** Intravenous injection results in the drug having a very rapid effect as it is quickly transported in the blood throughout the body.

(b) Drugs can also be injected intramuscularly and into subcutaneous fat layers.

(c) The method of administration used to treat respiratory diseases is inhalation.

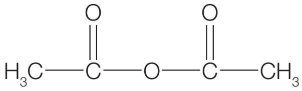
Challenge yourself

1 Because it contains two electron-withdrawing carbonyl groups ethanoic anhydride is more susceptible to nucleophilic attack. This enables it to react more vigorously than CH_3COOH with the –OH groups in morphine and form the ester.



$H_3C{-}C({=}O){-}OH$

ethanoic acid



$H_3C{-}C({=}O){-}O{-}C({=}O){-}CH_3$

ethanoic anhydride

2 Na_2CO_3 and $NaHCO_3$ solutions contain CO_3^{2-} and HCO_3^-, the conjugate bases of the weak acids HCO_3^- and H_2CO_3 respectively. As they are bases they are able to hydrolyse water and release OH^- ions:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-(aq)$$

3 Neuraminidase inhibitors are competitive inhibitors as they compete with the substrate sialic acid for binding to the enzyme neuraminidase. This competition occurs because they have a chemical structure similar to the substrate and so bind in the same way at the active site of the enzyme.