HIGHER LEVEL

WORKED SOLUTIONS

PEARSON BACCALAUREATE

HIGHER 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 177).

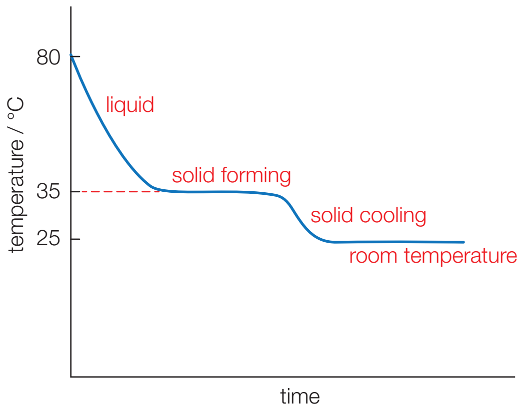
8 Bubbles will be present through the volume of the liquid. A brown gas is visible above the brown liquid. As the two states are at the same temperature, the particles have the same average kinetic energy and are moving at the same speed. The inter-particle distances in the gas are significantly larger 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 $L = 6.02 \times 10^{23}\ \text{mol}^{-1}$.

(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}

Mass = nM = 0.475 mol × 398.08 g mol^{-1} = 189.1 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 $$\text{percentage by mass} = \frac{\text{relative atomic mass of cadmium}}{M_r} \times 100$$

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

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	Phosphorus	Oxygen
mass / g	0.1927	0.02590	0.1124	0.1491	0.3337
moles	$\frac{0.1927}{12.01} =$ 0.01604	$\frac{0.02590}{1.01} =$ 0.0256	$\frac{0.1124}{14.01} =$ 0.008022	$\frac{0.1491}{30.97} =$ 0.004814	$\frac{0.3337}{16.00} =$ 0.02086
divide by smallest	3.332	5.32	1.666	1.000	4.333
nearest whole number ratio	10	16	5	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 $= 0.015\ \text{mol} \times 12.01\text{g mol}^{-1}$

$= 0.18$ g

mass of hydrogen $= 0.040\ \text{mol} \times 1.01\ \text{g mol}^{-1}$

$= 0.040$ 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	$\dfrac{0.18}{12.01} =$ 0.015	$\dfrac{0.040}{1.01} =$ 0.040	$\dfrac{0.08}{16.00} =$ 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 × $(6.02 \times 10^{23}\ \text{mol}^{-1})$ $\dfrac{6.20 \text{ x } 10^{23}\, y}{100.09}$

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 $\dfrac{3}{2} \times 3.75$ 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 $\dfrac{1}{3} \times 12.50$ mol = 4.167 moles of iron oxide.

4.167 moles of iron oxide have a mass of $4.167 \times M_r(Fe_2O_3) = 4.167\ \text{mol} \times 159.70\ \text{g mol}^{-1} = 665.5$ 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 $\frac{2}{10} \times 0.137 = 0.0274$ moles of butane.

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

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

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

Therefore 1000 g of Al react with $\frac{117.50}{26.98} \times 1000$ = 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 $0.0149 \times M_r(CaCO_3) = 0.0149\text{ mol} \times 100.09\text{ g mol}^{-1} = 1.49\text{ g}$

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

(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 $2.66 \times M_r(CH_3OH) = 2.66\text{ mol} \times 32.05\text{ g mol}^{-1} = 85.2\text{ g}$

(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 = $0.0528 \times M_r(C_2H_4Cl_2) = 0.0528\text{ mol} \times 98.96\text{ g mol}^{-1} = 5.23\text{ g}$

42 moles of $CaCO_3 = \frac{255\text{ g}}{(40.08 + 12.01 + (4 \times 16.00))\text{ g mol}^{-1}}$ = 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 = $\frac{198\text{ g}}{254\text{ g mol}^{-1}} \times 100$ = 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.

(We have to assume that the examiner means at STP because they have not said otherwise.)

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.

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

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

$$= 1.09\ \text{mol}$$

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

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

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

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. $\frac{PV}{nRT} < 1$

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 = $\frac{1000 \text{ cm}^3}{250 \text{ cm}^3}$ = 23.40 g of sodium chloride

23.40 g of NaCl is equivalent to

$$\frac{23.40 \text{ g}}{(22.99 + 35.45) \text{ g mol}^{-1}} = 0.400 \text{ mol}$$

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 $= cV = 0.147 \text{ mol dm}^{-3} \times \frac{36.42}{1000} \text{ dm}^3 = 5.35 \times 10^{-3}$ 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 $= cV = 0.0100 \text{ mol dm}^{-3} \times \frac{11.00}{1000} \text{ dm}^3 = 1.10 \times 10^{-4}$ mol

Since KOH reacts with HCl in a 1:1 ratio, moles of HCl $= 1.10 \times 10^{-4}$ 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 $36.46 \times 0.0220 = 0.802$ g dissolved in 1 dm^3

Concentration of HCl in g dm^{-3} = $0.0220 \text{ mol dm}^{-3} \times 36.46 \text{ g mol}^{-1} = 0.802 \text{ g dm}^{-3}$

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 $= 3.73 \times 10^{-3}$ 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.

Challenge problems

72 First write the balanced equations for the two steps of the process, recognizing that in the first step it is the $Ca_3(PO_4)_2$ in the phosphate rock that reacts with H_2SO_4.

1 $Ca_3(PO_4)_2(s) + 3H_2SO_4(aq) \rightarrow 3CaSO_4(s) + 2H_3PO_4(aq)$

2 $H_3PO_4(aq) + 3NH_3(l) \rightarrow (NH_4)_3PO_4(s)$

Determine theoretical mass of $(NH_4)_3PO_4$ (s) given that 1000 tonnes represents a 95% yield:

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

$$\text{theoretical yield} = \frac{\text{experimental yield}}{\text{percentage yield}} \times 100\%$$

$$= \frac{1000 \text{ tonnes}}{95\%} \times 100\% = 1053 \text{ tonnes}$$

Determine the number of moles in 1053 tonnes of $(NH_4)_3PO_4(s)$ recognizing that the mass that is given in tonnes must first be converted to grams:

$$n((NH_4)_3PO_4) = \frac{m}{M((NH_4)_3PO_4)}$$
$$= \frac{1053 \times 10^6 \text{ g}}{149.12 \text{ g mol}^{-1}}$$
$$= 7.061 \times 10^6 \text{ mol}$$

From equation 2, $n((NH_4)_3PO_4) = n(H_3PO_4) = 7.061 \times 10^6 \text{ mol}$

From equation 1, $n(Ca_3(PO_4)_2) = \frac{n(H_3PO_4)}{2} = \frac{7.061 \times 10^6 \text{ mol}}{2} = 3.531 \times 10^6 \text{ mol}$

Calculate the mass of $Ca_3(PO_4)_2(s)$:

$m(Ca_3(PO_4)_2) = nM(Ca_3(PO_4)_2) = (3.531 \times 10^6 \text{ mol}) \times 310.18 \text{ g mol}^{-1} = 1.095 \times 10^9 \text{ g} = 1095 \text{ tonnes}$

Determine the total mass of phosphate rock based on 90% of phosphate rock being $Ca_3(PO_4)_2$:

$$\%Ca_3(PO_4)_2 = \frac{\text{mass } Ca_3(PO_4)_2}{\text{mass phosphate rock}} \times 100\% = 90\%$$

$$\text{Mass of phosphate rock} = \frac{\text{mass } Ca_3(PO_4)_2}{\%\ Ca_3(PO_4)_2} \times 100\% = \frac{1095 \text{ tonnes}}{90\%} \times 100\% = 1217 \text{ tonnes}$$

73 Write balanced equations for the combustion reactions of ammonia and hydrazine:

$$2NH_3(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + 3H_2O(g)$$

$$N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

As we do not know the relative moles of ammonia and hydrazine:

let x = moles of ammonia, NH_3, in the reaction mixture

let y = moles of hydrazine, N_2H_4, in the reaction mixture

Determine equations for the total moles of $N_2(g)$ and $H_2O(g)$ formed in the two reactions using x and y:

$n(N_2) = 0.5x + y$

$n(H_2O) = 1.5x + 2y$

The question tells us that $n(N_2) = 0.40 \text{ x } n(H_2O)$:

$0.5x + y = 0.40(1.5x + 2y)$

$0.5x + y = 0.60x + 0.80y$

$0.2y = 0.1x$

$y = 0.5x$

If $y = 0.5x$ this means that the mixture contains half as much hydrazine, N_2H_4, as it does ammonia, NH_3.

Consider a mixture with exactly 1 mol of NH_3 and 0.5 mol of N_2H_4:

$$m(NH_3) = nM(NH_3) = 1 \text{ mol} \times 17.04 \text{ g mol}^{-1} = 17.04 \text{ g}$$

$$m(N_2H_4) = nM(N_2H_4) = 0.5 \text{ mol} \times 32.06 \text{ g mol}^{-1} = 16.03 \text{ g}$$

$$\%NH_3 = \frac{\text{mass } NH_3}{\text{total mass of mixture}} \times 100\% = \frac{17.04 \text{ g}}{17.04 \text{ g} + 16.03 \text{ g}} \times 100\% = 52\% \text{ to 2 d.p.}$$

Two assumptions are:

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

(ii) The gases behave as ideal gases therefore volumetric ratios are identical to molar ratios.

74 First we need to determine the moles of H_2SO_4 present in 980 tonnes of $H_2SO_4(l)$:

$$n(H_2SO_4) = \frac{m}{M(H_2SO_4)} = \frac{980 \times 10^6 \text{ g}}{98.08 \text{ g mol}^{-1}} = 9.99 \times 10^6 \text{ mol}$$

From equation 3, $n(SO_3) = n(H_2SO_4) = 9.99 \times 10^6 \text{ mol}$

From equation 2, $n(SO_2) = n(SO_3) = 9.99 \times 10^6 \text{ mol}$

From equation 1, $n(S) = n(SO_2) = 9.99 \times 10^6 \text{ mol}$

We can now calculate the mass of sulfur required:

$$m(S) = nM = 9.99 \times 10^6 \text{ mol} \times 32.06 \text{ g mol}^{-1} = 3.20 \times 10^8 \text{ g} = 3.20 \times 10^5 \text{ kg}$$

75 *This solution uses [KMnO$_4$] = 0.0500 mol dm^{-3} not 0.05 mol dm^{-3} as stated in the question so the answer can be expressed to more than one significant figure.*

$n(KMnO_4) = cV = 0.0500 \text{ mol dm}^{-3} \times \frac{18.00}{1000} \text{ dm}^3 = 9.00 \times 10^{-4} \text{ mol}$

From the balanced equation, $n(H_2O_2) = \frac{5}{2} n(KMnO_4) = \frac{5}{2} \times 9.00 \times 10^{-4} \text{ mol} = 2.25 \times 10^{-3} \text{ mol}$

Determine the concentration of the H_2O_2 solution:

$$[H_2O_2] = \frac{n}{V} = \frac{2.25 \times 10^{-3} \text{ mol}}{\frac{10.00}{1000} \text{dm}^3} = 0.225 \text{ mol dm}^{-3}$$

76 For the reaction with Na_2CO_3:

From Step 1 we can determine an equation for the moles of HCl(aq) reacting with the Na_2CO_3 initially present in the solution:

$$n(\text{HCl}) = c(\text{HCl}) \times V(\text{HCl}) = \text{Y mol dm}^{-3} \times \frac{\text{P}}{1000}\ \text{dm}^3 = \frac{\text{YP}}{1000}\ \text{mol}$$

Balanced equation 1 tells us that $n(Na_2CO_3) = n(\text{HCl}) = \frac{\text{YP}}{1000}$ mol.

We can then determine an equation for the concentration of the Na_2CO_3 initially present:

$$[Na_2CO_3] = \frac{n}{V} = \frac{\frac{\text{YP}}{1000}\ \text{mol}}{\frac{\text{X}}{1000}\ \text{dm}^3} = \frac{\text{YP}}{\text{X}}\ \text{mol dm}^{-3}$$

$$\left(= \frac{\text{PY}}{\text{X}}\ \text{mol dm}^{-3}\right)$$

For the reaction with $NaHCO_3$:

In Step 2 the HCl being added reacts with the $NaHCO_3$ initially present ***and*** the $NaHCO_3$ formed in Step 1.

The amount of $NaHCO_3$ formed in Step 1 will be equal to the amount of Na_2CO_3 initially present and it will also react with P cm^3 of HCl.

Therefore the $NaHCO_3$ that was initially present reacts with (Q – P) cm^3 of HCl.

$$n(\text{HCl}) = c(\text{HCl}) \times V(\text{HCl}) = \text{Y mol dm}^{-3} \times \frac{(\text{Q} - \text{P})}{1000}\ \text{dm}^3 = \frac{\text{Y(Q} - \text{P)}}{1000}\ \text{mol}$$

Balanced equation 2 tells us that $n(NaHCO_3) = n(\text{HCl}) = \frac{\text{Y(Q} - \text{P)}}{1000}$ mol.

We can then determine an equation for the concentration of the $NaHCO_3$ initially present:

$$[NaHCO_3] = \frac{n}{V} = \frac{\frac{\text{Y(Q} - \text{P)}}{1000}\ \text{mol}}{\frac{\text{X}}{1000}\ \text{dm}^3} = \frac{\text{Y(Q} - \text{P)}}{\text{X}}\ \text{mol dm}^{-3}$$

In the initial solution $[Na_2CO_3] = \frac{\text{YP}}{\text{X}}\ \text{mol dm}^{-3}$ and $[NaHCO_3] = \frac{\text{Y(Q} - \text{P)}}{\text{X}}\ \text{mol dm}^{-3}$ $\left(= \frac{(\text{Q} - \text{P})\text{Y}}{\text{X}}\ \text{mol dm}^{-3}\right)$

77 The balanced equation for the combustion of pentane under the reaction conditions stated is:

$$C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$$

Moles of pentane combusted:

$$n = \frac{m}{M(C_5H_{12})} = \frac{720\ \text{g}}{72.17\ \text{g mol}^{-1}} = 9.98\ \text{mol}$$

From the balanced equation:

$$n(CO_2) = 5 \times n(C_5H_{12}) = 5 \times 9.98\ \text{mol} = 49.9\ \text{mol}$$

$$n(H_2O) = 6 \times n(C_5H_{12}) = 6 \times 9.98\ \text{mol} = 59.9\ \text{mol}$$

Moles of gas formed in the reaction = (49.9 + 59.9) mol = 109.8 mol

Calculate the total moles of gas present after reaction using the ideal gas equation $PV = nRT$.

$$n(\text{gas}) = \frac{PV}{RT} = \frac{400 \times 10^3\ \text{Pa} \times 2.00\ \text{m}^3}{8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 740\ \text{K}} = 130\ \text{mol}$$

Determine the amount of unreacted O_2 present after combustion:

$n(\text{unreacted } O_2)$ = total moles of gas – moles of unreacted O_2 = 130 mol – 109.8 mol = 20 mol

Determine the amount of O_2 that reacted with the pentane using the balanced equation:

$$n(\text{reacted } O_2) = 8 \times n(C_5H_{12}) = 8 \times 9.98\ \text{mol} = 79.8\ \text{mol}$$

The amount of O_2 initially present is the sum of the amount that reacted and the unreacted excess:

$$n(\text{initial } O_2) = 20\ \text{mol} + 79.8\ \text{mol} = 100\ \text{mol}$$

Calculate the mass of O_2 that was initially present:

$$m(\text{initial } O_2) = nM(O_2) = 100\ \text{mol} \times 32.00\ \text{g mol}^{-1} = 3200\ \text{g} = 3.20\ \text{kg}$$

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 $Fe_2O_3(s) + \mathbf{3}CO(g) \rightarrow \mathbf{2}Fe(s) + \mathbf{3}CO_2(g)$.

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 × 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 × CH_2' = C_4H_8

Correct answer is D.

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

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 × (6.02 × 10^{23}) atoms
= 4.2 × 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:

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

$$= c_1V_1 + c_2V_2$$

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

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

$$= 0.0200\ \text{mol}$$

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

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

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:

$$25.00\ °\text{C} = (25.00 + 273.15)\ \text{K} = 298.15\ \text{K}$$

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

$$V = \frac{nRT}{P} = \frac{1.50\ \text{mol} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298.15\ \text{K}}{1.09 \times 10^5\ \text{Pa}} = 0.0341\ \text{m}^3 = (0.0341 \times 1000)\ \text{dm}^3 = 34.1\ \text{dm}^3$$

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:

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

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

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

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

(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 $C_2HCl_3 = (2 \times 12.01) + 1.01 + (3 \times 35.45) \text{ g mol}^{-1} = 131.38 \text{ g mol}^{-1}$.

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, $n(NO) = 1.5n(NH_3)$

Therefore assuming ideal gases, $V(NO) = 1.5V(NH_3)$

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:

$$V(NH_3) = \frac{V(NO)}{1.5} = \frac{30.0 \text{ dm}^3}{1.5} = 20.0 \text{ dm}^3$$

$$\text{The volume of excess } NH_3 = 30.0 \text{ dm}^3 - 20.0 \text{ dm}^3 = 10.0 \text{ dm}^3$$

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

$$V(N_2) = \frac{5}{6} V(NO) = \frac{5}{6} \times 30.0 \text{ dm}^3 = 25.0 \text{ dm}^3$$

20 **(a)** $n(HCl) = c \times V = 0.200 \text{ mol dm}^{-3} \times \frac{27.20}{1000} \text{ dm}^3 = 0.00544 \text{ mol}$

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

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

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:

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

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

$$n(\text{CaCO}_3) = \frac{1}{2} n(\text{HCl reacted})$$
$$= \frac{1}{2} \times 0.00306 \text{ mol} = 0.00153 \text{ mol}$$

(f) $m(\text{CaCO}_3) = nM(\text{CaCO}_3) = 0.00153 \text{ mol} \times 100.09 \text{ g mol}^{-1} = 0.153 \text{ g}$

$$\% \text{ CaCO}_3 \text{ in eggshell} = \frac{\text{mass of CaCO}_2}{\text{mass of eggshell}} \times 100\% = \frac{0.153 \text{ g}}{0.188 \text{ g}} \times 100\% = 81.4\%$$

(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:

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

$n(\text{Cl}^-) = n(\text{AgCl}) = 0.04275$ 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

$$x + y = 2.450 \qquad (1)$$

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:

$$n(\text{Cl}^- \text{ from NaCl}) + n(\text{Cl}^- \text{ from CaCl}_2) = 0.04275$$

$$\frac{x}{M(\text{NaCl})} + 2\left(\frac{y}{M(\text{CaCl}_2)}\right) = 0.04275$$

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

Applying simultaneous equations:

$$x + y = 2.450 \qquad (1)$$

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

$(2) \times 58.44 \qquad x + 1.053y = 2.498 \qquad (2')$

$(2') - (1) \qquad 0.053y = 0.048$

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

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

$$x = 1.54$$

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

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

$$\% \text{ CaCl}_2 = \frac{\text{mass CaCl}_2}{\text{total mass}} \times 100\% = \frac{0.91 \text{ g}}{2.450 \text{ g}} \times 100\%$$
$$= 37.1\%$$

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

$$m(\text{H}_2\text{O}) = m(\text{hydrated K}_2\text{CO}_3) - m(\text{dry K}_2\text{CO}_3)$$
$$= 10.00 \text{ g} - 7.93 \text{ g}$$
$$= 2.07 \text{ g}$$

$$n(\text{H}_2\text{O}) = \frac{m}{M(\text{H}_2\text{O})} = \frac{2.07 \text{ g}}{18.02 \text{ g mol}^{-1}}$$
$$= 0.115 \text{ mol}$$

(b) $$n(\text{K}_2\text{CO}_3) = \frac{m}{M(\text{K}_2\text{CO}_2)} = \frac{7.93 \text{ g}}{138.21 \text{ g mol}^{-1}}$$
$$= 0.0574 \text{ mol}$$

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

$$x = \frac{n(\text{H}_2\text{O removed})}{n(\text{dry K}_2\text{CO}_2)} = \frac{0.115\ \text{mol}}{0.0574\ \text{mol}} = 2.00$$

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:

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

$$n(\text{HCl}) = \frac{PV}{RT} = \frac{113\ 300\ \text{Pa} \times 7.40 \times 10^4\ \text{m}^3}{8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 330\ \text{K}}$$
$$= 0.0306\ \text{mol}$$

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.

$m(NH_4Cl) = nM(NH_4Cl) = 0.0306\ \text{mol} \times 53.50\ \text{g mol}^{-1} = 1.64\ \text{g}$

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
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

$$n(\text{H}_2\text{O}) = \frac{m}{M(\text{H}_2\text{O})} = \frac{108.1\ \text{g}}{18.02\ \text{g mol}^{-1}} \approx 6$$

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%).

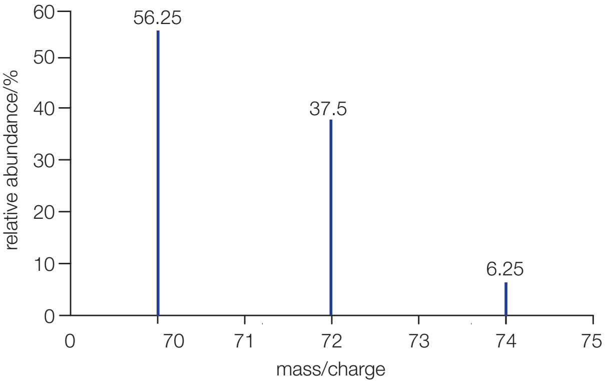
There are therefore four combinations of these isotopes that can occur in a Cl_2 molecule: ^{35}Cl/^{35}Cl (relative mass = 70), ^{35}Cl/^{37}Cl (relative mass = 72), ^{37}Cl/^{35}Cl (relative mass = 72) and ^{37}Cl/^{37}Cl (relative mass = 74).

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 = $0.75 \times 0.75 = 0.5625$ (56.25%)

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

Relative abundance of ^{37}Cl/^{37}Cl and ^{37}Cl/^{35}Cl = $0.25 \times 0.25 = 0.0625$ (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:

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

$$\begin{aligned} 2431 &= 1893.6 + 25x + 2600 - 2051.4 - 26x \\ &= 2442.2 - x \end{aligned}$$

$x = 11.20$

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

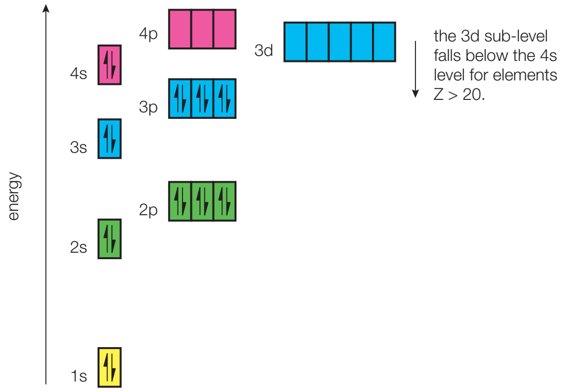
(You need to learn that the energy ordering for the orbitals is s < p < d < f.)

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: $1s^22s^22p^63s^23p^6\mathbf{3d^{10}}4s^24p^6\mathbf{4d^{10}}5s^25p^5$.

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

(Chromium ($[Ar]3d^54s^1$) 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: $[Ar]4s^23d^2$. 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 configurations 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.

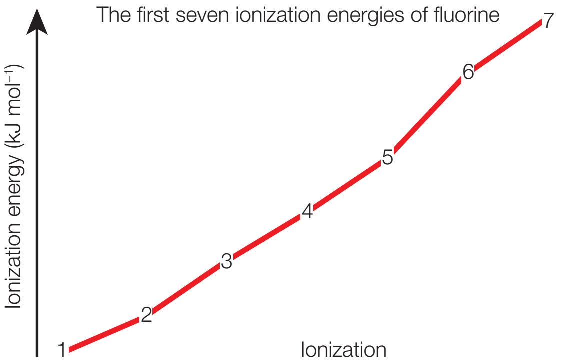
33 B There is a sharp increase in ionization energy between the second and third ionization energies, so the first two electrons are easier to remove than the others. Hence the element must be in Group 2.

34 B There is a sharp increase in ionization energy between the second and third ionization energies, so the first two electrons are easier to remove than the others. Hence the element must be in Group 2. Of those listed in the question, it must be calcium.

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

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

36 The first seven electrons all come from the outer shell, so there will be no sudden increases in ionization energy. The third and sixth ionization energies will be abnormally high. The third electron comes from the half-filled 2p orbitals, and the sixth comes from the full 2s orbital. In both cases, removal of an electron from the stable arrangement is found to be difficult.



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

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

(c) P has the configuration $[Ne]3s^23p^1_x3p^1_y3p^1_z$, S has the configuration $[Ne]3s^23p^2_x3p^1_y3p^1_z$. The electron removed from S comes from a doubly occupied 3p orbital, which is repelled by its partner and is easier to remove than the electron removed from P, which comes from a half-filled orbital.

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 $A_r = \sum$ isotopic mass × relative abundance

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

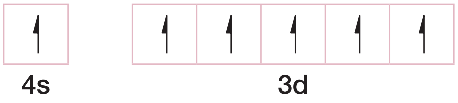
= 55.90 (to 2 decimal places).

12 **(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] $4s^23d^n$.)

(c)



13 **(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 $1s^22s^22p^63s^23p^63d^7$ (or [Ar] $3d^7$).

14 There are four electrons that are relatively easy to remove, then a jump in energy occurs before five electrons are removed from the energy level next closest to the nucleus.

This means there are four electrons in the valence level and the atom must have more than two energy levels. (Only two electrons could be removed after the valence electrons if atom only had two levels.)

Carbon and silicon are in Group 4, but only silicon has more than two electron shells.

Correct answer is B.

15 The electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$.

The first ionization energy is the lowest as it corresponds to removing the electron in the valence level that is furthest from the nucleus and experiences the least electrostatic attraction.

The ionization energy for the second electron is much larger as it involves removing an electron that is in an energy level closer to the nucleus and experiences a greater electrostatic attraction.

As successive electrons are removed within this level the ionization energies increase due to the greater effective nuclear charge experienced by these electrons.

The large increase between the ninth and tenth ionization energies is due to the tenth electron being removed from the energy level that is closest to the nucleus, where it will experience significant electrostatic attraction to the nucleus.

The eleventh electron has the highest ionization energy as it is also removed from the energy level closest to the nucleus and experiences the greatest electrostatic attraction to the nucleus – as the final electron removed it only experiences attraction to the nucleus and no repulsion due to other electrons.

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.

7 Using the graph of method 1, $\Delta\nu = -0.5897\nu + (19.022 \times 10^{14})\ \text{s}^{-1}$

Ionization of a hydrogen atom occurs when the emission lines converge, $\Delta\nu = 0$:

$0 = -0.5897\nu + (19.022 \times 10^{14})\ \text{s}^{-1}$

$\nu = 32.26 \times 10^{14}\ \text{s}^{-1}$

$E = h\nu = 6.63 \times 10^{-34}\ \text{J s} \times 32.26 \times 10^{14}\ \text{s}^{-1}$
$= 2.14 \times 10^{-18}\ \text{J}$

The ionization energy (I.E.) is based on the ionization of one mole of atoms:

$\text{I.E.} = 2.14 \times 10^{-18}\ \text{J} \times 6.02 \times 10^{23}\ \text{mol}^{-1}$
$= 1.29 \times 10^{6}\ \text{J mol}^{-1} = 1290\ \text{kJ mol}^{-1}$

8 The convergence limit in the Balmer series corresponds to the transition $n = 2$ to $n = \infty$.

To obtain the ionization energy, this needs to be added to the energy of the $n = 2$ to $n = 1$ transition (the first line in the Lyman series).

$E\ (n = 2 \text{ to } n = \infty) = h\nu = 6.63 \times 10^{-34}\ \text{J s} \times 8.223 \times 10^{14}\ \text{s}^{-1} = 5.45 \times 10^{-19}\ \text{J}$

$E\ (n = 1 \text{ to } n = 2) = h\nu = 6.63 \times 10^{-34}\ \text{J s} \times 24.66 \times 10^{14}\ \text{s}^{-1} = 1.63 \times 10^{-18}\ \text{J}$

Combined energy $= (5.45 \times 10^{-19})\ \text{J} + (1.63 \times 10^{-18})\ \text{J} = 2.18 \times 10^{-18}\ \text{J}$

Ionization energy (I.E.) is based on the ionization of one mole of atoms:

$\text{I.E.} = 2.18 \times 10^{-18}\ \text{J} \times 6.02 \times 10^{23}\ \text{mol}^{-1}$
$= 1.31 \times 10^{6}\ \text{J mol}^{-1} = 1310\ \text{kJ mol}^{-1}$

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 $1s^22s^22p^63s^23p^3$. 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 $[Kr]4d^{10}5s^25p^3$. Its valence electrons are $5s^25p^3$ 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 $1s^22s^22p^6$ whereas Si^{4-} has an electronic configuration of $1s^22s^22p^63s^23p^6$. Si^{4+} has two occupied energy levels and Si^{4-} has three and so Si^{4-} is larger.

9 A 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 $1s^2 2s^2 2p^6 3s^2 3p^6$, whereas Si^{4+} has an electronic configuration of $1s^2 2s^2 2p^6$. 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, $1s^2 2s^2 2p^6$, 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.

$Na_2O + H_2O \rightarrow 2NaOH$

$SO_3 + H_2O \rightarrow H_2SO_4$

34 It is probably simplest to start with the configurations of the atoms. Remember Hund's rule: electrons will occupy each orbital singly until there are so many that they have to form pairs.

Atom	3d					4s
Sc	↑					↑↓
Ti	↑	↑				↑↓
Ni	↑↓	↑↓	↑↓	↑	↑	↑↓
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

When the ions form, it is the 4s electrons which are lost first:

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

35 **D** Elements in the d block are metals; conducting heat and electricity well is a key property of metals.

A is not correct – some complexes are uncharged, e.g. hydroxides such as $Cu(H_2O)_4(OH)_2$. **B** is not the correct answer because some d block elements are not transition metals. For example, zinc doesn't have any coloured compounds. **C** is not correct – the elements all have strong metallic bonds.

36 **B** +2 is the only oxidation state shown by every first row transition element and is the most common.

37 **D** Counting the electrons (the superscript figures) we find that this is element 23, vanadium. The $3d^3 4s^2$ configuration should also have told you that this is vanadium. Vanadium shows oxidation states of +2, +3, +4 and +5 – something you need to learn.

38 **(a)** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

(b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (Zn loses its two outermost electrons to form Zn^{2+})

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

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

40 **C** All the species have lone pairs of electrons, apart from CH_4.

41 **C** H^+ has no lone pair of electrons, so it cannot be a ligand. This leaves only answer C. H_2O and Cl^- have lone pairs of electrons and bond to the copper ion in the complexes $[Cu(H_2O)_6]^{2+}(aq)$ and $[CuCl_4]^{2-}$.

42 **D** I is $[Cr(H_2O)_6]Cl_3$

II is $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$

III is $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$

The question asks about the charge on the complex ion, not on the chromium. The complex ion formula is in square brackets, so we need to remove the species outside the square brackets.

H_2O is simply water of crystallization, so it can be ignored. It has no charge anyway.

The Cl is in the form of chloride ions, so for each Cl we remove, the complex must have a positive charge:

I is $[Cr(H_2O)_6]^{3+}$

II is $[CrCl(H_2O)_5]^{2+}$

III is $[CrCl_2(H_2O)_4]^+$

43 **C** Ligands have non-bonding pairs of electrons that can donate electrons into empty d-orbitals on the transition metal ion to form a coordinate (dative) bond.

Ligands can be neutral, e.g. H_2O (**A**), don't have to contain an electronegative atom, e.g. CO (**B**), and can be single atoms/ions, e.g. Cl^- (**D**).

44 **(a)** Zn is not considered to be a transition metal as it doesn't form ions with partially full d orbitals.

(b) **(i)** +2.67. O has an oxidation state of –2. In order for the sum of the oxidation states to cancel out in the Fe_3O_4 molecule, each Fe must have a +2.67 oxidation state (+2.67 × 3 + –2 × 4 = 0).

(ii) +7. O has an oxidation state of –2. In order for the sum of the oxidation states to equal the overall charge of the MnO_4^- ion, each Mn must have a +7 oxidation state (+7 × 1 + –2 × 4 = –1).

(iii) +6. O has an oxidation state of –2. In order for the sum of the oxidation states to equal the overall charge of the CrO_4^{2-} ion, the Cr must have a +6 oxidation state (+6 × 1 + –2 × 4 = –2).

(iv) +2. CN^- has an oxidation state of –1. In order for the sum of the oxidation states to equal the overall charge of the $[FeCN_6]^{4-}$ ion, the Fe must have a +2 oxidation state (+2 × 1 + –1 × 6 = –4).

45 **(a)** The iron has a +2 oxidation state.

(b) The nitrogen atoms are in a square planar arrangement.

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

46 **(a)** Nickel is used to catalyse the hydrogenation of vegetable oils.

(b) Vanadium(V) oxide (V_2O_5) catalyses the oxidation of sulfur dioxide in the Contact process.

(c) Platinum, rhodium, and palladium can be used in vehicle exhaust catalysts.

47 **(a)** A homogeneous catalyst is in the same physical state as the reactants of the reaction it catalyses – usually in solution. A heterogeneous catalyst is in a different physical state to the reactants, for example a solid catalyst with gaseous reactants.

(b) Transition metals can form dative bonds with reactants on the surface of the metal, holding them in the correct orientation so that other reactants can react. The variable oxidation state of transition metals can be helpful if the reaction involves changes of oxidation state of the reactants.

(c) It is easy to recover heterogeneous catalysts, e.g. by filtration, and re-use them.

48 **D** In order to show paramagnetic properties the metal must have unpaired electrons. Mn has an electronic arrangement of $1s^22s^22p^63s^23p^64s^23d^5$. As a consequence of Hund's third law each of the 5d electrons are in a separate d orbital and so are unpaired and Mn is paramagnetic.

Looking at the electronic arrangements of the other elements in the question, you can see that all their electrons are paired.

49 **D** In order to show paramagnetic properties the metal must have unpaired electrons. The more unpaired electrons an element has the more paramagnetic it is. The number of unpaired electrons for each element can be determined from its electron configuration.

Sc: $[Ar]3d^14s^2$	1 unpaired electron	Ti: $[Ar]3d^24s^2$	2 unpaired electrons
V: $[Ar]3d^34s^2$	3 unpaired electrons	Cr: $[Ar]3d^54s^1$	6 unpaired electrons

Chromium is the most paramagnetic as it has the largest number of unpaired electrons.

50 Chromium has the electron configuration $[Ar]3d^54s^1$ so it has six unpaired electrons – which is the maximum number for the series. Zn has the electronic configuration $[Ar]3d^{10}$ and so has no unpaired electrons.

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

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

52 **(a)** The central metal ions are different in the two complexes, so there is a difference in the nuclear charge of the metal ion. This causes a different splitting of the d orbitals in the complex and the absorption of different wavelengths (colours) of light.

(b) The oxidation numbers of the central Fe ion in the two complexes are different, +3 in $[Fe(H_2O)_6]^{3+}$ and +2 in $[Fe(H_2O)_6]^{2+}$, and this causes a different splitting of the d orbitals in the complex and the absorption of different wavelengths (colours) of light.

(c) The two complexes have the same central metal ion but different ligands: NH_3 is the ligand in the first complex and H_2O is the ligand in the second complex. The bonding of different ligands in the complex results in different splittings of the d orbitals in the complex and the absorption of different wavelengths (colours) of light.

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

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

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

55 **(a)** Assume the question is only referring to the d electrons. Fe^{2+} has the electron configuration [Ar]$3d^6$. This can be illustrated using a box diagram representing the five 3d orbitals:

(b) The two complexes have the same central ion and the same coordination number so the colour of light will depend on the nature of the ligand. The splitting of the d orbitals will be greater for $[Fe(CN)_6]^{4-}$ as CN^- is a stronger ligand than H_2O. This will result in a different colour for this complex than that observed for $[Fe(H_2O)_6]^{2+}$, which has a smaller splitting between the two sets of d orbitals. (See the spectrochemical series on page 133, which lists various ligands by their splitting strength.)

56 **(a)** The nature of the central metal ion affects the size of the d orbital splitting in the complex and the colour of light absorbed by electronic transitions, as the ions have different nuclear charges and will exert a different attraction on the ligands. The first complex contains the Fe^{3+} ion and the second complex contains the Cr^{3+} ion so the two complexes will have different colours: $[Fe(H_2O)_6]^{3+}$ is yellow and $[Cr(H_2O)_6]^{3+}$ is green (the colours observed are complementary to the colours of light they absorb).

(b) The oxidation state of the central metal ion in the two complexes is different and this affects the size of the d orbital splitting in the complex and the colour of light absorbed by electronic transitions because of the different number of electrons present in the d orbitals. The first complex contains the Fe^{2+} ion, which has the electron configuration [Ar]$3d^6$, and the second complex contains the Fe^{3+} ion, which has the electron configuration [Ar]$3d^5$, so the two complexes will have different splitting energies between the two sets of d orbitals and will absorb different wavelengths (colours) of light.

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 **exothermic** reaction of sodium with water is $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$. NaOH(aq) is a colourless solution, bubbles will be observed due to formation of $H_2(g)$ and the temperature will increase due to it being an exothermic reaction.

Correct answer is D.

8 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.

9 There are four Cl^- ligands attached to the copper ion. The copper ion must be Cu^{2+} (and have an oxidation number of +2) to give an overall 2– charge. As there are four Cl^- ligands attached to the Cu^{2+} ion the coordination number is 4. All three statements are correct.

Correct answer is D.

10 Complex I: H_2O is a neutral ligand. The iron oxidation number must be +3 to give an overall charge of +3.

Complex II: H_2O is a neutral ligand and CN^- is negatively charged. The iron oxidation number must be +3 to give an overall charge of +2.

Complex III: CN^- is a negatively charged ligand. The iron oxidation number must be +3 to give an overall charge of –3.

Correct answer is D.

11 V_2O_5 is the catalyst used in the Contact process for the conversion of $SO_2(g)$ to $SO_3(g)$.

Correct answer is C.

12 Transition metal complexes are coloured due to the absorption of visible light, which results in the excitation of an electron from a low energy d orbital to a higher energy d orbital.

Correct answer is C.

13 **(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.

14 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.

15 **(a)** Because chlorine is more electronegative than iodine the iodide ions are displaced by chlorine and the solution will turn orange/brown due to the formation of aqueous iodine, $I_2(aq)$.

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

(An alternative equation that omits the K^+ spectator ions is:

$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$)

(b) Because fluorine is more electronegative than chlorine it is more reactive and the fluoride ions cannot be displaced by chlorine so no reaction occurs. No colour change will be observed.

16 **(a)** Elements are arranged according to increasing atomic number (*Z*).

(b) Electronegativity increases across Period 3 as the effective nuclear charge increases. The larger number of protons in the nucleus exerts a greater electrostatic attraction on a bonded pair of electrons.

As the electrons are being added in the same valence shell they do not screen other valence electrons such as a bonded pair and reduce their attraction to the nucleus.

The best definition of electronegativity is the attraction of an atom to a bonded pair of electrons. As noble gases do not readily form covalent bonds they are not capable of attracting a bonded pair of electrons and are therefore not assigned electronegativity values.

17 **(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 $1s^2 2s^2 2p^6 3s^1$.

The electron configuration of Na^+ is $1s^2 2s^2 2p^6$.

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 $1s^2 2s^2 2p^6 3s^2 2p^6$.

Si^{4+} has electron configuration $1s^2 2s^2 2p^6$.

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.

18 **(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 $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$)

19 **(a)** The first ionization energy is the energy required to remove one mole of electrons from one mole of atoms in the gaseous state: $M(g) \rightarrow M^+(g) + e^-$.

Periodicity is the repeating pattern of physical and chemical properties of elements.

(b) The electron configuration of argon is $1s^2 2s^2 2p^6$.

As the valence electrons of elements in the same period are in the same shell they do not effectively screen each other so the electrons of the noble gases experience the greatest effective nuclear charge as these elements have the most protons of the elements in their period. The valence electrons of the noble gases therefore experience the greatest attraction to the nucleus, which is why they have the highest ionization energies of the elements in each period.

(c) The valence electrons of sodium and chlorine are both in the third shell so they experience similar shielding effects. However, chlorine has 17 protons and sodium has 11 protons so the valence electrons of chlorine will experience a greater attraction to the nucleus and be held closer to the nucleus, resulting in a smaller atomic radius.

(d) Sulfide, S^{2-}, and chloride, Cl, are isoelectronic, both having 18 electrons. However, sulfide has 16 protons and chloride has 17 protons. This means the sulfide valence electrons experience less attraction to the nucleus and will be held less closely, resulting in a larger ionic radius.

(e) The Group 1 elements are metals and metallic bond strength (see Chapter 4) decreases down the group as the delocalized valence electrons are in energy levels that are more distant from the nucleus of the cations and experience a weaker electrostatic attraction to the nuclei. The weaker metallic bond strength results in lower melting points going down the group.

The Group 17 elements exist as diatomic molecules, X_2, which are attracted to each other by weak London dispersion forces (see Chapter 4). London dispersion forces increase down the group as the atoms become larger and contain more electrons, resulting in higher melting points.

20 **(a)** The square brackets indicate that $[Cu(H_2O)_6]^{2+}$ is a complex ion where the charge is delocalized over the whole complex whose chemical formula is written within the brackets.

(b) The d electrons in $[Cu(H_2O)_6]^{2+}$ are split into two energy levels. The transition of an electron from a low energy d orbital into a higher energy d orbital results in the absorption of visible light and the complex therefore appears coloured. The colour observed is complimentary to the colour of the light absorbed.

$[CuCl_4]^{2-}$ contains different ligands, as well as fewer ligands (a different coordination number), and also has a different geometry to $[Cu(H_2O)_6]^{2+}$. These all contribute to it having a different energy gap between its d orbitals for this complex. Transitions between the d orbitals of this complex will therefore involve absorption of light that has a different energy and therefore is a different colour.

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] $4f^76s^2$)

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

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

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

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 142 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 142. 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.

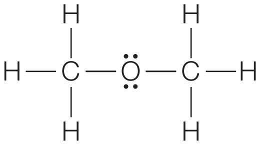
8 **D** The elements which react most readily will be those with the largest difference in electronegativity, i.e. between those on the bottom left and those on the top right. From the Periodic Table we can see that K is below Li and Cl is above Br.

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** $O{=}C{=}O$

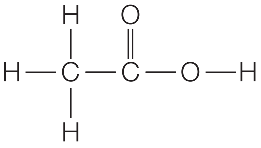
A



B

$C{\equiv}O$

C



D

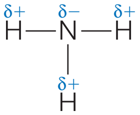
Substances **A** and **D** contain carbon–oxygen double bonds and substance **B** contains carbon–oxygen single bonds. Compound C (carbon monoxide) contains a triple bond. Triple bonds are shorter than both single and double bonds.

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)

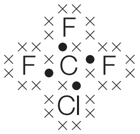


13

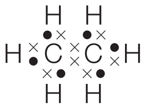
(a)	C 2.6	H 2.2	difference = 0.4
	C 2.6	Cl 3.2	difference = 0.6, more polar
(b)	Si 1.9	Li 1.0	difference = 0.9
	Si 1.9	Cl 3.2	difference = 1.3, more polar
(c)	N 3.0	Cl 3.2	difference = 0.2
	N 3.0	Mg 1.3	difference = 1.7, more polar

14 **(a)**

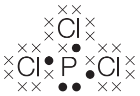
(b)



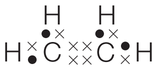
(c)



(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

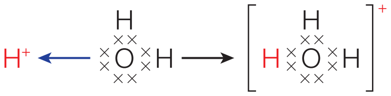
(c) CCl_4: C has 4 valence electrons and each Cl has 7; 4 + (4 × 7) = 32

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

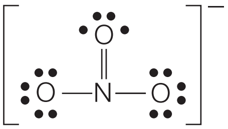
(e) SCl_2: S has 6 valence electrons and each Cl has 7; 6 + (2 × 7) = 20

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

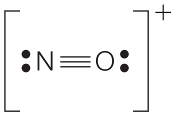
16



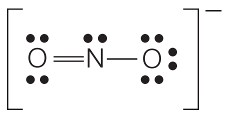
17



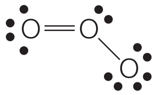
(a)



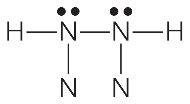
(b)



(c)



(d)

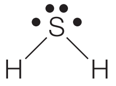


(e)

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 numbers 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

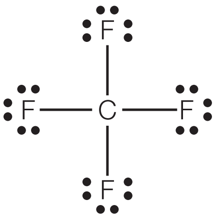


Four domains of electrons around the sulfur atom, electron domain geometry is tetrahedral.

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

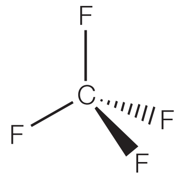
As lone pairs repel more than bonded pairs the bond angles are less than 109.5°. Observed bond angle is 105°.

(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.



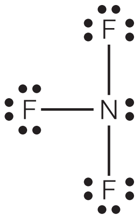
Bond angles are 109.5°.

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

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

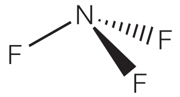
All electron pairs are bonded so shape is linear (as drawn in Lewis structure). Bond angle is 180°.

(d) NF_3: Lewis structure is



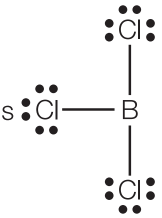
Four domains of electrons around the nitrogen atom, electron domain geometry is tetrahedral.

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

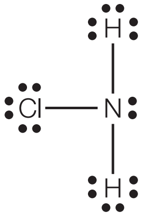


Three domains of electrons around the boron atom, electron domain geometry is trigonal planar.

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

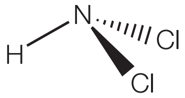
120° bond angle, triangular planar, three domains of electrons around the boron atom.

(f) NH_2Cl: Lewis structure is



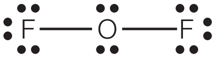
Four domains of electrons around the nitrogen atom, electron domain geometry is tetrahedral.

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



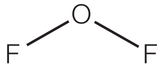
As lone pairs repel more than bonded pairs the bond angles are less than 109.5°. Observed bond angle is 107°.

(g) OF_2: Lewis structure is



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

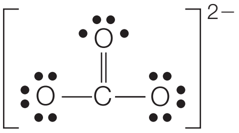
Two lone pairs and two bonded pairs so shape is bent.



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

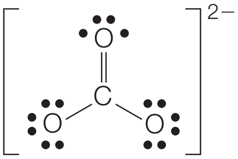
19 Drawing the Lewis structure of these ions will help you to sort out their structure.

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



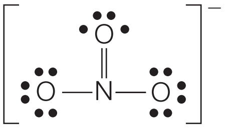
Three domains of electrons around the carbon atom, electron domain geometry is trigonal planar.

All electron domains are bonded so shape is trigonal planar.



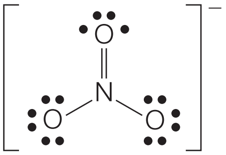
Bond angles are 120°.

(b) NO_3^-: Lewis structure is



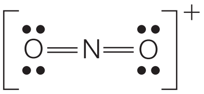
Three domains of electrons around the nitrogen atom, electron domain geometry is trigonal planar.

All electron domains are bonded so shape is trigonal planar.



Bond angles are 120°.

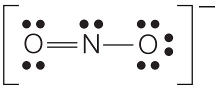
(c) NO_2^+: Lewis structure is



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

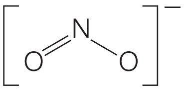
All electron domains are bonded so shape is linear (as drawn in Lewis structure). Bond angle is 180°.

(d) NO_2^-: Lewis structure is



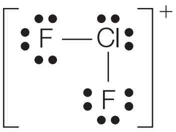
Three domains of electrons around the nitrogen atom, electron domain geometry is trigonal planar.

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



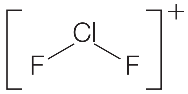
Lone pairs repel more so bond angle will be slightly less than 120°.

(e) ClF_2^+: Lewis structure is



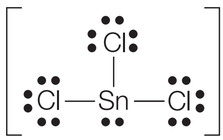
Four domains of electrons around the chlorine atom, electron domain geometry is tetrahedral.

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



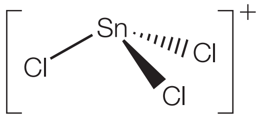
Lone pairs repel more so bond angle will be less than 109.5°. Observed angle is 105°.

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



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

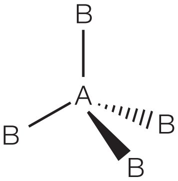
One lone pair and three bonded pairs so shape is trigonal pyramidal.



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.

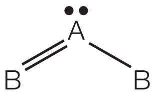
(a)



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.



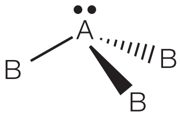
A bent shape can also be obtained from a trigonal planar electron domain geometry with **three** electron domains if one domain is a lone pair. A bent shape can also be obtained from a trigonal planar electron domain with three electron domains if two domains are bonded and there is one lone pair.

(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.

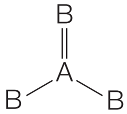
A linear shape can also be obtained from a trigonal bipyramidal electron domain geometry with **five** electron domains if two domains are bonded and there are three lone pairs.

(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)



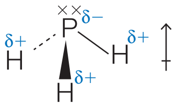
A trigonal planar shape can only be obtained from a trigonal planar electron domain geometry with **three** electron domains and with all domains bonded.

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:

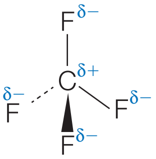
- work out the shape of the molecule (as in question 18)
- from the relative position of the polar bonds, determine whether or not there is a net dipole.

(a) PH_3



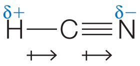
This is a pyramidal molecule, it is polar.

(b) CF_4



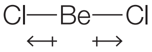
This is a tetrahedral molecule, all bond dipoles cancel, so it is non-polar.

(c) HCN



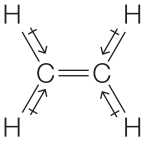
This is a linear molecule, the two dipoles (from the H—C bond and the C—N bond) do not cancel (in fact, they add together), so it is polar.

(d) $BeCl_2$



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

(e) C_2H_4



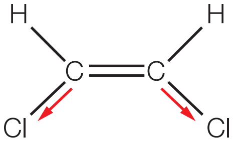
Each C is trigonal planar, each C—H bond is slightly polar, the C=C is non-polar, the structure is symmetrical, so non-polar.

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

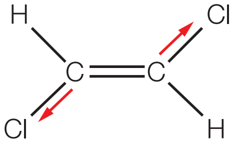
(g) Non-polar; F_2 is a symmetrical molecule so the bonding electrons are shared equally between atoms.

(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

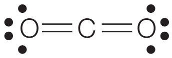
The *cis* isomer has a net dipole moment as both the electronegative atoms are on the same side of the molecule and so there is an overall dipole moment for the molecule. In the *trans* isomer the dipoles cancel out.

23 The C–O bond order for each species can be determined from their Lewis structures.

CO: Lewis structure is :C≡O:

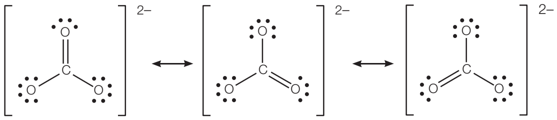
It contains a C≡O triple bond, bond order = 3.

CO_2: Lewis structure is



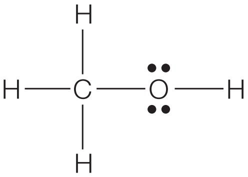
It contains two C=O double bonds, bond order = 2.

CO_3^{2-}: Three resonance structures:



The C–O bonds are delocalized and have a bond order of 1.33.

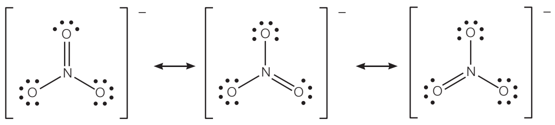
CH_3OH: Lewis structure is



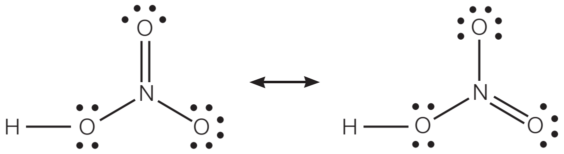
It contains a C–O single bond, bond order = 1.

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 182 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.

34 The steps to follow:

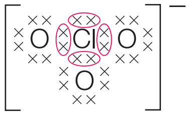
- work out the Lewis structure
- count the number of electron domains around the central atom, which gives the geometric arrangement of the electron domains
- determine the numbers and positions of the bonded atoms within this geometric arrangement to give the shape of the molecule
- adjust bond angles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

(a) XeF_2: Lewis structure is

Five domains of electrons around the xenon atom, electron domain geometry is trigonal pyramidal.

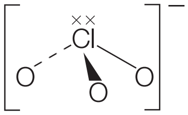
Three lone pairs and two bonded electron pairs so shape is linear (as indicated by Lewis structure). Bond angle is 180°.

(b) ClO_3^-: Lewis structure is



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

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

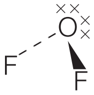


Lone pair repels more so bond angles are less than 109.5°. Observed angle is 107°.

(c) OF_2: Lewis structure is

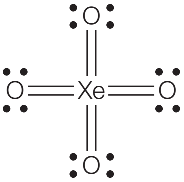
Four domains of electrons around the oxygen atom, electron domain geometry is tetrahedral.

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



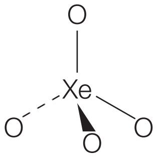
Lone pairs repel more so bond angle will be less than 109.5°. Observed angle is 105°.

(d) XeO_4: Lewis structure is



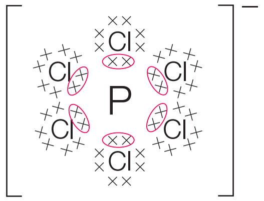
Four domains of electrons around the xenon atom, electron domain geometry is tetrahedral.

All electron domain are bonded so the shape is tetrahedral.



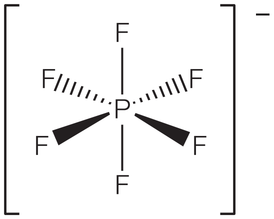
Bond angles are 109.5°.

(e) PCl_6^-: Lewis structure is



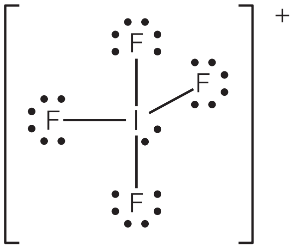
Six domains of electrons around the phosphorous atom, electron domain geometry is octahedral.

All electron domains are bonded so the shape is octahedral.



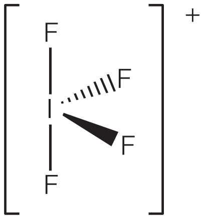
Bond angles are 90° and 180°.

(f) IF_4^+: Lewis structure is



Five domains of electrons around the iodine atom, electron domain geometry is trigonal bipyramidal.

One lone pair and four bonded pairs so the shape is see-saw (sawhorse).

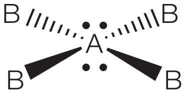


Bond angles in the equatorial plane are distorted due to the lone pair and the observed angle is around 117°. The axial bond angle is also reduced to around 170°.

35 This is similar to question 20.

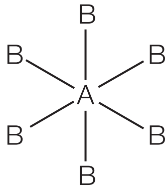
The table on page 189 confirms the relationships between the number of charge centres and the shape of the molecule.

(a)



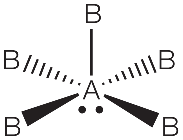
A square planar shape can be obtained from an octahedral electron domain geometry with **six** electron domains if four domains are bonded and there are two lone pairs.

(b)



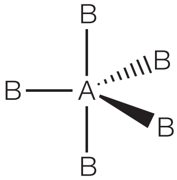
An octahedral shape can be obtained from an octahedral electron domain geometry with **six** electron domains if all six domains are bonded.

(c)



A square pyramidal shape can be obtained from an octahedral electron domain geometry with **six** electron domains if five domains are bonded and there is one lone pair.

(d)



A trigonal bipyramidal shape can be obtained from an octahedral electron domain geometry with **five** electron domains if all five domains are bonded.

(e) B—A—B

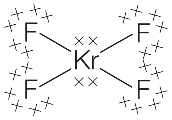
A linear shape can be obtained from a linear electron domain geometry with **two** electron domains if both domains are bonded.

A linear shape can also be obtained from a trigonal bipyramidal electron domain geometry with **five** electron domains if two domains are bonded and there are three lone pairs.

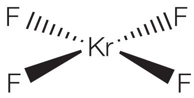
Note that in part (e), linear geometry can arise from two charge centres with no lone pairs (e.g. $BeCl_2$, C_2H_2) or from five charge centres with three lone pairs (e.g. I_3^-).

36 The bond angles are determined by the overall shape of the molecule, so this must be deduced first.

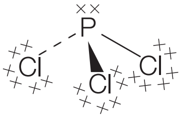
(a) Lewis structure is



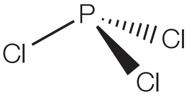
KrF_4 has 6 charge centres with 4 bonding pairs and 2 lone pairs, which is octahedral overall. This will be a square planar structure, with all F—Kr—F bond angles = 90°.



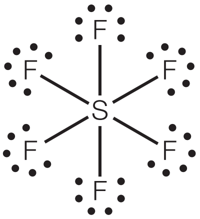
(b)



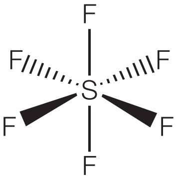
PCl_3 has 4 charge centres with 3 bonding pairs and 1 lone pair. This will be trigonal pyramidal with Cl—P—Cl bond angles around 107° (compressed slightly by the lone pair).



(c)



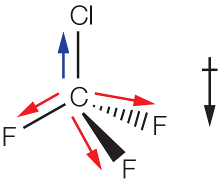
SF_6 has 6 charge centres, with all 6 as bonding pairs (no lone pairs) and so is octahedral. The F—S—F bond angle is 90°.



37 **(a)**

HF is polar; the F is more electronegative than H so the HF molecule has a dipole.

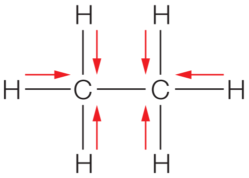
(b)



net dipole

CF_3Cl is polar; both the Cl and the F are electronegative to different extents so the C–F bond is more polar than the C–Cl bond. The dipoles do not cancel so there is a net dipole and the molecule is polar.

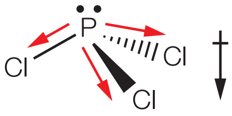
(c)



no net dipole

C_2H_6 is non-polar as the molecule is symmetrical and the dipoles associated with the weakly polar C–H bonds cancel.

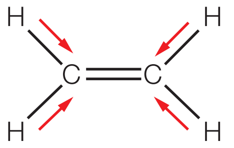
(d)



net dipole

PCl_3 is polar as it is an asymmetrical molecule and the dipoles associated with the three polar P–Cl bonds do not cancel so there is a net dipole.

(e)



no net dipole

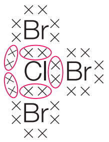
C_2H_4 is non-polar as the molecule is symmetrical and the dipoles associated with the weakly polar C–H bonds cancel.

(f) 

no net dipole

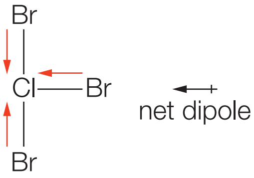
C_2H_2 is non-polar as the molecule is symmetrical and the dipoles associated with the weakly polar C–H bonds cancel.

38 **(a)** Lewis structure of $ClBr_3$:



Five domains of electrons around the chlorine atom, electron domain geometry is trigonal bipyramidal.

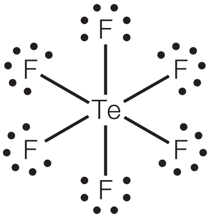
Two lone pairs and three bonded pairs so the shape is T-shaped.



The molecule is non-symmetrical so the dipoles created by the slightly polar Cl–Br bonds do not cancel and the molecule is polar.

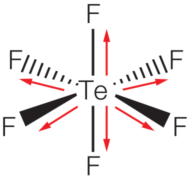
(b) IO_4^- is a molecular ion so it is a charged species. Because it is charged it cannot be designated as polar or non-polar as these terms only apply to neutral molecules.

(c) Lewis structure of TeF_6:



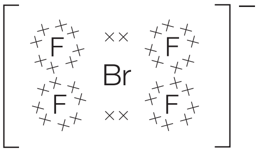
Six domains of electrons around the chlorine atom, electron domain geometry is octahedral.

All electron pairs are bonded pairs so the shape is octahedral.



The molecule is symmetrical so the dipoles created by the polar Te–F bonds cancel and the molecule is non-polar.

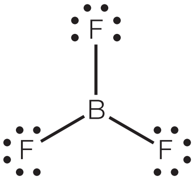
(d) BrF_4^- is a molecular ion so it is a charged species. Because it is charged it cannot be designated as polar or non-polar as these terms only apply to neutral molecules.



(e) PCl_4^+ is a molecular ion so it is a charged species. Because it is charged it cannot be designated as polar or non-polar as these terms only apply to neutral molecules.

(f) FCl_2^+ is a molecular ion so it is a charged species. Because it is charged it cannot be designated as polar or non-polar as these terms only apply to neutral molecules.

39 BF_3 has a trigonal planar shape.



To determine the formal charge on the boron and fluorine atoms we use the formula:

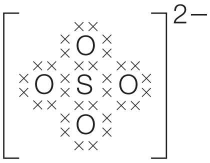
formal charge (FC) on atom = valence electrons of atom – (½ bonding electrons + lone pair electrons)

$$FC(B) = 3 - (\tfrac{1}{2} \times 6 + 0) = 0$$

$$FC(F) = 7 - (\tfrac{1}{2} \times 2 + 6) = 0$$

As all the atoms present in the molecule have a formal charge of zero this represents a stable structure even though the central boron atom does not obey the octet rule.

40 The Lewis structure for SO_4^{2-} where the sulfur atom obeys the octet rule is



To determine the formal charge on the sulfur and oxygen atoms we use the formula:

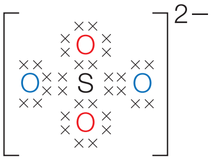
formal charge (FC) on atom = valence electrons of atom – (½ bonding electrons + lone pair electrons)

$$FC\ (S) = 6 - (½ \times 4 + 0) = +2$$

$$FC\ (O) = 6 - (½ \times 2 + 6) = -1$$

(Total formal charge for the one sulfur and four oxygen atoms = +2 + 4(–1) = –2, which is equivalent to the overall 2– charge on the ion).

The Lewis structure for SO_4^{2-} where the sulfur atom has an expanded octet with 12 electrons is



Two of the oxygens are singly bonded and two are doubly bonded to the central sulfur atom.

$$FC\ (S) = 6 - (½ \times 12 + 0) = 0$$

Singly bonded O: $FC\ (O) = 6 - (½ \times 2 + 6) = -1$

Doubly bonded O: $FC\ (O) = 6 - (½ \times 4 + 4) = 0$

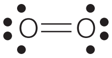
(Total formal charge for the one sulfur and four oxygen atoms = 0 + 2(–1) + 2(0) = –2, which is equivalent to the overall 2– charge on the ion).

Comparing the two structures we see that:

(i) the structure for the expanded octet contains fewer atoms with a formal charge (the expanded octet structure has more atoms where the formal charge = 0)

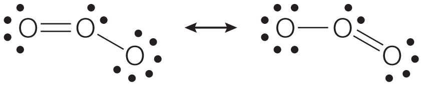
(ii) the formal charges that do exist on atoms in the expanded octet structure are smaller (all –1) than those in the octet structure (+2 on sulfur).

Both of these are factors that contribute to the expanded octet being the preferred structure.

41 Lewis structure of oxygen (O2) is 

The O=O double bond has a bond order of 2.

Ozone (O_3) has two resonance structures:



Ozone resonates between these two structures so each O–O bond is between a single and double bond, with a bond order of 1.5.

Bond strength increases with increasing bond order. With a bond order of 1.5 the O–O bonds in O_3 are weaker than the double bond in O_2 because of the lower bond order, therefore dissociation of ozone occurs with lower energy light (longer wavelength).

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

e.g. $CCl_2F_2(g) \rightarrow CClF_2\bullet(g) + Cl\bullet(g)$

CFCs break down in upper atmosphere

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

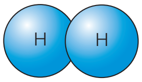
chlorine radical reacts with ozone and another radical is produced

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

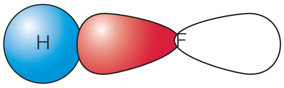
chlorine radical is regenerated and so acts a catalyst for ozone destruction

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

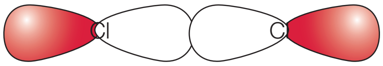
44 **(a)** H—H in H_2



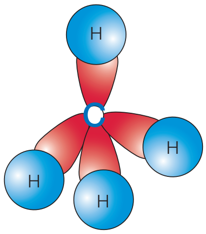
(b) H—F in HF



(c) Cl—Cl in Cl_2

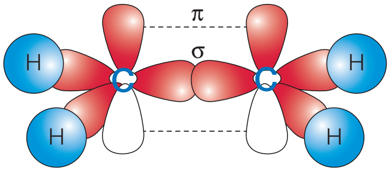


(d) C–H in CH_4



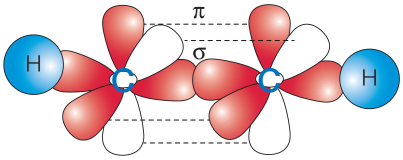
(The four orbitals around the central carbon are sp^3 hybrid orbitals.)

(e) C–H in C_2H_4



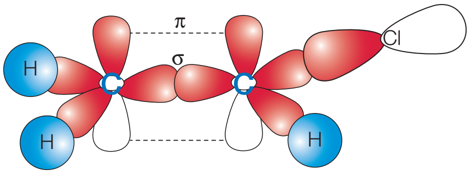
(Each carbon is sp^2 hybridized so has three sp^2 hybrids which form the sigma bonds and an unhybridized p orbital that forms the pi bond.)

(f) C–H in C_2H_2



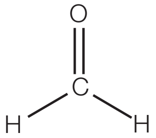
(Each carbon is sp hybridized so has two sp hybrids which form the sigma bonds and two unhybridized p orbitals that form the two pi bonds.)

(g) C–Cl in C_2H_3Cl



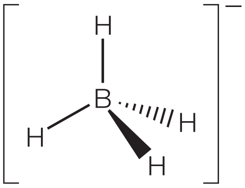
(Each carbon is sp^2 hybridized so has three sp^2 hybrids which form the sigma bonds and an unhybridized p orbital that forms the pi bond.)

45 **(a)** $H_2C{=}O$ is trigonal planar:



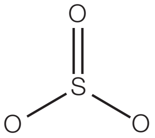
As the carbon atom has a trigonal planar electron domain geometry it is sp^2 hybridized.

(b) BH_4^- is tetrahedral:



As the boron atom has a tetrahedral electron domain geometry it is sp^3 hybridized.

(c) SO_3 is trigonal planar:

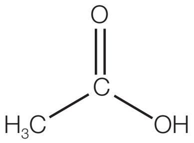


As the sulfur atom has a trigonal planar electron domain geometry it is sp^2 hybridized.

(d) $BeCl_2$ is linear: Cl—Be—Cl

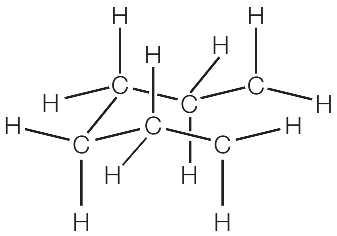
As the sulfur atom has a linear electron domain geometry it is sp hybridized.

(e) CH_3COOH is trigonal planar around the carbon highlighted:

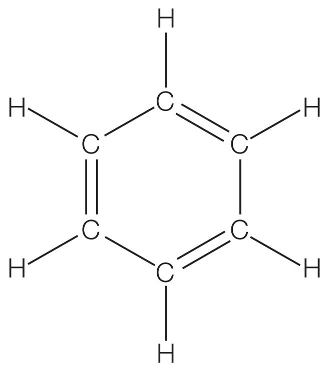


As the carbon atom has a trigonal planar electron domain geometry it is sp^2 hybridized.

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



In C_6H_6 benzene the carbon atoms are all sp^2 hybridized, forming a planar triangular arrangement with bond angles of 120°.



Practice questions

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 See diagrams on page 169.

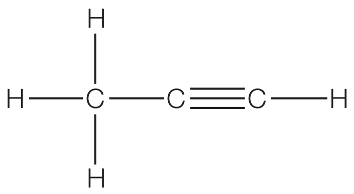
In diamond carbon atoms are all linked to four other atoms in a tetrahedral arrangement and the carbon atoms are sp^3 hybridized.

In graphite the carbon atoms are linked to three other atoms, forming sheets of interlocked hexagons and the carbon atoms are sp^2 hybridized.

In fullerenes the carbon atoms are linked to three other atoms, forming interlocked hexagons and pentagons that create a closed spherical cage and the carbon atoms are sp^2 hybridized.

Correct answer is A.

5 The structure of propyne is (see Chapter 10 for structures of organic compounds):



Each single bond is a σ bond. The triple bond contains one σ and two π bonds so there are a total of six σ and two π bonds.

Correct answer is B.

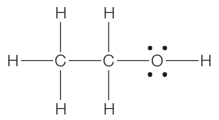
6 Compounds can form hydrogen bonds when:

(i) they contain a hydrogen atom covalently bonded to a highly electronegative atom, N, O or F

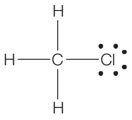
(ii) they have a lone pair on a highly electronegative atom, N, O or F.

The structures of the compounds are (see Chapter 10 for structures of organic compounds):

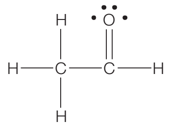
A



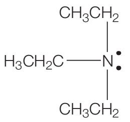
B



C



D

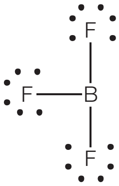


Only C_2H_5OH meets both requirements.

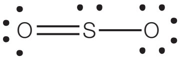
Correct answer is A.

7 Lewis structures of molecules:

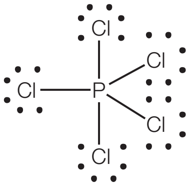
A



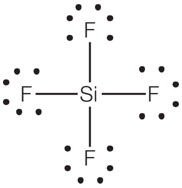
B



C



D

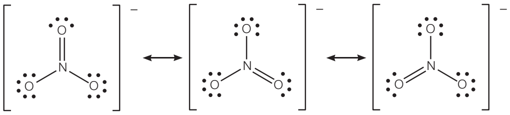


Only SO_2 has a lone pair of electrons on the central atom.

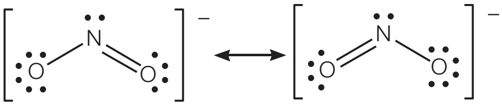
Correct answer is B.

8 Delocalized electrons occur when compounds have resonance structures. The correct answer will be the compound that does not have any resonance structures. All of the species listed have resonance structures except C_3H_6.

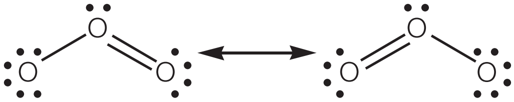
A



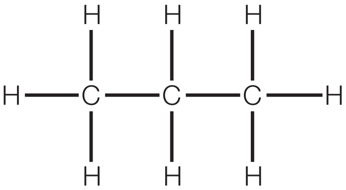
B



C

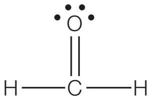


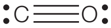
D

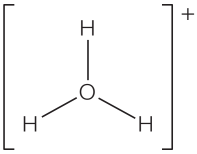


Correct answer is D.

9 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:





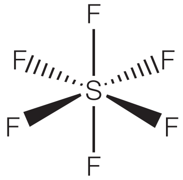


An oxygen atom has two unbonded electrons that can pair with an electron donated from another atom to form two covalent bonds.

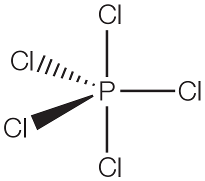
For oxygen to form a third bond this must be a coordination bond where it donates both the electrons in one of the lone pairs. H_3O^+ and CO both contain oxygen atoms that have three bonds.

Correct answer is C.

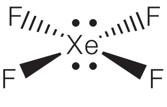
10 Consider the shapes obtained for the compounds:



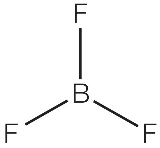
A: SF_6



B: PCl_5



C: XeF_4



D: BF_3

Only SF_6 is octahedral.

Correct answer is A.

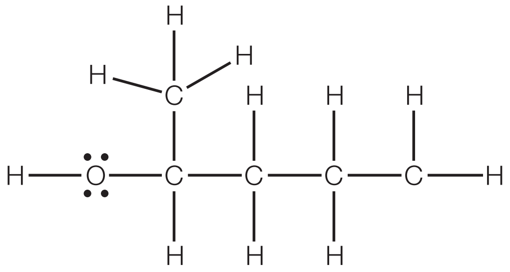
11 Statements I and III are correct. Statement II is incorrect as σ bonds can also be formed from the axial overlap of p orbitals. (Or from the overlap of s and p orbitals as well as the axial overlap of hybrid orbitals.)

Correct answer is B.

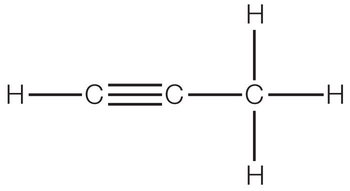
12 Atoms that have a trigonal planar arrangement of electron domains around them are sp^2 hybridized.

Consider the structures of the compounds (see Chapter 10 for structures of organic compounds):

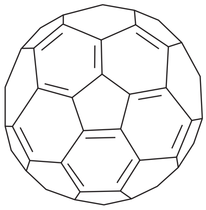
A



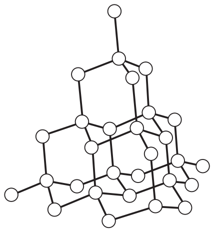
B



C

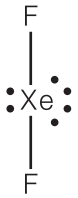


D



Correct answer is C.

13 When a central atom has two bonding and three non-bonding pairs there is a trigonal bipyramidal arrangement of the electron domains around the central atom but the shape is linear due to the two bonded atoms.



Correct answer is D.

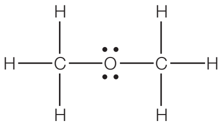
14 Compounds can form hydrogen bonds when:

(i) they contain a hydrogen atom covalently bonded to a highly electronegative atom, N, O or F

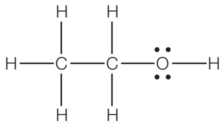
(ii) they have a lone pair on a highly electronegative atom, N, O or F.

Structures of compounds (see Chapter 10 for structures of organic compounds):

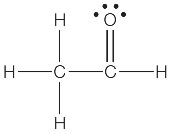
A



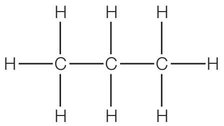
B



C



D

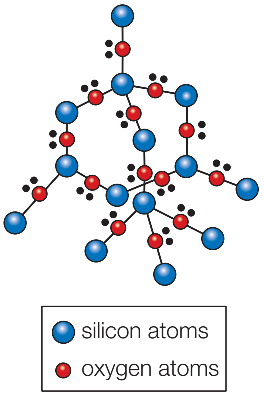


Only CH_3CH_2OH meets both requirements.

Correct answer is B.

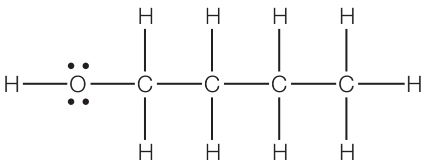
15 The silicon atoms in SiO_2 are surrounded by four bonding pairs so they are sp^3 hybridized.

The oxygen atoms in SiO_2 are surrounded by two bonding and two non-bonding pairs so they are sp^3 hybridized.

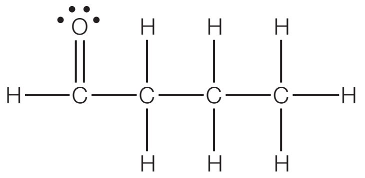


Correct answer is A.

16 Consider the structures of butan-1-ol and butanal (see Chapter 10 for structures of organic compounds):



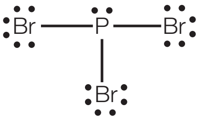
butan-1-ol



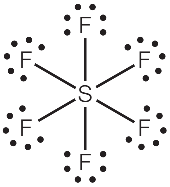
butanal

The intermolecular forces present in butan-1-ol are hydrogen bonding as it contains a hydrogen atom bonded to a highly electronegative oxygen as well as a lone pair on the highly electronegative oxygen. The intermolecular forces present in butanal are dipole–dipole interactions due to the polar C=O bond. Because hydrogen bonding is a stronger intermolecular force than dipole–dipole interactions butan-1-ol will have a higher boiling point than butanal.

17 **(a)** **(i)**



PBr_3



SF_6

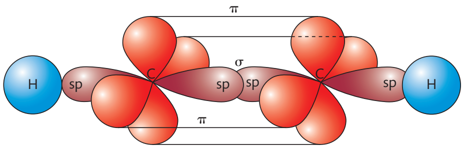
(ii) There are four electron domains around the central P atom in PBr_3. Because three of these are bonded pairs the shape of PBr_3 is trigonal pyramidal. Because the lone pair repels more than the bonded pairs the bond angle will be <109.5°.(Experimentally observed value is 101°.)

There are six electron domains around the central S atom in SF_6. Because all of these are bonded pairs the shape of SF_6 is octahedral and the bond angles are all 90°.

(iii) The P–Br bonds in PBr_3 are polar ($\Delta\chi = 0.7$). Because the molecule is not symmetrical the dipoles created by the three P–Br bonds do not cancel so the molecule has a net dipole and PBr_3 is a polar molecule.

The S–F bonds in SF_6 are highly polar ($\Delta\chi = 1.5$). However, because the molecule is symmetrical the dipoles created by the six S–F bonds cancel so there is no net dipole and SF_6 is a non-polar molecule.

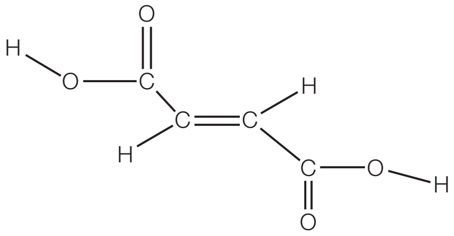
(b) **(i)** The structure of ethyne showing the orbital overlap and formation of σ and π bonds is given below.



σ bonds are formed from the axial overlap of two sp hybrid orbitals and sp hybrids with 1s hydrogen orbitals. The electron density in σ bonds is centred along the inter-nuclear axis (see page 198).

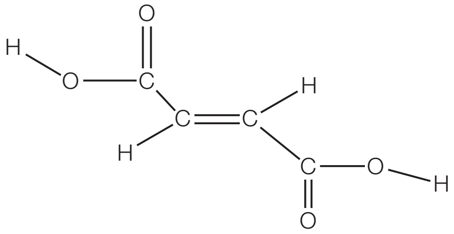
π bonds are formed by the side-on overlap of the unhybridized p orbitals on the two carbon atoms and the electron density of the π bonds is above and below the inter-nuclear axis (see page 199).

(ii) The structure of *trans*-but-2-ene-1,4-dioic acid is given below.

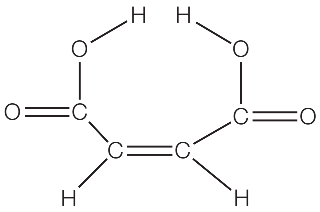


Each single bond is a σ bond. The double bonds contain one σ and one π bond so there are a total of 11 σ and three π bonds.

(iii)



trans-but-2-ene-1,4-dioic acid

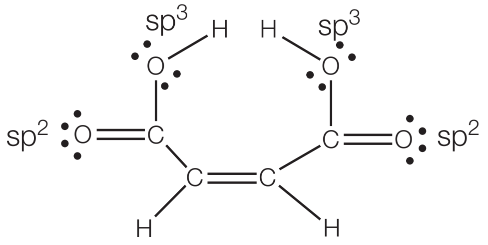


cis-but-2-ene-1,4-dioic acid

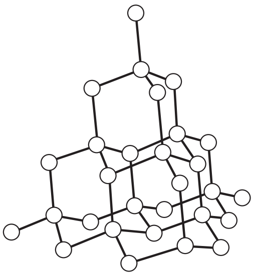
The two isomers of but-2-ene-1,4-dioic acid have different intermolecular forces. In the *trans*-isomer strong *inter*molecular forces exist due to hydrogen bonding between the molecules and it has a high melting point. In the *cis*-isomer *intra*molecular hydrogen bonding occurs between the acid functional groups. This results in weaker intermolecular forces between molecules and a lower melting point for the *cis*-isomer.

(iv) The close arrangement of the two acid functional groups in *cis*-but-2-ene-1,4-dioic acid allows for an internal condensation reaction to occur on heating and a water molecule is eliminated to form the cyclic anhydride.

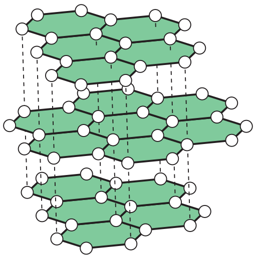
(c) Each oxygen atom with four electron domains is sp^3 hybridized and each oxygen atom with three electron domains is sp^2 hybridized.



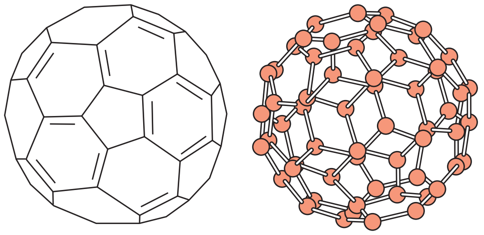
18 **(a)** Diamond is a covalent network structure where the carbon atoms are sp^3 hybridized and every carbon atom is covalently bonded to four others, forming a repeating tetrahedral arrangement with 109.5° bond angles. Diamond does not have delocalized electrons so it is not able to conduct electricity.



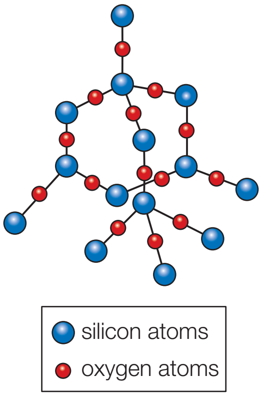
Graphite is a covalent network structure where the carbon atoms are sp^2 hybridized and each atom is covalently bonded to three other atoms, with bond angles of 120°, forming sheets of interlinked hexagons. London dispersion forces exist between the sheets. Electrons are delocalized over each sheet so 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.

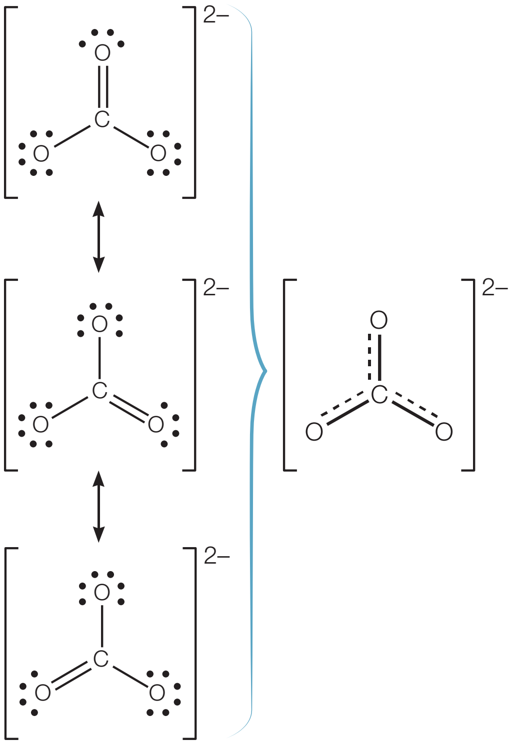
CO_2 is a discrete molecule with weak London dispersion forces between the molecules. These intermolecular forces are weak and easy to overcome so CO_2 has a low boiling point and is a gas at room temperature.

(c) The Lewis structure of carbon monoxide is:

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.

(d) The delocalization of pi electrons occurs when a multiple bond can occur in more than one position within a molecule. When this situation occurs two or more equally valid Lewis structures (resonance structures) can be drawn for the molecule. The reality is that the pi bond is shared over all the positions and is represented as a partial bond occurring in all positions.

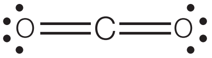
In the carbonate ion the central carbon atom is sp^2 hybridized, giving a trigonal pyramidal shape and there are three resonance structures:



Because the pi electrons are delocalized over the three positions this reduces electron–electron repulsions and increases the stability of the carbonate ion.

(e) Hybridization is the mixing of atomic orbitals to form new hybrid orbitals. The number of hybrid orbitals that are formed is equal to the number of atomic orbitals that mix to form the hybrids.

In carbon dioxide the carbon atom has two electron domains so it is sp hybridized. One p orbital has mixed with the s orbital to form two sp hybrid orbitals, leaving two unhybridized p orbitals able to form the π bonds.

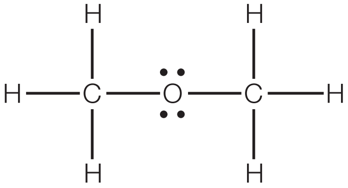


In diamond (see picture in Q18(a)) the carbon atoms have four electron domains so they are sp^3 hybridized. The three p orbitals have mixed with the s orbital to form four sp^3 hybrid orbitals.

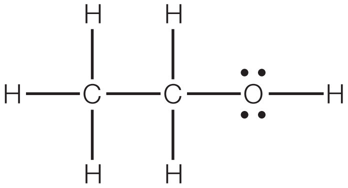
In graphite (see picture in Q18(a)) the carbon atoms have three electron domains so they are sp^2 hybridized. Two p orbitals have mixed with the s orbital to form three sp^2 hybrid orbitals, leaving one unhybridized p orbital able to form a pi bond.

In the carbonate ion (see picture Q18(d)) the carbon atom has three electron domains so it is sp^2 hybridized. Two p orbitals have mixed with the s orbital to form three sp^2 hybrid orbitals, leaving one unhybridized p orbital able to form a pi bond.

19 Consider the Lewis structures (see Chapter 10 for structures of organic compounds):



2-methoxymethane

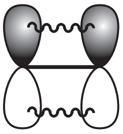


ethanol

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).

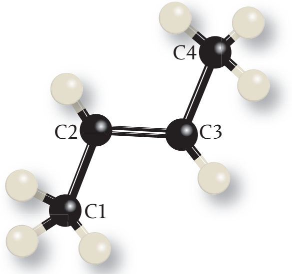
In ethanol hydrogen-bonding intermolecular forces can occur as there is a hydrogen atom bonded to a highly electronegative oxygen atom and a lone pair of electrons on a highly electronegative oxygen atom. As hydrogen bonding is significantly stronger than London dispersion forces and dipole–dipole interactions, ethanol will have a much higher boiling point (78 °C) than methoxymethane.

20 **(a)** The pi bond is formed from side-on overlap of p orbitals on C2 and C3:



π-bonding overlap

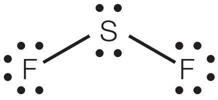
(b)



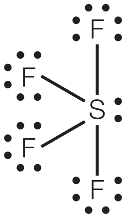
C1 has four electron domains so it is sp^3 hybridized.

C2 has three electron domains so it is sp^2 hybridized.

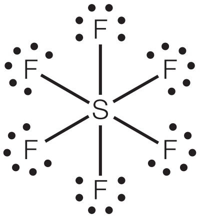
21



SF_2



SF_4



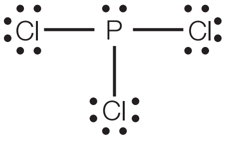
SF_6

In SF_2 there are four electron domains around the central atom and two of these are bonded so the molecule has a bent shape.

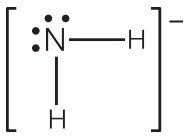
In SF_4 there are five electron domains around the central atom and four of these are bonded so the molecule has a see-saw shape.

In SF_6 there are six electron domains around the central atom and all six are bonded so the molecule has an octahedral shape.

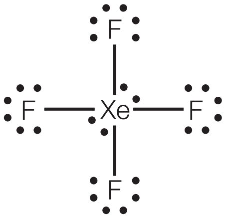
22 **(a)**



PCl_3



NH_2^-



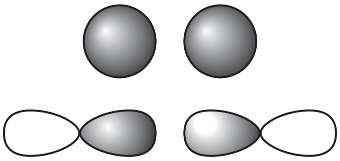
XeF_4

In PCl_3 there are four electron domains around the central atom and three of these are bonded so the molecule has a trigonal pyramidal shape. The bond angles will be <109.5°.

In NH_2^- there are four electron domains around the central atom and three of these are bonded so the ion has a bent shape. The bond angles will be ≈ 105°.

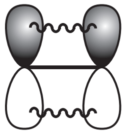
In XeF_4 there are six electron domains around the central atom and four of these are bonded so the molecule has a square planar shape. The bond angles will be 90°.

(b) **(i)** Sigma bonds between two carbon atoms are formed from axial overlap of two s or p orbitals (or sp_x hybrids).



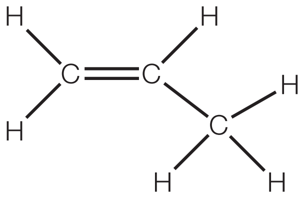
σ bonding overlap of s orbitals (top) and p orbitals (bottom)

Pi bonds between two carbon atoms are formed from side-on overlap of two p orbitals.



π-bonding overlap

(ii)

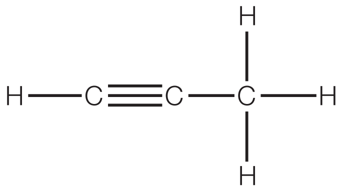


propene

All single bonds are σ bonds, double bonds contain one σ bond and one π bond. Overall propene has eight σ bonds and one π bond.

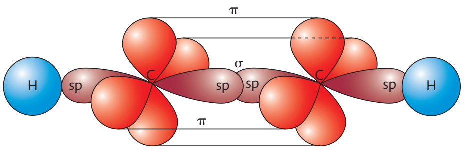
(iii) The bond angles on the carbons of propene with three electron domains are 120° as this is a trigonal planar arrangement. The bond angles on the carbon with four electron domains are 109.5° as this is a tetrahedral arrangement.

(iv)

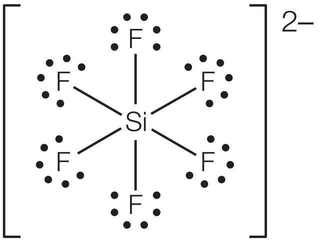


propyne

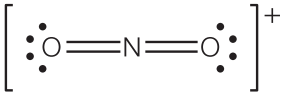
A triple bond consists of one σ bond and two π bonds. To form a triple bond the two carbon atoms must be sp hybridized; the σ bond forms from the overlap of a sp hybrid on each carbon atom and the two pi bonds are formed from the overlap of the two unhybridized p orbitals on each carbon.



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



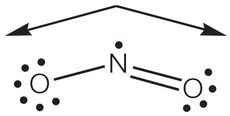
SiF_6^{2-}

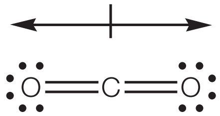
(ii) 

NO_2^+

SiF_6^{2-} has six electron domains and all six are bonded pairs so it has an octahedral shape. All bond angles will be 90° and 180° (for atoms on the same axis).

NO_2^+ has two electron domains and both are bonded pairs so the shape is linear and the bond angle is 180°.

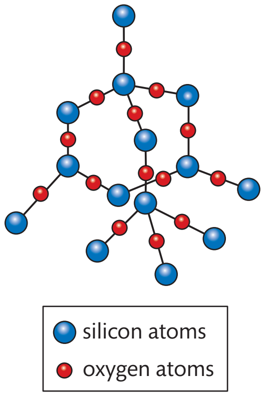
(b) 



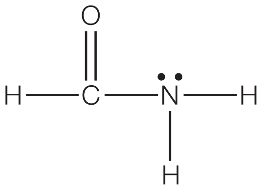
NO_2 has a bent shape and the dipoles created by the polar N–O bonds do not cancel so NO_2 has a net dipole and it is therefore a polar molecule.

CO_2 is a linear molecule and the dipoles created by the polar C–O bonds cancel each other so CO_2 does not have a net dipole and is therefore a non-polar molecule.

(c) SiO_2 is a covalent network solid with each silicon covalently bonded to four oxygen atoms and each oxygen atom covalently bonded to two silicon atoms, giving the empirical formula SiO_2.

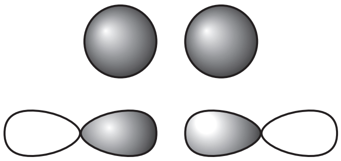


(d) **(i)** The name of $HCONH_2$ is methanamide (see Chapter 10 for naming and structures of organic compounds).



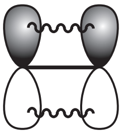
(ii) Hybridization is the mixing of atomic orbitals to form new hybrid orbitals. The number of hybrid orbitals that is formed is equal to the number of atomic orbitals that mix to form the hybrids.

(iii) Sigma bonds between atoms are formed from axial overlap of two s or p orbitals (or sp_x hybrids).



σ bonding overlap of s orbitals (top) and p orbitals (bottom)

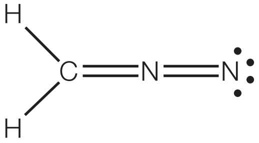
Pi bonds between two atoms are formed from side-on overlap of two p orbitals.



π-bonding overlap

(iv) In $HCONH_2$ there are three electron domains around the carbon atom so it is sp^2 hybridized. There are four electron domains around the nitrogen atom so it is sp^3 hybridized.

24 Formal charge (FC) on atom = valence electrons $-\left(\frac{1}{2}\text{ bonding electrons} + \text{lone pair electrons}\right)$

(a) **(i)** 

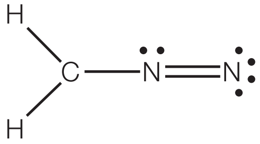
$$\text{FC (H)} = 1 - \left(\frac{1}{2} \times 2\right) = 0$$

$$\text{FC (C)} = 4 - \left(\frac{1}{2} \times 8\right) = 0$$

$$\text{FC (N1)} = 5 - \left(\frac{1}{2} \times 8\right) = +1$$

$$\text{FC (N2)} = 5 - \left(\frac{1}{2} \times 4 + 4\right) = -1$$

(ii)



$$\text{FC (H)} = 1 - \left(\frac{1}{2} \times 2\right) = 0$$

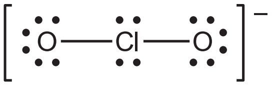
$$\text{FC (C)} = 4 - \left(\frac{1}{2} \times 6\right) = +1$$

$$\text{FC (N1)} = 5 - \left(\frac{1}{2} \times 6 + 2\right) = 0$$

$$\text{FC (N2)} = 5 - \left(\frac{1}{2} \times 4 + 4\right) = -1$$

Although both structures only contain two atoms with small formal charges the first structure will be preferred as the carbon in the second structure only has six electrons and an incomplete valence shell.

(b) (i)

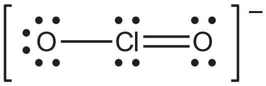


$$\text{FC (O1)} = 6 - \left(\frac{1}{2} \times 2 + 6\right) = -1$$

$$\text{FC (Cl)} = 7 - \left(\frac{1}{2} \times 4 + 4\right) = +1$$

$$\text{FC (O2)} = 6 - \left(\frac{1}{2} \times 2 + 6\right) = -1$$

(ii)



$$\text{FC (O1)} = 6 - \left(\frac{1}{2} \times 2 + 6\right) = -1$$

$$\text{FC (Cl)} = 7 - \left(\frac{1}{2} \times 6 + 4\right) = 0$$

$$\text{FC (O2)} = 6 - \left(\frac{1}{2} \times 4 + 4\right) = 0$$

The second structure will be preferred as it has fewer atoms with a formal charge.

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.

7 One problem is that it is difficult to know exactly how many valence electrons to assign to a transition metal when it forms a complex ion. The calculation of formal charges also involves treating the metal–ligand bonds as being purely covalent, but in reality these bonds often have some ionic character. Formal charge values obtained for the central metal in complex ions can be negative, which implies this model may not be appropriate for complex ions.

8 In the polar winter small amounts of water vapour freeze into ice crystals in the atmosphere. Reactions that occur on the surface of these crystals produce species such as $Cl_2\bullet$, which later dissociates into $Cl\bullet$, which is an ozone-depleting substance.

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 produces 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, $q = mc\Delta T$

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

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

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

$q = 9392\text{ J}$

Moles of glucose burnt: $n(C_6H_{12}O_6)$

$$= \frac{m}{M\,(C_6H_{12}O_6)} = \frac{1.10\text{ g}}{180.18\text{ g mol}^{-1}} = 6.11 \times 10^{-3}\text{ mol}$$

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.

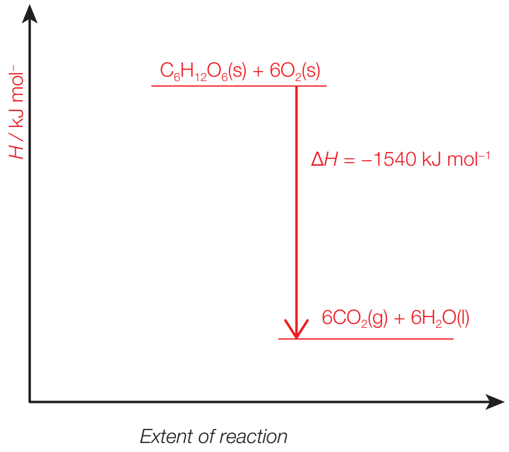
Enthalpy of combustion per mole, $\Delta H_c =$

$$\frac{-9392\text{ J}}{6.11 \times 10^{-3}\text{ mol}}$$

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

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

(b)



11 $q = mc\Delta T$

- Temperature increase, $\Delta T = 6.5\text{ °C} = 6.5\text{ K}$
- Specific heat capacity of water (from Section 2 in the IB data booklet) $= 4.18\text{ J g}^{-1}\text{ K}^{-1}$
- Mass of water = 150.00 g

$q = 150.0\text{ g} \times 4.18\text{ J g}^{-1}\text{ K}^{-1} \times 6.5\text{ K} = 4100\text{ J}$

$$0.0500\text{ g is } \frac{0.0500\text{ g}}{30.97\text{ g mol}^{-1}} = 1.61 \times 10^{-3}\text{ mol of}$$

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.

$$\Delta H^{\ominus}_c = \frac{-q}{n} = \frac{-4100\text{ J}}{1.61 \times 10^{-3}\text{ mol}}$$

$$= -2.5 \times 10^6\text{ J mol}^{-1} = -2500\text{ kJ mol}^{-1}$$

(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, $\Delta T = 50.0\text{ °C} = 50.0\text{ K}$
- Specific heat capacity of water (from Section 2 in the IB data booklet), $c = 4.18\text{ J g}^{-1}\text{ K}^{-1}$
- 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})

$q = 1000\text{ g} \times 4.18\text{ J g}^{-1}\text{ K}^{-1} \times 50.0\text{ K} = 209\text{ kJ}$

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.

$n(CuSO_4) = cV = 1.00\text{ mol dm}^{-3} \times 1.00\text{ dm}^3 = 1.00\text{ mol}$

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 g cm^{-1}, then 50.00 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 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 cm^3 of water.

As the density of water is 1.00 g cm^{-3} the 100.00 cm^3 has a mass of 100.00 g.

Mass of solution = 100.00 g + 5.035 g = 105.04 g

$q = mc\Delta T = 105.04\text{ g} \times 4.18\text{ J g}^{-1}\text{ K}^{-1} \times (21.79 - 25.55)\text{ K} = -1650\text{ J}$

$$n(NH_4Cl) = \frac{m}{M}\ \frac{5.350\text{ g}}{53.50\text{ g mol}^{-1}} = 0.1000\text{ mol}$$

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:

$\text{C(graphite)} + O_2\text{(g)} \rightarrow CO_2\text{(g)}$	$\Delta H^{\ominus} = -394\text{ kJ}$
$CO_2\text{(g)} \rightarrow \text{CO(g)} + \tfrac{1}{2}O_2\text{(g)}$	$\Delta H^{\ominus} = +283\text{ kJ}$
$\text{C(graphite)} + \tfrac{1}{2}O_2\text{(g)} \rightarrow \text{CO(g)}$	$\Delta H^{\ominus} = (-394 + 283)\text{ kJ} = -111\text{ kJ}$

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:

$CO_2(g) \rightarrow CO(g) + ½O_2(g)$	$\Delta H_1 = +283$ kJ mol^{-1}
$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$	$\Delta H_2 = ½ \times -572$ 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 $O_2(g)$.

$3C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3COCH_3(l)$, $\Delta H^{\ominus}_{f} = -248$ 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 $Fe_3O_4(s) + 2C(graphite) \rightarrow 3Fe(s) + 2CO_2(g)$

$\Delta H_{reaction} = \Sigma\Delta H^{\ominus}_{f}(products) - \Sigma\Delta H^{\ominus}_{f}(reactants)$

Recognizing that C(graphite) and Fe(s) are already in their standard states ($\Delta H^{\ominus}_{f} = 0$):

$\Delta H_{reaction} = 2\Delta H^{\ominus}_{f}(CO_2(g)) - \Delta H^{\ominus}_{f}(Fe_3O_4(s))$

$= (2 \times -394) - (-1118\ )$ kJ mol^{-1}

$= +330$ kJ mol^{-1}

26 $2NO_2(g) \rightarrow N_2O_4(g)$

$\Delta H_{reaction} = \Sigma\Delta H^{\ominus}_{f}(products) - \Sigma\Delta H^{\ominus}_{f}(reactants)$

$= \Delta H^{\ominus}_{f}(N_2O_4(g)) - 2\Delta H^{\ominus}_{f}(2NO_2(g))$

$= +9.2 - (2 \times +33.2)$ kJ mol^{-1}

$= -57.2$ kJ mol^{-1}

27 **D** $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

$\Delta H_{reaction} = \Sigma\Delta H^{\ominus}_{f}(products) - \Sigma\Delta H^{\ominus}_{f}(reactants)$

Recognizing that $O_2(g)$ is already in its standard state ($\Delta H^{\ominus}_{f} = 0$):

$\Delta H_{reaction} = 2\Delta H^{\ominus}_{f}(H_2O(l)) - 2\Delta H^{\ominus}_{f}(H_2O_2(g))$

$= (2 \times -286) - (2 \times -188)$ kJ mol^{-1}

$= -196$ kJ mol^{-1}

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

$\Delta H_{reaction} = \Sigma\Delta H^{\ominus}_{f}(products) - \Sigma\Delta H^{\ominus}_{f}(reactants)$

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.

$\Delta H_{reaction} = \Delta H^{\ominus}_{f}(CO_2(g)) - 2\Delta H^{\ominus}_{f}(MgO(s))$

$= -394 - (2 \times -602)$ 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.

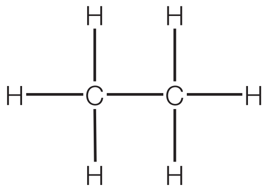
31 **C** Reaction I is the deposition of carbon dioxide, which is an exothermic process. (If it takes energy to convert a solid to gas then the opposite process will release energy.)

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 $H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3$

$\Delta H = \Sigma E$(bonds broken) – ΣE(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

$\Delta H = \Sigma E$(bonds broken) – ΣE(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

$\Delta H = \Sigma E$(bonds broken) – ΣE(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

$\Delta H = \Sigma E$(bonds broken) – ΣE(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

$\Delta H = \Sigma E$(bonds broken) – ΣE(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.)

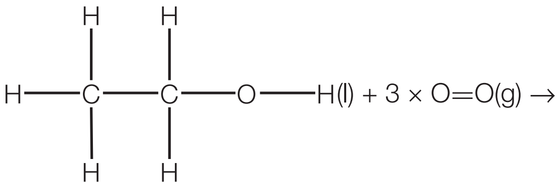
37 **C** $C_2H_4(g) + F_2(g) \rightarrow CH_2FCH_2F(g)$

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

$\Delta H = \Sigma E$(bonds broken) – ΣE(bonds formed) = (+2514 + (–3025)) kJ mol^{-1} = **–511 kJ mol^{-1}**

(Note that the bond enthalpies given in the question on page 234 differ from those in Section 11 of the IB data booklet, particularly for the C–F bond!)

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



$$H_3C{-}CH_2{-}O{-}H(l) + 3 \times O{=}O(g) \rightarrow$$

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

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 (see page 194). 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 $= \dfrac{498\ \text{kJ mol}^{-1}}{6.02 \times 10^{23}\ \text{mol}^{-1}} = 8.27 \times 10^{-22}$ 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 (see page 194). Thus, less energy is required to dissociate O_3 than O_2. Longer wavelength radiation of lower energy is needed to dissociate O_3.

42 **A** As the electron is attracted to the positively charged nucleus of the Cl atom, the process is exothermic. All the other processes are endothermic (i.e. require energy to take place).

43 **C** Electron affinity is the enthalpy change that occurs when one mole of gaseous atoms attracts one mole of electrons to form one mole of gaseous anions.

For potassium the equation that represents its electron affinity is **C**: $K(g) + e^- \rightarrow K^-(g)$.

A is incorrect as it represents the first ionization of potassium. B does not balance (no charges on the left and a total of 2$^-$ on the right.) D is incorrect as the electron is being added to a potassium ion and not an atom.

44 **D** The enthalpy of atomization for an element is the formation of 1 mole of gaseous atoms from the element in its standard state. The standard state of bromine is $Br_2(l)$ so the enthalpy of atomization corresponds to equation D: $\frac{1}{2}Br_2(l) \rightarrow Br(g)$.

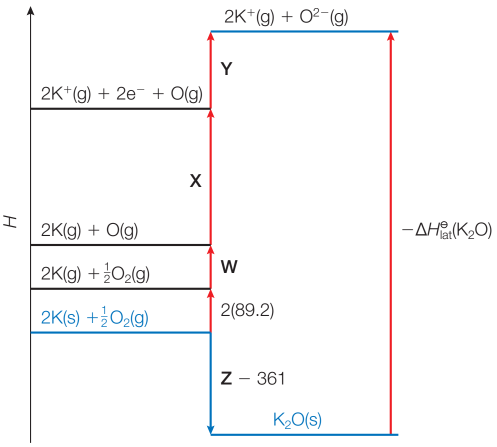
A is incorrect as bromine is not in its standard state and forms 2 moles of Br atoms.

B is incorrect as it forms 2 moles of Br atoms.

C is incorrect as bromine is not in its standard state.

45 **(a)** The lattice enthalpy can be defined as the energy required to turn 1 mole of an ionic solid into its constituent ions in the gaseous state, therefore the equation corresponding to the lattice enthalpy of potassium oxide is:

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



(Note that in the diagram for part (b) the arrow representing the lattice enthalpy has been drawn for the reverse of this process and has been labelled as $-\Delta H_{lat}^{\ominus}(K_2O)$*.)*

(b) **W** corresponds to the enthalpy of atomization of oxygen, $\Delta H_{atom}^{\ominus}(O)$: $\frac{1}{2}O_2(g) \rightarrow O(g)$.

It also corresponds to half the bond enthalpy of the O=O bond E(O=O) (the bond enthalpy is the energy required to break 1 mole of the bonds but that would give two oxygen atoms hence the need to halve the bond enthalpy.)

X corresponds to twice the first ionization energy of potassium, $\Delta H_i^{\ominus}(K)$: $2 \times (K(g) \rightarrow K^+(g) + e^-)$.

Y is the sum of the first and second electron affinities of oxygen, $\Delta H_{e1}^{\ominus}(O) + \Delta H_{e2}^{\ominus}(O)$ (the gaseous oxygen atoms are turned into gaseous O^{2-} ions by the successive addition of two electrons: $O(g) + e^- \rightarrow O^-(g)$ then $O^-(g) + e^- \rightarrow O^{2-}(g)$).

Z is the enthalpy of formation of potassium oxide, $\Delta H_f^{\ominus}(K_2O)$: $2K(s) + \frac{1}{2}O_2(g) \rightarrow K_2O(s)$ (the enthalpy of formation is the enthalpy change that occurs when one mole of a substance is formed from its constituent elements in their standard states).

(c) As $\Delta H_{lat}^{\ominus}(K_2O)$ corresponds to the equation $K_2O(s) \rightarrow 2K^+(g) + O^{2-}(g)$, the desired value can be calculated by starting at $K_2O(S)$ and summing the enthapies of the individual processes until reaching the desired products, $2K^+(g) + O^{2-}(g)$.

$\Delta H_{lat} = [-Z + 2(89.2) + W + X + Y]$ kJ mol^{-1}

$= -(-361) + (2 \times 89.2) + (\frac{1}{2} \times 498) + (2 \times 419) + (-141 + 753)$ kJ mol^{-1}

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

46 **B** Lattice enthalpy is the energy required to form gaseous ions from an ionic solid: $MX(s) \rightarrow M^+(g) + X^-(g)$. Lattice enthalpy increases in magnitude with increasing charge of the ions and decreasing ionic radius.

For the four ionic compounds given, the greatest lattice enthalpy will occur for MgO or CaO as these both have 2^+ and 2^- ions whereas Na_2O has 1^+ and 2^- ions and KCl has 1^+ and 1^- ions. As Mg^{2+} has a smaller ionic radius than Ca^{2+}, MgO will have the greatest lattice enthalpy.

47 Lattice enthalpy is the energy required to form gaseous ions from an ionic solid: $MX(s) \rightarrow M^+(g) + X^-(g)$. Lattice enthalpy increases in magnitude with increasing charge of the ions and decreasing ionic radius. The ionic compounds all have the same cation so the differences in lattice enthalpy are due to the halide ions. As halide ions become larger as we go down the group their increasing size results in a lower charge density on the anion (the 1^- charge is spread over a larger volume), therefore the electrostatic attraction to the positive Na^+ ion will decrease and the lattice enthalpies decrease as we go down the group: $\Delta H_{lat}^\ominus(NaF) > \Delta H_{lat}^\ominus(NaCl) > \Delta H_{lat}^\ominus(NaBr) > \Delta H_{lat}^\ominus(NaI)$.

48 Lattice enthalpy is the energy required to form gaseous ions from an ionic solid: $MX(s) \rightarrow M^+(g) + X^-(g)$. Lattice enthalpy increases in magnitude with increasing charge of the ions and decreasing ionic radius.

As MgO contains Mg^{2+} and O^{2-} ions it will have a larger lattice enthalpy than NaCl, which contains Na^+ and Cl^- ions, as there is significantly greater electrostatic attraction between 2^+ and 2^- ions than between 1^+ and 1^- ions.

The smaller ionic radii of Mg^{2+} and O^{2-} compared to Na^+ and Cl^-, respectively, also contributes to an increased electrostatic attraction between the ions in MgO and a larger lattice enthalpy, but this is a lesser effect than that of the greater charge on the ions.

49 **C** Lattice enthalpy is the energy required to form gaseous ions from an ionic solid: $MX(s) \rightarrow M^+(g) + X^-(g)$. Lattice enthalpy increases in magnitude with increasing charge of the ions and decreasing ionic radius.

For the four ionic compounds given, the greatest lattice enthalpy will occur for magnesium bromide ($MgBr_2$) and calcium bromide ($CaBr_2$) as these both have 2^+ and 1^- ions whereas sodium chloride (NaCl) and potassium chloride (KCl) both have 1^+ and 1^- ions. As Mg^{2+} has a smaller ionic radius than Ca^{2+}, $MgBr_2$ will have the greatest lattice enthalpy.

50 **A** Lattice enthalpy is the energy required to form gaseous ions from an ionic solid: $MX(s) \rightarrow M^+(g) + X^-(g)$. Lattice enthalpy increases in magnitude with increasing charge of the ions and decreasing ionic radius.

NaF contains Na^+ ions and F^- ions, $MgCl_2$ contains Mg^{2+} ions and Cl^- ions. The higher charge of the magnesium ion compared to the sodium results in a large lattice enthalpy for $MgCl_2$ compared to NaF.

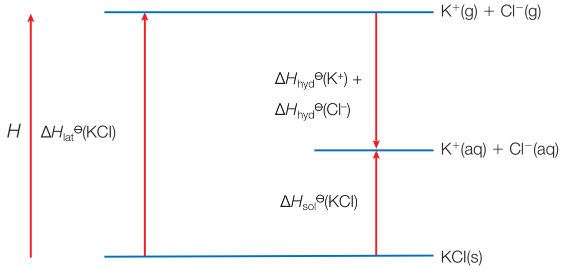
The greater charge on Mg^{2+} vs Na^+ has a much more significant effect on the lattice enthalpy than the smaller size of the fluoride ion in NaF compared with the chloride ion in NaCl.

51 Lattice enthalpy is the energy required to form gaseous ions from an ionic solid: $MX(s) \rightarrow M^+(g) + X^-(g)$. Lattice enthalpy increases in magnitude with increasing charge of the ions and decreasing ionic radius. As Ag^+ has a smaller ionic radius than K^+ the lattice enthalpy of AgBr is larger than that of KBr as the electrostatic attraction between the ions in AgBr is stronger.

Another reason is that the AgBr bond is not purely ionic and has more covalent character. This increases the bond strength above what would be predicted for a purely ionic bond and results in a larger lattice enthalpy.

52 K^+ and F^- have similar ionic radii but the enthalpy of hydration of the F^- ion (-504 kJ mol^{-1}) is significantly more exothermic than the enthalpy of hydration of K^+ (-340 kJ mol^{-1}). This suggests that there is an additional electrostatic attraction between the F^- ion and the polar water molecules other than ion–dipole interactions. This extra attraction is hydrogen bonding: due to the small size of the F^- ion, its lone pairs can form hydrogen bonds to the hydrogen atoms in the highly polar water molecules.

53 **(a)**



From the energy cycle we can see that:

$\Delta H_{sol}^{\ominus}(KCl) = \Delta H_{lat}^{\ominus}(KCl) + \Delta H_{hyd}^{\ominus}(K^+) + \Delta H_{hyd}^{\ominus}(Cl^-)$

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

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

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

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

The large inaccuracy is based on the calculated value being found by the difference between much larger values. Even a small variation in either of the large values will result in a large percentage difference in the calculated value compared to the experimental value.

54 **B** An entropy change close to zero ($\Delta S \approx 0$) will only occur if the reaction proceeds with little change in disorder. This will only happen if there is no change of state and/or the reactants and products contain the same moles of gases.

B: $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is the only reaction that does not involve a change of state or a change in the number of gas molecules.

55 **C** An increase in entropy is associated with an increase in disorder.

Reaction I decreases entropy because liquids are more ordered than gases, reaction II increases entropy because two moles of gas have more entropy than one mole of gas and reaction III increases entropy because aqueous ions have more entropy than ions in a lattice.

56 **A** A solid is turning into a gas; there is an increase in disorder and an increase in entropy so ΔS is positive. Intermolecular forces of attraction are overcome as the solid turns into a gas, so ΔH is positive and the change is endothermic. (It takes energy to convert a solid to a liquid.)

57 **D** An increase in entropy is associated with an increase in disorder.

In reaction D a solid and solution react to give products, one of which is a gas. Gases are more disordered than solids and solutions, which results in a large increase in entropy.

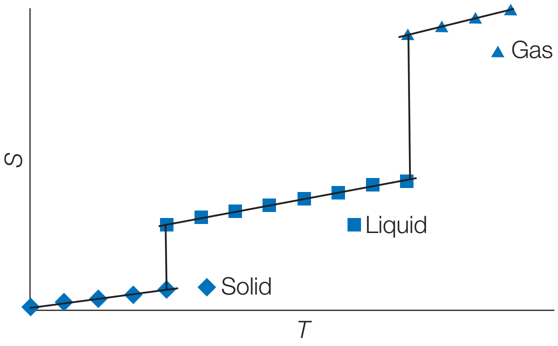
In reaction A the reactants are solutions and a solid is formed as one of the products. As solids are more ordered than solutions this results in a large decrease in entropy. In reaction B there are two moles of gases for both reactants and products so they have similar disorder and there will be only a small change in entropy. In reaction C there are two moles of gaseous reactants but only one mole of gaseous product so this results in an increase in order and a decrease in entropy.

58 **(a)** ΔS is negative. Two moles of gaseous products are more ordered and have less entropy than four moles of gaseous reactants.

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

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

59



60 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Page 252 of the textbook gives these entropy values:

$H_2(g) = 131\ J\ K^{-1}\ mol^{-1}$

$N_2(g) = 191\ J\ K^{-1}\ mol^{-1}$

$NH_3(g) = 193\ J\ K^{-1}\ mol^{-1}$

$\Sigma\Delta S^{\ominus}_{\text{reaction}} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants}) = ((2 \times +193) - (+191 + 3 \times +131))\ \text{J K}^{-1}\ \text{mol}^{-1} = -198\ \text{J K}^{-1}\ \text{mol}^{-1}$

The value is negative, as expected, since the two moles of gas produced have less entropy than the four moles of reactant gas.

61 The standard state of methane is $CH_4(g)$, so to show its formation from its elements in their standard states we write:

$C(\text{graphite}) + 2H_2(g) \rightarrow CH_4(g)$

Page 252 of the textbook gives these entropy values:

$C(\text{graphite}) = 5.7\ \text{J K}^{-1}\ \text{mol}^{-1}$

$H_2(g) = 131\ \text{K}^{-1}\ \text{mol}^{-1}$

$CH_4(g) = 186\ \text{J K}^{-1}\ \text{mol}^{-1}$

$\Sigma\Delta S^{\ominus}_{\text{reaction}} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

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

The value is negative, as expected, since one mole of gas product has less entropy than the two moles of reactant gas.

62 **C** $NH_4Cl(aq)$ has a larger entropy than $NH_4Cl(s)$ so the entropy change of the system (reaction) drives the process.

A is false – exothermic process are energetically favourable. B is not true – the bonds in $NH_4Cl(s)$ are stronger than the ion–dipole interactions between the hydrated ions and water, which is why the process is endothermic. D is wrong because the decrease in temperature represents heat loss from the surroundings, which is associated with a decrease in the entropy of the surroundings.

63 **(a)** Section 13 of the IB data booklet gives the enthalpy of combustion of hydrogen, which is the same as the enthalpy of formation of liquid water:

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l),\ \Delta H = -286\ \text{kJ mol}^{-1}$

The question gives us the enthalpy of formation of solid water (ice):

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(s),\ \Delta H = -292\ \text{kJ mol}^{-1}$

For the reaction $H_2O(s) \rightarrow H_2O(l)$

$\Delta H^{\ominus} = \Sigma\Delta H^{\ominus}_f(\text{products}) - \Sigma\Delta H^{\ominus}_f(\text{reactants})$

$= -286 - (-292) = +6\ \text{kJ mol}^{-1}$

(b) We need to recall the formula

$\Delta G^{\ominus}_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$

Ice will begin melting at a temperature when $\Delta G = 0$. Rearranging the formula we find that

$T = \dfrac{\Delta H^{\ominus}_{\text{reaction}}}{\Delta S^{\ominus}_{\text{reaction}}}$

$= \dfrac{6000\ \text{J mol}^{-1}}{22.0\ \text{J K}^{-1}\ \text{mol}^{-1}} = 273\ \text{K} = 0\ °\text{C}$ (which is rather what you would expect)

*(Note that the units for $\Delta H^{\ominus}_{\text{reaction}}$ were converted from kJ mol^{-1} to **J** mol^{-1} to be compatible with the units of $\Delta S^{\ominus}_{\text{reaction}}$, which are in **J** $\text{K}^{-1}\ \text{mol}^{-1}$.*

64 **A** We need to recall the formula

$\Delta G = \Delta H - T\Delta S$

The reaction is spontaneous if ΔG is negative.

When T is very low, $\Delta G \approx \Delta H$. For the reaction to be 'spontaneous at low temperatures', ΔH must be negative.

When T is very high, $\Delta G \approx -T\Delta S$. For the reaction to be 'non-spontaneous at higher temperatures', ΔS must be negative, making $-T\Delta S$ positive and so making ΔG positive.

65 **D** We need to recall the formula

$\Delta G = \Delta H - T\Delta S$

The reaction is spontaneous if ΔG is negative.

When T is very low, $\Delta G \approx \Delta H$. For the reaction to be 'not spontaneous at low temperatures', ΔH must be positive.

When T is very high, $\Delta G \approx -T\Delta S$. For the reaction to be 'spontaneous at higher temperatures', ΔS must be positive, making $-T\Delta S$ negative, and so making ΔG negative.

66 **B** For a reaction to be spontaneous ΔG has to be negative. At low temperature ΔG(system) ≈ ΔH(system), as $T\Delta S \approx 0$. As ΔH is negative, this reaction will occur at low temperatures. At high temperatures ΔG(system) ≈ $-T\Delta S$(system) as the temperature is sufficiently high as to make the term ΔH(system) negligible. Hence if ΔS(system) is negative then $-T\Delta S$(system) will be a positive value and so the reaction is not spontaneous.

67 **(a)** The reaction requires energy to decompose the carbonate ion so it is endothermic and ΔH is positive.

(b) One mole of gas is produced from a solid reactant, so there will be a large increase in disorder and ΔS will be positive.

(c) We need to recall the formula

$\Delta G = \Delta H - T\Delta S$

The reaction is spontaneous if ΔG is negative.

- When T is very low, $\Delta G \approx \Delta H$. If ΔH is positive, then the reaction will not be spontaneous at low temperatures.
- When T is very high, $\Delta G \approx -T\Delta S$. If ΔS is positive (making ΔG negative), then the reaction will be spontaneous at higher temperatures.

68 **D** We need to recall the formula

$\Delta G = \Delta H - T\Delta S$

The reaction is spontaneous if ΔG is negative.

- When T is very low, $\Delta G \approx \Delta H$. As ΔH is positive, then the reaction will not be spontaneous at low temperatures.
- When T is very high, $\Delta G \approx -T\Delta S$. As ΔS is positive (making ΔG negative), then the reaction will be spontaneous at higher temperatures.

The 1000 K figure comes from the temperature where $\Delta G = 0$. This is the boundary between where the reaction is spontaneous ($\Delta G < 0$) and where it is non-spontaneous ($\Delta G > 0$).

If $\Delta G = 0$ then $T = \dfrac{\Delta H}{\Delta S}$

$$T = \frac{100\ \text{kJ mol}^{-1}}{100\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

$$T = \frac{100\,000\ \text{J mol}^{-1}}{100\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

$$= 1000\ \text{K}$$

69 **C** For a reaction to be spontaneous ΔG has to be negative. At high temperatures ΔG(system) ≈ $-T\Delta S$(system) as the temperature is sufficiently high as to make the term ΔH(system) negligible. Hence, if ΔS(system) is positive then $-T\Delta S$(system) will be a negative value, i.e. the reaction is spontaneous.

70 $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$

$\Delta G_{\text{reaction}} = \Sigma\Delta G^{\ominus}_{\text{reaction}}$ (products) $- \Sigma\ \Delta G^{\ominus}_{\text{reaction}}$ (reactants)

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

The positive value of ΔG shows that the reaction is not spontaneous at this temperature.

71 $\text{CaCO}_3\text{(s)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$

The worked example gives values of $\Delta H^{\ominus}_{\text{reaction}} = +178\ \text{kJ mol}^{-1}$ and $\Delta S^{\ominus}_{\text{reaction}} = 160.8\ \text{J K}^{-1}\ \text{mol}^{-1}$.

It is necessary to convert the units of $\Delta S^{\ominus}_{\text{reaction}}$ from **J** K^{-1} mol^{-1} to **kJ** K^{-1} mol^{-1} so that they are consistent with the units of $\Delta H^{\ominus}_{\text{reaction}}$, which are **kJ** mol^{-1}. $\Delta S^{\ominus}_{\text{reaction}} = 160.8\ \text{J K}^{-1}\ \text{mol}^{-1} = 160.8 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1}$.

$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$

$= 178\ \text{kJ mol}^{-1} - (2000\ \text{K} \times 160.8 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})$

$= 178\ \text{kJ mol}^{-1} - 321.6\ \text{kJ mol}^{-1}$

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

72 **B** The definitions of enthalpy change of formation and free energy change of formation both refer to the formation of a substance from its elements in their standard states. In both cases, if elements are in their standard states they need no reaction to be formed, so the values for $\Delta H^{\ominus}_{f}$ and $\Delta G^{\ominus}_{f}$ are zero. $S^{\ominus} = 0$ describes a situation where there is perfect order and this only occurs at absolute zero ($T = -273.15$ K) so no element in its standard state will have $S^{\ominus} = 0$.

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

(b) Section 12 of the IB data booklet gives the formation entropy for ethanol as $+161 \text{ J K}^{-1} \text{ mol}^{-1}$.

$\Delta S^{\ominus}_{\text{reaction}} = \Sigma S^{\ominus}\text{ (products)} - \Sigma S^{\ominus}\text{ (reactants)}$

$= (+161 - (2 \times +5.7) + (3 \times +65.3) + (\frac{1}{2} \times +102.5)) \text{ J K}^{-1} \text{ mol}^{-1}$

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

(Note that the values for $S^{\ominus}(H_2)$ and $S^{\ominus}(O_2)$ given in this question, $+65.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $+102.5 \text{ J K}^{-1} \text{ mol}^{-1}$, are incorrect. The actual values are $S^{\ominus}(H_2) = +131 \text{ J K}^{-1} \text{ mol}^{-1}$ and $S^{\ominus}(O_2) = +205 \text{ J K}^{-1} \text{ mol}^{-1}$. Using these correct values gives $\Delta S^{\ominus}_{\text{reaction}} = -346 \text{ J K}^{-1} \text{ mol}^{-1}$.)

(c) Section 12 of the IB data booklet gives the formation enthalpy for ethanol as -278 kJ mol^{-1}.

$\Delta G = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$

$= -278 \text{ kJ mol}^{-1} - (500 \text{ K} \times (-98 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}))$

$= -278 \text{ kJ mol}^{-1} + 49 \text{ kJ mol}^{-1}$

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

(Note that the answer of $\Delta G = -105 \text{ kJ mol}^{-1}$ is obtained if $\Delta S^{\ominus}_{\text{reaction}} = -346 \text{ J K}^{-1} \text{ mol}^{-1}$ is used.)

(d) The negative free energy value indicates that this reaction is spontaneous at 500 K.

(e) When T is very low, $\Delta G \approx \Delta H$. If ΔH is negative, then the reaction will be spontaneous at low temperatures.

When T is very high, $\Delta G \approx -T\Delta S$. If ΔS is negative then $-T\Delta S$ will be positive, making ΔG positive, and then the reaction will not be spontaneous at higher temperatures.

74 **C** For a reaction to be spontaneous at all temperatures ΔG has to be negative at all temperatures. At low temperature $\Delta G(\text{system}) \approx \Delta H(\text{system})$, as $T\Delta S \approx 0$, hence exothermic reactions can occur at low temperatures. At high temperatures $\Delta G(\text{system}) \approx -T\Delta S(\text{system})$ as the temperature is sufficiently high as to make the term $\Delta H(\text{system})$ negligible. Hence if $\Delta S(\text{system})$ is positive then $-T\Delta S(\text{system})$ will be a negative value, i.e. the reaction is spontaneous. It is considered to be a complete reaction if $\Delta G(\text{reaction}) < -30 \text{ kJ mol}^{-1}$.

75 **D** If $\Delta G(\text{reaction}) = 0 \text{ kJ mol}^{-1}$ then an equilibrium will be present (see page 262). At this point the free energy will also be at a minimum and the entropy at a maximum. For a better understanding of this answer see the diagram provided on page 336.

76 **B** If the reaction has reversed by changing temperature then $\Delta G(\text{system})$ has changed sign from positive to negative, or vice versa. Given that $\Delta G = \Delta H - T\Delta S$, this can only happen if ΔH and ΔS are either both positive or both negative.

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
positive	negative	positive at all T
negative	positive	negative at all T
positive	positive	positive at low T negative at high T
negative	negative	negative at low T positive at high T

77 All three gases will be present as an equilibrium mixture when $\Delta G_{\text{reaction}}$ is in the range -30 kJ mol^{-1} to $+ 30 \text{ kJ mol}^{-1}$.

We can determine the temperatures which correspond to $\Delta G_{\text{reaction}} = -30 \text{ kJ mol}^{-1}$ and $\Delta G_{\text{reaction}} = +30 \text{ kJ mol}^{-1}$ using the equation $\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$. Note that this requires converting $\Delta S^{\ominus}_{\text{reaction}}$ from units of $\text{J K}^{-1} \text{ mol}^{-1}$ to $\text{kJ K}^{-1} \text{ mol}^{-1}$.

First consider when $\Delta G = -30\ \text{kJ mol}^{-1}$:

$$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$$

$$T = \frac{\Delta G_{\text{reaction}} - \Delta H^{\ominus}_{\text{reaction}}}{\Delta S^{\ominus}_{\text{reaction}}}$$

$$= \frac{-30\ \text{kJ mol}^{-1} - -123\ \text{kJ mol}^{-1}}{-(-128 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})} = 727\ \text{K}$$

Now consider when $\Delta G = +30\ \text{kJ mol}^{-1}$:

$$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$$

$$T = \frac{\Delta G_{\text{reaction}} - \Delta H^{\ominus}_{\text{reaction}}}{\Delta S^{\ominus}_{\text{reaction}}}$$

$$= \frac{+30\ \text{kJ mol}^{-1} - -123\ \text{kJ mol}^{-1}}{-(-128 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})} = 1195\ \text{K}$$

The three gases will be present at temperatures between 727 K and 1195 K.

78 All three gases will be present as an equilibrium mixture when $\Delta G_{\text{reaction}}$ is in the range –30 kJ mol^{-1} to + 30 kJ mol^{-1}.

We can determine the temperatures which correspond to $\Delta G_{\text{reaction}} = -30\ \text{kJ mol}^{-1}$ and $\Delta G_{\text{reaction}} = +30\ \text{kJ mol}^{-1}$ using the equation $\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$. Note that this requires converting $\Delta S^{\ominus}_{\text{reaction}}$ from units of J K^{-1} mol^{-1} to kJ K^{-1} mol^{-1}.

First consider when $\Delta G = -30\ \text{kJ mol}^{-1}$:

$$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$$

$$T = \frac{\Delta G_{\text{reaction}} - \Delta H^{\ominus}_{\text{reaction}}}{\Delta S^{\ominus}_{\text{reaction}}}$$

$$= \frac{-30\ \text{kJ mol}^{-1} - -93\ \text{kJ mol}^{-1}}{-(-198 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})} = 318\ \text{K}$$

Now consider when $\Delta G = +30\ \text{kJ mol}^{-1}$:

$$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$$

$$T = \frac{\Delta G_{\text{reaction}} - \Delta H^{\ominus}_{\text{reaction}}}{\Delta S^{\ominus}_{\text{reaction}}}$$

$$= \frac{+30\ \text{kJ mol}^{-1} - -93\ \text{kJ mol}^{-1}}{-(-198 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1})} = 621\ \text{K}$$

The three gases will be present at temperatures between 318 K and 621 K.

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.

$$q = mc\Delta T \text{ or } \Delta T = \frac{q}{mc}$$

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:

$$\text{Cu}_2\text{O(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow 2\text{CuO(s)} \quad \Delta H^{\ominus} = -144\ \text{kJ mol}^{-1}$$

$$\text{Cu(s)} + \text{Cu}_2\text{O(s)} \rightarrow \text{Cu}_2\text{O(s)} \quad \Delta H^{\ominus} = -11\ \text{kJ mol}^{-1}$$

$$\text{Cu(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CuO(s)} \quad \Delta H^{\ominus} = (-144 - 11)\ \text{kJ mol}^{-1}$$

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:

$\mathbf{2}CH_4(g) + \mathbf{2}O_2(g) \rightarrow \mathbf{2}HCHO(l) + \mathbf{2}H_2O(l) \quad \Delta H^\ominus = \mathbf{2}x$

$\mathbf{2}HCHO(l) + O_2(g) \rightarrow \mathbf{2}HCOOH(l) \quad \Delta H^\ominus = \mathbf{2}y$

$2HCOOH(l) + \tfrac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + H_2O(l) \quad \Delta H^\ominus = \boldsymbol{z}$

$2CH_4(g) + 3\tfrac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + 3H_2O(l) \quad \Delta H^\ominus = 2x + 2y + z$

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.

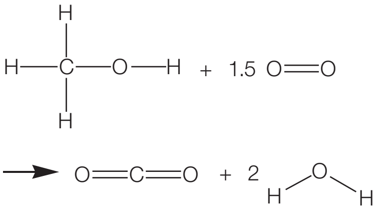
8 The equation provided involves the burning of 2 moles of CO(g). The enthalpy for the burning of 1.00 mole will be half of the enthalpy associated with this equation:

–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)** $\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$



$\Sigma E(\text{bonds broken}) = (3 \times E(C\text{–}H)) + E(C\text{–}O) + E(O\text{–}H) + (1.5 \times E(O{=}O))$

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

$= 2810\ \text{kJ mol}^{-1}$

$\Sigma E(\text{bonds formed}) = 2 \times E(C{=}O) + 4 \times E(O\text{–}H)$

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

$= 3460\ \text{kJ mol}^{-1}$

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed}) = 2810 - 3460\ \text{kJ mol}^{-1} = -650\ \text{kJ mol}^{-1}$

(b) **(i)** $n(CH_3OH) = \dfrac{m}{M(CH_3OH)} = \dfrac{(80.557 - 80.034)\ \text{g}}{32.05\ \text{g mol}^{-1}} = \dfrac{0.523\ \text{g}}{32.05\ \text{g mol}^{-1}} = 0.0163\ \text{mol}$

(ii) $q = mc\Delta T = 20.000\ \text{g} \times 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times (26.4 - 21.5)\ \text{K} = 410\ \text{J}\ (2\ \text{s.f.}) = 0.41\text{kJ}$

(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.

$$\Delta H^\ominus_c = \frac{\text{heat change}}{n(CH_3OH)} = \frac{-410\ \text{J}}{0.0163\ \text{mol}} = -25\ \text{kJ mol}^{-1}$$

(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) = $mc\Delta T = 50.0\ \text{g} \times 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times 48.2\ \text{K} = 1.01 \times 10^4\ \text{J}$ = 10.1 kJ

(c) If the solution became colourless then all of the Cu^{2+} ions have reacted with the zinc powder.

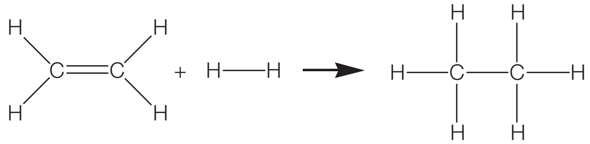
$n(\text{Cu}^{2+}) = cV = 1.00\ \text{mol dm}^{-3} \times \dfrac{50.0}{1000}\ \text{dm}^3 = 0.0500\ \text{mol}$

From the balanced equation, $n(\text{Zn}) = n(\text{Cu}^{2+}) = 0.0500$ mol.

(d) $\Delta H = \dfrac{\text{heat change}}{n(\text{Cu}^{2+})} = \dfrac{-10.1\ \text{kJ}}{0.0500\ \text{mol}}$
$= -202\ \text{kJ mol}^{-1}$

(The enthalpy change is negative as this is an exothermic reaction and heat is released by the reaction.)

11 **(a)** $\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$



$\Sigma E(\text{bonds broken}) = (4 \times E(\text{C–H})) + E(\text{C=C}) + E(\text{H–H})$

$= (4 \times 414) + 614 + 436\ \text{kJ mol}^{-1}$

$= 2706\ \text{kJ mol}^{-1}$

$\Sigma E(\text{bonds formed}) = (6 \times E(\text{C–H})) + E(\text{C–C})$

$= (6 \times 414) + 346\ \text{kJ mol}^{-1}$

$= 2830\ \text{kJ mol}^{-1}$

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$
$= 2706 - 2830\ \text{kJ mol}^{-1} = -124\ \text{kJ mol}^{-1}$

(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:

$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$
$= (E(\text{C=C}) + E(\text{H–H})) - (E(\text{C–C}) + (2 \times E(\text{C–H})))$)

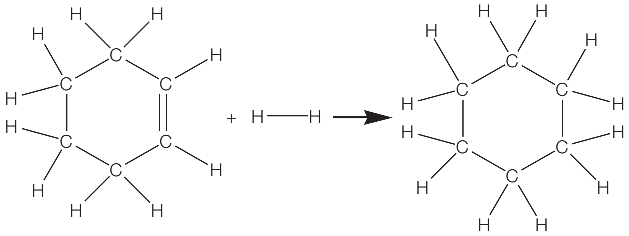
(b) $\Delta H_{\text{reaction}} = \Sigma H^{\ominus}_{\text{c}}\ (\text{reactants}) - \Sigma H^{\ominus}_{\text{c}}\ (\text{products})$
$= \Delta H^{\ominus}_{\text{c}}\ (\text{C}_2\text{H}_4(\text{g})) + \Delta H^{\ominus}_{\text{c}}\ (\text{H}_2(\text{g})) - \Delta H^{\ominus}_{\text{c}}\ (\text{C}_2\text{H}_6(\text{g}))$

$= (-1411 - 286)\ \text{kJ mol}^{-1} - (-1560)\ \text{kJ mol}^{-1}$

$= -137\ \text{kJ mol}^{-1}$

(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)** $\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$



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}

ΔH = ΣE(bonds broken) – ΣE(bonds formed) = (6920 – 7044) kJ mol^{-1} = –124 kJ mol^{-1}

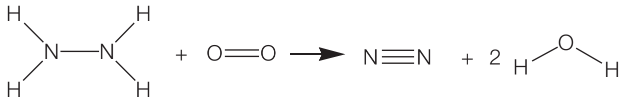
(The same value can be obtained by excluding bonds common to both reactants and products, and focusing on the bonds unique to both reactants and products:

ΔH = ΣE(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 ΔH = ΣE(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}

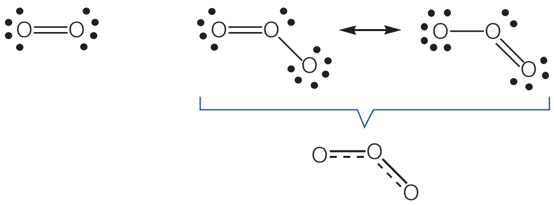
ΣE(bonds formed) = E(N≡N) + (4 × E(O–H))

= 945 + (4 × 463) kJ mol^{-1}

= 2797 kJ mol^{-1}

ΔH = ΣE(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.

14 Lattice enthalpy is the energy required to form gaseous ions from an ionic solid: MX(s) → M^+(g) + X^-(g). It increases in magnitude with increasing charge of the ions and decreasing ionic radius.

For the four ionic compounds given the greatest lattice enthalpy will occur for MgO or CaO as these both have 2+ and 2– ions whereas NaF and KF have 1+ and 1– ions. As Mg^{2+} has a smaller ionic radius than Ca^{2+}, MgO will have the greatest lattice enthalpy.

Correct answer is A.

15 **A** Bond dissociation and enthalpy of atomization are both endothermic.

B Electron affinity is exothermic and ionization energy is endothermic.

C This reaction is the reverse of endothermic lattice enthalpy so is exothermic.

D Bond dissociation is endothermic and electron affinity is exothermic.

Correct answer is A.

16 Reactions that form gaseous products from liquid and/or solid reactants have the greatest increase in entropy (greatest increase in disorder).

Correct answer is C.

17 An increase in entropy is associated with an increase in disorder.

- A Increasing temperature results in particles moving faster and an increase in disorder/entropy.
- B Gases are more disordered than liquids so entropy increases.
- C Mixtures are more disordered than pure substances so entropy increases.
- D A decrease in the number of moles of gases leads to greater order and a decrease in entropy.

Correct answer is D.

18 $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

$\Delta G^{\ominus}_{\text{reaction}} = \Sigma\Delta G^{\ominus}_{f}(\text{products}) - \Sigma\Delta G^{\ominus}_{f}(\text{reactants})$

$= ((2 \times -394) + (3 \times -229)) - (-175 + (3 \times 0))$ kJ mol^{-1}

$= -1300$ kJ mol^{-1}

Correct answer is B.

19 $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$\Delta S^{\ominus}_{\text{reaction}} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$

$= (2 \times 214) - ((2 \times 198) + 205)$ J K^{-1} mol^{-1}

$= -173$ J K^{-1} mol^{-1}

Correct answer is B.

20 $\Delta G^{\ominus}_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$

$= 10.00 \text{ kJ mol}^{-1} - \left(298 \text{ K} \times \dfrac{10.00}{1000} \text{ kJ K}^{-1} \text{ mol}^{-1}\right)$

$= 7.02$ kJ mol^{-1}

Correct answer is B.

21 **(a)** Enthalpy change I is the standard enthalpy of atomization of magnesium: $\Delta H^{\ominus}_{\text{atomization}}(\text{Mg})$.

Enthalpy change V is the standard enthalpy of formation of magnesium chloride: $\Delta H^{\ominus}_{f}(\text{MgCl}_2)$.

(b) From the IB data booklet:

II: $E(\text{Cl–Cl}) = +242$ kJ mol^{-1}

IV: $\Delta H^{\ominus}_{e}(\text{Cl}) = -349$ kJ mol^{-1}

$\Delta H^{\ominus}_{\text{lat}}(\text{MgCl}_2) = -\Delta H^{\ominus}_{f}(\text{MgCl}_2) + \Delta H^{\ominus}_{\text{atomization}}(\text{Mg}) + E(\text{Cl–Cl}) + \Delta H^{\ominus}_{i1}(\text{Mg}) + \Delta H^{\ominus}_{i2}(\text{Mg}) + 2\Delta H^{\ominus}_{e}(\text{Cl})$

$= 642 + 148 + 242 + 738 + 1451 + (2 \times -349)$ kJ mol^{-1}

$= +2523$ kJ

(c) Theoretical values are calculated based on the premise that the bonding in $MgCl_2$ is purely ionic in character. However, the bonding between Mg and Cl also has some covalent character and this results in the experimental lattice enthalpy being higher than the theoretical lattice enthalpy.

(d) Lattice enthalpy increases in magnitude with increasing charge of the ions in the salt and with decreasing ionic radius.

For MgO the ionic attraction is between 2+ and 2– ions so this will result in a higher lattice enthalpy than for $MgCl_2$, where the attraction is between 2+ and 1– ions.

The O^{2-} ion also has a smaller ionic radius than Cl^- so this results in a higher lattice enthalpy for MgO.

Challenge yourself

1 Nitrogen is an element with a positive energy of combustion:

$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^{\ominus}_{c} = 90$ 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) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
ΔH = –890 kJ mol^{-1}

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

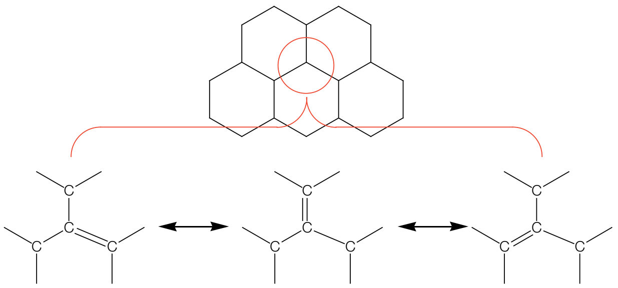
(2.1) $2H_2O(l) \rightarrow 2H_2O(g)$
ΔH = –808 – (–891) = +83 kJ mol^{-1}

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

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

This assumes that all other molecular interactions such as dipole–dipole and London 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 $1s^2 2s^2 2p^4$ 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.

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

8 Sodium chloride (salt) is an ionic substance that contains alternating sodium and chlorine ions. When salt is added to water, the partial charges on the water molecule are attracted to the Na^+ and Cl^- ions. The water molecules work their way into the crystal structure and between the individual ions, surrounding them. This disrupts the ionic attractions between the ions and slowly dissolves the salt, but as we have seen the enthalpy change is very small (see page 246 and Table 19 of the IB data booklet). The reason that this is a spontaneous process is that the aqueous solution is more disordered and has a higher entropy, as discussed later in the chapter.

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

If $\Delta G^{\ominus}_{\text{reaction}} = 0$ when $K_c = 1$, this implies a logarithmic function: $\Delta G^{\ominus}_{\text{reaction}}\ \alpha\ \ln K$.

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

This implies that $\Delta G^{\ominus}_{\text{reaction}}$ and K_c are inversely related: $\Delta G^{\ominus}_{\text{reaction}}\ \alpha\ -\ln K$.

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

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

Worked solutions

Chapter 6

Exercises

1 The information given on pages 275–278 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.

$$\text{Rate} = \frac{\Delta[A]}{\Delta t}$$

$$\text{Units of rate} = \frac{\text{units of concentration}}{\text{units of time}} = \frac{\text{mol dm}^{-3}}{\text{time}}$$
$$= \text{mol dm}^{-3}\ \text{time}^{-1}$$

(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).

$$\text{gradient} = \frac{(0 - 0.155)\ \text{mol dm}^3}{(185 - 0)\ \text{s}}$$
$$= -8.4 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

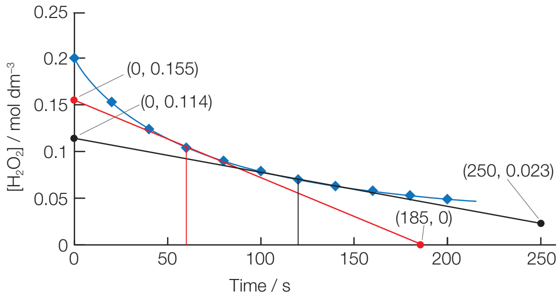
rate of reaction = 8.4×10^{-4} mol dm^{-3} s^{-1}

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: this is a good example of a question which bridges several topics, and could equally well be found under Option E: Environmental chemistry. 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.

13 The rate expressions are written by multiplying *k*, the rate constant, by the concentration of each reactant raised to the power of its order, which is given in the table.

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

Experiment 2: rate = $k[H_2O_2]$

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

Experiment 4: rate = $k[N_2O_5]$

Beware the mistake of using the values for the coefficients in the balanced equation – they are not directly related to the order.

14 As both NO and O_3 are in the rate equation with their concentration raised to the power 1, the reaction is first order with respect to each of them. The overall order is the sum of the individual orders, therefore second.

15 Here the sum of the orders with respect to the reactants must be 2. This would be the case if the reaction was second order with respect to one reactant and zero order with respect to the other, or if it was first order with respect to each reactant.

The three options are:

rate = $k[CH_3Cl]^2$

rate = $k[CH_3Cl][OH^-]$

rate = $k[OH^-]^2$

16 You can work out the units for *k* for any reaction of known order using the approach given in the table on page 290. This is generally better than trying to learn the units.

(a) Rate = $k[NO_2]^{2-}$: reaction is second order overall:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^2\text{ dm}^{-6}} = \text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}$$

(b) Rate = $k[CH_3CH_2Br]$: reacton is first order overall:

$$\text{units of } k = \frac{\text{units of rate}}{\text{units of concentration}} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol dm}^{-3}} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^2\text{ dm}^{-3}} = \text{s}^{-1}$$

(c) Rate = $k[NH_3]^0$: reaction is zero order:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^0} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{1} = \text{mol dm}^{-3}\text{ s}^{-1}$$

(d) Rate = $k[NO]^2[Br]$: reaction is third order overall:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^3} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^3} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^3\text{ dm}^{-9}} = \text{mol}^{-2}\text{ dm}^6\text{ s}^{-1}$$

(e) Rate = $k[H_2][I_2]$: reaction is second order overall:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^2\text{ dm}^{-6}} = \text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}$$

17 As the units of *k* are s^{-1}, the reaction must be first order – where the mol dm^{-3} terms have cancelled out (see the answer to question 16 above). As there is only one reactant, the rate expression can only be rate = $k[N_2O_5]$.

Note: this is a good example of a reaction where the rate equation does not match the overall reaction equation.

18 From the information given in the question, we can deduce that rate = $k[A]^0[B]^2$ or rate = $k[B]^2$.

Substituting the initial concentration of B and the initial rate into this equation, we get:

rate = $k[B]^2$

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

$$\text{which gives } k = \frac{4.5 \times 10^{-4}\text{ mol dm}^{-3}\text{ s}^{-1}}{4.0 \times 10^{-6}\text{ mol}^2\text{ dm}^{-6}} = 1.1 \times 10^2\text{ mol}^{-1}\text{ dm}^3\text{ min}^{-1}$$

Note: make sure answers for *k* always include units.

19 **C** Here it is best to work out the order with respect to each reactant first, before looking at the answers given.

The order for NO_2 can be deduced by comparing the first two rows where $[F_2]$ stays the same while $[NO_2]$ doubles from 0.1 to

0.2; the rate increases ×4 (from 0.1 to 0.4). So it is second order with respect to NO_2.

The order for F_2 can be deduced by comparing the first and third rows where $[NO_2]$ stays the same while F_2 doubles from 0.2 to 0.4; the rate doubles from 0.1 to 0.2. So it is first order with respect to F_2.

20 This is similar to question 19, but slightly harder as there is no data to compare two reactions where $[O_2]$ stays the same. So the order for NO will have to be worked out indirectly as follows.

From experiments 1 and 2, [NO] stays the same while doubling $[O_2]$ leads to a doubling of the rate. So the reaction is first order with respect to O_2.

Knowing this, we can see in experiments 2 and 3 $[O_2]$ doubles, which accounts for a doubling of the rate. But overall the rate has increased here ×8 from 4.0×10^{-3} to 3.2×10^{-2}. So the rate has increased ×4 due to the doubling of [NO]. Therefore it must be second order with respect to NO.

The rate expression follows from this: rate = $k[NO]^2[O_2]$

21 From the given rate expression we can deduce that the reaction is second order with respect to A and zero order with respect to B. So changes in [B] will not affect the rate of the reaction.

Comparing experiments 1 and 2, [A] doubles so the rate will increase ×4. The rate in experiment 2 will be four times the rate in experiment 1 (3.8×10^{-3} mol dm^{-3} s^{-1}) × 4 = 1.5×10^{-2} mol dm^{-3} s^{-1}.

Comparing experiments 2 and 3, [A] stays the same so the rate does not change as the change in [B] will not affect the rate. Rate in experiment 3 = rate in experiment 2 = 1.5×10^{-2} mol dm^{-3} s^{-1}.

22 Because we are told this is a one-step mechanism, the rate expression can be deduced directly from the stoichiometry of that step.

rate = $k[NO_2][CO]$

23 The rate-determining step is $NO_2 + NO_2 \rightarrow NO_3 + NO$.

The rate expression for this step is rate = $k[NO_2]^2$.

Because the rate-determining step is the first step this will also be the overall rate expression for the reaction. This mechanism is second order with respect to NO_2 so it is consistent with the experimental observation that the reaction is second order with respect to NO_2.

The mechanism is also consistent with the overall reaction as the two steps of the mechanism combine to give the overall reaction stoichiometry:

$$\begin{array}{l} \mathrm{NO_2 + NO_2 \rightarrow \cancel{NO_3} + \cancel{NO}} \\ \mathrm{\cancel{NO_3} + \cancel{NO} \rightarrow 2NO + O_2} \\ \hline \qquad \mathrm{2NO_2 \rightarrow 2NO + O_2} \end{array}$$

24 **C** Statement I is only true if the reaction can only happen via a one-step reaction involving two molecules of SO_2 and one O_2 colliding simultaneously. This has a very low probability compared to collisions between two molecules. It is more likely that the reaction could occur through two or more steps so it is not correct to say it **must** be between two SO_2 and one O_2 molecule.

Statement II is not correct as not every collision produces products: only those with sufficient kinetic energy to overcome the activation energy will produce products.

Statement III is correct as the slowest step of a mechanism is always the rate-determining step.

25 **(a)** The overall equation is deduced by adding together the steps in the reaction mechanism.

$$\begin{array}{ll} \mathrm{AB_2 + AB_2 \rightarrow \cancel{A_2B_4}} & \text{slow} \\ \mathrm{\cancel{A_2B_4} \rightarrow A_2 + 2B_2} & \text{fast} \\ \hline \mathrm{2AB_2 \rightarrow A_2 + 2B_2} & \end{array}$$

Here the A_2B_4 molecules cancel, so the net equation is $AB_2 + AB_2 \rightarrow A_2 + 2B_2$ (or $2AB_2 \rightarrow A_2 + 2B_2$).

(b) The slowest step is the rate-determining step. The rate expression for the rate-determining step is:

rate = $k[AB_2]^2$

Because the rate-determining step is the first step this is also the overall rate expression for the reaction.

(c) The units for k are derived from the fact that it is a second-order reaction.

rate = $k[AB_2]^2$

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^2}$$

$$= \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^2\text{ dm}^{-6}}$$

$$= \text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}$$

26 **C** Statement I is true (see page 301). Statement II is not true: activation energy is not temperature dependent. Statement III is true (see page 301).

27 **D** **A**: activation energy = E_a, **B**: kinetic energy is not mentioned in the Arrhenius equation, **C**: gas constant = R.

28 **B** Statement I is correct, the rate of collisions increases with temperature. Statement II is false, the activation energy is not temperature dependent. Statement III is correct, k (the rate constant) increases with temperature.

29 Using the equation $\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\ln\left(\frac{1.3\text{ mol dm}^3\text{ s}^{-1}}{23.0\text{ mol dm}^3\text{ s}^{-1}}\right)$$

$$= \frac{E_a}{8.31\text{ J K}^{-1}\text{ mol}^{-1}}\left(\frac{1}{800\text{ K}} - \frac{1}{700\text{ K}}\right)$$

$$-2.87 = -2.15 \times 10^{-5}\text{ J}^{-1}\text{ mol} \times E_a$$

$$E_a = 1.34 \times 10^5\text{ J mol}^{-1} = 134\text{ kJ mol}^{-1}$$

Practice questions

1 For a first-order reaction rate = $k[A]$ so the rate of reaction will decrease as the reaction proceeds and the reactants are consumed.

Correct answer is A.

2 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.

3 Consider conditions 1 and 2: $[Br_2]$ has been doubled and [NO] is constant. As rate has increased by a factor of four the reaction is second order with respect to Br_2 and rate α $[Br_2]^2$.

Consider conditions 2 and 3: $[Br_2]$ is constant and [NO] has been quadrupled. As the rate has not changed the reaction is zero order with respect to NO. Rate = $k[Br_2]^2[NO]^0 = k[Br_2]^2$

Correct answer is C.

4 Rate-determining steps are the slowest steps in a reaction mechanism and correspond to the steps with the highest activation energy.

Correct answer is C.

5 A rate expression can be derived for the slowest step: rate = $k[N_2O_2][H_2]$.

Because N_2O_2 is an intermediate it is necessary to substitute for $[N_2O_2]$ based on its formation in the first step: $[N_2O_2] = k'[NO]^2$. The rate expression is therefore rate = $k[H_2][NO]^2$.

Correct answer is A.

6 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.

7 Increasing temperature does not affect the activation energy, order of reaction or enthalpy change of the reaction. Increasing temperature does increase the frequency of collisions as well as the proportion of collisions with sufficient energy to overcome the activation energy.

Increasing temperature will therefore result in a faster reaction with a larger rate constant.

Correct answer is B.

8 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.

9 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.

10 Consider the rate expressions obtained for the slow step of each mechanism:

A rate = $k[N_2O_4][CO]^2$; substituting for $[N_2O_4]$, rate = $k[NO_2]^2[CO]^2$

B rate = $k[NO_2][CO]$

C rate = $k[NO_2]$

D rate = $k[NO_2]^2$

Correct answer is D.

11 **(a)** NO is acting as a catalyst for this mechanism as it is consumed in one step and then regenerated in a later step. This means that even though it participated in the reaction there is no overall change in the amount of NO present after the reaction has reached completion.

(b) **(i)** An intermediate is a species that is produced in one step and then consumed in a subsequent step. $N_2O_2(g)$ is an intermediate in this mechanism as it is produced in the first step and consumed in the second step.

(ii) If step 1 was the slow step, rate = $k[NO]^2$.

If step 2 was the slow step, rate = $k[N_2O_2][H_2]$.

Substituting for the concentration of the intermediate N_2O_2, rate = $k[NO]^2[H_2]$.

The theoretical rate expression obtained when the second step is the slow step agrees with the rate expression obtained experime ntally, rate = $k[NO]^2[H_2]$.

(c) If $k_2 >> k_1$ the first step is slow compared to the second step and the first step is the therefore the rate-determining step.

If the first step is the rate-determining step then the theoretical rate expression is rate = $k[NO_2]^2$, which agrees with the experimental rate expression.

(d) From the Arrhenius equation, $k = Ae^{-E_a/RT}$

$$\ln k = \ln A - \frac{E_a}{RT}$$

Therefore plotting lnk against 1/T will give a straight line where the slope = $\frac{-E_a}{R}$.

Using points (1.29×10^{-3}, –2.5) and (1.75×10^{-3}, –12.5):

$$\text{slope} = \frac{-12.5 - (-2.5)}{(1.75 - 1.29) \times 10^{-2}\ \text{K}^{-1}}$$

$$= \frac{-10.0}{4.6 \times 10^{-4}\ \text{K}^{-1}} = -2.17 \times 10^4\ \text{K}$$

E_a = –slope × R = 2.17×10^4 K × 8.31 J K^{-1} mol^{-1} = 1.8×10^5 J mol^{-1} = 180 kJ mol^{-1}

12 **(a)** The square brackets represent the concentration of NO(g). (The moles of NO gas relative to the volume occupied by the NO gas.)

(b) A rate has units of mol dm^{-3} s^{-1}. Substituting the units into the rate expression:

mol dm^{-3} s^{-1} = units of k × mol dm^{-3} × (mol $dm^{-3})^2$

mol dm^{-3} s^{-1} = units of k × mol^3 dm^{-9}

$$\text{units of } k = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^3\text{ dm}^{-9}} = \text{mol}^{-2}\text{ dm}^6\text{ s}^{-1}$$

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

(a) If ln$k$ decreases with 1/T this means that k increases with increasing T.

(b) From the Arrhenius equation, $k = Ae^{-E_a/RT}$:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Therefore plotting ln$k$ against 1/T will give a straight line where the slope = $\frac{-E_a}{R}$.

Using points (1.00 × 10^{-3}, –2.0) and (1.108 × 10^{-3}, –5.2):

$$\text{slope} = \frac{-5.2 - (-2.0)}{(1.108 - 1.00) \times 10^{-2}\text{ K}^{-1}}$$

$$= \frac{-3.2}{1.08 \times 10^{-4}\text{ K}^{-1}} = -3.0 \times 10^4\text{ K}$$

E_a = –slope × R = 3.0 × 10^4 K × 8.31 J K^{-1} mol^{-1} = 2.5 × 10^5 J mol^{-1} = 250 kJ mol^{-1}

Given the errors associated with determining the exact values of points on the line, values between 240 and 260 kJ mol^{-1} are acceptable.

(c) When 10% of N_2O has reacted, $[N_2O] = \frac{90}{100}$ × 0.200 mol dm^{-3} = 0.180 mol dm^{-3}

rate = $k[N_2O]^2$ = 0.244 dm^3 mol^{-1} s^{-1} × (0.180 mol $dm^{-3})^2$ = 7.91 × 10^{-3} mol dm^{-3} s^{-1}

14 **(a)** Water was added so that the same total volume was used for all of the trials. (Then the concentration of the reactant in the different trials is directly proportional to the volume used.)

(b) **(i)** CH_3COCH_3: In Experiments 1 and 3 $[CH_3COCH_3]$ has halved, $[H^+]$ and $[I_2]$ are constant. The initial rate has halved within experimental error so the reaction is first order with respect to CH_3COCH_3.

H^+: In Experiments 1 and 4 $[H^+]$ has halved, $[CH_3COCH_3]$ and $[I_2]$ are constant. The initial rate has halved so the reaction is first order with respect to H^+.

I_2: In Experiments 1 and 2 $[I_2]$ has increased by 1.5 times, $[CH_3COCH_3]$ and $[H^+]$ are constant. The initial rate is constant within experimental error so the reaction is zero order with respect to KI.

The rate expression for the reaction is rate = $k[CH_3COCH_3][H^+]$.

(ii) Alex's and Hannah's hypotheses were both incorrect as they both proposed that the rate of reaction would be dependent on $[I_2]$.

(c) For Experiment 1:

$$[CH_3COCH_3] = \frac{c_iV_i}{V_f}$$

$$= \frac{1.00\text{ mol dm}^{-3} \times 10.0\text{ cm}^3}{100.0\text{ cm}^3}$$

= 0.100 mol dm^{-3}

$$[H^+] = \frac{c_iV_i}{V_f} = \frac{1.00\text{ mol dm}^{-3} \times 10.0\text{ cm}^3}{100.0\text{ cm}^3}$$

= 0.100 mol dm^{-3}

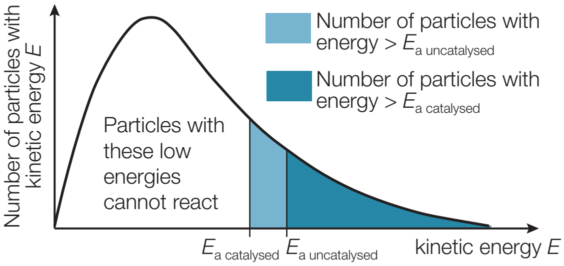
Initial rate = $k[CH_3COCH_3][H^+]$

$$k = \frac{\text{initial rate}}{[CH_3COCH_3][H^+]}$$

$$= \frac{4.96 \times 10^{-6}\text{ mol}^{-1}\text{ dm}^{-3}\text{ s}^{-1}}{01.00\text{ mol dm}^{-3} \times 0.100\text{ mol dm}^{-3}}$$

= 4.96 × 10^{-4} mol dm^3 s^{-1}

(i)



(ii) A catalyst provides an alternative reaction pathway with a lower activation energy.

15 Note that this question should refer to the mechanism provided as having two steps:

Step 1: $W + XY \rightarrow WY + X$

Step 2: $WY + Z \rightarrow W + YZ$

The labels 1–5 on the graph refer to *stages* 1–5 of the reaction (not steps).

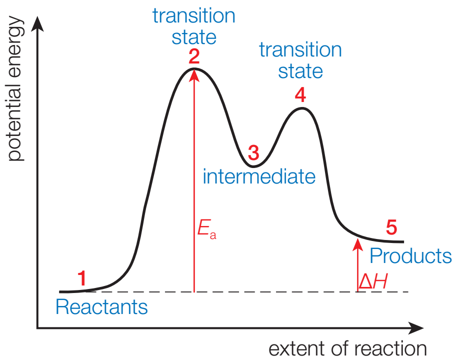
(a) $\cancel{W} + XY \rightarrow \cancel{WY} + X$

$\underline{\cancel{WY} + Z \rightarrow \cancel{W} + YZ}$

$XY + Z \rightarrow X + YZ$

Overall equation is $XY + Z \rightarrow X + YZ$.

(b) In the diagram 1–5 represent different stages of the reaction (not steps).



Stage 1 represents the reactants.

Stage 2 represents the transition state for step 1 of the reaction mechanism.

Stage 3 represents an intermediate.

Stage 4 represents a transition state for step 2 of the reaction mechanism.

Stage 5 represents the products.

(c) 1–5 represent different stages of the reaction (not steps).

Species present at stage 1 are reactants XY, Z and the catalyst W.

Species present at stage 2 is transition state formed by W and XY: W ---- X ----Y

Species present at stage 3 is intermediate WY, reactant Z and product X.

Species present at stage 4 is transition state formed by WY and Z: W ---- Y ----Z

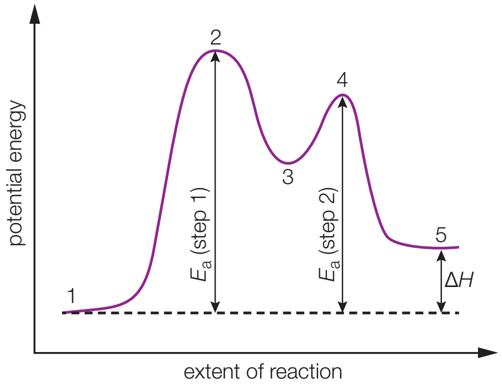
Species present at stage 5 are products X, YZ and the catalyst W.

(d) For the two steps provided in the reaction mechanism the rate-determining step will be the one with the highest activation energy. From the diagram provided in the answer for part (b) we can see that the first step in the mechanism ($W + XY \rightarrow WY + X$) has the highest activation energy so it will be the slowest step.

rate = $k[W][XY]$

(e) The reaction is catalysed. W is a catalyst as it is consumed in the first step and regenerated in the second step. (This means that even though it participated in the reaction, there is no overall change in the amount of W present after the reaction has reached completion.)

(f) The enthalpy change, ΔH, refers to the enthalpy change that occurs between the reactants and products. Because this reaction proceeds through an intermediate, and has two steps in the reaction mechanism, there are two activation energies. E_a (step 1) is the energy difference between the reactants and the transition state for the first step, $W + XY \rightarrow WY + X$. E_a (step 2) is the energy difference between the intermediate and the transition state for the second step, $WY + Z \rightarrow W + YZ$.



Challenge yourself

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

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

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) $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

(b) $K_c = \dfrac{[NO_2]^4\,[H_2O]^6}{[NH_3]^4[O_2]^7}$

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

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) $K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$ $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(b) $K_c = \dfrac{[CO][H_2]^2}{[CH_4][H_2O]}$ $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

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

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

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

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

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

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

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)

$$\frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{0.19^2}{0.00033 \times 0.083} = 1.3 \times 10^2$$

$$= 1300$$

Not at equilibrium. As $Q > K_c$ the reaction proceeds to the left.

9 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\quad K_\mathbf{c} = \frac{[SO_3]^2}{[SO_2]^4[O_2]^2} = 278$

(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

19 **(a)** The volume specified is 1.0 dm^3 so the number of moles given is the same as the concentration in mol dm^{-3}.

1.0 mol of HI has decreased to 0.78 mol at equilibrium, so 0.22 mol of HI have reacted.

This is therefore the value for the 'change' row. From this value, and the stoichiometry of the reaction, we can deduce the changes in the concentration of the other components. These enable us to calculate the equilibrium concentration of each component. Application of the equilibrium law leads to calculation of K_c.

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

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.11)^2}{(0.78)^2} = 2.0 \times 10^{-2} \text{ (at 440 °C)}$$

(b) A comparison of the values of K_c at the two different temperatures indicates that in this case an increase in temperature has led to an increase in the value of K_c. This is characteristic of an endothermic reaction.

20 Because K_c is very small we can deduce that the concentration of reactants at equilibrium is approximately equal to their initial concentrations.

As we do not know the amount of reactant to have reacted to reach equilibrium, we use '$-x$' to denote the change in reactant concentration.

This enables us to deduce the change in concentration in terms of x of the other components.

The values of equilibrium concentration are then expressed in terms of x.

Substituting the equilibrium concentrations into the equilibrium expression leads to evaluation of x and hence of the equilibrium values.

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

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

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

$$\frac{(2x)^2}{1.6 \times 1.6} = 1.7 \times 10^{-3}$$

$$4x^2 = 4.4 \times 10^{-3}$$

$$x = 0.033$$

$$[NO]_{eqm} = 2x = 0.066 \text{ mol dm}^{-3}$$

21 **(a)** From the initial concentrations of all components and the equilibrium concentrations of H_2 and CO_2, the equilibrium concentrations of the reactants can be calculated. By substituting the values for all the equilibrium concentrations into the equilibrium expression, the value of K_c can be calculated.

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

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

(b) Use the values given to obtain the reaction quotient, Q:

$$Q = \frac{[H_2][CO_2]}{[CO][H_2O]} = \frac{(3.0)^2}{(4.0)^2} = 0.56$$

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

22 **C** Entropy is at a maximum and free energy is at a minimum at equilibrium (see page 336).

23 Using the relationship $\Delta G = -RT \ln K$:

(a) If $K = 1$ then $\Delta G = 0$, because $\ln 1 = 0$.

(b) If $K > 1$ then ΔG = negative, because ln (positive number) = a positive number, so the right-hand side of the equation is negative overall (R is a constant with a positive value and T (absolute temperature) is, by definition, greater than 0).

(c) If $K < 1$ then ΔG = positive, because ln (negative number) = a negative number, so the right-hand side of the equation is positive overall.

24 **(a)** $\Delta G = -RT \ln K$

$\Delta G = -8.31 \text{ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln(1.00 \times 10^{-14}) = 79.8 \text{ kJ mol}^{-1}$

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

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 Using the initial concentrations for I_2 and Br_2 along with the equilibrium concentration of IBr provided (shown in **bold** below) we can calculate the changes occurring (shown in *italics* below) and the equilibrium concentrations of I_2 and Br_2:

	$I_2(g)$ +	$Br_2(g) \rightleftharpoons$	2IBr(g)
Initial	**0.50**	**0.50**	**0**
Change	*−0.40*	*−0.40*	*+0.80*
Equilibrium	0.10	0.10	**0.80**

$$K_c = \frac{[IBr]^2}{[I_2][Br_2]} = \frac{0.80^2}{0.10 \times 0.10} = 64$$

Correct answer is D.

6 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.

7 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.

8 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.

9 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.

10 **(a)** *(The original IB question this is based on had $\Delta H^\ominus = -198$ kJ mol^{-1}. The answer given here uses this original value and not what is provided in the book (+198 kJ mol^{-1}) to be consistent with the IB markscheme.)*

(i) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

(ii) 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 $SO_3(g)$.

(iii) 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 $SO_3(g)$.

(iv) 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.

(b) Using the initial concentrations for NO(g), $H_2(g)$ and $H_2O(g)$ along with the equilibrium concentration of NO(g) provided (shown in **bold** below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products:

	$2NO(g)$ +	$2H_2(g)$ $\rightleftharpoons$	$N_2(g)$ +	$2H_2O(g)$
Initial	**0.100**	**0.051**	**0**	**0.100**
Change	*−0.038*	*0.038*	*+0.019*	*+0.038*
Equilibrium	**0.062**	0.013	0.019	0.138

$$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{0.019 \times 0.138^2}{0.062^2 \times 0.013^2}$$

$$= 5.6 \times 10^2$$

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

(b) Using the initial concentrations for $SO_2(g)$ and $Cl_2(g)$ along with the equilibrium concentration of $SO_2Cl_2(g)$ provided (shown in **bold** below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products:

	$Cl_2(g)$ +	$SO_2(g)$ $\rightleftharpoons$	$SO_2Cl_2(g)$
Initial	**8.60×10^{-3}**	**8.60×10^{-3}**	**0**
Change	*-7.65×10^{-4}*	*-7.65×10^{-4}*	*$+7.65 \times 10^{-4}$*
Equilibrium	7.835×10^{-3}	7.835×10^{-4}	**7.65×10^{-4}**

$$K_c = \frac{[SO_2Cl_2]}{[Cl_2][SO_2]} = \frac{7.65 \times 10^{-4}}{7.835 \times 10^{-3} \times 7.835 \times 10^{-3}}$$

$$= 12.5$$

(c) The temperature has decreased from 370 °C to 300 °C. Because the reaction is exothermic ($\Delta H^\ominus$ is negative), decreasing the temperature will move the equilibrium position to the right and increase the equilibrium concentration of $SO_2Cl_2(g)$. This will also result in an increase in the value of K_c.

(d) There are 2 moles of gaseous reactants and 1 mole of gaseous products so increasing the volume to 1.50 dm^3 will shift the equilibrium to the left and decrease the equilibrium concentration of $SO_2Cl_2(g)$.

As the temperature has not changed the value of K_c will remain constant.

(e) A catalyst will increase the rate of both the forward and reverse reactions equally so it has no effect on the position of equilibrium or the value of K_c and will not affect the equilibrium concentration of $SO_2Cl_2(g)$.

12 **(a)** The graph shows that the yield of ammonia decreases as the temperature increases. A decrease in equilibrium product yield as temperature increases occurs for exothermic reactions therefore the forward reaction is exothermic.

(b) There are 4 moles of gaseous reactants and 2 moles of gaseous products so increasing the pressure will shift the equilibrium to the right and increase the yield of $NH_3(g)$.

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

(d) Using the initial concentrations for $N_2(g)$ and $H_2(g)$ along with the equilibrium concentration of $NH_3(g)$ provided (shown in **bold** below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products:

	$N_2(g)$ +	$3H_2(g)$ $\rightleftharpoons$	$2NH_3(g)$
Initial	**1.00**	**3.00**	**0**
Change	*–0.031*	*–0.093*	*+0.062*
Equilibrium	0.969	2.91	**0.062**

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^2} \quad \frac{0.062^2}{0.969 \times 2.91^3} = 1.6 \times 10^{-4}$$

(e) A catalyst will increase the rate of both the forward and reverse reactions equally so it has no effect on the position of equilibrium or the value of K_c.

13 **(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) Using the initial concentrations for $H_2(g)$ and $I_2(g)$ along with the equilibrium concentration of HI(g) provided (shown in **bold** below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products. *Note that the flask volume is 4.00 dm³ so the gas concentrations need to be calculated based on this volume.*

$$\text{Initial } [H_2] = \frac{1.60 \text{ mol}}{4.00 \text{ dm}^2} = 0.400 \text{ mol dm}^{-3}$$

$$\text{initial } [I_2] = \frac{1.00 \text{ mol}}{4.00 \text{ dm}^2} = 0.250 \text{ mol dm}^{-3}$$

$$\text{Equilibrium } [HI] = \frac{1.80 \text{ mol}}{4.00 \text{ dm}^2} = 0.450 \text{ mol dm}^{-3}$$

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial	**0.400**	**0.250**	**0**
Change	*–0.225*	*–0.225*	*+0.450*
Equilibrium	0.175	0.025	**0.450**

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.450^2}{0.175 \times 0.025} = 46.3$$

(f) 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.

14 **(a)** $\Delta G^\ominus = -RT\ln K = -8.31 \text{ J K}^{-1} \text{ mol}^{-1} \text{ x } 298 \text{ K x } \ln(1) = 0$ $\quad(\ln(1) = 0)$

(b) $\Delta G^\ominus = -RT\ln K = -8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln(1.7 \times 10^{12}) = -7.0 \text{ x } 10^4 \text{ J mol}^{-1} = -70 \text{ kJ mol}^{-1}$

15 **(a)** As the question only gives us initial concentrations (shown in **bold** below) we cannot determine the change in concentration occurring using equilibrium concentrations. Instead we have to solve the problem algebraically by letting the change in concentration = *x* then determining the changes in concentration (shown in *italics* below) and the equilibrium concentrations in terms of *x*.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial	**6.0**	**3.0**	**0**
Change	*–x*	*–x*	*+2x*
Equilibrium	6.0 – *x*	3.0 – *x*	***2x***

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$4.00 = \frac{(2x)^2}{(6.0 - x) \times (3.0 - x)}$$

$$4.00 = \frac{4x^2}{18.0 - 9.0x + x^2}$$

$$72.0 - 36.0x + 4x^2 = 4x^2$$

$$72.0 = 36.0x$$

$$x = 2.0 \text{ mol dm}^{-3}$$

The equilibrium concentrations are:

$[H_2] = 4.0 \text{ mol dm}^{-3}$, $[I_2] = 1.0 \text{ mol dm}^{-3}$, $[HI] = 4.0 \text{ mol dm}^{-3}$

(b) (i) Using the initial concentrations for HI(g) along with the equilibrium concentration of $H_2(g)$ provided (shown in **bold** below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products if we solve algebraically by letting the initial concentration of HI = x.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial	**0**	**0**	**x**
Change	*+0.218*	*+0.218*	*−0.436*
Equilibrium	**0.218**	0.218	$x - 0.436$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$51.50 = \frac{(x - 0.436)^2}{0.218 \times 0.218}$$

$$2.447 = (x - 0.436)^2$$

$$1.56 = x - 0.436$$

$$x = 2.00 \text{ mol dm}^{-3}$$

As the flask had a volume of 1.00 dm^3 the amount of HI added can be calculated using the initial concentration calculated of 2.000 mol dm^{-3}:

$$n(HI) = cV = 2.000 \text{ mol dm}^{-3} \times 1.00 \text{ dm}^3$$
$$= 2.00 \text{ mol}$$

The original amount of HI placed in the flask was 2.00 mol.

(ii) At equilibrium the concentration of I_2 = 0.218 mol dm^{-3}:

$$n(I_2) = cV = 0.218 \text{ mol dm}^{-3} \times 1.00 \text{ dm}^3$$
$$= 0.218 \text{ mol}$$

At equilibrium the concentration of

$$HI = (2.000 - 0.436) \text{ mol dm}^{-3}$$
$$= 1.564 \text{ mol dm}^{-3}$$

$$n(HI) = cV = 1.564 \text{ mol dm}^{-3} \times 1.00 \text{ dm}^3$$
$$= 1.56 \text{ mol}$$

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, but are included in the value of K.

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:

$10^{5.2} =$	2×10^5	$10^{-4.20} =$	6.3×10^{-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, $K_w = [H^+]\,[OH^-] = 1.00 \times 10^{-14}$

$\therefore [OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1.00 \times 10^{-14}}{10^{-9}} = 1.0 \times 10^{-5}$ 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 $[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1 \times 10^{-14}}{8 \times 10^{-8}} = 1.25 \times 10^{-7}$, 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 $[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.00 \times 10^{-14}}{6 \times 10^{-10}} = 1.7 \times 10^{-5}$, so $pH = 4.8$

15 Formula mass of NaOH = 40.00 g mol^{-1}

$n(NaOH) = \dfrac{6.0\ g}{40.0\ g\ mol^{-1}} = 0.15$ mol

One mole of dissolved NaOH gives one mole of OH^- ions.

$[OH^-] = \dfrac{n}{V} = \dfrac{0.15\ mol}{1.0\ dm^3} = 0.15$ mol dm^{-3}

$K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

Hence $[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.00 \times 10^{-14}}{0.15} = 6.7 \times 10^{-14}$, so $pH = 13.17$

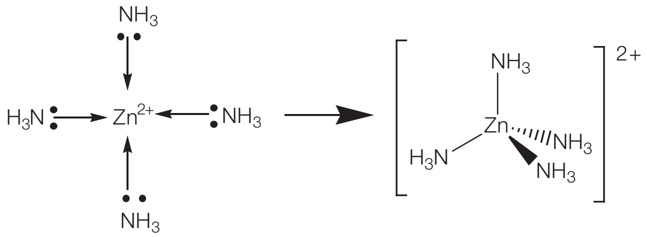
16 **B** The solution with the lowest conductivity will be the one with the fewest dissociated ions. The solution of ethanoic acid (CH_3COOH) will be the poorest conductor of electricity as ethanoic acid is a weak acid and only partially dissociates into its ions in solution. All the other examples are 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).

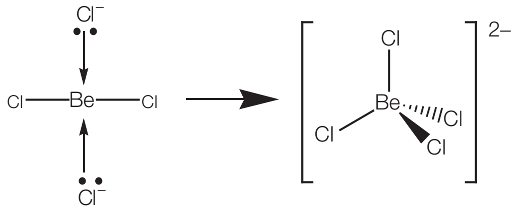
18 **(a)** H_2CO_3 is a weak acid and H_2SO_4 is a strong acid. H_2CO_3 has the stronger conjugate base, as the conjugate base is formed from the weaker of the two acids.

(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.

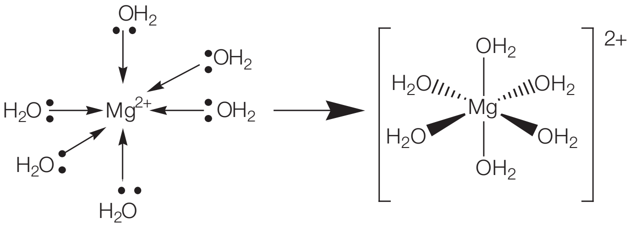
19 **(a)** The Lewis acid is Zn^{2+} as it accepts a lone pair from the ammonia; the Lewis base is NH_3 as it donates a lone pair to the zinc ion.



(b) The Lewis acid is $BeCl_2$ as it accepts lone pairs from the chloride ion; the Lewis base is Cl^- as it donates a lone pair to the $BeCl_2$.

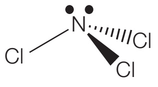


(c) The Lewis acid is Mg^{2+} as it accepts lone pairs from the water molecule; the Lewis base is H_2O as it donates a lone pair to the Mg^{2+} ion.

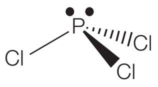


20 **D**

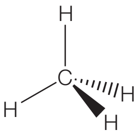
Cl^-



NCl_3



PCl_3



CH_4

CH_4 cannot act as a ligand because it does not possess a lone pair of electrons; all the other substances do contain a lone pair of electrons.

21 **C** Brønsted–Lowry theory is to do with proton donors and acceptors. Brønsted–Lowry acids donate protons (H^+), Brønsted–Lowry bases accept protons. In **C** there is no exchange of H^+ so no Brønsted–Lowry acids or bases are present. All the other equations have an exchange of H^+ ions.

22 If $K_w = 2.4 \times 10^{-14} = [H^+][OH^-]$

For water, $[H^+] = [OH^-] = \sqrt{2.4 \times 10^{-14}} = 1.5 \times 10^{-7}$ mol dm^{-3}

$pH = -\log[H^+] = -\log(1.5 \times 10^{-7}) = 6.81$

As $[OH^-] = [H^+]$, $pOH = pH = 6.81$

$pK_w = pH + pOH = 6.81 + 6.81 = 13.62$

However, water is still neutral, as $[H^+] = [OH^-]$.

23 $pH + pOH = pK_w = 14.00$ (at 298 K)

pH= 6.77 therefore pOH = 14.00 – 6.77 = 7.23

$pH = -\log[H^+]$ then $[H^+] = 10^{-pH} = 10^{-6.77}$
$= 1.7 \times 10^{-7}$ mol dm^{-3}

Similarly, if $p(OH) = -\log[OH^-]$ then $[OH^-] = 10^{-pOH} = 10^{-7.23} = 5.9 \times 10^{-8}$ mol dm^{-3}

$[H^+] > [OH^-]$ so the sample of milk is acidic

24 **(a)** $pH = -\log[H^+]$, $pH = -\log[0.40] = 0.40$

(b) $[OH^-] = 3.7 \times 10^{-4}$ mol dm^{-3}; $[H^+] = \dfrac{K_w}{[OH^-]}$

$$= \frac{1.00 \times 10^{-14}}{3.7 \times 10^{-4}} = 2.7 \times 10^{-11} \text{ mol dm}^{-3}$$

$pH = -\log[H^+] = -\log(2.7 \times 10^{-11}) = 10.57$

(c) As one mole of $Ba(OH)_2$ dissociates to give two moles of OH^- ions a 5.0×10^{-5} mol dm^{-3} solution of $Ba(OH)_2$ will have an OH^- concentration of 1.0×10^{-4} mol dm^{-3}.

$[OH^-] = 1.0 \times 10^{-4}$ mol dm^{-3}; $[H^+] = \dfrac{K_w}{[OH^-]}$

$$= \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} \text{ mol dm}^{-3}$$

$pH = -\log[H^+] = -\log(1.0 \times 10^{-10}) = 10.00$

25 **B** NaOH is a strong base so is fully dissociated. $[OH^-] = 0.010 = 1.0 \times 10^{-2}$ mol dm^{-3}. Use $K_w = [H^+][OH^-]$ to find $[H^+] = 1.0 \times 10^{-12}$, so pH = 12.00

26 $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

This is a modified equilibrium constant based on the balanced equation of ionization.

Here, the first step is therefore to write the equations. Then identify the base (B) and conjugate acid (BH^+) for each reaction.

(a) $C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$

$B = C_2H_5NH_2$; $BH^+ = C_2H_5NH_3^+$

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]}$$

(b) $HSO_4^- + H_2O \rightleftharpoons H_2SO_4 + OH^-$

$B = HSO_4^-$; $BH^+ = H_2SO_4$

$$K_b = \frac{[H_2SO_4][OH^-]}{[HSO_4^-]}$$

(c) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

$B = CO_3^{2-}$; $BH^+ = HCO_3^-$

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$

27 The higher the value of K_a, the stronger the acid. So HNO_2 is the weakest and H_2SO_3 is the strongest.

$HNO_2 < H_3PO_4 < H_2SO_3$

28 Dissociation constants are used to give a quantitative measure of the extent of ionization of an acid or base reaction that is in equilibrium. With strong acids and bases we assume full dissociation, so there is no equilibrium and the concept of an acid or base dissociation constant is not applicable. The H^+ concentration and pH of their solutions can be derived directly from their concentration.

29 **B** Because this is a weak acid we cannot determine the $[H^+]$ at equilibrium from the initial concentration, as this would be assuming complete dissociation. Instead, we have to deduce it from the value of K_a.

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial:	0.1		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.1 - x$		x		x

Because K_a is very small we can assume that $0.1 - x \approx 0.1$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.1} = 1.0 \times 10^{-5}$$

$x^2 = 1 \times 10^{-6}$

$\therefore x = \sqrt{1 \times 10^{-6}} = 1 \times 10^{-3}$

$[H^+] = 1 \times 10^{-3}$ mol dm^{-3}

$\therefore$ pH $= -\log[H^+] = -\log(1 \times 10^{-3}) = 3.0$

30 This is very similar to the Worked Example on page 373.

pH + pOH = 14.00

pH = 11.86 so pOH = 14.00 −11.86 = 2.14

(The question should have specified that it is at temperature 298 K!)

$\therefore$ $[OH^-]$ at equilibrium $= 10^{-\text{pH}} = 10^{-2.14}$
$= 7.2 \times 10^{-3}$ mol dm^{-3} (= 0.0072 mol dm^{-3})

	$C_2H_5NH_2$	$+ H_2O \rightleftharpoons$	$C_2H_5NH_3^+$ +	OH^-
Initial:	0.1		0	0
Change:	−0.0072		+0.0072	+0.0072
Equilibrium:	0.0928		0.0072	0.0072

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{0.0072^2}{0.0928} = 5.6 \times 10^{-4}$$

31 When you are working with an acid and K_a value, you will calculate the $[H^+]$ first and deduce the $[OH^-]$ from this. Again we are assuming that this is at 298 K – which should have been specified in the question.

This is very similar to the Worked Examples on page 374.

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial:	0.10		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.10 - x$		x		x

Because the value of K_a is very small, we can assume that

$[HA]_{\text{equilibrium}} \approx [HA]_{\text{initial}}$, i.e. $0.10 - x \approx 0.10$

$$\therefore K_a = \frac{x^2}{0.10} = 1.0 \times 10^{-7}$$

$x^2 = 1 \times 10^{-8}$

$\therefore x = [H^+] = \sqrt{1 \times 10^{-6}} = 1.0 \times 10^{-4}$ mol dm^{-3}

because $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$ we get

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} \text{ mol dm}^{-3}$$

32 The pK_a value must first be converted into K_a.

pK_a = 4.92 so $K_a = 10^{-4.92} = 1.2 \times 10^{-5}$

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial:	0.030		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.030 - x$		x		x

Because the value of K_a is very small, we can assume that

$[HA]_{\text{equilibrium}} \approx [HA]_{\text{initial}}$, i.e. $0.030 - x \approx 0.030$

$$\therefore K_a = \frac{x^2}{0.030} = 1.2 \times 10^{-5}$$

$x^2 = 3.6 \times 10^{-7}$

$\therefore x = [H^+] = \sqrt{3.6 \times 10^{-7}} = 6.0 \times 10^{-4}\ \text{mol dm}^{-3}$

$\therefore \text{pH} = -\log[H^+] = -\log(6.0 \times 10^{-4}) = 3.22$

33 **A** By definition $pK_a = -\log K_a$

34 The stronger acid has the lower pK_a value. Therefore HF is a stronger acid than HCN.

35 Once more we assume we are working at 298 K.

$pK_a + pK_b = 14.00$

For HCN and CN^- it follows that $9.21 + pK_b = 14.00$

$\therefore pK_b\ [CN^-] = 4.79$

For HF and F^- it follows that $3.17 + pK_b = 14.00$

$\therefore pK_b\ [F^-] = 10.83$

The stronger base has the lower pK_b value. Therefore CN^- is a stronger base than F^-.

This confirms our answer to Q34 that HCN is the weaker acid, so it will have the stronger conjugate base.

36 **(a)** The conjugate base of ethanoic acid, CH_3COOH, is CH_3COO^- (the ethanoate ion).

At 298 K, $pK_a + pK_b = 14.00$

$\therefore pK_b(CH_3COO^-) = 14.00 - pK_a(CH_3COOH) = 14.00 - 4.76 = 9.24$

(b) The conjugate base of methanoic acid, HCOOH, is $HCOO^-$ (the methanoate ion).

At 298 K, $pK_a + pK_b = 14.00$

$pK_b(HCOO^-) = 14.00 - pK_a(HCOOH) = 14.00 - 3.75 = 10.25$

The pK_b value of $HCOO^-$ is higher than the pK_b value of CH_3COO^- so $HCOO^-$ is a weaker base.

(In turn, this implies that methanoic acid is a stronger acid than ethanoic acid, which is confirmed by the pK_a values given here.)

37 **B** A buffer solution must contain approximately equal amounts of a weak acid or weak base with its conjugate base or acid. In the examples given here, you must consider how the given components will react together and the proportions of products and unused reactants that will result. We will consider each in turn.

- **A**: equimolar quantities of weak acid and strong base which react in 1 : 1 ratio, with the resulting mixture containing salt and water only: not a buffer.
- **B**: weak acid and strong base in 2 : 1 ratio by moles. These react in 1 : 1 ratio, so the resulting mixture contains (unreacted) weak acid and salt in equimolar amounts: this is a buffer.
- **C**: weak acid and strong base in 1 : 2 ratio by moles. These react in 1 : 1 ratio, so the resulting mixture contains salt and (unreacted) strong base: not a buffer.
- **D**: weak acid and strong base in 2 : 1 ratio by moles, but here the reacting ratio will be 2 : 1 as $Ba[OH]_2$ will neutralize 2 moles of CH_3COOH. The resulting mixture contains salt and water only: not a buffer.

38 **B** The concept here is similar to Q37. You must work out the products of each reaction.

I: The components do not react together. The mixture will contain equal moles of the weak acid CH_3COOH and its salt CH_3COONa. This is a buffer.

II: There is a 2 : 1 ratio of weak acid to strong base, so after reaction the mixture will contain equal quantities of weak acid and its salt. This is a buffer.

III: There is a 1 : 1 ratio of weak acid and strong base, so after reaction the mixture contains salt and water only. This is not a buffer.

39 (i), because it has a higher concentration of the acid and its conjugate base, and so has the capability of buffering to a greater extent than the mixture with the lower concentrations of solution.

40 **(a)** NaCl is a salt of a strong acid (HCl) and a strong base (NaOH). Neither ion hydrolyses appreciably. pH = 7

(b) $FeCl_3$ is a salt of strong acid (HCl) and a weak base. Cation hydrolyses, anion does not. pH < 7

(The Fe^{3+} cation exists as $Fe(OH_2)_6^{3+}$ in aqueous solution. $Fe(OH_2)_6^{3+}$ can act as an acid and will give a solution of pH < 7; $Fe(OH_2)_6^{3+}(aq) \rightleftharpoons Fe(OH_2)_5(OH)^{2+}(aq) + H^+(aq)$.)

(c) NH_4NO_3 is a salt of a weak base (NH_3) and a strong acid (HNO_3). Cation hydrolyses, anion does not. pH < 7

(d) Na_2CO_3 is a salt of a strong base (NaOH) and a weak acid (HCO_3^-). Anion hydrolyses, cation does not. pH > 7

41 **B** A salt solution with pH > 7 is characteristic of a salt formed from a strong base and a weak acid. **A**: sodium chloride = salt of strong acid (HCl) and strong base (NaOH), pH = 7. **B**: potassium carbonate = salt of strong base (KOH) and weak acid (HCO_3^-), pH > 7. **C**: ammonium nitrate = salt of weak base (NH_3) and strong acid (HNO_3), pH < 7. **D**: lithium sulfate = salt of strong base (LiOH) and strong acid (H_2SO_4), pH = 7.

42 The key to answering this question is to identify the strengths of the acid and base as 'strong' or 'weak'. The table on page 385 will be useful here, though ultimately you need to commit this to memory.

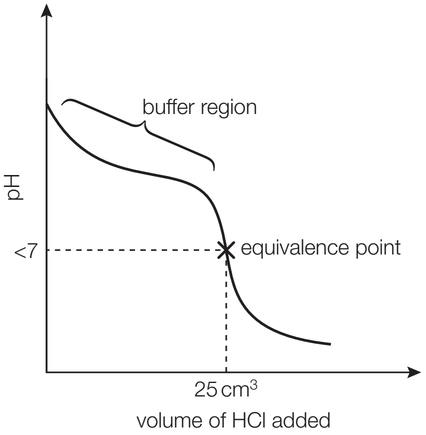
(a) strong acid (H_2SO_4) and weak base (NH_3), salt solution has pH < 7

(b) weak acid (H_3PO_4) and strong base (KOH), salt solution has pH > 7

(c) strong acid (HNO_3) and strong base ($Ba(OH)_2$), salt solution has pH = 7

43 **D** Statement I: the initial pH will not be the same – the strong acid, which dissociates completely, will have a lower initial pH than the weak acid of the same concentration, which does not dissociate completely. Statement II: the pH at equivalence point will not be the same – that for the strong acid will be about 7 and that for the weak acid will be > 7. Statement III: volume of NaOH needed is the same – both acids react in a 1 : 1 ratio with the base.

44



The graph makes the following points:

- the pH decreases during the titration as acid is added to base
- initial pH is the pH of NH_3, a weak base
- the buffer region is when some of the base has been neutralized by the acid
- equivalence occurs when 25 cm³ of acid has been added because they react in a 1 : 1 ratio and are supplied in equal concentrations
- the pH at equivalence is < 7 because the salt forms from a strong acid and a weak base.

45 Note that no data are given in this question, so no calculations are expected.

(i) If the concentration of the acid is known its K_a and therefore its pK_a can be calculated from the initial pH of the acid. This is similar to the type of calculation shown on page 373.

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

$$K_a = \frac{[CH_2COO^-][H^+]}{[CH_2COOH]}; [H^+] = 10^{-pH}$$

As $[CH_3COO^-] = [H^+]$ and assuming that the dissociation is small so $[CH_3COOH]_{eq} = [CH_3COOH]_{initial}$,

$$K_a \approx \frac{[H^+]^2}{[CH_2COOH]}$$

(ii) $[CH_3COO^-]$

$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

Halfway to the equivalence point half of the CH_3COOH has been converted to CH_3COO^- therefore at half-equivalence $[CH_3COOH] = [CH_3COO^-]$.

At half-equivalence $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = [H^+]$ ($[CH_3COOH]$ and $[CH_3COO^-]$ cancel)

If $K_a = [H^+]$ then $pK_a = pH$

The pH value that can be obtained from the titration curve at the half-equivalence point is therefore equivalent to the pK_a of the weak acid (CH_3COOH in this example).

46 **D** Different indicators have different pH values at which they change colour (so **A** is wrong). The size of the pH range over which the colour change occurs and the pK_a of an indicator are not related (so **B** is wrong). The colour observed in acidic solution will depend on the specific indicator (so **C** is wrong). The pH range of the colour change always includes the pK_a of the indicator (so **D** is correct).

47 **(a)** Its pH range for colour change occurs at between pH 3.8 and pH 5.4. This lies within the pH range at equivalence for titrations of (i) strong acid and strong base (pH 3–11) and (ii) strong acid and weak base (pH 3–7).

(b) An estimate for the pK_a of an indicator corresponds to about halfway through its colour-change range. As the pH range for the colour change for bromocresol green is pH 3.8–5.4 its $pK_a \approx 4.6$.

(This is not actually true for many indicators but it is the best estimate we can make in the absence of further information.)

(c) Bromocesol green changes from yellow to blue as pH increases, therefore its colour will be yellow at pH 3.6 (and at all pH values < 3.8). In the range 3.8–5.4 it will progress through various shades of green corresponding to the yellow/blue mix and above pH 5.4 it will be blue.

48 **(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.

49 **(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: $N_2(g) + O_2(g) \rightarrow 2NO(g)$

50 **(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.

51 The hydroxyl free radical $^{\bullet}OH$ is involved in the formation of sulfuric acid and nitric acid.

$^{\bullet}OH + SO_2 \rightarrow {}^{\bullet}HOSO_2$ $\quad$ $^{\bullet}OH + NO_2 \rightarrow HNO_2$
$^{\bullet}HOSO_2 + O_2 \rightarrow {}^{\bullet}HO_2 + SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$

$^{\bullet}OH$ 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 For a conjugate acid–base pair, $K_w = K_b K_a$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13}$$

Correct answer is D.

2 A buffer solution contains a mixture of both components of a conjugate acid–base pair.

A and **C**: Both solutions are a mixture of a strong acid and a strong base so cannot form a conjugate acid–base pair.

B: The sodium hydroxide will convert half of the ethanoic acid to its conjugate base (ethanoate ion) so this will contain a conjugate acid pair.

D: The sodium hydroxide will convert all of the ethanoic acid to its conjugate base (ethanoate ion) and no acid–base conjugate pair will be present.

Correct answer is B.

3 Hydrochloric acid is a strong acid and ethanoic acid is a weak acid. Because ethanoic acid does not dissociate fully it will have a different initial pH to the hydrochloric acid solution, where complete dissociation occurs. Weak acids pass through a buffering zone as they react with added sodium hydroxide and the pH changes observed will not be the same as those with hydrochloric acid, where no buffering occurs, and the equivalence points will not occur at the same pH. Because they are both monoprotic acids the same volume of sodium hydroxide solution will be required to reach the equivalence point, where all of the acid has reacted.

Correct answer is C.

4 The equilibrium for the bromophenol blue indicator is $HIn \rightleftharpoons H^+ + In^-$. As pH increases from 3.0 to 4.6 and $[H^+]$ decreases, the equilibrium will shift to the right. At pH 3.0 there will be an excess of HIn and at pH 4.6 an excess of In^-. As the colour changes from yellow to blue over this pH range, this means that HIn is yellow and In^- is blue. The equivalence point for the titration of ethanoic acid (weak base) with potassium hydroxide (strong base) will occur at pH >7 so bromophenol blue would not be a suitable indicator.

Correct answer is C.

5 The base dissociation reaction for ethylamine is:

$$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$$

$$K_b = \frac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$$

Correct answer is B.

6 It can be assumed that pure water means $[H^+] = [OH^-]$ and pH = pOH.

$$pK_w = pH + pOH = 2pH$$

$$14.54 = 2pH$$

$$pH = 7.27$$

Correct answer is C.

7 For a conjugate acid-base pair, $K_w = K_bK_a$.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = (1.5 \times 10^{-11})$$

Correct answer is C.

8 Nitric acid (HNO_3), ethanoic acid (CH_3COOH) and hydrochloric acid (HCl) are monoprotic acids acids and dissociate to give one H^+ per acid molecule. Sulfuric acid (H_2SO_4) is a diprotic acid and will dissociate to give two H^+ per acid molecule so a 20 cm^3 sample of this acid will require twice as much sodium hydroxide to neutralize it compared to the other acids.

Correct answer is B.

9 A buffer solution contains a mixture of both components of a conjugate acid–base pair.

A and **B**: Both solutions are a mixture of a strong acid and a strong base so cannot form a conjugate acid–base pair.

C: The HCl will convert two-thirds of the NH_3 to its conjugate acid (NH_4^+) so this solution will contain a conjugate acid pair.

D: The HCl will convert all of the NH_3 to its conjugate acid (NH_4^+) and no acid–base conjugate pair will be present.

Correct answer is C.

10 The base dissociation reaction for ammonia is:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Correct answer is D.

11 $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$

colour A colour B

Under acidic conditions the equilibrium will lie to the left and colour A will be observed. Under basic conditions the equilibrium will lie to the right and colour B will be observed. At the equivalence point $[HIn] = [In^-]$.

Correct answer is A.

12 A salt will only dissolve in water to create an acidic solution if one of the ions is acidic.

Nitrate (NO_3^-), chloride(Cl^-) and sodium (Na^+) ions are all spectator ions and have no effect on pH. Ethanoate (CH_3COO^-) and hydrogen carbonate (HCO_3^-) ions are basic and will form basic solutions. Ammonium (NH_4^+) is a weak acid so a solution of ammonium nitrate will be acidic.

Correct answer is A.

13 A buffer solution contains a mixture of both components of a conjugate acid–base pair.

A contains an excess of base so it will form a basic buffer.

B contains two acids so will not form a buffer solution.

C will contain equal concentrations of CH_3COOH and CH_3COO^- and as it is made from a weak acid it will be an acidic buffer with pH < 7.

D is a mixture of a weak acid with a weak base that is not its conjugate and will react to form a salt.

Correct answer is C.

14 **(a)** $K_w = [H^+][OH^-]$

(b) **(i)** $pK_a(HOCl) = 7.52$

OCl^- is the conjugate base of HOCl.

$$pK_b(OCl^-) = pK_w - pK_a(HOCl) = 14.00 - 7.52 = 6.48$$

$$K_b(OCl^-) = 10^{-pK_b} = 10^{-6.48} = 3.3 \times 10^{-7}$$

(ii) Base dissociation reaction for hypochlorite, OCl^-, is:

$$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$$

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]}$$

Let $[OH^-] = [HOCl] = x$:

$$K_b = \frac{x^2}{[OCl^-]}$$

$$x^2 = K_b[OCl^-] = 3.3 \times 10^{-7} \times 0.705 \text{ mol dm}^{-3} = 2.3 \times 10^{-7}$$

$$x = \sqrt{2.3 \times 10^{-7}} = 4.8 \times 10^{-4}$$

$$[OH^-] = 4.8 \times 10^{-7} \text{ mol dm}^{-3}$$

The assumption is that the amount of protonation of OCl^- that occurs is negligible so that the initial $[OCl^-]$ is equal to the $[OCl^-]$ after the acid–base equilibrium is reached, i.e. $[OCl^-]_{eq} = [OCl^-]_{initial} - x \approx [OCl^-]_{initial}$.

(iii) $K_w = [H^+][OH^-]$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{4.8 \times 10^{-4}}$$

$$= 2.1 \times 10^{-11} \text{ mol dm}^{-3}$$

$$pH = -\log[H^+] = -\log(2.1 \times 10^{-11})$$

$$= 10.68$$

15 (a) (i) 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:

$$B(aq) + H_2O(l) \rightarrow BH^+(aq) + OH^-(aq)$$

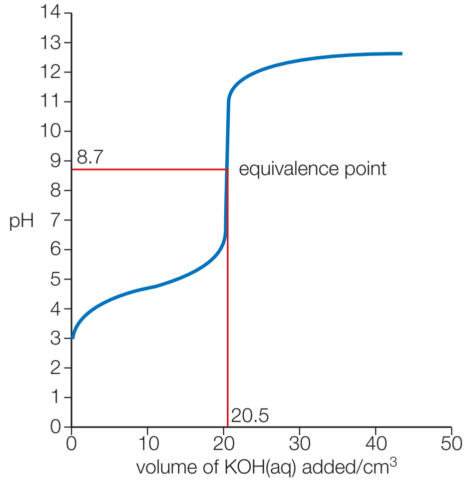
Ammonia (NH_3) is an example of a weak base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

(ii) 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.

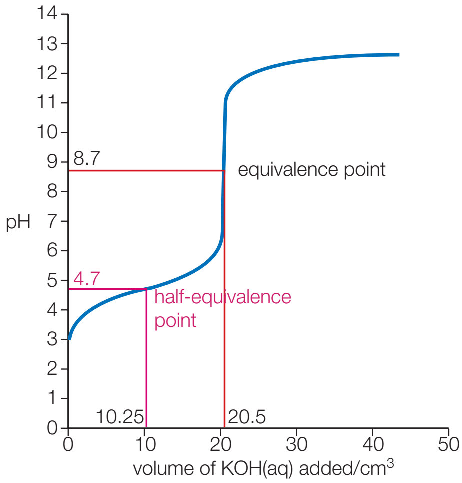
(iii) The equivalence point occurs at a volume of 20.5 cm^3 of KOH(aq) and a pH of 8.7.



(iv) The p*K*a can be found using the half-equivalence point, where half of the KOH(aq) required to reach the equivalence point has been added. At the half-equivalence point pH = $pK_a(CH_3COOH)$.

The half-equivalence point occurs at

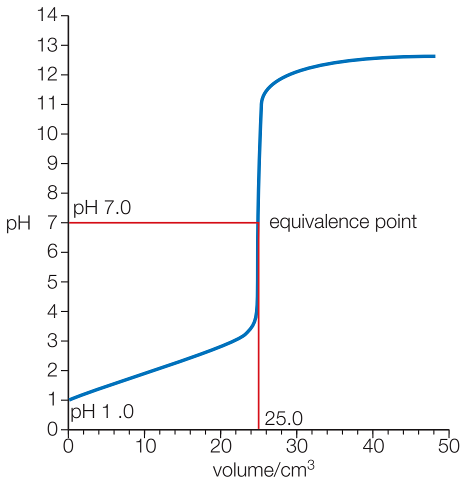
$$\frac{20.5 \text{ cm}^3}{2} = 10.25 \text{ cm}^3.$$



From the graph we see that the pH was 4.7 when 10.25cm^3 had been added.

$pK_a(CH_3COOH) = 4.7$

(v)



HNO_3 is a strong acid that dissociates completely. The starting concentration was 0.100 mol dm^{-3} so starting pH = –log(0.100) = 1.0.

Because the concentrations of HNO_3 and OH^- are the same, the equivalence point will occur after 25.0 cm^3 of OH^- has been added.

The equivalence point for the titration of a strong acid with a strong base occurs at pH = 7.0.

At the end of the titration all of the acid has been neutralized and there is a large excess of the base solution. The pH of the titrated solution will start approaching the pH of the OH^- solution being added.

The concentration of the OH^- solution was 0.100 mol dm^{-3} so pOH = –log(0.100) = 1 and the pH of the OH^- solution is therefore 14 – 1 = 13. The final pH of the titrated solution will be in the pH range 12–13.

(b) **(i)** An indicator (HIn) is a weak acid and the conjugate base (In^-) of the indicator has a different colour to the acid.

The acid–base equilibrium of the indicator can be represented as:

$$\underset{\text{colour 1}}{HIn(aq)} \rightleftharpoons H^+(aq) + \underset{\text{colour 2}}{In^-(aq)}$$

In acidic solution the equilibrium lies to the left and the colour of the solution will be that of the acid, HIn. As base is added and the equilibrium shifts to the right the solution will change colour to that of the conjugate base, In^-.

(ii) The best indicator for the titration is one whose colour change occurs within the steep portion of the titration curve. From the graph provided we can see that the best indicator for the titration of ethanoic acid with KOH(aq) will be phenolphthalein as its colour change occurs within the pH range 8.2–10.0, which lies within the steep portion of the titration curve.

16 **(a)** A strong acid dissociates completely in solution: $HA(aq) \rightarrow H^+(aq) + A^-(aq)$

From the examples provided HNO_3 is a strong acid: $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

A weak acid dissociates partially in solution: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

From the examples provided HCN is a weak acid: $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

(b) $pK_a(HCN) = 9.21$

$K_a(HCN) = 10^{-pK_a} = 10^{-9.21} = 6.2 \times 10^{-10}$

From the acid dissociation reaction for HCN determined in (a):

$$K_a(\text{HCN}) = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

(c) The assumption necessary to determine $[H^+]$ (and pH) is that the dissociation of HCN is negligible and $[\text{HCN}]_{eq} = [\text{HCN}]_{initial}$ at equilibrium, $[H^+] = [CN^-]$.

Let $[H^+] = x$, at equilibrium $[H^+] = [CN^-]$.

$$K_a(\text{HCN}) = \frac{x^2}{[\text{HCN}]}$$

$$6.2 \times 10^{-10} = \frac{x^2}{0.108}$$

$$x^2 = 6.2 \times 10^{-11}$$

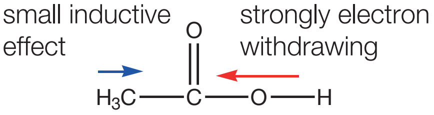
$$x = 8.2 \times 10^{-6}$$

$$[\text{H}^+] = 8.2 \times 10^{-6}\ \text{mol dm}^{-3}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(8.2 \times 10^{-6}) = 5.09$$

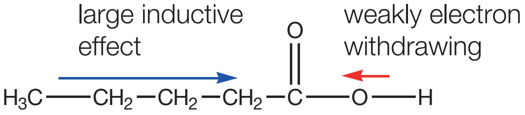
Challenge yourself

1 Increasing the length of the carbon chain increases the donation/push of electrons towards the carbonyl C atom, known as a positive inductive effect. This causes less electron withdrawal from the O–H bond, so weakening acid strength.



$H_3C-\overset{\overset{O}{\|}}{C}-O-H$

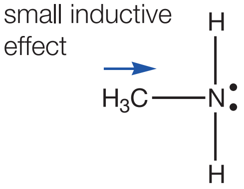
weaker O–H bond, stronger acid



$H_3C-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-O-H$

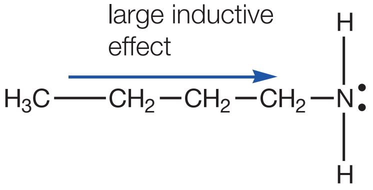
stronger O–H bond, weaker acid

The basic strength of amines depends largely on the availability of the lone pair electrons on nitrogen. Because of the inductive effect the longer carbon chain pushes electrons towards N more than a short chain does, so an amine with a longer carbon chain is a stronger base. (This will make more sense after studying inductive effects in Chapter 10.)



$H_3C-\underset{H}{\overset{H}{N}}{:}$

N electron poor so weaker base



$H_3C-CH_2-CH_2-CH_2-\underset{H}{\overset{H}{N}}{:}$

N electron rich so stronger base

2 **(a)** pH increases on dilution of a strong acid as $[H^+]$ decreases.

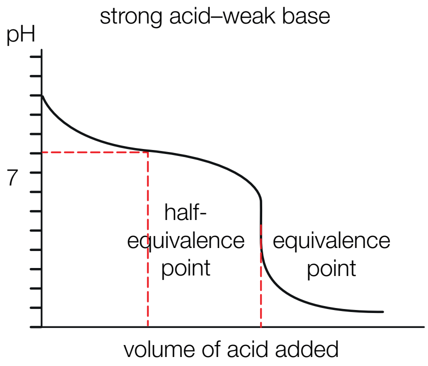
(b) pH increases on dilution of a weak acid as $[H^+]$ decreases, but the change is less than for a strong acid as acid dissociation increases with dilution.

(c) The pH of a buffer stays the same with dilution, as K_a or K_b and the [acid]/[salt] ratio stay constant.

3 [acid] = initial concentration of acid; [HA] = equilibrium concentration of acid. These will be equal only for weak acids, in which the extent of dissociation is so low that the acid is considered to be undissociated at equilibrium. For stronger acids this approximation may not be valid.

[salt] = initial concentration of salt solution; $[A^-]$ = concentration of anion/conjugate base at equilibrium. These will be equal for fully soluble salts in which the formula unit contains a single anion, e.g. NaCl, $MgSO_4$, and where the anion is a very weak base so negligible protonation occurs. If the salt contains more than one anion, e.g. $MgCl_2$, or a strongly basic anion this approximation will not be valid.

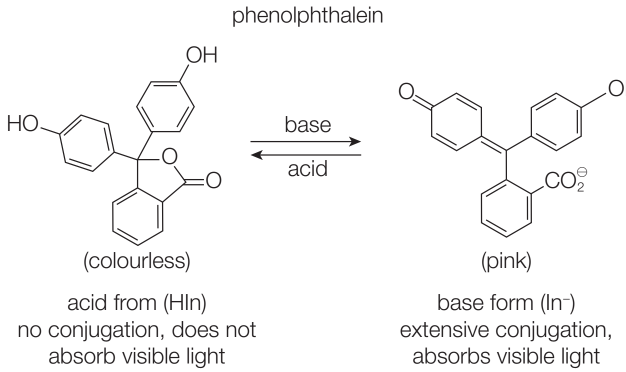
4 The titration needs to add acid from the burette to the base in the flask and the pH should be recorded after each addition of acid. A graph similar to the following will be obtained.



The half-equivalence point, when half the base has been neutralized and half remains unreacted, can be determined from the equivalence point obtained for the titration.

The pOH at the half-equivalence point is then calculated from the pH value obtained from the graph for the half-equivalence point using pH + pOH = 14 (assuming that the temperature is 298 K). The pK_b of the base = pOH at the half-equivalence point.

5 Indicators are typically weak organic acids that contain extensive conjugation, where multiple double bonds are each separated by single bonds. This arrangement allows for overlap of the p orbitals on each carbon and the delocalization of pi electrons throughout the conjugated system. As a result of this conjugation the energy gap between relevant molecular orbitals of the indicator are of the right energy for electronic transitions between these orbitals to occur with the absorption of visible light, giving the indicators their colour (the colour observed is complementary to the colour of the wavelength absorbed). The gain or loss of H^+ changes the extent of conjugation within the indicator and this changes the energy gap between the molecular orbitals. Electronic absorptions then occur with light of a different wavelength and a different colour is observed. See below for the change in conjugation that occurs in the indicator phenolphthalein in acid (HIn) and base (In^-) forms. (Colour is discussed in Topic 13, Chapter 3.)



6 Sulfur is present in proteins in living cells (a component of two out of the twenty amino acids). Decomposition of plant material to peat and then coal conserves this sulfur. Additional sources are the depositional environment such as sea water, where sulfates are reduced by bacteria to form H_2S, which can react further to form organic sulfur structures.

7 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 $N\equiv N$ bond (+942 kJ mol^{-1}), as well as the $O=O$ bond (+498 kJ mol^{-1}). The exothermic step of forming the triple $N\equiv O$ 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.

8 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 408. 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)

$$\text{Oxidation state of Fe} = \frac{(0 - -6)}{2} = +3$$

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^-:

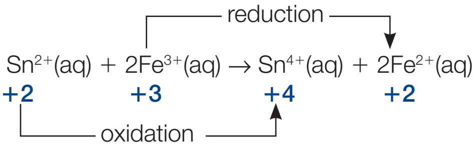
–1 = oxidation state of Mn + 4 × (–2)

Oxidation state of Mn = –1 – (–8) = +7

Oxidation states of elements: Mn = +7, O = –2

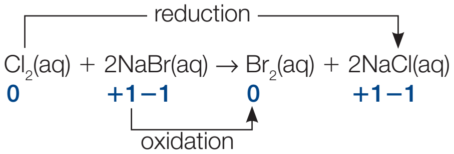
2 The best strategy here is to pick out one element at a time and work out its oxidation state on both sides of the equation. If it has increased, it has been oxidized; if it has decreased it has been reduced. If there is no change in oxidation state that atom has neither been oxidized nor reduced. Check that you have one element being oxidized and one being reduced on each side of the equation.

(a)



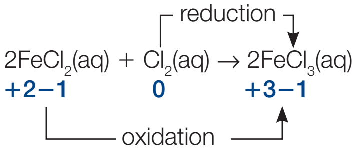
$Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

(b)



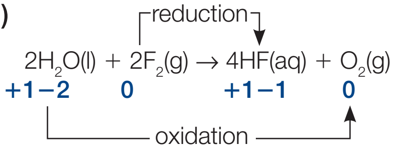
$Cl_2(aq) + 2NaBr(aq) \rightarrow Br_2(aq) + 2NaCl(aq)$

(c)



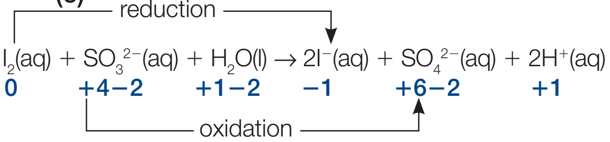
$2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

(d)



$2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$

(e)



$I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

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 412–414. 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 414. 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

$0 = 2 \times (\text{oxidation state of Cr}) + 3 \times (-2)$

$$\text{Oxidation state of Cr} = \frac{0 - (-6)}{2} = +3$$

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.

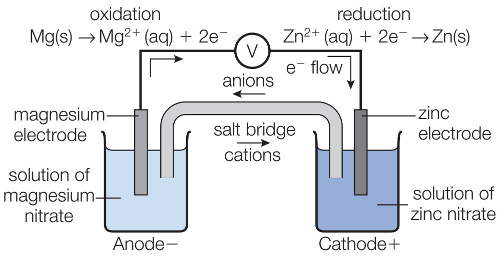
Mg/Mg^{2+} is the anode, where oxidation occurs

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) | Mg^{2+}(aq) || Zn^{2+}(aq) | 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:

$$\underset{}{Fe(s)} + \underset{\text{(blue)}}{Cu^{2+}(aq)} \rightarrow Fe^{2+}(aq) + \underset{\text{(red/brown)}}{Cu(s)}$$

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 $E^\ominus_{\text{cell}} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$

From the given standard electrode potential values, first deduce in which half-cell reduction will occur. The species with the higher $E^\ominus$ value will be reduced.

$E^\ominus(Cr^{3+}) = -0.75$ V, $E^\ominus(Cd^{2+}) = -0.40$ V

Due to its higher (less negative) *E* value, Cd^{2+} will be reduced. Now the $E^\ominus$ values can be substituted:

$E^\ominus(Cd^{2+}) - E^\ominus(Cr^{3+}) = -0.40\text{V} - (-0.75\text{V}) = +0.35$ V

17 This question needs a similar approach to that in Q16, using the *E* values to deduce where reduction and oxidation occur, respectively.

$E^\ominus_{\text{cell}} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$

From the given standard electrode potential values, first deduce in which half-cell reduction will occur. The species with the higher $E^\ominus$ value will be reduced:

$E^\ominus(BrO_3^-) = +1.44$ V, $E^\ominus(I_2) = +0.54$ V

Due to its higher (less negative) *E* value, BrO_3^- will be reduced. Now the $E^\ominus$ values can be substituted.

The half-equations are:

Reduction: $BrO_3^-(aq) + 6H^+ + 6e^- \rightarrow Br^-(aq) + 3H_2O(l)$

As the iodine half-cell is where oxidation occurs, its (reduction) equation will be reversed. It also needs to be multiplied by three as it only has $2e^-$ compared to the $6e^-$ in the reduction reaction, before adding it to that of the bromide half-cell.

Oxidation: $6I^- \rightarrow 3I_2(s) + 6e^-$

Overall equation: $BrO_3^-(aq) + 6H^+ + 6I^- \rightarrow Br^-(aq) + 3H_2O(l) + 3I_2(s)$

$E^\ominus_{\text{cell}} = E^\ominus(BrO_3^-) - E^\ominus(I_2) = +1.44\text{ V} - (+0.54\text{ V})$
$= +0.90$ V

18 $E^\ominus(Cu^{2+}) = +0.34$ V, $E^\ominus(Mg^{2+}) = -2.37$ V, $E^\ominus(Zn^{2+}) = -0.76$ V

The species with the higher $E^\ominus$ value is the most easily reduced. Cu^{2+} is the most easily reduced, so is the strongest oxidizing agent.

The species with the lowest $E^\ominus$ value is the hardest to reduce but its reverse reaction will have the species that is the most easily oxidized. Mg^{2+} has the lowest $E^\ominus$ value therefore Mg is the species most easily oxidized, so is the strongest reducing agent.

19 **(a)** No reaction can occur as both I_2 and Cu^{2+} can only be reduced based on the equations provided: I_2 to I^- and Cu^{2+} to Cu. With no species present that can be oxidized a redox equation cannot occur.

(b) BrO_3^- can be reduced to Br^- while Cd can be oxidized to Cd^{2+}.

Half-equations:

Reduction: $BrO_3^-(aq) + 6H^+(aq) \rightarrow Br^-(aq) + 3H_2O(l)$

The Cd^{2+} reduction reaction needs to be reversed for the oxidation of Cr(s) and multiplied by three as it only has $2e^-$ compared to the $6e^-$ in the reduction reaction.

Oxidation: $3Cd(s) \rightarrow 3Cd^{2+}(aq)$

Overall equation: $BrO_3^-(aq) + 6H^+(aq) + 3Cd(s) \rightarrow Br^-(aq) + 3H_2O(l) + 3Cd^{2+}(aq)$

$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$

$E^{\ominus}_{cell} = E^{\ominus}(BrO_3^-) - E^{\ominus}(Cd^{2+}) = +1.44\ V - (-0.40\ V) = +1.84\ V$

The $E^{\ominus}_{cell}$ is > 0, therefore the reaction is spontaneous.

(c) As given in the question, Cr would be oxidized to Cr^{3+} and Mg^{2+} would be reduced to Mg(s).

Half-equations:

Reduction: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$

The Cr^{3+} reduction reaction needs to be reversed.

Oxidation: $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$

The reduction reaction needs to be multiplied by two and the oxidation reaction by three so both have a total of $6e^-$.

Reduction: $3Mg^{2+}(aq) + 6e^- \rightarrow 3Mg(s)$

Oxidation: $2Cr(s) \rightarrow 2Cr^{3+}(aq) + 6e^-$

Overall: $3Mg^{2+}(aq) + 2Cr(s) \rightarrow 3Mg(s) + 2Cr^{3+}(aq)$

$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$

$E^{\ominus}_{cell} = E^{\ominus}(Mg^{2+}) - E^{\ominus}(Cr^{3+}) = -2.37\ V - (-0.75\ V) = -1.62\ V$

The $E^{\ominus}_{cell}$ is <0, therefore the reaction is non-spontaneous as written. No reaction occurs.

20 $Al(s) + Cr^{3+}(aq) \rightarrow Al^{3+}(aq) + Cr(s)$

Half-equations:

Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

Reduction: $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$

The standard free energy change is calculated using $\Delta G^{\ominus} = -nFE^{\ominus}$

where n = 3 mol (as shown in the half-equations 3 moles of electrons are transferred)

$F = 96\,500\ (C\ mol^{-1})$

$E^{\ominus} = 0.92\ V$

Therefore $\Delta G = -nFE^{\ominus} = -3\ mol \times 96\,500\ C\ mol^{-1} \times 0.92\ V = -2.7 \times 10^5\ J = -270\ kJ$

21 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:
$2F^-(l) \rightarrow F_2(g) + 2e^-$

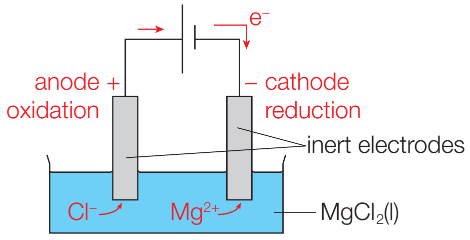
Reduction occurs at the cathode:
$Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$

(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:
$Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$

22 **(a)**



(b) anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

cathode: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$

overall: $Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(s) + Cl_2(g)$

23 **D** $MgCl_2$ 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.

24 Follow the steps on page 444 but recognize that as the electrolysis involves aqueous solutions it is possible that water could also be either oxidized at the anode or reduced at the cathode. Note it is prudent to show awareness that concentration could affect the discharge at the anode, but without information on this it is correct to predict the outcome based on $E^\ominus$ values.

1. Identify the ions present: $K^+(aq)$, $F^-(aq)$.

At the anode possible oxidation reactions are:

$2F^-(aq) \rightarrow F_2(g) + 2e^-$ $\quad -E^\ominus = -2.87$ V

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $\quad -E^\ominus = -1.23$ V

H_2O has the highest $-E^\ominus$ so will be preferentially reduced; $H^+(aq)$ and $O_2(g)$ will be discharged at the anode.

At the cathode possible reduction reactions are:

$K^+(aq) + e^- \rightarrow K(s)$ $\quad E^\ominus = -2.93$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E^\ominus = -0.83$ V

H_2O has the highest $E^\ominus$ so will be preferentially reduced; $OH^-(aq)$ and $H_2(g)$ will be discharged.

Products will be $O_2(g)$ and $H_2(g)$.

25 Different reactions occur for the electrolysis of $CuCl_2(aq)$ depending on the electrodes used.

(a) Carbon electrodes

Ions present: $Cu^{2+}(aq)$, $Cl^-(aq)$.

At the anode possible reactions are:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $\quad -E^\ominus = -1.36$ V

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $\quad -E^\ominus = -1.23$ V

Based on the $-E^\ominus$ values, the oxidation of H_2O will be preferred as it has the higher $-E^\ominus$ value. This is the case when $[Cl^-]$ is low, but at higher $[Cl^-]$ the oxidation of Cl^- becomes more likely given the greater number of Cl^- ions that will be found closer to the surface of the electrode.

At the cathode possible reduction reactions are:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad -E^\ominus = +0.34$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $\quad -E^\ominus = -0.83$ V

Cu^{2+} has the highest $E^\ominus$ so will be preferentially reduced; Cu(s) will be discharged.

Reactions that occur with low $CuCl_2$ concentration

Reduction at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Oxidation at anode: $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

Observations: Carbon cathode will change to a pinky brown colour as Cu(s) is deposited on it. The colour of the solution will fade as the blue $Cu^{2+}(aq)$ ions are reduced to Cu(s). Bubbles will be observed forming at the anode due to the discharge of $O_2(g)$.

Reactions that occur with high $CuCl_2$ concentration

Reduction at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Oxidation at anode: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Observations: Carbon cathode will change to a pinky brown colour as Cu(s) is deposited on it. The colour of the solution will fade as the blue $Cu^{2+}(aq)$ ions are reduced to Cu(s). Bubbles will be observed forming at the anode due to the discharge of $Cl_2(g)$ and a green gas will be observed leaving the solution.

(b) Copper electrodes

Ions present: $Cu^{2+}(aq)$, $Cl^-(aq)$.

With carbon electrodes, which are inert, the species that could be oxidized at the anode were $Cl^-(aq)$ and $H_2O(l)$. With copper electrodes it is also possible that the oxidation can involve the copper metal of the electrode.

At the anode possible reactions are:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $-E^\ominus = -1.36$ V

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $-E^\ominus = -1.23$ V

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $-E^\ominus = -0.34$ V

Based on the $-E^\ominus$ values, the oxidation of Cu will be preferred as it has the higher $-E^\ominus$ value.

At the cathode the possible reactions are:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $-E^\ominus = +0.34$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $-E^\ominus = -0.83$ V

Cu^{2+} has the highest $E^\ominus$ so will be preferentially reduced; Cu(s) will be discharged.

Reactions that occur with low copper electrodes

Reduction at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Oxidation at anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Observations: If it is tarnished and old the copper cathode will change to a pinky brown colour as fresh Cu(s) is deposited on it. The colour of the solution will remain constant – each blue $Cu^{2+}(aq)$ ion reduced to Cu(s) at the cathode is replaced by a $Cu^{2+}(aq)$ ion formed at the anode. The copper anode will start disintegrating as the Cu(s) it is made of is oxidized to $Cu^{2+}(aq)$ ions.

26 Molten NaCl, i.e. NaCl (l)

Ions present: Na^+ and Cl^-

Reduction at cathode: $Na^+(aq) + e^- \rightarrow Na(s)$

Oxidation at anode: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Aqueous NaCl, i.e NaCl(aq)

Ions present Na^+ and Cl^-

At the anode possible reactions are:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $-E^\ominus = -1.36$ V

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $-E^\ominus = -1.23$ V

Based on the $-E^\ominus$ values, the oxidation of H_2O will be preferred as it has the higher $-E^\ominus$ value.

At the cathode possible reduction reactions are:

$Na^+(aq) + e^- \rightarrow Na(s)$ $-E^\ominus = -2.71$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $-E^\ominus = -0.83$ V

Based on the $E^\ominus$ values, the reduction of H_2O will be preferred as it has the higher $E^\ominus$ value and $H_2(g)$ will be discharged at the cathode.

At any concentration of NaCl(aq) the reaction at the cathode for aqueous NaCl is different to the reaction that occurs at the cathode with molten NaCl. H_2O is preferentially reduced in the aqueous solution to form $H_2(g)$: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$.

(At low NaCl(aq) concentrations the reaction at the anode is also different for aqueous NaCl than with molten NaCl. H_2O is preferentially oxidized in the aqueous solution to form $O_2(g)$: $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$. At high NaCl(aq) concentrations the same reaction occurs at the anode as with molten NaCl: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$.)

27 Molten $AlCl_3$ consists of dissociated Al^{3+} and Cl^- ions: $AlCl_3 \rightarrow Al^{3+}(l) + 3Cl^-(l)$.

Ions present Al^{3+} and Cl^-

Reduction at cathode: $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$

Oxidation at anode: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

If 0.2 mol of $Cl_2(g)$ is formed at the cathode then this can be used to determine the total amount of electrons released in the oxidation of Cl^- at the anode:

$n(e^-) = 2 \times n(Cl_2) = 2 \times 0.2 \text{ mol} = 0.4 \text{ mol}$

The number of electrons released in the oxidation at the anode must equal the number of electrons accepted in the reduction at the cathode. We can use this to determine the number of moles of Al(s) discharged at the cathode.

$$n(\text{Al}) = \frac{n(e^-)}{3} = \frac{0.4\text{ mol}}{3} = 0.13\text{ mol*}$$

mass (Al) = nM(Al) = 0.13 mol × 26.98 g mol^{-1} = 3.5 g*

*(*Because the question only gave a value of 0.2 moles of Cl_2, which has one significant figure, then all answers calculated from this value should actually be expressed to one significant figure as well, i.e. moles(Al) = 0.1 mol and mass (Al) = 3 g. An extra figure has been given in these answers to avoid the large rounding errors associated with working with only one significant figure.)*

28 **C** As this is a multiple-choice question it is necessary to be able to deduce the answer without determining the exact amount of Cu(s) that would be formed in each electrolysis. The answer can be determined by calculating the total charge (C) involved in each process and then how many electrons are involved in each reduction.

Cu^+ requires 1 mole of electrons per mole of Cu

Cu^{2+} requires 2 moles of electrons per mole of Cu

charge = current × time

A Charge= 5.00 A × (10 × 60) s = 3000 C for a one-electron reduction ($Cu^+ \rightarrow Cu$)

B *Charge* = 5.00 A × (10 × 60) s = 3000 C for a two-electron reduction ($Cu^{2+} \rightarrow Cu$)

C *Charge* = 2.00 A × (30 × 60) s = 3600 C for a one-electron reduction ($Cu^+ \rightarrow Cu$)

D *Charge* = 2.00 A × (30 × 60) s = 3600 C for a two-electron reduction ($Cu^{2+} \rightarrow Cu$)

Option **C** has the greatest charge (related to the number of electrons) available for a reduction that only involves one electron per reduction therefore this will produce the most Cu(s) product.

29 In electroplating the metal is deposited at the cathode as the anode decomposes.

Reduction at cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Oxidation at anode: $Ag(s) \rightarrow Ag^+(aq) + e^-$

The mass of the silver anode will decrease as Ag is oxidized to Ag^+ ions that are released into the solution.

The mass of the spoon (which is the cathode) will increase as a layer of Ag is deposited on its surface. The metal surface of the spoon will become shiny/grey as the layer of Ag(s) is deposited.

Impurities may be visible collecting as a sludge at the bottom of the electrolyte solution as they fall from the decomposing impure silver anode.

Practice questions

1 $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ is a two-electron reduction.

$Ag^+(aq) + e^- \rightarrow Ag(s)$ is a one-electron reduction.

The total charge available for each cell = current × time.

A Has 500 C available for a two-electron reduction.

B Has 500 C available for a one-electron reduction.

C Has 750 C available for a two-electron reduction.

D Has 375 C available for a one-electron reduction.

Cell B will have the most metal ions being converted to the solid metal and the greatest mass of metal formed.

Correct answer is B.

2 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.

3 A spontaneous reaction occurs when $E^{\ominus}_{\text{cell}}$ is positive. Oxidation occurs at the electrode with

the most negative electrode potential. Reversing the reaction inverses the potential, multiplying the reaction has no effect on the potential as it is an intensive property:

$2Al(s) \rightarrow 2Al^{3+}(aq) + 6e–$ $\qquad -E^{\ominus} = +1.66\ V$

$3Ni^{2+}(aq) + 6e^- \rightarrow 3Ni(s)$ $\qquad E^{\ominus} = –0.23\ V$

$2Al(s) + 3Ni^{2+}(aq) \rightarrow$
$2Al^{3+}(aq) + 3Ni(s)$ $\qquad E^{\ominus}_{cell} = +1.43\ V$

Correct answer is D.

4 This reaction is discussed on page 450. The oxidation and reduction half-reactions for the electrolysis of $CuSO_4$(aq) are:

reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

oxidation: $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

overall: $2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + 4H^+(aq) + O_2(g)$

From the overall reaction we see that Cu(S) and O_2(g) are produced in a mole ratio of 2:1.

Correct answer is C.

5
$$\underset{+7}{MnO_4^-}(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow \underset{+2}{Mn^{2+}}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

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.

6 Electroplating with silver is discussed on page 454. The silver bar must be the positive electrode and the spoon must be the negative electrode. There is no need to acidify the electrolyte solution for the electrolysis of metal ions.

Correct answer is C.

7
$$\underset{+7}{2MnO_4^-}(aq) + \underset{-1}{Br^-}(aq) + H_2O(l) \rightarrow \underset{+4}{2MnO_2}(s) + \underset{+5}{BrO_3^-}(aq) + 2OH^-(aq)$$

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.

8 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.

9 Reduction occurs at the cathode and oxidation occurs at the anode.

For molten $MgBr_2$, Mg^{2+} will be reduced at the cathode and Br^- will be oxidized at the anode.

For aqueous $MgBr_2$, Mg^{2+} or H_2O can be reduced at the cathode. The species that is preferentially reduced is the one with the highest $E^{\ominus}$ potential, in this case H_2O will be reduced ($E^{\ominus}(Mg) = –2.37\ V$, $E^{\ominus}(H_2O) = –1.23\ V$). Br^- will still be the species oxidized at the anode.

Correct answer is B.

10 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.

11 A spontaneous reaction occurs when $E^{\ominus}_{cell}$ is positive. Oxidation occurs at the electrode with the most negative electrode potential. Reversing the reaction inverses the potential, multiplying the reaction has no effect on the potential as it is an intensive property.

$3Fe(s) \rightarrow 3Fe^{2+}(aq) + 6e^-$ $\qquad -E^{\ominus} = +0.44\ V$

$CrO_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow$
$2Cr^{3+}(aq) + 7H_2O(l)$ $\qquad E^{\ominus} = +1.33\ V$

$3Fe(s) + 3\ CrO_7^{2-}(aq) +$
$14H^+(aq) \rightarrow 3Fe^{2+(}aq) +$
$2Cr^{3+}(aq) + 7H_2O(l)$ $\qquad E^{\ominus}_{cell} = +1.77\ V$

($E^{\ominus}_{cell} = E^{\ominus}_{red} – E^{\ominus}_{ox} =+1.33\ V – (–0.44\ V) = +1.77\ V$)

Correct answer is C.

12 **(a)** **(i)** The standard electrode potential is the voltage obtained for a half-cell when it is connected to the standard hydrogen electrode. This measurement must be conducted under standard conditions of 298 K with 1 mol dm^{-3} solutions and an $H_2(g)$ pressure of 100 kPa.

The negative value of the standard electrode potential indicates that the electrons flow from the half-cell to the hydrogen electrode. This means that oxidation is occurring in the half-cell and that Fe is oxidized more readily than H_2. (Fe is a better reducing agent than H_2.)

(ii) The question tells us that cobalt is produced during the reaction so reduction must be occurring in the cobalt half-cell.

$E^\ominus_{cell} = 0.17\ \text{V}$, $E^\ominus_{ox} = E^\ominus(Fe^{2+}/Fe) = -0.45\ \text{V}$

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$$
$$0.17\ \text{V} = E^\ominus_{red} - (-0.45)\ \text{V}$$
$$0.17\ \text{V} = E^\ominus_{red} + 0.45\ \text{V}$$
$$E^\ominus_{red} = -0.28\text{V}$$

The standard electrode potential for the cobalt half-cell is –0.28 V.

(iii) When the voltaic cell is operating cobalt is being produced: $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$.

As $Co^{2+}(aq)$ is being reduced in this process it is the oxidizing agent.

(iv) The reduction half-reactions and the potentials for the two half-cells are:

$$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \quad E^\ominus = -1.66\ \text{V}$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^\ominus = -0.45\ \text{V}$$

The reactions occurring are:

$$2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^- \quad -E^\ominus = +1.66\ \text{V}$$
$$3Fe^{2+}(aq) + 6e^- \rightarrow 3Fe(s) \quad E^\ominus = -0.45\ \text{V}$$

overall equation:

$$2Al(s) + 3Fe^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Fe(s) \quad E^\ominus_{cell} = +1.21\ \text{V}$$

($E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = -0.45\ \text{V} - (-1.66\ \text{V} = +1.21\ \text{V})$

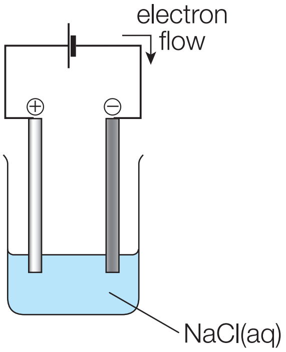
(v) The salt bridge is required to complete the electrical circuit and to allow the movement of ions into the half-cells to maintain the balance of charges as ions are formed and consumed by the redox reactions occurring.

(b) **(i)** 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.

(ii) 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.

(iii) 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.

(c) **(i)**



(ii) The ions present will be Na^+, Cl^-, H^+ and OH^-.

(iii) Reduction occurs at the cathode and there are two possible reductions that can occur:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^\ominus = -0.83\ \text{V}$$
$$Na^+(aq) + e^- \rightarrow Na(s) \quad E^\ominus = -2.71\ \text{V}$$

The reduction with the highest $E^\ominus$ value happens preferentially so the product formed at the cathode is $H_2(g)$ and the half-equation is $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$.

Oxidation occurs at the anode and there are two possible oxidations that can occur:

$2H_2O(l)^+(aq) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $\quad -E^{\ominus} = -1.23\text{ V}$

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-(s)$ $\quad -E^{\ominus} = -1.36\text{ V}$

The oxidation with the highest $E^{\ominus}$ value happens preferentially so the product formed at the anode is $O_2(g)$ and the half-equation is $2H_2O(l)^+(aq) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$.

(If the solution had contained a concentrated solution of NaCl then the second reaction would be favoured despite the higher potential.)

(iv) Reduction:

$4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

Oxidation:

$2H_2O(l)^+(aq) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

Overall:

$2H_2O(l)^+(aq) \rightarrow 2H_2(g) + O_2(g)$

($4H_2O(l)$ on reactants cancelled by $4H_2O(l)$ on products as $4H^+(aq) + 4OH^-(aq) \rightarrow 4H_2O(l)$)

Ratio of $H_2(g)$ to $O_2(g)$ is 2:1.

(d) **(i)** If concentrated NaCl(aq) was used the products would be $H_2(g)$ and $Cl_2(g)$.

The same reaction occurs at the cathode:

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

However, at the anode the higher concentration of $Cl^-(aq)$ favours the reduction of Cl^- rather than H_2O:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

(ii) If molten sodium bromide was used the products would be Na(s) and $Br_2(g)$. Molten sodium bromide contains Na^+ and Br^- ions:

cathode reaction (reduction)

$Na^+(l) + e^- \rightarrow Na(s)$

anode reaction (oxidation)

$2Br^-(l) \rightarrow Br_2(g) + 2e^-$

13 **(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: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

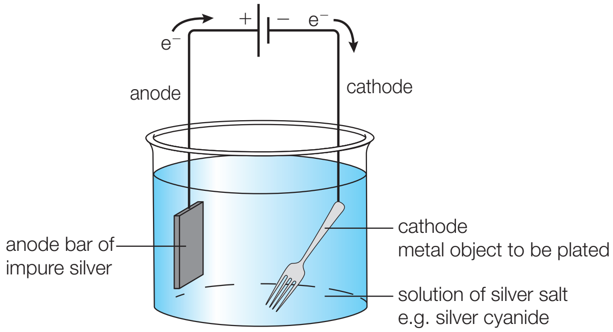
overall: $2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(s) + Cl_2(g)$

(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.

(e) For the electroplating of silver the anode has to be a silver bar or rod as this is where oxidation occurs and silver ions are generated: $Ag(s) \rightarrow Ag^+(aq) + e^-$.

The cathode has to be the object that the silver is being electroplated onto as this is where reduction and the formation of solid silver occurs: $Ag^+(aq) + e^- \rightarrow Ag(s)$.

The electrolyte needs to be a silver salt solution, e.g. aqueous silver nitrate, $AgNO_3(aq)$, to ensure that only Ag^+ ions are present and reduction cannot involve other metal ions.



14 **(a)** $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\ominus = -0.26\ V$

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ $E^\ominus = -1.66\ V$

The reactions occurring will be:

$2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^-$ $-E^\ominus = +1.66\ V$

$3Ni^{2+}(aq) + 6e^- \rightarrow 3Ni(s)$ $E^\ominus = -0.26\ V$

overall equation:

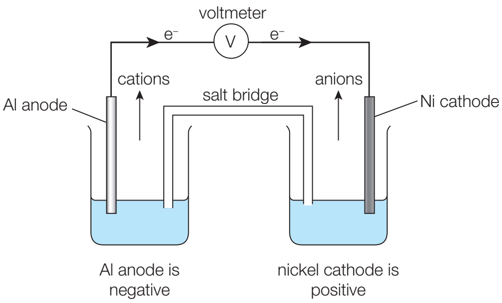
$2Al(s) + 3Ni^{2+}(aq) \rightarrow$

$2Al^{3+}(aq) + 3Ni(s)$ $E^\ominus_{cell} = +1.40\ V$

$(E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = -0.26\ V - (-1.66\ V) = +1.40\ V)$

(b) From the answer to (a), the cell potential is +1.40 V.

(c)



Electrons are generated at the anode by the oxidation of aluminium and they flow through the circuit to the nickel cathode. Anions flow to the aluminium electrode to balance the formation of Al^{3+} and cations flow to the nickel electrode to replace the Ni^{2+} ions being reduced.

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 $\underset{0}{Cl_2}(aq) + 2NaOH(aq) \rightarrow$

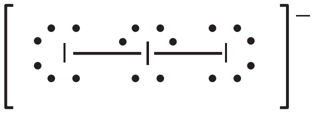
$\underset{-1}{NaCl}(aq) + \underset{+1}{NaClO}(aq) + H_2O(l)$

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) .

5 The Faraday constant, F, is the charge carried by 1 mole of electrons.

Charge of an electron (e) = $1.602176565 \times 10^{-19}$ C

Avogadro's number (N_A) = $6.02214129 \times 10^{23}$ mol^{-1}

$F = e \times N_A = 1.602176565 \times 10^{-19}\ \text{C} \times 6.02214129 \times 10^{23}\ \text{mol}^{-1} = 96485.3365\ \text{C mol}^{-1}$

(For precise values, also see the NIST Reference on Constant, Units and Uncertainty, www.pearsonhotlinks.co.uk/url.aspx?urlid=68468)

6 The relevant equations are $\Delta G^{\ominus} = -RT\ln K_c$ and $\Delta G^{\ominus} = -nFE_{\text{cell}} = -nFE^{\ominus}_{\text{cell}}$

Combining these equations we get $RT\ln K_c = nFE^{\ominus}_{\text{cell}}$

$$E^{\ominus}_{\text{cell}} = \frac{RT\ln K_c}{nF}$$

At 298K, $\frac{RT}{F} = \frac{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{96\,500\ \text{C mol}^{-1}}$

$$= 0.0257\ \text{V}$$

$$\log K_c = \frac{\ln K_c}{2.303}$$

$$E^{\ominus}_{\text{cell}} = \frac{0.0257\ \text{V} \times 2.303\ \log K_c}{n}$$

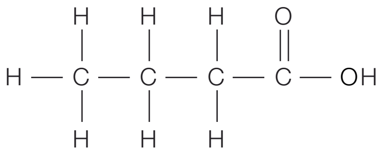
$$= \frac{0.0592}{n}\log K_c$$

Chapter 10

Exercises

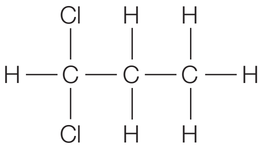
1 Remember to count the carbon of the functional group when naming an organic compound.

(a) $CH_3CH_2CH_2COOH$



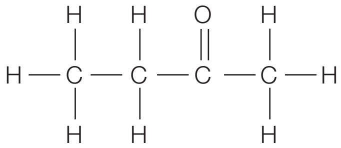
The compound contains the –COOH functional group so it is a **carboxylic acid**. Because it is a carboxylic acid its name will ends in -oic acid. The carbon chain is an alkane that contains four carbons so the compound's name has the stem but-. The compound's name is **butanoic acid**.

(b) $CHCl_2CH_2CH_3$



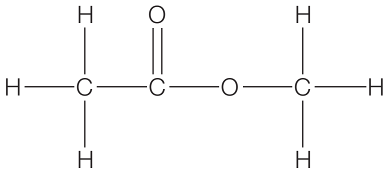
The compound contains two chlorine substituents so it is a **halogenoalkane** (more specifically a **chloroalkane**). Because it is a chloroalkane, its name will have the prefix chloro-. The carbon chain is an alkane that contains three carbons so the compound's name has the stem prop-. There are two chlorine atoms, both on the first carbon so the prefix becomes 1,1-dichloro-. The compound's name is 1,1-dichloropropane.

(c) $CH_3CH_2COCH_3$



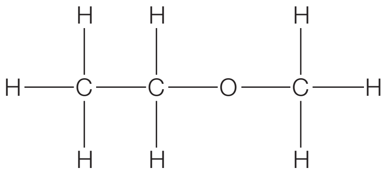
The compound contains a carbonyl functional group (–C=O). Because the carbonyl group is attached to two carbons the compound is a **ketone**. Because it is a ketone its name will end in -one. The carbon chain is an alkane that contains four carbons so the compound's name has the stem but-. The compound's 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) $CH_3CH_2COOCH_3$



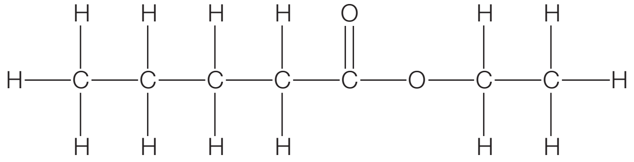
The compound contains an ester functional group (R–COO–R) so it is an **ester**. Because the carbonyl component of the ester contains two carbons the compound's name ends in ethanoate. Because the oxygen component of the ester is attached to a one-carbon chain the name starts with methyl. The compound's 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) $CH_3CH_2CH_2CH_2COOCH_2CH_3$

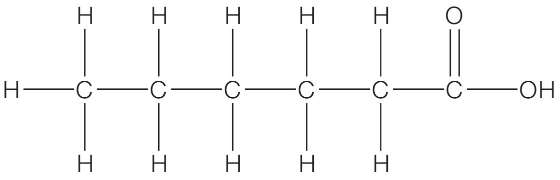


The compound contains an ester functional group (R–COO–R) so it is an **ester**. Because the carbonyl component of the ester contains five carbons the compound's name ends in pentanoate. Because the oxygen component of the ester is attached to a two-carbon chain the name starts with ethyl. The compound's 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.

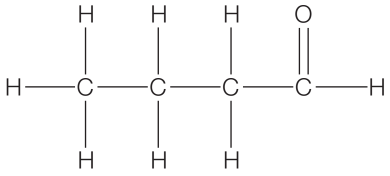
(a) Hexanoic acid: The compound has a six-carbon chain and the –COOH carboxylic acid functional group.

$CH_3(CH_2)_4COOH$



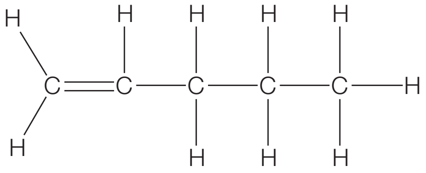
(b) Butanal: The compound has a four-carbon chain and the –CHO aldehyde functional group.

$CH_3CH_2CH_2CHO$



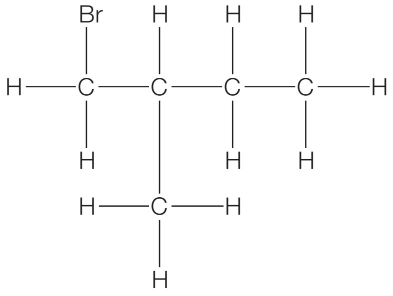
(c) Pent-1-ene: The compound has a five-carbon chain with a C=C double bond after the first carbon.

$CH_2CHCH_2CH_2CH_3$ or $CH_2CH(CH_2)_2CH_3$



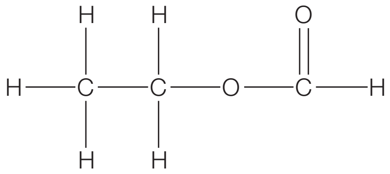
(d) 1-bromo-2-methylbutane: The longest chain has four carbons with a bromine on the first carbon and a methyl (one-carbon branch) on the second carbon.

$CH_2BrCH(CH_3)CH_2CH_3$



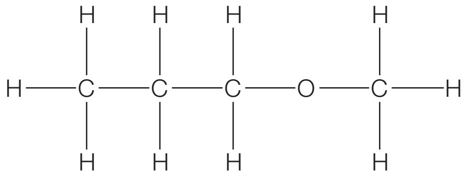
(e) Ethyl methanoate: The compound is an ester with a two-carbon chain attached to the O in the ester and the carbonyl group is part of a one-carbon chain.

$HCOOCH_2CH_3$



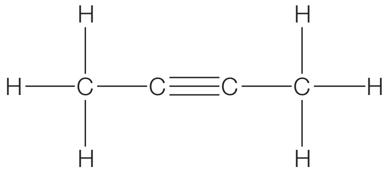
(f) Methxypropane: The compound is an ether with a one-carbon chain on one side of the ether linkage and a three-carbon chain on the other side.

$CH_3OCH_2CH_2CH_3$



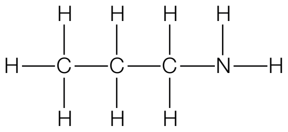
(g) But-2-yne: The compound has a four-carbon chain with a C≡C triple bond after the second carbon.

$CH_3C{\equiv}CCH_3$

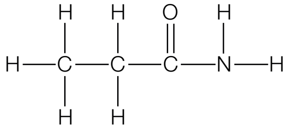


3 **A** Amines contain at least one carbon–nitrogen single bond (it is an analogue of ammonia).

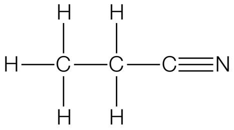
B is not an amine but a primary amide as it contains the $CONH_2$ group. **C** is a nitrile (C≡N group). **D** is a substituted amide as it contains CONH–R (it is a secondary amide).



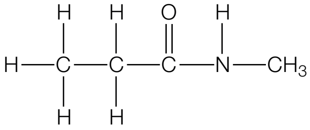
A is an amine



B is an amide

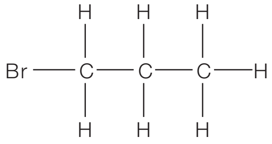


C is a nitrile

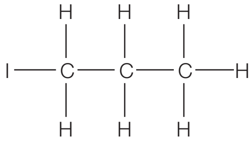


D is a secondary amide

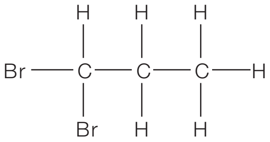
4 **D** Members of homologous series have the same functional group but differ by the number of $–CH_2–$ units present (different chain length). Because 1-bromopropane is a bromoalkane the correct answer will be another 1-bromoalkane with a different chain length.



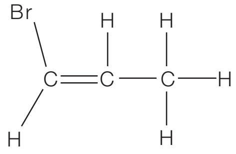
1-bromopropane



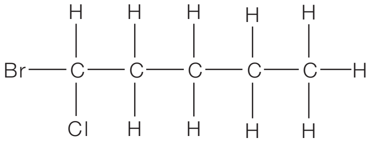
A: 1-iodopropane



B: 1,1-dibromopropane



C: 1-bromopropene

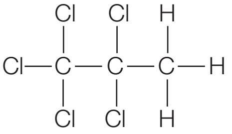


D: 1-bromopentane

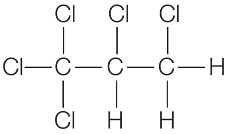
A is an iodo compound, **B** is a dibromo compound and **C** is a bromoalk**ene** so these cannot be members of the same homologous series as 1-bromopropane.

The correct answer is D, 1-bromopentane as it has two more $–CH_2–$ units than 1-bromopropane.

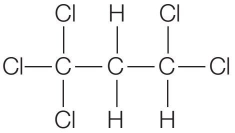
5 The three carbon chain can only exist in a straight chain, so there are no branched isomers. You need to be careful about recognizing when compounds that you have drawn are identical. Remember that there is free rotation about all the C–C bonds. All the compounds are pentachloropropanes. Perhaps the easiest way to approach this question is to work out the different ways of numbering the five chloro substituents.



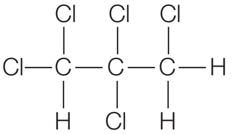
1,1,1,2,2-pentachloropropane



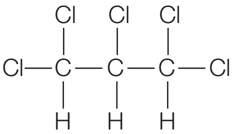
1,1,1,2,3-pentachloropropane



1,1,1,3,3-pentachloropropane

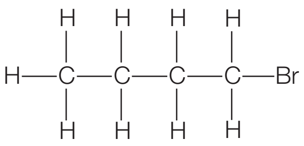


1,1,2,2,3-pentachloropropane

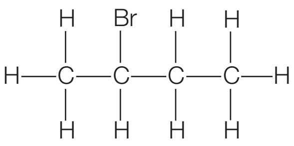


1,1,2,3,3-pentachloropropane

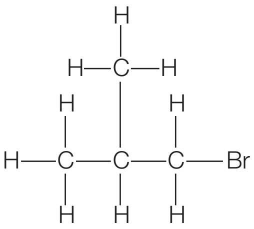
6 **B** A secondary halogenoalkane (bromoalkane in this case) must have a halogen atom bonded to a carbon atom that is also attached to one hydrogen atom and two alkyl groups. **A** is a primary halogenoalkane, **C** is a primary halogenoalkane, and **D** is a tertiary halogenoalkane.



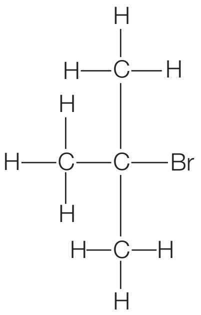
A is a primary bromoalkane



B is a secondary bromoalkane

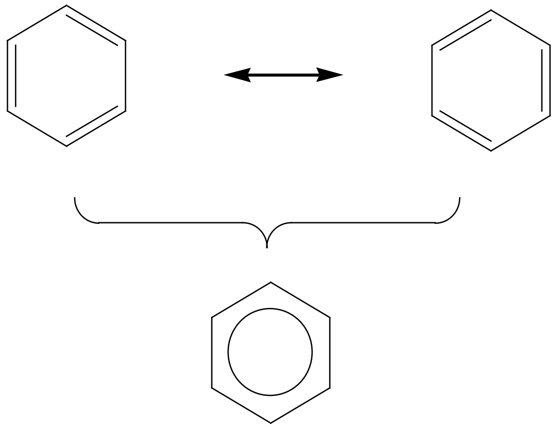


C is a primary bromoalkane



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.

$$\underbrace{H_3C}_{\text{non-polar}}—\underbrace{OH}_{\text{polar}}$$

lower solubility in hexane

$$\underbrace{CH_3—CH_2—CH_2—CH_2—CH_2—CH_2}_{\text{non-polar}}—\underbrace{OH}_{\text{polar}}$$

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)

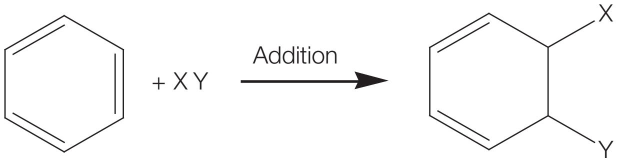
(b) methanal; orange → green (by distilling the reaction mixture the methanal is distilled off before it has time to be oxidized further to methanoic acid)

(c) no reaction; no colour change (as 2-methylbutan-2-ol is a tertiary alcohol and so cannot easily be oxidized into other products)

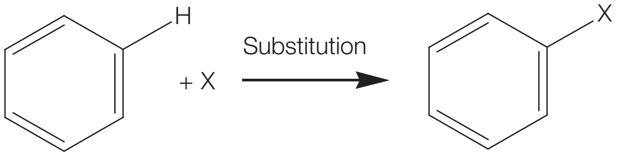
15 Nucleophilic substitution involves an electron-rich species (e.g. OH^-) which acts as a nucleophile attacking an electron-deficient carbon atom attached to an electronegative element (e.g. in chloroethane), leading to substitution of the halogen functional group by the nucleophile.

$C_2H_5Cl + OH^- \rightarrow C_2H_5OH + Cl^-$

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.



17 **(a)** The formulas of the three isomers follow from the definitions on page 476–477.

$CH_3CH_2CH_2CH_2Br$, primary

$CH_3CH_2CHBrCH_3$, secondary

$C(CH_3)_3Br$, tertiary

(b) S_N1 is characteristic of tertiary halogenoalkanes. S_N1 stands for substitution, nucleophilic, unimolecular.

(c) The rate-determining step in the S_N1 mechanism involves only the single reactant, the halogenoalkane. It breaks its carbon–halogen bond heterolytically forming two ions.

$RBr \rightarrow R^+ + Br^-$

18 **C** The compound which reacts most readily by S_N1 mechanisms is a tertiary halogenoalkane (reducing the choice to **A** and **C** as they form the most stable carbocation intermediates). The carbon–halogen bond which breaks most easily is the carbon–iodine. Unfortunately the font used in the text makes it very difficult to distinguish between Cl (chlorine) and CI (carbon bonded to iodine). Compound **A** contains a C–Cl group and compound **C** contains a C–I group. If you thought that the final two characters in **C** stood for chlorine, then the compound you would have been thinking about would be impossible, as it would be lacking its tertiary carbon atom. **A** is a tertiary chlorooalkane, **B** is a primary chlorooalkane, **C** is a tertiary iodoalkane, and **D** is a primary iodoalkane.

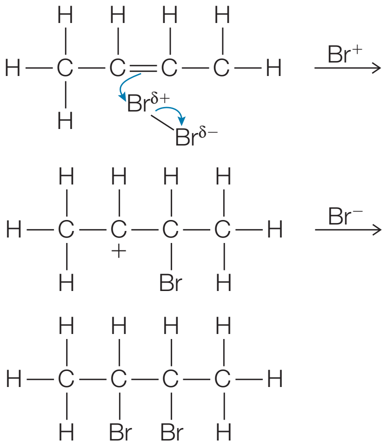
19 **(a)** The iodo- and bromo- compounds are more useful because they are more reactive than the chloro- compounds due to their weaker carbon–halogen bonds. This means that they can react with a wider range of compounds and give rise to a range of intermediates and products.

(b) The substitution reaction of OH for Cl occurs in both these compounds, displacing Cl^- which forms the white precipitate of AgCl, which darkens on exposure to air. The tertiary halogenoalkane $C(CH_3)_3Cl$ isomer reacts more quickly than the primary isomer $CH_3CH_2CH_2CH_2Cl$ because it undergoes an S_N1 mechanism, which is faster.

X must be the tertiary halogenoalkane because it reacts more quickly, due to its S_N1 mechanism. Y is the primary halogenoalkane, which reacts more slowly due to its S_N2 mechanism.

20 Alkenes have a double bond which is an electron-dense region and so is susceptible to attack by electrophiles which are themselves electron deficient. They undergo addition reactions because they are unsaturated; one of the bonds in the double bond breaks and incoming groups can add to the two carbon atoms.

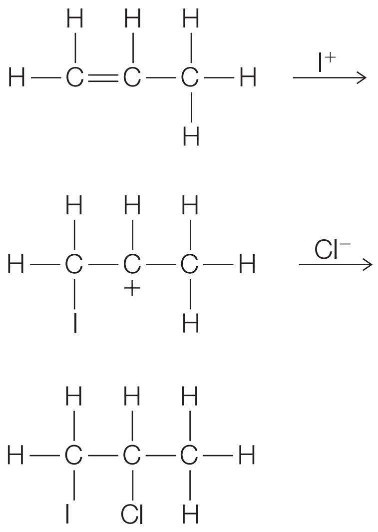
When bromine approaches but-2-ene, the bromine is polarized by the electron density in the double bond. Electrons in the bromine–bromine bond are repelled away from the double bond, leading to the heterolytic fission of the bromine molecule. The Br^+ product now attaches itself to one of the carbon atoms as the carbon–carbon double bond opens. This produces an unstable carbocation which then rapidly reacts with the Br^- ion. The product is 2,3-dibromobutane.



21 but-1-ene + HBr → 2-bromobutane

Application of Markovnikov's rule enables us to predict that the electrophile H^+ will add to the terminal carbon forming a secondary carbocation, as this is stabilized by the positive inductive effect of the alkyl groups. Br^- will then add to carbon 2 forming 2-bromobutane.

22 ICl is polarized as I^{d+} Cl^{d-} owing to the greater electronegativity of Cl than I. So when it undergoes heterolytic fission it will form I^+ and Cl^-. By application of Markovnikov's rule, the I^+ will attach to the terminal carbon, while Cl^- will add to carbon 2. The product is therefore 1-iodo-2-chloropropane.



23 Concentrated H_2SO_4 and concentrated HNO_3. The stronger acid H_2SO_4 protonates the HNO_3, leading to production of the nitronium ion NO_2^+. This is a strong electrophile which reacts with the pi electrons of the benzene ring, substituting for H.

24 **(a)** Because the reactant is a carboxylic acid it cannot be reduced by $NaBH_4$ so the more reactive $LiAlH_4$ is required. Use $LiAlH_4$ in dry ether and heat. The acid is reduced first to the aldehyde and then to the alcohol.

$$CH_3CH_2COOH \xrightarrow{[+H]} C_2H_5CH_2OH$$

(b) Nitrobenzene is heated under reflux with tin and concentrated HCl, and the product is reacted with NaOH.

$$C_6H_5NO_2 \xrightarrow{[+H]} C_6H_5NH_2$$

(c) Ethanal is heated with $NaBH_4$(aq).

$$CH_3CHO \xrightarrow{[+H]} CH_3CH_2OH$$

25 Start with ethanol. Take one portion and oxidize it using acidified potassium(VI) dichromate solution and heat under reflux to allow the reaction to go to completion.

$$C_2H_5OH \xrightarrow{[+O]} CH_3COOH$$

The product is ethanoic acid.

React the ethanoic acid product with another portion of the ethanol by warming it in the presence of some concentrated H_2SO_4. The esterification reaction yields ethyl ethanoate.

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5$$

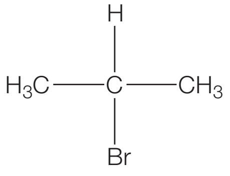
26 React the 1-chlorobutane with NaOH in warm aqueous solution to convert it into butan-1-ol.

$$C_4H_9Cl + NaOH \rightarrow C_4H_9OH + NaCl$$

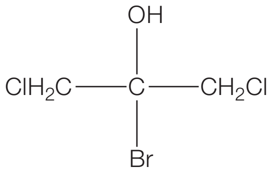
Oxidize the butan-1-ol using acidified potassium(VI) dichromate solution and heat under reflux to allow the reaction to go to completion.

$$C_4H_9OH \xrightarrow{[+O]} C_3H_7COOH$$

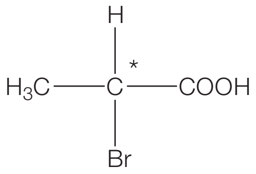
27 **C** Look to see which molecule contains a chiral carbon atom – one that is bonded to four different groups. All four compounds in this question have a three-carbon chain. It will help to draw a full structural formula. **A** has two CH_3 groups, **B** has two CH_2Cl groups, and **D** has two Cl atoms so these cannot be chiral compounds. **C** has a CH_3, H, Br, and COOH bonded to the central C atom so it is chiral.



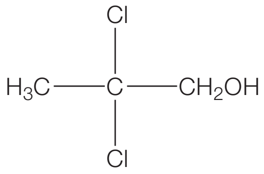
A



B



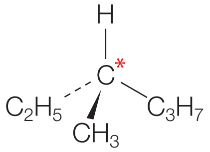
C



D

* = chiral carbon

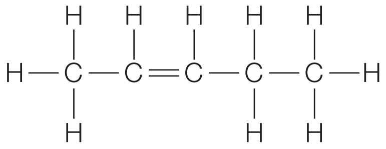
28 Start with a carbon atom and add four different groups which are found in alkanes, so you can add hydrogen (only once) and then three different alkyl groups – methyl, ethyl, and propyl.



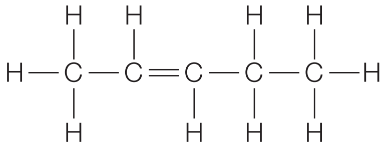
As you can see in the structure the alkane must have seven carbon atoms and have a branched chain. There are four different groups around the chiral carbon atom. Its name is 3-methylhexane.

29 The question mentions the *E*/*Z* convention, so you know you will be writing about geometric isomers. Start with the point of restriction of rotation – either a double bond or a cyclic structure. Then add the other groups to give the two isomers.

(a)



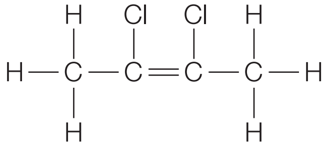
Z-pent-2-ene



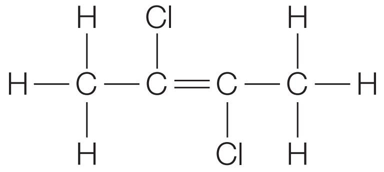
E-pent-2-ene

The groups with higher priority are CH_3 on the left and C_2H_5 on the right. In both cases, C has a higher atomic number than H. The *Z* isomer has the higher priority groups on the same side of the double bond and the *E* isomer has them on opposite sides.

(b)



Z-2,3-dichlorobut-2-ene



E-2,3-dichlorobut-2-ene

The groups with higher priority are Cl on both sides of the double bond. In both cases, Cl has a higher atomic number than C. The *Z* isomer has the higher priority groups on the same side of the double bond and the *E* isomer has them on opposite sides.

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 The reaction of halogenoalkanes with potassium hydroxide occurs via nucleophilic substitution reactions, S_N1 and S_N2, to form alcohols.

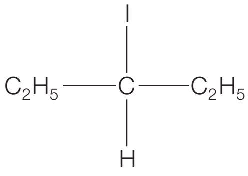
S_N1 occurs for tertiary halogenoalkanes and S_N2 for primary halogenoalkanes.

Iodide is a better leaving group than bromide due to the weaker C–I bond so iodoalkanes react faster than bromoalkanes.

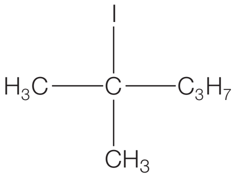
S_N1 reactions are faster than S_N2 so tertiary halogenoalkanes react faster than primary halogenoalkanes.

Correct answer is C.

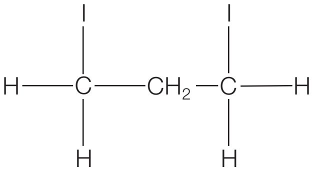
3 Optical isomerism occurs when the compound contains a chiral carbon (asymmetric carbon) with four different groups attached.



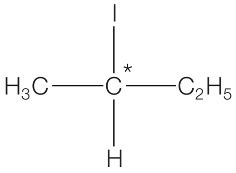
A



B



C

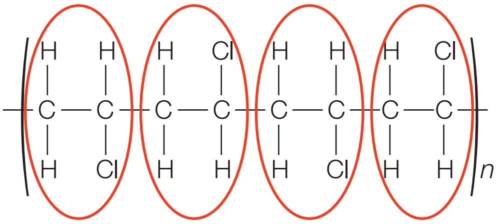


D

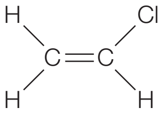
As the structures show, only 2-iodobutane (D) contains an asymmetric carbon.

Correct answer is D.

4 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.

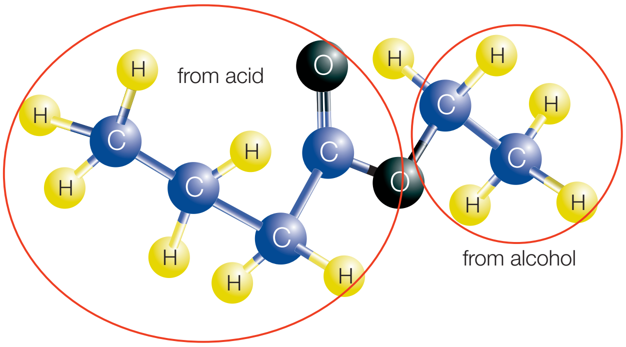
5 Step I converts a halogenoalkane into an alcohol so is a substitution reaction.

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.

6 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.

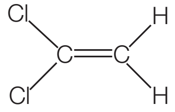
Correct answer is A.

7 In general S_N1 reactions of halogenoalkanes are faster than S_N2 reactions. S_N1 reactions occur via carbocation intermediates and are fastest for tertiary halogenoalkanes as these generate the most stable carbocations. The correct answer will be one of the tertiary halogenoalkanes: 2-iodo-2-methylpropane or 2-chloro-2-methylpropane.

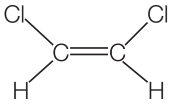
S_N1 reactions are faster for iodoalkanes than for chloroalkanes as the C–I bond is more readily broken than the C–Cl bond and I^- is a better leaving group than Cl^-. Therefore the fastest reaction will occur with 2-iodo-2-methylpropane.

Correct answer is B.

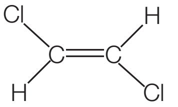
8 There are three isomers for a compound with the molecular formula $C_2H_2Cl_2$:



1,1-dichloroethene



cis-dichloroethene



trans-dichloroethene

Correct answer is C.

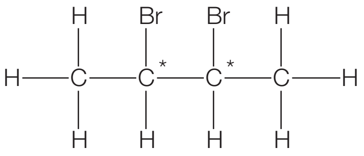
9 With complete combustion of hydrocarbons the products are carbon dioxide and water, so A is incorrect.

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.

10 Chiral carbons (asymmetric carbons) have four different groups attached.



2,3-dibromobutane
* = chiral carbon

From the structure we can see that 2,3-dibromobutane has two chiral carbons.

Correct answer is B.

11 The substitution reactions of alkanes occur via a free-radical mechanism.

A Converting alkane to halogenoalkane: substitution of Br via free-radical mechanism.

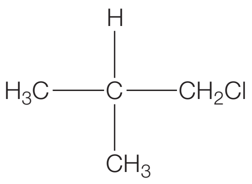
B Converting alkene to dibromoalkane: addition reaction.

C Converting iodoalkane to alcohol: nucleophilic substitution.

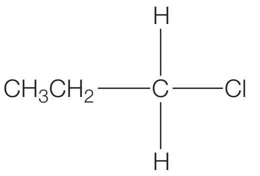
D Converting iodoalkane to alcohol: nucleophilic substitution.

Correct answer is A.

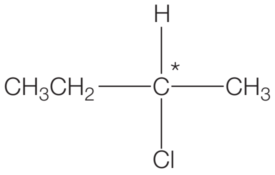
12 Compounds can rotate plane polarized light if they are optical isomers. Optical isomers are formed when a compound contains a chiral carbon with four different groups attached.



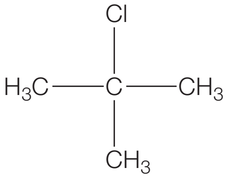
A



B



C

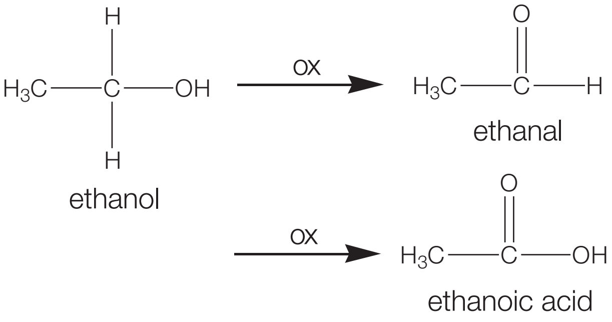


D

* = chiral carbon

Correct answer is C.

13 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.

14 Enantiomers of chiral compounds have identical physical properties with the exception of how they interact with plane polarized light.

The chemical reactions of enantiomers are not identical as they will react differently with other chiral compounds.

A racemic mixture (50/50 mix of the two enantiomers) will not rotate the plane of polarized light as the effects of the two enantiomers cancel.

One enantiomer will rotate the plane of polarized light in one direction whereas the other enantiomer will rotate it in the opposite direction.

Correct answer is D.

15 **(a)** **A** 1-bromobutane

B 2-bromobutane

C 2-bromo-2-methylpropane

D 1-bromo-2-methylpropane

(b) **(i)** S_N1 means first-order nucleophilic substitution (or unimolecular nuceophilic substitution). 'S_N' refers to the reaction being a nucleophilic substitution and '1' refers to it being first order. Tertiary bromoalkanes react almost exclusively via an S_N1 mechanism. A and D are both primary bromoalkanes, B is a secondary bromoalkane and C is a tertiary bromoalkane. Isomer C

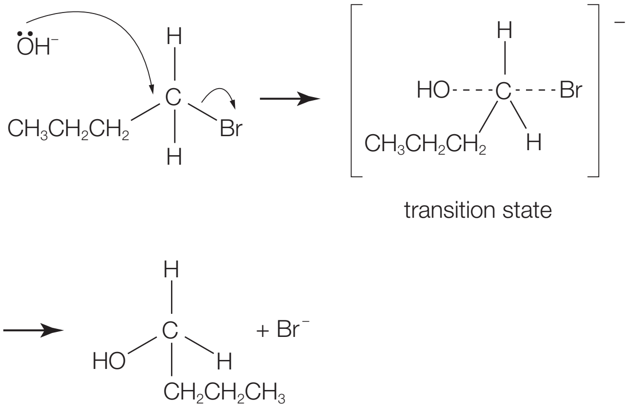
(2-bromo-2-methylpropane) will react via an S_N1 mechanism.

(ii) S_N1 reactions occur via a two-step mechanism. The rate-determining step (the slow step) is the first step which involves the heterolytic fission of the C–Br bond:

$$RBr \rightarrow R^+ + Br^-$$

(iii) Primary bromoalkanes react almost exclusively via an S_N2 mechanism. Isomers A and D are both primary bromoalkanes and will react via an S_N2 mechanism.

Consider the mechanism for the reaction of isomer A, 1-bromobutane:



(c) In b(i) the reaction mechanism is S_N1. The rate equation for an S_N1 reaction of a bromoalkane (RBr) with hydroxide (OH^-) is rate = k[RBr].

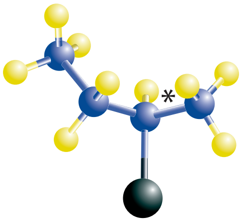
This reaction is zero order with respect to OH^- so if the concentration of OH^- is doubled there will be no effect on the reaction rate.

In b(ii) the reaction mechanism is S_N2. The rate equation for an S_N2 reaction of a bromoalkane (RBr) with hydroxide (OH^-) is rate = $k[RBr][OH^-]$.

This reaction is first order with respect to OH^- so if the concentration of OH^- is doubled the reaction rate will also double.

(d) The rate of reaction will be faster for 1-bromobutane than for 1-chlorobutane as Br is a better leaving group than Cl as the C–Br bond is weaker than the C–Cl bond and will break more readily.

(e) Enantiomers (optical isomers) are a type of stereoisomer that exist in compounds that contain chiral carbons with four different groups attached. From the structures provided we can see that isomer B, 2-bromobutane, has a chiral carbon (marked * in the diagram) and can therefore exist as two different stereoisomers that are enantiomers and can be identified using a polarimeter:



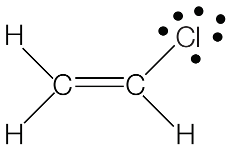
B

A polarimeter measures the angle that a plane of polarized light is rotated through due to its interactions with enantiomers (see page 522). One enantiomer will rotate the plane of polarized light clockwise and the other enantiomer will rotate the plane of polarized light anti-clockwise.

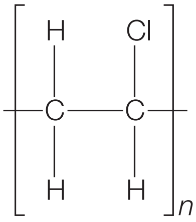
Enantiomers have identical physical properties except for their interaction with plane polarized light. They also have identical chemical properties except for their reactions with other chiral compounds.

16 **(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:

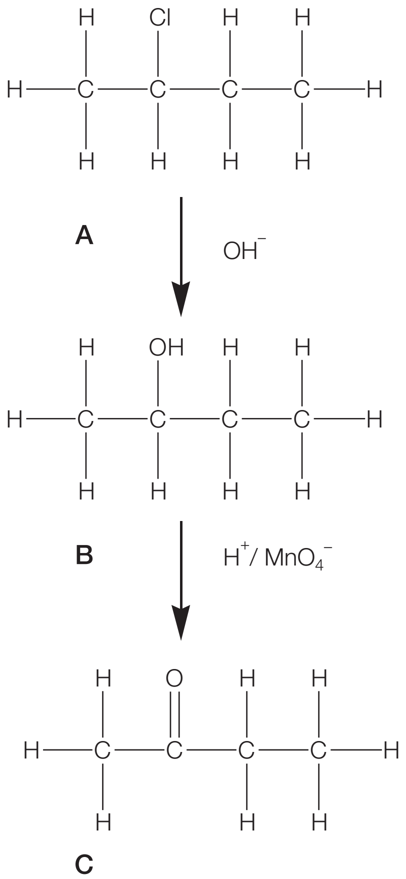
- production of ethanol from ethene (and subsequent production of ethanoic acid)
- synthesis of ethylene glycol (ethane-1,2-diol)
- use as reagents or precursors in synthesis of drugs and pesticides
- manufacture of margarine from unsaturated oils.

17 We can deduce the structural formulas for A–C by working backwards.

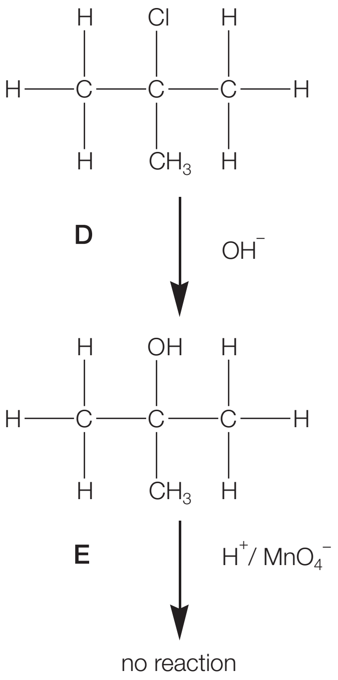
If C has the formula C_4H_8O and was formed from an oxidation reaction with acidified manganite(VII) it must be an aldehyde or a ketone. If it resists further oxidation it is a ketone.

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.



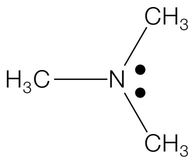
(b) Reaction is $CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$.

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.

Challenge yourself

1 All four carbon atoms in the molecule are sp^3 hybridized because they form four single bonds that are tetrahedrally arranged. The nitrogen atom is also sp^3 hybridized, as its four electron domains are also tetrahedrally arranged. Note that here the hybridization also includes the lone pair on the nitrogen atom.



2 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.

3 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 a negative ion:

$$A{-}B \longrightarrow A^{+} + B^{-}$$

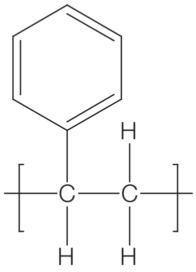
Because of their position above and below the bonding plane the pi electrons in the double bond are accessible to reactive species such as electrophiles and the heterolytic fission of a pi bond is the basis of the mechanism for addition reactions (see page 505).

4 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



5 When species such as cyanide (CN^-) or ammonia (NH_3) act as ligands or nucleophiles they are acting as Lewis bases by donating one pair of electrons to another species.

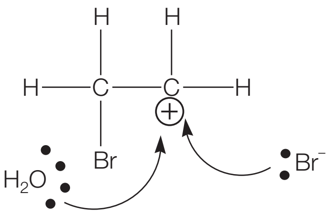
As a nucleophile they react with halogenoalkanes (e.g. R–Br) via nuclear substitution reactions and donate the lone pair to a carbon centre to form nitriles (R–CN) with CN and amines ($R{-}NH_2$) with NH_2.

As a ligand they react with transition metal centres by donating a lone pair of electrons to the metal centre and creating a coordination bond and the formation of complexes such as $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(CN)_4]^{3-}$.

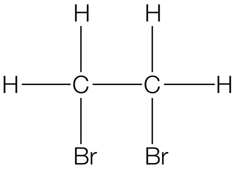
They can also react as Lewis bases in other reactions, such as $NH_3 + BCl_3 \rightarrow NH_3BCl_3$.

6 The order of the reaction with respect to each reactant can be deduced from experiments in which the concentration of each reactant in turn is changed and the initial rate of the reaction then measured. If, for example, the concentration of halogenoalkane is doubled while the concentration of OH^- remains constant, and the rate is found to have doubled, then it indicates that the reaction is first order with respect to halogenoalkane. Examples of this type of experiment and the interpretation of the results are given in Chapter 6.

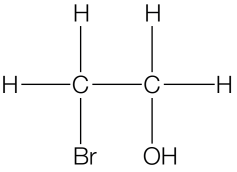
7 With bromine water, the water can also take part in the second part of the reaction as its lone pairs enable it to act as a nucleophile. Both Br^- and H_2O can attack the carbocation:



The product that results from attack of bromide is 1,2-dibromoethane and the product formed by attack of water is 2-bromoethanol.



1,2-dibromoethane

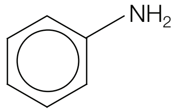


2-bromoethanol

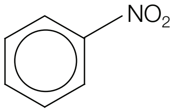
The relative concentrations of 2-bromoethanol and 1,2-dibromoethane depend on the strength of the bromine water used. The higher the concentration of bromine, the higher relative concentration of 1,2-dibromoethane that is formed.

Bromine water is brown/orange in colour and this colour will fade as bromine reacts with the alkene and is removed from the solution, being replaced by the colourless products.

8



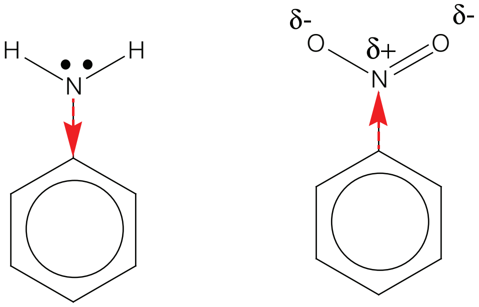
phenylamine



nitrobenzene

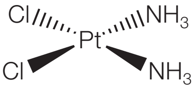
If phenylamine is more reactive towards electrophilic substitution than benzene this means the aromatic ring must be more attractive to electrophiles and it has a higher electron density. This is a result of the lone pair on the amine nitrogen being delocalized into the aromatic ring, increasing the electron density of the ring.

If nitrobenzene is less reactive towards electrophilic substitution than benzene this means the aromatic ring must be less attractive to electrophiles and it has a lower electron density. This is a result of π electrons from the ring being delocalized onto the NO_2 group, decreasing the electron density of the ring.

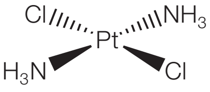


9 In both square planar and octahedral compounds, geometric isomers can arise due to groups having the possibility of being in adjacent (*cis*) or in across (*trans*) positions.

cis-platin and *trans*-platin are examples of geometric isomerism in square planar complexes:

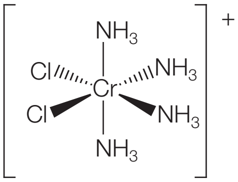


cis-platin
(*cis*-$[Pt(NH_3)_2Cl_2]$)

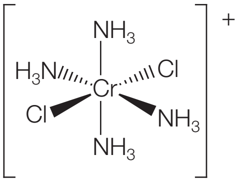


trans-platin
(*trans*-$[Pt(NH_3)_2Cl_2]$)

cis-$[Cr(NH_3)_4Cl_2]^+$ and *trans*-$[Cr(NH_3)_4Cl_2]^+$ are examples of geometric isomerism in octahedral complexes:



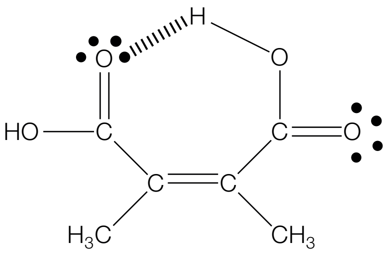
cis-$[Cr(NH_3)_4Cl_2]^+$



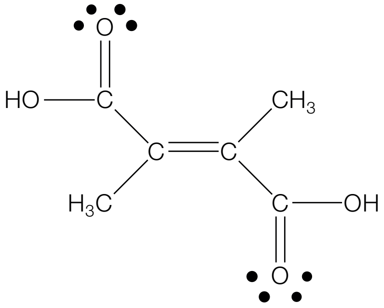
trans-$[Cr(NH_3)_4Cl_2]^+$

In tetrahedral compounds, all positions are adjacent to each other, so *cis* and *trans* geometric isomers are not possible. (However a different form of geometric isomerism, optical isomerism, is possible if all four groups attached to the central atom are different, as discussed in section 20.3.)

10 As shown in the diagram below **intra**molecular hydrogen bonding can occur in *cis*-butenedioic acid due to the close proximity of the two acid groups.



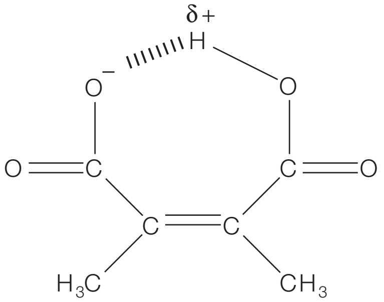
cis-butenedioic acid



trans-butenedioic acid

If **intra**molecular hydrogen bonding occurs this will reduce the amount of **inter**molecular hydrogen bonding that can happen. This results in the melting point and boiling point of *cis*-butenedioic acid being lower than that of *trans*-butenedioic acid, where the two acid groups can only engage in intermolecular hydrogen bonding. *Cis*-butenedioic acid is also more soluble in water due to the decreased strength of the intermolecular interactions.

Cis-butenedioic acid is a stronger acid because the *cis* anion formed from deprotonation is more stable than the *trans* form due to intramolecular interactions between the negative charge on the oxygen and the δ+ on the adjacent acid group.



cis-butenedioic acid anion

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, '$\times 10$' 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 = $\frac{2\%}{100\%} \times 57.536$ 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 538).

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 D It is harder to read the true value from the top of the meniscus so both the accuracy and the precision 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 A Random errors only can cancel when differences in quantities are calculated. This wouldn't have any effect on systematic 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 = 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 2.050 ± 0.050 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 0.5% + 0.5% = 1% = ±0.001.

20 number of moles = volume × concentration

= 1.00 mol dm^{-3} × 10.0 × 10^{-3} dm^3

= 10.0 × 10^{-3} mol = 1.00 × 10^{-2} 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 ± 0.06) × 10^{-2} mol

21 **(a)** $\Delta T = 43.2 - 21.2$ °C = 22.0 °C

absolute uncertainty = (±)0.2 °C

(b) % uncertainty = $\frac{0.2}{22.0} \times 100\% \approx 1\%$

(c) $\Delta H = \frac{-4.18 \times 22.0}{0.500} = -184$ kJ mol^{-1}

(d) 1%

(e) absolute uncertainty = $\frac{1}{100} \times 184 =$ ±2 kJ mol^{-1}

(f) experimental value for ΔH = −184 ± 2 kJ mol^{-1}

The literature value is outside this range. The random errors involved in reading the thermometer do not account for this difference.

There are systematic errors. The assumptions on which the calculation is based are not strictly valid. Some of the heat of reaction passes into the surroundings and the other uncertainties in the measurements cannot be ignored. It should also be noted that the standard value for ΔH refers to standard conditions of 298 K and 100 kPa.

22 **B** If $PV = nRT$ is rearranged to obtain a general equation of a straight line ($y = mx$) then $P =$ 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) g/(73 – 16) cm^3 = 150 g/57 cm^3 = 2.6 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}.

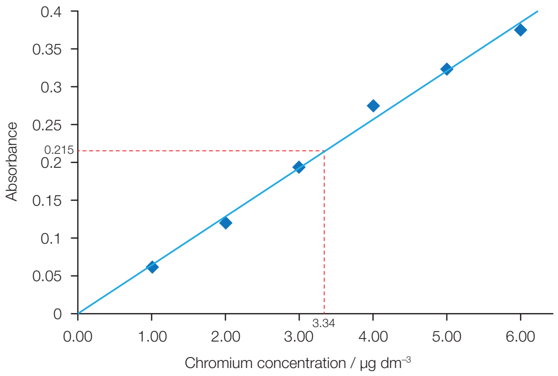
The fact that the best-fit line passes through all of the points, and their associated error bars, indicates that there were no significant random errors in the experiment.

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.

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 B Taking logs of both sides of the equation $\ln k = \ln A - \frac{E_a}{RT}$

A graph of ln k versus $\frac{1}{T}$ will give a straight line.

27 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.

28 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 $C_2H_5CO_2CH_3$.

29 A (the spectrum on the left) corresponds to CH_3CH_2CHO

B (the spectrum on the right) corresponds to CH_3COCH_3

Similarities

Both have a molecular ion corresponding to 58.

Differences

A has peaks corresponding to 29 ($CH_3CH_2^+$), 28 (loss of CH_3CH_2) and 57 ($CH_3CH_2CO^+$).

B has a peak corresponding to 43 (loss of CH_3).

30 **(a)**

Mass / charge	Fragment
15	CH_3^+
29	$C_2H_5^+$
43	$C_3H_7^+$
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}.

31

Molecule	Corresponding saturated non-cyclic molecule	IHD
C_6H_6	C_6H_{14}	4
CH_3COCH_3	C_3H_8O	2
$C_7H_6O_2$	$C_7H_{16}O$	5
C_2H_3Cl	C_2H_5Cl	1
C_4H_9N	$C_4H_9NH_2$	1
$C_6H_{12}O_6$	$C_6H_{14}O_6$	1

32 B With single bonds between large atoms, the molecules will vibrate the lowest frequency and so will have the longest wavelength absorption.

33 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 557).

34 **B** Both aldehydes and esters contain carbonyl groups, which absorb at 1720 cm^{-1} (see table on page 557).

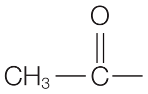
35 **(a)**

	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 $C_2H_4O_2$.

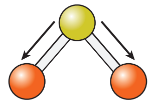
(b) IHD = 1

(c) The absorptions correspond to a carbonyl group and hydrogen-bonded hydroxyl group. Molecular structure is

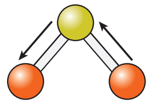


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$, ethanoic acid.

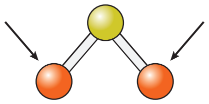
36



symmetric stretch
IR active



asymmetric stretch
IR active



symmetric bend
IR active

37 **B** C—O and C=O bonds absorb strongly whereas C=C only has a medium-weak absorption (see table on page 557).

38 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.

39 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.

40 C—H bond (see table on page 557).

41 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}.

42 **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.

43 **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.

44 **(a)** 2, the two CH_3 groups are in different environments

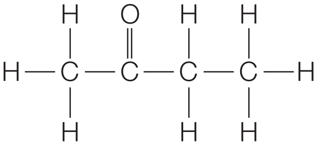
(b) 1, the molecule is symmetrical so the CH_3 groups are in the same environment

(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

45 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 561–562).

46 **(a)** $CH_3COCH_2CH_3$



$$\begin{array}{ccccccccc} & & H & & O & & H & & H & & \\ & & | & & \| & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & & & | & & | & & \\ & & H & & & & H & & H & & \end{array}$$

(b)

Type of hydrogen atom	Chemical shift / ppm	No. of H atoms	Splitting pattern
CH_3CO	2.2–2.7	3	1
$COCH_2CH_3$	2.2–2.7	2	4, in 1 : 3 : 3 : 1 pattern
CH_2CH_3	0.9–1.0	3	3, in 1 : 2 : 1 pattern

47

Compound	Number of peaks	Chemical shift / ppm	No. of H atoms	Splitting pattern
CH_3CHO	2	2.2–2.7	3	2, in 1 : 1 pattern
		9.4–10.0	1	4, in 1 : 3 : 3 : 1 pattern
CH_3COCH_3	1	2.1	6	1

48 IHD is 2, so either one double bond (either C=C or C=O) or a ring structure (unlikely as the largest ring would be a four-membered ring, which would be very strained). Possible structures (esters and carboxylic acid) are CH_3CH_2COOH, CH_3COOCH_3, $HCOOCH_2CH_3$. Could also be $H_2C{=}CHCH_2OH$.

- The peak at 8.0 ppm corresponds to R—COOH. There is no splitting as there are no hydrogen atoms bonded to neighbouring carbon atoms.
- The peak at 1.3 ppm corresponds to a $—CH_3$ group. The peak is split into a triplet because there is a neighbouring $—CH_2—$ group.
- The peak at 4.3 ppm corresponds to the $R—CH_2—COO$ group. The peak is split into a quartet as there is a neighbouring $—CH_3$ group.

  Molecular structure: CH_3CH_2COOH

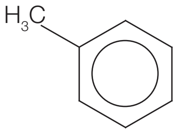
49 X-ray crystallography

50 Monochromatic means all the X-rays have the same wavelength. The angle of diffraction depends on the wavelength. If the X-rays have different wavelengths, different diffraction angles/pattern would be obtained. It would be impossible to match the angles with the wavelengths.

51 Hydrogen atoms have a low electron density.

52 The atoms must have a regular arrangement if an ordered diffraction pattern is to be produced. Crystals are used if possible.

53 **(a)** $C_6H_5CH_3$



(b) Hydrogen atoms have a low electron density and so do not appear.

(c) The saturated non-cyclic compound is C_7H_{16}. IHD = $\frac{1}{2}(16 - 8) = 4$ (the IHD of a benzene ring = 4 due to the presence of three double bonds and one ring)

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 $C_5H_{10}O_2^+$.

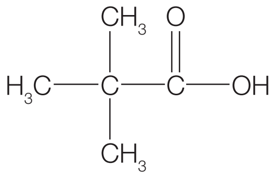
The peak at *m/z* = 57 is due to fragment $C_4H_9^+$.

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:



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OH$

(vi) $CH_3COOCH_2CH_2CH_3$ has four chemical environments so its ^1H 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)** 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^+.

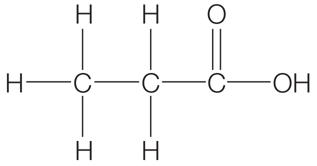
The peak at $m/z = 29$ is due to fragment $C_2H_5^+$.

(c) The peak in the ^1H NMR spectrum at 11.73 ppm is due to the hydrogen in the acid group, $-COO\underline{H}$. (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 ^1H 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 ^1H 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:



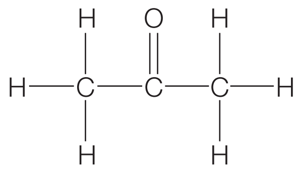
$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$

9 **(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.

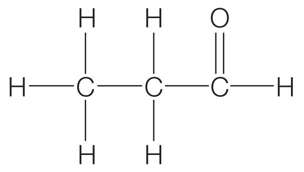
The structure given contains an alkene. The spectrum is not of this structure as a strong peak would be observed in the 1620–1680 cm^{-1} region if a C=C bond was present.

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

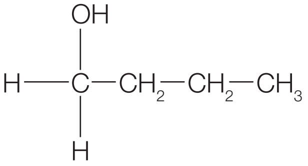


II

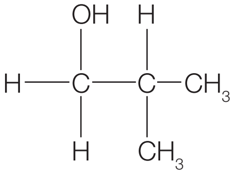
Structure I is not the correct structure as it would give an ^{1}H NMR spectrum with only one peak as all the $C\underline{H}_3$ hydrogens have the same chemical environment.

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.

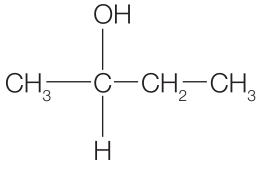
10 The structures of the four alcohols are given below.



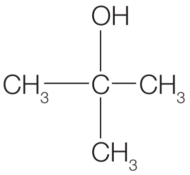
butan-1-ol



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, $-O\mathbf{H}$.

(ii) Spectrum 2 has four peaks in the ^{1}H 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.

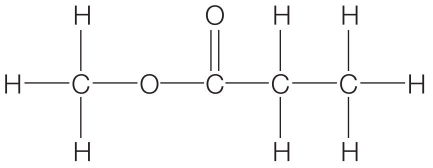
11 With the molecular formula $C_4H_8O_2$ the compound could be an acid or an ester. There is no ^{1}H NMR peak in the acid region, 9.0–13.0 ppm, so the compound is an ester.

The peak at 3.7 ppm is a singlet with an integrated area of three units, which indicates a methyl group, $-C\underline{H}_3$. Because it is a singlet the $n + 1$ rule tells us there are no hydrogens on the neighbouring atoms. Because it is at a high chemical shift this indicates it is adjacent to the oxygen atom of the ester group, $C\underline{H}_3$–O–CO–. (From the data booklet, R–CO–O–$C\underline{H}_2$– occurs at 3.7–4.8 ppm.)

The peak at 2.3 ppm is a quartet with an integrated area of two units, which indicates a methylene group, $-C\underline{H}_2-$. Because it is a quartet the $n + 1$ rule tells us there are three hydrogens on a neighbouring carbon(s), $-C\underline{H}_2-CH_3$. Because it is at a moderately high chemical shift this indicates it is adjacent to the carbon atom of the ester group, R–O–CO–$C\underline{H}_2$–CH_3. (From the data booklet, RO–C(O)–$C\underline{H}_2$– occurs at 2.0–2.5 ppm.)

The peak at 1.0 ppm is a triplet with an integrated area of three units, which indicates a methyl group, $-C\underline{H}_3$. Because it is a triplet the $n + 1$ rule tells us there are two hydrogens on a neighbouring carbon(s), $-CH_2-C\underline{H}_3$. Because it is at a low chemical shift this indicates it is reasonably distant from the ester group, R–O–CO–CH_2–$C\underline{H}_3$. (From the data booklet, $-C\underline{H}_3$ occurs at 0.9–1.0 ppm.)

The structure is:



12 **(a)** **(i)** The peak with highest m/z occurs at 88. This will be due to the molecular ion so the relative molecular mass of X is 88.

The empirical formula given is C_2H_4O, which has a relative formula mass of 44.

As m/z is double the formula mass the molecular formula is $2 \times C_2H_4O = C_4H_8O_2$.

The molecular ion is therefore $C_4H_8O_2^+$.

(ii) The peak at $m/z = 29$ is due to fragments $C_2H_5^+$ or CHO^+.

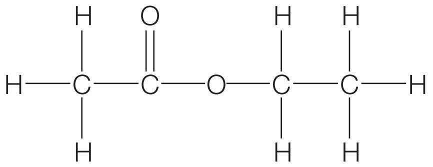
(iii) A peak at $m/z = 59$ would be due to the fragment $C_3H_7O^+$ that would result from the loss of CH_2CH_3. As $CH_2CH_3^+$ is observed at $m/z = 29$ this indicates that the C_3H_7O fragment formed with loss of CH_2CH_3 is not charged. (If it is not charged it cannot be deflected by the magnetic field and be observed at the detector.)

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

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

(ii) The IR spectrum shows that C=O and C–O are both present, which indicates that X contains an acid or an ester functional group. The strong, broad O–H absorption observed for acid O–H bonds at 2500–3000 cm^{-1} is absent from the IR spectrum so we can conclude that X contains the ester functional group.

(c) **(i)** A possible structure is:



$HCOOCH_2CH_3$ (drawn as $H_3C{-}CO{-}O{-}CH_2{-}CH_3$)

Reasoning:

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

From the ^1H NMR data the peak at 2.0 ppm is a singlet with an integrated area of three units, which indicates a methyl group, $–C\underline{H}_3$. Because it is a singlet the *n* + 1 rule tells us there are no hydrogens on the neighbouring atoms. Because it is at a moderately high chemical shift this indicates it is adjacent to the carbon atom of the ester group, $C\underline{H}_3–CO–O–$. (From the data booklet, $RO–CO–C\underline{H}_2–$ occurs at 2.0–2.5 ppm.)

The peak at 4.1 ppm is a quartet with an integrated area of two units, which indicates a methylene group, $–C\underline{H}_2–$. Because it is a quartet the *n* + 1 rule tells us there are three hydrogens on the neighbouring atoms. Because it is at a high chemical shift this indicates it is adjacent to the oxygen atom of the ester group, $–C\underline{H}_2–O–CO–$. (From the data booklet, $R–CO–O–C\underline{H}_2–$ occurs at 3.7–4.8 ppm.)

Because the peak at 4.1 ppm is a quartet and has three hydrogens on the neighbouring atoms we can deduce that the $–C\underline{H}_2–$ is adjacent to a methyl group, $–CH_3$.

(ii)

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

From the structure determined in (ii) we can see that the peak absent from the table will be due to the hydrogens on the methyl group at the end of the alkyl chain, $–CH_2–C\underline{H}_3$.

The *n* + 1 rule tells us this peak will be a triplet and it will have a relative peak area of 3 as three hydrogens share this chemical environment. From the data booklet we see that $–C\underline{H}_3$ occurs at 0.9–1.0 ppm.

(iii) The peak at 4.1 ppm is due to the methylene hydrogens, $CH_3–CO–O–C\underline{H}_2CH_3$. This peak is a quartet as there are three hydrogens on the neighbouring atoms.

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 = $\tfrac{1}{2}(2n + 2 - p)$

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 = $\frac{1}{2}(2n + 2 - p) = 1$

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:

IHD = $\frac{1}{2}(2n + 2 - p - s + r)$

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.

$$\lambda = \frac{1}{\text{wavenumber}} = \frac{1}{2100\ \text{cm}^{-1}}$$
$$= 4.762 \times 10^{-4}\ \text{cm} = 4.762 \times 10^{-6}\ \text{m}$$

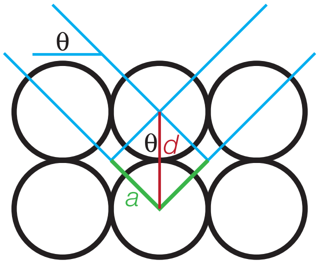
Frequency is related to wavelength by the equation $\nu = c/\lambda$

$$\nu = \frac{3.00 \times 10^{8}\ \text{m s}^{-1}}{4.762 \times 10^{-6}\ \text{m}} = 6.30 \times 10^{13}\ \text{s}^{-1}$$

7 For constructive interference to occur light waves must be travelling parallel to each other and be in phase with each other.

In the diagram below the blue lines represent two light waves travelling through a solid sample. The extra distance travelled by the lower light wave, the path difference, is represented by the green lines. The distance between the layers of atoms, d, is represented by the red line. If the lower light wave is to exit the sample in phase with the upper light wave then the path difference ($2a$) must be a multiple of the wavelength of the light involved:

$$2a = n\lambda \qquad \textbf{(i)}$$



The distance a can be calculated based on d, recognizing that they form two sides of a right-angled triangle, therefore:

$$\sin\theta = \frac{a}{d}$$

$$a = d\sin\theta$$

The extra distance travelled by the lower wave is $2a$, therefore:

$$2a = 2d\sin\theta \qquad \textbf{(ii)}$$

Combining (i) and (ii) by substituting for $2a$ gives the Bragg equation:

$$n\lambda = 2d\sin\theta$$

Worked solutions

Chapter 12

Exercises

1 A A composite is a mixture where one material acts as a matrix (e.g. fibreglass).

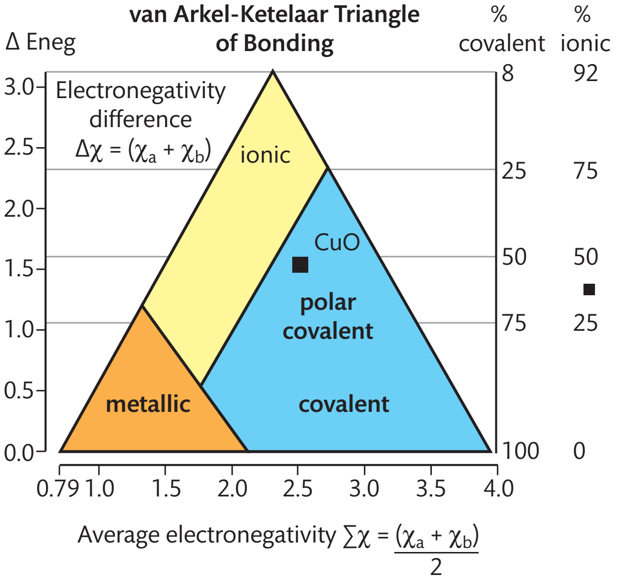
2

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 $$n(e^-) = \frac{I - t}{F} = \frac{0.0965\ \text{A} \times 1000\ \text{s}}{96\,500\ \text{C mol}^{-1}} = \frac{96.5}{96\,500} = 0.001\,00\ \text{mol}$$

$$n(\text{Ti}) = \frac{0.011\,975}{47.9} = 0.000\,250\ \text{mol}$$

$$\frac{n(e^-)}{n(\text{Ti})} = 4$$

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^{2}3p^1	1	paramagnetic
Si	[Ne]3s^{2}3p^2	2	paramagnetic
P	[Ne]3s^{2}3p^3	3	paramagnetic
S	[Ne]3s^{2}3p^4	2	paramagnetic
Cl	[Ne]3s^{2}3p^5	1	paramagnetic
Ar	[Ne]3s^{2}3p^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^{1}4s^2	1
V	[Ar]3d^{3}4s^2	3
Mn	[Ar]3d^{5}4s^2	5
Ga	[Ar]3d^{10}4s^{2}4p^1	1
As	[Ar]3d^{10}4s^{2}4p^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 × 10^7 c s^{-1} = 5.00 × 10^5 c s^{-1} = 500 kc s^{-1}. From the graph and line II, [Hg] is between 1.9 and 2.0 µg dm^{-3}

(c) 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.

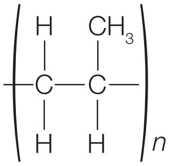
(b) Increases polarity and there are greater intermolecular forces between the molecules that cause them to align their orientation. The more polar molecule is also more responsive to changing orientation when an electric field is applied.

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.

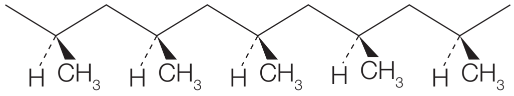
24 **A** There are strong C–C covalent bonds within the chains and relatively strong intermolecular forces between the large polymer chains.

25 **(a)**



$$\left(-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}- \right)_n$$

(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.

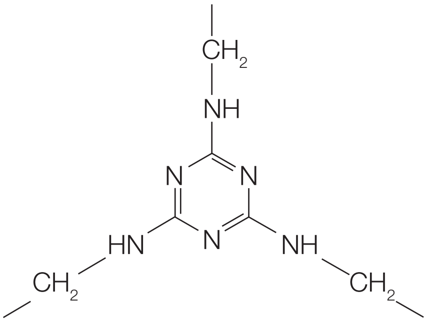
(b) The non-expanded form of polystyrene is a colourless, transparent, brittle plastic. The expanded form is opaque with a lower density. It is a better insulator and shock absorber. The expanded form is produced by heating polystyrene beads with a volatile hydrocarbon such as pentane. The pentane evaporates 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 $= 3.5 \times 10^{-9}$ 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

(b)

Method	Advantages	Disadvantages
recycling	conserves natural resources	plastics need to be sorted

(c) Bacteria do not have the enzymes needed to break the C—C bonds present.

(d) Natural polymers (e.g. starch, cellulose, or protein) can be added. Bacteria can break down the natural polymers and so the bag is broken down into smaller pieces.

33

Method	Advantages	Disadvantages
landfill	efficient method to deal with large volumes	not popular with locals; needs to be maintained and monitored after use
incineration	reduces volume; energy source	can cause pollutants, such as greenhouse gases and dioxins

34 *Advantages:* saves natural resources; saves energy; reduces pollution.

Disadvantages: materials need to be sorted.

35 **(a)** 1–5

(b) 1–4

36 Both molecules have C—H bonds, so they have strong absorptions between 2850 and 3090 cm^{-1}. The monomer has a C=C bond not found in the polymer so it will have a weak absorption at 1620–1680 cm^{-1}.

37 **(a)** A: As the resistance falls to zero at very low temperatures.

(b) A: The resistance is zero at very low temperatures due to the formation of Cooper electron pairs. The crystal structure is distorted at low vibrational energies by the presence of electrons that form pairs, which are more difficult to impede than single electrons.

B: The resistance decreases as the reduced vibrational energies of the ions in the lattice offer reduced resistance to the passage of single electrons.

38 The electrons are given energy as they are accelerated by the power source. They collide with the ions in the lattice and pass on some of their kinetic energy. The average vibrational energy and thus temperature of the ions increases.

39 Type 1 superconductors are metals or alloys. They only exhibit superconductivity at very low temperatures (<20 K). They lose their superconductivity suddenly as the temperature or magnetic field strength is increased.
Type 2 superconductors are ceramic metal compounds. Some can exhibit superconductivity at higher temperatures (<100 K). They lose their superconductivity gradually as the temperature or magnetic field strength is increased.

40

Location of atoms	Number of atoms	Contribution	Total atoms
corner	8	8 × (1/8)	1

There is one atom.

41 **(a)** The diagonal of the cube = $4r_M$

The length of a unit cell = $4r_M / \sqrt{3} = (4 \times 200 / \sqrt{3}) \times 10^{-12}$ m

$= 508 \times 10^{-12}$ m

(b) The volume of a cube = $(508 \times 10^{-12})^3$ m^3

Number of atoms = 2

The mass of an individual atom = $\frac{M(\text{K})}{N_A}$
$= \frac{39.10 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 6.50 \times 10^{-23}$ g

The unit cell contains two K atoms so:

mass of unit cell = $2 \times 6.50 \times 10^{-23}$ g $= 1.30 \times 10^{-22}$ g

density $= \frac{\text{mass}}{\text{volume}} = \frac{1.30 \times 10^{-22} \text{ g}}{(508 \times 10^{-12})^3 \text{ m}^3}$

$= 9.91 \times 10^5$ g m^{-3}

$= 991$ kg m^{-3}

42 **(a)** The diagonal of a face = $4r_M$

The length of a unit cell = $4r_M / \sqrt{2}$

$= (4 \times 144 / \sqrt{2}) \times 10^{-12}$ m

$= 407 \times 10^{-12}$ m

(b) The volume of a cube = $(407 \times 10^{-12})^3$ m^3

Number of atoms = 4

The mass of an individual atom = $\frac{M(\text{Au})}{N_A} = \frac{196.97 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 3.27 \times 10^{-22}$ g

The unit cell contains four atoms so:

mass of unit cell = $\frac{4 \times 196.97}{6.02 \times 10^{23} \text{ g}} = 4 \times 3.27 \times 10^{-22}$ g $= 1.31 \times 10^{-21}$ g

density $= \frac{\text{mass}}{\text{volume}} = \frac{1.31 \times 10^{-21} \text{ g}}{(407 \times 10^{-12})^3 \text{ m}^3}$

$= 1.94 \times 10^7$ g m^{-3}

$= 19.4 \times 10^3$ kg m^{-3}

43 Using the Bragg equation:

$n\lambda = 2d \sin \theta$

with $n = 1$, $\theta = 17.9°$

$$d = \frac{\lambda}{2 \sin \theta}$$

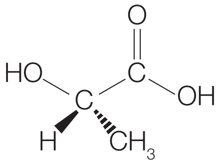
$$d = \frac{150 \times 10^{-12} \text{ m}}{2 \times \sin 17.9°} = 244 \times 10^{-12} \text{ m}$$

Assuming the atoms are touching

$$r = \frac{d}{2} = 122 \times 10^{-12} \text{ m}$$

44 $-(-NH-(CH_2)_6-NH-CO-(CH_2)_8-CO-)_n-$

45 From the structure we see that PLA is a polyester. The monomer must contain an acid functional group and an alcohol functional group.



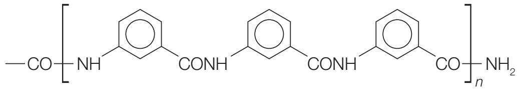
46 **(a)** $\left[O-CH_2-CH_2-CH_2-O-CO-CH_2-CH_2-CO\right]_n + H_2O$

(b) $\left[HN-CH_2-(CH_2)_4-CH_2-NH-CO-CH_2-CH_2-CO\right]_n + HCl$

47 **(a)** The primary amine and carboxylic acid groups.

(b) It is a condensation polymer so the byproduct will be H_2O

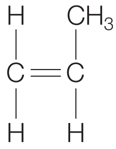
(c)



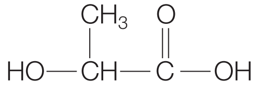
(d) The polymer formed has straight chains. Hydrogen bonds can form between the closely packed chains.

(e) The C, H, N, and O atoms have a lower relative atomic mass than Fe. The atoms in Kevlar® are not close packed, unlike in a metal, so it will have less mass per unit volume and a lower density.

48 **(a)**

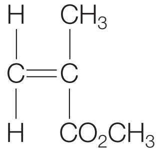


(b)



$\mathrm{HO{-}\overset{CH_3}{\overset{|}{C}}H{-}\overset{O}{\overset{\|}{C}}{-}OH}$

(c)



49 Heavy metal ions interfere with the function of key enzymes. They bind to the proteins instead of essential ions such as Mg^{2+} or Ca^{2+} and so interfere with key biochemical processes.

50 **(a)** The ligand has two O atoms which can form dative coordinate bonds. It is a bidentate ligand.

(b) Each ox forms two bonds. Coordination number = 6. Oxidation state = +3

51 $NiS(s) \rightleftharpoons Ni^{2+}(aq) + S^{2-}(aq)$

if the solubility is s: $[Ni^{2+}(aq)] = s$; $[S^{2-}(aq)] = s$

$K_{sp} = [Ni^{2+}(aq)]\ [S^{2-}(aq)] = s^2 = 2.0 \times 10^{-26}$

$s = \sqrt{2.0 \times 10^{-26}}$

$= 1.4 \times 10^{-13}$ mol dm^{-3}

52 **(a)** $K_{sp} = [Pb^{2+}(aq)]\ [S^{2-}(aq)]$

(b) $K_{sp} = [Cu^{+}(aq)]^2\ [S^{2-}(aq)]$

(c) $K_{sp} = [Al^{3+}(aq)]\ [PO_4^{\ 3-}(aq)]$

(d) $K_{sp} = [Ni^{2+}(aq)]\ [OH^{-}(aq)]^2$

53 **(a)** $K_{sp} = [Ag^{+}(aq)]\ [Cl^{-}(aq)]$

if the solubility is s then $[Ag^+] = s$ and also $[Cl^-] = s$; so $K_{sp} = s^2$

hence $1.6 \times 10^{-10} = s^2$

Therefore solubility = $[Ag^+]$

$= \sqrt{1.6 \times 10^{-10}} = 1.3 \times 10^{-5}$ mol dm^{-3}

(b) $[Ag^{+}(aq)]\ [Cl^{-}(aq)] = 1.6 \times 10^{-10}$

$$[Ag^{+}(aq)] = \frac{1.6 \times 10^{-10}}{0.100}$$

$= 1.6 \times 10^{-9}$ mol dm^{-3}

54 **(a)** $K_{sp} = [Ag^+][Br^-]$

If the solubility is s then $[Ag^+] = s$ and also $[Br^-] = s$; so $K_{sp} = s^2$

(b) $K_{sp} = [Ni^{2+}]\ [OH^-]^2$

If the solubility is s then $[Ni^{2+}] = s$ and $[OH^-] = 2s$; so $K_{sp} = 4s^3$

(c) $K_{sp} = [Hg^+]^2\ [S^{2-}]$

If the solubility is s then $[Hg^+] = 2s$ and $[S^{2-}] = s$; so $K_{sp} = 4s^3$

(d) $K_{sp} = [Ca^{2+}]^3\ [PO_4^{\ 3-}]^2$

If the solubility is s then $[Ca^{2+}] = 3s$ and $[PO_4^{\ 3-}] = 2s$; so $K_{sp} = 108s^5$

(e) $K_{sp} = [Cr^{3+}]\ [OH^-]^3$

If the solubility is s then $[Cr^{3+}] = s$ and $[OH^-] = 3s$; so $K_{sp} = 27s^4$

55 **(a)** $K_{sp} = [Pb^{2+}]\ [S^{2-}] = 1.30 \times 10^{-28}$

(b) $[Pb^{2+}] = [S^{2-}]$

$[Pb^{2+}] = \sqrt{1.30 \times 10^{-28}}$

$= 1.14 \times 10^{-14}$ mol dm^{-3}

(c) As the product of the concentrations (K_{sp}) is constant, an increase in $[S^{2-}]$ will lead to a decrease in $[Pb^{2+}]$ and Pb^{2+} will be precipitated out of solution.

56 Step 1: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$

Step 2: $Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$

Overall: $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^-$

57 **(a)** $O_2^{\ -\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+}$

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$

(b) The second step as $OH^{\bullet}$ is produced.

(c) oxidation number = $-\frac{1}{2}$

One electron is transferred to Fe^{3+}, which is reduced to Fe^{2+}.

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+}:

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \qquad E^{\ominus} = -1.66\ V$

$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \qquad E^{\ominus} = -0.45\ V$

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:

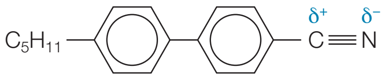
$$CH_3COOH + CH_3CH_2OH \overset{H^+}{\rightleftharpoons} CH_3COOCH_2CH_3 + H_2O$$

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:

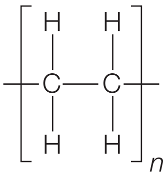
$$H_2C{=}CH_2 + H_2 \overset{Ni(s)}{\rightleftharpoons} CH_3CH_3$$

5 **(a)** Biphenyl nitriles are an example of thermotropic liquid crystals. The diagram below is 4-pentyl-4-cyanobiphenyl.

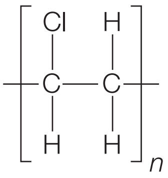


(b) The nitrile group (–CN) makes the molecule polar and the biphenyl group makes the molecule rigid. The strong intermolecular forces between molecules cause them to align in a common direction but the long flexible alkyl chain prevents the molecules from packing too closely and forming a solid.

6 **(a)** Poly(ethene) only contains non-polar C—H and C—C bonds whereas poly(vinylchloride) contains polar C—Cl bonds.



poly(ethene)

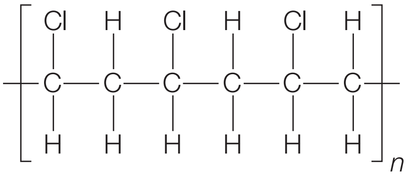


poly(vinylchloride)

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:



7 **(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.

8 **(a)** As Figure 12.5 on page 594 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.

9 **(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 629 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.

10 **(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.

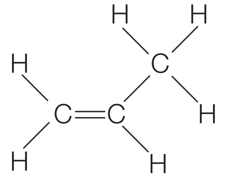
(b) See Figures 12.21 and 12.22 on page 615. In twisted nematic liquid crystal displays the liquid crystalline material is placed between two glass plates that have parallel scratches. The two plates are orientated so that the scratches on the two plates are at 90° to each other. Liquid crystal molecules 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.

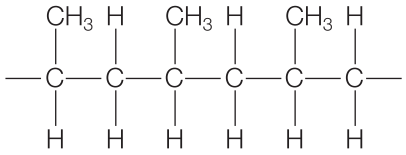
When a voltage is applied this changes the alignment of the liquid crystal molecules and the polarized light is no longer deflected 90° so that it can pass through the second polarizing filter and the pixel appears dark.

11 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.

12 **(a)** **(i)** The structural formula of propene is:



(ii) The structure of isotactic poly(propene) is:



As the structure shows the methyl substituents in isotactic poly(propene) are aligned on the same side of the carbon chain. In atactic poly(propene) the methyl substituents are randomly aligned. Atactic poly(propene) is likely to have weaker intermolecular forces between the polymer chains, which makes it softer and more flexible than the isotactic form, which has stronger intermolecular forces between the polymer chains.

(b) Expanded polystyrene is created by adding a volatile hydrocarbon such as pentane to polystyrene beads and then heating. As the pentane evaporates it cause bubbles of gas to form and this causes the polystyrene to expand. The polystyrene will take the shape of a mould it has been placed in. Expanded polystyrene has a very low density and is white in colour. It is a much better thermal insulator than regular polystyrene, which is brittle and opaque.

(c) Disposing of poly(vinyl chloride) by combusting it results in the production of carbon dioxide, CO_2, which is a strong greenhouse gas and a major contributor to climate change. Hydrogen chloride, HCl, is also formed in the combustion reaction and this can cause acid rain if released into the atmosphere. With incomplete combustion of PVC toxic compounds such as polychlorinated dioxins can be generated.

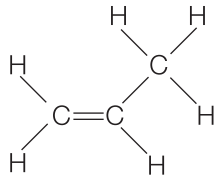
13 The difference between high-density poly(ethene) and low-density poly(ethene) is the amount of branching in the polymer chains. High-density poly(ethene) has very little branching and this allows stronger intermolecular forces and closer packing of the polymer chains. The stronger intermolecular forces also result in high-density poly(ethene) having a higher melting point.

14 **(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.

15 **(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.

16 Carbon (coke) and limestone (calcium carbonate) are added to iron ore in a blast furnace. The carbon will burn in the preheated air to produce carbon monoxide (CO):

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

As this is a highly exothermic reaction the heat released sustains the temperature within the blast furnace and the carbon monoxide formed then reacts with the iron ore and reduces it to pure iron:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

The limestone is added as it decomposes to calcium oxide (CaO) and CO_2 at high temperatures and the calcium oxide then reacts with silica impurities in the iron ore and removes them:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

$$CaO(s) + SiO_2(s) \rightarrow CaSiO_3(s)$$

17 Polymers do not corrode and are less dense than metals, which makes them more suitable than metals for many uses.

Polymers are easier to mould and as they do not biodegrade they are more durable than wood products for many uses.

18 **(a)** Kevlar can act as a lyotropic liquid crystal in concentrated sulfuric acid. The Kevlar chains will align themselves in solution at high concentrations, forming the lyotropic liquid crystal.

(b) Kevlar contains repeating benzene units and forms very rigid polymer chains that tend to align. Significant hydrogen-bonding interactions can occur between the amide oxygens and hydrogens on neighbouring chains (see Figure 12.17 on page 612).

(c) Acids will donate hydrogens to the oxygens and nitrogens in the amide groups and disrupt the hydrogen bonding between them. This will cause the Kevlar to lose its structure and decrease the effectiveness of the vest.

19 The concentration of Cl^- needed to precipitate AgCl can be determined using the K_{sp} value for AgCl and the concentration of silver ions present:

$$K_{sp}(AgCl) = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{8.0 \times 10^{-3}}$$
$$= 2.3 \times 10^{-8}\ \text{mol dm}^{-3}$$

The concentration of Cl^- needed to precipitate $PbCl_2$ can be determined using the K_{sp} value for $PbCl_2$ and the concentration of lead ions present:

$$K_{sp}(PbCl_2) = [Pb^+][Cl^-]^2 = 1.7 \times 10^{-5}$$

$$[Cl^-] = \sqrt{\frac{K_{sp}}{[Pb^{2+}]}} = \sqrt{\frac{1.7 \times 10^{-5}}{1.9 \times 10^{-2}}}$$
$$= 3.0 \times 10^{-2}\ \text{mol dm}^{-3}$$

AgCl will precipitate first as it is less soluble (has a lower K_{sp} value).

20 **(a)** The concentration of Ni^{2+} ions remaining in the water can be determined using the K_{sp} value for $Ni(OH)_2$ and recognizing that the concentration of OH^- ions will be twice the concentration of Ni^{2+} ions:

$$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Ni^{2+}][OH^-]^2 = [Ni^{2+}](2[Ni^{2+}])^2$$
$$= 4[Ni^{2+}]^3$$

$$6.50 \times 10^{-18} = 4[Ni^{2+}]^3$$

$$[Ni^{2+}] = \sqrt[3]{\frac{6.50 \times 10^{-18}}{4}}$$
$$= 1.18 \times 10^{-6}\ \text{mol dm}^{-3}$$

The mass of Ni^{2+} that is present in 1.00 dm^3 is determined by multiplying the concentration by the molar mass of nickel:

$$m(Ni^{2+}) = 1.18 \times 10^{-6}\ \text{mol dm}^{-3} \times 58.71\ \text{g mol}^{-1} \times 1.00\ \text{dm}^3$$
$$= 6.93 \times 10^{-5}\ \text{g}$$

(Rounding errors can result in a value between 6.90×10^{-5} g and 6.95×10^{-5} g being obtained.)

(b) Consider the equilibrium reaction between Ni^{2+} and OH^- ions:

$$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$$

If more hydroxide ions are added to the solution this will push the equilibrium to the left due to the common ion effect, forming more $Ni(OH)_2(s)$ and reducing the $Ni^{2+}(aq)$ concentration.

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.

4 To solve for the oxidation state of Ti in $CaTiO_3$ we need to make the assumption that Ca will have an oxidation state of +2 as a highly electropositive Group 2 metal and O will have an oxidation state of –2 as a highly electronegative Group 16 element.

As the overall charge on the mineral is 0:

oxidation state of Ca + oxidation state of Ti + 3(oxidation state of O) = 0

+2 + oxidation state of Ti + 3(–2) = 0

oxidation state of Ti = –2 – (–6) = +4

5 To solve for the oxidation state of Cu in $YBa_2Cu_3O_7$ we need to make the assumption that Ba will have an oxidation state of +2 as a highly electropositive Group 2 metal and O will have an oxidation state of –2 as a highly electronegative Group 16 element. The oxidation state of Y is given as +3.

As the overall charge on the superconductor is 0:

+3 + 2(+2) + 3(oxidation state of Cu) + 7(–2) = 0

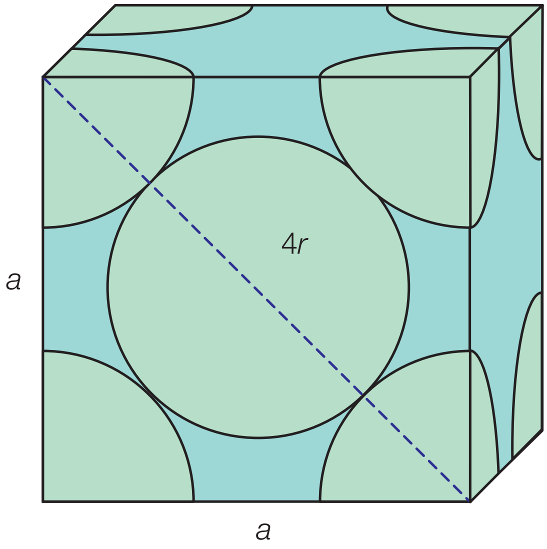
+3 + 4 + 3(oxidation state of Cu) – 14 = 0

3(oxidation state of Cu) = +7

Oxidation state of Cu = $+\frac{7}{3}$

A fractional oxidation state of $+\frac{7}{3}$ can only be obtained if the three Cu atoms are in different oxidation states: two are in the +2 oxidation state and the third is in the +3 oxidation state.

6 From the diagram of a face-centered cubic cell (FCC) we can see that it contains eight atoms in corner positions and six in the facial positions. Note that the diagram only shows the facial atom for the front face and not all six faces.



Corner atoms contribute $\frac{1}{8}$ of an atom to the unit cell, facial atoms contribute $\frac{1}{2}$ an atom (see table on page 648).

The total number of atoms in the unit cell =

$\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$ atoms.

Assuming the atoms are spherical with radius r, the volume occupied by four atoms is:

V (atoms) $= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

The volume of the cube is a^3 but we need to derive an expression for this volume in terms of r, the radius of the atoms. Applying Pythagoras:

$(4r)^2 = a^2 + a^2$

$16r^2 = 2a^2$

$a^2 = 8r^2$

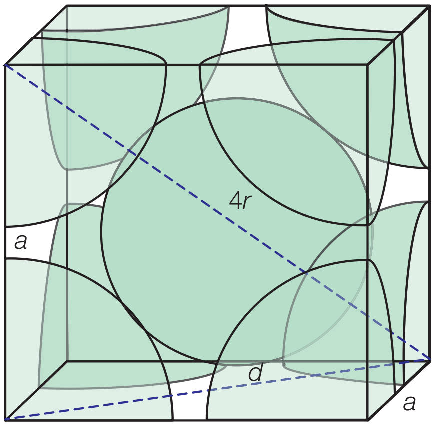
$a = \sqrt{8}r = 2\sqrt{2}r$

V (cell) $= a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3$

% volume of atoms in cell $= \frac{V(\text{atoms})}{V(\text{cell})} = \dfrac{\frac{16}{3}(r^3)}{16\sqrt{2}r^3}$

$\times$ 100%= 74.0%

7 From the diagram of a body-centered cubic cell (BCC) we can see that it contains eight atoms in corner positions and one atom in the centre of the cell position.



Corner atoms contribute $\frac{1}{8}$ of an atom to the unit cell, central atoms contribute one atom (see table on page 648).

The total number of atoms in the unit cell $= 8 \times \frac{1}{8} + 1 = 2$ atoms.

Assuming the atoms are spherical with radius r, the volume occupied by two atoms is:

V (atoms) $= 2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$

The volume of the cube is a^3 but we need to derive an expression for this volume in terms of r, the radius of the atoms. Applying Pythagoras:

$(4r)^2 = a^2 + d^2$ (by Pythagorus, $d^2 = a^2 + a^2$)

$16r^2 = 3a^2$

$a^2 = \frac{16}{3}r^2$

$a = \frac{4}{\sqrt{3}}r$

V (cell) $= a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3 = \frac{64}{3\sqrt{3}}r^3$

% volume of atoms in cell $= \frac{V(\text{atoms})}{V(\text{cell})} = \dfrac{\frac{8}{3}(r^3)}{\dfrac{8}{\frac{64}{3\sqrt{3}}r^3}} \times$

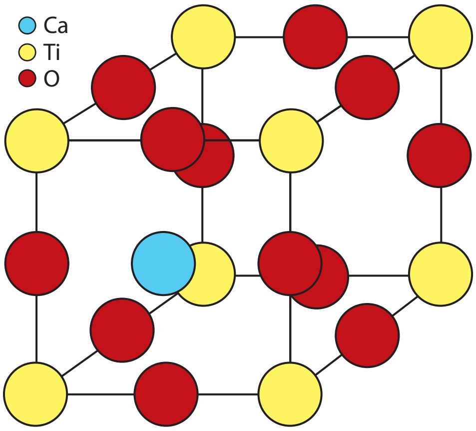
100% = 68.1%

8 From the diagram provided we can see that perovskite has:

8 Ti atoms situated at the corners of the cubic cell

12 O atoms situated at the edges

1 Ca atom situated in the centre of the cubic cell



Corner atoms contribute $\frac{1}{8}$ of an atom, edge atoms contribute $\frac{1}{4}$ of an atom and centre atoms contribute one atom (see table on page 648).

The number of Ti atoms $= 8 \times \frac{1}{8} = 1$

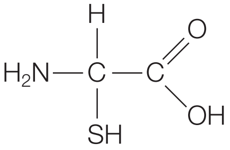
The number of O atoms $= 12 \times \frac{1}{4} = 3$

The number of Ca atoms = 1 × 1 = 1

The formula of perovskite is $CaTiO_3$.

9 Polyesters are condensation polymers and are therefore similar to many biopolymers such as triglycerides, polysaccharides and polypeptides. Many bacteria capable of breaking down various biopolymers are also capable of breaking down polyesters.

10 Mercury and mercury ions react readily with sulfur-containing compounds. The amino acid cysteine contains a thiol group (–SH), which includes S, so it is likely to bond to Hg^{2+} ions.



cysteine

11 Entropy was discussed in section 15.2 on page 247. If there is an increase in the number of ways that energy can be distributed then there will be an increase in entropy.

$[M(H_2O)_6]^{n+} + EDTA^{4+} \rightarrow [M(EDTA)]^{n-4} + 6H_2O$

For the reaction there are two reactant species and seven product species. This means that there is an increase in the number of ways that energy can be distributed and the reaction will occur with an increase in entropy (positive ΔS).

According to the equation $\Delta G = \Delta H - T\Delta S$ (see page 256), the Gibbs free energy change (ΔG) for the reaction is likely to be negative with a large positive value of ΔS. A negative ΔG would result in the reaction being spontaneous, with the chelated product being more stable than the reactants.

12 The concentration of pure water can be calculated from the equation $[H_2O] = \frac{n(H_2O)}{V(H_2O)}$.

If we assume water has a density of 1.000 kg/dm^3 then 1.000 dm^3 has a mass of 1.000 kg (1.000×10^3 g).

$$n(H_2O) = \frac{m(H_2O)}{M(H_2O)} = \frac{1.000 \times 10^3 \text{ g}}{(16.00 + 2 \times 1.01)\text{g mol}^{-1}}$$
$$= 55.49 \text{ mol}$$

$$[H_2O] = \frac{n(H_2O)}{V(H_2O)} = \frac{55.49 \text{ mol}}{1.000 \text{ dm}^3} = 55.49 \text{ mol dm}^{-3}$$

13 For the reaction $M_pX_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$:

$K_{sp} = [M^{m+}(aq)]^p[X^{n-}(aq)]^q$

If s is the solubility of M_pX_q then $[M^{m+}] = ps$ and $[X^{n-}] = qs$.

$K_{sp} = (ps)^p(qs)^q = p^ps^pq^qs^q = p^pq^qs^{p+q}$

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 **(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

7 **(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

8 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.

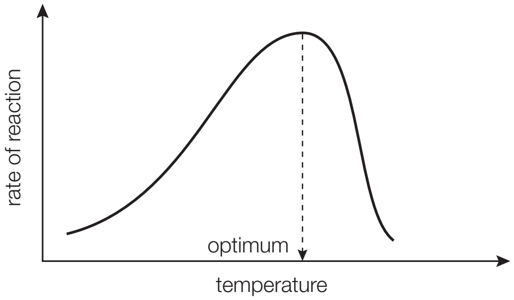
9 Hydrogen bonds in the secondary structure are between groups that are part of the peptide bonds of amino acids four residues apart in a polypeptide chain. Hydrogen bonds in the tertiary structure are between groups such as –OH in the side chains of amino acids.

10 **(a)** 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.

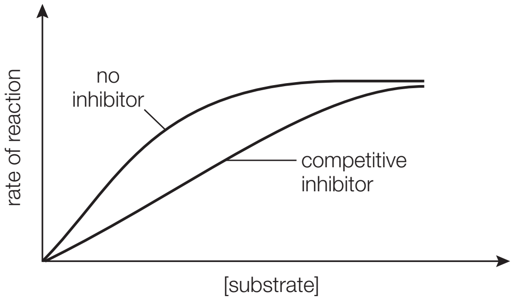
(b) In a sketch graph it is essential to label the axes (but without units) and give the shape clearly. Use a ruler when drawing the axes. The graph given here shows how the explanation must make reference to the structure of the protein in reference to the enzyme activity.



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.

11 This type of question seems to be quite common, so it is a good idea to be familiar with it.

(a) and (b)



(c) **(i)** V_{max} is unchanged because the enzyme (at high enough substrate concentration) is still capable of achieving full activity.

(ii) The competitive inhibitor, because it competes directly with the substrate for binding at the active site, raises the K_m. This means that a higher substrate concentration will be needed to achieve the maximum rate.

12 *Similarities:* both increase rate of reaction by providing pathway of lower E_a; both have no effect on K_c or yield.

Differences: enzymes are proteins, inorganic catalysts have a varied structure; enzymes show saturation kinetics, inorganic catalysts usually do not; enzymes are regulated by inhibitors, inorganic catalysts are usually not; enzymes are sensitive to pH and temperature, inorganic catalysts usually work well at a wide range of temperature and pressure.

13 **(a)** Hands are likely to 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.

14 Use $\text{pH} = \text{p}K\text{a} + \log\dfrac{[\text{salt}]}{[\text{acid}]}$

Assume that all the NaOH is used up reacting with the acid to form salt.

moles of salt formed $= 0.05 \times \dfrac{\nu}{1000}$ and

moles of acid remaining $= \dfrac{100}{1000} \times 0.05 -$ moles of salt formed

The data we have is:

pH = 4.23

$K_a = 1.77 \times 10^{-4}$, so $pK_a = -\log(1.77 \times 10^{-4}) = 3.75$

Inserting all the numbers into the formulae:

$$4.23 = 3.75 + \log\frac{5\times10^{-5}\times\nu}{5\times10^{-3} - (5\times10^{-5}\times\nu)}$$

$$0.48 = \log\frac{5\times10^{-5}\times\nu}{5\times10^{-3} - (5\times10^{-5}\times\nu)}$$

Anti-logging and solving for *v* gives the volume of NaOH needed = 75 cm^3 of 0.05 mol dm^{-3} NaOH

15 A series of dilutions (at least five) is prepared of a protein standard solution. These are treated with a reagent (such as Biuret solution) which generates colour according to the protein content. Absorbance of each solution is measured under carefully controlled conditions of temperature, wavelength, and volume of reagent added. The calibration curve is plotted of absorbance versus protein concentration. The same conditions are applied to the experimental solution, whose protein concentration can then be read from the calibration curve.

16 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.

17 **(a)** Melting point above 25 °C: lauric, myristic, palmitic, and stearic acids are solids at room temperature.

(b) Melting point increases as London dispersion forces increase with size of the R group, due to an increase in the number of electrons.

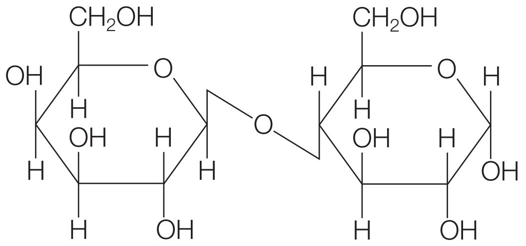
(c) An increase in the number of C=C double bonds adds kinks to the structure, which reduces the ability of the molecules to pack together. The intermolecular forces are weaker and the melting points decrease.

18 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.

19 **(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.

20



Lactose

molecular formula = $C_{12}H_{22}O_{11}$. The bond between the sugars is a glycosidic bond.

21 **(a)** Carbon–carbon double bonds and hydroxyl groups.

(b) Water-soluble: vitamin C; fat-soluble vitamin A/vitamin D. Vitamin C has many —OH and polar groups able to form hydrogen bonds with water. Vitamins A and D are predominantly non-polar/have hydrophobic groups and so cannot form hydrogen bonds with water. Instead they dissolve more readily in non-polar fats.

22 Fortification of certain staple foods such as rice and flour with micronutrients; supply of nutritional supplements, particularly in places where certain deficiencies are known (e.g. iodine); possible changes and improvements in nutrient content through genetic modification.

23 **(a)** This is a great opportunity to show knowledge of the chemistry of the bonding, including possibly some structural formulas. Note the question is only about the bonding between nucleotides to form the polynucleotide chain, not about the interaction between two polynucleotides to form DNA, so any mention of base pairings or hydrogen bonding would be out of place here.

Polynucleotides form by condensation reactions between nucleotides. Phosphate groups react with ribose sugar molecules at C_3 and C_5 forming phosphodiester links between the sugar molecules. The backbone of the polynucleotide strand is an alternating sequence of sugar and phosphate groups.

(b) Again this question is a good chance to show understanding of the chemical interactions within the structure. The hydrophobic interactions between the non-polar nitrogenous bases stacked in the interior are a bigger factor in stability than the hydrogen bonds between the two polynucleotide strands.

The double helix of the DNA is stabilized by hydrogen bonds between the complementary pairs of bases. Guanine and cytosine pairs are held together by three hydrogen bonds, and adenine and thymine pairs by two hydrogen bonds. The molecule is also stabilized by hydrophobic interactions between the stacked bases in the interior of the helix.

24 This is a pretty straightforward question, providing you know the base pairings in DNA. The main trick here is to remember that in mRNA, U has substituted for T and so base pairs with A. Dividing the number of bases in the strand by three gives the number of triplets (codons), and hence the number of amino acids coded.

(a) TTAGCGTATATTAAGCGATCG

(b) UUAGCGUAUAUUAAGCGAUCG

(c) There are seven base triplets so seven amino acids can be inserted.

25

Benefits	Concerns
Improved flavour, texture and nutritional value	Uncertainties about the outcomes
Longer shelf-life	Links to increased allergies (for people involved in their processing)
Increased crop yields in plants and feed efficiency in animals	Pollen from GM crops may escape to contaminate 'normal' crops

26 When a substance is oxidized, electrons are transferred and the oxidation number of the substance is increased. This happens to Fe in cytochromes when they act as electron carriers. Oxygenation does not involve transfer of electrons and there is no change in oxidation state; it involves the bonding of a molecule of oxygen as a ligand. This happens in hemoglobin when it forms oxyhemoglobin.

27

pH	λ_{max}	Colour absorbed	Colour of pigment
1	550	green	red
7	350	none visible	colourless

28 **(a)** The carotenoids are coloured due to the presence of an extended pi system of electrons in their molecules. They are not water soluble as the molecules contain a non-polar hydrocarbon chain. They are soluble in non-polar fats and oils.

(b) The colour is due to the presence of anthocyanins. These are water soluble as the molecules contain polar hydroxyl groups which form hydrogen bonds with water. The colour changes in the presence of acid as the degree of conjugation of the pi system is reduced when anthocyanins are protonated. This changes the wavelength of the light absorbed.

29 A: $R_f = \dfrac{2.5}{15.0} = 0.17$

B: $R_f = \dfrac{7.5}{15.0} = 0.50$

C: $R_f = \dfrac{10.0}{15.0} = 0.67$

Polar molecules interact fairly strongly with the polar Si—O bonds of the stationary phase and so have smaller R_f values.

30 Oxygen dissociation curve of hemoglobin is sigmoidal, representing cooperative binding between the four heme groups within the quaternary structure. Oxygen dissociation curve of myoglobin is hyperbolic, representing saturation kinetics with no cooperative binding, as myoglobin contains a single heme group and no quaternary structure.

31 The carbon–carbon double bonds that remain in partially hydrogenated fats are changed from *cis* to *trans* configurations. *Trans* fats are associated with a number of negative health effects, including cardiovascular disease. Complete hydrogenation results in fats that have no carbon–carbon double bonds.

32 Cellulose is a polymer of β-glucose. It has –OH groups sticking out on both sides of its chains, so hydrogen bonds between them form microfibrils, which give it rigidity. It is used for support. Starch is a polymer of α-glucose, forming compact and spiral molecules.

33 Light activates the conversion of 11-*cis*-retinal to the all-*trans* isomer, which causes its dissociation from opsin and the triggering of a nervous impulse.

34 Ionic bonds, hydrogen bonds, London dispersion forces, hydrophobic interactions.

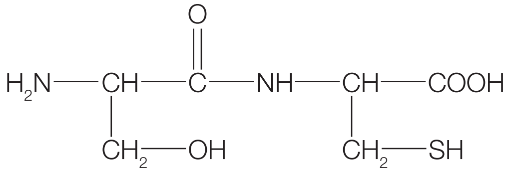
35 Biomagnification refers to the increasing concentration of a xenobiotic substance at different levels in a food web. It is often associated with toxic effects for organisms that feed at a high trophic level, as their cells contain the highest concentrations.

36 Break down oil spills, help break down some plastics, in biological detergents that improve energy efficiency, in Green Chemistry involving less toxic chemical pathways and solvents.

Practice questions

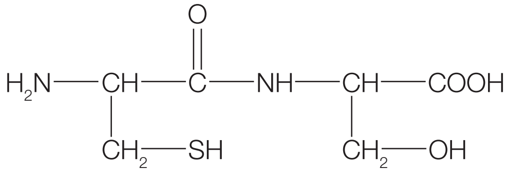
1 **(a)** When two amino acids such as cysteine and serine react to form a dipeptide the reaction that takes place is a condensation reaction. As it is a condensation reaction water is also produced.

(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.



$H_2N-CH(CH_2OH)-C(=O)-NH-CH(CH_2SH)-COOH$

Ser-Cys



$H_2N-CH(CH_2SH)-C(=O)-NH-CH(CH_2OH)-COOH$

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

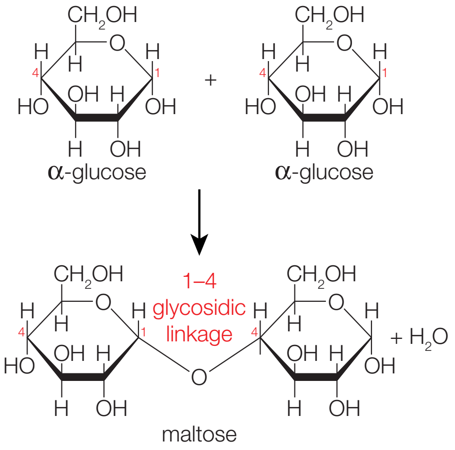
(d) **(i)** The secondary structure of proteins is maintained by hydrogen bonding that occurs between peptide bonds along the length of the protein chain.

(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.)

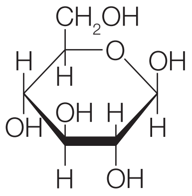
2 **(a)** **(i)** Maltose is a disaccharide formed from the condensation reaction between the –OH on carbon 1 of one α-glucose and the –OH on carbon 4 of another α-glucose to form a 1–4 glycosidic linkage.



(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.

(b) **(i)** The monomer of cellulose is β-glucose;



(ii) Starch is a polymer of α-glucose and it forms a compact spiral structure. Cellulose is a polymer of β-glucose and it forms linear chains. Hydrogen bonding can occur between cellulose chains to form microfibres but hydrogen bonding doesn't occur between the starch spirals. The strong hydrogen bonding between the cellulose chains gives the microfibres a high tensile strength.

3 **(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.

4 **(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(linoleic acid) = (18 × 12.01) + (32 × 1.01) + (2 × 16.00)g mol^{-1} = 280.50 g mol^{-1}

In exactly 100 g, n(linoleic acid)

$$= \frac{m(\text{linoleic acid})}{M(\text{linoleic acid})} = \frac{100\ \text{g}}{280.50\ \text{g mol}^{-1}}$$

$= 0.357$ 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.

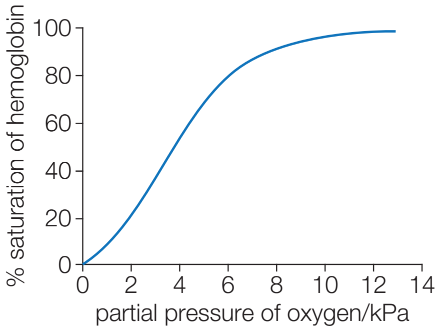
Hydrolytic rancidity occurs when the fat is hydrolysed and breaks down into glycerol and the three constituent fatty acids. (This is the opposite of the condensation reaction that forms the fat.) Hydrolytic rancidity is favoured by high temperatures and it is also catalysed by the enzyme lipase.

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.

5 **(a)** Globular proteins are compact spherical molecules with a dominant tertiary structure and are water soluble. Hemoglobin consists of four polypeptides whose shapes are determined by its tertiary structure. The quarternary structure dictates how the four polypeptides combine to form hemoglobin. Hemoglobin is water soluble, hence its ability to function as an oxygen carrier in blood.

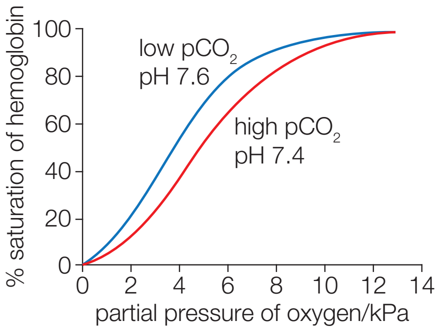
(b) The cooperative nature of oxygen binding to hemoglobin is shown in a curve where the percentage of saturation increases as the partial pressure of oxygen increases before reaching a plateau, giving a sigmoidal shape.



(c) The binding of oxygen to one heme group causes a slight change in the conformation of this heme and in the overall structure. This change in structure makes it easier for oxygen to access the binding sites in the other heme groups.

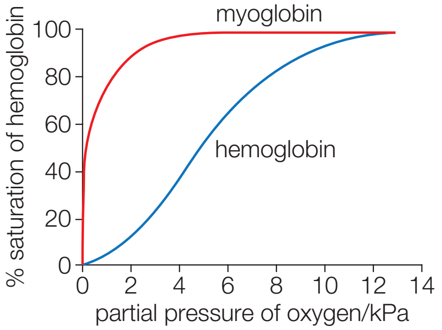
(d) When cells respire they release CO_2, which dissolves to form carbonic acid.

This increases the acidity of the blood and decreases the affinity of hemoglobin for O_2.



(e) When oxygen is present hemoglobin is converted to oxyhemoglobin, which gives meat a bright red colour, which makes it appear fresher and more appealing.

(f) Myoglobin has a higher affinity for O_2 than hemoglobin. Its oxygen dissociation curve lies to the left of hemoglobin and it is hyperbolic rather than sigmoidal in shape as there is no cooperative binding occurring in myoglobin.



6 Possible benefits of genetically modified foods include that they can have greater resistance to dieases and pests, can give greater crop yields, have longer shelf lives and can have enhanced flavours and nutrients.

Possible concerns include that they may have unknown consequences in the food chain, risk of escape to the wild and breeding of species resistant to control, possibility of allergic reactions in consumers, and the lack of information in the labelling of genetically modified foods.

7 **(a)** A nucleotide contains deoxyribose sugars, phosphate (PO_4^{3-}), and a nitrogenous base (purines such as adenine or guanine, or pyrimidines such as cytosine, thymine and uracil).

These components combine through condensation reactions to form nucleotides.

(b) The phosphate groups that link the sugars in DNA are negatively charged so they will migrate towards the positive electrode during electrophoresis.

(c) **(i)** The complementary DNA strand is CGGATGAATCGAT.

(ii) The RNA derived from the complementary DNA strand is GCCUACUUAGCUA.

8 **(a)** Pigments are coloured due to the absorption of specific wavelengths of visible light and the transmission of other wavelengths.

(b) **(i)** The absorption at 375 nm occurs in the UV region of the electromagnetic spectrum, which is invisible to the human eye so no colour will be observed due to this absorption.

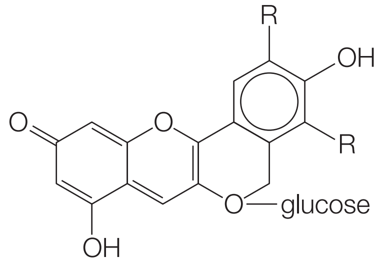
(ii) The absorption at 530 nm occurs in the visible region of the electromagnetic spectrum, which is visible to the human eye so it will cause the anthocyanin to be coloured. As 530nm corresponds to blue–green light the absorption of this wavelength will result in the colour observed being red.

(c) Oxidation of the anthocyanin can change the extent of conjugation within the molecule and affect the colour of light being absorbed.

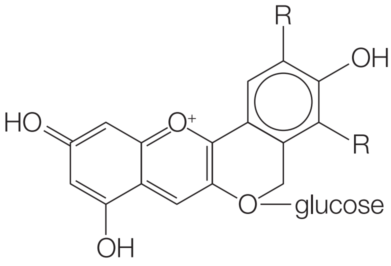
Change of pH or temperature can affect the structure and extent of conjugation and result in a different colour of light being absorbed.

If metal ions are present they can bind to the anthocyanin, which will also alter the colour of light being absorbed.

9 Anthocyanins contain polar –OH groups that allow them to form hydrogen bonds with water and as a result they are water soluble.

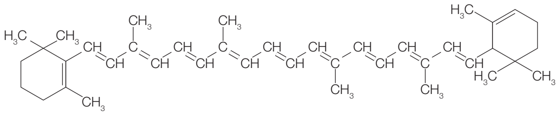


quinoidal base (blue)

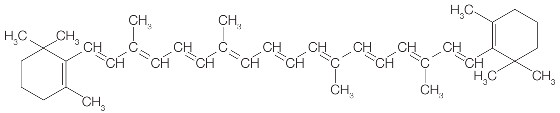


flavylium cation (red)

Carotenoids contain long hydrocarbon chains and rings that are non-polar. As a result carotenoids will be more soluble in other non-polar compounds and are fat soluble.

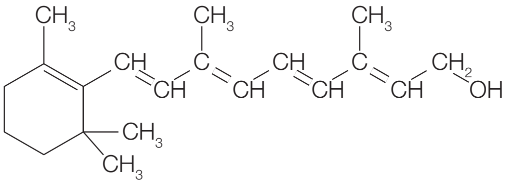


α-carotene



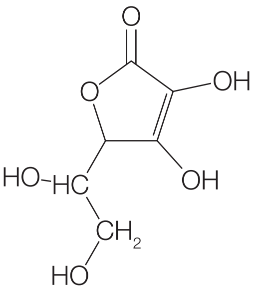
β-carotene

10 **(a)** Although vitamin A contains a polar –OH group, the vast majority of the molecule consists of non-polar C–C and C–H bonds so it is a non-polar molecule and insoluble in water.



retinal (vitamin A)

Vitamin C contains many polar –OH groups so it is a polar molecule and capable of forming hydrogen bonds with water so it is soluble in water.



ascorbic acid (vitamin C)

(b) The body is capable of storing vitamins that are fat soluble within fat deposits so vitamin A is more likely to be stored in the body.

(c) Vitamin deficiency diseases are prevalent in many parts of the world for a number of reasons. Local regions may have soils or water sources that are depleted in nutrients. On a global scale there can be a poor distribution of food resources. Even in regions rich in food sources vitamin deficiency diseases can occur due to overcooking and over-processing of food as well as poor education about nutrition and the failure to consume a balanced diet.

11 **(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.

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

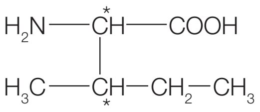
oxidation state of C +2(–2)= 0

oxidation state of C – 4 = 0

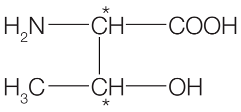
oxidation state of C = +4 in CO_2

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:



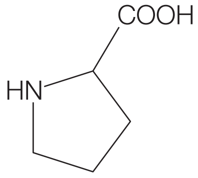
isoleucine



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):



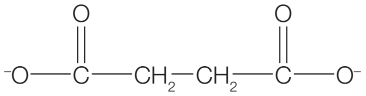
When it forms peptide linkages the nitrogen in proline becomes a tertiary nitrogen with no hydrogens bonded to it so it cannot be a hydrogen bond donor, but it retains a lone pair of electrons so it can be a hydrogen bond acceptor. Because of this the presence of proline leads to a bend or kink in the polypeptide chain.

5 In the region labelled (a) the rate of reaction is proportional to the substrate concentration [S], therefore the rate is first order with respect to the substrate, rate = $k[S]$.

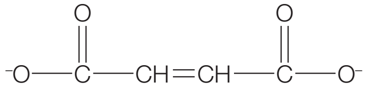
In the region labelled (b) the rate of reaction is not proportional to the substrate concentration, therefore the rate is mixed order with respect to the substrate, rate = $k[S]^x$.

In the region labelled (c) the rate of reaction has no dependence on the substrate concentration as the enzyme is saturated with substrate, therefore the rate is zero order with respect to the substrate, rate = $k[S]^0 = k$.

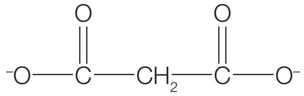
6



succinate
(butanedioate)

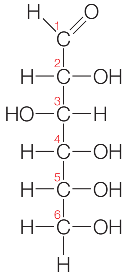


fumarate
(butenedioate)

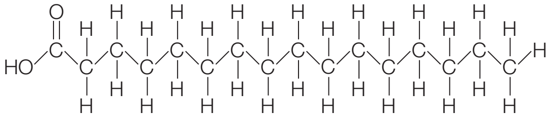


malonate
(propanedioate)

7 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.

8 The structures of isoleucine and threonine are given in the answer to Challenge yourself question 3. The number of stereoisomers is equal to 2^n where *n* represents the number of chiral carbons. Both amino acids contain two chiral carbons, which means they have 2^2 stereoisomers, i.e. isoleucine and threonine both have four stereoisomers.

9 See the structures of α-glucose and β-glucose on page 752. In β-glucose the –OH groups on carbons 1 and 2 are on opposite sides of the ring in a *trans* configuration. In α-glucose these –OH groups are on the same side of the ring in a *cis* configuration. There is less steric repulsion between the –OH groups when they are in the *trans* configuration so β-glucose is more stable than α-glucose.

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 $(\rho) = \frac{\text{mass}}{\text{volume}} = \frac{m}{V} = \frac{PM}{RT}$

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

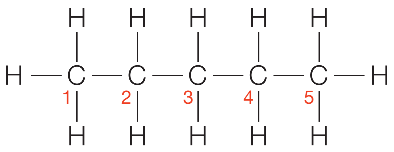
No. of moles of CH per second =

$\frac{39\,900}{12.01 + 1.01} = 3062\ \text{mol s}^{-1}$

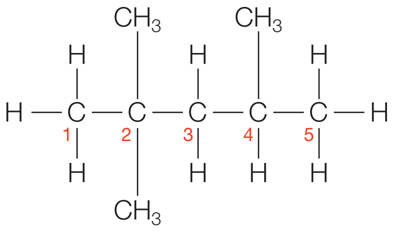
Mass of CO_2 per second = 3062 × 44.01

$= 135\,000\ \text{g} = 135\ \text{kg s}^{-1}$

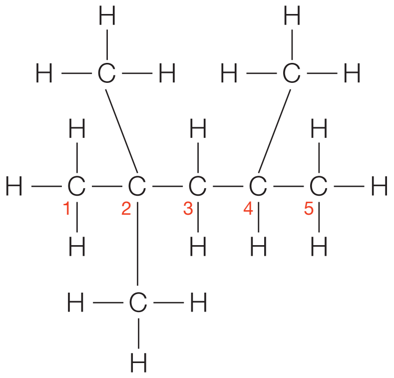
6 The structure is based on pentane:



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.

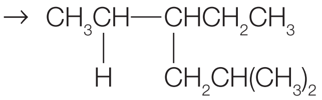
(c) The components of gasoline have boiling points above normal temperatures. They are volatile liquids. They can be easily vaporized in the car cylinder for reaction with oxygen. Lower molar mass compounds are gases which occupy too much volume, while higher molar mass compounds do not vaporize or burn 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: $(CH_3)_3CH + CH_3CH{=}CHCH_2CH_3$



$$\rightarrow \begin{array}{lcl} CH_3CH & - & CHCH_2CH_3 \\ \quad | & & | \\ \quad H & & CH_2CH(CH_3)_2 \end{array}$$

9 The general pattern is:

straight-chain alkanes < cycloalkanes < alkenes < aromatics

pentane < cyclopentane < pentene < benzene

10 The general pattern is that the octane number of straight-chain alkanes decreases with an increase in chain length. Alcohols have very high octane numbers.

heptane < hexane < pentane < ethanol

11 **(a)** High specific energy/energy density. As a liquid it is convenient to handle and deliver. Easy to vaporize, which assists combustion.

(b) It is formed by the 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)** $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$: $\Delta H_c^{\ominus} = -283\ \text{kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$: $\Delta H_c^{\ominus} = -286\ \text{kJ mol}^{-1}$

$CO(g) + H_2(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$:

$\Delta H_c^{\ominus} = -283 + (-286)\ \text{kJ mol}^{-1} = -569\ \text{kJ mol}^{-1}$

(b) 1 mole of carbon monoxide would be converted to 1 mole of methane.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$: $\Delta H_c^{\ominus} = -891\ \text{kJ mol}^{-1}$

(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	$\frac{10\,000}{3910} = 2.56$	$(12.01 \times 7) + (8 \times 1.01)$ $= 92.15$	2.56×92.15 $= 236$
Ethanol	–1367	$\frac{10\,000}{1367} = 7.31$	$(12.01 \times 2) + (6 \times 1.01) + 16.00$ $= 46.08$	7.31×46.08 $= 337$

(b)

Fuel	Moles of CO_2 produced / mol	Mass of CO_2 produced / g
Methylbenzene	$7 \times 2.56 =$ 17.92	17.92×44.01 $= 789$
Ethanol	$2 \times 7.31 =$ 14.62	14.62×44.01 $= 643$

(c) Oxygenates produce less carbon dioxide / have a smaller carbon footprint.

19 **(a)** Deuterium nucleus is a proton and a neutron.

Predicted mass of deuterium nucleus = 1.008 665 amu + 1.007 265 amu

= 2.01593 amu

$\Delta m = 2.01593 - 2.01355$ amu $= 0.00238$ amu $= 0.00238 \times 1.66 \times 10^{-27}$ kg

$\Delta E = 0.00238 \times 1.66 \times 10^{-27} \times (3.00 \times 10^{8})^{2}$ J

$= 0.00238 \times 1.66 \times 10^{-27} \times (3.00 \times 10^{8})^{2} \times 6.02 \times 10^{23}$ J mol^{-1}

$= 2.14 \times 10^{11}$ J mol^{-1}

$= 2.14 \times 10^{8}$ kJ mol^{-1}

(b) The binding energy for ${}^{4}_{2}He$ is calculated on page 791.

Nuclide	No. of nucleons	Binding energy / kJ mol^{-1}	Binding energy / kJ mol^{-1} per nucleon
${}^{4}_{2}He$	4	2.73×10^{9}	$\frac{2.73 \times 10^{9}}{4} = 6.83 \times 10^{8}$
${}^{2}_{1}H$	2	2.14×10^{8}	$\frac{2.14 \times 10^{8}}{2} = 1.07 \times 10^{8}$

(c) We have the following energy changes as the nuclei of the two elements are formed:

$2p + 2n \rightarrow 2\,{}^{2}_{1}H$: $\Delta E = 2 \times 2.14 \times 10^{8}$ kJ mol^{-1}

$2p + 2n \rightarrow {}^{4}_{2}He$: $\Delta E = 2.73 \times 10^{9}$ kJ mol^{-1}

Using Hess' law we have for the following:

$2\,{}^{2}_{1}H \rightarrow 2p + 2n$: $\Delta E = -2 \times 2.14 \times 10^{8}$ kJ mol^{-1}

$2p + 2n \rightarrow {}^{4}_{2}He$: $\Delta E = 2.73 \times 10^{9}$ kJ mol^{-1}

Adding the equations:

$2\,{}^{2}_{1}H \rightarrow {}^{4}_{2}He$: $\Delta E = (-2 \times 2.14 \times 10^{8}) + (2.73 \times 10^{9})$ kJ mol^{-1}

$\Delta E = 2.30 \times 10^{9}$ kJ mol^{-1}

(d) ${}^{4}_{2}He$ is more stable than ${}^{2}_{1}H$

20 **(a)** ${}^{1}_{0}n$ – 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.

21 **(a)** $\Delta E = \frac{hc}{\lambda}$

$$= \frac{6.63 \times 10^{-34} \times 3.00 \times 10^{8}}{\lambda}\ \text{J}$$

$$= \frac{6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 3.00 \times 10^{8}}{\lambda}\ \text{J mol}^{-1}$$

$$= \frac{6.02 \times 10^{20} \times 6.63 \times 10^{-34} \times 3.00 \times 10^{8}}{\lambda}\ \text{kJ mol}^{-1}$$

$$= \frac{0.000\,120}{\lambda}\ \text{kJ mol}^{-1}$$

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.

22 **(a)** Using $E = mc^2$, the energy produced from 1 g = $6.72 \times 10^{-6} \times (3.00 \times 10^8)^2$ J

$= 6.05 \times 10^{11}$ J

$= 6.05 \times 10^{8}$ kJ

(b) Mass of coal needed $= \dfrac{6.05 \times 10^8 \text{ kJ}}{30 \text{ kJ g}^{-1}}$

$= 20 \times 10^6$ g

$= 20 \times 10^3$ kg

23 Mass of hydrogen isotopes on left-hand side of equation:

${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} = 2.014102 + 3.016049$

$= 5.030151$ amu

Mass of helium isotope and neutron on right-hand side of equation:

${}^{4}_{2}\text{He} + {}^{1}_{0}\text{n} = 4.002602 + 1.008665$

$= 5.011267$ amu

Difference = 0.018884 amu

1 amu is equivalent to 1 g mol^{-1}, 0.018884 amu → 0.018884 g mol^{-1}

Using $\Delta E = mc^2$ we need mass in kg: 0.018884 g mol^{-1} = 1.8884×10^{-5} kg mol^{-1}

$\Delta E = 1.8884 \times 10^{-5}$ kg mol^{-1} × $(3.00 \times 10^8 \text{ m s}^{-1})^2$

$= 1.70 \times 10^{12}$ J mol^{-1}

$= 1.70 \times 10^{9}$ kJ mol^{-1}

24 **(a)** W: atomic number = 92 – 2 = 90, mass number = 233 – 4 = 229: ${}^{229}_{90}\text{Th}$

X: atomic number = (92 + 0) – 56 + 36 = 0, mass number = (235 + 1) – (141 + 92) = 3: $3{}^{1}_{0}\text{n}$

Y: atomic number = 92 – (–1) = 93, mass number = 239: ${}^{239}_{93}\text{Np}$

Z: atomic number = 92 – 58 = 34, mass number (233 + 1) – (140 + 2) = 92: ${}^{92}_{34}\text{Se}$

(b) Process II (fission) is used to produce electricity in nuclear power plants. (Process IV is also a fission reaction and is another potential reaction.) This process can be initiated as required by controlling the input of neutrons, whereas the other processes are natural ones and occur randomly. Process II is self-sustaining if the critical mass is available. It produces more neutrons than are needed initially and so a chain reaction occurs which can lead to the fission of more nuclei.

(c) The mass of the products is less than the mass of the reactants. The difference is converted to energy according to the equation: $\Delta E = \Delta mc^2$.

25 Less than 1% of natural uranium is the fissionable isotope: ${}^{235}_{92}\text{U}$. There is less than the critical mass present. There is insufficient ${}^{235}_{92}\text{U}$ to sustain the chain reaction.

26 **(a)** UO_2 is a giant ionic structure; UF_6 is molecular covalent. The +4 oxidation state of U forms ionic compounds but the +6 oxidation state forms covalent compounds as the U^{6+} ion would be too polarizing.

(b) Both compounds would have similar radioactivity as it depends on the nucleus of the uranium atoms and not on the electron arrangements.

(c) For fission reactors, the fuel (typically based on uranium) is usually based on the metal oxide; oxides are used rather than the metals themselves because the oxide melting point is much higher than that of the metal and because it cannot burn, being already in the oxidized state.

27 **(a)** The elements all have non-polar molecular covalent structures. The intermolecular forces are due to the interaction between an instantaneous dipole and induced dipole and so depend on the number of electrons.

The boiling points increase as the number of electrons increases.

(b) UF_6 has a lower boiling than expected based on the trend in (a). Although it is a non-polar molecule it does contain polar bonds. The fluorine atoms all have a partial negative charge so repel the fluorine atoms in other molecules, which reduces the intermolecular forces.

(c) It is volatile. The fluorine atoms only have one mass number so the mass difference in the compound is only due to mass differences in the uranium atoms.

(d) The separation depends on the ratio of the masses of the compounds containing the two isotopes = $\frac{352}{349}$. As the ratio is close to one, the molecules have very similar physical properties and so are hard to separate.

28 **(a)** Fuel enrichment means that the amount of ^{235}U in the fuel is increased, which means more than the critical mass of ^{235}U is available for fission so the reaction can be sustained.

(b) Enriched fuel can be used in the manufacture of nuclear weapons.

29 **(a)** Mass converted to energy = $\frac{1}{1000} \times 1.0$ kg

$= 1.0 \times 10^{-3}$ kg

$\Delta E = \Delta mc^2$

$= 1.0 \times 10^{-3}\text{ kg} \times (3.00 \times 10^{8}\text{ m s}^{-1})^2$

$= 9.0 \times 10^{13}$ J

$= 9.0 \times 10^{10}$ kJ

(b) Mass of coal that produces this energy

$= \frac{9.0 \times 10^{10}\text{ kJ}}{30\text{ kJ g}^{-1}}$

$= 3.0 \times 10^{9}$ g

$= 3.0 \times 10^{6}$ kg

= 3000 tonne

30 Rn → Ra + n

Difference in amu units for the reaction = Δm = 5.2×10^{-3} amu

5.2×10^{-3} amu is equivalent to 5.2×10^{-3} g mol^{-1} = 5.2×10^{-6} kg mol^{-1}

$\Delta E = \Delta mc^2$

$= 5.2 \times 10^{-6}\text{ kg mol}^{-1} \times (3.00 \times 10^{8}\text{ m s}^{-1})^2$

$= 4.7 \times 10^{11}\text{ kJ mol}^{-1}$

$= 4.7 \times 10^{8}\text{ kJ mol}^{-1}$

31 **(a)** The first neutron is needed to initiate a chain reaction and the reaction would not happen without it.

(b) Mass of reactants = 235.0439 + 1.0087 = 236.0526 amu

Mass of products = 95.9342 + 137.9112 + (2 × 1.0087) = 235.8628 amu

Δm = 0.1898 amu

0.1898 amu is equivalent to 0.1898 g mol^{-1} = 1.898×10^{-4} kg mol^{-1}

$\Delta E = 1.898 \times 10^{-4}\text{ kg mol}^{-1} \times (3.00 \times 10^{8}\text{ m s}^{-1})^2$

$= 1.71 \times 10^{13}\text{ J mol}^{-1}$

$= 1.71 \times 10^{10}\text{ kJ mol}^{-1}$

32 **(a)** $^{228}_{90}Th \rightarrow {}^{224}_{88}Rn + {}^{4}_{2}He$

(b) Mass of products = 228.022 800 amu

Δm = 0.005 926 amu

0.005926 amu is equivalent to 0.005926 g mol^{-1} = 5.926×10^{-6} kg mol^{-1}

(c) $\Delta E = \Delta mc^2$

$\Delta E = 5.926 \times 10^{-6}\text{ kg mol}^{-1} \times (3.00 \times 10^{8}\text{ m s}^{-1})^2$

$= 5.33 \times 10^{11}\text{ J mol}^{-1}$

$= 5.33 \times 10^{8}\text{ kJ mol}^{-1}$

(d) Mass of coal burned for the same amount of energy = $\frac{5.33 \times 10^{8}\text{ kJ}}{28\text{ kJ g}^{-1}} = 1.90 \times 10^{7}$ g

$= 1.9 \times 10^{4}$ kg

33 **(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%

34 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.)

35 $^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{90}_{38}\text{Sr} + {}^{144}_{54}\text{Xe} + 2{}^{1}_{0}\text{n}$

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.

36 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.

37 Use the information in the question to compile a table:

Time / years	Activity / hr^{-1} g^{-1}
0	60.0
5730	30.0
5730 × 2	15.0
5730 × 3	7.5
5730 × 4	3.75

The shell is approximately 5730 × 4 years = 22 920 years old.

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

38 **(a)** $^{238}_{94}\text{Pu} \rightarrow {}^{235}_{92}\text{U} + {}^{4}_{2}\text{He}$

(b) One year is short compared to the half-life and so the number of plutonium nuclei does not change significantly.

(c) $\lambda = \frac{\ln 2}{t_{½}}$

$= \frac{\ln 2}{88 \text{ yr}} = 0.007\,877 \text{ yr}^{-1}$

$\ln \frac{[A]_t}{[A]_0} = -0.007\,877 \text{ yr}^{-1} \times 20 \text{ yr}$

$= -0.157533$

$\frac{[A]_t}{[A]_0} = e^{-0.157} = 0.854$

$= 85.4\%$

39 **(a)** $\lambda = \frac{\ln 2}{28.4 \text{ yr}} = 0.0244 \text{ yr}^{-1}$

$A = A_0 e^{-0.0244 \times 80}$

$= 5.1 \times 10^{16} \times e^{-0.0244 \times 80}$

$= 7.24 \times 10^{15} \text{ s}^{-1}$

(b) Initial activity is very high and still highly radioactive after 80 years. This poses severe health risks and problems of disposal.

40 $E_{\text{needed}} = 1216 \text{ kJ mol}^{-1}$

$= \frac{1216 \times 1000 \text{ J mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}}$

$E = h\nu$

$\nu = \frac{1216 \times 1000 \text{ J mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \times 6.63 \times 10^{-34} \text{ J s}}$

$= 3.05 \times 10^{15} \text{ s}^{-1}$

$\lambda = \frac{3.00 \times 10^{8} \text{ m s}^{-1}}{3.05 \times 10^{15} \text{ s}^{-1}}$

$= 9.85 \times 10^{-8} \text{ m}$

This is in the UV region of the electromagnetic spectrum, as displayed in Section 3 of the IB data booklet.

41 **(a)** $CH_2{=}CH{-}CH{=}CH_2$ is a conjugated system with two double bonds separated by a single bond which extends along the full length of the molecule.

(b) The double bonds disappear as the molecules undergo an addition reaction with bromine.

(c) Benzene absorbs radiation in the UV region. In nitrobenzene, conjugation between the benzene ring and the nitro group allows radiation of longer wavelength to be absorbed. This radiation occurs in the visible region of the spectrum and so the compound is coloured.

42 **(a)** Increased conjugation (increased *n*) moves the absorption band λ_{max} towards longer wavelength.

(b) The first members of the series are colourless as they absorb in the UV region, but the later members ($n > 2$) are coloured as they absorb in the visible region.

(c) $C_6H_5{-}(CH{=}CH)_5{-}C_6H_5$ absorbs in the purple region and is probably yellow. $C_6H_5{-}(CH{=}CH)_6{-}C_6H_5$ absorbs in 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.

43 The conjugated system includes eleven C=C bonds and so absorbs in the visible region. The molecule absorbs blue light and so appears orange.

44 **(a)** Fossil fuels and biomass are derived from the Sun through photosynthesis. Other sources 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.

45 **(a)** $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(b) Chlorophyll

(c) Conjugated system of double and single bonds

(d) Process: fermentation

Equation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

Conditions: acidity / absence of oxygen / below 40 °C, yeast provides enzyme

46 **(a)** Methane.

(b) Carbon monoxide and hydrogen.

(c) Particulates (soot), hydrocarbons, carbon monoxide.

(d) Fossil fuels are running out. Biomass is a renewable source.

47 **(a)** 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

48

- Biodiesel is renewable.
- Biodiesel is carbon neutral. Plants use the same amount of CO_2 to make the oil that is released when the fuel is burned.
- Biodiesel is rapidly biodegradable and completely non-toxic, meaning spillages represent far less risk than petroleum diesel spillages.
- Biodiesel has a higher flash point than petroleum diesel, making it safer in the event of a crash.
- Blends of 20% biodiesel with 80% petroleum diesel can be used in unmodified diesel engines.
- Biodiesel can be used in its pure form but engines may require certain modifications to avoid maintenance and performance problems.

- Biodiesel can be made from recycled vegetable and animal oils or fats.

49 **(a)** Distant from localized areas of pollution; data present an accurate measure of global levels of CO_2.

(b) $\% \text{ increase} = \dfrac{\text{increase}}{\text{initial value}} \times 100\%$

$= \dfrac{384 - 316}{316} \times 100\% = 21.5\%$

(c) Combustion of fossil fuels.

(d) The annual variation is due to CO_2 uptake by growing plants. The uptake is highest in the northern hemisphere springtime.

(e) Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

CO_2 dissolves in water: $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

(f) Decreased level of photosynthesis: less CO_2 taken in by plants.

(g) CO_2 absorbs infrared radiation, which leads to increased vibrations and bending and stretching of the bonds.

50 **(a)** Carbon dioxide has polar C=O bonds and the oxygen atoms have lone pairs. It can form hydrogen bonds with water molecules.

(b) Relatively strong hydrogen bonds are formed: Δ*H* 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.

51 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.

52 pH = 8.2: $[H^+] = 10^{-8.2}$

pH = 8.1: $[H^+] = 10^{-8.1}$

$\% \text{ increase} = \dfrac{10^{-8.1} - 10^{-8.2}}{10^{-8.2}} \times 100\%$

$= (10^{0.1} - 1) \times 100\%$

$10^{01} = 1.26$, so change is 26%

53 **(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

54 **(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 825).

55 **(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)

56 **(a)** $E = E^\ominus - \frac{RT}{nF}\ln Q$

Cell reaction: $Zn(s) + Ni^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Ni(s)$

$$Q = \frac{[Zn^{2+}(aq)]}{[Ni^{2+}(aq)]}$$

$$E^\ominus = -0.26 - (-0.76) = +0.50 \text{ V}$$

$$Q = \frac{0.100}{0.00100} = 100$$

$$E = +0.50 - \frac{8.31 \times 298}{2 \times 9.65 \times 10^4} \times \ln 100 \text{ V}$$

$$= 0.50 - 0.059$$

$$= 0.44 \text{ V}$$

(b) $E = E^\ominus - \frac{RT}{nF}\ln Q$

Cell reaction: $Mn(s) + Pb^{2+}(aq) \rightleftharpoons Mn^{2+}(aq) + Pb(s)$

$$Q = \frac{[Mn^{2+}(aq)]}{[Pb^{2+}(aq)]}$$

$$E^\ominus = -0.13 - (-1.18) = 1.05 \text{ V}$$

$$Q = \frac{0.100}{0.00010} = 1.0 \times 10^3$$

$$E = 1.05 - \frac{8.31 \times 298}{2 \times 9.65 \times 10^4} \times \ln(1.0 \times 10^3) \text{ V}$$

$$= 1.05 - 0.0886$$

$$= 0.96 \text{ V}$$

(c) $E = E^\ominus - \frac{RT}{nF}\ln Q$

Cell reaction: $Zn(s) + Fe^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Fe(s)$

$$Q = \frac{[Zn^{2+}(aq)]}{[Fe^{2+}(aq)]}$$

$$E^\ominus = -0.45 - (-0.76) = +0.31 \text{ V}$$

$$Q = \frac{1.50}{0.100} = 15.0$$

$$E = 0.31 - \frac{8.31 \times 298}{2 \times 9.65 \times 10^4} \times \ln 15.0 \text{ V}$$

$$= 0.31 - 0.035 = 0.28 \text{ V}$$

57 **(a)** $E = E^\ominus - \frac{RT}{nF}\ln Q$

Cell reaction: $Zn(s) + Pb^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Pb(s)$

$$Q = \frac{[Zn^{2+}(aq)]}{[Pb^{2+}(aq)]}$$

$$E^\ominus = -0.13 - (-0.76) = +0.63 \text{ V}$$

$$Q = \frac{[Zn^{2+}(aq)]}{0.100}$$

$$0.60 = 0.63 - \frac{8.31 \times 298}{2 \times 9.65 \times 10^4} \times \ln Q$$

$$0.03 = \frac{8.31 \times 298}{2 \times 9.65 \times 10^4} \times \ln Q$$

$$\ln Q = \frac{0.03 \times 2 \times 9.65 \times 10^4}{8.31 \times 298}$$

$$\ln Q = 2.34$$

$$Q = e^{2.34} = 10.1$$

$$10.1 = \frac{[Zn^{2+}(aq)]}{0.100}$$

$$[Zn^{2+}(aq)] = 1.01 \text{ mol dm}^{-3}$$

(b) The equilibrium needs to be shifted to the right. $[Zn^{2+}(aq)]$ could be decreased or $[Pb^{2+}(aq)]$ could be increased.

In detail:

$$0.65 = 0.63 - \frac{8.31 \times 298}{2 \times 9.65 \times 10^4} \times \ln Q$$

$$-0.02 = \frac{8.31 \times 298}{2 \times 9.65 \times 10^4} \times \ln Q$$

$$\ln Q = \frac{-0.02 \times 2 \times 9.65 \times 10^4}{8.31 \times 298}$$

$$\ln Q = -1.55873$$

$$Q = e^{-1.55873}$$

$$Q = 0.21 = \frac{[Zn^{2+}(aq)]}{0.100}$$

$[Zn^{2+}(aq)] = 0.021 \text{ mol dm}^{-3}$ (the previous $[Zn^{2+}(aq)]$ was 1.01 mol dm^{-3})

(c) Increase the temperature. This would increase the size of the second negative term in the Nernst equation.

58 **(a)** The half reaction at the cathode is: $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$

The equilibrium will be to the right for high $[Zn^{2+}(aq)]$. Solution B should be used at the cathode as it has the higher concentration.

(b) $E = E^{\ominus} - \frac{RT}{nF}\ln Q$

$E = -\frac{RT}{nF}\ln 2$

$E = \frac{-8.31 \times 298}{2 \times 9.65 \times 10^{-4}}\ln 2$

$= 0.0089\ \text{V}$

59 **(a)** $CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$-167 \qquad 0 \qquad -394.4 \qquad 2(-237.1)$

$\Delta G_f^{\ominus}$ / kJ mol^{-1}

$\Delta G_{reaction} = \sum \Delta G_f^{\ominus}(\text{products}) - \sum \Delta G_f^{\ominus}(\text{reactants})$

$= (-394.4 + 2(-237.1) - (-167)\ \text{kJ mol}^{-1}$

$= -702\ \text{kJ mol}^{-1}$

(b) $\text{Efficiency} = \frac{-\Delta G_{sys}}{-\Delta H_{sys}} \times 100\%$

$= \frac{-702}{-726} \times 100\% = 97\%$

60 **(a)** $\underset{0}{Pb}(s) + \underset{IV}{PbO_2}(s) + 2H_2SO_4(aq) \rightarrow$

$2\underset{II}{PbSO_4}(s) + 2H_2O(l)$

The lead(II) sulfate is produced from two reactants. It is produced by oxidation from lead, and by reduction from lead (IV) oxide.

(b) The negative terminal is where oxidation occurs during discharge. The oxidation reaction is lead to lead(II) sulfate:

$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2e^-$

(c) $PbSO_4$ is insoluble, so it is deposited on each electrode and is available for reduction or oxidation when the battery is recharged.

(d) Advantages: cheap; large current can be produced; rechargeable.

Disadvantages: low energy/weight ratio, use toxic and corrosive chemicals, can produce a dangerous hydrogen/oxygen gas mixture if overcharged, sulfuric acid needs topping up in older-style batteries.

61 **(a)** Bacteria oxidize the substrate: they live at the negative electrode or cathode.

(b) Sucrose ($C_{12}H_{22}O_{11}$) is oxidized by the bacteria. 12 C atoms are oxidized from 0 to +4 so 48 electrons are released. 24 O atoms are needed so 13 H_2O are needed to provide the final 13 O atoms. 48 H atoms are needed on both sides. Finally, check that the charges are balanced by adding electrons: needs to be zero on both sides.

$C_{12}H_{22}O_{11}(aq) + 13H_2O(l) \rightarrow 12CO_2(g) + 48H^+(aq) + 48e^-$

(c) 48 electrons will reduce 12 O_2 molecules. 48 H atoms are needed on both sides.

$48H^+(aq) + 12O_2(g) + 48e^- \rightarrow 24H_2O(l)$

(d) $C_{12}H_{22}O_{11}(aq) + 13H_2O(l) \rightarrow 12CO_2(g) + 48H^+(aq) + 48e^-$

$48H^+(aq) + 12O_2(g) + 48e^- \rightarrow 24H_2O(l)$

$C_{12}H_{22}O_{11}(aq) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$

62 **(a)** $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(b) Less waste heat produced and more chemical energy converted to useful energy.

63 Semiconductors have electrical conductivities intermediate between metals (conductors) and insulators.

In metals, the low ionization energies result in the formation of metallic bonding – cations surrounded by a ‘sea’ of free-moving electrons.

In insulators, the bonding is covalent and electrons are unable to move beyond their individual covalent bonds.

In semiconductors, the bonds are covalent but the lower ionization energies mean that electrons can be removed from the covalent bonds (for example by the energy of a photon of light). When this occurs, the material can conduct electricity.

64 **(a)** In insulators, the bonding is covalent and electrons are unable to move beyond their individual covalent bonds. This is the case with diamonds.

Pure germanium has a covalently bonded lattice with each Ge atom sharing four pairs of electrons with its neighbouring atoms. The lattice is non-conductive unless the electrons can be excited by a photon. Excited electrons leave the covalent bond and can move throughout the lattice, carrying charge. The bond with an absent electron, or ‘hole’, can also move and carry charge. The ionization energy of carbon is too high for this to happen with diamond.

(b) Adding small amounts of boron to germanium will make its electrical resistance lower. Boron and other Group 13 elements have only three outer electrons, compared to germanium’s four. If some germanium atoms are swapped for boron atoms, the missing electron creates a hole which can conduct electricity. Because the conductor is a positive hole, this is known as a p-type semiconductor.

65 Nitrogen and other Group 15 elements have five outer electrons, compared to germanium’s four. If some germanium atoms are swapped for nitrogen, the extra electron is free to conduct electricity. Because the conductor is a negative electron, this is known as an n-type semiconductor.

Arsenic would be the most likely Group 15 element to use because its atomic radius is closest to that of germanium. Replacing some germanium atoms with arsenic is unlikely to distort the shape of germanium’s crystal lattice.

66 Pure silicon has a covalently bonded lattice with each Si atom sharing four pairs of electrons with its neighbouring atoms. The lattice is non-conductive unless electrons can be excited by a photon. Excited electrons leave the covalent bond and can move throughout the lattice, carrying charge. The bond with an absent electron, or ‘hole’, can also move and carry charge.

Si is doped with As to produce an n-type semiconductor and with Ga to produce a p-type semiconductor. Light stimulates electron flow from the n-type to the p-type semiconductor through an external circuit.

67 Photovoltaic cells generate electricity without creating the pollution (such as nuclear waste, CO_2 emissions) associated with many other forms of electricity generation. Once installed, the power produced is free because it requires no input of fuel. These cells use a renewable energy source which is more efficient. Energy can be stored in a rechargeable battery.

However, the cells are expensive and will not generate electricity if there is not enough light. The rechargeable batteries used to store electricity are expensive, heavy, and inefficient.

68 Conductivity increases as the gallium has one less electron than silicon. Electron holes are introduced which make it a p-type conductor so electrons can move into these holes. Arsenic has one more electron than silicon. An extra electron is introduced so it is a n-type conductor. The extra electrons are free to move.

69 **(a)**

Process	Photovoltaic	DSSC
Light absorption	Silicon atom is ionized to create hole and electron (Si^+ and e^-) pair	Electron excited in conjugated organic molecule
Charge separation	Electron and hole move in opposite directions due to electric field in p–n semiconductor	Election is accepted by semiconductor Positive ion loses its charge as the ion is reduced by electrolyte

(b) If the electron directly recombines with an ion the light energy is converted to useless heat energy.

Practice questions

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 ${}^{234}_{92}\mathrm{Ra}$ is 1600 years the amount present after t years, A(t), can be determined using the equation $\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_\mathrm{o}} = -\lambda t$.

The decay constant, λ, can be found from the value of the half-life, $t_{½}$:

$$\lambda = \frac{\ln\ 2}{t_{½}} = \frac{\ln\ 2}{1600\ \mathrm{yr}} = 4.33 \times 10^{-4}\ \mathrm{yr}^{-1}$$

If 93.75% of the ${}^{234}_{92}\mathrm{Ra}$ decays then $\frac{[\mathrm{A}]_t}{[\mathrm{A}]_\mathrm{o}} = \frac{(1 - 0.9375)}{1} = 0.0625$

$$\ln\frac{[\mathrm{A}]_t}{[\mathrm{A}]_\mathrm{o}} = -\lambda t$$

$$\ln(0.0625) = -4.33 \times 10^{-4}\ \mathrm{yr}^{-1} \times t$$

$$t = \frac{\ln(0.0625)}{-4.33 \times 10^{-4}\ \mathrm{yr}^{-1}} = 6400\ \text{years}$$

It takes 6400 years for 93.75% of ${}^{234}_{92}\mathrm{Ra}$ 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 ${}^{235}_{92}\mathrm{U}$ results in a fission reaction occurring:

$${}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3{}^{1}_{0}\mathrm{n} + \text{energy}$$

The three neutrons released in the reaction can trigger three more fission reactions if they are each absorbed by ${}^{235}_{92}\mathrm{U}$ 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 × 10^3* ***J*** *g^{-1} not 60 × 10^3* ***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}

Specific energy of propane $= \dfrac{|\Delta H_c|}{M(C_3H_8)}$

$= \dfrac{2219 \text{ kJ mol}^{-1}}{44.11 \text{ g mol}^{-1}} = 50.31 \text{ kJ g}^{-1}$

$M(C_4H_{10}) = (4 \times 12.01) + (10 \times 1.01)$ g mol^{-1} =58.14 g mol^{-1}

$\Delta H_c\ (C_4H_{10}) = -2878 \text{ kJ mol}^{-1}$

Specific energy of butane $= \dfrac{|\Delta H_c|}{M(C_4H_{10})}$

$= \dfrac{2878 \text{ kJ mol}^{-1}}{58.14 \text{ g mol}^{-1}} = 49.50 \text{ kJ g}^{-1}$

(b) The ideal gas equation is $pV = nRT$

Substituting for $n = \dfrac{m}{M}$ gives:

$$pV = \frac{m}{M}RT$$

Rearranging to give $\dfrac{m}{V}$ and recognizing that this is equal to the density, ρ, gives:

$\rho = \dfrac{pM}{RT}$, 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})

(c) The gas which is the smallest in size is likely to escape the fastest so propane will escape at a faster rate than butane.

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 $= \dfrac{-\Delta G_{sys}}{-\Delta H_{sys}} \times$ 100%

The combustion reaction of ethanol is:

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

$\Delta G_c = \sum \Delta G_f(\text{products}) - \sum \Delta G_f(\text{reactants})$

$= (2 \times \Delta G_f(CO_2(g))) + (3 \times \Delta G_f(H_2O(l))) - \Delta G_f(C_2H_5OH(l))$

$= (2 \times -394.4) + (3 \times -237.1) - (-175) \text{ kJ mol}^{-1}$

$= -1325.1 \text{ kJ mol}^{-1}$

Thermodynamic efficiency $= \dfrac{\Delta G_c}{\Delta H_c} \times 100\%$

$= \dfrac{-1325.1 \text{ kJ mol}^{-1}}{-1367 \text{ kJ mol}^{-1}} \times 100\% = 96.93\%$

= 97% to nearest whole number

(f) The function of the bacteria is to oxidize the glucose and as oxidation occurs at the anode, the bacteria will be present at the anode of the microbial cell.

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 × 704 million years = 1408 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

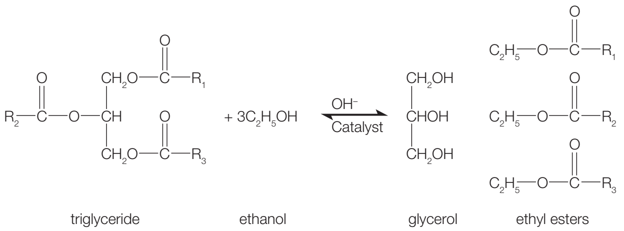
6 × oxidation state of C = 0

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.



17 **(a)** See page 839 for a schematic of a hydrogen–oxygen fuel cell with an alkaline electrolyte. In a hydrogen–oxygen fuel cell the species that is reduced at the cathode is water:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

At the anode the species that is oxidized is hydrogen:

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

(b) The rechargeable nickel–cadmium battery is discussed on page 837. For the forward (discharging) reaction the cathode is cadmium metal and the anode is nickel oxyhydroxide, NiO(OH). For the reverse (charging) reaction the cathode is nickel hydroxide, $Ni(OH)_2$, and the anode is cadmium hydroxide, $Cd(OH)_2$. The question seems to be asking what the electrodes are for the charging process: cathode is $Ni(OH)_2$ and anode is Cd(OH).

For the spontaneous discharging reaction the relevant equations are:

reaction at cathode

$$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2 + 2e^-$$

reaction at anode

$$2NiO(OH) + 2H_2O(aq) + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$$

---

overall reaction

$$Cd(s) + 2NiO(OH)(s) + 2H_2O(aq) \rightarrow Cd(OH)_2 + 2Ni(OH)_2$$

18 **(a)** The lithium-ion battery is discussed on page 838. The battery avoids oxides forming on solid lithium metal electrodes by instead mixing the lithium with graphite at the anode. At the cathode the Li metal that is formed from reduction of Li^+ ions is mixed into an MnO_2 lattice, which also prevents oxidation of the lithium metal.

(b) At the anode lithium ions are formed from the reduction of the solid lithium mixed in the graphite and they then dissolve into a polymer electrolyte:

$$Li(graphite) \rightarrow Li^+(polymer) + e^-$$

The Li^+ ions can migrate through the polymer electrolyte to the cathode, where they are reduced within the MnO_2 lattice:

$$Li^+(polymer) + MnO_2(s) + e^- \rightarrow LiMnO_2(s)$$

(c) Fuel cells and rechargeable batteries are similar in that they are both electrochemical cells that convert chemical energy directly into electrical energy through spontaneous electrochemical (redox) reactions.

Fuel cells and rechargeable batteries are dissimilar in that the electrochemical reactions in a rechargeable battery are reversible and the electrochemical reactions in a fuel cell are irreversible. Fuel cells will continue producing electrical energy as long as fuel is supplied to the cell but rechargeable batteries will eventually deplete the reactants and stop producing electrical energy until they are recharged.

19 Silicon can be used in photovoltaic cells because it has a lower ionization energy than other non-metals such as phosphorous and sulfur, and can more readily lose its valence electrons. As a result silicon is a semiconductor whose electrical conductivity increases with temperature.

Doping silicon with small amounts of Group 13 elements creates a p-type semiconductor in which electron holes are created due to the Group 13 dopants having fewer electrons than silicon. Electrons from neighbouring atoms can migrate into the hole, which moves the hole to a new location in the lattice and this process repeats, resulting in the holes and electrons migrating through the lattice, increasing the conductivity of the p-type semiconductor relative to pure silicon.

When the semiconductor absorbs light energy from the sun the silicon atoms release more electrons and in the process create more holes. If a p-type semiconductor is in contact with an n-type semiconductor then the electrons and holes created are unable to immediately recombine. Instead the electrons must flow through an external circuit before recombination can occur and this generates an electrical current.

20 **(a)** As Figure 14.3 on page 792 shows the nucleon with the highest binding energy is ^{56}Fe.

(b) Binding energy is the energy released when a nucleus is made from protons and neutrons (or the energy required to separate the nucleus into separate nucleons).

(c) The nuclear equation for the fission reaction of $^{235}_{92}$U is:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 2\,{}^{1}_{0}\text{n}$$

A chain reaction can occur as the two neutrons created in the fission process can combine with two other $^{235}_{92}$U atoms and cause more fission reactions that would generate more four neutrons capable of initiating further fission reactions and the process becomes self-sustaining.

(d) The energy released due to the mass defect in the fission reaction can be calculated using the equation $E = mc^2$:

$E(\text{one } {}^{235}_{92}\text{U fission}) = mc^2 = (3.1 \times 10^{-28}\text{ kg}) \times (3.00 \times 10^{8}\text{ m s}^{-1})^2 = 2.8 \times 10^{-11}\text{ J} = 2.8 \times 10^{-14}\text{ kJ}$

$E(\text{one mole of } {}^{235}_{92}\text{U fission}) = (2.8 \times 10^{-14}\text{ kJ}) \times (6.02 \times 10^{23}\text{ mol}^{-1}) = 1.7 \times 10^{10}\text{ kJ mol}^{-1}$

(e) The specific energy of the fuel is the amount of energy per gram of fuel. If 3% of the fuel rod is $^{235}_{92}$U then 1.00 g of a fuel rod contains 0.0300 g of $^{235}_{92}$U.

$$n({}^{235}_{92}\text{U}) = \frac{m({}^{235}_{92}\text{U})}{M({}^{235}_{92}\text{U})} = \frac{0.0300\text{ g}}{235\text{ g mol}^{-1}}$$
$$= 1.28 \times 10^{-4}\text{ mol}$$

Based on the answer to (c) we can determine the energy released by 1.28×10^{-4} mol of $^{235}_{92}$U:

energy released = $(1.7 \times 10^{10}\text{ kJ mol}^{-1}) \times (1.27 \times 10^{-4}\text{ mol}) = 2.2 \times 10^{6}\text{ kJ}$

Because this amount of energy is released from 1.00 g of a fuel rod, the specific energy of the fuel rod is 2.2×10^{6} kJ g^{-1}.

(f) The amount of $^{235}_{92}$U can be increased through enrichment processes. $^{235}_{92}$U and $^{238}_{92}$U are converted into their respective hexafluorides, $^{235}UF_6$ and $^{238}UF_6$, which can then be separated based on their different masses. This separation can happen through diffusion of gaseous UF_6 molecules through a semipermeable membrane and then subsequent repeating of this process to give a larger concentration of $^{235}_{92}$U. Another method is to place $^{235}UF_6$ and $^{238}UF_6$ in a centrifuge and on spinning at high speed the lighter $^{235}UF_6$ will not settle as deep into the centrifuge tube and can be separated from the heavier $^{238}UF_6$, which settles at the bottom of the tube.

21 **(a)** The reaction $^{2}_{1}\text{H} + {}^{1}_{1}\text{H} \rightarrow {}^{3}_{2}\text{He}$ is a nuclear fusion reaction in which small nuclei combine to form a larger nucleus.

(b) The amount of energy released can be calculated based on the change in mass that occurs during the reaction, using the equation $E = mc^2$.

Change in mass = | mass of products – mass of reactants |

$= |3.01603 \text{ amu} - (2.014102 + 1.00728) \text{ amu}|$

$= 0.00535$ amu

From the IB data booklet 1 amu = 1.66×10^{-27} kg.

$0.00535 \text{ amu} = 0.00535 \times 1.66 \times 10^{-27} \text{ kg}$
$= 8.88 \times 10^{-30} \text{ kg}$

$E(\text{one fission reaction}) = mc^2 = 8.88 \times 10^{-30} \text{ kg} \times (3.00 \times 10^8 \text{ m s}^{-1})^2 = 7.99 \times 10^{-13} \text{ J}$

$E(\text{one mole of fission reaction}) = 7.99 \times 10^{-13} \text{ J} \times 6.02 \times 10^{23} \text{mol}^{-1}$

$= 4.18 \times 10^{11} \text{ J mol}^{-1}$

$= 4.18 \times 10^{8} \text{ kJ mol}^{-1}$

(c) The nuclei with the greatest binding energy must be the product of the reaction, $^{3}_{2}\text{He}$, as this is the source of the energy produced in the reaction.

(d) The main difficulty is confining the hot plasma state required for the reaction for a long enough time for the nuclear fusion reaction to occur.

22 Two methods for converting solar energy to electricity involve the use of photovoltaic cells and dye-sensitized solar cells.

Photovoltaic cells are made from silicon doped with small amounts of Group 13 elements to make a p-type semiconductor and small amounts of Group 15 elements to make an n-type semiconductor. When the silicon atoms in the semiconductors absorb light, ionization can occur and this creates free electrons and holes, increasing the conductivity. If an n-type and a p-type semiconductor are in contact the potential at the n–p junction prevents the electrons and holes recombining and the electrons must flow through an external circuit, generating electricity, before recombination can occur.

Dye-sensitized solar cells are made from titanium dioxide, TiO_2, covered with a highly absorbing dye that is typically a highly conjugated organic compound. When the dye absorbs light energy an electron is promoted to an excited state and this extra energy makes it possible for the electron to leave the dye and move into the TiO_2, ionizing the dye. The dye can then take an electron from the electrolyte and return to the ground state, where it can absorb more light energy. The electron that moved into the TiO_2 layer must then travel through an external circuit, generating electricity, before it can recombine with the electrolyte and replace the electron that the electrolyte lost to the dye.

23 **(a)** The rate at which energy is being generated by the fission of $^{235}_{92}\text{U}$ can be determined from the energy output of the power plant and its efficiency:

$$\text{efficiency} = \frac{\text{energy output}}{\text{energy generated}} \times 100\%$$

$$\text{energy generated} = \frac{\text{energy output}}{\text{energy efficiency}} \times 100$$
$$= \frac{2.00 \times 10^4 \text{ kJ s}^{-1}}{42} \times 100$$
$$= 4.8 \times 10^4 \text{ kJ s}^{-1}$$
$$= 4.8 \times 10^7 \text{ J s}^{-1}$$

The rate at which $^{235}_{92}\text{U}$ is being consumed can be determined from the energy generated and the energy released per reaction:

energy generated = number of fission reactions × energy per reaction

number of fission reactions per second
$$= \frac{\text{energy generated}}{\text{energy per reaction}}$$
$$= \frac{4.8 \times 10^7 \text{ J s}^{-1}}{2.8 \times 10^{-11} \text{ J}}$$
$$= 1.7 \times 10^{18} \text{ s}^{-1}$$

moles of $^{235}_{92}\text{U}$ consumed per second =
$$\frac{1.7 \times 10^{18} \text{ s}^{-1}}{6.02 \times 10^{-23} \text{ mol}^{-1}} = 2.8 \times 10^{-6} \text{ mol s}^{-1}$$

moles of $^{235}_{92}$U consumed per hour = $3600 \dfrac{\text{s}}{\text{hr}} \times 2.8 \times 10^{-6}$ mol s^{-1} = 1.0×10^{-2} mol hr^{-1}

mass of $^{235}_{92}$U consumed per hour = $n(^{235}_{92}\text{U}) \times M(^{235}_{92}\text{U})$ = 1.0×10^{-2} mol hr^{-1} × 235 g mol^{-1} = 2.4 g hr^{-1}

(b) As $^{238}_{92}$U is present in the fuel rods it can absorb a neutron and then be converted into $^{239}_{92}$Pu through the subsequent emission of beta particles.

$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \rightarrow ^{239}_{92}\text{U}$

$^{239}_{92}\text{U} \rightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e}$

$^{239}_{93}\text{Np} \rightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\text{e}$

The conversion of $^{238}_{92}$U to $^{239}_{94}$Pu is desirable as $^{239}_{94}$Pu can be used as a fuel in breeder nuclear reactors, which do not require moderators.

(c) Because radioactive decay is an exponential function the decay constant, λ, for $^{239}_{94}$Pu can be determined from its half-life, $t_{½}$:

$$\lambda = \frac{\ln 2}{t_{½}} = \frac{\ln 2}{2.40 \times 10^{4}\ \text{yr}} = 2.89 \times 10^{-5}\ \text{yr}^{-1}$$

(d) If the activity falls to 1.00% of its initial value then $\dfrac{[\text{A}]_t}{[\text{A}]_\text{o}} = 0.0100$

$$\ln \frac{[\text{A}]_t}{[\text{A}]_\text{o}} = -\lambda t$$

$$\ln(0.0100) = -2.89 \times 10^{-5}\ \text{yr}^{-1} \times t$$

$$t = \frac{\ln (0.0100)}{-2.89 \times 10^{-5}\ \text{yr}^{-1}} = 1.59 \times 10^{5}\ \text{years}$$

It will take 1.59×10^5 years for the $^{239}_{94}$Pu to decay to 1.00% of its initial value.

Challenge yourself

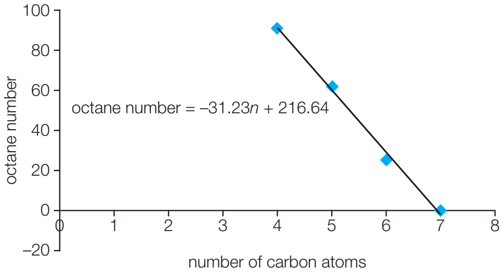
1 The remaining energy is given off as heat. This means that 320 kJ is used for the purpose of the TV, which is to provide images (light) and sound, and 680 kJ is lost as heat:

$$\text{energy efficiency} = \frac{\text{energy utilised for purpose}}{\text{total energy}} \times 100\% = \frac{320\ \text{kJ}}{1000\ \text{kJ}} \times 100\% = 32.0\%$$

2 One form of the second law of thermodynamics states that the entropy of the universe is always increasing. If learning chemistry causes the entropy in your brain, which can be viewed as a system, to decrease, then this must be accompanied by a greater entropy increase in the surroundings and the overall entropy of the universe increases.

3 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: $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$. 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: $\text{SO}_3\text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4\text{(aq)}$.

4 **(a)** From the table on page 780 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.

5 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.

6 The energies of the different energy levels of the hydrogen atom and helium ion were provided in the table on page 794, 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.

7 The enrichment process makes use of the difference in mass between $^{235}UF_6$ and $^{238}UF_6$. Because there are no isotopes of fluorine this means that there are only two possible forms of this molecule, based on the two isomers of uranium. With only two compounds this makes the separation much easier than it would be if UF_6 molecules of other masses were also present due to isomers of fluorine.

8 The separation of $^{235}UF_6$ and $^{238}UF_6$ by gaseous diffusion takes many stages as at each stage the difference in the diffusion time for the two molecules is 1.004. To achieve effective separation the process can require over 4000 stages so this requires the construction of an industrial site with a very large footprint that is difficult to hide.

9 The boiling point of UF_6 is very low for such a heavy molecule, partly because of the high oxidation state on the central uranium. Other covalent fluorides with the central atom in a high oxidation state are therefore predicted to also have low boiling points relative to their size, e.g. SF_6, SeF_6, ClF_5 and IF_7.

10 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.

11 **(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.

12 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.

$$CaCO_3(s) + H_2O(l) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$$

13 Efficiency $= \dfrac{-\Delta G_{sys}}{-\Delta H_{sys}} \times 100\%$

$$= \frac{-\Delta H_{sys} + T\,\Delta S_{sys}}{-\Delta H_{sys}} \times 100\%$$

$$= 1 + \frac{T\,\Delta S_{sys}}{-\Delta H_{sys}} \times 100\%$$

For the reaction $H_2(g) + ½O_2(g) \rightarrow H_2O(g)$ there is a smaller change in entropy, ΔS_{sys} than for the reaction $H_2(g) + ½O_2(g) \rightarrow H_2O(l)$ and liquid water is formed rather than steam.

As ΔS_{sys} decreases the term $\dfrac{T\,\Delta S_{sys}}{-\Delta H_{sys}}$ decreases and the efficiency increases.

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 $0.3623 \times 180.17\ \text{g mol}^{-1}$ 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″), alkene (–C=C–) and a benzene ring (see page 881).

(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:

$$pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$$

$$pH = 4.82 + \log_{10}\frac{0.020}{0.010}$$

$$pH = 4.82 + 0.30 = 5.12$$

Change in pH on adding an extra 2×10^{-4} moles of acid:

$$pH = 4.82 + \log_{10}\frac{0.020}{0.0102}$$

$$pH = 4.82 + 0.29 = 5.11$$

(b) Buffer solutions do not change pH on dilution.

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 **(a)** Bark of Pacific yew tree. Harvesting has depleted the trees, which grow slowly.

(b) Taxol has 11 chiral carbon atoms, giving rise to a very large number of possible stereoisomers. At many stages in its synthesis different enantiomers could be produced, which may have different physiological properties. So these steps need to be controlled by chiral auxiliaries.

21 A chiral auxiliary is itself an enantiomer which bonds to the reacting molecule to create the stereochemical environment necessary to follow a certain pathway. The reaction then takes place, forming the desired enantiomer, and the chiral auxiliary is then removed.

Different enantiomers may have different biological effects, some of which may be harmful. An example is the genetic deformities caused by the (*S*) enantiomer of the drug thalidomide in the racemic mixture, although, in this case giving an enantiomerically pure drug would not have solved the problem as it racemizes in the body.

22 **(a)** ${}^{90}_{39}\mathrm{Y} \rightarrow {}^{90}_{40}\mathrm{Zr} + {}^{0}_{-1}\beta$

Be sure to check that the superscripts on the left of the equation add up to the sum of the superscripts on the right of the equation, and also that the subscripts on the left add up to the sum of the subscripts on the right.

(b) 4 days = 96 hours

number of half-lives = $\frac{96}{64}$ = 1.5

proportion remaining = $(0.5)^{1.5}$ = 0.3536

therefore amount remaining = 65.0 × 0.3536 = 23 g

23 Proportion remaining after 24 hr = 0.33/5.0 = 0.066

Proportion remaining = 0.066 = 0.5^x, where x = number of half-lives

Taking logs: $x \log 0.5 = \log 0.066$

$$x = \frac{\log 0.066}{\log 0.5} = 3.92$$

There are 3.92 half-lives in 24 hours

1 half-life is $\frac{24}{3.92}$ = 6.12 hours (6 hours 7 minutes)

24 **(a)** Half-life is 6 hours – long enough for diagnosis but decays quickly. Radiation is gamma rays used for detection and low-energy electrons which minimize radiation dose. The isotope is chemically able to bond to various biomolecules.

(b) Strong beta emitters that also emit gamma radiation to enable imaging.

25 **(a)** Targeted alpha therapy uses alpha emitters attached to carriers such as antibodies, which specifically target certain cells.

(b) Very high ionizing density and so a high probability of killing cells along their track. Short range and so minimize unwanted irradiation of normal tissue surrounding the targeted cancer cells.

26 **B** Methylbenzene and water are immiscible as methylbenzene is non-polar and water is polar. The other solvent pairs are miscible.

27 **(a)** An ideal solution contains fully miscible components. Each component exerts the same vapour pressure in the mixture, according to its relative concentration, as it does when pure. The intermolecular forces between the particles of the different components are the same as those between the particles in the pure substances.

(b) The boiling point of a mixture decreases with increasing height in a fractionating column as the mixture becomes enriched in the more volatile component.

28 **(a)** 2850–3090 cm^{-1} is characteristic of the C—H bond

3200–3600 cm^{-1} is characteristic of the O—H bond

(b) The peak at 2850–3100 cm^{-1} is used to characterize ethanol in the presence of water vapour.

(c) Propanone also contains C—H bonds, which give the same characteristic band at 2950 cm^{-1} as ethanol. The propanone in their breath would give a false positive reading in a test for ethanol.

29 **(a)** Molecular ion at m/z = 194, which is the formula mass of caffeine

(b) C—H in methyl groups: 2850–3090 cm^{-1}

C=O: 1700–1750 cm^{-1} (two different peaks in this region as caffeine contains two –C=O groups)

(c) Four peaks, relative areas 3:3:3:1 as there are hydrogen atoms in four different environments in the caffeine molecule (three CH_3 groups and a hydrogen atom attached to the five-membered ring).

(d) Amine, amide, alkene, ketone

30 Solvents cause problems of disposal. Organic solvents can be incinerated, causing release of pollutants, greenhouse gases, and toxins (although power can be generate). Solvents can contaminate ground water and soil. Some solvents can be hazardous to the health of workers.

31 Protective shoe-covers, clothing, gloves, paper towels, and contaminated implements. Interim storage in sealed containers for radioactivity to decay before conventional disposal.

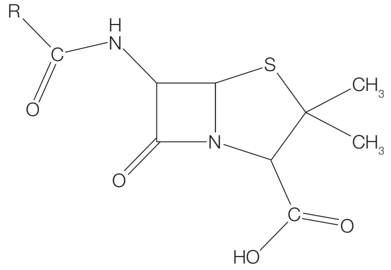
32 The success of antibiotics in treating disease has led to their widespread use, and in some cases over-use. Exposure of bacteria to antibiotics increases the spread of resistant strains. Antibiotic resistance renders some antibiotics ineffective, especially with multiply resistant strains, e.g. MRSA.

33 Patient compliance refers to the importance of patients following medical instructions, in particular to completing the course of an antibiotic treatment. This helps prevent the spread of antibiotic-resistant bacteria.

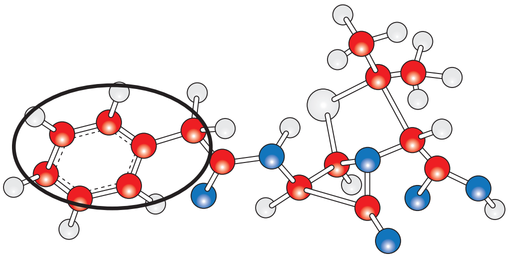
34 Green Chemistry principles seek to reduce toxic emissions and waste substances in the manufacture of drugs. This includes reduction in the amount of solvent used, the adoption of synthesis pathways with shorter routes, the replacement of inorganic catalysts with enzymes, and the recycling of waste.

Practice questions

1 **(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.

2 Chiral auxiliaries are compounds that force reactions to proceed with a specified stereochemistry and create chiral products. Chiral auxiliaries are enantiomers themselves so when they bind to the reactant they make it chiral and therefore create a preference for the reaction to proceed in a stereospecific manner. When the chiral auxiliary is removed the final product will be a single enantiomer.

3 **(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.

4 **(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.

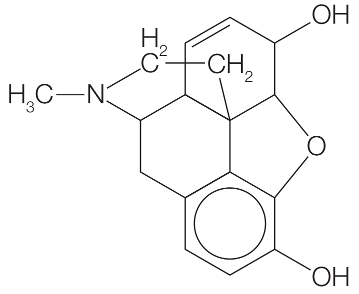
These are all found in bacteria.

(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.

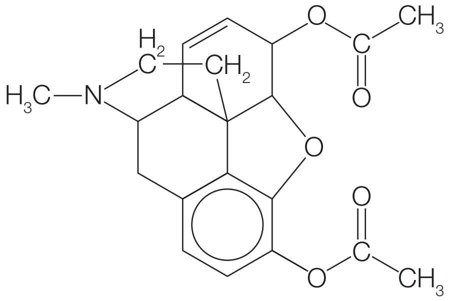
(c) The human immunodeficiency virus (HIV) that causes AIDs mutates very quickly, which makes it difficult to develop an effective long-lasting treatment. As HIV uses the host cells, drugs that target HIV may also harm the host cells so it is difficult to target HIV without causing harm to the host.

5 **(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

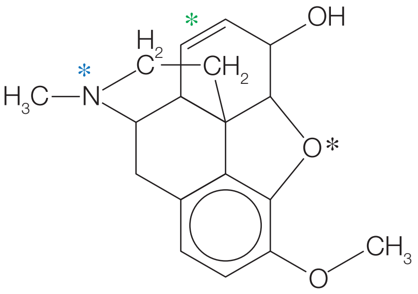


diamorphine (heroin)

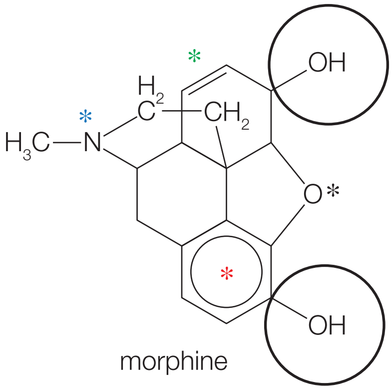
6 The therapeutic window is the range of dosages between the minimal amount necessary to produce a therapeutic effect and the amount that produces medically unacceptable adverse effects. It is determined from the ratio between ED_{50} and LD_{50}, the dosage where 50% of the population experiences noticeable 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.

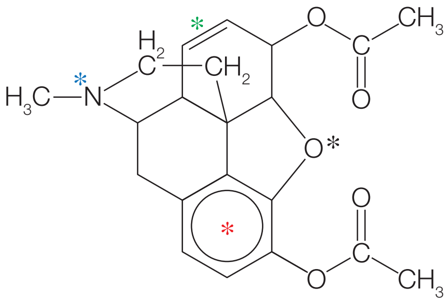
7 **(a)** The structures of codeine, morphine and diamorphine are shown below, with groups present in all three compounds (tertiary amine, alkene and ether) highlighted with asterisks.



codeine



morphine



diamorphine (heroin)

The functional groups present in these compounds are:

∗ = alkene
∗ = amine
∗ = benzene ring
∗ = ether

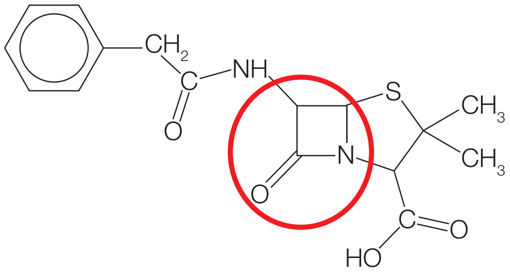
(b) The functional group present in morphine but not diamorphine is the alcohol group. The alcohol groups in morphine are circled in the diagram above.

(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.)

8 **(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.

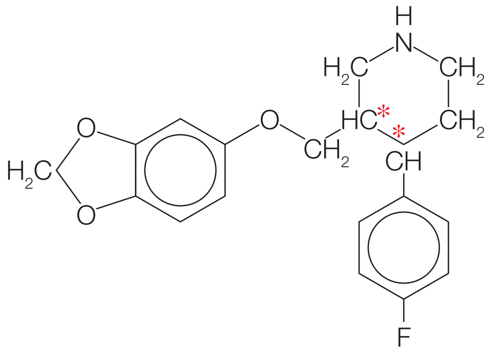
(c) The beta-lactam ring in penicillin is circled in the diagram below.



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.

9 **(a)** Chiral carbons are carbons which have four different groups attached to them. The two chiral carbons on paroxetine are marked in the structure below with asterisks.

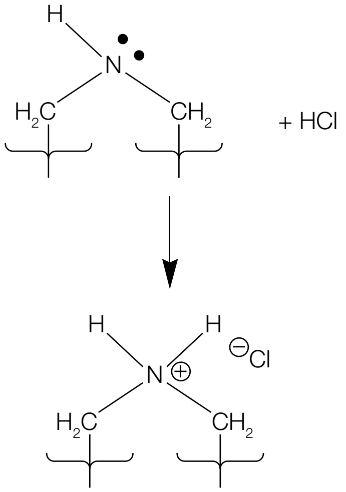


(b) The classic example of the importance of chirality in drug action is thalidomide. One optical isomer was effective in reducing morning sickness in pregnant women, the other isomer caused fetal abnormalities. Another example is ibuprofen, where one optical isomer is more effective than the other. Because different optical isomers can have different effects on the body it is necessary to isolate each isomer and conduct clinical trials with each one to determine their individual effects before they can be approved for human use.

(c) Chiral auxiliaries are compounds that force reactions to proceed with a specified stereochemistry and create chiral products. Chiral auxiliaries are enantiomers themselves so when they bind to the reactant they make it chiral and therefore create a preference for the reaction to proceed in a stereospecific manner. When the chiral auxiliary is removed the final product will be a single enantiomer.

(d) **(i)** Converting paroxetine to a hydrochloride salt converts a relatively non-polar molecule into an ionic compound and increases its solubility in aqueous solutions. This enables it to be more effectively distributed around the body.

(ii) The amine nitrogen contains a lone pair of electrons and the nitrogen can therefore act as a Bronsted–Lowry base. This enables paroxetine to be converted to a hydrochloride salt, as shown in the diagram below, which illustrates the changes that occur at the amine group within paroxetine:



10 **(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.

11 **(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.

12 **(a)** **(i)** The oxidation reaction that occurs in the breathalyser when ethanol is present involves the oxidation of ethanol to ethanoic acid:

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$$

The reduction reaction that occurs in the breathalyser when ethanol is present involves the reduction of the dichromate ion to chromium(III) ions:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

(ii) The orange acidified dichromate ions turn green as chromium(III) ions are formed.

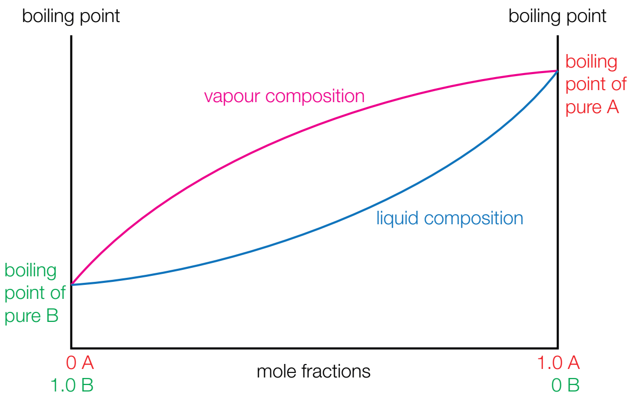
(b) The intoximeter will show peaks occurring at 2950 cm^{-1} due to C–H bonds if ethanol is present in the breath of the person being tested. The intensity of these peaks relative to a reference sample will depend on the amount of ethanol in the breath sample so this allows the amount of ethanol present to be determined.

13 **(a)** Iodine-123 may be favoured over iodine-131 as the shorter half-life means the body will be exposed to potentially damaging radiation for a shorter period of time.

(b) The equation for decay of iodine-131 by beta emission is given below. Note that the gamma radiation emitted in this process is also shown as a product.

$$^{131}_{53}I \rightarrow {}^{131}_{54}Xe + {}^{0}_{-1}\beta + {}^{0}_{0}\gamma$$

14 **(a)** The boiling point composition diagram for a mixture of two miscible liquids, A and B, is given below.



(b) As vapour rises up the column it will cool and then condense to a liquid and return to the boiling mixture. The higher up the column the vapour reaches, the lower its temperature and the higher its composition of B, which has the lower boiling point of the two components. With the appropriate height of column pure B can be isolated as a vapour that exits the top of the column, leaving pure A as a liquid.

15 A more efficient process than extracting Taxol directly from the bark of Pacific yew trees involves semi-synthesis, where a precursor compound is isolated from the leaves of Himalayan and European yew trees and then converted into Taxol via synthetic reactions. As the isolation of the precursor does not damage the trees as much as bark removal does it is regarded as a more sustainable process.

A more promising development in the green synthesis of Taxol is the discovery that certain species of fungi produce Taxol in fermentation reactions. Isolating Taxol from these fermentation processes avoids the inefficiency of the many steps required for synthetic and semi-synthetic approaches, and does not require the use and disposal of large amounts of solvents.

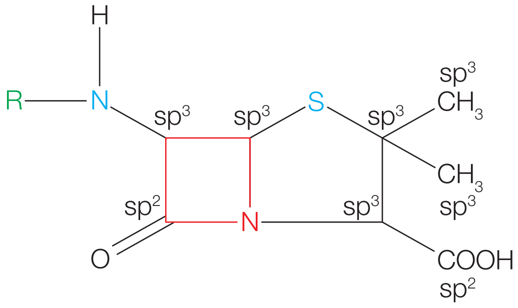
Challenge yourself

1 A carbon atom with four electron domains is sp^3 hybridized.

A carbon atom with three electron domains is sp^2 hybridized.

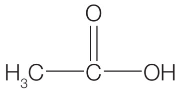
A carbon atom with two electron domains is sp hybridized.

Note that the structural representation provided for penicillin has some carbon atoms only represented by vertices and in this type of representation H atoms are often omitted.



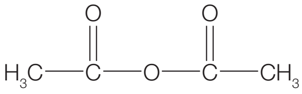
penicillin

2 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.



$\mathrm{H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$

ethanoic acid



$\mathrm{H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3}$

ethanoic anhydride

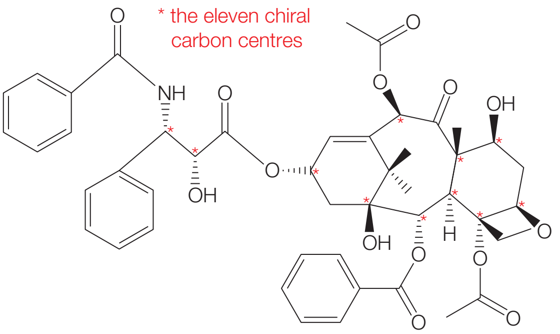
3 Na_2CO_3 and $NaHCO_3$ solutions contain CO_3^{2-} and HCO_3^-, the conjugate bases of the weak acids HCO_3^- and H_2CO_3 respectively. As they are bases they are able to hydrolyse water and release OH^- ions:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3\ (aq) + OH^-(aq)$$

4 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.

5 The chiral carbon atoms in Taxol are identified in the structure below using red asterisks:



6 The ionic salt K_2CO_3 dissolves readily in water, which is a very polar solvent, but not as readily in ethanol as it is a less polar solvent. The presence of the ions in water reduces the solubility of the ethanol in water so the two solvents separate and ethanol forms a separate layer on top of the water. This process is used in biochemistry to precipitate proteins from solution.