# Section 1.1

1	<b>a</b> 2.0	<b>b</b> 5.3	<b>c</b> 1.3	<b>d</b> 10.0	<b>e</b> 5.0
	<b>f</b> 50.2				

**2 a** 144 **b** Neodymium

3	Mass of sample/g	A ; S	mount of ample/mol	Num atom	ber of Is
	-	_		6.02	× 10 <sup>23</sup>
	-	2	2.00	_	
	56.0	-		6.02	× 10 <sup>23</sup>
	80.0	-		12.0	$4 \times 10^{23}$
	63.5	C	).50	_	
4	<b>a</b> 1	<b>b</b> 0.5	<b>c</b> 0.25	<b>d</b> 0.1	<b>e</b> 0.25
	<b>f</b> 0.5	<b>g</b> 0.25	<b>h</b> 0.1	<b>i</b> 2	<b>i</b> 5

Atoms of copper are approximately twice as heavy as atoms of sulphur. Thus the same mass contains only half as many moles of copper as it does of sulphur.

- 5 Black copper(II) oxide (CuO) contains equal numbers of copper and oxygen particles (Cu<sup>2+</sup> and O<sup>2-</sup> ions). Red copper(I) oxide (Cu<sub>2</sub>O) contains twice as many copper particles as oxygen particles (Cu<sup>+</sup> and O<sup>2-</sup> ions).
- **6 a** The mass of the sample is needed to be sure that iodine and oxygen are the only elements in the compound.

# Section 1.2

- 1 a  $2Mg + O_2 \rightarrow 2MgO$ 
  - **b**  $2H_2 + O_2 \rightarrow 2H_2O$
  - **c**  $2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3$
  - **d** CaO + 2HNO<sub>3</sub>  $\rightarrow$  Ca(NO<sub>3</sub>)<sub>2</sub> + H<sub>2</sub>O
  - e CaCO<sub>3</sub> + 2HCl  $\rightarrow$  CaCl<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>O
  - **f**  $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ **g** 2HCl + Ca(OH)<sub>2</sub>  $\rightarrow$  CaCl<sub>2</sub> + 2H<sub>2</sub>O
  - **g**  $2\text{HCI} + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}\text{Cl}_2 + 2\text{H}$ **h**  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{Na}\text{OH} + \text{H}_2$
  - i  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
  - $\mathbf{j}$  2CH<sub>3</sub>OH + 3O<sub>2</sub>  $\rightarrow$  2CO<sub>2</sub> + 4H<sub>2</sub>O

# Section 1.3.

- **1 a** All the magnesium reacts.
  - **b** So that we know the number of moles of each substance involved in the reaction.
  - c Mass of 1 mole of magnesium oxide.
  - **d** Because 2 moles of magnesium oxide are produced.
  - **e** To find the mass of magnesium oxide produced from 1 g of magnesium.
  - ${f f}~$  80/48 would be multiplied by 50 rather than by 6.
- **2** 20 g

**3 a** 2.8g **b** 3.1g **c** 2.5g

- **4** 3667 g (3.667 kg)
- **5 a**  $C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$ **b** 175 kg
  - **c** 154 kg

- **b** The relative number of moles of iodine and oxygen.
- **c** To change the relative number of moles into the ratio of moles of oxygen relative to 1 mole of iodine.
- **d** In order to produce a ratio involving whole numbers
- $\mathbf{e} \ \mathbf{I}_2 \mathbf{O}_5, \mathbf{I}_4 \mathbf{O}_{10}, \mathbf{I}_6 \mathbf{O}_{15}, \text{etc.}$
- **f** The molar mass is needed.

7	a f	H <sub>2</sub> O CuO	<b>b</b> CO <b>g</b> CaO	c h	$\begin{array}{c} \mathrm{CS}_2\\ \mathrm{SO}_2 \end{array}$	<b>d</b> CH <sub>4</sub> <b>i</b> MgH <sub>2</sub>	e	Fe <sub>2</sub> O <sub>3</sub>
8	a	92.3	<b>b</b> 7.7	с	СН			
9	a f	SiH <sub>4</sub> CaCO <sub>3</sub>	b CO g HClO <sub>3</sub>	c h	CO <sub>2</sub> NaHCO <sub>3</sub>	<b>d</b> MgO	e	C <sub>2</sub> H <sub>6</sub> O
10	a f	$\substack{\text{CH}_2\\\text{C}_3\text{H}_4}$	$\begin{array}{c} \boldsymbol{b} \ P_2O_3 \\ \boldsymbol{g} \ CH_2O \end{array}$	c h	$\begin{array}{c} \text{AlCl}_3\\ \text{C}_{12}\text{H}_{22}\text{O}_1\end{array}$	<b>d</b> BH <sub>3</sub>	e	$C_4H_5$
11	a	$H_2O_2$	b CO	с	$C_2H_2$	$\mathbf{d} C_6 H_6$	e	$C_6H_{12}$
12	a	2	<b>b</b> 11	с	2	<b>d</b> 10	e	2
13	a f	30 242	<b>b</b> 78 <b>g</b> 132	c	130	<b>d</b> 100	e	158
14	a f	$2 \\ 1 \times 10^{6}$	<b>b</b> 4	c	10	<b>d</b> 0.02	e	5

- **2 a**  $2Ca + O_2 \rightarrow 2CaO$ 
  - **b** Ca +  $2H_2O \rightarrow Ca(OH)_2 + H_2$
  - $\mathbf{c} \ \mathrm{C} + \mathrm{CO}_2 \rightarrow 2\mathrm{CO}$
  - **d**  $N_2 + 3H_2 \rightarrow 2NH_3$
  - $\mathbf{e} \ \mathrm{C_3H_8} + 5\mathrm{O_2} \rightarrow 3\mathrm{CO_2} + 4\mathrm{H_2O}$
- 3 **a**  $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$  **b**  $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ 
  - **c**  $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
  - **d**  $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$
  - **e** BaO(s) + 2HCl(aq) → BaCl<sub>2</sub>(aq) + H<sub>2</sub>O(l)
- **6 a** 56 tonnes
  - $\mathbf{b} \, \mathrm{S} + \mathrm{O}_2 \rightarrow \mathrm{SO}_2$
  - **c** 64 g
  - **d** 64 tonnes
  - e 2 tonnes
  - **f** 112 tonnes
- **7 a** 217 tonnes
- **b** 0.58 tonnes
- 8 **a**  $\operatorname{Fe}_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ 
  - **b** 160 g
  - **c** 1.43 g
  - **d** 1.43 tonnes
  - **e** 2.86 tonnes
  - **f** 11.9 tonnes

 $e C_3H_4$ 

**d**  $500 \, \text{cm}^3$ 

# Section 1.4

- 1 The particles in a gas are much further apart than in a liquid or solid. In a gas, therefore, the volume of the particles is a very small part of the total volume and does not significantly affect it. In a liquid or solid the particles are close together and their volumes must be taken into account when deciding on the total volume.
- 2 a  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ **b** Volume of oxygen is twice that of methane. **c** The volume of water vapour formed is twice the
  - volume of methane burnt.

# Section 1.5

- 1 a  $i 0.02 \, dm^3$ **ii** 1.5 dm<sup>3</sup>
  - **i** 220 000 cm<sup>3</sup> **ii** 1600 cm<sup>3</sup> b
- 2 There is 0.4 mole of sodium hydroxide dissolved in every dm<sup>3</sup> of the solution.

3	<b>a</b> 0.5	<b>b</b> 0.4	<b>c</b> 1	<b>d</b> 0.2	<b>e</b> 0.05	<b>f</b> 0.002
4	<b>a</b> 2	<b>b</b> 2	<b>c</b> 5	<b>d</b> 0.2	<b>e</b> 4	<b>f</b> 0.2
5	<b>a</b> 0.25	<b>b</b> 0.2	<b>c</b> 5	<b>d</b> 0.4	<b>e</b> 0.5	<b>f</b> 0.125
6	<b>a</b> 40 g	<b>b</b> 4g	<b>c</b> 20 g	<b>d</b> 0.4 g	<b>e</b> 800 g	<b>f</b> 1g
7	<b>a</b> 117 g <b>e</b> 0.0024	<b>b</b> 3 9 <b>f</b> 2	.95 g 385 g	<b>c</b> 1.4 g <b>g</b> 0.0126	d Sg h	9930g 0.1825g
	i 25.0g	<b>j</b> 1	3.9g	8 0.0120		0.10298
8			2			

-	Concentration/g dm °	Concentration/mol dm °
	-	5.15
	_	1.51
	31.5	-
	13.4	-
	-	0.174
	-	0.065
	0.6	-

# Section 2.1

1				
Isotope	Symbol	Atomic number	Mass number	Number of neutrons
carbon-12	<sup>12</sup> <sub>6</sub> C	6	12	6
carbon-13	<sup>13</sup> <sub>6</sub> C	6	13	7
oxygen-16	<sup>16</sup> <sub>8</sub> 0	8	16	8
strontium-90	<sup>90</sup> <sub>38</sub> Sr	38	90	52
iodine-131	$^{131}_{53}$ I	53	131	78
iodine-123	<sup>123</sup> <sub>53</sub> I	53	123	70

2	Protons	Neutrons	Electrons
а	35	44	35
b	35	46	35
с	17	18	17
d	17	20	17

**a** 0.25 **b** 2 **c**  $48 \, \text{dm}^3$ **d**  $240 \, \text{dm}^3$ **e** 30 dm<sup>3</sup> Na<sup>+</sup> Cl-9 Na<sup>+</sup> CO<sub>2</sub><sup>2-</sup>  $Ag^+$ NO<sub>3</sub>  $Mg^{2+}$ Br⁻  $SO_4^{2-}$  (or  $HSO_4^{-}$ )  $H^+$ 10 a  $1 \operatorname{mol} dm^{-3}$ **b** 0.02 mol dm<sup>-3</sup>  $\mathbf{c}$  0.3 mol dm<sup>-3</sup>  $\mathbf{d}$  0.4 mol dm<sup>-3</sup> 11 a 0.0019 mol **b** 0.0019 mol **d**  $0.076 \,\mathrm{mol}\,\mathrm{dm}^{-3}$  or  $2.77 \,\mathrm{g}\,\mathrm{dm}^{-3}$ **c** 0.076 mol 12 a 0.0022 mol **b** 0.0044 mol **d** 0.176 mol dm<sup>-3</sup> c 0.176 mol **13 a**  $7.75 \times 10^{-4}$  (0.000775) mol dm<sup>-3</sup> **b**  $0.0574 \,\mathrm{g}\,\mathrm{dm}^{-3}$ 

 $c 25 \text{ cm}^3$ 

 $c 1 dm^3$ 

**b** 0.0025

**b** 0.04 mol

**b** Volumes of hydrogen and chlorine are the same.

**a**  $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ 

**c** 4

Volume of hydrogen chloride is twice the volume of

**b** 5 cm<sup>3</sup>

**d** 2

3 **a**  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ 

hydrogen or chlorine.

4 **a**  $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ 

**b** 3

**b** 500 cm<sup>3</sup> **c** 300 cm<sup>3</sup>

 $0.414 \,\mathrm{dm^3} \,(414 \,\mathrm{cm^3})$ 

5

6

7

8

**a** 3

- 3 **a**  $A_{\rm e}({\rm Br}) = 80.0$ 
  - **b**  $A_{r}(Ca) = 40.1$
- **4 a** 100 x

**14 a** 0.0025

15 a 0.02 mol

**e** 20 cm<sup>3</sup>

- **b** 193x
- **c** 191(100 x)
- **d** 193x + 191(100 x)
- **e**  $[193x + 191(100 x)] \div 100$ f 60% iridium-193, 40% iridium-191
- 5 37.5% antimony-123, 62.5% antimony-121
- 23.5% rubidium-87 6

# Section 2.2

- 1 **a**  ${}^{238}_{94}Pu \rightarrow {}^{234}_{92}U + {}^{4}_{2}He$  **b**  ${}^{221}_{87}Fr \rightarrow {}^{217}_{85}At + {}^{4}_{2}He$  **c**  ${}^{230}_{90}Th \rightarrow {}^{226}_{88}Ra + {}^{4}_{2}He$ 2 **a**  ${}^{90}_{38}Sr \rightarrow {}^{90}_{39}Y + {}^{0}_{-1}e$  **b**  ${}^{131}_{51}I \rightarrow {}^{131}_{54}Xe + {}^{0}_{-1}e$  **c**  ${}^{231}_{90}Th \rightarrow {}^{231}_{91}Pa + {}^{0}_{-1}e$ 3 **a**  ${}^{7}_{3}Li + {}^{1}_{1}p \rightarrow {}^{24}_{2}He$ 
  - $\mathbf{b}_{7}^{14}N + {}_{0}^{1}n \rightarrow {}_{6}^{14}C + {}_{1}^{1}p$

# Section 2.3

1 No. Isotopes have the same number of protons and the same number of electrons.



4	Electronic shell configuration	Group	Period	
	_	3	2	
	-	6	3	
	2.4	_	-	
	2.8.4	-	-	
	-	1	2	
	-	1	3	
	_	1	4	

5 Elements A, C and E are in the same group.

# Section 2.4

- 1s block:metalsp block:mixture of metals and non-metalsd block:metalsf block:metals
- **a** The electron is in the first electron shell. **b** The electron is in an s type orbital. **c** There are two electrons in this orbital.

3	<b>a</b> s block	<b>b</b> p block

- c p block d f block
- e d block f p block
- **g** f block **h** s block

# Section 3.1

- **1 a**, **c**, **e** 2.8.8
  - **b**, **d** 2.8
  - **f** 2.8.14
  - **g** 2.8.13
  - **h** 2.8.17
- **2**  $K^+$ ,  $Ca^{2+}$ ,  $(Sc^{3+})$ ,  $Cl^-$ ,  $S^{2-}$ ,  $P^{3-}$

- $c^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}p$   $d^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + {}^{1}_{0}n$   $4^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn \rightarrow {}^{218}_{84}Po \rightarrow {}^{214}_{82}Pb$   $5^{232}_{90}Th {}^{6}_{2}He {}^{4}_{-1}e \rightarrow {}^{208}_{82}Pb$   $6^{}a 5g b 0.625g c 4.5 \times 10^{-4}s$
- 7 b Approx. 4.3 gc Approx. 185 days
- **6 a** X is in Group 1.
  - b Y is in Group 0.Group 1 elements have a single electron in their outer shell, which they lose readily. Noble gases in Group 0 have 2 or 8 electrons in their outer shell and it is difficult to remove one of these electrons.

**d** 0.039 g

- 7 **a** lst ionisation 2nd ionisation 3rd ionisation Ca(g)  $\rightarrow$  Ca<sup>+</sup>(g) + e<sup>-</sup> Ca<sup>+</sup>(g)  $\rightarrow$  Ca<sup>2+</sup>(g) + e<sup>-</sup> Ca<sup>2+</sup>(g)  $\rightarrow$  Ca<sup>3+</sup>(g) + e<sup>-</sup>
  - **b** Once an electron has been removed the remaining electrons are held more tightly. Hence it is more difficult to remove a second electron.
  - **c** Second ionisation enthalpy involves removal of an electron from shell 4 but third involves removal of an electron from shell 3 which is closer to the nucleus.
- 8 The second ionisation enthalpy for sodium is high because removing a second electron involves removing an electron from the full second shell. This requires much more energy than removing the second electron from the third shell of magnesium which is further from the nucleus.
- 4 Z = 16. The element is sulphur.

5	a Chlorine	<b>b</b> Potassium
	<b>c</b> Titanium	<b>d</b> Tin

- **6 a**  $1s^2 2s^2 2p^1$ 
  - **b**  $1s^2 2s^2 2p^6 3s^2 3p^3$
  - **c**  $1s^2 2s^2 2p^6 3s^2 3p^5$
  - **d**  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
  - **e**  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
- **3 a**  $\begin{bmatrix} \text{Li} \end{bmatrix}^+ \begin{bmatrix} \text{H} \\ \text{H} \end{bmatrix}^$ **b**  $\begin{bmatrix} \text{K} \end{bmatrix}^+ \begin{bmatrix} \text{XX} \\ \text{X} \\ \text{XX} \end{bmatrix}^-$

- $\mathbf{d} \begin{bmatrix} \mathbf{x} \\ \mathbf{x} \\ \mathbf{x} \\ \mathbf{x} \\ \mathbf{x} \\ \mathbf{x} \\ \mathbf{x} \end{bmatrix}^{-} \begin{bmatrix} \mathbf{x} \\ \mathbf{x} \end{bmatrix}^{-}$  $\begin{bmatrix} Ca \end{bmatrix}^{2+} \begin{bmatrix} \bullet X \\ \bullet X \\ X \\ X \\ X \\ X \end{bmatrix}^{2-}$  $\begin{bmatrix} Na \end{bmatrix}^{+} \begin{bmatrix} Na \end{bmatrix}^{+} \begin{bmatrix} \bullet X \\ X & X \\ X & X \end{bmatrix}^{3-}$ g Na |<sup>+</sup>  $\begin{bmatrix} AI \end{bmatrix}^{3+} \begin{bmatrix} \bullet X \\ X \\ X \\ X \\ X \end{bmatrix}^{-} \begin{bmatrix} \bullet X \\ X \\ X \\ X \\ X \end{bmatrix}^{-} \begin{bmatrix} \bullet X \\ X \\ X \\ X \\ X \end{bmatrix}^{-} \begin{bmatrix} \bullet X \\ X \\ X \\ X \\ X \end{bmatrix}^{-}$ h 4 хx ΧХ b H X CI X хх Н С  $H \overset{\bullet X}{\underset{\bullet X}{\times}} C \overset{\bullet X}{\underset{\bullet X}{\times}} H$ н H \* S \* H d хх e X Br X xx •x xx x Br • Al • Br x хх хх ΧХ f X CI X хх н •× g x. c x x С н H <sup>×</sup> C <sup>×</sup> C <sup>×</sup> H i Н • X
  - H \* C \* O \* H X • • • •

**5 a** In a normal covalent bond, each atom supplies a single electron to make up the pair of electrons involved in the bond. In a dative covalent bond one atom supplies both electrons.

8 Chlorine has a stronger electron pulling power. Thus in a covalent bond between carbon and chlorine, the electron pair forming the bond is more strongly attracted by the chlorine atom than by the carbon atom.

9	<b>a</b> H—F δ+δ-	<b>b</b> N≡N non-polar
	c H—Cl $\delta + \delta$ –	<b>d</b> Cl—F $\delta + \delta$ -
	e H—I $\delta + \delta$ –	<b>f</b> S=C=S non-polar

10 a Three

- **b** The delocalised electrons form a pool of electrons which are free to move around the positive ions in the metal. When a potential difference is applied across the metal, electrons move towards the positive terminal, ie a current flows.
- 11 a Metallicb Covalentc Covalentd Ionice Ionicf Covalent

Silicon tetrafluoride contains polar covalent bonds.

12 a NaCl **b** MgCl<sub>2</sub> c FeCl<sub>3</sub>  $\mathbf{d}$  Al<sub>2</sub>O<sub>3</sub> e NH<sub>4</sub>Čl f NaOH  $\mathbf{g}$  K<sub>2</sub>CO<sub>2</sub> h MgSO<sub>4</sub> 13 a NH<sub>2</sub> **b** H<sub>2</sub>Š  $\mathbf{c}$   $\overline{CO}_2$ d HCĪ e CO f SO<sub>2</sub> g N<sub>2</sub>Õ h SÕ<sub>3</sub>

#### **SECTION 3**

#### Section 3.2

- **1 a** Li(g) because it has an extra electron shell.
  - **b** Li<sup>+</sup>(aq) because the ion is surrounded by water molecules.
  - ${\boldsymbol c}\ \ Cl^-(g)$  because it has an extra electron.
  - **d** Cl<sup>-</sup>(aq) because the ion is surrounded by water molecules.
- **2 a**  $K^+(g)$  because it has an extra electron shell.
  - **b** Br<sup>-</sup>(g) because it has an extra electron shell.
  - **c** Na<sup>+</sup>(g) because it has one less proton in the nucleus and therefore attracts the same number of electrons less strongly.
  - **d**  $Fe^{2+}(g)$  because it has one more electron.
- **3 a** K<sup>+</sup>(aq)
  - **b** K<sup>+</sup>(aq)
  - c K<sup>+</sup>(aq)

#### Section 3.3

- **4 a** Na<sup>+</sup>
  - **b** Na<sup>+</sup>Cl<sup>-</sup>

**c** Na<sup>+</sup>Cl<sup>−</sup>

- **5 a i** 11, 12, 13, 15, 16, 17 **ii** Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup> 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup>
  - $P^{3-}, S^{2-}, Cl^{-}$   $1s^2 2s^2 2p^6 3s^2 3p^6$
  - **b i** Same electronic configuration.
  - ii Different number of protons in the nucleus leading to different ionic charges.
  - **c** Contraction of ion size as the number of protons relative to the number of electrons increases.
  - **d** P<sup>3-</sup> is the biggest and Cl<sup>-</sup> is the smallest because of the increasing attraction on the same number of electrons of an increasing number of protons in the nucleus.
  - ${\bf e}\,$  They each contain an extra shell of electrons.





#### Section 3.4

- **2** Isomers of  $C_5H_{12}$ :





**3** There are 4 isomers of  $C_4H_9Br$ :













2 a Br CH<sub>3</sub>-









L-Cysteine is readily available as a hydrolysis product of 5 proteins.

D-Cysteine has to be made synthetically. It is probably made together with L-cysteine from which it must be separated.





**c** No: the carbon which was chiral is now bonded in the same way in both directions around the ring.

# Section 4.1

- 1 a *Standard enthalpy change of combustion* is the enthalpy change when 1 mole of the compound is burnt completely in oxygen, under standard conditions (ie the compound and the products in their most stable states at 1 atmosphere pressure and at a stated temperature, often 298 K).
  - **b** *Standard enthalpy change of formation* is the enthalpy change when 1 mole of a compound is formed from its elements, with both the compound and its elements being in their standard states (ie their most stable state at 1 atmosphere pressure and at a stated temperature, often 298 K).
- 2 The formation of a compound from its elements may be an exothermic reaction ( $\Delta H_{\rm f}$  negative) or an endothermic reaction ( $\Delta H_{\rm f}$  positive). However, energy is liberated whenever a substance burns, so combustion reactions are always exothermic ( $\Delta H_c$  negative).



4 **a** 2C(s) + 3H<sub>2</sub>(g) + 
$$\frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$$
  
**b** C<sub>2</sub>H<sub>5</sub>OH(l) + 3O<sub>2</sub>(g) → 2CO<sub>2</sub>(g) + 3H<sub>2</sub>O(l)  
**c** 4C(s) + 5H<sub>2</sub>(g) → C<sub>4</sub>H<sub>10</sub>(g)  
**d** C<sub>4</sub>H<sub>10</sub>(g) + 6 $\frac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$ 

**e** 6C(s) + 6H<sub>2</sub>(g) + 3O<sub>2</sub>(g) → C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(s) **f** C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(s) + 6O<sub>2</sub>(g) → 6CO<sub>2</sub>(g) + 6H<sub>2</sub>O(l)

5 ΔH<sup>e</sup><sub>c</sub>(C) is enthalpy change when 1 mole of carbon burned completely under standard conditions, ie C(s) + O<sub>2</sub>(g) → CO<sub>2</sub>(g)
 ΔH<sup>e</sup><sub>f</sub>(CO<sub>2</sub>) is enthalpy change when 1 mole of carbon dioxide is formed from its elements with both the carbon dioxide and its constituent elements in their standard states, ie

 $C(s) + O_2(g) \rightarrow CO_2(g)$ 

- 6 a Thermometer, measuring cylinder, gas meter.b Volume of water used, temperature rise of water, volume of gas used.
  - $\boldsymbol{c}\,$  Cooling losses, impurity of the gas, etc.
- 7 **a**  $\Delta H = -667 \,\mathrm{kJ \, mol^{-1}}$ 
  - **b** Much heat was lost to the surroundings in the experiment whereas the accurate  $\Delta H$  value in the data book would have been determined using a calorimeter in which very little heat is lost.
- 8 a  $M_r(C_7H_{16}) = 100$ 
  - **b i** 481.7 kJ released **ii** 481700 kJ released (Assumed combustion is complete and  $CO_2$  and  $H_2O$  are the only products. Also, that combustion is carried out under standard conditions.)
  - **c** Density of heptane

9 **a** H<sub>2</sub>(g) + 
$$\frac{1}{2}$$
O<sub>2</sub>(g) → H<sub>2</sub>O(l)  
**b** ΔH<sup>⊕</sup><sub>f,298</sub>(H<sub>2</sub>O) = -286 kJ mol<sup>-1</sup>

- **c** –143 kJ (assuming combustion takes place under standard conditions)
- $d + 286 \text{ kJ mol}^{-1}$
- **10 a** Enthalpy change of formation of propane.
  - **b** Enthalpy change of combustion of 3 moles of carbon and 4 moles of hydrogen.
  - **c** Enthalpy change of combustion of propane.

**d** 
$$\Delta H_1 + \Delta H_3 = \Delta H_2$$
  
**e**  $\Delta H = \Delta H - \Delta H$ 

$$= 3(-393) \text{ kJ mol}^{-1} + 4(-286) \text{ kJ mol}^{-1} - (-2220) \text{ kJ mol}^{-1} = -103 \text{ kJ mol}^{-1}$$

**11 a**  $4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$ 



#### **SECTION 4**

- $\mathbf{c} \ \Delta H_1 + \Delta H_3 = \Delta H_2$  $\Delta H_1 = \Delta H_2 - \Delta H_3$  $= 4(-393) \text{ kJ mol}^{-1} + 5(-286) \text{ kJ mol}^{-1}$ -(-2877) kJ mol<sup>-1</sup>  $= -125 \, \text{kJ} \, \text{mol}^{-1}$
- **12 a** Enthalpy change of combustion of methane.
  - **b** Enthalpy change of formation of methane.
  - **c** Enthalpy change of combustion of carbon or enthalpy change of formation of carbon dioxide; the enthalpy of combustion of 2 moles of hydrogen or enthalpy change of formation of 2 moles of water.
  - **d**  $\Delta H_1 = -\Delta H_2 + \Delta H_3$
  - $e \Delta H_1 = -(-75) \text{ kJ mol}^{-1} + (-393) \text{ kJ mol}^{-1}$  $+ 2(-286) \text{ kJ mol}^{-1}$  $= -890 \, \text{kJ} \, \text{mol}^{-1}$

#### Section 4.2

- 1 a  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ b  $H-C-H+2O=O \rightarrow O=C=O+2H-O-H$ **c** 4 (C–H)
  - 2 (O=O)
  - **d** 2 (C=O)
  - 4 (O-H)
  - $e + 2648 \text{ kJ mol}^{-1}$  (or  $+ 2737 \text{ kJ mol}^{-1}$  depending on the value used for E(C-H))
  - $f -3466 \, \text{kJ} \, \text{mol}^{-1}$
  - $g 818 \text{ kJ mol}^{-1}$  (or  $-729 \text{ kJ mol}^{-1}$ ) (The value of the standard enthalpy change of combustion at 298 K is for H<sub>2</sub>O(1) and hence that value will be more exothermic than the value obtained here.)
- **2 a**  $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

## Section 4.3

2

- **1 a** Increase **b** Decrease **c** Increase d Increase e Decrease **f** Decrease **a** Molten wax (Liquids have higher entropies than solids.) (Gases have higher entropies than liquids.) **b**  $Br_2(g)$ c Brass (Mixtures have higher entropies than the pure substances.) d Octane
  - (Complex molecules have higher entropies than simpler molecules.)

13 a CH<sub>2</sub>CHO(1) +2 $\frac{1}{2}$ O<sub>2</sub>(g)  $\rightarrow$  2CO<sub>2</sub>(g) + 2H<sub>2</sub>O(1)



- c Standard enthalpy change of combustion of ethanol  $= \Delta H_1 = -\Delta H_2 + \Delta H_3$  $= -(-192) \text{ kJ mol}^{-1} + 2(-393) \text{ kJ mol}^{-1} + 2(-286) \text{ kJ mol}^{-1}$  $= -1166 \, \text{kJ} \, \text{mol}^{-1}$
- 3 a  $CH_3OH(l) + 1\frac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ b н  $H-C-O-H + 1^{1}_{2}O=O \rightarrow O=C=O + 2H-O-H$ н c 3 (C-H) 1 (C-O) 1 (O-H) l.5 (O=O) **d** 2 (C=O) 4 (O-H)  $e + 2786 \, kJ \, mol^{-1}$  $\mathbf{f}$  –3466 kJ mol<sup>-1</sup>  $g - 680 \text{ kJ mol}^{-1}$ 4  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- Bond enthalpies/kJ mol<sup>-1</sup>:  $(+945) + 3(+436) \rightarrow 2(3 \times +391)$  $\Delta H^{\circ} = -93 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$
- 5  $N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$ Bond enthalpies/kJ mol<sup>-1</sup>:  $(+158) + 4(+391) + (+498) \rightarrow (+945) + 4(+464)$  $\Delta H^{\circ} = -581 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$
- **6**  $C_2H_4(g) + Br_2(g) \rightarrow C_2H_4Br_2(g)$ Bond enthalpies/kJ mol<sup>-1</sup>:  $(+612) + 4(+413) + (+193) \rightarrow 4(+413) + 2(+290)$  $+ (+347) \Delta H^{\circ} = -122 \,\text{kJ} \,\text{mol}^{-1}$
- **3** 1 in 256
- **a** Ar molecule larger than He. 4
  - **b** Gases have higher entropies than liquids.
  - **c**  $Cl_2$  molecule larger than  $F_2$ .
- **a** Greater. A gas is formed as a product.
  - **b** Smaller. Number of molecules of gas in product smaller than the number of molecules of gas in reactants.
  - **c** Smaller. One reactant is a gas; product only solid.

# Section 4.4

- 1 The entropies increase for the first four alkanes as the molecules become heavier and composed of more atoms (the number of energy levels increases with the number of atoms). Pentane is a liquid and so has a lower entropy than butane.
- 2 a Entropy decrease, because the number of moles of gas is reduced by half as reaction proceeds.
  - **b** Entropy increase; the number of moles of gas doubles during the reaction and a solid has much lower entropy than a gas.
  - **c** Entropy decrease; 2 moles of gaseous reactants are replaced by 1 mole of solid.
  - **d** Entropy decrease; 5 moles of gaseous oxygen are removed, the only product is a solid.
  - e Entropy increase; 5 moles of gaseous product are formed.

## Section 4.5

- **a** When 1 mole of sodium fluoride is formed from 1 mole of  $Na^+(g)$  and 1 mole of  $F^-(g)$ , 915 kJ mol<sup>-1</sup> of energy are released. This is the lattice enthalpy of sodium fluoride.
  - **b** The lattice enthalpy becomes more negative as the ionic radii decrease.
- a LiF; Li<sup>+</sup> has a smaller radius than Na<sup>+</sup> and attracts F<sup>-</sup> ions more strongly.
  - **b** Na<sub>2</sub>O; Na<sup>+</sup> has a smaller radius than Rb<sup>+</sup> and attracts  $O^{2-}$  more strongly.
  - **c** MgO; Mg<sup>2+</sup> is smaller and more highly charged than Na<sup>+</sup>, and attracts O<sup>2–</sup> more strongly.
  - **d** KF; F<sup>-</sup> has a smaller radius than Cl<sup>-</sup> and attracts K<sup>+</sup> more strongly.
- **3 a** SrF<sub>2</sub>; Sr<sup>2+</sup> is smaller and more highly charged than Rb<sup>+</sup> and will attract F<sup>-</sup> more strongly.
  - **b** By the same arguments as in **a**, BaO should have the more exothermic lattice enthalpy.
  - **c** Cu<sup>2+</sup> is more highly charged than Cu<sup>+</sup>, so CuO should have the more exothermic lattice enthalpy.
- 4 a Li<sup>+</sup> attracts water molecules more strongly than Na<sup>+</sup> because of its smaller size.
  - **b**  $Mg^{2+}$  attracts water molecules more strongly than  $Ca^{2+}$  because of its smaller size.
  - **c** Ca<sup>2+</sup> and Na<sup>+</sup> have similar sizes, but Ca<sup>2+</sup> is more highly charged and so attracts water molecules more strongly.
- 5 a The ions in the lattice attract each other less strongly as the size of the anion increases from F<sup>-</sup> to Cl<sup>-</sup>.
  - **b**  $\Delta H_{hyd}$  becomes less exothermic as the anion becomes bigger and attracts water molecules less strongly.



**3** Students' answers should be based on the following deductions.

	$\Delta {f S}_{sys}/J{f K}^{-1}{f mol}^{-1}$	$\Delta \mathbf{S}_{surr}$ /J K $^{-1}$ mol $^{-1}$	Explanation
a	+203	-44	Spontaneous: total entropy change positive
b	+63	+329	Spontaneous: total
c	+25	-604	Not spontaneous: total entropy change negative
d	+209	+416	Spontaneous: total
e	-4	-6.7	Not spontaneous: total entropy change negative

4 Values for both  $\Delta S_{sys}$  and  $\Delta S_{surr}$  are negative. Therefore  $\Delta S_{total}$  must always be negative, whatever value of *T* is chosen, and the process can never be spontaneous.



Both silver halides have endothermic enthalpy changes of solution and the enthalpy level diagrams will have the form shown below.



- $\begin{array}{l} \mathbf{d} \ \Delta H_{\text{solution}} = -\Delta H_{\text{LE}} + \Delta H_{\text{hyd}}(\text{Ag}^+) + \Delta H_{\text{hyd}}(\text{X}^-) \\ \Delta H_{\text{solution}}(\text{AgF}) &= +6 \, \text{kJ} \, \text{mol}^{-1}; \\ \Delta H_{\text{solution}}(\text{AgCl}) &= +95 \, \text{kJ} \, \text{mol}^{-1} \end{array}$
- e AgF may be soluble in water. AgCl will be insoluble.
- $\begin{array}{ccc} \mathbf{6} & \mathbf{a} \, \, \mathrm{Mg(OH)}_2 & & + \, 152 \, \mathrm{kJ \, mol^{-1}} \\ & & \mathrm{Ca(OH)}_2 & & + \, 7 \, \mathrm{kJ \, mol^{-1}} \end{array}$ 
  - **b** Ca(OH)<sub>2</sub>: enthalpy change of solution much less endothermic.
  - c Entropy changes of the processes.

# Section 4.6





As Group 1 is ascended, the enthalpy changes of formation of the chlorides become less negative and the first ionisation enthalpies of the elements become more positive.

#### **SECTION 4**



**c** The enthalpy change of formation of CaCl<sub>2</sub> is much more negative than that of CaCl. CaCl<sub>2</sub> has lower energy and is more stable relative to the elements Ca and Cl<sub>2</sub>, and so it is more likely to be formed.

# Section 5.1

**1 a**  $Ca^{2+}(aq) + 2OH^{-}(aq)$ **b**  $Mg^{2+}(aq) + SO_4^{2-}(aq)$ **c**  $2Na^{+}(aq) + O^{2-}(aq)$ **d**  $K^+(aq) + OH^-(aq)$  $e \operatorname{Ag}^+(aq) + \operatorname{NO}_2^-(aq)$ **f**  $2Al^{3+}(aq) + 3SO_4^{2-}(aq)$ 2 **a** NaBr **b**  $Mg(OH)_2$ c Na<sub>2</sub>S **d** BaŌ e CaCO<sub>2</sub> **f** Ca( $NO_2$ )<sub>2</sub> g K<sub>2</sub>CO<sub>2</sub> **a**  $\operatorname{Ba}^{2+}(\operatorname{aq}) + \operatorname{SO}_{4}^{2-}(\operatorname{aq}) \rightarrow \operatorname{BaSO}_{4}(\operatorname{s})$ 3 **b**  $Mg^{2+}(aq) + 2O\dot{H}(aq) \rightarrow Mg(O\dot{H})_{2}(s)$ 

**d** 
$$\operatorname{Ba}^{2+}(\operatorname{aq}) + \operatorname{CrO}_4^{2-}(\operatorname{aq}) \rightarrow \operatorname{BaCrO}_4(\operatorname{s})$$

# Section 5.2

- 1 The small size of the carbon atom makes it possible for carbon to form double bonds with oxygen to produce discrete covalent molecules. Silicon, on the other hand, bonds to 4 oxygen atoms to form single bonds and hence a covalent network structure. The attractive forces between the molecules of carbon dioxide (intermolecular forces) are weak so that little energy is needed to separate the individual molecules. Strong covalent network structure so a lot of energy is needed to melt it.
- **2 a** Any attractive forces between the solvent and the atoms in the covalent network structure are too weak to overcome the strong covalent bonds holding the network together.
  - **b** At room temperature, the kinetic energy of atoms and molecules is small but it may be enough to overcome the weak attractive forces between simple molecules or isolated atoms.
- **3 a** Diamond structure with silicon and carbon atoms alternating.

**4** 2Na<sup>+</sup>(aq) + SO<sub>4</sub><sup>2-</sup>(aq) + 10H<sub>2</sub>O(l) → Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O(s)

- 5 **a** H<sup>+</sup>(aq) + OH<sup>-</sup>(aq) → H<sub>2</sub>O(l) **b** Zn(s) + 2H<sup>+</sup>(aq) → Zn<sup>2+</sup>(aq) + H<sub>2</sub>(g) **c** CuO(s) + 2H<sup>+</sup>(aq) → Cu<sup>2+</sup>(aq) + H<sub>2</sub>O(l) **d** CaCO<sub>3</sub>(s) + 2H<sup>+</sup>(aq) → Ca<sup>2+</sup>(aq) + H<sub>2</sub>O(l) + CO<sub>2</sub>(g)
- 6 a i Cubic
  - **ii** Eight
  - iii Eight
  - **b** The attractions between the oppositely charged caesium and chloride ions greatly outweigh the repulsions between ions with the same charge. The net attractive force is very high. The solid is hard and has a high melting point as this strong attraction has to be overcome to separate the particles.
  - **b** The silicon and carbon atoms are held together by strong covalent bonds in an extended network structure. This makes the substance very hard.
- **4 a** Graphite structure with alternating boron and nitrogen atoms.
  - **b** In graphite, each carbon atom has 4 bonding electrons. Only 3 are needed to form the layer structure. The fourth electron is 'free' and causes graphite to be a good electrical conductor. Both boron and nitrogen have only 3 bonding electrons. All 3 are needed to form the structure of the layer. There are no electrons available to become delocalised and conduct electricity.
- **5** It was assumed that buckminsterfullerene was a covalent network structure and would be insoluble like graphite and diamond, but solution in benzene showed it, surprisingly, to be a molecular form of carbon.

Attractive forces between the solvent molecules and the carbon atoms are sufficient to overcome the weak intermolecular forces between the buckminsterfullerene molecules.

# Section 5.3



- **a** Pentane has the strongest intermolecular forces and hence the highest boiling point. Dimethylpropane has the weakest intermolecular forces and hence the lowest boiling point.
- **b** The molecules of pentane, because it is a straight chain alkane, can approach closely to each other which increases the opportunities for instantaneous–induced dipole interactions and hence stronger intermolecular attractions. Methylbutane has one methyl side chain and so it is more difficult for these molecules to approach each other and instantaneous–induced dipole interactions are weaker. Dimethylpropane has two methyl side-chains and so it is even more difficult for molecules of this compound to approach each other.
- 4 The strength of instantaneous dipole–induced dipole forces between molecules increases as the relative molecular masses of the molecules increase. To be sure that the higher boiling point of the polar substance is due only to the increased strength of dipole–dipole attractions it will be necessary to ensure that the instantaneous dipole–induced dipole forces in both polar and non-polar substances are of similar strength. This can be done by comparing substances of similar molecular mass.
- 5 a A and D; C and G.b A and G have the stronger intermolecular forces compared to D and C, respectively.

# Section 5.4

- **1 a** As the temperature rises, solids and liquids expand. The temperature increase raises the kinetic energy of the particles present. In solids, the rotational and vibrational energy increases. In liquids, rotational, vibrational and translational energy increases. The increases in vibrational and translational energy increase the volume occupied by the particles. As they occupy an increasing volume, the density of the solid or liquid decreases.
  - **b i** When ice melts, much of the open, hydrogenbonded structure collapses. This enables the molecules to occupy less space so the density increases on melting.
    - **ii** The boiling point of water is higher than expected, as more energy is needed to break the hydrogen bonding.
    - **iii** The specific heating capacity of water is higher than expected, as more energy is absorbed by the water to break hydrogen bonds in the liquid.
- **2 a i** H<sub>2</sub>O instantaneous dipole–induced dipole permanent dipole–permanent dipole hydrogen bonding.
  - H<sub>2</sub>S instantaneous dipole–induced dipole permanent dipole–permanent dipole.
  - H<sub>2</sub>Se instantaneous dipole–induced dipole permanent dipole–permanent dipole.
  - H<sub>2</sub>Te instantaneous dipole–induced dipole permanent dipole–permanent dipole.
  - **ii** Intermolecular forces must be overcome when a liquid boils.
    - Hydrogen bonding present between molecules of  $H_2O$  but not between those of  $H_2S$ ,  $H_2Se$  or  $H_2Te$ .

- 6 Polarity will occur as follows:
   C–F; H–Cl; H–N; C–O with charges in the order δ+ δ– in each case.
- 7 CHCl<sub>3</sub>, CH<sub>3</sub>OH, (CH<sub>3</sub>)<sub>2</sub>CO, *cis*-1,2-difluoroethene and 1,2-dichlorobenzene possess dipoles.
- 8 a i Eighteen
  - **ii** The attractions will be similar.
  - iii  $H_2S$  has a permanent dipole. It is a bent molecule with two lone pairs.  $SiH_4$  does not have an overall permanent dipole as it is a symmetrical molecule.
  - **b** Both compounds have similar instantaneous dipole–induced dipole forces. However, H<sub>2</sub>S also has permanent dipole–permanent dipole attractions so its boiling point is higher than that of SiH<sub>4</sub>.
- **9 a** Instantaneous dipole–induced dipole.
  - **b** Instantaneous dipole–induced dipole.
  - **c** Instantaneous dipole–induced dipole, permanent dipole.
  - ${\bf d}$  Instantaneous dipole–induced dipole.
  - **e** Instantaneous dipole–induced dipole, permanent dipole–permanent dipole.
  - **f** Instantaneous dipole–induced dipole.
  - ${\boldsymbol{g}}$  Instantaneous dipole–induced dipole.
  - **h** Instantaneous dipole–induced dipole, permanent dipole.

Hydrogen bonding forces are much stronger than other intermolecular forces and so the boiling point of water is higher than that of the other hydrides.

- **b** The strength of instantaneous dipole–induced dipole and permanent dipole–permanent dipole attractions in a substance gets weaker as its relative molecular mass gets smaller. This produces a lower boiling point. The boiling point of  $H_2O$  should be lower than that of  $H_2S$  but it is in fact much higher. This suggests that, compared to  $H_2S$ , a different and much stronger type of intermolecular bonding exists in  $H_2O$ .
- **c ii** All have instantaneous dipole–induced dipole forces.
  - iii The shape of the graph is nearly a straight line with positive slope. There is no hydrogen bonding between the hydride molecules of Group 4. The increase in boiling points down the group is a result of their regularly increasing molecular masses.
- **3** A, D, E and F
- **a** Hydrogen bonding will be present in NH<sub>3</sub>, CH<sub>3</sub>OH, and HF.







- 6 **a** Instantaneous dipole–induced dipole, permanent dipole–permanent dipole, hydrogen.
  - **b** Instantaneous dipole–induced dipole.
  - **c** Instantaneous dipole–induced dipole, permanent dipole, hydrogen.
  - **d** Instantaneous dipole–induced dipole.
  - **e** Instantaneous dipole–induced dipole, permanent dipole–permanent dipole.

#### Section 5.5, Part 1 (Addition polymers).





6 But-1-ene and propene



8 a Poly(ethene), poly(propene), poly(chloroethene)

instantaneous dipole-induced
dipole
instantaneous dipole-induced
dipole
instantaneous dipole-induced
dipole
permanent dipole-permanent
dipole

- **c** Poly(chloroethene)
- **9 a** Isotactic polymer is a stereoregular polymer, that is, the side-chains all have the same orientation. In an atactic polymer the side-chains are randomly orientated.
  - **b** The regular arrangement of the side-chains in an isotactic polymer allows the polymer chains to pack together closely, which means intermolecular forces are stronger. The polymer chains do not slide past each other easily, making the polymer stronger and less flexible than the atactic form of the same polymer.



- 3 Polarity increases from  $-CH_3$  to -Cl to -CN so the intermolecular attractions become stronger which leads to an increase in  $T_g$ .
- 4 a i Instantaneous dipole-induced dipole.
   ii Instantaneous dipole-induced dipole. Permanent dipole-permanent dipole.
  - **b**  $(CH_2O)_n$  would have a higher  $T_g$  because of the permanent dipole–permanent dipole interactions between the chains.

the lattice of positive ions. Each positive ion is

attracted to the negatively charged delocalised

electrons and vice versa.

- 5 There is hydrogen bonding in poly(caprolactam). In poly(caprolactone) there are only permanent dipole–permanent dipole and instantaneous dipole–induced dipole attractions.
- 6 **a** Model building should show that the  $T_{\rm m}$  values reflect the alignment of hydrogen bonding between the polymer chains for nylon-6. There are fewer opportunities for hydrogen bonding in nylon-11.
  - **b** Intermolecular hydrogen bonding is more extensive in nylon-6,6. The chains in nylon-6,10 can slide past one another more easily.

Electrical conductivity

conducts when molten or in aqueous solution does not conduct

does not conduct

does not conduct

does not conduct conducts when molten or in aqueous solution conducts when solid or liquid does not conduct

#### Section 5.6

1	a ] b	Ionic lattice i Ne	monatomic	2	Name	State at room temperature	Solubility in water
		H H	simple molecular (covalent)	a	sodium iodide	solid	soluble
		₩ H H´L H´L	simple molecular (covalent)	b c d	carbon monoxide diamond tetrachloro-	gas solid liquid	insoluble insoluble insoluble
	с	<ul><li>iv O=C=O</li><li>i See Figure 6, page 92</li><li>ii Covalent network or</li></ul>	simple molecular (covalent) 2, <b>Chemical Ideas</b> . giant covalent.	e f	methane ethanol copper(II) chloride	liquid solid	soluble soluble
	d (	The diagram should be si <b>Chemical Ideas</b> . There we positive ions as the metal electrons, two from each	milar to Figure 15, page 39, vill be 2+ charges on the is magnesium. The outer magnesium atom, contribute	g h	vanadium poly(propene	solid e) solid	insoluble insoluble
	1	to a poor of electrons wr	nen move randonny urrougn	3 a	Isolated atom	S	

- **b** Motallia giant la
  - **b** Metallic; giant lattice
  - ${\boldsymbol c}$  Covalent network (or giant covalent); giant lattice
  - **d** Macromolecular; covalent molecular
  - e Ionic; giant lattice
  - **f** Simple molecular; covalent molecular
- 4 A Macromolecular; covalent molecular
  - B Metallic; giant lattice
  - **C** Ionic; giant lattice
  - **D** Metallic; giant lattice
  - E Simple molecular; covalent molecular

#### **SECTION 6**

- **a** In ionic substances, the charge-carriers (ions) are held 5 in the solid lattice and are not free to move. In metals, the charge-carriers (electrons) are delocalised and are free to move throughout the lattice.
  - **b** When an ionic melt conducts electricity, the ions move to opposite electrodes where they are discharged, leading to decomposition. When a metal conducts, electrons move towards the more positive terminal and are replaced at an equal rate at the more negative terminal.

# Section 6.1

- **1** a 7.22 × 10<sup>-28</sup> J **b**  $6.6 \times 10^{-17}$  J **c**  $9.2 \times 10^{10}$
- 5.5 × 10<sup>13</sup> Hz 2
- 3 **a** The four lowest energy lines in the Balmer Series arise from transitions to level 2 from levels 3, 4, 5 and 6. b



The lines converge towards high frequency. The lines in the Balmer Series are at lower frequency than the lines in the Lyman Series.

## Section 6.2\_

1	Energy of photon emitted or absorbed/J	Frequency/Hz	Type of radiation	Type of energy change in molecule
a b c d	$\begin{array}{c} 4.6 \times 10^{-17} \\ 2.3 \times 10^{-20} \\ 2.1 \times 10^{-22} \\ 5.5 \times 10^{-19} \end{array}$	$\begin{array}{c} 6.9\times10^{16}\\ 3.5\times10^{13}\\ 3.2\times10^{11}\\ 8.3\times10^{14} \end{array}$	u.v. i.r. microwave visible	electronic vibrational rotational electronic

- **2 a** 5.43 × 10<sup>-20</sup> J **b**  $8.19 \times 10^{13}$  Hz; infrared
  - **c**  $3.66 \times 10^{-6}$  m

**3 a** 
$$E = \frac{+214 \text{ kJ mol}^{-1} \times 1000}{6.02 \times 10^{23} \text{ mol}^{-1}} = +3.55 \times 10^{-19} \text{ J}$$

**b** E = bv $3.55 \times 10^{-19} \text{ J} = 6.63 \times 10^{-34} \text{ J} \text{ Hz}^{-1} \times \nu \text{ Hz}$  $\nu = 5.36 \times 10^{14} \,\mathrm{Hz}$ 

**c** This is in the visible region of the electromagnetic spectrum.

## Section 6.3

2

- **1** F, OH,  $NO_2$  and  $CH_3$  are radicals.
  - а i Photodissociation
  - ii Homolytic **b** Reaction A initiation Reaction B
    - propagation Reaction C ,
  - **c** H• and HO<sub>2</sub>• d
    - i  $2O_3 \rightarrow 3O_2$
    - ii Catalyst
  - e The rates of radical reactions depend on the concentrations of the radicals involved.
  - **f** Termination

- c Any attractive forces between the solvent and the atoms in the giant covalent lattice are too weak to overcome the strong covalent bonds holding the lattice together.
- **d** At room temperature, the kinetic energy of atoms and molecules is small. It is not enough to overcome the energy of attraction between particles in giant or macromolecular structures, but it may be enough to overcome the weak intermolecular forces between simple molecules.
- c The line must go from a lower energy level to a higher level.
- **a** Ground state 4 h
  - i  $\Delta E = bv$  $= 6.63 \times 10^{-34}$  J Hz<sup>-1</sup> × 3.27 × 10<sup>15</sup> Hz  $= 2.17 \times 10^{-18}$  J
  - **ii** One photon of frequency  $3.27 \times 10^{15}$  Hz provides this energy. For 1 mole of hydrogen atoms  $\Delta E = 6.02 \times 10^{23} \text{ mol}^{-1} \times 2.17 \times 10^{-18} \text{ J}$ 
    - $= 1310 \,\mathrm{kI} \,\mathrm{mol}^{-1}$ .

Data book value for the ionisation enthalpy of hydrogen is 1318 kJ mol<sup>-1</sup>.

- **4 a**  $1.89 \times 10^4$  J
  - **b**  $1.62 \times 10^{-24}$  J
  - **c** 0.978 J
  - d 19330 moles of photons
- **5** a  $CO_2$  absorbs infrared radiation of specific frequencies corresponding to transitions between vibrational energy levels. (Vibrational energy is quantised.) The specific frequencies absorbed make the molecules vibrate in particular ways. The vibrational energy increases.
  - **b** The molecules which have absorbed radiation have more kinetic energy. (A more complete answer could include energy being subsequently transferred to other molecules in the air by collision.)
- **3 a** Oxidation of  $N_2$  in internal combustion engines. **b** Exothermic
  - $\mathbf{i} \quad \mathbf{O}_3 + \mathbf{O} \rightarrow \mathbf{O}_2 + \mathbf{O}_2$ С ii Catalyst
    - iii  $\Delta H = -292 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$
  - **d** It catalyses breakdown of ozone, thus removing it from the stratosphere.
- **4 a** Initiation: reaction 1 Propagation: reactions 2, 3 and 4 Termination: reactions 5 and 6
  - **i** Endothermic: reaction 1 (C–C bond broken) b **ii** Exothermic: reaction 6 (C-C bond formed)

- **c**  $CH_3$  methyl radical  $C_2H_5$  • ethyl radical H• hydrogen radical
- 5 **a**  $Cl_2 + b\nu \rightarrow Cl \cdot + Cl \cdot$  initiation  $CH_4 + Cl \cdot \rightarrow CH_3 \cdot + HCl$   $CH_3 \cdot + Cl_2 \rightarrow CH_3Cl + Cl \cdot$   $Cl \cdot + Cl \cdot \rightarrow Cl_2$  $CH_3 \cdot + CH_3 \cdot \rightarrow C_2H_6$  termination

# Section 6.4\_

**1 a** 4.24 μm **b** 7.08 × 10<sup>13</sup> Hz

Absorption/cm	I <sup>-1</sup> Bond
3660	0–H
3060	C–H
	(arene)
	ОН

$$CH_{2} - CH_{2} - CH - CH_{2}$$
 butan-2-ol

$$CH_3 - CH_2 - C - CH_3$$

butan-2-one

b	Compound	Absorption/cm <sup>-1</sup>	Bond
	Α	3660	0–H
		2970	C–H (alkane)
	В	2990	C–H (alkane)
		1730	C=0

# Section 6.5.

1 **a** 78, 72, 106 **b** Two isotopes of chlorine leading to  $C_3H_7^{35}Cl$  (78) and  $C_4H_7^{37}Cl$  (80)

- **2** 43,  $[C_{3}H_{7}]^{+}$ 43,  $[CH_{3}CO]^{+}$ 77,  $[C_{6}H_{5}]^{+}$
- **3 a**, **b A** Ethanoic acid

B Ethanol

- **A** 43, [CH<sub>3</sub>CO]<sup>+</sup> 45, [COOH]<sup>+</sup> 60, [CH<sub>3</sub>COOH]<sup>+</sup>
- **B** 31,  $[CH_3O]^+$  or  $[CH_2OH]^+$ 46,  $[C_2H_5OH]^+$
- **4 a** 88, molecular ion 43, [CH<sub>3</sub>CO[<sup>+</sup>

**b**  $[CH_3COOCH_2CH_3]^+ \rightarrow [CH_3CO]^+ + OCH_2CH_3$ 

5 a	Mass of peak	Possible fragment
	58	$[C_4H_{10}]^+$
	43	$[C_{3}H_{7}]^{+}$
	29	$[C_2H_5]^+$
	15	[CH <sub>3</sub> ] <sup>+</sup>

**b** The chloromethane formed can also react with Cl• radicals.

 $CH_3Cl + Cl \cdot \rightarrow \cdot CH_2Cl + HCl$ 

 $\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl \bullet$ 

Similarly,  $CH_2Cl_2$  can react with  $Cl \cdot$ , and so on, until  $CCl_4$  is produced. The chlorinated products react with  $Cl \cdot$  radicals more quickly than  $CH_4$  does, so a mixture of products is always obtained.

**c A** butan-2-ol

**B** butan-2-one

4

5

a	Compound	Absorption/cm <sup>-1</sup>	Bond
	С	3580 2990 1775	O–H C–H (alkane) C=O
	D	3670 2950	0–H C–H (alkane)
	E	2990 1770	C–H (alkane) C=O

**b** C A carboxylic acid

**D** An alcohol

**E** An ester

Bond	Absorption/cm <sup>-1</sup>
O–H (phenol)	3600–3640
C–H (arene)	3000–3100
C=O (ester)	1735–1750

b	CH <sub>3</sub>
$CH_3 - CH_2 - CH_2 - CH_3$	$CH_3 - CH - CH_3$

**c** Adopting a 'Lego' approach to these fragment ions, the full structural formula of the hydrocarbon must be:

$$CH_3 - CH_2 - CH_2 - CH_3$$

Fragmentation of this by breaking C–C bonds leads to the four ions in the table.

The branched isomer would not produce the  $C_2H_5^+$  ion by breaking C–C bonds. However, the other three ions will also appear in the spectrum of this isomer.

- **6 a** H O  $CH_3 - CH_2 - C = O$   $CH_3 - C - CH_3$  **b** 58 - 43 = 15;  $CH_3$ 
  - **c i** 58 57 = 1; H **ii** 57 - 29 = 28; CO or C<sub>2</sub>H<sub>4</sub>

**d i** 
$$[CH_3CO^+]$$

- **ii** 28  $[CO]^+$  or  $[C_2H_4]^+$
- 29 [CH<sub>3</sub>CH<sub>2</sub>]<sup>+</sup>
  - 57  $[CH_3CH_2CO]^+$

**e C** is  $CH_3COCH_3$  **D** is  $CH_3CH_2CHO$ 

7 Accurate atomic masses give  $C_4H_8O$  as the formula. Peaks to be identified:

Mass of peak	Possible fragment
15	[CH <sub>3</sub> ] <sup>+</sup>
29	$[CH_3CH_2]^+$
43	[CH <sub>3</sub> CO] <sup>+</sup>
57	$[CH_3CH_2CO]^+$
72	[CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub> ] <sup>+</sup>

The compound has the structure

$$CH_3 - CH_2 - C - CH_3$$

# Section 6.6\_

1

a	3	
b	Chemical shift	Relative number of protons
	1.0	3
	2.1	3
	2.4	2

**c d** 
$$CH_3 - CH_2 - CO - CH_3$$
  
1.0 2.4 2.1

2 **a b** Tartaric acid 3 signals 1 : 1 : 1 Succinic acid 2 signals 2 : 1 Citric acid 3 signals 1 : 4 : 3

3	a	Chemical shift	Relative number of protons
		1.2	3
		2.6	1
		3.7	2

- **b** CH<sub>3</sub> (1.2), OH (2.6), CH<sub>2</sub> (3.7)
- **c** CH<sub>3</sub>-CH<sub>2</sub>-OH
- **E** is ethanol.

4 a	Chemical shift	Relative number of protons	
	1.3	9	
	2.0	1	

**b** CH<sub>3</sub> (1.3), OH (2.0)

$$\begin{array}{c} \mathbf{c} & \begin{array}{c} \mathsf{CH}_3 \\ | \\ \mathsf{CH}_3 - \begin{array}{c} \mathsf{C} - \mathsf{OH} \\ | \\ \mathsf{CH}_3 \end{array}$$

 ${f F}$  is 2-methylpropan-2-ol.

-			-
5	Chemical shift	Relative number of protons	
	1.2	3	
	2.7	2	
	7.0–7.4	5	
CH	3 (1.2),	$-CH_2 - R$ (2.7), $H - H$	(7.0-



**G** is ethylbenzene.

8 The sketch should show two molecular ion peaks of equal height at 108  $[C_2H_5^{79}Br]^+$  and 110  $[C_2H_5^{81}Br]^+$ . Also peaks at 93  $[CH_2^{79}Br]^+$  and 95  $[CH_2^{81}Br]^+$ . (Actual data have 29 as the base peak (100%) and peaks at 108 and 110 (94%). The next largest peak is 27 (70%).

Peaks at 79 and 81 are very small (3%).)

6	Chemical shift	Relative number of protons	
	1.3	3	
	2.1	3	
	4.1	2	
	СН <sub>3</sub> (1.3), СН <sub>3</sub> —	$CO_{(2.1)}, -CO_{CH_2} - R_{(4)}$	.1)
	СH <sub>3</sub> −С−	O-CH <sub>2</sub> -CH <sub>3</sub>	

H is ethyl ethanoate.

7	Chemical shift	Relative number of protons
	4.0	3
	6.4	1
	7.0	1
	7.4	2
	9.8	1

CHO (9.8)

8

'.4)

a	Protons in the molecule	Expected chemical shift	Relative numbers of each type of proton
	CH <sub>3</sub> O	ca 3.7	3
	C <sub>6</sub> H <sub>4</sub>	6.0–9.0	2

It is good enough to identify *two* types of proton (C $\mathbf{H}_3$  and C<sub>6</sub> $\mathbf{H}_4$ ), in the ratio of 3 : 2. However, there are actually two different environments for the protons on the aryl group, one being adjacent to the ester group, and the better answer would be 3 : 1 : 1.

# Section 6.7

- **1 a** Green 520 nm–580 nm approx. **b** Red 620 nm–700 nm approx.
- 2 Blue and blue-green; approx. 440 nm 520 nm
- 3 It will appear green. The sketch should show two peaks with  $\lambda_{max}$  at about 640 nm and 410 nm.

# Section 6.8

2

#### 1 a Spectrum (b) b Violet



- 4 **a**  $6.97 \times 10^{14}$  Hz **b**  $8.57 \times 10^{14}$  Hz
  - **c**  $4.29 \times 10^{14} \,\mathrm{Hz}$
  - **b** A reflectance spectrum of a black pigment would show a low percentage of reflected light for all wavelengths in the visible region.
- **a** Spectrum (**a**)  $\lambda_{max} = 440 \text{ nm}$  (approx.) Spectrum (**b**)  $\lambda_{max} = 420 \text{ nm}$  (approx.)
  - **b** Spectrum (**b**) corresponds to haemoglobin.
- **4 a** Red ochre.
  - **b** It absorbs violet, blue and green light  $(\lambda = 400 \text{ nm}-530 \text{ nm})$  but reflects yellow and red light  $(\lambda = 530 \text{ nm}-700 \text{ nm}).$

### Section 6.9

- **a** A chromophore is the part of a dye molecule responsible for its colour. It contains unsaturated groups such as C=O and -N=N- which are often part of an extended delocalised electron system involving arene rings.
  - $^{\mathbf{b}}$
  - ${f c}$  An extended delocalised system of electrons.

# Section 7.1

- **a** Rate of evaporation = rate of condensation.**b** It is a closed system, in which there is a dynamic equilibrium between water vapour and liquid.
  - $\boldsymbol{c}~$  No longer a closed system,  $H_2O(g)$  escapes.
  - **d i** Towards  $H_2O(l)$ 
    - **ii** Towards  $H_2O(g)$ .
- **2 a** Equilibrium lies to the reactants' side because at equilibrium there is a greater concentration of reactants than products.
  - **b** Equilibrium is reached at the point where the graphs become horizontal.
- 3 B
- $\begin{array}{ccc} 4 & a & {\rm left} \rightarrow {\rm right} & b & {\rm right} \rightarrow {\rm left} & c & {\rm no \ change} \\ & d & {\rm left} \rightarrow {\rm right} & e & {\rm left} \rightarrow {\rm right} \end{array}$
- **5 a** The concentrated hydrochloric acid moves the position for the equilibrium to the left, the bismuth trichloride is predominantly present as BiCl<sub>3</sub>(aq).

- 2 a Cyanidin contains an extended delocalised (conjugated) electron system. The electrons in such systems require less energy to excite them than those in single bonds or in isolated double bonds. The excitation energy corresponds to the visible region.
  - **b** Molecule absorbs orange light; the diagram should show a smaller excitation energy.
  - **b** The equilibrium would move to the right due to the large amount of water, hence a white precipitate of BiOCl(s) would be seen.
- 6 **a** There would be no change to fizziness as the concentration of  $CO_2(g)$  is not influenced by the amount of air present since the system had already come to equilibrium.
  - **b** The increase in concentration of  $CO_2(g)$  would make the first equilibrium move to the right and form more  $CO_2(aq)$  which in turn would make the second equilibrium move to the right and increase the concentration of  $H^+(aq)$ .
  - **c** Dilute alkali would react with  $H^+(aq)$  and the reduction in concentration of  $H^+(aq)$  would cause the second equilibrium to move to the right. The resulting reduction in the concentration of  $CO_2(aq)$  would cause the first equilibrium to move to the right and more  $CO_2(g)$  would dissolve and so the equilibrium pressure of carbon dioxide would decrease.

#### Section 7.2 1 a Concentration CO<sub>2</sub> (aq)/mol dm<sup>-3</sup> 0.09 0.08 0.07 0.06 0.05 0.04 0.03 2 3 n Pressure CO<sub>2</sub>(g)/atm **b** Gradient = $(0.09-0.03) \text{ mol dm}^{-3}$ $[CO_2(aq)] =$ (2.6-0.8) atm $p_{\rm CO_2(g)}$ $= 0.033 \,\mathrm{mol} \,\mathrm{dm}^{-3} \,\mathrm{atm}^{-1}$ = equilibrium constant at 292 K **c** Drawing a 'best fit' line eliminates errors more effectively than taking an average. **2 a** $K_{\rm c} = \frac{[{\rm NO}_2({\rm g})]^2}{[{\rm NO}({\rm g})]^2 [{\rm O}_2({\rm g})]} \, {\rm mol}^{-1} \, {\rm dm}^3$ **b** $K_{\rm c} = \frac{[{\rm C}_2{\rm H}_4(g)][{\rm H}_2(g)]}{[{\rm C}_2{\rm H}_6(g)]} \text{ mol dm}^{-3}$ **c** $K_{c} = \frac{[H_{2}(g)][I_{2}(g)]}{[HI(g)]^{2}}$ (no units) $\mathbf{d} K_{c} = \frac{[\text{HCO}_{3}^{-}(\text{aq})][\text{H}^{+}(\text{aq})]}{[\text{CO}_{2}(\text{aq})][\text{H}_{2}\text{O}(l)]} \text{ (no units)}$ $\mathbf{e} K_{c} = \frac{[In_{2}(aq)]^{3}}{[In_{6}(aq)]} \text{ mol}^{2} \text{ dm}^{-6}$ $\mathbf{f} \ K_{c} = \frac{[CH_{3}COOC_{3}H_{7}(l)][H_{2}O(l)]}{[CH_{3}COOH(l)][C_{3}H_{7}OH(l)]}$ (no units) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ 3

5 **a** 
$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

**b** 
$$K_{c} = \frac{[H_{2}O(g)]^{2}}{[H_{2}(g)]^{2}[O_{2}(g)]}$$

- **c i** Equilibrium moves towards reactants (reaction is exothermic)
  - **ii** Equilibrium moves towards products (fewer gaseous molecules).
- d i Decreases ii No effect

6 **a** 
$$K_{c} = \frac{[PCl_{3}(g)][Cl_{2}(g)]}{[PCl_{5}(g)]}$$

 $b 0.196 \text{ mol dm}^{-3}$ 

7 **a** 
$$K_{c} = \frac{[H_2S(g)]^2}{[H_2(g)]^2[S_2(g)]}$$

**b** At equilibrium, 
$$[S_2(g)] = \left(\frac{0.442^2}{9.4 \times 10^5 \times 0.234^2}\right) \mod \mathrm{dm}^{-3}$$

$$= 3.80 \times 10^{-6} \,\mathrm{mol}\,\mathrm{dm}^{-3}$$

8 a Products

**b** 
$$K_{c} = \frac{[NO(g)]^{2}[O_{2}(g)]}{[NO_{2}(g)]^{2}}$$

- $c 0.083 \, mol \, dm^{-3}$
- **d** Yes. The equilibrium concentration of NO<sub>2</sub>(g) is much lower than the concentrations of NO(g) and O<sub>2</sub>(g).

9 **a** 
$$K_{c} = \frac{[CH_{3}CH(OC_{2}H_{5})_{2}(l)][H_{2}O(l)]}{[C_{2}H_{5}OH(l)]^{2}[CH_{3}CHO(l)]}$$

- **b** Reactants
- c Low
- $d 0.074 \text{ mol}^{-1} \text{dm}^3$
- 10 Likely to be low.

4 **a**  $K_c = \frac{[\text{NH}_3(g)]^2}{[\text{N}_2(g)] [\text{H}_2(g)]^3}$ **b**  $K_c = 2.09 \text{ mol}^{-2} \text{ dm}^6$ 

## Section 7.3

**1 a** 
$$K_{\rm p} = \frac{p_{\rm H_2O}^2}{p_{\rm H_2}^2 p_{\rm O_2}} \, \mathrm{atm}^{-1}$$
  
**b**  $K_{\rm p} = \frac{p_{\rm CH_3OH}}{p_{\rm CO} \, p_{\rm H_2}^2} \, \mathrm{atm}^{-2}$   
**c**  $K_{\rm p} = \frac{p_{\rm H_2} p_{\rm CO_2}}{p_{\rm H_2O} \, p_{\rm CO}} \, \text{(no units)}$   
**d**  $K_{\rm p} = \frac{p_{\rm C_2H_5OH}}{p_{\rm C_2H_4} p_{\rm H_2O}} \, \mathrm{atm}^{-1}$   
**e**  $K_{\rm p} = \frac{p_{\rm SO_3}^2}{p_{\rm SO_2}^2 p_{\rm O_2}} \, \mathrm{atm}^{-1}$ 

 $\mathbf{f} \ K_{\mathrm{p}} = \frac{p_{\mathrm{NO}}^2}{p_{\mathrm{N}_2} p_{\mathrm{O}_2}} \ (\text{no units})$ 

**2 a** 
$$K_{\rm p} = \frac{p_{\rm CO} p_{\rm H_2}^3}{p_{\rm CH_4} p_{\rm H_2O}}$$

- **i** K<sub>p</sub> increases
   **ii** K<sub>p</sub> unchanged
   **iii** K<sub>p</sub> unchanged
- **c i** A larger proportion of reactants (fewer gaseous molecules)
  - **ii** A larger proportion of products (reaction is endothermic)

**3 a** 
$$K_{\rm p} = \frac{p_{\rm O}^2}{p_{\rm O_2}}$$

**b**  $3 \times 10^{-8}$  atm

The position of the equilibrium is much further to the right at this altitude compared to lower regions of the atmosphere because of the higher intensity of the ultraviolet radiation with the right frequency to cause this dissociation.

K

87.1

87.6 87.3

## Section 7.4\_

1	Experiment number
	1
	2
	3

An average value of 87.3

2 **a** Partition coefficient =  $\frac{[\text{butanedioic acid}]_{\text{ethoxyethane}}}{[\text{butanedioic acid}]_{\text{water}}}$ = 0.148

## Section 7.5

- 1 The position of equilibrium would move toward the products, ie  $Ca^{2+}$  ions will displace  $Mg^{2+}$  ions from the clay surface.
- **2** The equilibrium involved is

 $R-H^+(s) + Na^+(aq) \rightleftharpoons R-Na^+(s) + H^+(aq)$ 

Washing with acid moves the equilibrium back to the left (the regenerated form). A high volume of concentrated acid is used to ensure that the equilibrium moves as far as possible to the left so that regeneration is as near complete as possible.

- 3 a resin -OH<sup>-</sup>(s) + Cl<sup>-</sup>(aq) → resin -Cl<sup>-</sup>(s) + OH<sup>-</sup>(aq)
   b One might expect I<sup>-</sup>(aq) to be held more strongly by the resin than Cl<sup>-</sup>(aq), because I<sup>-</sup> has fewer surrounding water molecules.
  - **c**  $H^+(aq)$  reacts with  $OH^-(aq)$  to form  $H_2O(l)$

# Section 7.6\_

- **1 a** X = 0.75; Y = 0.25
  - **b** Compared to compound X, compound Y has a greater affinity for the stationary phase and/or a lower affinity for the mobile phase.
  - **c** To maintain constant conditions in which the space around the thin layer is saturated with solvent vapour.
- **2 a** Retention time depends on the affinity of the compound for the stationary phase compared to its affinity for the carrier gas. More volatile compounds usually have shorter retention times. Other factors include the length and packing of the column, the flow rate of the gas and the temperature.
  - **b** The extent to which a compound distributes itself between the mobile phase and the stationary phase, and hence the retention time for that compound, depends on the temperature, so this must be constant throughout the column. Most columns are kept above room temperature to give reasonably short retention times. The temperature (and other conditions) must

- **4 a**  $K_{\rm p} = \frac{p_{\rm NH_3}^2}{p_{\rm N_2} p_{\rm H_2}^3}$ 
  - **b**  $1.7 \times 10^{-4}$  atm<sup>-2</sup> (The calculation follows the steps in the worked example on page 179.)
  - **c** 23.7 atm
  - **d** 100 atm, 24%
  - **b** [butanedioic acid]<sub>ethoxyethane</sub> =  $0.148 \times 0.036 \text{ mol dm}^{-3}$ =  $0.0053 \text{ mol dm}^{-3}$

3 **a** 
$$K_{ow} = \frac{[DDT(octan-1-ol)]}{[DDT(aq)]}$$
  
**b**  $K_{ow}$  is greater than 1

**c** Lower

4 The caesium, as Cs<sup>+</sup> ions, was deposited by rain. In the soil, the caesium ions exchanged with other cations such as hydrogen ions on the surface of the clays.

 $Soil-H^+(s) + Cs^+(aq) \rightarrow Soil-Cs^+(s) + H^+(aq)$ 

The caesium is thus held in the soil rather than being rapidly leached away. Like any nutrient cation, it is slowly released from the soil by exchange with hydrogen ions in subsequent rainfall. The initial ion exchange reaction is reversed

Soil-Cs<sup>+</sup>(s) + H<sup>+</sup>(aq)  $\rightarrow$  Soil-H<sup>+</sup>(s) + Cs<sup>+</sup>(aq)

The rate of release will be greater in areas of higher rainfall. This will lead to a greater concentration in grass and a consequently higher level in livestock. This higher level is likely to exceed that acceptable in food.

be recorded and kept constant in order to obtain reproducible results. If the temperature varies, the rates of elution of the substances will vary and results will be inconsistent between experiments.

- **c** Compounds with very high boiling points would have very long retention times. Compounds which decompose on heating may break down into smaller compounds in the column.
- **3 a** Ratio of *cis* : *trans* isomers was 1 : 1.4.
  - **b** They are likely to be similar because they are isomers.
- 4 a Methylpropane
  - **b** The more carbon atoms in the molecule, the longer the compound takes to travel through the column. Larger molecules are less volatile, spend more time dissolved in the stationary liquid phase and less time in the gas phase.
  - **c** All the times would be longer and the peaks would be further apart.

2

# Section 7.7

- 1 a i AgI(s)  $\rightleftharpoons$  Ag<sup>+</sup>(aq) + I<sup>-</sup>(aq)
  - ii  $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$
  - iii  $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^{-}(aq)$
  - iv  $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^{-}(aq)$
  - **i**  $K_{sp} = [Ag^{+}(aq)] [I^{-}(aq)] mol^{2}dm^{-6}$  **ii**  $K_{sp} = [Ba^{2+}(aq)] [SO_{4}^{-2}(aq)] mol^{2}dm^{-6}$  **iii**  $K_{sp} = [Pb^{2+}(aq)] [I^{-}(aq)]^{2} mol^{3}dm^{-9}$ b

    - iv  $K_{sp}^{F} = [Fe^{3+}(aq)] [OH^{-}(aq)]^3 mol^4 dm^{-12}$
  - **c** The reactant is a solid and so its concentration can be regarded as constant.

a	Product of ion concentrations / mol <sup>2</sup> dm <sup>-6</sup>	K <sub>sp</sub>
i ii iii	$4.0 \times 10^{-12}$ $9.0 \times 10^{-12}$ $2.0 \times 10^{-9}$	$5.0 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$ $1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ $1.6 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$
iv	2.0 × 10 <sup>-6</sup>	$5.0 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$

- **b** A precipitate will product of the ic solubility produc
- **a**  $[Ag^+(aq)] = 0.0$ 3  $[Cl^{-}(aq)] = 0.0$

**b** 
$$[Ca^{2+}(aq)] = 0.001 \, \text{mol} \, \text{dm}^{-3}$$

**a**  $[Tl^+(aq)] = 0.5 \times 7.0 \times 10^{-3} \text{ mol dm}^{-3}$ . 4 (Remember the concentration will be halved on mixing with an equal volume of sodium chloride.)

# Section 8.1

form in $\mathbf{i}$ and $\mathbf{iv}$ as in these cases the	C
ct.	
$105 \mathrm{mol}\mathrm{dm}^{-3};$	
$001 \mathrm{mol}\mathrm{dm}^{-3}$	

of sodium chloride above which a precipitate will just  
form is 
$$0.10 \text{ mol dm}^{-3}$$
.  
The volume of the mixture becomes  $200 \text{ cm}^3$ , therefore  
both ionic concentrations become  $5 \times 10^{-3} \text{ mol dm}^{-3}$ .  
Hence  $[\text{Ag}^+(\text{ag})] \times [\text{BrO}_2^-(\text{ag})] = 2.5 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ 

As with the thallium ion, the concentration of chloride ion will be halved on mixing. Hence the concentration

at 298 K, which is less than  $K_{sp}$  so no precipitate would

 $K_{\rm sp} = (0.5 \times 7.0 \times 10^{-3} \,\mathrm{mol}\,\mathrm{dm}^{-3}) \times [\mathrm{Cl}^{-}(\mathrm{aq})]$ 

 $[Cl^{-}(aq)] = \frac{1.75 \times 10^{-4} \,\text{mol}^{\,2} \,\text{dm}^{-6}}{0.5 \times 7.0 \times 10^{-3} \,\text{mol} \,\text{dm}^{-3}}$ 

 $= 0.05 \text{ mol dm}^{-3}$ 

- be observed. **a**  $[Ag^+(aq)] = 1.41 \times 10^{-5} \text{ mol dm}^{-3}$ 5  $[Cl^{-}(aq)] = 1.41 \times 10^{-5} \, mol \, dm^{-3}$ 
  - **b**  $2.02 \times 10^{-3} \,\mathrm{g}\,\mathrm{dm}^{-3}$

b

The new  $[Cl^{-}(aq)] = 5.0 \times 10^{-1} \, \text{mol} \, \text{dm}^{-3}$ . (The Cl<sup>-</sup> ions from AgCl will be negligible in comparison.) The product of the concentrations of silver and chloride ions

= 
$$(5.0 \times 10^{-1} \text{ mol dm}^{-3}) \times (0.5 \times 1.41 \times 10^{-5} \text{ mol dm}^{-3})$$
  
=  $3.5 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$ 

which exceeds the  $K_{sn}$  at this temperature and so a white precipitate of silver chloride would be observed.

base

NH<sub>2</sub>

H<sub>2</sub>Ó

HSO<sub>4</sub>-

HNO<sub>2</sub>

 $ClO_4^-$ 

base

OH

base

HCO<sub>3</sub>-

base SO,2-

 $H_2O$ 

Cl-

CH<sub>3</sub>COOH

CH<sub>2</sub>COO-

- Conjugate pairs: acid 1 Acid donates hydrogen ions/protons and the base 4 accepts hydrogen ions/protons.  $NH_4^+$ a H<sub>3</sub>O<sup>+</sup> **a**  $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ 2 H<sub>2</sub>SO<sub>4</sub> b base acid H<sub>2</sub>NO<sub>2</sub><sup>+</sup> **b**  $NH_3 + H_2O \rightarrow NH_4^+ + OH^$ base acid HClO<sub>4</sub> С **c**  $\operatorname{NH}_4^+ + \operatorname{OH}^- \rightarrow \operatorname{NH}_3 + \operatorname{H}_2\operatorname{O}$ acid base CH<sub>3</sub>COOH<sub>2</sub>+ **a**  $CH_2COOH + OH^- \rightarrow CH_2COO^- + H_2O$ 5 **d**  $\mathrm{SO_4^{2-} + H_3O^+} \rightarrow \mathrm{HSO_4^- + H_2O}$ Conjugate pairs: acid base acid CH<sub>2</sub>COOH  $\mathbf{e} \, \mathrm{H_2O} + \mathrm{H^-} \rightarrow \mathrm{H_2} + \mathrm{OH^-}$ H<sub>2</sub>O acid base **b**  $HCO_3^- + HCl \rightarrow H_2CO_3 + Cl^ \mathbf{f} \operatorname{H}_{3}\mathrm{O}^{+} + \mathrm{OH}^{-} \rightarrow 2\mathrm{H}_{2}\mathrm{O}$ Conjugate pairs: acid acid base HC  $\mathbf{g} \operatorname{NH}_{3} + \operatorname{HBr} \rightarrow \operatorname{NH}_{4}^{+} + \operatorname{Br}_{4}^{-}$ H<sub>2</sub>CO<sub>3</sub> base acid  $\mathbf{c} \operatorname{H_2O} + \operatorname{HSO_4^-} \rightarrow \operatorname{SO_4^{2-}} + \operatorname{H_3O^+}$  $\mathbf{h} \operatorname{H_2SO_4} + \operatorname{HNO_3} \rightarrow \operatorname{HSO_4}^- + \operatorname{H_2NO_3}^+$ Conjugate pairs: acid acid base i  $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$ HSO4 acið base  $H_3O^+$ 3 **a** Acid–base
- - **b** Acid–base
  - c Redox
  - d Redox

#### Section 8.2

- **1 a**  $[H^+(aq)] = 1 \times 10^{-2} \text{ mol dm}^{-3}$ ; therefore pH = 2 **b**  $[H^+(aq)] = 2 \times 10^{-1} \text{ mol dm}^{-3}$ ; therefore pH = 0.7 **c**  $[H^+(aq)] = 4 \times 10^{-1} \text{ mol dm}^{-3}$ ; therefore pH = 0.4 **d**  $[H^+(aq)] = 4 \times 10^{-1} \text{ mol dm}^{-3}$ ; therefore pH = 0.4 **2 a**  $1.7 \times 10^{-5} = \frac{[\text{H}^+(\text{aq})]^2}{1 \times 10^{-1}}$  $[H^+(aq)]^2 = 1.7 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$  $[H^+(aq)] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$ pH = 2.9**b**  $1.7 \times 10^{-5} = \frac{[\text{H}^+(\text{aq})]^2}{5 \times 10^{-2}}$  $[H^+(aq)]^2 = 8.5 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$  $[H^+(aq)] = 9.2 \times 10^{-4} \,\mathrm{mol}\,\mathrm{dm}^{-3}$ pH = 3.0**c** 6.3 × 10<sup>-5</sup> =  $\frac{[\text{H}^+(\text{aq})]^2}{1 \times 10^{-3}}$  $[H^+(aq)]^2 = 6.3 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$  $[H^+(aq)] = 2.5 \times 10^{-4} \,\mathrm{mol}\,\mathrm{dm}^{-3}$ pH = 3.6**d**  $1.6 \times 10^{-4} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{2.5}$ 
  - $$\begin{split} [\mathrm{H^+(aq)}]^2 &= 4.0 \times 10^{-4} \, \mathrm{mol^2} \, \mathrm{dm^{-6}} \\ [\mathrm{H^+(aq)}] &= 2.0 \times 10^{-2} \, \mathrm{mol} \, \mathrm{dm^{-3}} \\ \mathrm{pH} &= 1.7 \end{split}$$
- 3 a The reaction of the acid with water goes to completion.
  b [H<sup>+</sup>(aq)] = [A<sup>-</sup>(aq)]

[HA(aq)] = [A(aq)][HA(aq)] at equilibrium = original [HA(aq)].

4 a Strong acid – hydrochloric acid
 Weak acid – nitrous acid (nitric(III) acid)

# Section 8.3

- **1 a**  $1.6 \times 10^{-4} \mod \text{dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{0.1 \mod \text{dm}^{-3}}{0.1 \mod \text{dm}^{-3}}$ Therefore  $[\text{H}^+(\text{aq})] = 1.6 \times 10^{-4} \mod \text{dm}^{-3}$ 
  - pH = 3.8 **b**  $6.3 \times 10^{-5} \mod dm^{-3} = [H^+(aq)] \times \frac{0.03 \mod dm^{-3}}{0.01 \mod dm^{-3}}$ Therefore  $[H^+(aq)] = 2.1 \times 10^{-5} \mod dm^{-3}$ pH = 4.7
  - **c** The concentrations of acid and salt in the mixture will both be 0.05 mol dm<sup>-3</sup>. This is equivalent to diluting the buffer in **1 a** with an equal volume of water. The pH remains unchanged at 3.8.
  - **d**  $1.3 \times 10^{-5} \operatorname{mol} \mathrm{dm}^{-3} = [\mathrm{H}^{+}(\mathrm{aq})] \times \frac{5.0 \times 10^{-3} \operatorname{mol} \mathrm{dm}^{-3}}{1 \times 10^{-1} \operatorname{mol} \mathrm{dm}^{-3}}$ Therefore  $[\mathrm{H}^{+}(\mathrm{aq})] = 2.6 \times 10^{-4} \operatorname{mol} \mathrm{dm}^{-3}$  $\mathrm{pH} = 3.6$
  - e  $1.6 \times 10^{-4} \operatorname{mol} \mathrm{dm}^{-3} = [\mathrm{H}^{+}(\mathrm{aq})] \times \frac{2 \times 1.5 \times 10^{-2} \operatorname{mol} \mathrm{dm}^{-3}}{2 \times 5 \times 10^{-3} \operatorname{mol} \mathrm{dm}^{-3}}$

$$[H^+(aq)] = 5.3 \times 10^{-5} \text{ mol dm}^{-5}$$
  
pH = 4.3

**b** The position of the equilibrium for the reaction of the strong acid with water is completely to the right:  $HCl(aq) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$ The amount in moles of H<sup>+</sup>(aq) ions is equal to the amount in moles of HCl put into solution. Thus,  $[H^+(aq)] = 0.01 \text{ mol dm}^{-3} \text{ and pH} = 2.$ The position of the equilibrium for the reaction of the weak acid with water is more to the left:  $HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$ The amount in moles of H<sup>+</sup>(aq) ions is very much less than the amount in moles of HNO<sub>2</sub> put into solution. To obtain a solution with pH = 2, the nitrous acid solution must be more concentrated than the hydrochloric acid solution.

	[OH <sup>-</sup> (aq)]/mol dm <sup>-3</sup>	[H <sup>+</sup> (aq)]/mol dm <sup>-3</sup>	pН
a	1	$1 \times 10^{-14}$	14
b	0.01	$1 \times 10^{-12}$	12
с	0.2	$5 \times 10^{-14}$	13.3

6 a In alkaline solution, the equilibrium shifts to the right as H<sup>+</sup>(aq) is removed by reaction with OH<sup>-</sup>(aq), so the indicator will be present as the pink In<sup>-</sup> form.

$$\mathbf{b} \ K_{a} = \frac{[\mathrm{H}^{+}(\mathrm{aq})][\mathrm{In}^{-}(\mathrm{aq})]}{[\mathrm{HIn}(\mathrm{aq})]}$$

**c** 
$$K_a = 5.01 \times 10^{-10} \text{ mol dm}^{-3}$$
  
 $= \frac{[\text{H}^+(\text{aq})][\text{In}^-(\text{aq})]}{[\text{HIn}(\text{aq})]}$   
At the end point [HIn(aq)] = [In^-(aq)]  
Hence  $5.01 \times 10^{-10} \text{ mol dm}^{-3} = [\text{H}^+(\text{aq})]$   
pH at end point = 9.3

- 7 **a i**  $K_a = 5.0 \times 10^{-10} \text{ mol dm}^{-3}, pK_a = 9.3$  **ii**  $K_a = 1.3 \times 10^{-10} \text{ mol dm}^{-3}, pK_a = 9.9$  **iii**  $K_a = 4.8 \times 10^{-4} \text{ mol dm}^{-3}, pK_a = 3.3$ 
  - **b** HF, HCN, phenol

g

**f** In 750 cm<sup>3</sup> of solution the concentrations of acid and salt are

$$[acid] = \frac{0.1 \times 250}{750} \mod dm^{-3}$$
$$[salt] = \frac{0.1 \times 500}{750} \mod dm^{-3}$$
$$1.7 \times 10^{-5} \mod dm^{3} = [H^{+}(aq)] \times \frac{0.1 \times 500 \mod dm^{-3}}{0.1 \times 250 \mod dm^{-3}}$$
$$[H^{+}(aq)] = 8.5 \times 10^{-6} \mod dm^{-3}$$
$$pH = 5.1$$
$$1.7 \times 10^{-5} \mod dm^{-3} = [H^{+}(aq)] \times \frac{0.1 \mod dm^{-3}}{0.2 \mod dm^{-3}}$$

$$[H^+(aq)] = 3.4 \times 10^{-5} \text{ mol dm}^{-3}$$
  
pH = 4.5

The pH of the buffer solution, on adding a higher proportion of acid, has decreased. Changing the ratio of [salt] : [acid] provides a way of 'fine tuning' the pH of a buffer solution.

- 2 a Buffer solutions are made of either a weak acid and one of its salts or a weak base and one of its salts.
  - **i** Ethanoate ions from the salt react with the extra b H<sup>+</sup>(aq) ions to form ethanoic acid and water and so prevent a fall in the pH.
    - ii The addition of  $OH^{-}(aq)$  ions removes  $H^{+}(aq)$ but these are replaced by further dissociation of the ethanoic acid so the pH will remain constant.

## Section 9.1

1	<b>a b</b> i $K \rightarrow K^+ + e^-$ ii $H_2 \rightarrow 2H^+ + 2e^-$ iii $O + 2e^- \rightarrow O^{2-}$ iv $Cu^+ \rightarrow Cu^{2+} + e^-$ v $Cr^{3+} + e^- \rightarrow Cr^{2+}$	oxidation oxidation reduction oxidation reduction
2	<b>a</b> Ag(+1) <b>f</b> N(-3)	<b>k</b> S(+6), F(-1)
	<b>b</b> Br(0) <b>g</b> Mg(+2), Cl(-	1) <b>1</b> $S(+6), O(-2)$
	<b>c</b> $P(0)$ <b>h</b> $C(+4), O(-2)$ <b>d</b> $H(+1)$ <b>;</b> $P(+5), Cl(-1)$	<b>m</b> N(+5), O(-2) <b>n</b> P(+5) O(-2)
	<b>e</b> H(-1) <b>i</b> Al(+3), O(-2) <b>e</b> H(-1) <b>i</b> Al(+3), O(-2)	) <b>n</b> $\Gamma(\pm j), O(-2)$
2	$C_{1}(0) > C_{1}(1)$	roduced
3	a CI(0) → CI(-1) Fe(0) → Fe(+3)	oxidised
	<b>b</b> $Cl(0) \rightarrow Cl(-1)$	reduced
	$\begin{array}{c} H(0) \rightarrow H(+1) \end{array}$	oxidised
	$\mathbf{c} \operatorname{Cl}(0) \rightarrow \operatorname{Cl}(-1)$	reduced
	$Fe(+2) \rightarrow Fe(+3)$	oxidised
	$\mathbf{d} \ \mathbf{F}(0) \rightarrow \mathbf{F}(-1)$	reduced
	$O(-2) \rightarrow O(0)$	oxidised
4	a i Cl <sub>2</sub>	
	<b>ii</b> Fe	
	<b>b i</b> $Cl_2$	
	ii FeCl	
	$\mathbf{d}  \mathbf{i}  \mathbf{F}_2$	
	ii H <sub>2</sub> O	
5	a $Cl(+5) \rightarrow Cl(-1)$	reduced
	$O(-2) \rightarrow O(0)$	oxidised
	<b>b</b> $S(+6) \rightarrow S(+4)$	reduced
	$Br(-1) \rightarrow Br(0)$	oxidised

- iii Addition of a small amount of water will change the concentration of the acid and the salt by the same factor which means the ratio of [salt] to [acid] will remain constant and the pH will remain constant.
- **3** Ethanoic acid, because its  $K_a$  is close to the required  $[H^+(aq)]$  (pK<sub>a</sub> close to the required pH).

	$c  S(+6) \rightarrow S$ $I(-1) \rightarrow I(0)$ $d  I(0) \rightarrow I(-1)$ $S(+4) \rightarrow S$	(-2) )) (+6)	reduced oxidised reduced oxidised	
6	<b>a</b> Cu <sub>2</sub> O Cu: 2(+1) O: -2 H:	$+ 2H^+ \rightarrow Cu^{2+}$ $+ 2$ $2(+1)$	$+ Cu + H_2$ 0 -2 2(+	O oxidised and reduced no change -1) no change
	<b>b</b> 3Br <sub>2</sub> + <b>Br</b> : 3(0) + <b>O</b> : <b>H</b> :	$6OH^- \rightarrow BrO$ +5 6(-2) $3(-2)6(+1)$	$3^{-} + 5Br^{-} + 5(-1)$ 3(-) 3(-) 6(+)	3H <sub>2</sub> O oxidised and reduced 2) no change -1) no change
	<b>c</b> $4IO_3^{-}$ <b>I</b> : $4(+5)$ <b>O</b> : $12(-2)$	→ $3IO_4^- + I^-$ 3(+7) -1 12(-2)	oxidised : no chang	and reduced e
7	<ul> <li>a tin(II) oxid</li> <li>b tin(IV) oxid</li> <li>c iron(II) chl</li> <li>d iron(III) chl</li> <li>e lead(IV) ch</li> <li>f copper(I) c</li> <li>g manganese</li> </ul>	e le oride loride loride vxide (II) hydroxide	<ul> <li>h nitrate(I</li> <li>i nitrate(V</li> <li>j sulphate</li> <li>k sulphate</li> <li>l mangana</li> <li>m chromate</li> <li>n vanadate</li> </ul>	II) (IV) (VI) tte(VII) e(VI) e(VI) e(V)
8	<b>a</b> KClO <sub>2</sub> <b>b</b> NaClO <sub>3</sub> <b>c</b> Fe(OH) <sub>3</sub>			

#### **d** $Cu(NO_3)_2$

3 a

## Section 9.2

- 1 a  $Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$   $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ **b**  $6H^+(aq) + 6e^- \rightarrow 3H_2(g)$   $2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^$ **c**  $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$   $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^$ **d**  $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$  $e S(s) + 2e^- \rightarrow S^{2-}(s)$ 
  - $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}$  $Zn(s) \rightarrow Zn^{2+}(s) + 2e^{-}$
- **2 a** Mg(s) + Cu<sup>2+</sup>(aq)  $\rightarrow$  Mg<sup>2+</sup>(aq) + Cu(s) **b**  $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ **c**  $3Mg(s) + 2Au^{3+}(aq) \rightarrow 3Mg^{2+}(aq) + 2Au(s)$ **d**  $2\text{Fe}^{2+}(aq) + \text{Cl}_2(g) \rightarrow 2\text{Fe}^{3+}(aq) + 2\text{Cl}^-(aq)$
- **v** 1.36V

**i** 3.16V

**ii** 1.10V

**iii** 0.18V

iv 0.32 V

- **b i**  $Ag^+(aq)/Ag(s)$ ii  $Cu^{2+}(aq)/Cu(s)$ 
  - iii Ni<sup>2+</sup>(aq)/Ni(s)
  - **iv**  $Fe^{2+}(aq)/Fe(s)$ 
    - $\mathbf{v} \operatorname{MnO}_4^{-}(aq)/\operatorname{Mn}^{2+}(aq)$

 $E^{\circ} = -0.13 \text{ V}$ 

**c** i 
$$2Ag^+(aq) + Mg(s) \rightarrow 2Ag(s) + Mg^{2+}(aq)$$

**ii** 
$$\operatorname{Cu}^{2+}(\operatorname{aq}) + \operatorname{Zn}(s) \rightarrow \operatorname{Cu}(s) + \operatorname{Zn}^{2+}(\operatorname{aq})$$
  
**iii**  $\operatorname{Ni}^{2+}(\operatorname{aq}) + \operatorname{Eo}(s) \rightarrow \operatorname{Ni}(s) + \operatorname{Eo}^{2+}(\operatorname{aq})$ 

$$\begin{array}{c} \text{iii} \quad \text{Ni}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \rightarrow \text{Ni}(\text{s}) + \text{Fe}^{2+}(\text{aq}) \\ \hline \end{array}$$

- iv  $Fe^{2+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$ **v**  $2MnO_4^{-}(aq) + 5Sn^{4+}(aq) + 16H^{+}(aq)$
- $\rightarrow 2Mn^{2+}(aq) + 5Sn^{2+}(aq) + 8H_2O(l)$
- **4**  $Cd^{2+}(aq)/Cd(s)$  $E^{\circ} = -0.40 \,\mathrm{V}$
- $Co^{2+}(aq)/Co(s)$  $E^{\circ} = -0.28 \, \text{V}$ 5

#### Section 9.3

- i  $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}; Cl_{2}(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$ overall:  $Cl_2(g) + 2I^{-}(aq) \rightarrow 2Cl^{-}(aq) + I_2(aq)$ 
  - ii  $2Br^{-}(aq) \rightarrow Br_{2}(aq) + 2e^{-};$  $MnO_{4}^{-}(aq) + \bar{8}H^{+}(aq) + 5e^{-}$  $\rightarrow$  Mn<sup>2+</sup>(aq) + 4H<sub>2</sub>O(l) overall:  $2MnO_4^{-}(aq) + 16H^{+}(aq) + 10Br^{-}(aq)$  $\rightarrow$  2Mn<sup>2+</sup>(aq) + 8H<sub>2</sub>O(l) + 5Br<sub>2</sub>(aq)
  - iii  $2I^{-}(aq) \rightarrow 2I_{2}(aq) + 2e^{-}; Br_{2}(aq) + 2e^{-} \rightarrow 2Br^{-}(aq)$ overall:  $2I^{-}(aq) + Br_{2}(aq) \rightarrow I_{2}(aq) + 2Br^{-}(aq)$
- 2 **a** Yes c No d Yes
- **b** Yes
- $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$ 3  $\tilde{Cr}_{2}O_{7}^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightarrow 2Cr^{3+}(aq) + 7H_{2}O(l)$ overall:  $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq)$  $\rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$

# Section 9.4

- i Cobalt(III) fluoride dissolves in water to form 1 a cobalt(III) ions,  $[Co(H_2O)_6]^{3+}$ .  $E^{\circ}$  for the  $[Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}$  half-cell is more positive than  $E^{\bullet}$  for the  $O_2(g)$ ,  $H^+(aq)/H_2O(l)$ half-cell. Electrons are supplied to the more positive half-cell, so cobalt(III) ions are reduced to cobalt(II) ions and water is oxidised to release oxygen.
  - ii The overall equation is

$$\begin{split} 4[\mathrm{Co}(\mathrm{H}_{2}\mathrm{O})_{6}]^{3+}(\mathrm{aq}) &+ 2\mathrm{H}_{2}\mathrm{O}(\mathrm{l}) \\ & \rightarrow 4[\mathrm{Co}(\mathrm{H}_{2}\mathrm{O})_{6}]^{2+}(\mathrm{aq}) + \mathrm{O}_{2}(\mathrm{g}) + 4\mathrm{H}^{+}(\mathrm{aq}) \end{split}$$

- **iii** The hydrated  $Co^{2+}$  ion is more stable than the hydrated Co<sup>3+</sup> ion.
- **b** Oxygen in the air is unable to oxidise the pink cobalt(II) ion as the  $E^{\bullet}$  for the oxygen half equation is less positive than that required for oxidising  $[Co(H_2O)_6]^{2+}(aq)$ .
- **c** The  $E^{\circ}$  for the oxygen half equation is more positive than that needed to oxidise the yellow-brown  $[Co(NH_3)_6]^{2+}(aq)$  to the dark brown  $[Co(NH_3)_6]^{3+}(aq)$ . The overall equation is

$$O_2(g) + 4H^+(aq) + 4[Co(NH_3)_6]^{2+}(aq)$$
  
→  $2H_2O(l) + 4[Co(NH_3)_6]^{3+}(aq)$ 

**d**  $[Co(NH_3)_6]^{3+}$  is more stable than  $[Co(NH_3)_6]^{2+}$ .

- 6  $Pb^{2+}(aq)/Pb(s)$
- $Fe^{3+}(aq)/Fe^{2+}(aq)$ 7  $E^{\circ} = + 0.77 \,\mathrm{V}$ 
  - $F_{2}(g)/2F^{-}(aq)$  $E^{\circ} = +2.85 \, \text{V}$
- 9 K, Ce, Cd, Ni, Sn, Ag

8

10	$2H^{+}(aq)/H_{2}(g)$	$E^{\circ} = 0$ V by definition
	$Pb^{2+}(aq)/Pb(s)$	$E^{\circ} = -0.13 \mathrm{V}$
	$Cd^{2+}(aq)/Cd(s)$	$E^{\circ} = -0.40 \mathrm{V}$
	Ag <sup>+</sup> (aq)/Ag (s)	$E^{\circ} = +0.80 \mathrm{V}$
	$Cr^{3+}(aq)/Cr(s)$	$E^{\circ} = -0.74 \mathrm{V}$

- 4 b i No ii No
  - iii Yes
- 5 a Yes **b** No c Yes d Yes
  - e Yes
- 6 **a,b** i  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ ii  $2CH_3OH(aq) + O_2(g) \rightarrow 2HCHO(aq) + 2H_2O(l)$ iii  $2HCHO(aq) + O_2(g) \rightarrow 2HCOOH(aq)$

2 b **i** As the  $E^{\circ}$  for aqueous iron(III),  $[Fe(H_2O)_6]^{3+}(aq)$ , is more positive than that of the iodine half-cell, the iron(III) will oxidise the aqueous iodide ion to iodine. The overall equation is

$$2[Fe(H_2O)_6]^{3+}(aq) + 2I^{-}(aq) \rightarrow 2[Fe(H_2O)_6]^{2+}(aq) + I_2(aq) E cell = +0.77 V - (+0.54 V) = +0.23 V$$

ii As the  $E^{\circ}$  for the iodine half-cell is more positive than that of hexacyanoferrate half-cell, iodine will oxidise the hexacyanoferrate(II) to hexacyanoferrate(III) The overall equation is

$$I_2(aq) + 2[Fe(CN)_6]^{4-}(aq)$$
  
→ 2I<sup>-</sup>(aq) + [Fe(CN)\_6]^{3-}(aq)  
E cell = +0.54 V - (+0.36 V) = +0.18 V

c A major reason why many predicted reactions do not occur is because of high activation enthalpies, ie there is a kinetic barrier to the reaction despite it appearing thermodynamically feasible. Also, these calculations assume standard conditions: if conditions are not standard, the results may be different.

1

# Section 10.1\_

-			
	а	b	c
A temperature	rate will increase with temperature	rate will increase with temperature	rate will increase with temperature
B total pressure of gas	rate of forward reaction not affected	rate increases	rate of forward reaction not affected
C concentration of solution	increasing the concentration of acid will increase the rate	solutions not involved	increasing the concentration of peroxide will increase the rate
D surface area of solid	the more finely divided the magnesium, the faster the rate	the more finely divided the catalyst, the faster the rate	solids not involved
<b>2</b> Both the acid and the enhydrolysis of a protein.	azyme can act as catalysts for the	4 <b>a B</b> and <b>C</b> <b>b A</b> and <b>D</b>	

3	<b>a</b> The greater the concentration of reactants, the greater the rate of collisions and hence the faster the reaction	c D d B
	proceeds. <b>b</b> A change of temperature has little effect. Most	еВ fD

collisions result in a reaction.

# Section 10.2

- **1 a** A **b** A **c** B **d** Mainly B, with A to a minor extent.
- 2 a This reaction has a high activation enthalpy that prevents it occurring at a significant rate at room temperature, but the reaction is exothermic, and once the spark has provided the energy needed to get it started, the reaction produces enough energy to sustain itself regardless of how much is present.
  - **b** The platinum catalyst lowers the activation enthalpy to such an extent that it is close to the thermal energy of molecules at room temperature.
- **3** Above a certain temperature, enzymes are denatured and become inactive.
- **4 a** The surface area of the coal is much greater in the powder than in the lump. Many more collisions with oxygen molecules are possible and the speed of reaction will be much greater.
  - **b** Although the gas molecules are moving freely, the molecules have insufficient kinetic energy to overcome the activation enthalpy for reaction.
  - **c** The particles in the solids are in fixed positions in their respective lattices. The only movement will be due to low energy vibrations or rotations about these fixed positions. The number of collisions is very low indeed. There is also unlikely to be sufficient energy available to overcome the activation enthalpy for reaction.
- Section 10.3
- **1 a** The reaction is first order with respect to bromoethane and zero order with respect to hydroxide ion.
  - **b** The reaction is first order with respect to methyl methanoate, zero order with respect to water and first order with respect to H<sup>+</sup>.
  - **c** The reaction is first order with respect to urea, zero order with respect to water and first order with respect to urease.

- **d** The fine flour dust allows maximum chances of collisions with oxygen molecules. A spark will cause instant ignition followed by a very rapid reaction amounting to an explosion.
- 5 Catalytic converters catalyse redox reactions involving CO,  $NO_x$  and oxygen from the air (see **Developing Fuels** for details). The catalyst lowers the activation enthalpies of these reactions, but the activation enthalpies are still high, and the reactions do not occur at a significant rate until the catalyst is hot.
- **6** The added curve is above the original, with a greater slope at the start of the reaction but plateauing at the same final volume of hydrogen given off.
- 7 **a** The area shaded is underneath the  $T_1$  curve and to the right of  $E_a$ .
  - **b** The area shaded a different colour is underneath the  $T_2$  curve and to the right of  $E_a$ , encompassing the first-coloured area. The  $T_2$  curve has a lower and broader maximum than the  $T_1$  curve and the maximum value is shifted to the right. It tails off above the  $T_1$  curve.

- **d** The reaction is a single step in the mechanism. It is first order with respect to the methyl radical and first order with respect to the chlorine molecule.
- **e** The reaction is order  $\frac{1}{2}$  with respect to carbon monoxide and first order with respect to chlorine.
- **f** The reaction is second order with respect to nitrogen dioxide.
- **2 a** Rate = k[CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl] [OH<sup>-</sup>] **b** Rate = k[C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>] [H<sup>+</sup>]

- 3 a i First order
  - ii Second order

**b** Rate = 
$$k[H_2][NO]^2$$

$$k = 0.384 \,\mathrm{mol}^{-2} \,\mathrm{dm}^6 \,\mathrm{s}^{-1}$$

- **4 b** All are *ca* 1150 s (Allow within 1100–1200 s.) First order.
  - **e** Rate =  $k[N_2O_5]$  or  $-d[N_2O_5]/dt = k[N_2O_5]$

# Section 10.4

- **a** Platinum on aluminium oxide (heterogeneous catalyst).
  - ${\bm b} \ {\tt Zeolite} \ ({\tt heterogeneous \ catalyst}).$
  - **c** Platinum on aluminium oxide (heterogeneous catalyst).
- a 2CO(g) + 2NO(g) → 2CO<sub>2</sub>(g) + N<sub>2</sub>(g)
   b These gases are hazardous to health, produce acid rain and can take part in producing photochemical smog.
  - **c i** A substance is adsorbed when it is bound to the surface of another substance.
    - **ii** The mechanism should show CO and NO being adsorbed to the catalyst surface.



# Section 10.5



#### Section 11.1

- 1 a d block b p block c s block d f block
- 2 **a** Peaks: carbon, silicon Troughs: helium, neon, argon
  - **b** Elements in the same group occur at similar positions on graph eg Group 4 at peaks, Group 0 in troughs.
- **3 a** They are all in Group 1.
  - **b** The molar atomic volumes for each period of elements vary in similar regular patterns.
- - **c** Second period: number of chlorine atoms same as group number for Groups 1–4. After Group 4, falls by

- **f**  $6.2 \times 10^{-4} \text{ s}^{-1}$ (Method is difficult to use. Allow for an answer between 5 and  $7 \times 10^{-4} \text{ s}^{-1}$ .)
- 5 a Structural isomerism
  - **b** 0.5 atm
  - **d**  $t_{\frac{1}{2}}$  is constant and about 55 × 10<sup>3</sup> s. First order.

The bonds in the molecules are weakened and new bonds form between the atoms.

N-N O-C-O $\bigcirc$ catalyst surface

Products are released from the surface.

- **d** The reaction between nitrogen and carbon monoxide on the surface of the catalyst is faster at high temperature.
- e i Lead poisons the catalyst in the converter. It is adsorbed strongly to the surface of the catalyst and prevents CO and NO being adsorbed.
  - ii Use unleaded fuel.
- **b** The rate will be faster for the enzyme catalysed reaction, as the activation enthalpy is significantly lower. This means that more pairs of colliding molecules have sufficient energy to react at room temperature.
- **a** The catalyst is in the same phase as the reactants.
  - **i** An intermediate is formed. In this example, the intermediate is the radical, ClO.
    - **ii** The first peak represents the energy that must be supplied to enable bonds in the reactants (Cl and  $O_3$ ) to stretch and break as new bonds form in the products (ClO and  $O_2$ ). The trough represents the energy released when ClO and  $O_2$  are formed from Cl and  $O_3$ . The second peak represents the energy required for ClO and O to come together and allow the formation of Cl and  $O_2$  which are the products.

one chlorine atom for each subsequent group. Similar pattern for third period, rise continues to Group 5 before falling.

**d** Same formulae.

b

- **5 a** Li<sub>2</sub>O, BeO, B<sub>2</sub>O<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, F<sub>2</sub>O Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, Cl<sub>2</sub>O<sub>7</sub>
  - **c** Second period: number of oxygen atoms per atom of element increases by a half up to Group 5 before falling. Third period, increases from Groups 1 through to 7.
  - **d** Same formulae except for halogens where fluorine is unable to form the higher oxides.

1

# Section 11.2\_

Element	Trend in reactivity with water	Trend in thermal stability of carbonate	Trend in pH of hydroxide with water	Trend in solubility of hydroxide	Trend in solubility of carbonate	
Mg		nre			•	
Са		e ngly perat				
Sr	tses	npose reasir r tem	ses	tses	Ises	
Ва	increa	decor at inc highe	increa	increa	increé	
Ва	increa	decom at incr higher	increas	increa	increas	

- 2 Sulphate solubility decreases down group.
- **a** magnesium + steam

→ magnesium hydroxide + hydrogen Mg(s) +  $2H_2O(g) \rightarrow Mg(OH)_2(s) + H_2(g)$ 

 $\mathbf{b}$  calcium oxide + hydrochloric acid

→ calcium chloride + water CaO(s) + 2HCl(aq) → CaCl<sub>2</sub>(aq) + H<sub>2</sub>O(l)

**c** beryllium carbonate

→ beryllium oxide + carbon dioxide BeCO<sub>3</sub>(s) → BeO(s) + CO<sub>2</sub>(g)

**d** barium hydroxide + sulphuric acid

# Section 11.3

1 The triple bond in N<sub>2</sub> is very strong (bond enthalpy =  $945 \text{ kJ mol}^{-1}$ ), so a great deal of activation enthalpy must be supplied before N<sub>2</sub> will react. P<sub>4</sub>, on the other hand, needs only enough energy to break one of the P–P bonds (bond enthalpy =  $198 \text{ kJ mol}^{-1}$ ) to start it reacting. The reason that P does not form triple bonds like those in N<sub>2</sub> is related to its larger size.

```
2 a i +3 \rightarrow +5

ii +5 \rightarrow 0

iii -3 \rightarrow -3

iv \ 0 \rightarrow -3

v +2 \rightarrow +4

b i \ A
```

- ii B
- iii C
- iv B

```
v A
```

```
3 a +2 to +1
```

# Section 11.4

- **1 a i** Deep brown colour  $2I^{-}(aq) + Cl_{2}(aq) \rightarrow I_{2}(aq/s) + 2Cl^{-}(aq)$ 
  - ii No changeiii Light brown/red colour deepens in tone, becoming dark brown
  - $2I^{-}(aq) + Br_2(aq) \rightarrow I_2(aq/s) + 2Br^{-}(aq)$ iv Light brown/red colour
  - $2Br^{-}(aq) + Cl_{2}(aq) \rightarrow Br_{2}(aq) + 2Cl^{-}(aq)$
  - **b i**  $\operatorname{Ag}^+(\operatorname{aq}) + \operatorname{Cl}^-(\operatorname{aq}) \rightarrow \operatorname{AgCl}(s)$ 
    - ii  $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

iii 
$$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$$

**4 a** Cs (or Fr)

**b** Cs (or Fr) **c** +1

- **d** i M<sub>2</sub>O ii MOH iii M<sub>2</sub>CO<sub>3</sub>
- 5 a lithium + water → lithium hydroxide + hydrogen 2Li(s) + 2H<sub>2</sub>O(l) → 2LiOH(aq) + H<sub>2</sub>(g)
  - **b** hydrochloric acid + sodium hydroxide  $\rightarrow$  sodium chloride + water HCl(aq) + NaOH(aq)  $\rightarrow$  NaCl(aq) + H<sub>2</sub>O(l)
  - **c** Little reaction even at high temperatures
  - **d** sodium oxide + sulphuric acid

**b**  $2NO(g) + 2H^+(aq) + 2e^- \rightarrow N_2O(g) + H_2O(l)$ 

4 i 
$$NO_2^{-}(aq) + H_2O(1) \rightarrow NO_3^{-}(aq) + 2H^+(aq) + 2e^-$$
  
ii  $NO_2^{-}(aq) + 6H^+(aq) + 5e^- \rightarrow \frac{1}{2}N_2(g) + 3H_2O(1)$ 

- **ii**  $\operatorname{NO}_3(\operatorname{aq}) + \operatorname{OH}^-(\operatorname{aq}) + \operatorname{Se}^- \rightarrow \overline{2}\operatorname{N}_2(\operatorname{g}) + 3\operatorname{H}_2\operatorname{O}(\operatorname{Iii})$ **iii**  $\operatorname{NH}_4^+(\operatorname{aq}) + \operatorname{OH}^-(\operatorname{aq}) \rightarrow \operatorname{NH}_3(\operatorname{g}) + \operatorname{H}_2\operatorname{O}(\operatorname{I})$
- iv  $N_2(g) + 6H^+(aq) + 6e^- \rightarrow 2NH_3(g)$
- $\mathbf{v}$  NO(g) + H<sub>2</sub>O(l)  $\rightarrow$  NO<sub>2</sub>(g) + 2H<sup>+</sup>(aq) + 2e<sup>-</sup>
- **a** The NO is oxidised by air as in reaction (2), to produce further NO<sub>2</sub> which takes part in reaction (3).
  - **b** Ammonium nitrate fertiliser.
  - **c i** 1 mole of NH<sub>3</sub>  $\rightarrow \frac{2}{3}$  mole of HNO<sub>3</sub> 1000 kg × (63/17) ×  $\frac{2}{3}$  = 2471 kg
    - ii Incomplete reaction at each of the three stages. Loss of intermediates.
  - **d** The reactants and intermediates include serious environmental pollutants, particularly  $NO_x$ . Escape of these, even in small quantities, would lead to acid rain and direct effects on living things. The  $NO_x$  could be absorbed in aqueous sodium hydroxide.
  - c i  $2Na(s) + Br_2(l/g) \rightarrow 2NaBr(s)$ ii  $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$ 
    - **iii**  $2K(s) + I_2(s/g) \rightarrow 2KI(s)$
    - iv  $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$
- **2 a** I + 1, Cl 1
  - **b** Br +3, F -1
  - **c** Br +1
  - **d** I +5
  - **e** I +7

3 a  $Cl_2(g) + 2NaOH(aq)$ 

$$\rightarrow$$
 NaCl(aq) + NaClO(aq) + H<sub>2</sub>O(l)

**b i** Chlorine

4 a

- **ii** Cl from 0 in  $Cl_2$  to -1 in NaCl, ie reduction Cl from 0 in  $Cl_2$  to +1 in NaClO, ie oxidation
- **c i** 2NaClO(aq)  $\rightarrow$  2NaCl(aq) + O<sub>2</sub>(g)
  - **ii** Oxygen and chlorine.
  - iii Oxygen from -2 in NaClO to 0 in O<sub>2</sub>, ie oxidation Chlorine from +1 in NaClO to -1 in NaCl, ie reduction.

isotopes and abundances	<sup>210</sup> At
melting point/K	575 (allow 480–600)
boiling point/K	610 (allow 550–700)
solubility at 293 K/g per 100 g water	allow any low value

# Section 11.5\_

Element	Electronic configuration	Element	Electronic configuration
Sc	[Ar] 3d <sup>1</sup> 4s <sup>2</sup>	Fe	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>
Ti	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>	Co	[Ar] 3d <sup>7</sup> 4s <sup>2</sup>
V	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>	Ni	[Ar] 3d <sup>8</sup> 4s <sup>2</sup>
Cr	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>	Cu	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>
Mn	[Ar] 3d <sup>5</sup> 4s <sup>2</sup>	Zn	[Ar] 3d <sup>10</sup> 4s <sup>2</sup>

2	a	i	Cu <sup>2+</sup>	$[Ar] 3d^9 4s^0$
		ii	$Cu^+$	[Ar] 3d <sup>10</sup> 4s <sup>0</sup>
		iii	Fe <sup>3+</sup>	$[Ar] 3d^5 4s^0$
		iv	V <sup>3+</sup>	$[Ar] 3d^2 4s^0$
		v	$Cr^{3+}$	$[Ar] 3d^3 4s^0$
		vi	Ni <sup>2+</sup>	$[Ar] 3d^8 4s^0$

- b Cu<sup>2+</sup> has a partially filled 3d sub-shell and behaves as a typical d block transition metal ion.
   Cu<sup>+</sup> has a filled 3d sub-shell and cannot show such properties.
- **3 a** The three transition metals atoms (Cr, Fe, Co) are the same size as each other, but are smaller than the atoms of sodium (Na) and magnesium (Mg).
  - **b** The melting and boiling points of the transition metals are much higher than those of sodium and magnesium.
  - **c** The three transition metals are much denser than sodium and magnesium.
  - **d** Cr  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ 
    - Fe  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
    - $Co \qquad 1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 3d^7 \, 4s^2$
    - Na  $1s^2 2s^2 2p^6 3s^1$
    - Mg  $1s^2 2s^2 2p^6 3s^2$
  - **e** The properties of elements are governed by the arrangement of electrons in the outermost incomplete shells. In the first row of the d block, the inner *3*d orbital is being filled and most elements have two electrons in the outer 4s shell. (Chromium is an exception, having only one electron in the 4s shell.)

- **b i** The orange aqueous bromine water turns a dark brown/black and a black precipitate may form. Br<sub>2</sub>(aq) + 2At<sup>-</sup>(aq)  $\rightarrow$  2Br<sup>-</sup>(aq) + At<sub>2</sub>(s)
  - $\begin{array}{ll} \textbf{ii} & \text{The orange-brown colour of iodine is replaced by} \\ & a \mbox{ much darker colour and/or a black precipitate.} \\ & I_2(aq) + 2At^-(aq) \rightarrow 2I^-(aq) + At_2(s) \end{array}$
  - iii The two colourless solutions produce a yellow precipitate.
     Ag<sup>+</sup>(aq) + At<sup>-</sup>(aq) → AgAt(s)
  - iv The sodium burns with an orange flame and a white solid is produced.  $2Na(s) + At_2(g) \rightarrow 2NaAt(s)$

Thus, transition elements have similar properties because they have essentially the same *outer* electronic arrangement as each other, in the same way as the elements in a vertical group. They differ only by the number of electrons in the *inner incomplete 3d* sub-shell.

Metals in different groups in the periodic table have different numbers of outer electrons and hence different properties.

4 **a** The  $E^{e}$  for the  $O_2(g)$ ,  $4H^+(aq)/2H_2O(l)$  half-cell is more positive and receives electrons from the Fe<sup>3+</sup>(aq)/Fe<sup>2+</sup>(aq) half-cell. So overall  $O_2$  is reduced to water and the Fe<sup>2+</sup>(aq) is oxidised to Fe<sup>3+</sup>(aq).  $O_2(g) + 4H^+(aq) + 4Fe^{2+}(aq)$ 

→  $2H_2O(l) + 4Fe^{3+}(aq)$  E cell = +1.23 V - (+0.77 V) = +0.46 VThe  $E^{\circ}$  for the  $O_2(g)$ ,  $4H^+(aq)/2H_2O(l)$  half-cell is less positive than that for the Mn<sup>3+</sup>(aq)/Mn<sup>2+</sup>(aq) half-cell and so it is not oxidising enough to form Mn(III) from Mn(II). The Mn<sup>3+</sup>(aq)/Mn<sup>2+</sup>(aq) half-cell receives electrons from the  $O_2(g)$ ,  $4H^+(aq)/2H_2O(l)$  half-cell. In the presence of water, Mn<sup>3+</sup>(aq) is reduced to Mn<sup>2+</sup>(aq) and the water oxidised to oxygen.  $4Mn^{3+}(aq) + 2H_2O(l)$ 

→  $4Mn^{2+}(aq) + O_2(g) + 4H^+(aq)$ E cell = +1.56 V - (+1.23 V) = +0.33 V

- **b i** An acidified solution of iron(II) will be oxidised by air.
  - **ii** An acidified solution of marganese(II) will not be oxidised by air.
- **c** The flow of electrons is to the half-cell with the most positive  $E^{\circ}$  value. Cu<sup>+</sup>(aq) will be expected to be oxidised to Cu(s) and reduced to Cu<sup>2+</sup>(aq) (disproportionation).  $2Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$ E cell = +0.52 V - (+0.16 V) = +0.36 V

## Section 11.6

- **1 a** 2
  - **b** 4
    - **c** 6
    - **d** 6
- **2 a**  $[Mn(H_2O)_6]^{2+}$ 
  - **b**  $[Zn(NH_3)_4]^{2+}$
  - **c**  $[FeF_6]^{3-5}$
  - **d**  $[Cr(H_2O)_5OH]^{2+}$
- **3 a** +1
  - **b** +2
  - **c** +3
  - **d** +3
- 4 a Hexaaquavanadium(III) ionb Hexacyanoferrate(II) ion
  - **c** Tetrachlorocobaltate(II) ion
  - **d** Diamminesilver(I) ion
  - e Tetraaquadichlorochromium(III) ion
- 5 **a**  $TiO_2(s)$  contains titanium with a  $3d^0$  electron configuration. It is white as no 3d electron transitions are possible.
  - **b**  $Sc^{3+}$  [Ar]

	L J	
$Zn^{2+}$	[Ar] 3d <sup>10</sup>	no 3d electron transitions

 $Cu^+$  [Ar]  $3d^{10}$  possible, hence colourless

```
6 a 6
```

```
b +4
```

```
\boldsymbol{c}\ \text{Hexachlorotitanate}(\text{IV})\ \text{ion}
```

# Section 12.1\_\_\_\_\_



- 7 A five-membered chelate ring seems to lead to a more stable complex than a six-membered one.
- 8 a Monodentate
  - **b** Bidentate
  - c Polydentate
  - **d** Bidentate
- 9 A complex of a metal ion with edta contains six 5-membered chelate ring systems (see Figure 32 on page 270 of **Chemical Ideas**). The complex is much more stable than the corresponding complexes with  $NH_3$  or  $H_2O$  which contain no chelate rings. The extra stability is due to the large increase in entropy when  $edta^{4-}$ displaces six ligands.

I	Empirical formula	Molecular formula	M <sub>r</sub>
	$ \begin{array}{c} C_{3}H_{8} \\ CH_{2} \\ CH \\ C_{10}H_{21} \\ CH_{2} \end{array} $	$C_{3}H_{8}$ $C_{12}H_{24}$ $C_{6}H_{6}$ $C_{20}H_{42}$ $C_{5}H_{10}$	44 168 78 282 70
	CH	$C_2H_2$	26
	C <sub>5</sub> H <sub>4</sub>	C <sub>10</sub> H <sub>8</sub>	128
2	<b>a</b> $CH_2$ <b>b</b> $C_2H_4$		
3	<b>a</b> CH <b>b</b> $C_6H_6$		
4	a, b	С : Н	
	Ratio by mass	82.8 : 17.2	
	Ratio by moles	6.9 : 17.2	
	Simplest ratio	1 : 2.5	
	Whole number ratio	2 : 5	
	: Empirical formula is C	$_{2}H_{5}$	
	But $M_r(C_2H_5) = 29$		
	So, the molecular formul	$13 15 C_4 H_{10}$ .	
5	<b>a</b> 0.085 g C 0.	014 g H	
	<b>b</b> 0.0071 mol C 0.	014 mol H	
	c CH <sub>2</sub>		
	$\mathbf{d} \operatorname{C}_{6}\operatorname{H}_{12}$		
	e (or a hexe	ne such as	>>>)
6	a B D E		
	<b>b</b> ACF		







**12 a**  $C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$  **b**  $C_5H_{12} + 5\frac{1}{2}O_2 \rightarrow 5CO + 6H_2O$ 

- **13 a** For 'cat' cracking, high temperature (500 °C) and zeolite catalyst. For steam cracking, high temperature (900 °C) with short residence time and steam as dilutent.
  - **b** True: (ii), (iv), (v)
  - **c** Three from:



b D c A d B e C and E
f eg C or E could have been produced by cracking D

g A

E /

#### Section 12.2







- 8 **a** Bromine; room temperature; non polar solvent
  - **b** Steam; catalyst, phosphoric acid on silica; 300 °C; high pressure (60 atm)
  - **c** Hydrogen; catalyst, nickel; 150 °C; 5 atm pressure; (or platinum at lower temperatures and atmospheric pressure)
  - d Hydrogen; catalyst, nickel; 150°C.



**b** The hydrogen bromide is polarised with the hydrogen atom being slightly positively charged. The hydrogen atom behaves as an electrophile and reacts with the double bond.

One of the carbon atoms has become positively charged and so it reacts with the bromide ion to form a C–Br covalent bond.

10 Shake the compound with about 1 cm depth of bromine water in a stoppered test-tube. If the compound is unsaturated, the bromine will be decolorised. The reaction occurs quickly at room temperature.

#### Section 12.3

1 a i 1,4-dimethylbenzene ii 1-ethy1-3-methylbenzene iii 1,2,4-trimethylbenzene



- 2 **a** 1,3,5-trimethylbenzene **b** 1-methyl-3-propylbenzene
  - c bromobenzene
  - d 1,3-dinitrobenzene
  - **e** 4-methylphenylamine
  - f 2,6-dimethylphenol





isomer is possible.



# Section 12.4

- **1 a** Product:
- CI
- **b** Reagents and conditions: Br<sub>2</sub>; AlBr<sub>3</sub> or Fe; reflux



 $\mathbf{g}$  Reagents and conditions: CH<sub>3</sub>COCl; AlCl<sub>3</sub>; reflux

SO<sub>2</sub>-OH

**h** Product:



3 a Difference in electronegativity between I and Cl

**c** As the molecule is permanently polarised, a catalyst is not needed.

$$\begin{array}{cc} \delta-&\delta+\\ Cl&-I \end{array}$$

 $\begin{array}{l} \textbf{d} \ \mbox{Formation of chlorobenzene requires a chlorine with a} \\ \delta + \ \mbox{charge}. \end{array}$ 



- 5 a The benzene ring is resistant to hydrogenation because this destroys the stable delocalised electron system. The reaction has a high activation enthalpy.
- 6 a Electrophilic substitution
  - **b** Electrophilic addition
  - ${\boldsymbol{c}}\xspace$  Radical substitution
  - ${\boldsymbol{d}}$  Radical addition

# Section 13.1

- **1 a** trichloromethane
  - **b** 2-chloropropane
  - **c** 1,1,1,-trichloro-2,2,2-trifluoroethane
  - **d** 2-chloro-1,1,1-trifluoropropane
  - e 2,2–dibromo–3–chlorobutane



3 a CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl(l) + NaOH(aq)
 → CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH(aq) + NaCl(aq)
 b The chlorine atom in 1-chloropropane has been replaced by a hydroxyl group, -OH.

4 a H Cl  

$$H - C - C - C - Cl$$
  
 $H - C - C - Cl$   
 $H - Cl$   
b F F H  
 $H - C - C - C - H$   
 $H - C - C - C - H$   
 $H - C - C - C - H$   
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 $H - H - H$   
 $H - C - H$   
 $H - H - H$   
 $H - C - H$   
 $H - H - H$   
 $H - H$   
 $H - H - H$   
 $H -$ 

 $\mathbf{c} \begin{bmatrix} \mathbf{x} \mathbf{x} & \mathbf{x} \\ \mathbf{H} \mathbf{x} & \mathbf{O} \mathbf{x} \\ \mathbf{x} \mathbf{x} \end{bmatrix}^{-1}$ 



**c d** Explanation along similar lines to that on pages 302–303 in **Chemical Ideas**. Ammonia is the nucleophile because of its lone pair.

8 a 1-iodopentane (or bromo or chloro); aqueous NaOH; reflux.

- **b** 2-iodopropane (or bromo or chloro): concentrated aqueous solution of NH<sub>3</sub> (heat under pressure in a sealed tube).
- c 1-iodopropane (or bromo or chloro); alcoholic solution of KCN (or NaCN); reflux.
- 9 **a**  $CH_3I \xrightarrow{bv} CH_3 \cdot + I \cdot CH_3Cl \xrightarrow{bv} CH_3 \cdot + Cl \cdot$ 
  - **b** Bond enthalpy of C–I bond is less than that of C–Cl bond. C–I bond can be broken by ultraviolet radiation in the troposphere although this has relatively less energy than the ultraviolet radiation in the stratosphere.

# Section 13.2

- **1 a** pentan-1-ol **b** heptan-3-ol
  - **c** butane-2,3-diol
  - **d** cyclohexanol

 $\frac{1}{2}$ 

g decanol

ethoxypropane

e 2-methylbutan-2-ol

f ethoxypropane

0~~~~

methoxybutane

0~~~

Some students may give this isomer:



- a Hydrogen bonding between ethanol and water molecules (see Chemical Ideas, page 306). As the hydrocarbon chain becomes longer, the importance of the –OH group relative to that of the alkyl group becomes less and hexanol is unable to mix with water.
  - ${\boldsymbol{b}}$  No hydrogen bonding occurs.

# Section 13.3

- **1 a** methanoic acid
  - **b** pentanoic acid
  - ${\bf c}\,$  2-methylbutanoic acid
- **2 a** butanoic acid
  - **b** octanoic acid
  - **c** pentanedioic acid





4



- 4 a B D F b A c C d E e A and B; C and F f A
  - gЕ
- 5 a Ethanol has hydrogen bonds between molecules, ethane does not. Hydrogen bonds require more energy to be broken than the weak attractive forces between ethane molecules, so boiling point of ethanol is higher.
  - **b** Water forms more hydrogen bonds than ethanol so its boiling point is higher.
  - **c** Both have –OH group and form hydrogen bonds between molecules. Boiling point increases down a homologous series as  $M_r$  increases. Hence butan-1-ol has a higher boiling point than ethanol.
  - **d** Butan-1-ol forms hydrogen bonds, ethoxyethane does not. Hence boiling point of butan-1-ol is higher.



#### **SECTION I3**

#### Section 13.4



O<sup>−</sup>Na⁺

2-methylpropanal

cyclohexanone

(salicylic acid)

—н

—н

2-hydroxybenzoic acid

# Section 13.5.

- **1 a** methyl propanoate
  - **b** propyl ethanoate
  - **c** ethyl propanoate
  - **d** methyl methanoate **e** methyl butanoate

# **a** and **b** -

#### **a** and **b** Ester Alcohol Acid ethyl methanoate ethanol methanoic acid $-C - O - CH_2CH_3$ $\parallel O$ H - C - OH $CH_3CH_2 - OH$ Ö 3-methylbutyl ethanoate 3-methylbutanol ethanoic acid $CH_3 - C - OH$ $\mathrm{CH}_3 - \mathrm{C} - \mathrm{O} - \mathrm{CH}_2\mathrm{CH}_2\mathrm{CH}\mathrm{CH}_3$ CH<sub>3</sub>CHCH<sub>2</sub>CH<sub>2</sub>OH 0 ö CH<sub>3</sub> ethyl 2-methylbutanoate ethanol 2-methylbutanoic acid $\begin{array}{c} \mathsf{CH}_3\mathsf{CH}_2\mathsf{CH}-\mathsf{C}-\mathsf{O}-\mathsf{CH}_2\mathsf{CH}_3\\ | & \|\\ \mathsf{CH}_3 & \mathsf{O} \end{array}$ $CH_3CH_2CH - C - OH$ $CH_3CH_2 - OH$ CH<sub>3</sub> Ö phenylmethyl ethanoate phenylmethanol ethanoic acid 0 $CH_2 - O - C - CH_3$ CH<sub>2</sub>OH $CH_3 - C - OH$

**c** They are structural isomers.

**5 a** The C–O bond next to the C=O in the ester is broken.



- **b** The C=O bond is very polar with a  $\delta$ + charge on the carbon atom. Hydrolysis occurs by nucleophilic attack on this carbon atom by a lone pair on the oxygen-18 of a water molecule and the C–O bond break.
- **c** A hydrogen ion attaches itself to the oxygen of the carbonyl group, and thus makes the carbon atom in the group more susceptible to attack by a nucleophile (eg water).



A water molecule attacks the positive carbon atom, the  $CH_3$ - $CH_2$ - $O^-$  group is displaced and combines with H<sup>+</sup> to form ethanol.

#### SECTION 13

7

ĊH<sub>3</sub>



4-methylphenol

CH<sub>3</sub>COCl (ethanoyl chloride) or CH<sub>3</sub>CO-O-COCH<sub>3</sub> (ethanoic anhydride) Mix the reagents carefully. If the anhydride is used, warm the mixture under reflux.

ethanoyl chloride, CH<sub>3</sub>COCl ethanoic anhydride (CH<sub>3</sub>CO)<sub>2</sub>O  $\mathbf{c}$  H<sub>2</sub>O, water HCl, hydrogen chloride

$$CH_3COOH$$
, ethanoic acid **d** O

$$\begin{array}{c} H_2 - O - C - CH_3 & CH_2OH \\ + H_2O & + CH_3COOH \end{array}$$

e Becomes increasingly vinegary.



200

- **2 a**, **b** 1 mole glycerol (propane-1,2,3-triol) 2 moles oleic acid
  - 1 mole linoleic acid
- **3 a** Saturated fats are esters of fatty acids with no (or few) carbon double bonds.
  - **b** Monounsaturated fats contain fatty acids with one carbon double bond (such as oleic acid).
  - ${\bf c}\,$  Polyunsaturated fats contain a high proportion of fatty acid groups with two
  - or more carbon double bonds (such as linoleic acid).



- **c** The hydrocarbon chain Instantaneous dipole–induced dipole forces
- **d** Soaps are sodium and potassium salts of long chain carboxylic acids. The ions in solution are readily hydrated.
- **5 a** 150 °C; pressure (5 atmospheres); nickel as catalyst
  - **i**  $M_{\rm r} = 882$
  - ii  $1.13 \times 10^3$  moles of oil react with  $2.45 \times 10^3$  moles of hydrogen
  - **iii** 4

b

- iv 4 moles
- **v** To fully saturate 1 tonne of oil would require  $1.13 \times 10^3 \times 4$  moles hydrogen =  $4.52 \times 10^3$  moles

Percentage of double bonds hydrogenated =  $\frac{2.45 \times 10^3}{4.52 \times 10^3} \times 100 = 54.2\%$ 

vi Easier to spread (less hard); healthier

## Section 13.7\_

- **1 a** methanal
  - **b** propanal
  - $\mathbf{c}$  4-methylpentanal
- **a** butan-2-one**b** pentan-3-one







- between amine and solvent molecules.
- **c**  $[Cu(H_2O)_6]^{2+} + 4C_4H_9NH_2$  $\rightarrow$   $[\tilde{\text{Cu}}(\text{C}_4\text{H}_9\text{NH}_2)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{H}_2\text{O}$ blue deep blue

 $(cf [Cu(NH_3)_4(H_2O)_2]^{2+})$ 

202

CH N−H CΓ CH<sub>3</sub>-CH<sub>2</sub>-COOH + CH2 – NH — C — CH₃

HCI

HCI

d Product: O

#### Section 13.9 н R 1 a 0 -ċ—o-Н· C -- N н н CH<sub>3</sub> CH<sub>3</sub> b i СГ H<sub>3</sub>N — CH — СООН $H_2N - CH - COOH$ HCI ii CH<sub>2</sub>OH CH<sub>2</sub>OH $H_{2}N - CH - COO^{-} Na^{+}$ $(CH_{2})_{4}NH_{3} CI^{-}$ $(CH_{2})_{4}NH_{3} CI^{-}$ $H_{3}N - CH - COOH$ $H_{2}N - CH - COOH + NaOH$ $(CH_{2})_{4}NH_{2}$ $H_{2}N - CH - COOH + 2HCI$ H<sub>2</sub>O iii 2HCI CH<sub>2</sub>COO<sup>-</sup>Na<sup>+</sup> | H<sub>2</sub>N — CH — COO<sup>-</sup>Na<sup>+</sup> + СН₂СООН | iv $H_2N - CH - COOH +$ 2NaOH 2H<sub>2</sub>O $\begin{array}{cccc} CH_{3} & O & CH_{3} & CH_{3} \\ | & || \\ H_{2}N - CH - C - OH & CH & O \\ | & || \\ H_{2}N - CH - C - OH \end{array}$ 2 OH The salts will be formed in the presence of HCl(aq), for example СІ<sup>-</sup> H<sub>3</sub><sup>+</sup>, - CH<sub>2</sub> - С - ОН



**c** Key points which should be included are: correct choice of solvent; the container used for the separation should have a lid; authentic samples of the amino acids used alongside the reaction mixture;  $R_{\rm f}$  values carefully measured.

#### Section 13.10\_



4 The diazonium salt is a relatively weak electrophile and will only react with particularly electron-rich activated benzene rings.

# Section 14.1

- **1 a** 73.9% **b** 73.1%
- 2 Route I (Route I 40%; Route II 30%)
- **3** 16.2 g
- 4 a (Selection of starting materials); reaction; extraction of product from reaction mixture; purification of product.

# Section 14.2

- **1 a** A solution of hydrogen bromide (HBr) in a polar solvent at room temperature.
  - ${\bf b}$  Reflux with dilute aqueous sodium hydroxide solution

- **b** A small amount of product is never recovered from the reaction mixture. This is due to factors such as wetting of the walls of the reaction vessel, incomplete crystallisation of the product, loss on filter papers, loss by evaporation, etc.
- **c** Reflux with an acidified solution of potassium dichromate(VI)
- **d** Treat with hydrogen cyanide solution with a small amount of alkali.

- **2 a** Addition; electrophilic
  - **b** Substitution; nucleophilic
  - $\boldsymbol{c} \ \, \text{Oxidation}$
  - **d** Addition; nucleophilic
- 3 a Radical substitutionb The mechanism is:



**b** Electrophilic substitution

с

4 a

 $\mathbf{c}$  AlCl<sub>3</sub> helps to polarise the chlorine molecule, to produce the electrophile, Cl<sup>+</sup>



**5 a i** Reagents and condition: treat with a nitrating mixture (conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub>); keep temperature below 55 °C.



- **iii** Reactant: CH<sub>3</sub>Cl (or CH<sub>4</sub>)
- iv Reactant: CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-X (X = Cl, Br, I) v Products:

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ HO - C - CH_2 - CH_2 - C - OH + 2HCI \end{array}$$

vi Products:

$$\bigcirc CH_3 \\ \parallel \\ C-CH-CH_2-CH_3 + HCI$$

- **b i** Electrophilic substitution
  - ii Electrophilic addition
  - iii Radical substitution
  - iv Nucleophilic substitution
  - **v** Nucleophilic substitution
  - vi Electrophilic substitution

6 a i 
$$\bigcirc$$
  $- COO^- Na^+ + H_2O$   
ii  $CH_3COO^- Na^+ + \bigcirc$   $- NH_2$   
iii  $\bigcirc$   $+ H_2O$   
iv  $CH_3 - CH_2 - OH$ 

$$\mathbf{v}$$
  $\bigcirc$  +  $3H_2$   $\xrightarrow{Pt}$   $\bigcirc$ 

**b i** Acid–base

- ii Hydrolysis
- iii Dehydration
- iv Esterification
- **v** Reduction
- **c** Examples may be:

i 
$$CH_3COOH + NaOH \longrightarrow CH_3COO^- Na^+ + H_2O$$

ii 
$$CH_3 - C - NH - CH_3 + NaOH$$
  
 $\downarrow O$   
 $CH_3COO^-Na^+ + CH_3NH_2$ 

iii 
$$CH_3 - CH_2 - OH \xrightarrow{Al_2O_3} CH_2 = CH_2 + H_2O$$



7 **a** React with hydrogen in presence of finely divided nickel at 150 °C and 5 atm.

$$CH_3 - CH_2 - CH = CH - CH_2 - COOH + H_2$$
  
 $\downarrow$   
 $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - COOH$ 

**b** Treat with a solution of HBr in a polar solvent at room temperature.

$$CH_{3}-CH_{2}-CH=CH-CH_{2}-COOH + HBr$$

$$\downarrow$$

$$CH_{3}-CH_{2}-CH-CH_{2}-CH_{2}-COOH$$
(+ isomer)

**c** Hydrolyse by refluxing with a dilute aqueous solution of NaOH.

$$CH_{3} - CH_{2} - CH - CH_{2} - CH_{2} - COOH + 2NaOH$$
(prepared as in **b**)

 $\begin{array}{c} & \text{OH} \\ I \\ \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{COO}^- \text{Na}^+ + \text{NaBr} + \text{H}_2\text{O} \\ \text{Then acidify with dilute acid.} \end{array}$ 

$$\begin{array}{c} OH\\ CH_3-CH_2-CH-CH_2-CH_2-COO^-Na^+ + HCH\\ \downarrow\\ OH\\ CH_3-CH_2-CH-CH_2-CH_2-COOH + NaCH \end{array}$$

**d** Dehydrate by heating with  $Al_2O_3$  at 300 °C or by heating with concentrated sulphuric acid.

 $CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-COOH \rightarrow CH_{3}-CH=CH-CH_{2}-CH_{2}-COOH$ (prepared as in c) + H<sub>2</sub>O



NO<sub>2</sub>

# Section 15.1

**a** Continuous

NO<sub>2</sub>

- **b** Batch
- **c** Continuous
- **d** Continuous

# Section 15.2

a Conditions: lower pressure, or less separation required.
 Feedstock: methanol can be obtained from a variety of feedstocks.
 Product: higher yield
 Co-products: far fewer.

# Section 15.3

- **2 a i** As 3 moles of gas form 1 mole of gas, increasing the pressure will cause more methanol to form.
  - **ii** As the conversion of synthesis gas to methanol is exothermic, an increase in temperature will reduce the equilibrium yield of methanol.
  - **b i** The pressure of 100 atm will increase the yield. The temperature is not too high, otherwise the yield is decreased. It is sufficient to provide a high

# Section 15.4

**a** Thermal energy released from the reaction can be used to pre-heat, via a heat exchanger, the water which will be made into steam as one of the reactants.

**b** Disadvantages: very expensive catalyst, and more than one stage to process.

NH<sub>c</sub>

rate of reaction with the catalyst used. It is carefully controlled to prevent the exothermic reaction raising the temperature and reducing the yield.

- **ii** The catalyst lowers the temperature required to give a high rate of reaction. However, some sacrifice in yield is made to maintain this rate. The high pressure also increases the reaction rate.
- **b** The unreacted feedstock can be recycled again over the catalyst, saving costs of energy needed in the high temperature and pressure conditions.

# Section 15.5

- a Many of the fixed costs for a 200 tonne day<sup>-1</sup> plant are less than double those of a 100 tonne day<sup>-1</sup> plant: for example, the larger plant will require less than twice the area of land for building, and the cost of building access roads will be less than twice as great.
  - **b** You have to pay the same fixed costs such as wages and land rental regardless of how much you are producing. But variable costs such as costs of raw materials and energy will double if you double output.

¢φ
\$
\$
\$
\$
\$

The Netherlands	$3.7 \times 10^5 \text{ US}$ \$
Switzerland	$3.7 \times 10^5 \text{ US}$ \$
Ireland	7.9 × 10 <sup>5</sup> US\$
Sweden	$2.7 \times 10^5 \text{ US}$ \$
<b>b</b> Ireland	

- **c** The costs of operating in each country (general level of wages; workforce productivity; taxation policies); the age and inherent efficiency of the plant in each of the countries if similar products are being made; the type of product each country produces; some of these factors are controlled by political forces, others are the results of decisions and developments in the past.
- **d** It may be that a country's chemical industry is biased towards products that need a larger number of employees. Thus, one should also look at other statistics such as profits per employee.