# Section 5.5 -

- **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 increase. In liquids, rotational, vibrational and translational energy increase. 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 instantaneous dipole-induced dipole H<sub>2</sub>O permanent dipole-permanent dipole hydrogen bonding.
  - $H_2S$ 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.
- Section 5.7 -

ii Intermolecular bonds 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  $H_2Te$ . Hydrogen bonding forces are much stronger than other intermolecular bonds 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 bonds in a substance gets weaker as its relative molecular mass gets smaller. This produces a lower boiling point. The boiling point of H<sub>2</sub>O should be lower than that of H<sub>2</sub>S, but it is in fact much higher. This suggests that, compared to H<sub>2</sub>S, a different and much stronger type of intermolecular bonding exists in H<sub>2</sub>O.
- ii All have instantaneous dipole-induced dipole С bonds.
  - 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.



- **b** HO–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–OH and С
- HO CH C OH
- Polarity increases from -CH<sub>3</sub> to -Cl to -CN so the 3 intermolecular bonds become stronger, which leads to an increase in  $T_{o}$ .
- 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 bonds between the chains.

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

### Section 5.8



2

iv	O-C-O	simple molecular	(covalent)
			( /

- i See Figure 1, page 88, Chemical Ideas.ii Covalent network or giant covalent.
- **d** The diagram should be similar to Figure 15, page 41, **Chemical Ideas**. There will be 2+ charges on the positive ions as the metal is magnesium. The outer electrons, two from each magnesium atom, contribute to a 'pool' of electrons which move randomly through the lattice of positive ions. Each positive ion is attracted to the negatively charged delocalised electrons and vice versa.

	Name	State at room temperature	Solubility in water	Electrical conductivity
a	sodium iodide	solid	soluble	conducts when molten or in aqueous solution
b	carbon monoxide	gas	insoluble	does not conduct
с	diamond	solid	insoluble	does not conduct
d	tetrachloro- methane	liquid	insoluble	does not conduct
e	ethanol	liquid	soluble	does not conduct
f	copper(II) chloride	solid	soluble	conducts when molten or in aqueous solution
g	vanadium	solid	insoluble	conducts when solid or liquid
h	poly(propene)	solid	insoluble	does not conduct

С

3 a Isolated atoms

4

- **b** Metallic; giant lattice
- c Covalent network (or giant covalent); giant lattice
- d Macromolecular; covalent molecular
- e Ionic; giant lattice
- **f** Simple molecular; covalent molecular
- **a** Macromolecular; covalent molecular
- **b** Metallic; giant lattice
  - **c** Ionic; giant lattice
  - **d** Metallic; giant lattice
- e Simple molecular; covalent molecular
- 5 a In ionic substances, the charge-carriers (ions) are held 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.
- **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 bonds between simple molecules.

#### Section 6.6 \_

a	3	
b	Chemical shift	Relative number of protons
	1.0	3
	2.1	3
	2.4	2
C (	LCH <sub>3</sub> -CH <sub>2</sub> -CO-CI 1.0 2.4 2	H <sub>3</sub> .1
a l	• Tartaric acid 3 sig	mals 1:1:1
	Succinic acid 2 si	gnals $2:1$
a		15 1. 7. 9
	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)
С	CH <sub>3</sub> -CH <sub>2</sub> -OH	
	<b>E</b> is ethanol.	
a	Chemical shift	Relative number of protons
	1.3 2.0	9 1
b	CH <sub>2</sub> (1.3), OH (2	.0)
c	CH <sub>3</sub>	
	H <sub>3</sub> C — C — OH	
	CH <sub>3</sub>	
	<b>F</b> is 2-methylprop	ban-2-ol.
0	Chemical shift	Relative number of protons
1	.2	3 2
7	7.0-7.4	5
. ,		
H <sub>3</sub> (*	1.2), (C <b>F</b>	H <sub>2</sub> —R (2.7), H (7.0-7.4)
<b>⊣</b> 3 (†	1.2), () — CH	$H_2 = H(2.7), H = (7.0-7.4)$

G is ethylbenzene.

# 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.



H is ethyl ethanoate.

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



8 a

CHO (9.8)

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 ( $CH_3$  and  $C_6H_4$ ), 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.

- **4 a**  $6.97 \times 10^{14}$  Hz.
  - **b**  $8.57 \times 10^{14}$  Hz.
  - **c**  $4.29 \times 10^{14}$  Hz.

It absorbs violet, blue and green light.

Cyanidin contains an extended delocalised

show a smaller excitation energy.

(conjugated) electron system. The electrons in such

in single bonds or in isolated double bonds. The

excitation energy corresponds to the visible region. Molecule absorbs orange light; the diagram should

systems require less energy to excite them than those

 $(\lambda = 530 \,\text{nm} - 700 \,\text{nm}).$ 

 $(\lambda = 400 \text{ nm}-530 \text{ nm})$  but reflects yellow and red light.

# Section 6.8



- **b** A reflectance spectrum of a black pigment would show a low percentage of reflected light for all wavelengths in the visible region.
- 3 a Spectrum (a)  $\lambda_{max} = 440 \text{ nm (approx.)}$ Spectrum (b)  $\lambda_{max} = 420 \text{ nm (approx.)}$

**b** Spectrum (b) corresponds to haemoglobin.

#### 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.

  - c An extended delocalised system of electrons.

#### Section 7.2



- 3  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ 
  - **a**  $K_{\rm c} = \frac{[{\rm NH}_3({\rm g})]^2}{[{\rm N}_2({\rm g})] [{\rm H}_2({\rm g})]^3}$

a Red ochre.

4

2 a

b

h

- **b**  $K_c = 2.09 \text{ mol}^{-2} \text{ dm}^6$ **a**  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$
- **b**  $K_{c} = \frac{[H_{2}O(g)]^{2}}{[H_{c})^{1/2}[O(g)]^{2}}$

**c** 
$$\mathbf{K}_{c} = \frac{[H_{2}(g)]^{2}}{[H_{2}(g)]^{2}} \begin{bmatrix} O_{2}(g) \end{bmatrix}$$

- **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**  $0.196 \,\mathrm{mol}\,\mathrm{dm}^{-3}$

7 **a** 
$$K_{c} = \frac{[\Pi_{2} \circ (g)]}{[\Pi_{2}(g)]^{2} [S_{2}(g)]}$$
  
**b** At equilibrium [S\_{c}(g)]:

**b** At equilibrium, 
$$[S_2(g)] = \left(\frac{0.112}{9.4 \times 10^5 \times 0.234^2}\right) \mod dm^{-5}$$
  
= 3.80 × 10<sup>-6</sup> mol dm<sup>-3</sup>

 $0.442^{2}$ 

**b** 
$$K_{\rm c} = \frac{[{\rm NO}({\rm g})]^2 [{\rm O}_2({\rm g})]}{[{\rm NO}_2({\rm g})]^2}$$

- c 0.083 mol dm<sup>-3</sup>
- $\mathbf{d}$  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).
- **a**  $K_{\rm c} = \frac{[{\rm CH}_{3}{\rm CH}({\rm OC}_{2}{\rm H}_{5})_{2}({\rm l})] [{\rm H}_{2}{\rm O}({\rm l})]}{[{\rm C}_{2}{\rm H}_{5}{\rm OH}({\rm l})]^{2}[{\rm CH}_{3}{\rm CHO}({\rm l})]}$
- **b** Reactants
- **D** Reacta

9

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

It absorbs violet, blue and green light.

Cyanidin contains an extended delocalised

show a smaller excitation energy.

(conjugated) electron system. The electrons in such

in single bonds or in isolated double bonds. The

excitation energy corresponds to the visible region. Molecule absorbs orange light; the diagram should

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a Red ochre.

4

2 a

b

h

- **b**  $K_c = 2.09 \text{ mol}^{-2} \text{ dm}^6$ **a**  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$
- **b**  $K_{c} = \frac{[H_{2}O(g)]^{2}}{[H_{c})^{1/2}[O(g)]^{2}}$

**c** 
$$\mathbf{K}_{c} = \frac{[H_{2}(g)]^{2}}{[H_{2}(g)]^{2}} \begin{bmatrix} O_{2}(g) \end{bmatrix}$$

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- **b** Reactants
- **D** Reacta

9

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- **10** Likely to be low.

# Section 7.3 –

- **1 a** X = 0.75; Y = 0.25
  - **b** Compared with compound X, compound Y has a greater affinity for the stationary phase and/or a lower affinity for the mobile phase.
  - С To maintain constant conditions in which the space around the thin layer is saturated with solvent vapour.
- 2 Retention time depends on the affinity of the а compound for the stationary phase compared with 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.
  - The extent to which a compound distributes itself b 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

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.

- С 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 а Ratio of *cis*: trans isomers was 1:1.4.

4

- b They are likely to be similar because they are isomers. **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.
- All the times would be longer and the peaks would be С further apart.

# Section 8.1 \_\_\_\_

1	Acid donates hydrogen ions/protons and the base accepts
	hydrogen ions/protons.

- **a**  $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ 2 acid base
  - **b**  $NH_3 + H_2O \rightarrow NH_4^+ + OH^$ base acid
  - $\mathbf{c}$  NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup>  $\rightarrow$  NH<sub>3</sub> + H<sub>2</sub>O acid base
  - **d**  $SO_4^{2-}$  +  $H_3O^+ \rightarrow HSO_4^{-}$  +  $H_2O$ base acid
  - $\mathbf{e} \quad \mathrm{H}_{2}\mathrm{O} + \mathrm{H}^{-} \rightarrow \mathrm{H}_{2} + \mathrm{O}\mathrm{H}^{-}$ acid base
  - $H_3O^+ + OH^- \rightarrow 2H_2O$ f acid base
  - $NH_3 + HBr \rightarrow NH_4^+ + Br^$ g base acid
  - **h**  $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$ acid base
  - $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$ i acid base
- **a** Acid–base 3
  - **b** Acid–base c Redox
    - d Redox

# Section 8.2 \_

1	a	$[H^+(aq)] = 1 \times 10^{-2} \text{ mol dm}^{-3}; \text{ therefore } pH = 2$
	b	$[H^+(aq)] = 2 \times 10^{-1} \text{ mol dm}^{-3}; \text{ therefore pH} = 0.7$
	с	$[H^+(aq)] = 4 \times 10^{-1} \text{ mol dm}^{-3}$ ; therefore pH = 0.4
	d	$[H^+(aq)] = 4 \times 10^{-1} \text{ mol dm}^{-3}$ ; therefore pH = 0.4
2	a	$1.7 \times 10^{-5} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{1 \times 10^{-1}}$
		$[H^+(aq)]^2 = 1.7 \times 10^{-6} \text{mol}^2 \text{dm}^{-6}$
		$[H^+(aq)] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$
		pH = 2.9
	b	$1.7 \times 10^{-5} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{5 \times 10^{-2}}$
		$[H^+(aq)]^2 = 8.5 \times 10^{-7} \text{mol}^2 \text{dm}^{-6}$
		$[H^+(aq)] = 9.2 \times 10^{-4} \text{ mol dm}^{-3}$
		pH = 3.0
	c	$6.3 \times 10^{-5} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{1 \times 10^{-3}}$

4		Conjugate pairs:	acid	base
	a		$\mathrm{NH_4}^+$	NH <sub>3</sub>
			$H_3O^+$	$H_2O$
	b		$H_2SO_4$	$HSO_4^{-}$
			$H_2NO_3^+$	HNO <sub>3</sub>
	с		$HClO_4$	$\text{ClO}_4^-$
			CH <sub>3</sub> COOH <sub>2</sub> <sup>+</sup>	CH <sub>3</sub> COOH
5	a	$CH_3COOH + OH$	$H^- \rightarrow CH_3COO^$	$+ H_2O$
		Conjugate pairs:	acid	base
			CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>
			$H_2O$	OH-
	b	$\text{HCO}_3^- + \text{HCl} \rightarrow$	$H_2CO_3 + Cl^-$	
		Conjugate pairs:	acid	base
			HCl	Cl-
			$H_2CO_3$	HCO3 <sup>-</sup>
	с	$H_2O + HSO_4^- \rightarrow$	$SO_4^{2-} + H_3O^+$	
		Conjugate pairs:	acid	base
			$HSO_4^-$	$SO_{4}^{2-}$
			$H_{a}O^{+}$	H <sub>2</sub> O

- $[H^+(aq)]^2 = 6.3 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$
- $[H^+(aq)] = 2.5 \times 10^{-4} \,\text{mol}\,\text{dm}^{-3}$ 
  - рН = 3.6
- **d**  $1.6 \times 10^{-4} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{2.5}$ 

  - $[H^+(aq)]^2 = 4.0 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$
  - $[H^+(aq)] = 2.0 \times 10^{-2} \, mol \, dm^{-3}$
  - pH = 1.7

4

- 3 The reaction of the acid with water goes to completion. а b  $[H^{+}(aq)] = [A^{-}(aq)]$ 
  - [HA(aq)] at equilibrium = original [HA(aq)].
  - Strong acid hydrochloric acid Weak acid - nitric(III) acid
  - b The position of the equilibrium for the reaction of the strong acid with water is completely to the right:  $HCl(aq) + H_2O(l) \rightarrow Cl^{-}(aq) + H_3O^{+}(aq)$

# Section 7.3 –

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		$[H^+(aq)] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$
		pH = 2.9
	b	$1.7 \times 10^{-5} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{5 \times 10^{-2}}$
		$[H^+(aq)]^2 = 8.5 \times 10^{-7} \text{mol}^2 \text{dm}^{-6}$
		$[H^+(aq)] = 9.2 \times 10^{-4} \text{ mol dm}^{-3}$
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	с		$HClO_4$	$\text{ClO}_4^-$
			CH <sub>3</sub> COOH <sub>2</sub> <sup>+</sup>	CH <sub>3</sub> COOH
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		Conjugate pairs:	acid	base
			CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>
			$H_2O$	OH-
	b	$\text{HCO}_3^- + \text{HCl} \rightarrow$	$H_2CO_3 + Cl^-$	
		Conjugate pairs:	acid	base
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			$H_2CO_3$	HCO3 <sup>-</sup>
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			$H_{a}O^{+}$	H <sub>2</sub> O

- $[H^+(aq)]^2 = 6.3 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$
- $[H^+(aq)] = 2.5 \times 10^{-4} \,\text{mol}\,\text{dm}^{-3}$ 
  - рН = 3.6
- **d**  $1.6 \times 10^{-4} = \frac{[\mathrm{H}^+(\mathrm{aq})]^2}{2.5}$ 

  - $[H^+(aq)]^2 = 4.0 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$
  - $[H^+(aq)] = 2.0 \times 10^{-2} \, mol \, dm^{-3}$
  - pH = 1.7

4

- 3 The reaction of the acid with water goes to completion. а b  $[H^{+}(aq)] = [A^{-}(aq)]$ 
  - [HA(aq)] at equilibrium = original [HA(aq)].
  - Strong acid hydrochloric acid Weak acid - nitric(III) acid
  - 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  $H^+(aq)$  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  $H^+(aq)$  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 nitric(III) acid solution must be more concentrated than the hydrochloric acid solution.

5	$[OH^{-}(aq)]/mol dm^{-3}$	$[H^+(aq)]/mol dm^{-3}$	рН
а	1	$1 \times 10^{-14}$	14
b	0.01	$1 \times 10^{-12}$	12
С	0.2	$5 \times 10^{-14}$	13.3

### Section 8.3 -

- **1 a**  $1.6 \times 10^{-4} \text{ mol dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{0.1 \text{ mol dm}^{-3}}{0.1 \text{ mol dm}^{-3}}$ Therefore  $[H^+(aq)] = 1.6 \times 10^{-4} \,\text{mol}\,\text{dm}^{-3}$ pH = 3.8
  - **b**  $6.3 \times 10^{-5} \,\mathrm{mol}\,\mathrm{dm}^{-3} = \frac{[\mathrm{H}^+(\mathrm{aq})] \times 0.03 \,\mathrm{mol}\,\mathrm{dm}^{-3}}{10^{-5} \,\mathrm{mol}\,\mathrm{dm}^{-3}}$ 0.01 mol dm<sup>-3</sup> Therefore  $[H^+(aq)] = 2.1 \times 10^{-5} \,\text{mol}\,\text{dm}^{-3}$ pH = 4.7
  - The concentrations of acid and salt in the mixture will С both be  $0.05 \,\mathrm{mol}\,\mathrm{dm}^{-3}$ . This is equivalent to diluting the buffer in **1 a** with an equal volume of water. The pH remains unchanged at 3.8.
  - $1.3 \times 10^{-5} \text{ mol dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{5.0 \times 10^{-3} \text{ mol dm}^{-3}}{1 \times 10^{-1} \text{ mol dm}^{-3}}$ d Therefore  $[H^+(aq)] = 2.6 \times 10^{-4} \,\text{mol}\,\text{dm}^{-3}$ nH - 36

e 
$$1.6 \times 10^{-4} \text{ mol dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{2 \times 1.5 \times 10^{-2} \text{ mol dm}^{-3}}{2 \times 5 \times 10^{-3} \text{ mol dm}^{-3}}$$
  
[H<sup>+</sup>(aq)] =  $5.3 \times 10^{-5} \text{ mol dm}^{-3}$ 

**f** In  $750 \text{ cm}^3$  of solution the concentrations of acid and salt are

$$[acid] = \frac{0.1 \times 250 \text{ mol dm}^{-3}}{750}$$
$$[salt] = \frac{0.1 \times 500 \text{ mol dm}^{-3}}{750}$$

### Section 9.2

- **1** a  $Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ 
  - $6H^+(aq) + 6e^- \rightarrow 3H_2(g)$  $2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^{-1}$ b
  - $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$  $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{+}$ С
- **d**  $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$  $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}$
- **e**  $S(s) + 2e^- \rightarrow S^{2-}(s)$  $Zn(s) \rightarrow Zn^{2+}(s) + 2e^{-s}$ 2
- **a**  $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$
- **b**  $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
- $3Mg(s) + 2Au^{3+}(aq) \rightarrow 3Mg^{2+}(aq) + 2Au(s)$ С
- **d**  $2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^{-}(aq)$
- 3 **a i** 3.16V

b

- **ii** 1.10V
- **iii** 0.18V iv 0.32V
- v 1.36V
- **i**  $Ag^+(aq)/Ag(s)$
- **ii**  $Cu^{2+}(aq)/Cu(s)$
- **iii**  $Ni^{2+}(aq)/Ni(s)$
- iv  $Fe^{2+}(aq)/Fe(s)$
- $MnO_4^{-}(aq)/Mn^{2+}(aq)$ v

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

**b** 
$$K_a = \frac{[\text{H}^+(\text{aq})] [\text{In}^-(\text{aq})]}{[\text{HIn}(\text{aq})]}$$

$$\mathbf{c} \quad K_{a} = 5.01 \times 10^{-10} \operatorname{mol} \mathrm{dm}^{-3}$$
$$= \frac{[\mathrm{H}^{+}(\mathrm{aq})] [\mathrm{In}^{-}(\mathrm{aq})]}{[\mathrm{HIn}(\mathrm{aq})]}$$
At the end point [HIn(aq)]

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

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

 $1.7 \times 10^{-5} \text{ mol } dm^3 = [\text{H}^+(\text{aq})] \times \frac{0.1 \times 500 \text{ mol } dm^{-3}}{0.1 \times 250 \text{ mol } dm^{-3}}$  $[H^+(aq)] = 8.5 \times 10^{-6} \,\text{mol}\,\text{dm}^{-3}$ pH = 5.1

**g**  $1.7 \times 10^{-5} \,\text{mol}\,\text{dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{0.1 \,\text{mol}\,\text{dm}^{-3}}{0.2 \,\text{mol}\,\text{dm}^{-3}}$  $[H^+(aq)] = 3.4 \times 10^{-5} \,\text{mol}\,\text{dm}^{-3}$ 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.

- **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.
    - 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** i  $2Ag^{+}(aq) + Mg(s) \rightarrow 2Ag(s) + Mg^{2+}(aq)$ ii  $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$ iii  $Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$ iv  $Fe^{2+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$  $2MnO_4^{-}(aq) + 5Sn^{2+}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq)$  $+ 5Sn^{4+}(aq) + 8H_2O(l)$  $\tilde{E}^{\ominus} = -0.40 \,\mathrm{V}$  $Cd^{2+}(aq)/Cd(s)$ 4  $E^{\oplus} = -0.28 \text{V}$  $\mathrm{Co}^{2+}(\mathrm{aq})/\mathrm{Co}(\mathrm{s})$ 5  $E^{\oplus} = -0.13 \,\mathrm{V}$  $Pb^{2+}(aq)/Pb(s)$ 6  $Fe^{3+}(aq)/Fe^{2+}(aq) E^{\oplus} = +0.77V$ 7  $E^{\oplus} = +2.85 \mathrm{V}$ 8  $F_2(g)/2F^-(aq)$ 9 K, Ce, Cd, Ni, Sn, Ag  $E^{\ominus} = 0$  V by definition **10**  $2H^+(aq)/H_2(g)$  $E^{\oplus} = -0.13$  V  $Pb^{2+}(aq)/Pb(s)$  $Cd^{2+}(aq)/Cd(s)$   $E^{\ominus} = -0.40V$  $E^{\oplus} = +0.80 \,\mathrm{V}$  $Ag^{+}(aq)/Ag(s)$  $E^{\oplus} = -0.74 \mathrm{V}$  $Cr^{3+}(aq)/Cr(s)$

The amount in moles of  $H^+(aq)$  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  $H^+(aq)$  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 nitric(III) acid solution must be more concentrated than the hydrochloric acid solution.

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

### Section 8.3 -

- **1 a**  $1.6 \times 10^{-4} \text{ mol dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{0.1 \text{ mol dm}^{-3}}{0.1 \text{ mol dm}^{-3}}$ Therefore  $[H^+(aq)] = 1.6 \times 10^{-4} \,\text{mol}\,\text{dm}^{-3}$ pH = 3.8
  - **b**  $6.3 \times 10^{-5} \,\mathrm{mol}\,\mathrm{dm}^{-3} = \frac{[\mathrm{H}^+(\mathrm{aq})] \times 0.03 \,\mathrm{mol}\,\mathrm{dm}^{-3}}{10^{-5} \,\mathrm{mol}\,\mathrm{dm}^{-3}}$ 0.01 mol dm<sup>-3</sup> Therefore  $[H^+(aq)] = 2.1 \times 10^{-5} \,\text{mol}\,\text{dm}^{-3}$ pH = 4.7
  - The concentrations of acid and salt in the mixture will С both be  $0.05 \,\mathrm{mol}\,\mathrm{dm}^{-3}$ . This is equivalent to diluting the buffer in **1 a** with an equal volume of water. The pH remains unchanged at 3.8.
  - $1.3 \times 10^{-5} \text{ mol dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{5.0 \times 10^{-3} \text{ mol dm}^{-3}}{1 \times 10^{-1} \text{ mol dm}^{-3}}$ d Therefore  $[H^+(aq)] = 2.6 \times 10^{-4} \,\text{mol}\,\text{dm}^{-3}$ nH - 36

e 
$$1.6 \times 10^{-4} \text{ mol dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{2 \times 1.5 \times 10^{-2} \text{ mol dm}^{-3}}{2 \times 5 \times 10^{-3} \text{ mol dm}^{-3}}$$
  
[H<sup>+</sup>(aq)] =  $5.3 \times 10^{-5} \text{ mol dm}^{-3}$ 

**f** In  $750 \text{ cm}^3$  of solution the concentrations of acid and salt are

$$[acid] = \frac{0.1 \times 250 \text{ mol dm}^{-3}}{750}$$
$$[salt] = \frac{0.1 \times 500 \text{ mol dm}^{-3}}{750}$$

### Section 9.2

- **1** a  $Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ 
  - $6H^+(aq) + 6e^- \rightarrow 3H_2(g)$  $2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^{-1}$ b
  - $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$  $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{+}$ С
- **d**  $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$  $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}$
- **e**  $S(s) + 2e^- \rightarrow S^{2-}(s)$  $Zn(s) \rightarrow Zn^{2+}(s) + 2e^{-s}$ 2
- **a**  $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$
- **b**  $Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$
- $3Mg(s) + 2Au^{3+}(aq) \rightarrow 3Mg^{2+}(aq) + 2Au(s)$ С
- **d**  $2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^{-}(aq)$
- 3 **a i** 3.16V

b

- **ii** 1.10V
- **iii** 0.18V iv 0.32V
- v 1.36V
- **i**  $Ag^+(aq)/Ag(s)$
- **ii**  $Cu^{2+}(aq)/Cu(s)$
- **iii**  $Ni^{2+}(aq)/Ni(s)$
- iv  $Fe^{2+}(aq)/Fe(s)$
- $MnO_4^{-}(aq)/Mn^{2+}(aq)$ v

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

**b** 
$$K_a = \frac{[\text{H}^+(\text{aq})] [\text{In}^-(\text{aq})]}{[\text{HIn}(\text{aq})]}$$

$$\mathbf{c} \quad K_{a} = 5.01 \times 10^{-10} \operatorname{mol} \mathrm{dm}^{-3}$$
$$= \frac{[\mathrm{H}^{+}(\mathrm{aq})] [\mathrm{In}^{-}(\mathrm{aq})]}{[\mathrm{HIn}(\mathrm{aq})]}$$
At the end point [HIn(aq)]

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

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

 $1.7 \times 10^{-5} \text{ mol } dm^3 = [\text{H}^+(\text{aq})] \times \frac{0.1 \times 500 \text{ mol } dm^{-3}}{0.1 \times 250 \text{ mol } dm^{-3}}$  $[H^+(aq)] = 8.5 \times 10^{-6} \,\text{mol}\,\text{dm}^{-3}$ pH = 5.1

**g**  $1.7 \times 10^{-5} \,\text{mol}\,\text{dm}^{-3} = [\text{H}^+(\text{aq})] \times \frac{0.1 \,\text{mol}\,\text{dm}^{-3}}{0.2 \,\text{mol}\,\text{dm}^{-3}}$  $[H^+(aq)] = 3.4 \times 10^{-5} \,\text{mol}\,\text{dm}^{-3}$ 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.

- **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.
    - 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** i  $2Ag^{+}(aq) + Mg(s) \rightarrow 2Ag(s) + Mg^{2+}(aq)$ ii  $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$ iii  $Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$ iv  $Fe^{2+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$  $2MnO_4^{-}(aq) + 5Sn^{2+}(aq) + 16H^{+}(aq) \rightarrow 2Mn^{2+}(aq)$  $+ 5Sn^{4+}(aq) + 8H_2O(l)$  $\tilde{E}^{\ominus} = -0.40 \,\mathrm{V}$  $Cd^{2+}(aq)/Cd(s)$ 4  $E^{\oplus} = -0.28 \text{V}$  $\mathrm{Co}^{2+}(\mathrm{aq})/\mathrm{Co}(\mathrm{s})$ 5  $E^{\oplus} = -0.13 \,\mathrm{V}$  $Pb^{2+}(aq)/Pb(s)$ 6  $Fe^{3+}(aq)/Fe^{2+}(aq) E^{\oplus} = +0.77V$ 7  $E^{\oplus} = +2.85 \mathrm{V}$ 8  $F_2(g)/2F^-(aq)$ 9 K, Ce, Cd, Ni, Sn, Ag  $E^{\ominus} = 0$  V by definition **10**  $2H^+(aq)/H_2(g)$  $E^{\oplus} = -0.13$  V  $Pb^{2+}(aq)/Pb(s)$  $Cd^{2+}(aq)/Cd(s)$   $E^{\ominus} = -0.40V$  $E^{\oplus} = +0.80 \,\mathrm{V}$  $Ag^{+}(aq)/Ag(s)$  $E^{\oplus} = -0.74 \mathrm{V}$  $Cr^{3+}(aq)/Cr(s)$

#### Section 9.3 -

- $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}; Cl_{2}(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$ overall:  $Cl_2(g) + 2I^{-}(aq) \rightarrow 2Cl^{-}(aq) + I_2(aq)$ 
  - b  $2Br^{-}(aq) \rightarrow Br_2(aq) + 2e^{-};$  $MnO_{4}^{-}(aq) + 8H^{+}(aq) + 5e^{-}$  $\rightarrow$  Mn<sup>2+</sup>(aq) + 4H<sub>2</sub>O(l) overall:  $2MnO_4^{-}(aq) + 16H^{+}(aq) + 10Br^{-}(aq)$  $\rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$
  - $2I^{-}(aq) \rightarrow 2I_{2}(aq) + 2e^{-}; Br_{2}(aq) + 2e^{-} \rightarrow 2Br^{-}(aq)$ С overall:  $2I^{-}(aq) + Br_2(aq) \rightarrow I_2(aq) + 2Br^{-}(aq)$ c No
- 2 **a** Yes d Yes
- **b** Yes
- 3  $2I^{-}(aq) \rightarrow I_{2}(aq) + 2e^{-}$  $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ overall:  $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq)$  $\rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$

# Section 10.3 -

- 1 a The reaction is first order with respect to bromoethane and zero order with respect to hydroxide ion.
  - The reaction is first order with respect to methyl b methanoate, zero order with respect to water and first order with respect to  $H^+$ .
  - С The reaction is first order with respect to urea, zero order with respect to water and first order with respect to urease.
  - **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.
- Rate = k[CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl] [OH<sup>-</sup>] 2 а
- Rate =  $k[C_{12}H_{22}O_{11}]$  [H<sup>+</sup>] b
- a i First order 3
  - ii Second order
  - Rate =  $k[H_2]$  [NO]<sup>2</sup> b
  - $k = 0.384 \,\mathrm{mol}^{-2} \,\mathrm{dm}^{6} \,\mathrm{s}^{-1}$

### Section 10.4

 $(NH_2)_2CO + H_2O \xrightarrow{urease} 2NH_3 + CO_2$ 1 a



- 4 b i No ii No
  - iii Yes
  - a Yes b No

5

- Yes С
- Yes d
- Yes e
- 6  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ a bi ii  $2CH_3OH(aq) + O_2(q) \rightarrow 2HCHO(aq) + 2H_2O(1)$ iii  $2HCHO(aq) + O_2(g) \rightarrow 2HCOOH(aq)$

- **4 b** All are *ca.* 1150s (Allow within 1100–1200s.) First order.
  - Rate =  $k[N_2O_5]$  or  $-d[N_2O_5]/dt = k[N_2O_5]$ e
  - $6.2 \times 10^{-4} \text{ s}^{-1}$  (Method is difficult to use. Allow for an f answer between 5 and  $7 \times 10^{-4} \text{ s}^{-1}$ .)
- 5 а Structural isomerism.
  - **b** 0.5 atm.
- **d**  $t_{\frac{1}{2}}$  is constant and about 55×10<sup>3</sup> s. First order. 6
  - **a** rate = k [CH<sub>3</sub>COCH<sub>3</sub>] [H<sup>+</sup>] **b** Yes. One of the steps has one mole of propanone reacting with one mole of hydrogen ions. Iodine is not involved in this step. This is consistent with the rate equation.
  - Step 1. С
  - **d** Neutralise with an alkali to remove the acid catalyst from the system.
- Mechanism 1, as it is the only mechanism that has a 7 step involving two molecules of B only (step 1). This is consistent with the rate equation. Mechanism 2 has no such step.
  - Mercury ions act as a catalytic poison. They bind to the С active site of the enzyme and render it inoperative.
  - Titrate the ammonia that is liberated in the reaction d using a dilute strong acid such as hydrochloric acid.
- 2 Catechol and 3-hydoxybenzoic acid have similar molecular shapes to each other. 3- hydroxybenzoic acid can enter the active site of the enzyme and bind to the active site. Since it is not converted to products it does not diffuse away from the active site. This means there are fewer active sites for the catechol to enter. With fewer enzyme substrate complexes formed there will be less product formed, so a slower rate of reaction.

# Section 11.3

- 1 The triple bond in  $N_2$  is very strong (bond enthalpy = 945 kJ mol<sup>-1</sup>), so a great deal of activation enthalpy must be supplied before  $N_2$  will react.  $P_4$ , 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**  $\mathbf{a} + 3 \rightarrow + 5$ A
  - $\mathbf{b} + 5 \rightarrow 0$
  - $c -3 \rightarrow -3$ С B
  - $\mathbf{d} \ 0 \rightarrow -3$
  - $e + 2 \rightarrow + 4$ A
- **a** +2 to +1 3
- **b**  $2NO(g) + 2H^+(aq) + 2e^- \rightarrow N_2O(g) + H_2O(l)$
- 4 **a**  $NO_2^{-}(aq) + H_2O(l) \rightarrow NO_3^{-}(aq) + 2H^+(aq) + 2e^{-}$ 
  - **b**  $NO_3^{-}(aq) + 6H^{+}(aq) + 5e^{-} \rightarrow N_2(g) + 3H_2O(l)$
  - **c**  $\operatorname{NH}_4^+(\operatorname{aq}) + \operatorname{OH}_-(\operatorname{aq}) \to \operatorname{NH}_3(g) + \operatorname{H}_2O(l)$
  - **d**  $N_2(g) + 6H^+(aq) + 6e^- \rightarrow 2NH_3(g)$

B

e  $NO(g) + H_2O(l) \rightarrow NO_2(g) + 2H^+(aq) + 2e^-$ 

### Section 11.5 \_\_\_\_\_

1	Element	Electronic configuration	Element	Electronic configuration
	Sc Ti V Cr Mn	[Ar] 3d <sup>1</sup> 4s <sup>2</sup> [Ar] 3d <sup>2</sup> 4s <sup>2</sup> [Ar] 3d <sup>3</sup> 4s <sup>2</sup> [Ar] 3d <sup>5</sup> 4s <sup>1</sup> [Ar] 3d <sup>5</sup> 4s <sup>2</sup>	Fe Co Ni Cu Zn	[Ar] 3d <sup>6</sup> 4s <sup>2</sup> [Ar] 3d <sup>7</sup> 4s <sup>2</sup> [Ar] 3d <sup>8</sup> 4s <sup>2</sup> [Ar] 3d <sup>10</sup> 4s <sup>1</sup> [Ar] 3d <sup>10</sup> 4s <sup>2</sup>
2	<b>a i</b> Cu <sup>2+</sup>	$[Ar] 3d^9 4s^0$		

- [Ar] 3d<sup>10</sup> 4s<sup>0</sup> ii Cu<sup>+</sup> iii Fe<sup>3+</sup>  $[Ar] 3d^5 4s^0$ 
  - $iv V^{3+}$ [Ar] 3d<sup>2</sup> 4s<sup>0</sup>
  - $\mathbf{v}$  Cr<sup>3+</sup>  $[Ar] 3d^3 4s^0$
  - vi Ni<sup>2+</sup>  $[Ar] 3d^8 4s^0$
- $Cu^{2+}$  has a partially filled 3d sub-shell and behaves as a b typical d-block transition metal ion. Cu<sup>+</sup> has a filled 3d sub-shell and cannot show such properties.
- **a** The three transition metals' atoms (Cr, Fe, Co) are the 3 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.
  - The three transition metals are much denser than С sodium and magnesium.
  - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ d Cr
    - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>6</sup> 4s<sup>2</sup> Fe
    - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>7</sup> 4s<sup>2</sup> Со
    - $1s^2 2s^2 2p^6 3s^1$ Na
    - Mg  $1s^2 2s^2 2p^6 3s^2$
  - 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 3d orbital is being filled and most elements have two

- The NO is oxidised by air as in reaction 2, to produce a further  $NO_2$  which takes part in reaction 3.
  - b Ammonium nitrate(V) fertiliser.
  - **c i** 1 mole of  $NH_3 \rightarrow$  mole of  $HNO_3$

$$1000 \text{ kg} \times \frac{63.0}{17.0} \times = 247 \text{ kg}$$

- ii Incomplete reaction at each of the three stages. Loss of intermediates.
- **d** The reactants and intermediates include serious environmental pollutants, particularly NO<sub>x</sub>. Escape of these, even in small quantities, would lead to acid rain and direct effects on living things. The NO<sub>x</sub> could be absorbed in aqueous sodium hydroxide.

electrons in the outer 4s shell. (Chromium is an exception, having only one electron in the 4s shell.) Thus, transition elements have similar properties because they have essentially the same outer electronic arrangement as one another, 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  $E^{\ominus}$  for the O<sub>2</sub>(g),4H<sup>+</sup>(aq)/2H<sub>2</sub>O(l) half-cell is more positive and receives electrons from the Fe<sup>3+</sup>(aq)/  $Fe^{2+}(aq)$  half-cell. So overall,  $O_2$  is reduced to water and the  $Fe^{2+}(aq)$  is oxidised to  $Fe^{3+}(aq)$ .  $O_2(g) + 4H^+(aq) + 4Fe^{2+}(aq) \rightarrow 2H_2O(l) + 4Fe^{3+}(aq)$  $E_{\text{cell}} = +1.23 \text{V} - (+0.77 \text{V}) = +0.46 \text{V}$ The  $E^{\ominus}$  for the O<sub>2</sub>(g),4H<sup>+</sup>(aq)/2H<sub>2</sub>O(l) half-cell is less positive than that for the  $Mn^{3+}(aq)/Mn^{2+}(aq)$ half-cell and so it is not oxidising enough to form Mn(III) from Mn(II). The  $Mn^{3+}(aq)/Mn^{2+}(aq)$  half-cell receives electrons from the  $O_2(g)$ ,  $4H^+(aq)/2H_2O(l)$ half-cell. In the presence of water,  $Mn^{3+}(aq)$  is reduced to  $Mn^{2+}(aq)$  and the water oxidised to oxygen.  $4Mn^{3+}(aq) + 2H_2O(l) \rightarrow 4Mn^{2+}(aq) + O_2(g) + 4H^+(aq)$  $E_{\text{cell}} = +1.56 \text{V} - (+1.23 \text{V}) = +0.33 \text{V}$ 
  - b i An acidified solution of iron(II) will be oxidised by air
    - ii An acidified solution of manganese(II) will not be oxidised by air.
  - The flow of electrons is to the half-cell with the С most positive  $E^{\ominus}$  value. Cu<sup>+</sup>(aq) will be expected to be oxidised to Cu(s) and reduced to  $Cu^{2+}(aq)$ (disproportionation).  $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$  $E_{\text{cell}} = +0.52 \,\text{V} - (+0.16 \,\text{V}) = +0.36 \,\text{V}$

#### Section 11.6.

- 1 a 2 b 4
  - С 6 d 6
- 2  $[Mn(H_2O)_6]^{2+}$ а
- $[Zn(NH_3)_4]^{2+}$ b
  - $[FeF_6]^{3-1}$ С
  - $[Cr(H_2O)_5OH]^{2+}$ d
- 3 +1а
  - b +2
  - +3С
  - d +3
- 4 a Hexaaquavanadium(III) ion
  - **b** Hexacyanoferrate(II) ion
  - Tetrachlorocobaltate(II) ion С
  - **d** Diamminesilver(I) ion
  - e Tetraaquadichlorochromium(III) ion
- **a**  $TiO_2(s)$  contains titanium with a  $3d^0$  electron 5 configuration. It is white as no 3d electron transitions are possible. b
  - Sc<sup>3+</sup> [Ar]
  - $Zn^{2+}$ [Ar] 3d<sup>10</sup>
  - $Cu^+$ [Ar] 3d<sup>10</sup>

No 3d electron transitions possible, hence colourless.

- 6 6 а
  - b +4
  - Hexachlorotitanate(IV) ion С

# *Section* 12.3 -



- A five-membered chelate ring seems to lead to a more 7 stable complex than a six-membered one.
  - **a** Monodentate

8

- Bidentate h
- c Bidentate
- 9 A complex of a metal ion with edta contains six fivemembered chelate ring systems (see Figure 6, page 259 Chemical Ideas). The complex is much more stable than the corresponding complexes with NH<sub>3</sub> or H<sub>2</sub>O, which contain no chelate rings. The extra stability is due to the large increase in entropy when edta<sup>4-</sup> displaces six ligands.
- 1 a i 1,4-dimethylbenzene С OH ii 1-ethyl-3-methylbenzene iii 1,2,4-trimethylbenzene b i d C ii C e iii 4 a 0.154 nm 2 1,3,5-trimethylbenzene a 1-methyl-3-propylbenzene b bromobenzene С -0.134 nm 1,3-dinitrobenzene d 4-methylphenylamine е The ring is not a regular hexagon, but has alternating 2,6-dimethylphenol f long and short bonds. 3 a b b **c** All the bonds in the ring are the same and so only one isomer is possible.  $CH_3$ CH<sub>3</sub>

#### Section 11.6

- **1 a** 2 **b** 4
  - c 6d 6
- **2 a**  $[Mn(H_2O)_6]^{2+}$
- **b**  $[Zn(NH_3)_4]^{2+}$ 
  - **c**  $[FeF_6]^{3-}$
  - **d**  $[Cr(H_2O)_5OH]^{2+}$
- **3 a** +1
  - **b** +2
  - **c** +3
  - **d** +3
- **4 a** Hexaaquavanadium(III) ion
  - **b** Hexacyanoferrate(II) ion
  - **c** Tetrachlorocobaltate(II) ion
  - **d** Diamminesilver(I) ion
  - e Tetraaquadichlorochromium(III) ion
- 5 a TiO<sub>2</sub>(s) contains titanium with a 3d<sup>0</sup> electron configuration. It is white as no 3d electron transitions are possible.
  - Sc<sup>3+</sup> [Ar]
  - $Zn^{2+}$  [Ar]  $3d^{10}$
  - $Cu^+$  [Ar]  $3d^{10}$
  - No 3d electron transitions possible, hence colourless.
- **6 a** 6

b

- **b** +4
- c Hexachlorotitanate(IV) ion

# Section 12.3 \_

- d Cl Cl Cl Cl Cl Cl
- 7 A five-membered chelate ring seems to lead to a more stable complex than a six-membered one.
  - **a** Monodentate

8

- **b** Bidentate
- **c** Bidentate
- 9 A complex of a metal ion with edta contains six fivemembered chelate ring systems (see Figure 6, page 259 Chemical Ideas). The complex is much more stable than the corresponding complexes with NH<sub>3</sub> or H<sub>2</sub>O, which contain no chelate rings. The extra stability is due to the large increase in entropy when edta<sup>4-</sup> displaces six ligands.
- 1 a i 1,4-dimethylbenzene С OH ii 1-ethyl-3-methylbenzene iii 1,2,4-trimethylbenzene b i d C ii C e iii 4 a 0.154 nm 2 1,3,5-trimethylbenzene a 1-methyl-3-propylbenzene b bromobenzene С -0.134 nm 1,3-dinitrobenzene d 4-methylphenylamine е The ring is not a regular hexagon, but has alternating 2,6-dimethylphenol f long and short bonds. 3 a b b **c** All the bonds in the ring are the same and so only one isomer is possible.  $CH_3$ CH<sub>3</sub>



### Section 13.3 -

- methanoic acid 1 a
- 2-methylbutanoic acid с
- butanoic acid 2 a pentanedioic acid С
- acid 3 a Н Н Н Н Н 0 Н С С 0 – H Н Н н н н b Н Н Н Н С C С C - H 0-Н Н Н Н 0-– H с 0 0 Н



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**b** pentanoic acid

**b** octanoic acid



### Section 13.3 -

- methanoic acid 1 a
- 2-methylbutanoic acid с
- butanoic acid 2 a pentanedioic acid С
- acid 3 a Н Н Н Н Н 0 Н С С 0 – H Н Н н н н b Н Н Н Н С C С C - H 0-Н Н Н Н 0-– H с 0 0 Н



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**b** pentanoic acid

**b** octanoic acid

5 
$$O$$
  
H-C  
O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> butyl methanoate  
O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub> propyl ethanoate

$$CH_3 - CH_2 - C''_O - CH_2 - CH_3$$

ethyl propanoate

methyl butanoate

Student may also draw isomers with branched chains, for example.

$$CH_3 - C$$
  
 $O - CH - CH_3$   
 $CH_3$   
 $CH_3$   
 $2$ -propyl ethanoate

## Section 13.4



### Section 13.5

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

2 a b





- **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 breaks.
- carbonyl group, and thus makes the carbon atom in the group more susceptible to attack by a nucleophile (e.g. water).



A water molecule attacks the positive carbon atom, the CH3-CH2-O- group is displaced and combines with H+ to form ethanol.



#### Section 13.6



**3 a** Saturated fats are esters of fatty acids with no carbon–carbon double bonds.

**c** Polyunsaturated fats contain a high proportion of fatty acid groups with two or more carbon–carbon double bonds (such as linoleic acid).

hydrogen.

**iii** 4

v

iv 4 moles

150 °C; pressure (5 atmospheres); nickel as catalyst.

To fully saturate 1 tonne of oil would require

 $=\frac{2.45\times10^3}{4.52\times10^3}\times100=54.2\%.$ 

vi Easier to spread (less hard); healthier.

 $1.13 \times 10^3 \times 4$  moles hydrogen =  $4.52 \times 10^3$  moles Percentage of double bonds hydrogenated

ii  $1.13 \times 10^3$  moles of oil react with  $2.45 \times 10^3$  moles of



- С dipole bonds.
- d Soaps are sodium and potassium salts of long-chain carboxylic acids. The ions in solution are readily hydrated.

# Section 13.7 -

- 1 a methanal
  - propanal b
- 4-methylpentanal С



- 5 a Н Н Н Н Н· C С С С - OH Primary Н Н Н Н b Н ОН Н Н Secondary Н С - H С С С Н Н Н н н С НН-С-НОН Н Secondary С С -H Н С -нн Н ΗН - C Н 6 Н OH а Н Н -С-С-С-Н Н Н С |||Ν b Н Н ОН Н L Н С С С С - H Н Н Н С Ν
  - Similar argument to that seen in Chemical Ideas 13.7 С on addition reactions, pages 318-319.

- 5 a **b** i  $M_r = 882$
- The hydrocarbon chain; instantaneous dipole-induced

## Section 13.8 \_\_\_\_\_

Cl-



**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;  $R_f$  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.
  - ${\boldsymbol{b}} \quad \text{Reflux with dilute aqueous sodium hydroxide solution.}$
  - **c** Reflux with an acidified solution of potassium dichromate(VI).
  - **d** Treat with hydrogen cyanide solution with a small amount of alkali.

- **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.
- **2 a** Addition; electrophilic.
  - **b** Substitution; nucleophilic.
  - **c** Oxidation.
  - **d** Addition; nucleophilic.

#### Section 15.8 \_

- **1** Set 1 B, A, D, C Set 2 D, C, A, B
- **2 a** Benzene method:

Butene method:

 $\frac{98.0}{(78.0 + 144.0)} \times 100 = 44.1\%$  $\frac{98.0}{(56.0 + 96.0)} \times 100 = 64.5\%$ 

**b** The atom economy increased.

# Section 15.9 \_\_\_\_

- **1** Substrate binds reversibly to enzyme, reaction is catalysed and products then leave the enzyme.
- 2 Energy-saving reactions happen at lower temperature. They reduce the number of steps in synthesis. They are more product-specific (thus producing less waste). They can be re-used. They may involve less plant down-time.