



Chapter 1.1

page 13

- Put the milk in a fridge.
 - Warm the mixture but not too much (about 35 °C).
 - e.g. cover the iron with grease.
 - e.g. use more dilute HCl.
- Collect the hydrogen in a gas syringe.
 - Monitor the change in pH.
 - Use a colorimeter.
- Hydrogen has a very low density; there would be little change in the mass of the reaction vessel.
- The gas syringe.
 - The gas syringe; little of the gas would collect in the measuring cylinder method.

page 15

- The mixture will not change colour until all the thiosulfate has reacted with iodine. If there is too much thiosulfate, the solution will not change colour, or will take a very long time to change.
- 1
 - 2
 - 3
 - Rate = $k[\text{NO}]^2[\text{Cl}_2]$
 - $9.15 \times 10^{-5} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

page 19

- It would be hard to determine if the graph was truly a straight line from two points.
- rate = $k[\text{A}]$
 - The graph of rate versus concentration should be a straight line showing that it is first order.
 - 0.01065 s^{-1}
 - In the rate-determining step, A splits up.

page 23

- Have an excess of methanoic acid.
 - You should get the same half-life each time – approximately 180 s.
- I-131 decays in a first order process, so the half-life is constant and doesn't depend on concentration. 24 days is three half-lives. After 8 days, $\frac{1}{2}$ of the original amount remains; after another 8 days, $\frac{1}{4}$ remains; and after 24 days the fraction remaining is $\frac{1}{8}$.

**page 27**

- 1 Lead is adsorbed onto the metal catalyst and is not desorbed. Active sites stop working.
- 2 The catalyst is used up but is then regenerated to be used over again.

page 29

- 1 **a** As T increases E_A / RT decreases and $\ln k$ becomes more positive; that means that k gets larger and so the reaction is faster.
b The larger E_A , the larger the value of E_A / RT and $\ln k$ becomes less positive; that means that k gets smaller and so the rate of reaction gets smaller.
- 2 $E_A = -78 \text{ kJ mol}^{-1}$

page 31

- 1 **a** Rate = $k[\text{NO}_2(\text{g})][\text{CO}(\text{g})]$
b Step 1. It is the only step that matches the rate equation.
- 2 An $\text{S}_{\text{N}}1$ reaction produces a primary carbocation which rearranges to form a tertiary carbocation before reacting with hydroxide ions; tertiary carbocations are more stable than secondary carbocations.

page 33

- 1 **a** This method is faster, and does not require removal of samples from the reaction mixture.
b To make sure they all have the same volume.
c Sodium hydrogencarbonate totally removes all H^+ ions.
- 2 Iodine does not appear in the rate-determining step.



Chapter 1.2

page 37

- 1 There has to be a favourable temperature gradient for heat to flow in a particular direction; in this case, the external temperature would have to be higher than the temperature of the tea in the cup.
- 2 No. The act of tidying releases heat energy which increases the entropy of the surroundings by more than the tidying decreases the entropy of the system.
- 3 ice < water < steam

page 39

- 1
 - a $\text{CO}_2(\text{g})$
 - b $\text{NaCl}(\text{aq})$
 - c $\text{H}_2\text{O}(\text{l})$
- 2
 - a Decrease: reactants are a gas and a solid, and only a solid is produced.
 - b Increase; when a solid dissolves, the ions are free to move in the solution.
 - c Increase; one of the products is a gas.

page 41

- 1
 - a Increase: solid to solution – decrease in order, so increase in entropy.
 - b Decrease: two gases to a liquid – increase in order, so decrease in entropy.
 - c Increase: liquid to gas – decrease in order, so increase in entropy.
 - d Decrease: solid and gas to a solid – increase in order, so decrease in entropy.
 - e Increase: solid to two gases – decrease in order, so increase in entropy.
 - f Increase: all gases but large molecules form an increased number of smaller molecules – decrease in order, so increase in entropy.

2 a

Reaction	Enthalpy change	Entropy change of system
Dissolving ammonium nitrate in water	endothermic	increase
Ammonium carbonate reacting with ethanoic acid	endothermic	increase
Magnesium burning in air	exothermic	decrease

- b Answer to include points such as:

Enthalpy relates to the energy within a system and gives you an idea of whether overall energy is given out or taken in during a reaction.

Entropy is a measure of the order or disorder within a system.

Changes in energy and changes in order will both affect the likelihood of a reaction occurring spontaneously.

page 43

- 1 $3.3 \text{ J mol}^{-1} \text{ K}^{-1}$
- 2 $\text{NH}_3(\text{g})$: it can vibrate and rotate in more ways than the simpler molecule.

**page 47**

- 1 Always spontaneous.
- 2 **a** The value for $\Delta S_{\text{total}}^{\ominus}$ at 298 K is negative ($-63 \text{ J mol}^{-1} \text{ K}^{-1}$). Therefore, it is not spontaneous at that temperature.
- b** 405 K; at this temperature $\Delta S_{\text{sys}}^{\ominus}$ has a negative value less than 175 and so $\Delta S_{\text{total}}^{\ominus}$ is positive.

page 49

- 1 **a** $+4 \text{ kJ mol}^{-1}$
- b** -38 kJ mol^{-1}
- 2 **a** $+609 \text{ J mol}^{-1} \text{ K}^{-1}$; $+63.8 \text{ J mol}^{-1} \text{ K}^{-1}$; $+672.5 \text{ J mol}^{-1} \text{ K}^{-1}$
- b** There is a large increase in entropy when RbCl dissolves. The $T\Delta S$ part of the equation outweighs the positive value of ΔH , so the value for ΔG is negative.

Chapter 1.3**page 54**

- 1 **a** Iodine molecules move from one layer to the other. The movement from the organic solvent to the aqueous solution is equal in both directions.
- b** An equilibrium would be reached more quickly at a higher temperature; there may be a different position of equilibrium.
- 2 **a** $K_{\text{c}} = \frac{[\text{Ag}(\text{NH}_3)_2(\text{aq})]}{[\text{Ag}^+(\text{aq})][\text{NH}_3(\text{aq})]^2}$; $\text{mol}^{-1} \text{ dm}^3$
- b** $K_{\text{c}} = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{CH}_3\text{COOH}(\text{l})][\text{C}_2\text{H}_5\text{OH}(\text{l})]}$; none
- c** $K_{\text{c}} = \frac{[\text{CH}_3\text{OH}(\text{g})][\text{H}_2(\text{g})]}{[\text{CH}_4(\text{g})][\text{H}_2\text{O}(\text{g})]}$; none

Stretch & Challenge page 54

- 1 $0.897 \text{ mol dm}^{-3}$

page 57

- 1 **a** Heterogeneous.
- b** $K_{\text{c}} = \frac{[\text{H}_2\text{O}(\text{g})]^4}{[\text{H}_2(\text{g})]^4}$
- c** No units.
- 2 **a** $K_{\text{p}} = \frac{p(\text{C}_2\text{H}_5\text{OH})}{p(\text{C}_2\text{H}_4) \times p(\text{H}_2\text{O})}$
- b** $3.5 \times 10^{-4} \text{ kPa}^{-1}$
- 3 $K_{\text{p}} = p(\text{CO}_2(\text{g}))$
- 4 **a** $K_{\text{p}} = \frac{p(\text{NH}_3)^2}{p(\text{N}_2) \times p(\text{H}_2)^3}$
- b** $K_{\text{p}} = \frac{p(\text{PCl}_5)}{p(\text{PCl}_3) \times p(\text{Cl}_2)}$

**page 59**

- 1 **a** There is virtually no reaction at room temperature; high temperatures give better yields of hydrogen.
- b** Exothermic; value of K_p increases with temperature.
- 2 The value is very low at room temperature, higher at 1500 K.

page 61

- 1 Yes; there are different numbers of ions in aqueous solution on the right- and left-hand sides of the equation; the equilibrium expression will involve V .
- 2 Rapid cooling slows dramatically the rates of both forward and backward reactions; the concentrations of reactants and products do not change while the titration is carried out.
- 3 0.05 mol dm^{-3}
- 4 54.3, 54.6, 53.9; no units.

page 63

- 1 **a** A solid reacts to form a solid and a gas; this involves an increase in entropy because gases have higher standard molar entropies than solids.
- b**
$$\begin{aligned}\Delta S_{\text{total}}^{\ominus} &= \Delta S_{\text{system}}^{\ominus} + \Delta S_{\text{surroundings}}^{\ominus} \\ &= 175 \text{ J mol}^{-1} \text{ K}^{-1} - 71\,000 \text{ J mol}^{-1} / 700 \text{ K} \\ &= 175 \text{ J mol}^{-1} \text{ K}^{-1} - 101 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 74 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$
The value is positive so the reaction is spontaneous.

Chapter 1.4

page 67

- 1 The manufacturer wants to produce the maximum yield of the desired product and, therefore, wants any equilibrium to be as far to the right as possible. However, if the rate of reaction is very slow, it may affect the total amount produced. A compromise is required.
- 2 **a** Endothermic reaction; entropy increases. This suggests a spontaneous reaction at high temperatures. A high temperature will move the equilibrium to the right because the reaction is endothermic. More molecules on the right-hand side suggests that increasing the pressure will decrease the yield.
- b** $\text{CO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{OH(g)}$
- 3 **a**
$$K_p = \frac{p(\text{CH}_3\text{OH})}{p(\text{CO}) \times p(\text{H}_2\text{O})^2}$$
- b** Lower; reaction is exothermic.



page 69

$$1 \quad \mathbf{a} \quad K_p = \frac{p(\text{SO}_3)}{p(\text{SO}_2) \times p(\text{O}_2)^{\frac{1}{2}}}$$

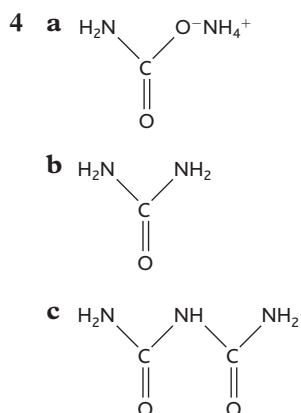
- b** Decrease in the entropy of the system because there are more gaseous molecules on left-hand side.
- c** Exothermic.
- d** Spontaneous at low temperatures.
- e** The maximum yield will be obtained at low temperatures.
- f** At low temperature, the rate of conversion will be slow. This is overcome by using a suitable catalyst which lowers the activation energy.
- g** Increasing the proportion of oxygen (the cheaper raw material) pushes the equilibrium to the right.

If a much greater concentration of oxygen is used, it slows the process down because there are fewer collisions between sulfur dioxide and oxygen particles.

- h** Since there is a good conversion rate at low pressures, the extra expense of increasing pressure cannot be justified.

page 71

- 1** Maximise yield: only two steps in the process, step 1 maximises the production of urea. Unused gases recycled; pressures maintained to maximise yield. Step 2 breaks down ammonium carbonate to urea and water. Steps to increase rate of second reaction; steps to prevent formation of biuret as a waste product.
Minimise cost: pressures kept as low as possible; excess gases all recycled. Steps to prevent formation of biuret as waste product; minimum temperatures used to drive reactions.
Maintain safety: lowest possible temperatures and pressures used. Dust removed to avoid air pollution.
- 2**
 - a** Atom economy is a measure of how good a reaction is at turning reactants into desired products. The recycling steps collect carbon dioxide and ammonia and pass them through the process again until they are converted to urea. The first step has 78% conversion of carbon dioxide.
The steps which minimise the likelihood of biuret being formed.
 - b** This is 'Stretch & Challenge' and up to students to find out what they can.
 - c** The Haber process is a single-step process, while making urea takes two steps and so is less efficient. The Haber process's use of a catalyst allows a high atom economy at relatively low temperatures and pressures: down to 40 atm with modern catalysts. The urea process doesn't have a catalyst. The urea process first has a decrease, then an increase in entropy of the system, whereas the Haber process is a decrease in entropy of the system. This makes it easier to achieve good atom economy in the Haber process.
- 3** A fan removes air contaminated with urea dust and removes particles of urea.



- 5 This would remove all the ammonia and carbon dioxide from the solution. This would encourage more urea to be hydrolysed.

Chapter 1.5

page 75

- 1 Conjugate acid/conjugate base:
- a** $\text{HSO}_4^-(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ with $\text{H}_3\text{O}^+(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$
- b** $\text{HClO}_4(\text{l})$ and $\text{ClO}_4^-(\text{l})$ with $\text{CH}_3\text{COOH}_2^+(\text{l})$ and $\text{CH}_3\text{COOH}(\text{l})$
- 2 A solution of ethanoic acid in water has very low electrical conductivity; this shows there are few ions in solution, and so the equilibrium lies to the left.
- 3 Arrhenius definition: acids and bases dissolve and separate partially or completely into charged particles in a process called dissociation: H^+ from acids, OH^- from bases. The limitation was that acids had to be dissolved in water. Brønsted–Lowry definition: an acid is a proton donor; a base is a proton acceptor.

page 79

- 1 **a** 1.0
- b** 13.3
- c** 1.0 – remember that sulfuric acid is a dibasic acid.
- 2 **a** A strong acid is completely dissociated into ions in aqueous solution at up to moderate concentrations; a concentrated acid contains a large number of moles of acid per unit volume of solution.
- b** Yes.

page 83

- 1 $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
- $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$
- $[\text{H}^+(\text{aq})]^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
- $[\text{H}^+(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$; $\text{pH} = 7.0$



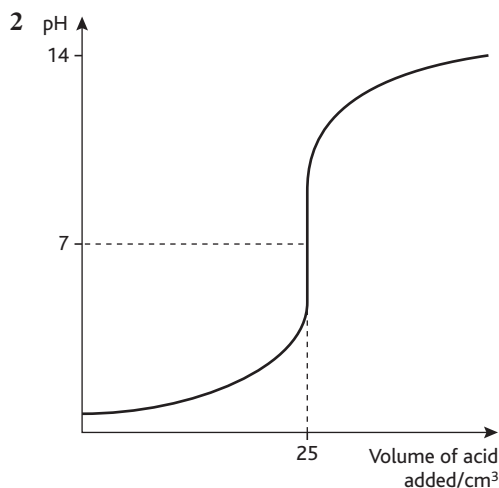
- 2 **a** $[\text{H}^+(\text{aq})] = 1 \times 10^{-2} \text{ mol dm}^{-3}$; $\text{pH} = 2$
b $[\text{H}^+(\text{aq})] = 4.12 \times 10^{-4} \text{ mol dm}^{-3}$; $\text{pH} = 3.38$
c $[\text{OH}^-] = 6.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}^+(\text{aq})] = 1.67 \times 10^{-12} \text{ mol dm}^{-3}$; $\text{pH} = 11.78$
- 3 $[\text{H}^+] = 3.4 \times 10^{-3} \text{ mol dm}^{-3}$; $\text{pH} = 2.5$

page 85

- 1 Approximately $2.4 \times 10^{-6} \text{ mol dm}^{-3}$
- 2 **a** This will add very little. The same result should be obtained three times because nothing has changed. If different results are obtained then it would be worrying.
b If different results are obtained, it suggests that the pH meters may not be accurate. If the same results are obtained then it suggests that the results are reliable.
c If the same results are obtained, it suggests that the solution was mixed properly and that the results are reliable.

page 87

- 1 There is no slow change in colour of an indicator to give an early warning; the change in colour that happens on the steep part of the curve occurs on addition of one drop. It is this fact that makes titration a successful technique.



page 89

- 1 **a** A phenolphthalein; B methyl orange or bromothymol blue.
b The fall in pH at A is not as clear because there is not such a big decrease.
c At A: $\text{Na}_2\text{CO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaHCO}_3(\text{aq}) + \text{NaCl}(\text{aq})$
 At B: $\text{NaHCO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow 2\text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- 2 **a** (i) Any of the three; (ii) congo red; (iii) thymol blue.
b 4.0 and 8.8

**page 91**

- Method 1 is better because a graph is plotted from a large number of points, and it does not rely on getting an exact end-point by eye. If you go beyond the end point, the solution stays the same colour.
 - Method 2 could be improved by carrying out the titration a number of times and using a suitable average volume.
- Usually the alkali goes in the flask and the acid in the burette. The phenolphthalein then changes from pink to colourless.
 - Sodium hydroxide solution and other bases can cause glass taps to stick or seize up.
- The more acidic the pH, the more pronounced the antimicrobial activity. Also, in general, acids with lower pK_a values have higher antimicrobial activity at the same pH.

Stretch & Challenge page 94

- 4.77
- 5.07

page 95

- 4.0
- 3.9
- The pK_a of a buffer should be close to the ideal pH of the skin/hair and/or the product. For example, glycolic acid ($pK_a = 3.83$), ethanoic acid (4.76), citric acid (3.14) and succinic acid (4.16) are used to make acidic buffers for use where the product needs to be acidic – such as on skin with a typical pH of 5.5. Students need to find things out for themselves and then show an understanding of the basic principles.

page 97

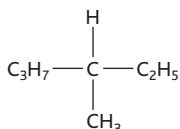
- Pickling in vinegar lowers the pH; microorganism activity is reduced.
- To remove the products of respiration; especially carbon dioxide.
- Depends on research tool chosen.
- Carbon dioxide undoubtedly dissolves in water to form an acidic solution, but it is a very weak acid ($K_a = 4.5 \times 10^{-7} \text{ mol dm}^{-3}$) compared to the weak acid responsible largely for the acidification of rain – sulfurous acid ($K_a = 1.5 \times 10^{-2} \text{ mol dm}^{-3}$). Others say that the role of the oceans is to act as a carbon dioxide 'sponge' and to control the atmospheric content of the gas.



Chapter 1.6

page 99

1



- 2 Glycine is not optically active because it contains a central carbon atom attached to two hydrogen atoms. Serine has a chiral centre because there are four different groups attached to the central carbon atom – so it is the one that is optically active.

page 101

1 a -12° , i.e. anticlockwise.

b 0°

c Racemic mixture.

- 2 To remove all vibrations of light not in the same plane.

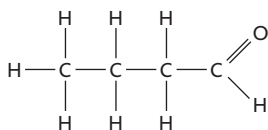
page 103

1 $\text{S}_{\text{N}}1$ mechanism.

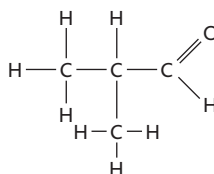
- 2 In small-scale production during the development of thalidomide, the $\text{S}_{\text{N}}2$ mechanism resulted in only the L-isomer being formed. Different compounds and processes used in large-scale production resulted in the formation of a planar intermediate. This planar molecule led to an $\text{S}_{\text{N}}1$ mechanism, which, as usual, led to the formation of a racemic mixture of products, and so to the production of some of the D-isomer, which is teratogenic.

page 107

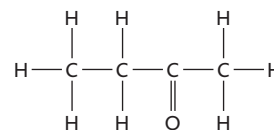
1



butanal



2-methylpropanal



butanone

- 2 B and D are aldehydes; A and C are ketones.

page 109

1 Propanal; see table 1.6.1.

2 Boiling temperatures are affected by atmospheric pressure and are more difficult to measure accurately.

3 Perhaps propanone, but possibly impure; impure compounds melt at a lower temperature and over a range.

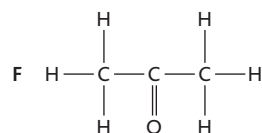
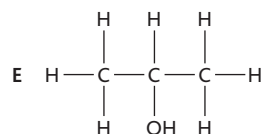
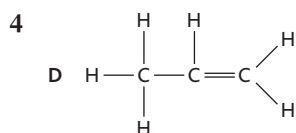
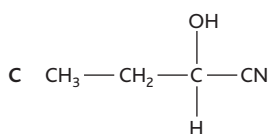
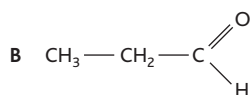

page 113

1 **a** Fehling's/Benedict's test or Tollens' test.

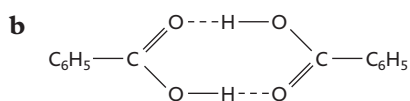
b Iodoform test.

2 Pentan-2-one $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$ or 3-methylbutan-2-one $(\text{CH}_3)_2\text{CHCOCH}_3$

3 **A** $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$


page 115

1 **a** The hydrocarbon portion is large.



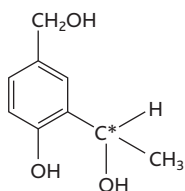
2 **a** Use excess ethanol and allow ethanal to boil off and condense.

b Reflux with excess potassium dichromate(IV).

page 118

1 $\text{CaCO}_3(\text{s}) + 2\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) \rightarrow \text{Ca}(\text{CH}_3\text{CH}_2\text{COO})_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

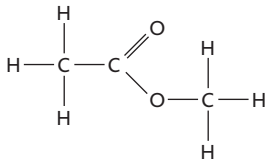
2 The product has a chiral centre and exists as two optical isomers.





page 121

1 Methyl ethanoate.

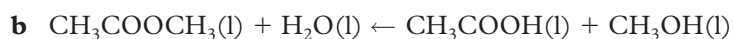
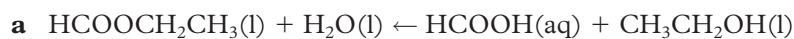


2 Hexanoic acid and ethanol.

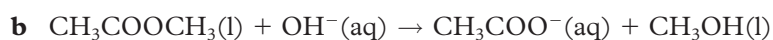
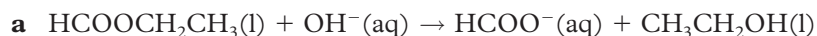
3 They all contain esters; the natural flavours are produced by mixtures of esters and other compounds in a complex set of interactions.

page 124

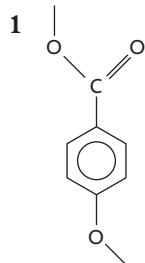
1 Acid hydrolysis:



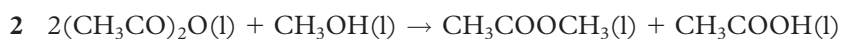
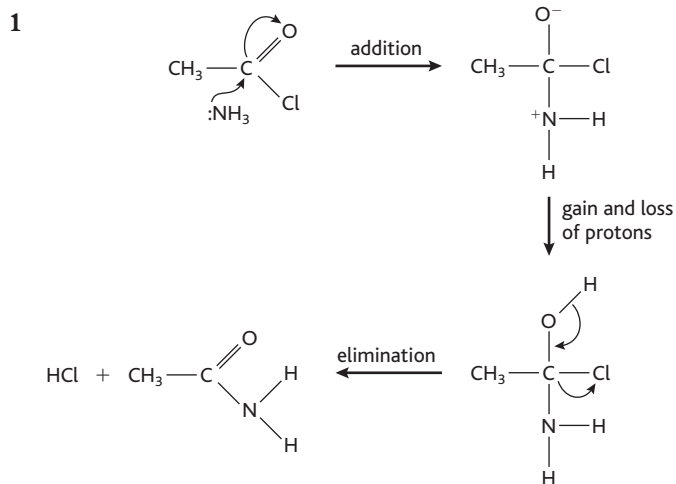
Base hydrolysis:



page 126



page 129





Chapter 1.7

page 132

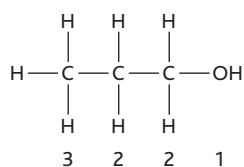
- 1 For example: quicker, more reliable, use small samples, can be used without destroying a sample.

page 136

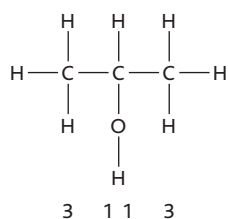
- 1 Ethanal; the nmr spectrum indicates three protons in one environment (forms the quartet) and one proton in another (forms the doublet).

- 2 a Tetramethylsilane; used as a reference standard.

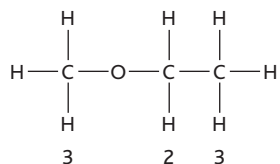
b



propan-1-ol



propan-2-ol



methoxyethane

- c Propan-1-ol; the peaks fit the pattern triplet, septuplet, triplet, singlet.

- 3 Nmr spectroscopy is a technique used to get information about the structure of molecules. The main differences between the X-ray and the MRI techniques are the images they produce. An X-ray clearly shows the contrast between soft tissue and bone density. That is why it is often used to examine broken bones. An MRI image shows a better contrast between different kinds of soft tissue. That is why it produces such detailed images of the brain and other tissues.
- 4 Faster; uses a smaller sample; uses less solvent; uses an internal reference.

page 139

- 1 m/z 58 = molecular ion $\text{C}_4\text{H}_{10}^+$; m/z 15 = CH_3^+ ; m/z 29 = C_2H_5^+ ; m/z 43 = C_3H_7^+ .
- 2 (a) is propanal and (b) is propanone.
(a) has a peak corresponding to 29 (C_2H_5^+) and 28 (loss of $\text{C}=\text{O}$).
(b) has peaks at 43 and 15 corresponding to fragmentation forming CH_3^+ and CH_3CO^+ .

page 143

- 1 a Y (less polar) and then X (polar).
b X and then Y.
- 2 Retention times vary with conditions.