

Chapter 2.1

page 147

- $\begin{array}{ll} 1 & Zn(s) \to Zn^{2+}(aq) \,+\, 2e^- \\ & Cu^{2+}(aq) \,+\, 2e^- \to Cu(s) \\ & Zn(s) \,+\, Cu^{2+}(aq) \to Zn^{2+}(aq) \,+\, Cu(s) \end{array}$
- $\begin{array}{ll} \textbf{2} & H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l) \\ & H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^- \\ & 2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \end{array}$

This is the overall equation for the decomposition of hydrogen peroxide – it is an example of disproportionation (see page 175 in *Edexcel AS Chemistry*).

page 149

- 1 The solution is colourless until one drop of unreacted potassium manganate(VII) is present. Then the solution turns pink.
- 2 a Amount of Fe²⁺ is $\frac{0.010}{1000} \times 25.0 = 2.50 \times 10^{-4} \text{ mol}$ Ratio of Fe²⁺ to MnO₄⁻ is 5 to 1, so need $\frac{2.50 \times 10^{-4}}{5} = 5.00 \times 10^{-5} \text{ mol MnO}_4^-$ Provided by $\frac{1000}{0.020} \times 5.00 \times 10^{-5} \text{ cm}^3 = 2.50 \text{ cm}^3$
 - **b** Amount of H₂O₂ is $\frac{0.200}{1000} \times 25.0 = 5.00 \times 10^{-3}$ mol Ratio of H₂O₂ to MnO₄⁻ is 5 to 2, so need $5.00 \times 10^{-3} \times \frac{2}{5} = 2.00 \times 10^{-3}$ mol MnO₄⁻ Provided by $\frac{1000}{0.020} \times 2.00 \times 10^{-3}$ cm³ = 100 cm³
 - **c** Amount of $C_2O_4^{2-}$ is $\frac{0.100}{1000} \times 25.0 = 2.50 \times 10^{-3}$ mol Ratio of $C_2O_4^{2-}$ to MnO_4^{-} is 5 to 2, so need $2.50 \times 10^{-3} \times \frac{2}{5} = 1.00 \times 10^{-3}$ mol MnO_4^{-} Provided by $\frac{1000}{0.020} \times 1.00 \times 10^{-3}$ cm³ = 50.0 cm³
- 3 Amount of MnO_4^- is $\frac{0.020}{1000} \times 28.75 = 5.75 \times 10^{-4}$ mol Ratio of MnO_4^- to Fe^{2+} is 1 to 5, so amount of $Fe^{2+} = 5.75 \times 10^{-4}$ mol $\times 5 = 2.875 \times 10^{-3}$ mol Mass of $Fe^{2+} = 2.875 \times 10^{-3}$ mol $\times 55.8$ g mol⁻¹ = 0.160 g % $Fe^{2+} = \frac{0.160}{1.340}$ g $\times 100 = 12.0\%$

page 152

- 1 Sodium thiosulfate reacts with an acid to produce sulfur and sulfur dioxide.
- 2 Amount of $S_2O_3^{2^-}$ is $\frac{0.050}{1000} \times 32.4 = 1.62 \times 10^{-3} \text{ mol}$ Ratio of $S_2O_3^{2^-}$ to I_2 is 2 to 1, so amount of $I_2 = \frac{1.62 \times 10^{-3} \text{ mol}}{2} = 8.10 \times 10^{-4} \text{ mol}$ Ratio of I_2 to ClO⁻ is 1 to 1, so amount of ClO⁻ = 8.10 $\times 10^{-4} \text{ mol}$ Concentration of bleach = $\frac{8.10 \times 10^{-4}}{2} \times 1000 = 0.405 \text{ mol dm}^{-3}$

page 158

- **1 a** The potential difference between the electrodes of the two half-cells that make up an electrochemical cell.
 - b The reference half-cell used for measuring standard electrode potentials; consists of hydrogen gas at 1 atm pressure and 298 K bubbling around a platinum electrode in 1.00 mol dm⁻³ H⁺(aq) ions.



- c One half of an electrochemical cell; one of the two electrodes of the cell.
- **d** The electrode potential of a half-cell as measured against a standard hydrogen electrode, indicated as E^{\ominus} .
- 2 a $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s); Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
 - $\textbf{b} \quad Cl_2(aq) \,+\, 2e^- \rightarrow 2Cl^-(aq); \, 2I^-(aq) \rightarrow I_2(aq) \,+\, 2e^-$
 - $\textbf{c} \quad Zn(s) \rightarrow Zn^{2+}(aq) \, + \, 2e^-; Pb^{2+}(aq) \, + \, 2e^- \rightarrow Pb(s)$
- **3** The standard electrode potential of a half-cell is a measure of the oxidising power or reducing power of the species in it in other words, its ability to compete for electrons; in general, the stronger an oxidising agent, the more positive its electrode potential, while a strong reducing agent has a large negative electrode potential.
- $\label{eq:alpha} \textbf{4} \quad \textbf{a} \quad +0.12 V, Pb^{2+}(aq) \, + \, Ni(s) \rightarrow Pb(s) \, + \, Ni^{2+}(aq)$
 - **b** +0.03V, Ag⁺(aq) + Fe²⁺(aq) \rightarrow Ag(s) + Fe³⁺(aq)

- **1 a** $E_{\text{cell}}^{\leftrightarrow} = (-0.34\text{V}) + (+0.80\text{V}) = +0.46\text{V}$
 - **b** Feasible because the value is positive.
- **2 a** Slightly to the right.
 - **b** No.
- **3** Zinc acts as a sacrificial metal; zinc ions pass into solution rather than iron(II) ions because zinc is more electropositive; this is shown by their standard electrode potentials:

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$	$E^{\odot} = +0.44$ V
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$	$E^{\oplus} = +0.76$ V

Electron flow is from zinc to iron, further protecting the iron.

- 4 a Reactions A and D may proceed.
 - **b** There is no guarantee that a reaction predicted to be feasible will proceed at a reasonable rate.

page 165

- $\label{eq:2.1} \begin{array}{ll} \textbf{a} & \text{Anode: } C_2H_5OH(l) + 3H_2O(l) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^- \\ & \text{Cathode: } \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O \end{array}$
 - $\textbf{b} \quad C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
- 2 Hydrogen fuel cells are very efficient compared to the combustion reaction; hydrogen is explosive when mixed with air. Methanol is toxic and highly flammable. Ethanol fuel cells work at a lower temperature; ethanol is flammable.

page 167

- 1 a Fuel cell.
 - **b** IR spectroscopy.

The roadside test is a screening test that needs to be easy to administer, but the test to provide evidence for use in courts must be more accurate and reliable.



2 *Fuel cell breath tester* – any alcohol is oxidised and electrons are released. An external circuit with a microprocessor measures the current and calculates the blood alcohol content.

Infrared breath analyser – IR radiation is passed through the sample and the resulting spectrum allows the concentration of ethanol to be measured accurately by a microprocessor.

IR spectrometry gives very accurate results but the instrumentation is not very portable; the process is both mechanised and accurate, so this evidence is admissible in court. However, other groups, most notably aromatic rings and carboxylic acids, can give similar absorbance readings.

Unfortunately, breathalysers only give the composition of the air breathed out and it is assumed that this is exhaled from deep within the lungs; however, alcohol may have come from the mouth, throat or stomach.

Chapter 2.2

page 170

- **1 a** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
 - **b** Both 4s electrons are lost.
- **2 a** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$
 - **b** 7, corresponding to the loss of the 4d and 5s electrons.
- **3** Disagree too simplistic; some are f-block elements; the properties of some d-block elements do not fit the general pattern, e.g. Zn. A better description is an element that forms one or more stable ions which have incompletely filled d sub-shells.
- 4 They are all hard metals with high melting and boiling temperatures; they show more than one oxidation state in their compounds; they tend to form coloured compounds and ions; many show catalytic activity.
- 5 The *general* trend is an increase in ionisation energy, though by no means regular; the increase is due to the increased nuclear charge as the row is crossed; the unevenness (and the occasional decrease) is attributed to the extra stability of half-filled and filled d orbitals exposed by some electron losses. This applies equally to the first, second and third ionisation energies.

page 174

- 1 Copper(II) ions have unfilled 3d orbitals; copper(I) ions have filled 3d orbitals.
- **2** Both involve the sharing of a pair of electrons. In a covalent bond each bonded atom supplies one electron to the bond. In a dative covalent bond both electrons come from one atom.
- **3 a** At least one pair of electrons.
 - **b** Monodentate ammonia molecules; bidentate ethanedioate ions; polydentate edta.



Chapter 2.2

- **c** They all use lone pairs of electrons to form co-ordinate/dative covalent bonds to a metal ion; monodentate ligands use one lone pair, bidentate ligands use two, and polydentate ligands use more than two (edta uses six lone pairs).
- 4 The colours can be used to identify transition metals and to indicate changes in oxidation state of transition metal ions.

page 177

- 1 At this stage there are approximately equal concentrations of yellow dioxovanadium(V) and blue oxovanadium(IV) ions.
- 2 Stage 1: $VO_2^+(aq) + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$ Stage 2: $VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$ Stage 3: $V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$
- 3 a Mn: [Ar] 3d⁵4s²; Fe: [Ar] 3d⁶4s²
 Mn²⁺: [Ar] 3d⁵; Fe²⁺: [Ar] 3d⁶
 Mn³⁺: [Ar] 3d⁴; Fe³⁺: [Ar] 3d⁵
 - **b** Mn^{2+} is more stable than Fe^{2+} because of the former's half-filled 3d orbitals; Mn^{3+} is less stable than Fe^{3+} because of the latter's half-filled 3d orbitals.

page 179

- **1 a** $[CuCl_2]^-(aq)$
 - **b** $[CuCl_4]^{2-}(aq)$
 - **c** $[Cu(H_2O)_6]^{2+}(aq)$
- $\textbf{2} \quad \textbf{a} \quad Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

b $E_{\text{cell}}^{\oplus} = (-0.34\text{V}) + (+0.80\text{V}) = +0.46\text{V}$

3 When some or all of the ligands in a complex ion are replaced by different ligands. For example, when concentrated HCl is added to a solution containing the complex ions [Cu(H₂O)₆]²⁺(aq), the blue colour is replaced by a green colour. Some of the aquo-complex ions have their water molecules replaced by chloride ions to form [CuCl₄]²⁻(aq), which are yellow – these and the remaining blue complex ions mix to make the green colour. Adding water to this mixture reverses the ligand exchange reaction.

page 181

- $1 \quad 2 Cr^{3+}(aq) \, + \, 5 H_2 O_2(aq) \rightarrow 2 Cr O_4{}^{2-}(aq) \, + \, O_2(g) \, + \, 10 H^+(aq)$
- 2 The process must involve oxidation; in industry this is achieved by fusing crushed chromium(III) ore, containing chromium(III) oxide, with sodium carbonate in the presence of oxygen:

 $2Cr_2O_3(s) + 4Na_2CO_3(s) + 3O_2(g) \rightarrow 4Na_2CrO_4(s) + 4CO_2(g);$

if necessary, an aqueous extract from this is treated with sulfuric acid to form dichromate(VI), but this is not redox.



- **1 a** The d-block ions are relatively small and have a strong electric field around them; this attracts species rich in electrons; the metal ion can accommodate anions or molecules that act as electron-pair donors; forming co-ordinate/dative covalent bonds and a group of atoms/molecules/ions called a complex ion.
 - **b** Transitions between the partly-filled d orbitals in transition metal ions are the source of their colours.
- 2 The 3d orbitals are split into three orbitals of lower energy and two orbitals of higher energy; absorption of visible light, and colour formation, are explained in terms of photons causing electrons to jump from the orbitals with lower energy to those with higher energy; the difference between these energies depends on a number of factors which transition metal it is, what ligands it is complexed with, concentration of solution, etc.

page 185

- 1 There are two Cr^{2+} ions (i.e. +4) and four CH_3COO^- ions (i.e. -4).
- 2 The chromium(II) in the complex is oxidised to chromium(III) so the red precipitate will turn a grey-green colour.

page 188

- 1 Exposure enables oxygen in the air to increase the oxidation numbers of Mn(II) and Fe(II) to those of Mn(OH)₃ (Mn(III)) and Fe(OH)₃ (Fe(III)) respectively.
- 2 Zinc sulfate solution is colourless, manganese(II) sulfate solution very pale pink. This may not be clearly visible, so add sodium hydroxide solution to each solution both form a white precipitate. In the case of zinc sulfate the precipitate formed dissolves in excess NaOH; in the case of manganese(II) sulfate the precipitate does not dissolve.
- 3 Cu^{2+} , Ni^{2+} or Co^{2+}
- 4 Mn^{2+}
- 5 $Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_{3}(s)$
- $\textbf{6} \quad [Ni(H_2O)_6]^{2+} + 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$

page 190 (Stretch & Challenge)

In the first stage, manganese(IV) oxide reacts with hydrogen peroxide to form manganese(VII) oxide. Here manganese is in the highest possible oxidation number:

 $3H_2O_2(aq)\,+\,2MnO_2(s)\rightarrow Mn_2O_7(s)\,+\,3H_2O(l)$

In the second stage, manganese(VII) oxide decomposes to reform manganese(IV) oxide and oxygen:

 $2Mn_2O_7(s) \rightarrow 4MnO_2(s)\,+\,3O_2(g)$

The overall equation can be simplified to:

 $2H_2O_2(aq) \rightarrow 2H_2O(l)\,+\,O_2(g)$



- 1 The reaction can be continuous; the area of contact between the reactants is very small and the solid phase effectively increases this; the products do not have to be separated from the catalyst.
- **2** Provides a large surface area for catalysis to take place; gases can pass through the mesh easily.
- $\begin{array}{ll} \textbf{3} & SO_2(g) + V_2O_5(s) \rightarrow SO_3(g) + 2VO_2(s); \\ & 2VO_2(s) + \frac{1}{2}O_2(g) \rightarrow V_2O_5(s) \end{array}$
- 4 Lead compounds adsorb onto the catalyst surface and cannot be removed; they poison the catalyst and stop it working.

page 192

1 Benefits: lower operating temperatures, so environmentally sound and less expensive; very fast.

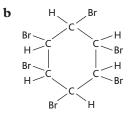
Disadvantages: may be inactivated/denatured at higher temperatures; sensitive to poisoning.

- **2** Biological systems are sensitive to different isomers; the two forms fit differently into enzyme active sites.
- **3** A sudden flash of light (e.g. photoflash) may cause the glasses to darken unnecessarily; moving from internal to external light can trigger change even if not strongly sunny; response may not be rapid enough to cope with sudden decrease in light levels (e.g. when driving into a tunnel).

Chapter 2.3

page 197

- 1 The delocalised ring of electrons above and below the benzene molecule attracts electrophiles.
- 2 **a** You would expect bromine to be decolourised by benzene simply on mixing (see page 129 in *Edexcel AS Chemistry*).



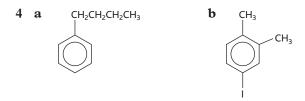
c No; there is no delocalised electron system; all the carbon–carbon bonds are single bonds.



a Addition: benzene and bromine in uv light; benzene with hydrogen.
 Substitution: benzene with fuming concentrated sulfuric acid; reaction of bromine with a halogen carrier.

P Reactant	Alkanes	Alkenes	Benzene
Hydrogen	No reaction	Addition reaction in presence of finely divided nickel catalyst at about 200 °C to form alkane	Rapid addition reaction in presence of nickel catalyst at 150 °C to form cyclohexane
Bromine	In the dark, no reaction; in the light, substitution reactions to form bromoalkanes	Addition reaction to form bromoalkanes regardless of light conditions	In the dark, with a catalyst such as iron filings, substitution to form bromobenzene; in the light, addition reaction to form 1, 2, 3, 4, 5, 6- hexabromocyclohexane
Concentrated sulfuric acid	d No reaction	Reaction at room temperature to form an alkyl hydrogensulfate	Under reflux for several hours, electrophilic substitution in form of sulfonation to produce benzenesulfonic acid

- 2 The iron filings react with the bromine to produce iron(III) bromide, which can then catalyse the reaction.
- 3 a 1-chloro-3-methylbenzene
 - **b** 1-chloro-3,5-dimethylbenzene
 - c 2-iodoethylbenzene
 - **d** 1,2,3,4,5,6-hexachlorocyclohexane



5 $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$; reflux bromine and benzene in presence of iron(III) bromide in the dark.

 $C_6H_6 + SO_3 \rightarrow C_6H_5SO_3H$; mix fuming sulfuric acid and benzene.

 $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$; mix benzene with concentrated sulfuric and nitric acids below 55 °C.

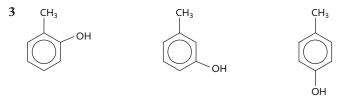
- **6 a** Increased melting and softening temperatures; harder and more rigid; more resistant to chemicals.
 - **b** Low-temperature reaction; rapid reaction; good purity product (high atom economy).

page 207

1 The pairs of non-bonding electrons on the oxygen in the —OH group are delocalised and this activates the benzene ring, making it more susceptible to attack by electrophiles; NO₂ groups deactivate the ring, so normal nitration methods have to be used; CH₃ groups activate the ring a little.



2 Benzene neither mixes nor reacts with either reagent; phenol reacts immediately with both at room temperature, forming a white precipitate; the difference is explained in the answer to question **1**.



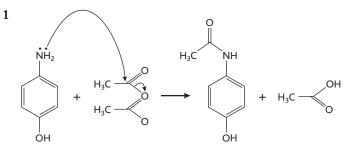
Chapter 2.4

page 212

- **1 a** The methylamine is likely to react with more chloromethane to form secondary or tertiary amines.
 - **b** Carry out the reaction with an excess of ammonia.
- **2 a** $C_{11}H_{15}NO_2$
 - **b** Secondary amine; there is only one hydrogen atom connected to the nitrogen atom.
- **3** Oxygen is removed from nitrobenzene and hydrogen is added; the half-equation for the change to the organic compounds involves the gain of electrons:

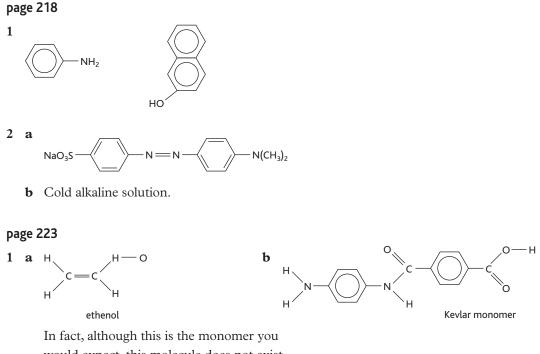
 $C_6H_5NO_2(l)\,+\,4H^+(aq)\,+\,4e^-\rightarrow C_6H_5NH_2(l)\,+\,2H_2O(l)$





2 In the past there were few effective drugs, so the placebo effect was important and no comparisons were made. Now the effectiveness of drugs is carefully measured and evaluated as there are a number of different options. There is much legislation to ensure that new drugs are safe to use and effective to protect patients. There is a greatly increased awareness of the risk of side effects, and adverse reactions to drugs means public and scientists want to ensure no problems. As people die young much less often, there is an increased awareness of risk with taking medicines – as death from diseases is relatively rare so death from the cure would be noticeable!

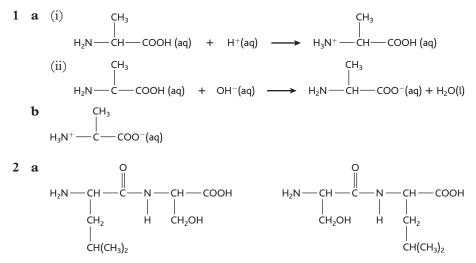




In fact, although this is the monomer you would expect, this molecule does not exist. See the next section for an explanation.

2 Poly(propene) is very unreactive with no reaction with acids, alkalis, etc. It will burn in excess air to form carbon dioxide and water. Poly(ethenol) burns in a similar way but is also hydrolysed by refluxing with acids or alkalis.

page 226



b leu-ser; ser-leu

- **3** a Clockwise from top left: glycine, alanine, unknown, isoleucine, leucine.
 - **b** $C_6H_{13}NO_2$
 - **c** Isoleucine and leucine.

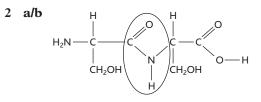


- **1 a** Alanine, tyrosine and aspartic acid.
 - **b** The larger spot indicates a larger quantity of aspartic acid.
 - **c** The $R_{\rm f}$ values are almost identical.
- **2** Touching the paper in the wrong places will put secretions on the paper which will be detected by the ninhydrin.
- **3 a** Isoleucine and threonine.
 - b Biological systems are usually responsive to chirality. Often only one form is active in biological systems; the presence of two chiral centres means that there are four possible isomers of these molecules, but only one of these has both chiral centres that are active biologically (usually the L-form).
- 4 Fingerprints are an important strand of evidence to show that someone has been present at a crime scene; they contain traces of protein; the fingerprint can be shown up using ninhydrin to make an image of the print for identification purposes; traces of other skin contacts can be made in the same way.

page 233

1 Insulin is a relatively small protein, made up of two short chains of amino acids, one containing 21 amino acids and the other 30 amino acids; as a result it is relatively easy these days to work out the composition and structure of the molecules.

A molecule such as haemoglobin is not only much larger, with four polypeptide chains and therefore many more amino acids to identify and sequence, but its structure is also complicated by the presence of the iron-containing haem groups.

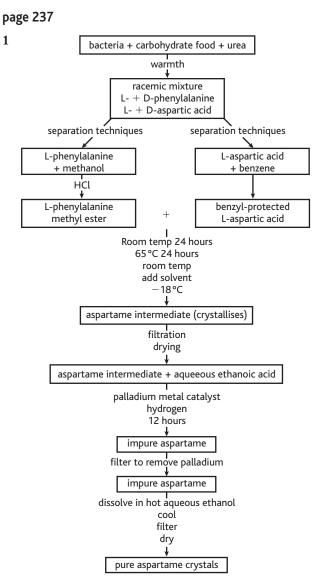


- 3 a It was the first time the entire sequence of a protein had been worked out.
 - **b** Sanger determined the relative molar mass and the molecular formula of insulin; he determined which amino acids are present by hydrolysis with hydrochloric acid and paper chromatography; he compared the M_r values from found amino acids with his calculations; he established the sequence of amino acids using techniques including the partial hydrolysis of the protein into shorter polypeptides, determining the sequence in these, and building up sequence after sequence until the whole molecule could be worked out.

Modern methods involve the controlled sequential enzymatic breakdown of a protein molecule into fragments; followed by mass spectrometry to find the M_r values of the fragments; allowing determination of the different amino acid linkages using very small quantities.



Chapter 2.5



- 2 It is a multi-stage process; this is likely to reduce the overall yield greatly.
- **3 a** Cyclamate sweeteners are made in a relatively short process with one or two reaction stages; aspartame involves a complex process with many different steps, some requiring long reaction times and considerable purification, etc.
 - **b** Cyclamate synthesis, because it has fewer steps and therefore less reduction in yield at each step.
 - **c** Saccharine no calories; sweet taste; bitter aftertaste; correlation but no causation found between intake and some cancers; very useful for diabetics.

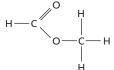
Cyclamate – sweeter than sucrose; less sweet than saccharin; less aftertaste than saccharin; has been reported that some intestinal bacteria could desulfonate cyclamate to produce cyclohexylamine, which is believed to be toxic.

Aspartame – 200 times sweeter than sucrose; dissolves in water readily; sweet taste without leaving bitter aftertaste; tends to interact with other chemicals in food; decomposes when heated strongly; no evidence that aspartame is unsafe.

4 To prevent unwanted reactions, e.g. the amine group of aspartic acid combining with the acid group of the phenylalanine.



1 Not a carboxylic acid; so methyl methanoate:



2 0.5666 g of carbon dioxide contains $\frac{12}{44} \times 0.5666$ g = 0.1545 g carbon Percentage of carbon in compound = $\frac{0.1545 \text{ g}}{0.206 \text{ g}} \times 100 = 75.0\%$ 0.4635 g of water contains $\frac{2}{18} \times 0.4635$ g = 0.0515 g hydrogen

Percentage of hydrogen in compound = $\frac{0.0515 \text{ g}}{0.206 \text{ g}} \times 100 = 25.0\%$

Element	c	н
%	75	25
A _r	12	1
Combining ratio	$\frac{75}{12} = 6.25$	$\frac{25}{1} = 25$
Simplest whole number	1	4

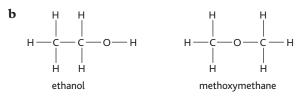
The empirical formula is CH₄, so the molecular formula must be CH₄.

3 a

Element	c	н	0
Mass/g	2.4	0.6	1.6
A _r	12	1	16
Combining ratio	$\frac{2.4}{12} = 0.2$	$\frac{0.6}{1} = 0.6$	$\frac{1.6}{16} = 0.1$
Simplest whole number	2	6	1

The empirical formula is C_2H_6O .

 $M_{\rm r} = 46$ so the molecular formula must be C₂H₆O.



c Ethanol will form hydrogen chloride fumes; methoxymethane will not.

4 a $0.8 \times 0.75 \times 0.9 \times 0.8 \times 0.8 = 0.35$; so the yield is 35%.

b None of the reactions has a 100% yield, so at each step there is less chemical to move forward to the next step; the more reaction steps there are, the lower the final yield will be; so the fewer reaction steps, the higher the final yield is likely to be, and if each step is as efficient as possible, that will also increase final yield.

page 244

1 Butanoic acid has a —COOH group so the compound is acidic, but weak; it will react with alcohols to form esters; it will react with nucleophiles like amines to form amides; it will react with PCl₅ to form butanoyl chloride; aqueous solution will react with sodium



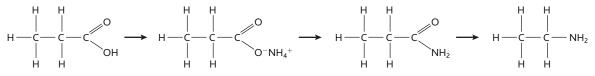
carbonate to give carbon dioxide; with alkalis to form butanoate salts; and with reactive metals to form hydrogen.

Methyl propanoate and propyl methanoate are esters; they will hydrolyse to the parent acid and alcohol.

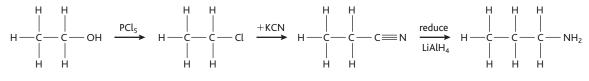
2 Depends on the choice made.

page 247

- 1 A Distil with acidified potassium dichromate(VI) solution and excess alcohol.
 - B React the carboxylic acid with lithium tetrahydridoaluminate in dry ether.
 - C Reflux the acid and the alcohol with concentrated hydrochloric acid.
 - D React the carboxylic acid with phosphorus(V) chloride.
 - E React the acyl chloride with ammonia.
 - F React the alkene with a hydrogen halide.
 - G Reflux the halogenoalkane with a solution of potassium hydroxide in ethanol.
 - H Reflux the halogenoalkane with potassium cyanide dissolved in ethanol.
 - I Heat the halogenoalkane in a sealed vessel with excess ammonia.
 - J Hydrolyse the nitrile with a dilute acid solution.
- 2 U React benzene with a mixture of concentrated nitric acid and sulfuric acid below 55 °C.
 - V React nitrobenzene with tin and concentrated hydrochloric acid.
 - W React phenylamine with nitrous acid (sodium nitrite and hydrochloric acid) below 5 °C.
 - X Reflux benzene with an acyl chloride and aluminium chloride.
 - Y Reflux benzene with a halogenoalkane and aluminium chloride.
 - Z React benzene with bromine and iron filings.
- **3** Reflux benzene with ethanoyl chloride and aluminium chloride to form phenylethanone; reduce this with zinc and hydrochloric acid.
- 4 React propanoic acid with ammonia solution to form ammonium ethanoate; heat this to produce ethanamide; reflux with bromine and concentrated potassium hydroxide:



5 React ethanol with phosphorus(V) chloride; reflux with potassium cyanide in ethanol; reduce with lithium tetrahydridoaluminate in dry ether:



page 249

1 Although the D-form, for example, may have no side-effects while the L-form does have side-effects, prescribing just the D-form may not solve the problem as the forms may interact in the body.



- 2 Makes it more possible to synthesise single enantiomers economically so that only the desired enantiomer is delivered in the drug; prevents production of unwanted by products or enantiomers.
- 3 With some drugs, both isomers have biological activity, so the racemic mixture will have similar action to the single enantiomer, so the same dose is needed; in others one isomer has no effect, so the racemic mixture is effectively half the strength, so a double dose has to be taken to get the same level of therapeutic drug as the single-isomer medicine.
- 4 Thalidomide has two enantiomers one safe and effective, the other teratogenic. The teratogenic form is produced during the manufacturing process. New developments are making it much easier to produce a single enantiomer rather than a racemic mixture, making a thalidomide situation much less likely.

The body reacts with drugs and may convert one enantiomer into another so that even single enantiomer drugs can cause problems – this was also the case with thalidomide.

page 252

- 1 Synthesis 2 is preferable. Both routes involve unpleasant chemicals but potassium cyanide and lithium tetrahydridoaluminate are particularly so. The use of ethoxyethane as a solvent can also cause problems because of its flammability. Overall the steps involved in synthesis 2 require the more straightforward processes.
- 2 Overall yield = $25\% \times 75\% \times 80\% = 15\%$ Maximum mass of paracetamol = 1000 tonnes $\times \frac{15}{100} = 150$ tonnes.
- **3** The —OH group activates the ring; using concentrated nitric acid and concentrated sulfuric acid will produce a multi-substituted product.
- **a** A reflux with tin and concentrated hydrochloric acid (or iron and hydrochloric acid).
 B add ethanoic anhydride or ethanoyl chloride.
 - C react with cold sodium nitrite and dilute hydrochloric acid.
 - D heat gently.
 - **b** Step A involves tin and concentrated hydrochloric acid. Using diluted hydrochloric acid would be safer and would still give the desired product. In step B ethanoic anhydride is refluxed with phenylamine. This is safer than using ethanoyl chloride. In step B only refluxing is needed.
 - **c** There are many steps in the process; the yield would be reduced at each step.

page 255

- 1 Mass spectrometry.
- 2 It can produce huge numbers of similar compounds in a short time which are analysed and screened for biological activity. The synthesis route of any useful compounds is already known, making it much faster to bring a potential drug through to a cell, organ and animal testing. The speed and lack of human input should keep the costs down making the resulting drugs more affordable. In theory it should speed up the development of drugs.
- **3** Specificity is often important in biological systems and many drugs have optical enantiomers, only one of which has therapeutic effects; a chiral centre is needed for optical activity, but combinatorial chemistry has not so far been good at developing molecules with these.