

# Index

## A

absorbance, 226  
accuracy, 222–3, 458–9  
acetate (ethyl ethanoate), 174, 177  
acetic acid (ethanoic acid), 131–3, 140–1, 171–2  
acid–base conjugates, 149–50  
acid–base reactions, 112–13, 342  
acid–base titrations, 158–9, 164–5  
acid rain, 123–4, 126–7, 167–8, 283  
acid salts, 151–2  
acidic oxides, 115–16, 121–3  
acidic solutions, 137  
acids, 107–8, 113–14, 131–4, 146–79  
definitions and history of, 107, 146–7, 150–1  
in everyday life, 104–45  
salts as, 152–4  
weak and strong, 140–2  
active metals, 406  
activity series, 43–4  
addition polymers, 13, 15–20  
addition reactions, 8–9, *see also* hydration reactions  
adsorption, 196–7, 290, 490  
aerated drinks, 119  
aerobic bacteria, 271  
agriculture, 269, 284  
air pollutants, 236–8  
atmospheric oxides, 121–6  
monitoring, 249

smog, 123, 239–41  
sulfur extraction, 332  
alanine, 482  
*Alcaligenes*, 28–9  
alcohol groups, 170  
alcohols, 12, 170, 173–6,  
*see also* ethanol  
algal blooms, 263, 286–9  
alkaline (basic) solutions, 136–7  
alkaline cells, 54, 60  
alkalis (soluble bases), 108,  
*see also* bases; sodium carbonate; sodium hydroxide  
alkanes, 6–7  
alkanoic acids, 170–6  
alkanols, 12, 170–6, 462–3,  
*see also* ethanol  
alkenes, 7–10  
alkoxide ions, 462–3  
alkyl alkanoates, 175  
alkyl groups, 9  
allotropes of oxygen, 244,  
*see also* ozone  
 $\alpha\beta$  isomerism, 475  
alpha-emitting radioisotopes, 76–7  
 $\alpha$ -fructose, 475  
 $\alpha$ -glucose, 468, 471–2, 475  
alpha linkages, 468, 472  
alpha rays (particles), 76, 88–9  
aluminium, 418, 420, 422–3  
amides, 23, 484  
amines, 23, 132, 481  
amino acid sequencing, 488  
amino acids, 23, 481–3  
coded by DNA, 500  
tests for, 488–9, 491–5

ammonia, 132, 200–4  
ammonium ion, 243  
amphiprotic substances, 154–5  
amphoteric oxides, 115–16  
amylopectin, 472  
amylose, 472  
anaerobic bacteria, 271, 430  
analytical chemistry, 196–7, 511–31, *see also* forensic chemistry; identification  
anionic surfactants, 367–9  
anions, 113–14, 152–3, 349  
monitoring and identification, 213–15, 219–20, 279–81  
annealing steel, 402  
anodes, 49, 273, 349  
anodic sites, 416  
anodising, 418  
ANSTO (Lucas Heights), 86  
Antarctic, ozone depletion in, 254–6, 258–9  
applied voltage, 424  
aquifers, 283  
Arrhenius, Svante, 146–7, 150–1, 400  
artefacts, 433–40  
ascorbic acid, 132–3  
aspartic acid, 494  
atmosphere, 234–61, *see also* air pollutants; ozone  
layered structure of, 235–7  
atmospheres (units of pressure), 128  
atomic absorption spectroscopy, 225–

30, 283, 530  
atomic bomb, 80–1  
atomic emission spectrographs, 524, 526  
atomic emission spectrometers, 527  
atomic emission spectroscopy, 224–5, 283, 526–9, 531  
atomic mass, 518, *inside right back cover*  
atomic number, 75  
average molecular weight of polymers, 15, 18  
Avogadro's hypothesis, 128

## B

bacteria, 271, *see also* microorganisms  
corrosion of shipwrecks, 430–1, 436  
cyanobacteria in algal blooms, 286  
*Escherichia coli*, 275–6  
nitrous oxide release by, 123  
polymers made by, 28–9  
baking soda, 379  
band (zone) of stability, 75–6  
barium, 214–17, 221–3  
base conjugates, 148–9  
bases, 104–45  
defined, 108, 147  
naturally occurring, 132  
salts as, 152–4  
synthetic, 132–3  
basic oxides, 115–16  
basic solutions, 136–7  
*Batavia* (ship), 439  
batteries, 41, 47–8, 56, 58–

- 60, *see also* galvanic (voltaic) cells  
 Benedict's solution, 476  
 benzene, 16  
 beta-emitting  
     radioisotopes, 77–8  
 $\beta$ -fructose, 468, 475  
 $\beta$ -glucose, 470–1, 475  
 beta linkages, 472–3  
 beta rays (particles), 76, 85–6  
 biochemical oxygen demand (BOD), 270–4  
 biodegradability, 28, 369–70  
 biomass, 26  
 biopolymers, 27–8  
 biuret test, 488–9  
 boiling points, 172–3, 359  
 branched chains, 13–14, 18  
 brine purification, 373–4  
 bromide oxidation, 339–40  
 Brønsted–Lowry concept, 147–51  
 bubbles (foam), 367–8  
 buffer solutions, 166–8  
 builders, in detergents, 369, 370  
 burettes, 158–9, 163–4  
 ‘button’ cells, *see* silver oxide cells
- C**
- calcium chloride, 373–5  
 calcium hydroxide, 133  
 calcium oxide, 133  
 cancer treatment, 86–7  
 Cape Grim Station, 249  
 capillary columns, 512  
 capillary membrane filters, 292–3  
 car batteries, 58–9  
 car exhausts, 239–41  
 carbohydrates, 465–73, 476–7  
 carbon compounds, *see* organic compounds  
 carbon dioxide, 124  
     in oceans, 426–8  
     in the atmosphere, 121, 126  
 carbon dioxide–water equilibrium, 116–19  
 carbon monoxide, 241, 243  
 carbonates, 132, 213–15, 279  
 carbonyl carbons, 467–8, 474–5  
 carbonyl groups, 474  
 carboxylic acid groups, 23, 172, 481  
 carboxylic acids, 173–6, *see*
- also* fatty acids  
 catalysts, 6, 202–3, 334–5  
 catalytic cracking (cat crackers), 6  
 catalytic exhausts on cars, 240–1  
 catchments, 289–91  
 cathodes, 49, 273, 349  
 cathodic protection, 423–4  
 cathodic sites, 416  
 cationic surfactants, 368, 370  
 cations, 349  
     monitoring and identification, 206–11, 216–17, 219–20, 281–3, 464  
 cells, *see* batteries; electrolytic cells; galvanic (voltaic) cells; photovoltaic cells  
 cellulase enzymes, 26–7  
 cellulose, 22–3, 25–7, 470–1  
 cementite, 401–2  
 centre of reactivity, *see* functional groups  
 centrifugation, 210–11  
 centrifuges, 210  
 CFCs, 250–4, 257–8  
 chain branching, 13–14, 18  
 chain carriers, 254  
 chain of custody, 458, 506  
 chain reactions, 253–4  
 chain stiffening, 18–19  
 charge coupled devices (CCDs), 527–8  
 chemical equilibrium, *see* equilibrium  
 chemical reactions, vs nuclear reactions, 78–9  
 chemistry, 195–9, *see also* analytical chemistry  
 chlor–alkali industry, 352–7  
 chlorides, 214–15, 280, 434–5  
 chlorine, 254–5, 290–1, 352–7  
 chloroethene (vinyl chloride), 13, 15  
 chlorofluorocarbons (CFCs), 250–4, 257–8  
 chromatograms, 512–15  
 chromatographs, 514–15  
 chromatography, 489–91, 512–14, 531  
     before mass spectrometry, 520–1  
     compared with
- electrophoresis, 495  
 chromosomes, 497, 500,  
     *see also* DNA  
 citric acid, 132–3  
 clarifying water, 289–90  
 classifying substances, *see* identification  
 cleaning agents, 364–5, *see also* soaps  
 cloud chambers, 85  
 cloudiness, *see* turbidity  
 coagulation (flocculation), 289–91  
 coins, silver, restoration of, 438–9  
 collaboration in chemistry, 198–9  
 colony forming units, 275  
 colorimeters, 280  
 combustion, 122–3, 237–8  
 completeness, 459  
 complex ions, 209, 243  
 concentrated solutions, 142  
 condensation reactions, 22–4, 469, 485  
 condition for equilibrium, 319, 321–2, 328–9  
 conductivity, 267–8, 411  
 conjugate acids and bases, 148–9  
 contact processes, 333–5  
 contamination of specimens, 457–8  
 conversion factors, *inside left back cover*  
 coordinate covalent bonds, 242–3  
 copper, 219, 340  
     restoration of artefacts, 437–8  
 copper chloride, 347–8, 408  
 copper sulfate, 408  
 coral, removal of, 435  
 corrosion, 392–3, 404–6,  
     *see also* oxidation; rusting of iron  
     metals in contact, 418–19  
     restoration after, 435–8  
     in shipwrecks, 425–6, 429–31  
 coulometer, 399  
 covalent bonds, *see* coordinate covalent bonds; peptide bonds (links)  
 ‘cracking’ crude oil fractions, 5–7  
 cracking patterns, 518–20  
 crime, *see* forensic chemistry  
 cross-linking, 19
- crude oil, 5–7, 22, 122, 332  
 crystalline linear chains, 14  
 cultural eutrophication, 287  
 custody, chain of, 458, 506  
 cyclotrons, 81–2, 84–5  
 cysteine, 482
- D**
- data banks, 506–7, 520  
 data, useful, *inside left back cover*  
 Davy, Humphry, 146–7, 150, 398–9  
 degree of ionisation, 141  
 dehydration reactions, 30–1, 341  
 deoxyribonucleic acid, *see* DNA  
 deoxyribose, 466, 497–9  
 depth filters, 293  
 destructive testing, 511–12  
 Desulfovibrio family, 430, 436  
 detergents (synthetic surfactants), 278, 364–5, 367–70  
 diaphragm cells, 352–4  
 dichlorodifluoromethane, 251  
 digestion, 472–3, 486  
 dilute solutions, 142  
 dipeptides, 484  
 diprotic acids, 151–2  
 disaccharides, 467–9, 476  
 displacement reactions, 41–4  
 dissolved oxygen, 270–3  
 DNA (deoxyribonucleic acid), 497–508  
     deoxyribose in, 466  
     electrophoresis, 493  
     forensic analysis of, 497, 501–6, 531  
     privacy issues, 507  
 DNA polymerase, 502  
 Dobson Units, 259  
 domestic water, *see* water quality  
 double bonds, *see* addition reactions  
 double helix structure of DNA, 497, 499, 502  
 drinking water, 263, 289–91, *see also* water quality  
 dry cells (Leclanché cells), 53–4, 60  
 drying  
     long-submerged objects, 433–4  
     to constant mass, 222

**E**

*E.coli*, 275–6  
effluents, *see* sewage; waste management  
electrical conductivity, 267–8, 411  
electricity, history of, 398–400  
electrochemical cells, *see* electrolytic cells; galvanic (voltaic) cells  
electrochemistry, 41–73  
electrode processes (reactions), 47  
electrode (redox) potentials, 64–7, 70  
electrodes, 47, 49–52, 409  
electrolysis, 347–51, 398–401, 407–11  
dissolved oxygen, 272–3  
restoration using, 434–7  
electrolytes, 47, 395–6, 408, 411  
electrolytic cells, 348  
electromagnetic radiation, 247–8, 522–3  
electromagnetism, 400  
electromotive force (EMF), 64, 66, 68–70  
electron transfer reactions, *see* redox reactions  
electrons, excitation of, *see* emission spectra  
electrophoresis, 492–5, 503  
electroplating, 409  
elements, *see also* Periodic Table  
emission spectra, 226, 526, 529  
symbols for, *inside right front cover*  
elution, 491  
EMF, 64, 66, 68–70  
emission limits, 240–1  
emission spectra, 224–7, 525–9  
emulsifiers, 366  
emulsions, 365–6  
end points (equivalence points), 158–9, 164–5  
*Endeavour*, 435, 438  
energy efficiency, in synthesis, 335–6  
energy levels, *see* emission spectra  
environmental issues, *see also* acid rain; air pollutants; water quality  
chemical monitoring and management and, 191–308

detergents, 369–70  
sodium carbonate manufacture, 374–5  
sulfur extraction, 332  
enzymes, 472–3, 480, 486, 488  
equilibrium, 313–45  
equilibrium constants (K), 318–26, 329–30  
equilibrium expressions, 319, 321–2, 328–9  
equilibrium positions, 117  
equilibrium reactions, 116–19, 141, 201–2  
equivalence points (end points), 158–9, 164–5  
*Escherichia coli*, 275–6  
esters, 173–7, 358–9, 363  
ethanoic acid (acetic acid), 131–3, 140–1, 171–2  
ethanol, 31, 170–1  
as a fuel, 34–7  
source of ethylene, 22, 30–1  
synthesis of, 11–12, 33–4  
ethene, *see* ethylene  
ethical issues in forensic chemistry, 459  
ethoxide, 463  
ethoxylates (polyoxyethylene ethers), 367–8  
ethyl acetate (ethyl ethanoate), 174, 177  
ethylene (ethene), 11–15  
sources of, 5–7, 26–7, 30–1  
ethylene glycol, 12  
eutrophication, 286–9  
excited states, 224, 226  
exons, 501, 505  
exothermic processes, 157  
expression for the equilibrium constant, *see* equilibrium expressions

**F**

Faraday, Michael, 399–400  
farming, 269, 284  
fats and oils, 360–4  
fatty acids, 361–3  
Fehling's solution, 476  
fermentation, 33  
fertilisers, 221–3, 287  
production of, 203, 331  
fibres, synthetic, 314  
fibrous proteins, 480  
filters, *see* membrane filters; sand filtration  
fingerprinting, 507  
fissionable (fissile)

elements, 81  
flame colours, emission spectra and, 527–8  
flame ionisation detectors, 512–13  
flame tests, 216–17  
flat batteries, 56  
flavours, from esters, 176–7  
flocculation (coagulation), 289–91  
fluoride, added to water, 290–1  
foam (bubbles), 367–8  
food additives, 133  
carbohydrates, 470, 472–3  
irradiation, 88  
forensic chemistry, 454–541  
DNA analysis in, 497, 501–6  
ethical issues, 459  
instrumental analysis, 511–31  
sample collection, 454–5, 457–8, 501  
formic acid (methanoic acid), 171–2  
Frasch process, 331–2  
free radicals, 246–7  
freons, 250–1  
frequencies, of radiation, 247–8, 523  
fructose, 465–6, 474–5  
fruit flavours, 176  
fuel cells, 60–1  
fuels, *see also* crude oil  
ethanol as source of, 34–5  
functional (globular) proteins, 480, 488  
functional groups, 177, 463–4  
fundamental constants, *inside left back cover*

**G**

Galvani, Luigi, 398  
galvanic (voltaic) cells, 46–61  
calculating EMF for, 66, 68–70  
compared with electrolytic cells, 349  
corrosion and, 416–17, 419, 422–4, 430–1  
pH meters as, 138  
rechargeable, 58–60  
galvanised steel, 421–3  
gamma rays, 76, 78, 86–8  
gas chromatography,

- 196–7  
 gas-liquid chromatography, 512–14  
 gas-solid chromatography, 491  
 gases  
     composition of atmosphere, 235–6  
     concentration of, and pressure, 328–9  
     solubility in oceans, 426–9  
     volumes in reactions, 128–31  
 genes, 500–1  
 genetic information. *see also* DNA  
 Gieger-Müller counters, 85–6  
 glass electrodes, 138  
 glassware, 163–4  
 globular (functional) proteins, 480, 488  
 glucose, 465–6  
     cellulose made from, 25–7  
     isomers, 468, 470–2, 474–5  
 glycerol, 360–4  
 glycine, 481–2  
 glycogen, 471–2, 477  
 Grätzel cells, 63  
 gravimetric analysis, 220–4  
 greenhouse emissions, 34–5  
 ground states, 224, 226, 525–6
- H**  
 Haber process, 200, 203–4  
 half-life, 83  
 halides, 113  
 haloalkanes, 249–52  
 halons, 252, 256  
 hard water, 263, 277–9, 368–9, 379  
 HCFCs, 257  
 health effects, *see* medical issues  
 heat of combustion, ethanol, 36–7  
 heat of reaction, 157  
 heavy metals, 282–3  
 hertz, 523  
 hexoses, 465–6  
 HFCs, 257  
 high density polyethylene (HDPE), 14, 20  
 high performance liquid chromatography, 514–16  
 hollow fibre membrane filters, 292–3  
 homologous series, 170, 172  
 HPLC, 514–16  
 human body, 168, *see also* medical issues  
     DNA of, 500–1, 505  
 hydration reactions, 11, 30–1, 154  
 hydrochloric acid, 131, 134, 140  
 hydrochlorofluorocarbons, 257  
 hydrofluorocarbons, 257  
 hydrogen bonds, 487, 499  
 hydrogen–oxygen fuel cells, 61  
 hydrolysis, 154  
     carbohydrates, 467, 469, 473  
     peptides and proteins, 485–6  
     saponification, 359  
 hydronium ions, 107, 133, 135–6  
 hydrophilic heads, 365  
 hydrophobic tails, 365  
 hydrothermal vents, 396–7  
 hydroxide ions, 136  
 hydroxyl free radical, 246
- I**  
 identification, *see also* analytical chemistry; forensic chemistry  
     atomic emission spectroscopy, 527–8  
 gas-liquid chromatography, 513  
 high performance liquid chromatography, 514–16  
 mass spectrometry, 518–20  
 metal ions, 464  
 organic compounds, 459–60, 462–4  
 proteins and amino acids, 488, 492, 494–5  
 indicators, 108–11, 139  
     pH ranges of, 109, 138–9  
     titration using, 158–9, 164–5  
 industrial chemistry, 195–7, 310–90  
 industrial plants, 311, 377  
 industrial synthesis  
     ammonia, 200–4  
     sodium hydroxide, 352–4  
     sulfuric acid, 333–6  
 industry
- effluents from, 284  
 membrane filters, 294–5  
 uses of radioisotopes, 87–90  
 infrared spectroscopy, 463–4  
 inorganic chemistry, 197  
 inorganic compounds, 459–61  
 instrumental analysis, 511–31  
 international agreements, phasing out CFCs, 257–8  
 introns ('junk' DNA), 501, 503, 507  
 iodide oxidation, 339–40  
 ion migration, *see* salt bridges  
 ionic attractions in proteins, 487  
 ionic product constant of water, 135  
 ionisation reactions, 133–6, 140–1  
 ions, 408–9, *see also* anions; cations; zwitterions  
     concentration in water bodies, 283–4  
 i.r. spectroscopy, 463–4  
 iron, 219, *see also* rusting of iron; steels (iron alloys)  
     distinguishing cations, 209  
     for shipbuilding, 401–4  
     restoration of artefacts, 434–5, 437–8  
 irradiation of medical supplies and food, 88  
 irrigation salinity, 269  
 isoelectric points, 482, 494  
 isomers, 170  
     glucose, 468, 470–2, 474–5  
 isotopes, 75, 518, *see also* radioactive isotopes
- J**  
 jobs in chemistry, 195–7
- K**  
 K. *see* equilibrium constants
- L**  
 lactose, 467  
 land clearing, 269, 283  
 Lavoisier, Antoine, 146–7, 150  
 Le Chatelier's principle, 117–19, 166–7, 314  
 ammonia synthesis,
- 201–2  
 equilibrium expressions and, 328–9  
 leaching, 284, 396, 433–4  
 lead–acid cells (lead accumulators), 58–9  
 lead artefacts, 438  
 lead iodide, 219  
 leak detectors, 88  
 Leclanché cells, *see* dry cells  
 light emission from atoms, 524–5  
 limestone, 371–3, 375  
 linear accelerators (cyclotrons), 81–2, 84–5  
 linear chains, 14  
 linking, *see* cross-linking  
 liquid junction photovoltaic devices, 63  
 liquid–solid chromatography, 490–1  
 lithium cells, 55–6  
 litmus, 108  
 living things, *see also* human body; microorganisms; organic compounds  
     oxygen concentration and, 270–2, 427–8  
     role of DNA in, 500–1  
 low density polyethylene (LDPE), 13–14, 20
- M**  
 maltose, 467–8, 475–6  
 manufactured products, *see* production of materials  
 Mary Rose (ship), 439–40  
 mass filters, 520–1  
 mass number, 75  
 mass spectrometers, 517, 520–1  
 mass spectrometry, 517–20, 531  
 mass–volume calculations, 131  
 materials, production of, *see* production of materials  
 medical issues  
     diagnosis using DNA, 1505  
     effects of atmospheric oxides, 123, 125  
     uses of radioisotopes, 84–90  
 membrane cells, 356–7  
 membrane filters, 292–5  
 mercury cells, 354–6

- mercury pollution, 355–6, 530  
mesosphere, 236  
metal artefacts, restoration of, 435–9  
metallic oxides, 132  
metals  
displacement reactions, 41–3  
heavy metals, 282–3  
identification of ions, 464  
predicting corrosion tendency, 405–6  
used in shipbuilding, 402–4  
methanoic acid (formic acid), 171–2  
methanol, 30, 170–1  
microorganisms, *see also* bacteria  
algal blooms, 286–9  
water quality, 275–6, 289–91, 294  
wood in sea water, 439–40  
yeast, fermentation using, 33  
migration of ions, *see* salt bridges  
mixtures, 210–11, 215, 520  
mobile phase in chromatography, 490  
molar volume, 128–9  
molecular weight, 519  
monitoring, 191–308  
cations and anions, 219–20  
chemical industry, 195–232  
manufactured products, 204, 206  
pollution, 227–8, 531  
stratospheric ozone, 258–9  
water quality, 262–95  
monochromators, 226–7, 280, 524, 526–7  
monomers, 13  
monoprotic acids, 151  
monosaccharides, 465–7, 474–5  
Montreal Protocol, 257–8  
motor car exhausts, 239–41
- N**  
natural gas, sulfur from, 332  
natural products, replacing with synthetic, 313–14  
negative terminal
- (electrode), 49, 349  
nephelometric turbidity units (NTUs), 267  
neutral solutions, 108, 136–7  
neutral species, free radicals as, 246–7  
neutralisation, 112–13, 155–9, 168–9  
neutron bombardment, 84  
nickel–cadmium cells, 59–60  
ninhydrin test, 488, 492  
nitric acid, 132, 200  
nitric oxide, 122–3, 239–41  
nitrogen dioxide, 121–3, 126, 239–41  
nitrogen, in oceans, 426–8  
nitrogen oxides, 122–6  
nitrous oxide, 123, 126  
non-destructive testing, 511–12  
non-ionic surfactants, 367–8  
non-reducing sugars, 475–6  
nuclear chemistry, 74–92  
nuclear equations, 77  
nuclear fission, 78, 80  
nuclear reactions, 78–9, *see also* radioactive isotopes  
nuclear reactors, 80–1, 84  
nucleotides (bases), 497–9  
nutrients in waterways, 287, *see also* sewage
- O**  
oceans (sea water)  
aluminium in, 418  
cathodic protection in, 423–4  
corrosion in, 416–17, 425–6, 430–1  
as electrolyte solutions, 395–6  
ions in, 284  
objects submerged in, 433, 439–40  
redox reactions and, 396–7  
salts in, 264, 395–6, 428  
solubility of gases and salts, 426–8  
oil, crude, 5–7, 22, 122, 332  
oils and fats, 360–4  
open-chain monosaccharides, 474–5  
organic chemistry, 197  
organic compounds, identification of, 459–
- 60, 462–4, 529  
organic wastes, 271, 287  
oxidation, 42–3, 49, *see also* corrosion  
oxidation states, 44–5  
oxides, 115–16, *see also* nitrogen oxides  
oxidising agents (oxidants, oxidisers), 339–41  
oxyacids, 113  
oxyanions, 113  
oxygen, 244–7, *see also* ozone  
biochemical oxygen demand, 270–4  
in oceans, 426–9  
reactions with ethylene, 12–13  
oxygen sensors, 272–3  
ozone, 123, 236, 238, 242–9  
depletion, 247–9, 253–9  
photochemical smog and, 239–41
- P**  
painting, rust prevention using, 420–1  
paper chromatography, 490–2  
paper electrophoresis, 492–3  
particulates, 237, 240  
parts per million (ppm) (gaseous), 121  
passivating metals, 406, 418, 420–2  
PCR amplification, 502  
pentoses, 465–6  
peptide bonds (links), 23, 484, 487  
peptides, 484–6  
Periodic Table, 116, *inside left front cover*  
PET (poly(ethylene terephthalate)), 24  
pH, 134–40  
of water, 265–6  
pH meters, 138, 265  
PHB (poly(3-hydroxybutanoate)), 28–9  
phenyl groups, 16  
phenylethene, 15–16  
phosphates, 214–15, 280–1  
in detergents, 369–70  
in DNA, 497–9  
monitoring in waterways, 219  
photochemical smog, 123, 239–41  
photographic film, detection of radiation using, 85  
photovoltaic cells, 63  
physical chemistry, 197  
pipettes, 163  
plasma, in atomic emission spectrometers, 528–9  
pollution, *see also* air pollutants; water quality chemistry and, 234–5 heavy metals, 282–3, 530 monitoring, 227–8, 531 poly(1-chloroethene), *see* PVC polyester (PET), 24 polyethene, *see* polyethylene polyethylene glycol, 440 polyethylene (polyethene), 13–15, 17–18, 20 polymerase chain reaction (PCR), 502 polymerisation, 13–15 polymers, 5, 13, 15–16, 18–20, 28, *see also* cellulose in membrane filters, 292 polypeptides as, 485 polysaccharides as, 470 polypeptides, 485 polypropylene, 17, 28–9 polysaccharides, 467, 470–3, 475, 477 polystyrene, 15, 17, 21 polythene, 13 poly(vinylchloride), *see* PVC position of equilibrium, 117, 324–6 positive terminal (electrode), 49, 349 positron emission tomography (PET), 86 potassium iodide, 409–10 powder coating, 420 precipitates, 210–11, 220 precipitation reactions, 207–11 precision, *see* reproducibility of analysis prefixes, *inside left back cover* pressure equilibrium reactions, 201 gas concentration proportional to, 328–9 primary standards, 159 primary structure of

- proteins, 487–8  
 primers, 502–3  
 privacy, of DNA data, 507  
 production of materials,  
     2–102, 310–11  
     monitoring, 199–200,  
         206  
     raw materials, 22  
     use of radioisotopes in,  
         87–8  
 propanoic acid, 171–2  
 propanol, 170–1  
 proteins, 480–96  
     condensation polymers,  
         23–4  
     hydrolysis, 485–6  
     identification of, 488–9,  
         494–5  
 proton donors and  
     acceptors, *see*  
     amphiprotic  
     substances  
 proton transfer reactions,  
     156  
 PVC (poly(vinylchloride)),  
     15, 17, 19–21  
 pyroaurite, 421
- Q**
- quadrupole mass filters,  
     520–1  
 qualitative analysis, 220  
 quantised energy, 525  
 quantitative analysis, 220  
 quantum of energy, 525  
 quenching steel, 402
- R**
- radiation, 74, 76, *see also*  
     electromagnetic  
     radiation  
     detection of, 85–6  
     hazard signs, 90  
     ozone as shield from,  
         238  
 radicals, 246–7  
 radioactive isotopes  
     (radioisotopes), 74,  
         82–90  
     radioactive  
         disintegration, 76–9  
 radioactivity, 74  
 rain water, 167–8, 283, 396  
 rates of reactions, 201–2,  
     334–5  
 raw materials, scarcity of,  
     22  
 rayon (viscose rayon), 27,  
     471  
 reaction quotients, 320–1,  
     323  
 reactivity of metals, 43  
 rechargeable batteries,
- 58–60  
 recovered artefacts, 433–40  
 redox reactions (electron  
     transfer reactions),  
     43, *see also* corrosion;  
     galvanic (voltaic)  
     cells; vanadium redox  
     cells  
     calculating EMF for, 66,  
         68–70  
     electricity from, 46–7,  
         56  
     history, 400–1  
     oceans and, 396–7  
     oxidation of sugars,  
         475–6  
     sulfuric acid, 339–42  
         two site, 397  
 reducing agents  
     (reductants,  
     reducers), 339  
 reducing sugars, 475–6  
 reduction, 42–3, 49  
 reduction half reactions,  
     66, 68–70  
 reductive heating, 437  
 refluxing, 175–6  
 refrigeration, 251  
 relative atomic mass  
     (weight), *inside right  
     back cover*  
 relative humidity, 235  
 reliability, use of term in  
     syllabus, 222–3  
 renewable resources,  
     ethanol, 34–5  
 reproducibility of analysis,  
     222–3  
 restoration, *see* recovered  
     artefacts  
 restriction enzymes, 505  
 retention time, 513–14,  
     520  
 reversible reactions,  
     314–15  
 ribonucleic acid, 466  
 ribose, 466  
 rigidity (chain stiffening),  
     18–19  
 ring structures in  
     monosaccharides,  
         474–5  
 rubber, 19, 313–14  
 rubbish dumps, leaching  
     from, 284  
 rust, 405  
 rusticles, 430–1  
 rusting of iron, 404–6,  
     415–18, *see also*  
         corrosion  
     prevention of, 420–1
- S**
- sacrificial electrodes, 423–4  
 safety precautions  
     radioisotopes, 90  
     soap making, 363  
     sulfuric acid, 342–3  
 salinity, 268–70  
 salt bridges, 46, 48–9, 51–2  
 salt water, *see* sea water  
 salting out the soap, 363  
 salts, 112–14, 146, *see*  
     *also* salinity; sodium  
     chloride  
     as acids and bases,  
         152–4  
     in sea water, 395–6, 428  
     in total dissolved solids  
         (TDS), 267–8  
 leaching from recovered  
     artefacts, 433–4  
 sample collection, 454–5,  
     457–8  
     DNA (deoxyribonucleic  
     acid), 501  
     water quality, 264–5  
 sand filtration, 291  
 sanitising water, 289–90  
 saponification, 358–9, 363  
 saturated fatty acids, 362–3  
 scintillation counters, 86  
 sea water, *see* oceans (sea  
     water)  
 secchi discs, 266  
 secondary structure of  
     proteins, 487–8  
 self-ionisation of water,  
     135–6  
 sensitivity, 224, 226–7,  
     230  
 separation, 491–2, 515,  
     *see also* instrumental  
     analysis  
 sewage, 271–2, 284, 287,  
     294  
 shipbuilding, 401–5, 421  
 shipwrecks, 392–3, 425–6,  
     429–30, 433–40  
 short tandem repeats  
     (STRs), 503–4, 506  
 significant figures, 134, 162  
 silver artefacts, restoration,  
     436–9  
 silver oxide cells, 54–5  
 silver plating, 409  
 smog, 123, 239–41  
 smoke alarms, 88–9  
 soaps, 277, 279, 314, 358–  
     9, 363–6  
 soda ash, 378, *see also*  
     sodium carbonate  
 sodium carbonate, 371–5,  
     378–9  
 sodium chloride, *see also*  
     salinity

- drying long-submerged  
     objects, 433–5  
 electrolysis, 349–51  
     in oceans, 395–6  
 sodium fluoride, 290–1  
 sodium hydroxide, 132–3,  
     346–7, 352–4  
     saponification and, 363  
 sodium stearate, 277, *see*  
     *also* soaps  
 sodium sulfate, electrolysis,  
     408  
 soft water, 263, 277–8, *see*  
     *also* hard water  
 soil acidity indicators,  
     110–11  
 soil analysis, 461  
 solar radiation, 247–8  
 solubility  
     addition polymers, 19  
     alcohols and acids, 359  
     in chromatography,  
         196–7  
     gases and salts, 426–8  
     identification of one  
         cation, 209–10  
     in chromatography, 490,  
         515  
 solutions  
     alkaline and acidic,  
         136–7, 138–40  
     concentrated and dilute,  
         142  
     identification of anions  
         in, 213–15  
     identification of cations  
         in, 206–11  
 Solvay process, 371–5  
 solvents, 31  
 specimens, *see* sample  
     collection  
 spectra, *see* emission  
     spectra  
 spectrometry, *see* mass  
     spectrometry  
 spectrophotometers, 258–  
     9, 280  
 spectroscopes, 524, 527  
 spectroscopy, *see*  
     atomic emission  
     spectroscopy  
 splitting the atom, *see*  
     nuclear fission  
 stability of polymers,  
     19–20  
 stable isotopes, 75–6  
 stable nuclei, 74  
 stainless steel, in ships, 404,  
     421  
 standard electrode (redox)  
     potentials, 64–7, 70  
 standard hydrogen  
     electrode, 64–5

- standard solutions, 159, 162–3
- standard state, 65
- starch, 26, 471–2, 477
- stationary phase in chromatography, 490
- steam (thermal) cracking, 6–7
- steels (iron alloys), *see also* iron corrosion, 392–3, *see also* rusting of iron for shipbuilding, 401–4
- sterilizing, *see* sanitising water
- stratopause, 236–7
- stratosphere, 236, 247–9, 253–9
- Streamwatch, 264–5
- strong acids, 140, 142
- structural function of proteins, 487–8
- styrene (phenylethene), 15–16
- substitution reactions, 7
- sucrose, 465, 467–9, 475–6
- synthesis of ethanol from, 33–4
- sugars, 465–7, 475–6
- sulfates, 214–15, 221–3, 280
- sulfur, 331–2, 487
- sulfur dioxide, 121–6, 333–6
- sulfur trioxide, 333–6
- sulfuric acid, 331–45
- safety precautions, 342–3
- synthesis of, 132, 333–6
- surfactants (surface active agents), 364–6, *see also* detergents
- hard water and, 368–9
- swimming pool test kits, 168
- symbols for elements, *inside right front cover*
- synthetic materials, 2–102, *see also* detergents
- acids, 132
- biodegradable polymers, 28–9
- replacing natural products, 313–14
- T**
- ‘tadpole’ structure, 365
- temperature
- atmosphere, 235–6
  - equilibrium and, 201, 326, 329–30
  - ozone depletion and,
- 255
- water, 265
- tempering steel, 402
- tertiary structure of proteins, 487–8
- thermal cracking, 6–7
- thoroughness, in forensic chemistry, 459
- Titanic*, 403, 425–6, 431, 433
- titrants, 158
- titrations, 157–9, 164–5
- dissolved oxygen, 272
- titre, 158
- Tollens’ reagent, 476
- total dissolved solids (TDS), 267–9
- total ozone mapping spectrophotometers (TOMS), 259
- trace elements, 230
- transuranic elements, 80–2
- trichlorofluoromethane, 251
- trichlorotrifluoroethane, 251
- triglycerides, 362
- tripeptides, 485
- triprotic acids, 151–2
- tropopause, 236–7
- troposphere, 236
- turbidity, 266–7, 289–91
- U**
- ultraviolet light, 247–9, 253, 258–9
- universal indicators, 139
- unsaturated fatty acids, 362–3
- unstable isotopes, 75–6
- unstable nuclei, 74
- uranium, 76–7, 80–1
- u.v. light, 247–9, 253, 258–9
- V**
- valence (valency), 44–5
- vanadium redox cells, 61–2
- Vasa* (ship), 439–40
- vinyl chloride (chloroethene), 13, 15
- viscose rayon, 27, 471
- vitamin C (ascorbic acid), 132–3
- Volta, Alessandro, 398
- voltage, 64, 424
- voltaic cells, *see* galvanic (voltaic) cells
- Volta’s pile, 398–9
- volumes of gases in reactions, 128–31
- volumetric analysis, 157–63
- volumetric glassware, 159, 163–4
- W**
- washing soda, 378–9
- waste heat, 375
- waste management, 192–3, 284
- organic wastes, 271, 287
- sodium carbonate manufacture, 374–5
- water, *see also* hard water; sea water; water quality
- carbon dioxide–water equilibrium, 116–17
- self-ionisation of, 135–6
- water quality, 262–95
- algal blooms, 286–9
- aquatic life forms, 270–1
- catchments, 283–4, 289–91
- defined, 262–4
- domestic water, 263, 289–91
- environmental water, 263–4, 355–6
- ion concentrations, 283–4
- mercury pollution, 355–6
- sampling, 264–5
- tests used, 264–83
- wavelength, 247–8, 523–4
- weak acids, 140–2, 172
- welding, 401
- wooden ships and artefacts, 439–40
- wool, 314
- working steel, 402
- wrecks, *see* shipwrecks
- Y**
- yield, monitoring of, 199–200
- Z**
- zeolites, 6
- Ziegler–Natta process, 14
- zinc, 219, 421–4
- zincaleume, 422–3
- zone (band) of stability, 75–6
- zwitterions (dipolar ions), 482–3, 494

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FOURTH EDITION

For Madeline, Aaron, Emily, Jacob,  
Stephanie, Cameron, Victoria and Oscar,  
whose energy and enthusiasm  
have been truly inspiring

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# Contents

Acknowledgments	vi
About this book	vii
To the student	x
The NSW Board of Studies' list of verbs	xiii
<b>Module 1 The Production of Materials</b>	<b>1</b>
<b>CHAPTER 1</b> Ethylene, polymers and ethanol	5
<b>CHAPTER 2</b> Electrochemistry	41
<b>CHAPTER 3</b> Nuclear chemistry	74
<i>Extended Response Exam-style Questions and Revision Test for Module 1</i>	93
<i>Module 1 and the New South Wales HSC syllabus</i>	98
<b>Module 2 The Acidic Environment</b>	<b>103</b>
<b>CHAPTER 4</b> Acids and bases in everyday life	107
<b>CHAPTER 5</b> Acids: changing concepts, use in analysis and making esters from	146
<i>Extended Response Exam-style Questions and Revision Test for Module 2</i>	181
<i>Module 2 and the New South Wales HSC syllabus</i>	186
<b>Module 3 Chemical Monitoring and Management</b>	<b>191</b>
<b>CHAPTER 6</b> Monitoring and management in the chemical industry	195
<b>CHAPTER 7</b> Chemistry and the atmosphere	234
<b>CHAPTER 8</b> Monitoring water quality	262
<i>Extended Response Exam-style Questions and Revision Test for Module 3</i>	297
<i>Module 3 and the New South Wales HSC syllabus</i>	304
<b>Option 1 Industrial Chemistry</b>	<b>309</b>
<b>CHAPTER 9</b> Chemical equilibrium and sulfuric acid	313
<b>CHAPTER 10</b> Alkalies and detergents	346
<i>Extended Response Exam-style Questions and Revision Tests for Option 1</i>	382
<i>Option 1 and the New South Wales HSC syllabus</i>	386
<b>Option 2 Shipwrecks, Corrosion and Conservation</b>	<b>391</b>
<b>CHAPTER 11</b> Materials and the basic electrochemistry	395
<b>CHAPTER 12</b> Corrosion and restoration	415
<i>Extended Response Exam-style Questions and Revision Tests for Option 2</i>	444
<i>Option 2 and the New South Wales HSC syllabus</i>	448
<b>Option 3 Forensic Chemistry</b>	<b>453</b>
<b>CHAPTER 13</b> Classifying and identifying substances (including sugars)	457
<b>CHAPTER 14</b> Proteins and DNA	480
<b>CHAPTER 15</b> Instrumental analysis	511
<i>Extended Response Exam-style Questions and Revision Tests for Option 3</i>	533
<i>Option 3 and the New South Wales HSC syllabus</i>	537
<b>Answers</b>	543
<b>Index</b>	596

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# About this book

*Conquering Chemistry Fourth edition* has been written to meet the requirements of the October 2002 revision of the New South Wales Board of Studies Chemistry Stage 6 Syllabus and to accommodate the new style of HSC examination question used since 2000. Some comments about the approach and organisation of the book are warranted.

## Approach to the syllabus

*Conquering Chemistry* presents a comprehensive coverage of the content of the syllabus, meaning the *Students learn to* (middle) column.

The coverage of material in the student activity (right-hand) column is more varied.

- Procedures for performing experiments (*first hand investigations*) are not included because a bulky textbook does not make a good instruction sheet to have open on a laboratory bench where spills and other accidents can cause extensive damage to the book. Instead, the publisher offers a book of blackline masters that includes, among other activities, details for all the compulsory experiments (Smith, D., *Conquering Chemistry HSC Course Blackline Masters*, McGraw-Hill, Sydney, 2003). However, the text does treat all the background theory and includes calculations required for experiments, both as worked examples and as exercises; in addition it includes experiments in the Extended Response Exam-style Questions (see below) and in the Revision Tests, with useful information being provided in answers to these questions.
- For activities that require students to develop and use skills, such as writing equations and performing stoichiometric and other calculations, full treatment of the underlying theory and methods of approach, along with worked examples and student exercises, are included.
- For activities that require students to process, analyse or discuss information, the relevant information is generally included in the text.
- Some activities require students to collect and organise information, with the emphasis being upon the process of collecting and organising the information rather than on the information itself. Generally, information for this type of activity is not included in the text, though the activity is usually

highlighted by being the subject of a *For Investigation* box.

- Activities involving building and evaluating models are treated to some extent, but are limited by the constraints of two-dimensional paper presentation.

## Presentation

*Conquering Chemistry* follows syllabus order apart from a few minor exceptions where the logical introduction of concepts seems to demand variation.

The book presents a thorough treatment of syllabus material, but equally importantly, it contains very little material that is outside the syllabus. On the few occasions where non-syllabus material has been included (because logic seems to demand it), footnotes are used to indicate this.

## General structure

Each module begins with a general introduction setting out its purpose and scope. There are then two or three chapters treating the material, followed by a set of Extended Response Exam-style Questions and one 90 minute or two 45 minute Revision Tests. Finally, there is a section called *Module x and the HSC Syllabus*. This presents tables showing where each syllabus item is treated in the book, where information can be found for the compulsory experiments, how and where items in the student activity column have been treated and a brief comment on how the material relates to the Prescribed Focus Areas of the syllabus.

## Structure of chapters

Each chapter starts with a section called *In this chapter*, which lists the main topics to be discussed. At the end of the chapter is a list of *Important new terms* with page references to definitions or explanations and finally a set of *Test yourself* questions for students to see whether they have gained the required knowledge.

Sets of exercises are located throughout the chapters at places where the author considers it is appropriate to pause and consolidate learning by applying it to problem-solving.

## Exercises, Test yourself, Extended Response Exam-style Questions, Revision Tests

- *Exercises* are simple calculations and qualitative problems interspersed through the text. They are intended to consolidate understanding and use of the concepts just discussed. At least some of them should be done as students work through the chapter.
- *Test yourself* is a set of questions to let students check that they have learnt the necessary facts from the chapter. They are not problems; they just test factual knowledge.
- *Extended Response Exam-style Questions* (at the end of each module) are in the style that is currently being used for extended response questions in HSC Chemistry examinations: they use the HSC list of verbs (such as assess, compare, contrast, describe, discuss, evaluate, explain, justify, outline) and place heavy emphasis upon recall of learnt information. They do not involve problem-solving. Recall of learnt information is much more important in the post-2000 HSC examination than it was previously.

- *Revision test* is a mini-HSC exam (at the end of each module). It combines problem-solving questions with extended response questions and is intended to help students develop the exam skills they will need for the actual HSC exam.

## Exercises with asterisks

Answers are provided for all numerical exercises and for more than half the non-numerical ones (explain why, draw structures, write equations, etc). Unanswered exercises are generally the latter parts of multi-part questions or ones that are similar to a previous question for which an answer has been given.

*Exercises (or parts thereof) without answers have an asterisk before them.*

Answers and/or detailed commentaries are given for all *Extended Response Exam-style Questions* and *Revision Tests*.

## The *Conquering Chemistry* website

There is a *Conquering Chemistry* website at the address:

[www.nelsonsecondary.com.au/conqueringchemhsc](http://www.nelsonsecondary.com.au/conqueringchemhsc)

For each module or chapter the site contains comments about the syllabus, explanations for the approach or sequence adopted by the book, further information about the topics of the chapter (generally outside the syllabus, but often relevant and interesting) and further exercises (some more challenging).

Most importantly, this website will be updated to meet any further fine-tuning of the syllabus that may occur after publication of the book.

## Other Internet sites

Occasionally throughout the book there are addresses of Internet sites that contain useful and relevant information to supplement this book or to meet syllabus requirements. Brief notes about what the site contains and how to reach the relevant information are included. Websites do have a tendency to appear, disappear or change addresses quite rapidly, so be prepared to have the occasional site turn up ‘address unknown’! The lists provided are not exhaustive, so students are encouraged to do their own searching for other relevant sites.

# To the student

Do not be alarmed by the size of this book; you only have to study two thirds of it (because it contains three options, of which you study only one). The aim of *Conquering Chemistry* is to help you understand and use the basic concepts of chemistry and develop an appreciation of the way chemistry is involved in your life and in the world we live in. The emphasis is on ‘help’. You must make the real effort and do the hard work to gain that understanding and appreciation; no book or teacher can do it for you. But if you do make the effort, you will soon come to enjoy chemistry and the fascinating insights it provides into the world around us. The key to success is studying effectively.

## Effective study methods

For a good understanding of chemistry you need to study regularly, methodically and without distractions, and you need to *apply* your knowledge to problem-solving and to test yourself frequently on what you have learnt.

When you have a new piece of work to study, first skim through the chapter or portion of a chapter to quickly get an idea of what it is about. Then read it carefully to understand what is being said, paying particular attention to the examples and illustrations, because they often get the message across better than mere descriptions. Write out and learn the important definitions and laws as they are introduced. Just as you cannot speak Italian or Indonesian until you know the vocabulary, so too you cannot talk chemistry unless you know the meaning of technical terms and the important laws.

When you think that you understand the material and know the necessary facts, try some of the exercises. Try them when they occur in the text—they have been placed at strategic points where the author thinks your understanding will be helped by working some examples. Generally in each set of exercises the early ones are very simple, but gradually they get harder as you progress through the set. Answers are provided for all numerical exercises and for most of the non-numerical ones. Many of the exercises have several parts. There is no need to work all parts on your first time through the book. Work the first half or so of them, and keep the rest for revision. Do not despair if you find the exercises difficult at first: go back over the text, particularly the worked examples, then if

you are still having difficulty, ask your teacher or a friend to help you with the first one or two, then try the rest on your own. Eventually you must be able to solve exercises on your own, so do not rely on helpers for too long!

## Self-testing

When you think that you have mastered a topic, check that you have absorbed the essential facts and concepts from the chapter by trying the *Test yourself* questions. These questions highlight the key points of the chapter and allow you to check that you have absorbed them. Whenever you revise a chapter—and frequent revision is necessary in order to remember what you have learnt—use these *Test yourself* sets. You haven't really learnt the material of the chapter until you can answer those simple questions!

You will enjoy chemistry when you can succeed at it (just as you enjoy tennis, netball or dancing when you can do it properly) and success in chemistry, as well as in sports, requires perseverance and practice.

## Key aspects

Three of the key aspects of succeeding at chemistry are:

- being able to write formulae for compounds without having to memorise them;
- being able to write chemical equations for common types of reactions, regardless of which particular compounds are involved; and
- being able to do simple quantity calculations based on chemical formulae and equations.

Hence this book places great emphasis on developing these skills—they take time, patience and perseverance for mastery, but the rewards are worth it.

In chemistry, as in mathematics and physics, the emphasis is on using the information acquired—working exercises and solving problems. Assimilation of facts is necessary but it is not sufficient. So develop the habit of working exercises—and persevering with them until you get them correct—right from the beginning of your course.

## Preparing for the New South Wales HSC examination

Understanding chemistry and being able to apply concepts to problem-solving situations is no longer sufficient to guarantee a good mark in the New South Wales HSC examination. You now (since 2000) need to be able to assess, compare and contrast, demonstrate, discuss, evaluate, explain, justify, etc. various aspects of the subject in what are called ‘extended response’ questions. Even when you understand the chemical concepts and can apply them to problems, these extended response questions are often not easy to answer ‘cold’ (that is, without having seen or thought about the question in advance). So to maximise your marks in the HSC exam, you need to develop skills for answering such questions and the best way to do this is by a lot of practice, with feedback on your efforts. To help you develop these necessary skills *Conquering Chemistry* presents a set of such extended response questions for each module. Advice about how to tackle these questions and what examiners would expect in your answers, along with sample answers for many of them, are included in the

Answers section of this book. The use of such questions in the HSC examination means that chemistry students now need to memorise a lot more information than they did before 2001.

The HSC examination will be a mixture of these extended response questions and problem-solving questions similar to the exercises throughout the chapters of this book.

When you have finished studying a complete module and worked most of the exercises in the chapters and many of the Extended Response Exam-style Questions, and consider that you have a reasonable grasp of the material, try the *Revision Test* at the end of the module. Revision Tests are similar to HSC examinations: they are mixes of problem-solving and extended response questions and have the topics in random order.

## Other useful study hints

Some further hints are:

- *Use the index!* If, in studying a particular chapter, a technical term is used which you cannot remember the meaning of, look it up in the index to find the relevant section in the book so you can better understand the argument at hand. That is not wasting time—it is effective learning.
- *Look up cross-references.* If the topic you are currently reading refers to a previous section, look it up to make sure you know what it is all about. Interconnecting today's study with last week's or last month's work is an important part of learning.
- *Set out your exercises systematically and neatly.* This will help you develop logical arguments and make it easy for you to check for errors in your work or for your teacher to diagnose where you are having problems. The worked examples in this text have been set out in ways that should serve as good models for your own work.
- If you are having difficulty with exercises based on a particular topic, take the time to read the relevant part of the text carefully and study it thoroughly. Do not just grab a formula or copy a worked example. Time spent getting to understand the basic idea is definitely not time wasted—even when the object is to get some homework exercises done!

Classroom wits will soon discover that there are two ways of taking the title of this book. The author is confident that, with reasonable effort, you will be able to take it as intended—as you mastering chemistry. Good study and good luck!

# The NSW Board of Studies' list of verbs

The NSW Board of Studies has prepared a list of definitions of the verbs that are used in its syllabus documents. Since 2000 these verbs have figured prominently in HSC examinations (in the extended response questions). The list of definitions is reproduced here (with permission). The verbs are intended for a wide range of subjects, so the definitions are quite broad. Following HSC examination usage, the Extended Response Exam-style Questions in this book use these verbs. In the comments and answers to these questions the meaning of these verbs in specific contexts is explained more fully.

**Account** *Account for:* state reasons for, report on

*Give an account of:* narrate a series of events or transactions

**Analyse** Identify components and the relationship among them; draw out and relate implications

**Apply** Use, utilise, employ to a particular situation

**Appreciate** Make a judgement about the value of

**Assess** Make a judgement of value, quality, outcomes, results or size

**Calculate** Ascertain/determine from given facts, figures or information

**Clarify** Make clear or plain

**Classify** Arrange or include in classes/categories

**Compare** Show how things are similar or different

**Construct** Make; build; put together items or arguments

**Contrast** Show how things are different or opposite

**Critically (analyse/evaluate)** Add a degree or level of accuracy depth, knowledge and understanding, logic, questioning, reflection and quality to (analysis/evaluation)

**Deduce** Draw conclusions

**Define** State meaning and identify essential qualities

**Demonstrate** Show by example

**Describe** Provide characteristics and features

**Discuss** Identify issues and provide points for and/or against

**Distinguish** Recognise or note/indicate as being distinct or different from; to note differences between

**Evaluate** Make a judgement based on criteria; determine the value of

**Examine** Inquire into

- Explain** Relate cause and effect; make the relationships between things evident; provide why and/or how
- Extract** Choose relevant and/or appropriate details
- Extrapolate** Infer from what is known
- Identify** Recognise and name
- Interpret** Draw meaning from
- Investigate** Plan, inquire into and draw conclusions about
- Justify** Support an argument or conclusion
- Outline** Sketch in general terms; indicate the main features of
- Predict** Suggest what may happen based on available information
- Propose** Put forward (for example a point of view, idea, argument, suggestion) for consideration or action
- Recall** Present remembered ideas, facts or experiences
- Recommend** Provide reasons in favour
- Recount** Retell a series of events
- Summarise** Express concisely the relevant details

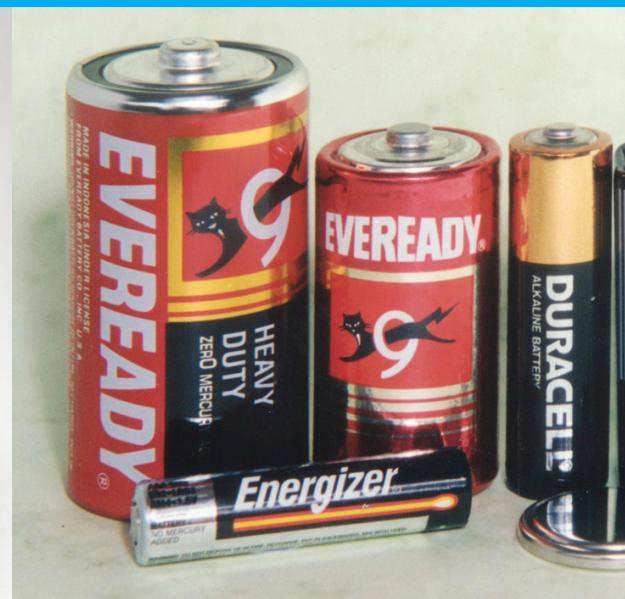
MODULE 1

# Production of materials

Throughout history humans have used their ingenuity to make new materials and objects to satisfy their diverse and growing needs—materials such as ceramics and glass, metals and alloys, plastics and synthetic fibres, and inventions such as wheels, weapons, weaving looms, locomotives, motor cars, aeroplanes, telephones, televisions and computers.

When the demands for particular natural resources put strains on their supply, new materials were developed. For example when agriculture expanded greatly in order to feed a growing world population, synthetic fertilisers such as ammonium sulfate and superphosphate were developed to overcome shortages of natural fertilisers (manure and saltpetre). When demand for natural fibres (cotton, wool, silk) put strains on supply, synthetic fibres (rayon, nylon, polyester) were developed. Now that demands for crude oil are likely to deplete supplies within a few decades, attention is turning to developing new sources for the important materials such as plastics we currently get from oil.

In recent decades we have seen the development of many new technologies to meet the expanding demands of a more sophisticated society. When demands for more and more telecommunications put strains on the ability of copper wires to carry the signals, fibre optics were developed. Similarly the demands of the space race of the 1960s and '70s produced strong, light, heat-resistant materials.



The needs of medicine prompted the development of more sophisticated diagnostic tools and materials for artificial body parts, while the development of computers since the 1960s continues to stimulate the production of new high-purity materials.

In this module we shall examine some of the synthetic materials that are in widespread use and some of the ways of making them.

We will start (in Chapter 1) with a survey of some polymers (plastics and fibres) that we make from crude oil. This will lead us into a discussion of possible future trends for such materials, particularly in view of likely depletion of oil supplies and widespread pollution by plastics. Use of plant material as a possible source of liquid fuels will also be considered.

Electrochemical methods (which are processes involving chemical reactions and electricity) are widely used to produce sources of easily portable energy.

Chapter 2 will introduce the basic ideas and describe several widely used batteries.

Chapter 3 will introduce what are called radioactive materials and will describe some of the important roles they play in medicine and industry.

Throughout this module particular attention will be given to new materials and to likely future developments in these areas of chemistry.



## MANY EVERYDAY PRODUCTS ARE MADE FROM SYNTHETIC MATERIALS

This colourful picnic ware and the collection of batteries used in a variety of consumer goods are just some of the thousands of products that are made from materials synthesised by chemical reactions.

Synthetic radioactive materials such as caesium-137 are made in nuclear reactors and used to detect structural faults in complex machinery (in much the same way as X-rays detect broken bones in people).



# Ethylene, polymers and ethanol

## IN THIS CHAPTER

Ethylene from cracking crude oil fractions  
Properties of alkanes and alkenes  
Reactions of alkanes  
Reactions of alkenes  
Industrially important reactions of ethylene  
Polymerisation of ethylene  
Other addition polymers  
Relating properties and uses to structure  
Uses of polyethylene, PVC and polystyrene

Will raw materials run out?  
Condensation polymers  
Structure and possible uses of cellulose  
Biopolymers  
A synthetic biodegradable biopolymer  
Ethanol as a source of ethylene  
Ethanol as a solvent  
Synthesis of ethanol from plant material  
Ethanol as a fuel  
Heat of combustion of ethanol

In Chapter 9 of *Conquering Chemistry Preliminary Course (CCPC)* we saw how crude oil provides us with a variety of products—gases for LPG, petrol for cars, kerosene for jet aircraft, diesel for trucks, lubricating oils and greases and tar (Table 9.6, p. 257 *CCPC*). Crude oil also provides us with the raw materials for making many plastics or *polymers* as they are called technically.

The most widely used starting substance for making polymers is ethylene<sup>†</sup> which is obtained from crude oil, either as a by-product of petrol refining or by the deliberate decomposition of some of its higher boiling point fractions. The term ‘cracking’ is used in these contexts.

## 1.1 ETHYLENE FROM ‘CRACKING’ CRUDE OIL FRACTIONS

**Cracking** is the name given to the chemical process of breaking large hydrocarbon molecules into smaller ones; for example breaking dodecane, C<sub>12</sub>H<sub>26</sub> into octane, C<sub>8</sub>H<sub>18</sub>, and butene, C<sub>4</sub>H<sub>8</sub>. There are two types of cracking: *catalytic cracking* and *thermal cracking*.

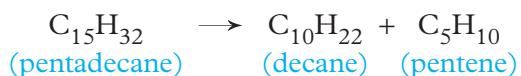
<sup>†</sup> This is the historical name for the compound. Its systematic name is ethene. However, as explained on p. 262 *CCPC* this is one of several compounds where the historical (trivial) name, rather than the systematic name, is the IUPAC-preferred name; hence, it will be used in this book.

## Ethylene from catalytic cracking in oil refineries

Oil refineries need to balance their outputs of various products (petrol, diesel, fuel oil etc) to match the demands of the marketplace. As was mentioned on p. 258 of *CCPC*, generally more petrol is required than is obtained from fractional distillation. Hence oil refineries increase the proportion of gasoline by converting some of the lower demand fractions into gasoline. The process is called *catalytic cracking*.

**Catalytic cracking** is the process in which high molecular weight (*high boiling point*) fractions from crude oil are broken into lower molecular weight (*lower boiling point*) substances in order to increase the output of high-demand products.

The column in which this occurs is called a **cat cracker**. Alkanes with 15 to 25 carbon atoms per molecule are broken into two smaller molecules, one an alkane and the other an alkene; for example:



The alkene further splits into smaller alkenes until either ethylene or propene (or both) is formed; for example,



The overall products of catalytic cracking are alkanes of shorter chain lengths (used for petrol) and small alkenes. The proportions of ethylene to propene to alkanes vary with the reaction conditions.

The catalysts used for cracking alkanes are inorganic compounds called **zeolites**: they are crystalline aluminosilicates (compounds of aluminium, silicon and oxygen with some metal ions attached). The reaction is typically carried out at 500°C in the absence of air and with pressures somewhat above atmospheric.

The ethylene and propene which are by-products of catalytic cracking are starting materials for making plastics (polymers). However this production of ethylene and propene is insufficient to meet current needs for these chemicals. Often some fractions of crude oil are decomposed completely to produce ethylene and propene in a process called steam cracking or thermal cracking.

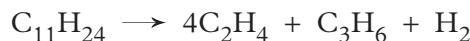
## Ethylene from steam or thermal cracking

**Steam cracking** or **thermal cracking** is a non-catalytic process in which a mixture of alkanes with steam is passed through very hot metal tubes (700 to 1000°C) and at just above atmospheric pressure to decompose the alkanes completely into small alkenes such as ethylene,

Catalytic crackers at an oil refinery



propene and butene. Some hydrogen is also produced. For example, for the thermal cracking of undecane,  $C_{11}H_{24}$ :



Steam is present as an inert diluent; it allows the process to operate at just above atmospheric pressure (which facilitates easy flow of the gases through the hot tubes), while keeping the concentrations of the reacting gases low enough to ensure that the desired reactions occur.

Sometimes the feedstock for thermal cracking is a mixture of ethane and propane obtained from natural gas (which is mainly methane: see p. 268 *CCPC*). In this case the reactions are:



and



## 1.2 PROPERTIES OF ALKANES AND ALKENES

We saw on p. 265 CCPC that alkenes had similar physical properties (boiling points, densities and solubilities) to the corresponding alkanes. This was because alkenes, like alkanes, are *non-polar molecules* with *weak dispersion forces* being the only intermolecular forces involved. Recall that ethylene, propene and the butenes are gases at room temperature (as are the corresponding alkanes). The higher alkenes (like the higher alkanes) are liquids.

However alkenes and alkanes differ markedly in their chemical reactivity.

## 1.3 REACTIONS OF ALKANES

For alkanes there are only two important reactions:

- 1** Alkanes burn in air to form carbon dioxide and water. In doing so they liberate large amounts of heat, for example:

For propane:  $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$

$$\text{For octane: } \text{C}_8\text{H}_{18}(g) + 12\frac{1}{2}\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(g)$$

It is this combustion reaction that makes alkanes useful to us as fuels (Chapter 9 CCPC).

- 2** Alkanes react with chlorine and bromine when the mixtures are exposed to ultraviolet (u.v.) light, for example:

For methane:

$$\text{CH}_4(g) + \text{Cl}_2(g) \rightarrow \text{CH}_3\text{Cl}(g) + \text{HCl}(g)$$

(chloromethane)

For hexane:  $\text{C}_6\text{H}_{14}(l) + \text{Br}_2(\text{soln}) \rightarrow \text{C}_6\text{H}_{13}\text{Br}(\text{soln}) + \text{HBr}(\text{soln})$   
**(bromoheptane)**

A reaction such as these in which an atom in a molecule is replaced by another atom or group of atoms is called a **substitution reaction**.

A variety of other products can be formed by these reactions, depending upon the conditions used, but for our present purposes the key point to note is that alkanes do not react with (decolorise) chlorine or bromine solutions in the absence of u.v. light but that they do react (quite slowly for the liquid ones) in the presence of u.v. light. This contrasts with the behaviour of alkenes (below).

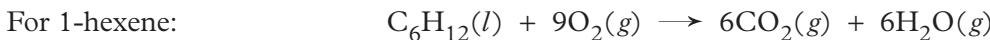
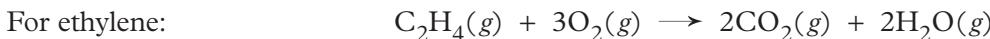


## Exercises

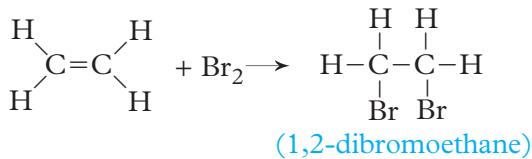
- 1 a Write an equation (in terms of molecular formulae) for the catalytic cracking of
  - i butadecane, C<sub>14</sub>H<sub>30</sub>, into a C<sub>8</sub> alkane and a C<sub>6</sub> alkene
  - \*ii dodecane, C<sub>12</sub>H<sub>26</sub>, into a C<sub>7</sub> alkane and a C<sub>5</sub> alkene
- b Draw structural formulae and name the products of your reactions in (a).
- 2 Write equations to show the decomposition of the alkenes in Exercise 1 to propene and/or ethylene.
- \*3 Why is it necessary to exclude air from catalytic and thermal cracking?
- 4 Write an equation for thermal cracking of hexadecane, C<sub>16</sub>H<sub>34</sub> (to form ethylene, propene and perhaps hydrogen); more than one equation is possible.
- 5 An oil refinery was processing a Middle East crude oil that contained a high proportion of C<sub>20</sub> to C<sub>25</sub> alkanes. After fractional distillation (see pp. 256–7 CCPC) the refinery wanted to increase the proportion of the gasoline fraction, C<sub>6</sub> to C<sub>12</sub>, so it passed the C<sub>20</sub> to C<sub>25</sub> fraction through a catalytic cracker. Operating conditions were such that this cat cracker produced a mixture of C<sub>6</sub> to C<sub>12</sub> alkanes along with C<sub>2</sub> to C<sub>5</sub> alkenes.
  - a How would the refinery separate this mixture into a portion that could be added to its gasoline output, a portion that contained C<sub>4</sub> and C<sub>5</sub> alkenes that could be further cracked, and a gaseous mixture of ethylene and propene? Some contamination of the gasoline portion with C<sub>5</sub> alkenes and vice versa would cause no problem.
  - b Write equations for the cracking of one of the starting alkanes and for the complete cracking of one of the C<sub>5</sub> alkenes.
  - \*c Draw a flow chart for the complete processing of this C<sub>20</sub> to C<sub>25</sub> fraction.
- 6 Write equations for the combustion of:
  - a butane
  - b hexane
  - \*c octane
- 7 Write equations for the reaction of butane with chlorine in the presence of u.v. light. How many monosubstituted chloro-compounds (that is, compounds with only one Cl atom per molecule) can be formed? Draw their structures.
- 8 a When ethane is reacted with bromine in the presence of u.v. light, under certain conditions compounds having two Br atoms per molecule are formed. Draw structures to show that two such compounds (isomers) are possible.  
b Under other conditions compounds with three Br atoms per molecule are possible. How many isomers with three Br atoms are possible?

## 1.4 REACTIONS OF ALKENES

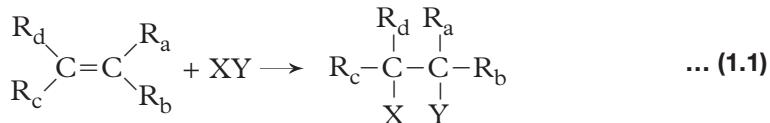
Alkenes burn in air to form carbon dioxide and water in the same way as alkanes do; for example:



*The presence of the double bond in alkenes makes them much more reactive than alkanes.* There are many substances which react with alkenes by opening out the double bond to form two single bonds: these are called **addition reactions**, the simplest one being between bromine and ethylene:



The general form of addition reactions is:



where XY is a molecule such as Cl<sub>2</sub>, Br<sub>2</sub>, H<sub>2</sub>, HCl, HBr, HOH (H<sub>2</sub>O) and where R<sub>a</sub>, R<sub>b</sub>, R<sub>c</sub> and R<sub>d</sub> represent the rest of the alkene molecule—either H atoms or what are called **alkyl groups**.

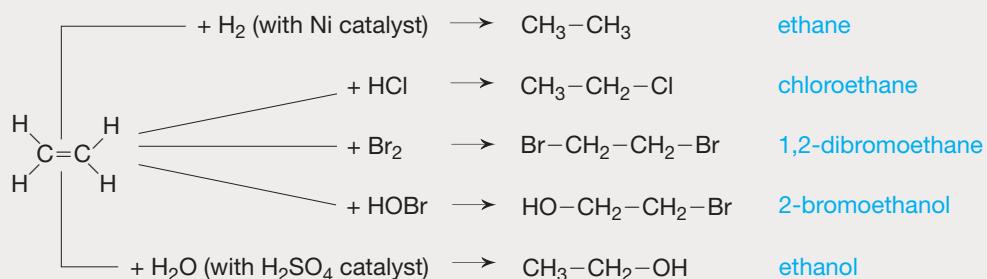
An **alkyl group** is an alkane molecule with one hydrogen atom missing; it does not exist on its own, but is part of another molecule.

Alkyl groups are named by deleting the *ane* from the parent alkane and adding *-yl*. The simplest alkyl groups and their parent alkanes are shown in Table 1.1.

**TABLE 1.1 Names and formulae of simple alkyl groups**

Alkane	Name	Alkyl group	Name
CH <sub>4</sub>	methane	CH <sub>3</sub> —	methyl
CH <sub>3</sub> —CH <sub>3</sub>	ethane	CH <sub>3</sub> —CH <sub>2</sub> —	ethyl
CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>3</sub>	propane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —	propyl
CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>3</sub>	butane	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —CH <sub>2</sub> —	butyl

Addition reactions of alkenes are summarised in Figure 1.1. Although ethylene is used as the alkene (for simplicity), *all* alkenes undergo these reactions.



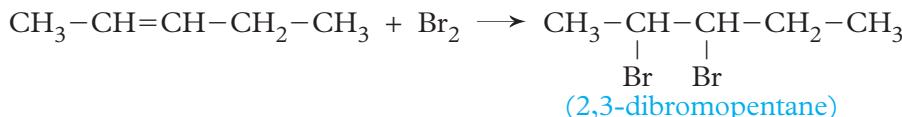
**FIGURE 1.1**  
Common addition reactions of alkenes  
(examples of Reaction 1.1)

## Laboratory test for alkenes

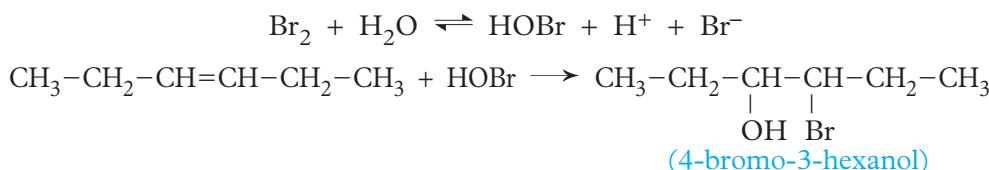
Reaction with bromine is often used in the laboratory to distinguish between alkenes and alkanes. The bromine can be used either in a non-aqueous solvent such as chloroform or hexachloroethane or as an aqueous solution called bromine water. In either case drops of the bromine solution are added to the colourless sample to be tested with gentle shaking. If the sample decolorises

the bromine solution, the sample is an alkene; if the sample takes on the brown colour of the bromine (that is, does not react with the bromine), it is an alkane. The test must be performed in subdued light because in the presence of ultraviolet light (for example sunlight) alkanes will react slowly with bromine (previous section).

As an example, 2-pentene will decolorise drops of a solution of bromine in hexachloroethane, the reaction being:



Alternatively 3-hexene will decolorise drops of bromine water, the reaction being:



On the other hand pentane and hexane will not decolorise either solution.

While the aqueous bromine solution is more convenient to use, the chemistry is a little more complicated than for the non-aqueous solution.

## Exercises

9 Write balanced equations for the combustion (in excess oxygen) of:

- a propene                  b 1-pentene                  \*c 1-octene

Use molecular formulae for the carbon compounds.

10 Write equations for the reaction of (i) hydrogen (using a catalyst) (ii) chlorine (iii) bromine water, with each of the alkenes

- a propene                  b 2-butene                  \*c 1-pentene

Use structural formulae for the carbon compounds.

11 Write equations for the reaction of hydrogen chloride with:

- a propene                  b 1-butene                  \*c 3-hexene

If two products are possible, give both.

12 Write equations for the reaction of aqueous acid solution with:

- a propene                  \*b 2-butene

If two products are possible, give both. Name all your products.

13 Draw structural formulae for the products of the following reactions:

- a 1-butene with

i bromine                  ii hydrogen bromide                  iii water (with H<sup>+</sup> catalyst)

- b 2-pentene with

i bromine water                  ii hydrogen (with Ni catalyst)

14 Compounds A, B and C are either octane or 2-hexene.

- a When a few drops of a solution of bromine in chloroform were added to compound A and the mixture shaken, there was no apparent reaction. When a solution of bromine in water was added to another sample of the same compound, again after



shaking the mixture there was no apparent reaction. What do you conclude about the compound?

- b** When similar tests were performed on a different compound, B, this compound decolorised both of the bromine solutions. What do you conclude about compound B?
- c** The same two tests were performed on compound C on a sunny patio outside the laboratory. Compound C slowly decolorised both bromine solutions. When the tests were repeated inside the laboratory in very subdued light, neither solution was decolorised. Explain these results and draw a conclusion about the nature of compound C.

## 1.5 INDUSTRIALLY IMPORTANT REACTIONS OF ETHYLENE

The reactive double bond in ethylene means that it can easily be converted into a range of very useful products such as ethanol and the starting materials for several important plastics (polymers) as shown in Figure 1.2. Let us look at some of these reactions in more detail.

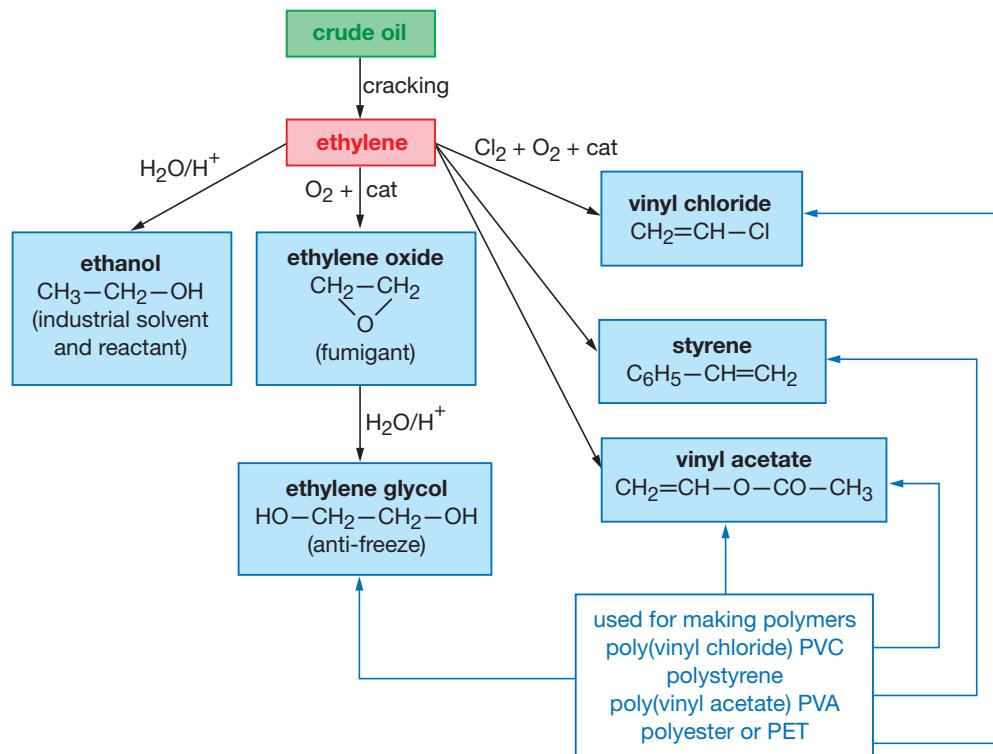
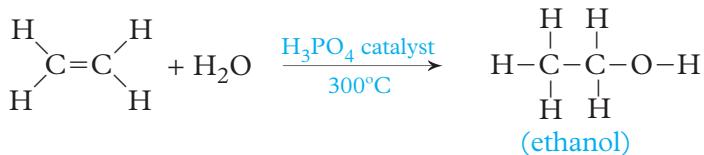


FIGURE 1.2  
Important industrial chemicals made from ethylene (cat = catalyst)

### 1 Reaction of ethylene with water to form ethanol

Industrially ethylene is converted to ethanol by heating it with water (steam) at  $300^\circ\text{C}$  and at high pressure and using phosphoric acid as a catalyst:



This addition of a water molecule across a double bond is called a **hydration reaction**. It is a special type of *addition reaction*.

Ethanol is widely used in industry as a reactant and as a solvent in the synthesis of products ranging from pharmaceuticals and perfumes to varnishes and plastics. In the home it is used as an antiseptic and as a solvent in such items as food colourings and flavourings and in many medications.

The alcohol in alcoholic beverages is made by fermentation (discussed below), not by the above industrial process. Similarly the ethanol that is currently being added to petrol is made by fermentation.

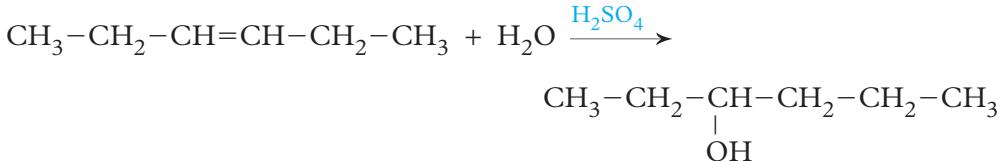
Ethanol belongs to a group of compounds called **alkanols**: they can be regarded as alkanes with one H atom replaced by an OH group: for example methanol,  $\text{CH}_3\text{-OH}$ , from methane,  $\text{CH}_4$ ; ethanol (above) from ethane,  $\text{CH}_3\text{-CH}_3$ .

### To name an alkanol

- Delete the *e* of the parent alkane and add **-ol**: methanol, ethanol, propanol, butanol and so on, and
- Add a number prefix to denote the position of the alcohol group (as the OH is called) in the same way as a number was used for the position of the double bond on p. 265 CCPC<sup>†</sup>. No number is needed for methanol or ethanol. (Why?)

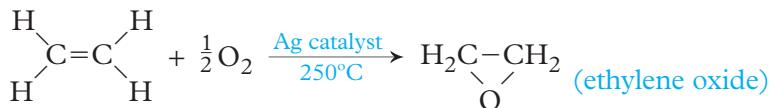
Alkanols are a sub-group of a class of compounds called **alcohols**. *Alcohols (and therefore alkanols) contain the  $-\text{OH}$  functional group* (centre of reactivity, p. 267 CCPC).

In the laboratory liquid alkenes are converted to the corresponding alkanols by heating with dilute sulfuric acid, the  $\text{H}^+$  from  $\text{H}_2\text{SO}_4$  being the catalyst for the reaction; for example 3-hexene can be converted to 3-hexanol:

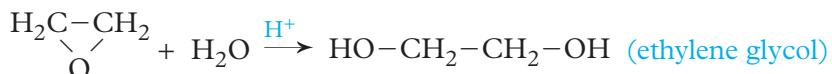


## 2 Catalysed reactions of ethylene with oxygen

Ethylene glycol (systematic name 1,2-ethanediol) is used in large quantities for the manufacture of polymers (polyester fibres and PET, poly(ethylene terephthalate) plastics) and as an automotive antifreeze. It is made from ethylene. The first step is to react ethylene with oxygen in the presence of a silver catalyst to form ethylene oxide:

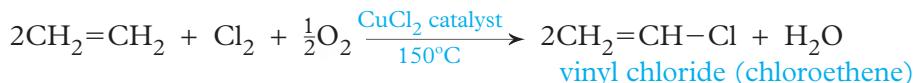


While some ethylene oxide is used as a fumigant, much larger amounts are converted to ethylene glycol by treating it with dilute acid solution:



<sup>†</sup> Remember, CCPC is the abbreviation being used for *Conquering Chemistry Preliminary Course*. Page numbers refer to the fourth edition, 2004.

Other catalysed reactions are used to convert ethylene to the starting materials for making a variety of other plastics as indicated in Figure 1.2. For example to form vinyl chloride, the starting material for making the very common plastic, poly(vinyl chloride), PVC, ethylene is heated to 150°C with chlorine and oxygen in the presence of a copper chloride catalyst:

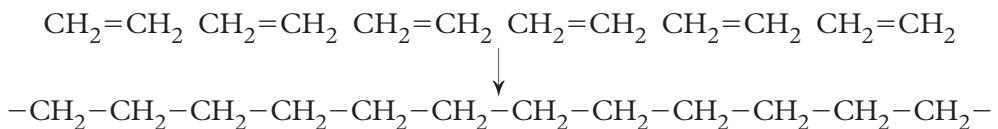


The most important reaction of ethylene is its conversion to polyethylene (or polyethene) in a reaction which is called *polymerisation*.

## 1.6 POLYMERISATION OF ETHYLENE

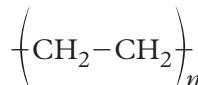
**Polymerisation** is a chemical reaction in which many identical small molecules combine together to form one large molecule. The small molecules are called **monomers** while the large product molecule is called a **polymer**.

The monomer ethylene polymerises to form the polymer, polyethylene:



These polymers are essentially long alkane molecules: each molecule contains from a few hundred to a few thousand monomer units.

The structure is frequently written in an abbreviated form:



where  $n$  is the number of monomer units in the molecule—say about 300 to 3000.

*Polyethene* is the systematic name for this substance but *polyethylene* is the IUPAC<sup>†</sup> preferred name. *Polythene* was the trade name for the product patented by the chemical manufacturer ICI (Imperial Chemical Industries Pty Ltd).

Polyethylene is called an **addition polymer**. This means that it forms by molecules adding together without the loss of any atoms. Basically each double bond ‘opens out’ to form single bonds with the neighbouring molecules.

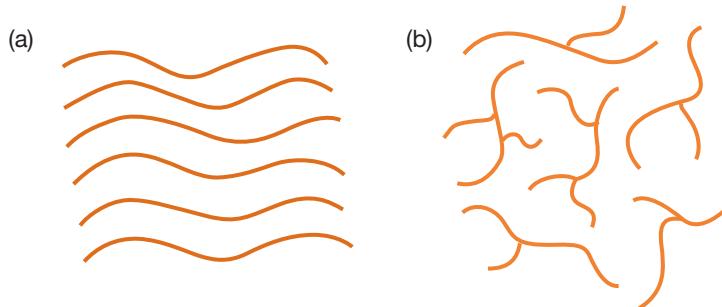
There are two processes used to make polyethylene.

- In the older gas phase process (still widely used) high pressure (1000 to 3000 times atmospheric) and high temperature (300°C) along with an initiator (an organic peroxide, a compound containing a  $-\text{O}-\text{O}-$  group, or sometimes oxygen gas) are used. The product has significant **chain branching**. This means that at some carbon atoms one hydrogen atom is replaced by an alkyl group (Table 1.1). Consequently the alkane chains cannot pack close together or in an orderly way: this is called *low density polyethylene* (LDPE). In this process the ‘initiator’ is not strictly a catalyst because it gets incorporated into the actual polymer formed—one initiator molecule per one or two polymer molecules, meaning per 2000 or 3000 monomer units.

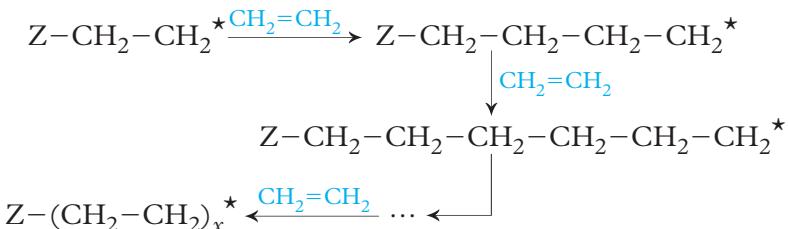
<sup>†</sup> International Union of Pure and Applied Chemistry; this body, among other things, formulates rules for the naming of compounds.

The second (newer) process uses pressures of only a few times atmospheric and temperatures of about 60°C and uses a catalyst which is a mixture of titanium(III) chloride and a trialkylaluminium compound such as triethylaluminium,  $(\text{CH}_3-\text{CH}_2)_3\text{Al}$ . This **Ziegler-Natta process** as it is called forms unbranched polyethylene molecules which are able to pack closely together in an orderly fashion. This product, called *high density polyethylene* (HDPE), is more crystalline and has a higher density than the branched-chain product. Figure 1.3 illustrates the difference between linear and branched chains. The properties and uses of the two forms of polyethylene will be discussed below.

**FIGURE 1.3**  
Different arrangements of polymer chains:  
(a) crystalline linear chains as in HDPE,  
(b) amorphous (non-crystalline) branched chains as in LDPE

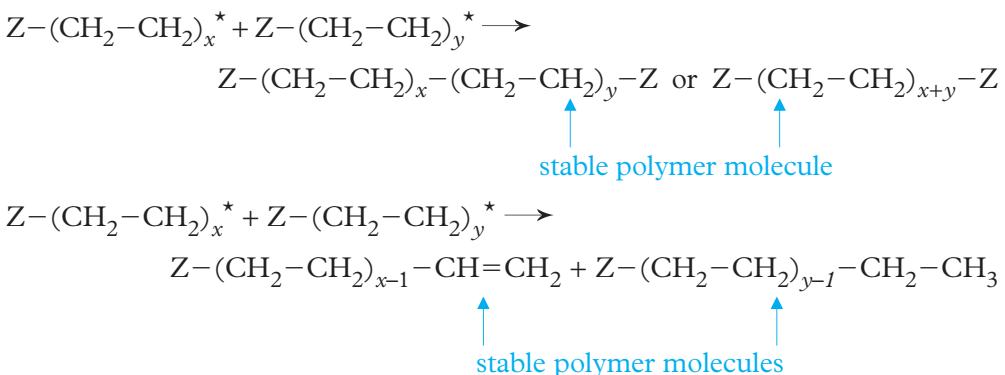


In both these processes the initiator or catalyst activates an ethylene molecule by attaching to it. An ordinary ethylene molecule then attaches to this, forming a new activated species. Polymerisation continues by ethylene molecules one after the other adding to the growing chain:



Z is all or part of the catalyst molecule \* indicates an activated species

Finally the process stops by two such activated chains colliding with each other; they either join together to form a stable polymer molecule or they exchange a hydrogen atom to form two stable molecules:



Because activated chains of variable lengths can collide (different values of  $x$  and  $y$ ) and because of the two possible processes, the polymer molecules formed have different chain lengths (different values of  $x$  or  $y$  or  $x+y$ ) and so different masses. *Hence in any polymer sample there is a distribution of molecular weights as*

shown in Figure 1.4. Consequently we talk about the **average molecular weight** of a polymer; this is the average relative mass of all of the molecules present in the sample.

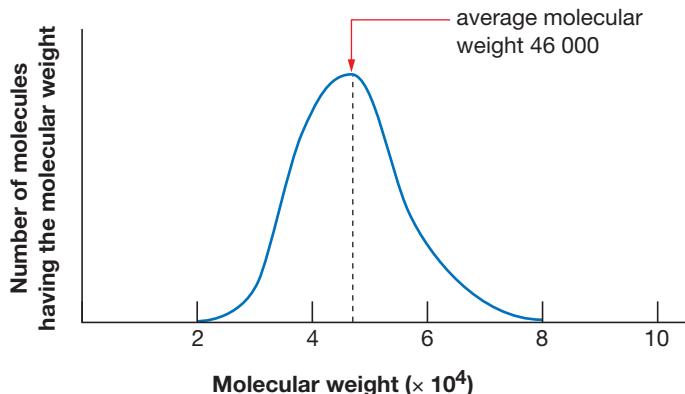


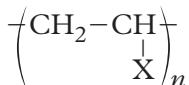
FIGURE 1.4  
A typical molecular weight distribution for a polymer. The graph shows the number of molecules having a particular molecular weight as a function of molecular weight

## 1.7 TWO OTHER ADDITION POLYMERS

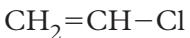
Several other common polymers are addition polymers made from monomers in which one of the H atoms of ethylene has been replaced by a different atom or group such as Cl or  $\text{CH}_3-$ . We can represent such monomers as  $\text{CH}_2=\text{CH}-\text{X}$  and the polymer as:



As with polyethylene, we can abbreviate this to:



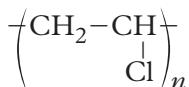
PVC, or poly(vinyl chloride), is made from the monomer, *vinyl chloride*,



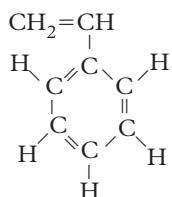
The systematic name for this monomer is *chloroethene* and therefore for the polymer is poly(1-chloroethene)<sup>†</sup>. Apart from polyethylene this is the cheapest and most widely used polymer. It has the structure:



which can again be abbreviated to



Another common addition polymer is *polystyrene*, made from the monomer *styrene* which has the structure:

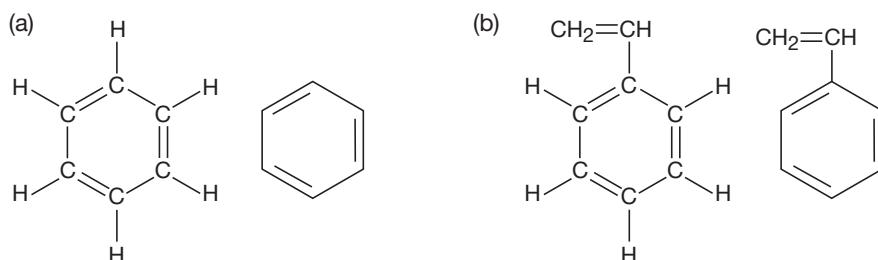


<sup>†</sup> The 1- is not necessary in chloroethene. Why? It is included in the name of the polymer to indicate that the Cl atoms are on alternate C atoms and never on adjacent Cs.

The side group here—the X above—is the so-called *phenyl group*. It comes from the compound benzene,  $C_6H_6$ , in the same way as alkyl groups come from alkanes—by removal of a hydrogen atom. Benzene is a cyclic hydrocarbon with six C atoms in a planar hexagonal ring and with a H atom attached to each C. We can think of the C—C bonds as being alternate double and single bonds though this is not an accurate description of the true structure. The phenyl group can replace an H atom in ethylene in the same way as Cl does.

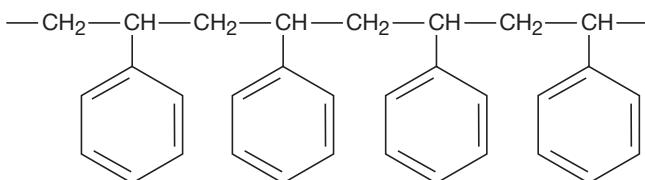
The above structure for styrene is cumbersome to draw, so chemists have a shorthand way of drawing benzene rings (or phenyl groups): they just draw the ring structure, leaving out the C and H atoms. It is understood that there is a C atom at every apex of the structure and attached to it are sufficient H atoms to bring the valence of the C up to its usual 4. The full and abbreviated structures for benzene and styrene are in Figure 1.5.

FIGURE 1.5  
Full and abbreviated  
structures for (a) benzene  
and (b) styrene



Styrene is the common name for this monomer; its systematic name is *phenylethene*. The IUPAC preferred name is styrene.

A segment of the structure of polystyrene is:



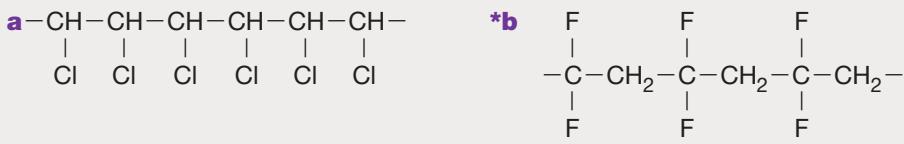
## Naming polymers

So far we have had polyethylene, poly(vinyl chloride) and polystyrene. Polymers are named by putting ‘poly’ in front of the name of the monomer, but when do we use brackets around the monomer name and when not? Brackets are used:

- when the monomer name is more than one word, as in poly(vinyl chloride), PVC or
- when the monomer name begins with a number, as in poly(1-chloroethene), the systematic name for PVC.

## Exercises

- 15** Would you expect 1,1-dibromoethene,  $CH_2=CBr_2$  to form an addition polymer? If so draw a segment of its structure. Include at least four monomer units.
- 16 a** A sample of PVC has an average molecular weight of  $7.2 \times 10^4$ ; what is the average number of monomer units in a molecule of this sample?  
**b** What would be the average molecular weight of a sample of polystyrene in which the average number of monomer units per molecule was 800?
- 17** Draw the structure of the monomer you would use to make the following polymers:



- 18** Perspex, commonly used as a substitute for glass, is an addition polymer of methyl methacrylate,  $\text{CH}_2=\text{C}-\text{CO}-\text{O}-\text{CH}_3$
- $\text{CH}_3$

Draw a segment of the structure of this polymer.

- 19** Using information in Table 1.3, draw segments of the structures of polypropylene, polytetrafluoroethylene and polyacrylonitrile.

Table 1.2 summarises information about the three addition polymers described so far. Their uses and the way these uses depend upon properties will be discussed in Section 1.10.

**TABLE 1.2 Common addition polymers, the monomers they are made from, and some of their uses**

Polymer	Name and structure of the monomer	Common uses
polyethylene	ethylene (ethene) $\text{CH}_2=\text{CH}_2$	<i>LDPE</i> : milk bottles, soft toys, wrapping film (cling wrap) <i>HDPE</i> : kitchen utensils and containers, more rigid toys, rubbish bins, tougher carry bags
poly(vinyl chloride) PVC	vinyl chloride (chloroethene) $\text{CH}_2=\text{CH}-\text{Cl}$	electrical insulation, garden hoses, drainage and sewerage pipes, household guttering and downpipes
polystyrene	styrene (phenylethene) $\text{CH}_2=\text{CH}$ 	car battery cases, tool handles, modern furniture, CD cases, disposable drink cups (both foam and clear), foam packing material

## 1.8 SOME FURTHER ADDITION POLYMERS†

Table 1.3 presents information on four further addition polymers in widespread use in the everyday world.

**TABLE 1.3 Another four addition polymers, the monomers they are made from, and their common uses**

Polymer	Name and structure of the monomer	Common uses
polypropylene	propylene (propene) $\text{CH}_2=\text{CH}-\text{CH}_3$	motor car bumpers, rope and twine, household goods, moulded chairs, carpets
polyacrylonitrile (acrylics)	acrylonitrile (cyanoethene) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	as a wool substitute in clothing, blankets, soft furnishings, carpet
poly(vinyl acetate), PVA	vinyl acetate $\text{CH}_2=\text{CH}-\text{O}-\text{CO}-\text{CH}_3$	vinyl coatings on upholstery fabrics, paint, adhesives
polytetrafluoroethylene, PTFE (Teflon™)	tetrafluoroethene $\text{F}_2\text{C}=\text{CF}_2$	high-grade electrical insulation, non-stick surfaces on cookware, pipe thread sealant

† not required for NSW HSC

## 1.9 RELATING PROPERTIES AND USES TO STRUCTURE

In selecting a polymer for a particular use important properties to consider are:

- melting or softening point
- stability to heat and light
- chemical stability
- mechanical strength
- flexibility or rigidity.

Another factor is cost: we generally select the cheapest polymer that will do the job.

As with all compounds, the properties of polymers are affected by their structure. Important structural features for addition polymers are:

- average molecular weight (or chain length)
- crystallinity (extent of chain branching)
- chain stiffening
- cross-linking.

### Average molecular weight

The average molecular weight of a polymer reflects the number of monomer units that combine to make one polymer molecule. This depends upon the conditions used in the polymerisation process. Not all the molecules in a batch of polymer have the same molecular weight: there will be a range of different chain lengths as was explained in Section 1.6, and this is why we need to talk about the *average molecular weight*.

For a given type of polymer, the longer the polymer chain (higher the molecular weight) and the smaller the spread of molecular weights, then the higher the melting point and the harder the substance is.

### Chain branching

As already mentioned, we can get **chain branching** in polyethylene. If polyethylene forms in long unbranched chains then these chains are able to intertwine and align closely. This leads to an orderly arrangement; the substance is crystalline. A high degree of crystallinity leads to high density, a high melting point and a relatively hard and tough material. On the other hand, if there is a lot of chain branching then the molecules are not able to get so close to one another, they are not able to align themselves in an orderly fashion and so the material is non-crystalline or amorphous as shown in Figure 1.3. This leads to low density, low melting point, greater flexibility and softness. High density polyethylene is easily recognised by the way it ‘crackles’ when it is crumpled. Low density polyethylene is much softer and ‘clingy’. Gladwrap™ and similar wraps are low density polyethylene.

### Chain stiffening

**Chain stiffening** of an addition polymer involves putting a bigger side-group into the linear chain to reduce its flexibility. Changing from H of polyethylene to CH<sub>3</sub> of polypropylene stiffens the chain only slightly. When the side-group is changed

to a chlorine atom (PVC) or to a benzene ring in polystyrene, both much bigger than a  $\text{CH}_3$  group, the ability of the chain to ‘flop around’ is greatly restricted. The material becomes stiffer and much more rigid. PVC without additives (plasticisers) to soften it is quite rigid. Polystyrene, which contains a benzene ring, is a hard plastic used for screwdriver handles, car battery cases, some plastic furniture and the like. Polyethylene, even the high density form, is never as hard or as rigid as polystyrene or unplasticised PVC because it lacks chain stiffening.

However when polystyrene is formed with gas being blown through it, it forms soft beads or foam. The softness however is due to the gas trapped inside the beads, not to the polymer itself.

## Cross-linking

The rigidity or hardness of a polymer can be increased by what is called **cross-linking**. This is a process in which two or more linear chains are joined together to form a more extended two-dimensional network as shown in Figure 1.6. Cross-linking is much more common in the condensation polymers to be discussed below than in addition polymers. However it does occur in the vulcanising of rubber. Natural rubber is an addition polymer of polyisoprene: it is rather soft and sticky. If it is heated with a few per cent sulfur, the sulfur forms  $-\text{S}-\text{S}-$  bridges between pairs of linear chains. This introduces considerable cross-linking into the material and makes it harder and more ‘springy’ (elastic).



The four properties just discussed can all be controlled in the manufacture of these various polymers. It is therefore possible to ‘tailor-make’ molecules—to make materials with specific physical properties.

## Solubility of addition polymers

None of the polymers mentioned so far contains OH groups or exposed O atoms and so these polymers cannot form hydrogen bonds with water. Although some of them contain polar C–Cl or C≡N bonds, there are many more non-polar bonds. Consequently these polymers are quite insoluble in water and are generally hydrophobic (water repelling): this means that they are not easily wetted by water.

## Stability

Most of the bonds in these polymers are strong C–C and C–H bonds and so these molecules are fairly stable. Polytetrafluoroethene (Table 1.3) has



The addition polymer poly(vinyl chloride) or PVC is widely used for plumbing fittings, particularly for drain pipes

**FIGURE 1.6**  
Cross-linking joins long chains to one another: this can make the polymer more rigid (polystyrene) or elastic (rubber)

C–F bonds which are much stronger than C–H bonds. This makes the polymer the most stable of those discussed so far. On the other hand PVC has C–Cl bonds which are weaker than C–H bonds. PVC is vulnerable to attack by ultraviolet light (which can break C–Cl bonds) and so special additives are needed to protect PVC exposed to sunlight (though PVC is extremely stable underground or in the dark).

When heated to high temperatures, PVC decomposes to form hydrogen chloride which is extremely corrosive: it is the cause of much of the damage that results from fires involving PVC. Acrylics, when heated strongly, decompose to form hydrogen cyanide which is an extremely poisonous gas; this is of considerable concern with the increasing use of acrylics in furnishings and carpets.

## 1.10 USES OF POLYETHYLENE, PVC AND POLYSTYRENE

Having seen how structural features affect properties of polymers, we can now look at how these properties determine which polymers will be used for particular purposes.

### Low density polyethylene, LDPE

Low density polyethylene, because of its extensive chain-branching, lack of stiffening side groups and lack of cross-linking, is relatively soft and very flexible with a fairly low melting point; it is not particularly strong. These properties make it well suited for making wrapping materials and disposable shopping bags, flexible toys, milk bottles and squeeze bottles in both the laboratory and the home.

### High density polyethylene, HDPE

High density polyethylene has virtually no chain branching. This means that molecules can pack closely together in an orderly fashion, which results in this polymer being harder and stronger and having a higher melting point than LDPE. HDPE is widely used to make kitchen utensils and containers, tougher carry bags, more rigid toys, a variety of building products, ‘wheely’ bins for household waste and recycling, and pipes for transporting natural gas to households (replacing older steel and copper ones). The absence of chain stiffening and cross-linking limits the hardness and brittleness of HDPE.

### Poly(vinyl chloride), PVC

Poly(vinyl chloride), with its Cl side groups producing considerable chain stiffening and with its polar C–Cl bonds producing quite strong intermolecular forces, is a hard inflexible polymer. Its C–Cl bonds make it vulnerable to attack by ultraviolet (u.v.) light so it degrades fairly quickly in daylight; for outdoor use PVC needs an inhibitor added to it to absorb the u.v. light. The rigidity of PVC can be adjusted quite considerably by adding non-volatile plasticisers to it. Consequently some formulations of PVC are quite soft and can be used for electrical insulation and garden hoses; PVC is the common insulation on household electrical wiring. More rigid formulations are used for many household items, for drainage and sewage pipes, for household guttering and down-pipes and increasingly for window frames.

Both PVC and polyethylene are cheaper than the other common plastics so they tend to be used unless the product requires properties they do not have.

## Polystyrene

Polystyrene with its large phenyl side group is the most stiffened of the common plastics. Hence it is very hard and rigid. With only C–C and C–H bonds it is also very stable to heat and u.v. light. With minimal chain branching it is very crystalline and can be formed into very clear transparent objects. It is widely used for making tool handles, car battery cases, high quality modern furniture and assorted ornaments, CD cases and clear disposable drink glasses.

Despite its inherent hardness polystyrene is used to make foam drink cups, bean-bag filler and foam packing materials, both moulded-to-fit ones and pellets. These uses arise because, if gas is bubbled through the styrene mixture as it is polymerising, a very light-weight foam is formed which solidifies as a very spongy material. The sponginess arises from the gas bubbles that are trapped inside the polymerised material. It is the compressibility of the gas that gives polystyrene foam its softness and lightness; the actual polystyrene is still quite hard.

### WEBSITES

For further information about structure and uses of polymers:

<http://www.pscl.ws/macrog/index.htm>

(scroll down a bit, then click on a level. Level One is very good for uses of polymers.)



<http://www.pacia.org.au>

(click on *Education*, then, on the left side of the screen under *Education and Resources for Students*, click on *Orica Chem Fact Sheets*; select *Polyethylene* or *Polypropylene* or any other chemical of interest.)

<http://www.kcpc.usyd.edu.au/discovery/Syllabus.html>

(click on *Addition polymerisation scenic route*. Lots of interesting information though much of it is outside the HSC syllabus.)

### Exercises

20 Arrange the three polymers, polyethylene, PVC and polystyrene in order of increasing chain stiffness. Explain your reasoning. Which of these would you expect to be the most flexible or pliable and which the least? Explain why.



21 Draw a section of a polyethylene molecule with chain branching.

22 What type(s) of intermolecular forces would you expect in:

- a polyethylene      b poly(vinyl chloride)      \*c polystyrene?

Draw a diagram to illustrate for (b)

23 Which of LDPE, HDPE, PVC or polystyrene would be most suitable for making each of the following products? Give your reasoning. If you are unable to make a clear choice discuss the possibilities.

- a disposable juice bottles
- b reusable juice bottles (for daily use in school lunch packs)
- c plastic raincoats
- d transparent protective covers for outdoor light bulbs
- \*e outer casings for desktop computers and printers
- \*f self-assembly toys for young children such as buildings, boats, robots and dolls.
- \*g insulating sheath for keeping a wine bottle cool

## 1.11 WILL RAW MATERIALS RUN OUT?

The raw materials for making the polymers just described come from crude oil (basically ethylene and propene). There is considerable concern that the world is going to use up all its available oil reserves within the next few decades. Some analysts predict that supplies will be effectively used up by the middle of this century: others suggest a few decades later. How long oil supplies will last depends upon our rate of consumption—whether it continues to increase rapidly as it has done in the last half century or whether our use starts to decline.

By far the major use of crude oil is as a fuel for cars, planes and trains. Currently there is pressure to reduce energy use and to develop alternative fuels, first because of the greenhouse problem (p. 288 CCPC) and secondly because as supplies of oil diminish the cost will increase. However progress in this direction has been slow.

Currently the petrochemical industry (mainly plastics) consumes only about 3 to 5% of the total oil used in the world today.

Some scientists argue that because oil supplies are going to run out in the foreseeable future, we should be developing alternative sources of the raw materials for plastics. They point to ethanol obtained from agricultural crops as a possible source of ethylene for making polymers.

Others argue that as oil supplies diminish, costs will increase and oil will become too expensive to use as a fuel: overall energy use will fall and alternative fuels will become cost effective. The petrochemical industry will be less affected by price rises (because the cost of raw materials is a smaller proportion of the cost of the finished products) and so will still be able to afford to use oil. Consequently, these people argue, the remaining oil will become the exclusive domain of the petrochemical industry and will last for many more decades.

Regardless of which argument is correct, it would be prudent for the plastics industry to develop alternative sources of ethylene and propene.

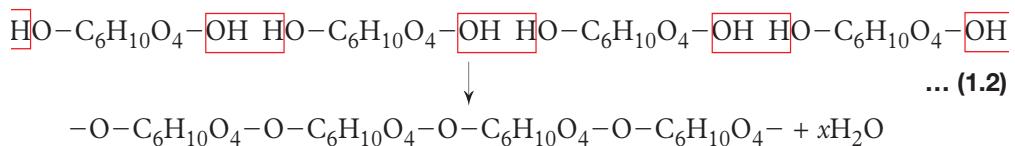
Ethanol is the prime candidate for an alternative source of ethylene. Ethanol can be produced by fermentation of starch and sugars from a variety of agricultural crops and it can be easily converted to ethylene. We will discuss this approach in Section 1.16.

There is however an even more tantalising source for starting materials for making many of the polymers that are so useful today, and that is cellulose. Cellulose is a major component of plant material, whereas starch and sugars are minor components. In order to explore the possible use of cellulose for making petrochemicals, we need to look at the general structure of natural polymers (starch, cellulose, proteins). This leads us to what are called *condensation polymers*.

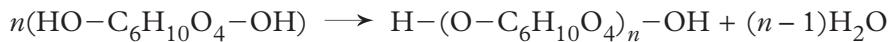
## 1.12 CONDENSATION POLYMERS

**Condensation polymers** are polymers that form by the elimination of a small molecule (often water) when pairs of monomer molecules join together.

*Cellulose* is a naturally occurring condensation polymer. The monomer from which it forms is glucose. To illustrate condensation polymerisation let us write glucose, which has the molecular formula  $C_6H_{12}O_6$  as  $HO-C_6H_{10}O_4-OH$ . The polymerisation occurs by the elimination of water molecules from between pairs of glucose molecules:

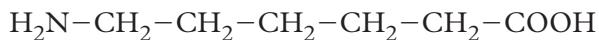


Alternatively we can write this as:

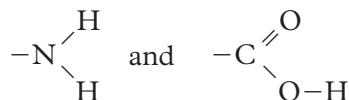


This is saying that  $n$  molecules of glucose combine to form one molecule of cellulose (which contains  $n$  glucose units) by eliminating  $(n-1)$  molecules of water.

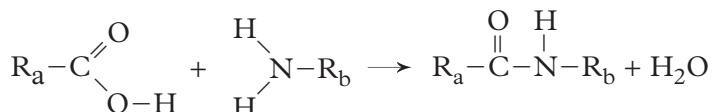
A synthetic condensation polymer is *nylon-6*. This is a particular type of nylon formed from the monomer 6-aminohexanoic acid which has the structure:



This can be written as  $\text{H}_2\text{N}-(\text{CH}_2)_5-\text{COOH}$ . This molecule contains two functional groups (pp. 266–7 CCPC), the **amine group**  $-\text{NH}_2$  and the **carboxylic acid group**  $-\text{COOH}$ . Although written in these ways for convenience, their full structures are:



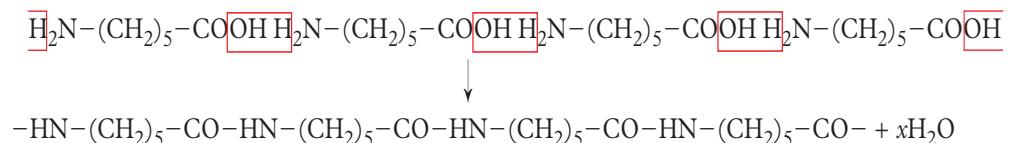
Carboxylic acids react with amines:



where  $\text{R}_a$  and  $\text{R}_b$  are the rest of the molecules (commonly alkyl groups). For convenience this reaction is often written as:



Molecules of 6-aminohexanoic acid having both functional groups can react with one another to form a polymer. The polymerisation reaction is:



The chemical bond that has formed here is the same as occurs when proteins form: a carboxylic acid group  $-\text{COOH}$  combines with an amine group  $\text{H}_2\text{N}-$  to form what is called an **amide link**  $-\text{CO}-\text{NH}-$ . In biochemical contexts this is called a **peptide link**. In nylon-6 all the monomer units are identical. Nylon-6 was the first nylon to be made but it is not the common nylon today. Nylon is actually a trade name. The generic name is **polyamide**.

Proteins are condensation polymers made from amino acids. **Amino acids are compounds with a  $-\text{COOH}$  group at one end and a  $-\text{NH}_2$  group at the other.** When proteins form from amino acids, different amino acids are strung together sequentially in the one chain. The properties of the protein depend as much upon the *sequence* of amino acids as upon the number of them in the chain. Proteins will be discussed in Chapter 14. 6-aminohexanoic acid is an amino acid, though not a

naturally occurring one, and therefore it is not involved in any proteins.

The condensation polymer made from ethylene glycol and terephthalic acid is known as **polyester** when used as a fibre (such as terylene) and as PET or poly(ethylene terephthalate) when used for drink bottles. This polymer plus nylon are the main synthetic condensation polymers in use today.



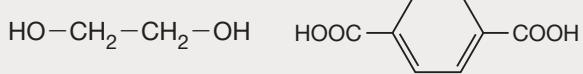
The condensation polymers nylon (left) and polyester (right) are widely used for carpets and textiles because they form as linear (unbranched) molecules that stick together via hydrogen bonding to form fibres



### Exercises

- 24** What would be the average molar mass of cellulose that contained on average 300 glucose units per molecule? What would have been the mass of the glucose from which this cellulose had been formed?
- 25** The structure for cellulose can be written as  $\text{H}-(\text{O}-\text{C}_6\text{H}_{10}\text{O}_4)_n-\text{OH}$ . Write the structure of nylon-6 in the same way.
- 26 a** Poly(ethylene glycol) or Carbowax can be considered a condensation polymer formed from ethylene glycol,  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ . Draw a structure for a segment of this polymer. Include at least four monomer units.  
**b** Carbowax can also be considered as an addition polymer of ethylene oxide. Explain how this can be so. (Carbowax is made by polymerising ethylene oxide, not from ethylene glycol.)
- 27** Glycine is the simplest amino acid:  $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ . Draw a structure for the simplest possible protein, a condensation polymer formed from glycine.
- 28 a** What is the essential feature that a molecule must have in order for it to be involved in the formation of a condensation polymer?  
**b** Would it be possible to make a condensation polymer from each of:  
**i** 1-propanol,  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$   
**ii** 1-chloropropanol,  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$   
**iii** 1,3-dichloropropanol,  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$   
either alone or with some other compound? Explain why or why not and if some other compound is needed, suggest a possibility.

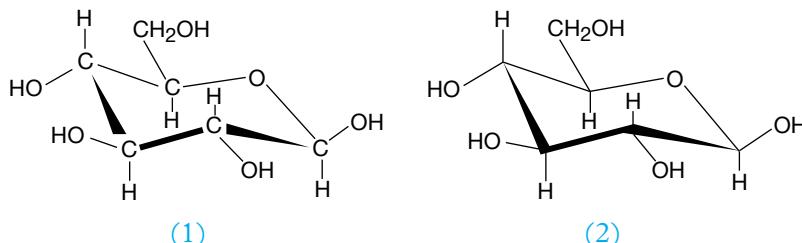
- 29** Poly(ethylene terephthalate), polyester or PET, is made from ethylene glycol and terephthalic acid:



Draw a segment of this polymer, including two of each of the monomer units.

## 1.13 STRUCTURE AND POSSIBLE CHEMICAL USES OF CELLULOSE

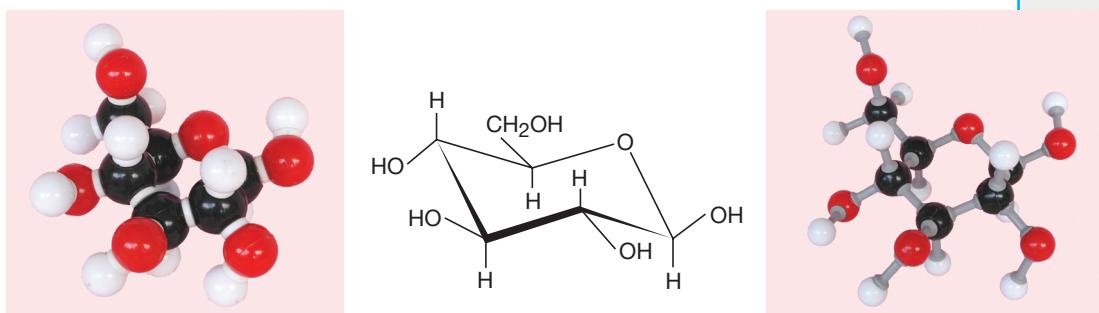
As already mentioned, cellulose is a polymer of which the monomer units are glucose which earlier we wrote as HO-(C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>)-OH. The structural formula for glucose is (1):



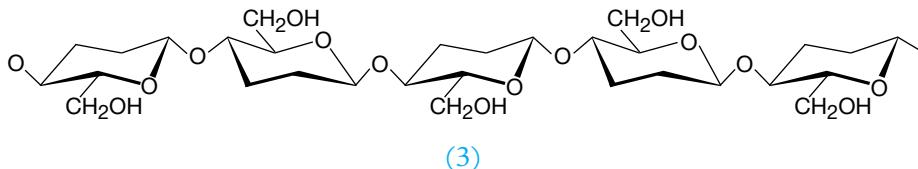
It has 5 carbon atoms and an oxygen atom forming a puckered ring; there are OH groups on 5 of the C atoms. The side of the ring (top or bottom) on which each OH group is positioned is important: interchange an OH and an H on the one C atom and you get a different compound (galactose or mannose, for example). Because structure (1) is quite cluttered, chemists commonly abbreviate it to (2) above, that is we leave out the ring C atoms: it is understood that there is a C atom at every apex of the structure.

Figure 1.7 shows space-filling and ball-and-stick models of β-glucopyranose, the form that is used to make cellulose. An explanation of the β in β-glucopyranose is given in Section 13.8†.

FIGURE 1.7  
Space-filling and ball-and-stick models of β-glucopyranose along with the structural formula oriented in approximately the same way



When glucose molecules combine to form cellulose, the OH on the right-hand C atom of one molecule (as drawn above) combines with the OH of the left-hand carbon atom of the next glucose molecule; this forms structure (3).



This is the structure of the product in Equation 1.2.

For clarity several of the H and OH groups have been omitted from each ring. The important points to note are:

- for bonding to occur alternate glucose units must be inverted (tipped ‘upside down’)

† part of the option, Forensic Chemistry: not required for the HSC core.

- this bonding produces a very linear molecule. The geometry of the rings and the C–O–C bond angles cause this linearity.

Cellulose is the major component of plant material or of *biomass*.

**Biomass** is material produced by living organisms; mainly it is plant material though the term also includes animal excreta and material made by algae.

## Cellulose as a source of chemicals

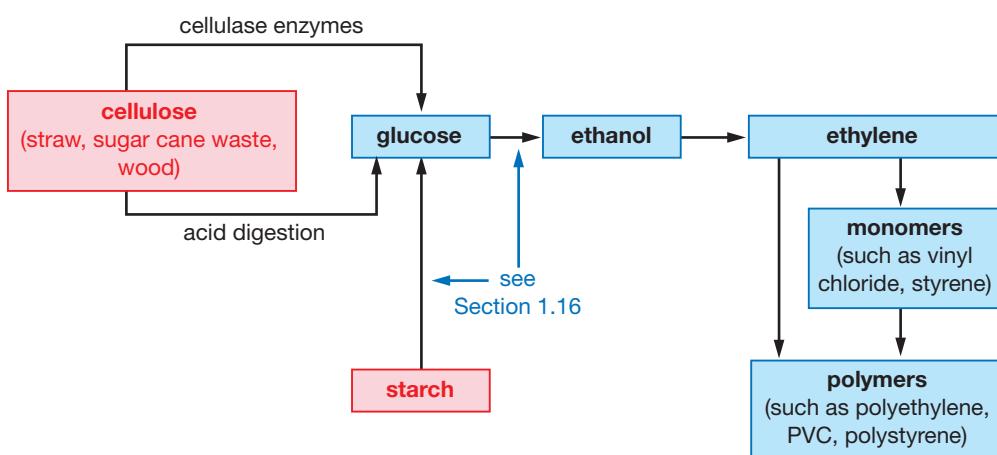
Cellulose is widely used as cotton, particularly for textiles, and as paper and cardboard. But can it be used as a source of chemicals?

As we shall see in Section 1.16, starch is a useful alternative source for some chemicals we currently make from petroleum, notably ethanol and ethylene. Starch is also a polymer of glucose, though there is a subtle difference between its structure and that of cellulose and this leads to quite different properties and chemical reactivity. The structures of starch and cellulose will be discussed in more detail in Section 13.9. Plants produce far more cellulose than starch, so there would be great benefits if we could use cellulose as a source of materials we currently make from oil.

Each glucose unit of cellulose has six carbon atoms joined together (Figure 1.7 and structure (3) above), so it could be regarded as a basic structure for making starting molecules for petrochemicals—molecules such as ethylene (2 C atoms), propylene (3 C atoms) and butene (4 C atoms, a starting point for synthetic rubber).

Figure 1.8 is a flow chart that shows how cellulose and starch could be converted into ethylene which could be used to make many of the polymers we currently make from ethylene derived from oil.

**FIGURE 1.8**  
Possible production of polymers from non-oil sources such as cellulose and starch



Unfortunately it is much more difficult to break cellulose into glucose than it is to break up starch. This is because the long near-linear chains of cellulose hydrogen bond to one another to form very compact fibres, making it hard for chemicals to ‘get at’ the glucose–glucose links. However, there are two processes for breaking cellulose into glucose:

- 1 *digestion by cellulase enzymes*. These enzymes exist in bacteria (present in the first stomach of herbivores) and in certain fungi. The process can be performed industrially by first treating finely ground cellulose-containing materials (such as grain husks and stalks, bagasse and old newspapers) with

sodium hydroxide solution (or sometimes just hot water) to swell (open up) the cellulose fibres, then digesting them with cellulase enzymes to produce a solution of glucose.

- 2 *digestion with strong acid.* This involves heating a suspension of cellulose-containing materials (those mentioned above plus wood chips) with moderately concentrated aqueous sulfuric acid solution which breaks cellulose into glucose. Insoluble matter, particularly lignin from wood pulp, is filtered off, many impurities are removed, then the acid is neutralised to produce a solution of glucose.

In both cases the solution of glucose can be treated with yeast to form ethanol and if required this can be dehydrated to ethylene (Section 1.16).

While this conversion of cellulose to ethanol and then to ethylene does work, it has the major disadvantage that if much of the energy required for the process (keeping reaction mixtures hot and driving the process machinery) comes from oil, then more oil would be used making ethylene in this way than is used by cracking the oil directly to ethylene (Section 1.1). Making ethanol from cellulose is considerably more expensive than making it from starch or sugars, despite the lower cost of the starting cellulose-containing material. Nevertheless considerable scientific effort is currently being directed into developing more efficient ways of using cellulose as an alternative source of chemicals we now obtain from oil.

## 1.14 BIOPOLYMERS

**Biopolymers** are polymers that are made totally or in large part by living organisms.

Originally the word meant biologically-synthesised polymers such as cellulose, starch, proteins and nucleic acids. However the word now includes polymers that are chemically-modified versions of natural polymers and polymers that can be produced by ‘manipulating’ biological organisms.

Partially synthetic biopolymers based on cellulose have been used commercially for nearly a century.

Some biopolymers that have been made from cellulose (itself a biopolymer) are:

- *rayon*, also called *viscose rayon* or just *viscose*. This is a reconstituted cellulose; cellulose that is unsuitable for spinning into thread for fabric weaving, such as wood pulp, waste paper and sometimes straw, is treated chemically and mechanically to produce fibres that can be used to make fabric. Rayon generally has a silky look and feel.
- *cellophane*. This is a form of rayon that is produced as a thin transparent film which is widely used for packaging.
- *cellulose nitrate*. This is a synthetically modified cellulose that was widely used for photographic and movie film early last century: it was also used as an explosive (gun cotton) and as a plastic called *celluloid*. Unfortunately it was highly flammable and was soon replaced by other plastics.
- *cellulose acetate*. This is much less flammable than cellulose nitrate and is still widely used, for example for overhead projector slides.

In cellulose nitrate and acetate the three OH groups on each glucose unit of the cellulose molecule (can you identify them in (1) and (2) in Section 1.13?) are replaced by  $\text{--ONO}_2$  (nitrate group) and  $\text{--O--CO--CH}_3$  (acetate group) respectively.

- *carboxymethyl cellulose*, CMC. This is another cellulose-based biopolymer; in it the  $-\text{CH}_2\text{OH}$  side chain on each glucose unit has been replaced by  $-\text{CH}_2-\text{COOH}$ . CMC is used as a thickener in many foods, because the supply of natural alginate thickeners obtained from seaweed cannot keep up with increasing demand.

Cellulose has been fairly widely used as a raw material for making products that people need or want. However, to date it has not been practical to use cellulose to synthesise polymers or other substances that we currently make from petroleum.

## Moves from natural to synthetic polymers

The commercial use of biopolymers such as cotton (cellulose), wool and silk (protein) has been declining as the petroleum-based polymers such as polyester (or PET) and polyamide (nylon) have been taking over. Similarly natural rubber has been quite dramatically supplemented by a synthetic, SBR, styrene-butadiene rubber which is a co-polymer (two monomers) of styrene and butadiene. Again the starting materials come from crude oil.

### A problem

There is a major problem with petroleum-based polymers: they are not **biodegradable**. This means that when they are discarded into the environment or put into rubbish dumps, they are not decomposed naturally by the action of living organisms such as bacteria or fungi. Carelessly discarded synthetic plastics are causing harm and often death to marine and bird life and remain eyesores in landscapes almost indefinitely.

One approach to building biodegradability into synthetic polymers has been to alternate biopolymer sections with synthetic sections in the same polymer molecule: biological decay of the biopolymer sections leads to disintegration of the whole polymer. Another very recent approach has been to develop biopolymers that have similar properties to the synthetic polymers but which still retain biodegradability.

## 1.15 A SYNTHETIC BIODEGRADABLE POLYMER

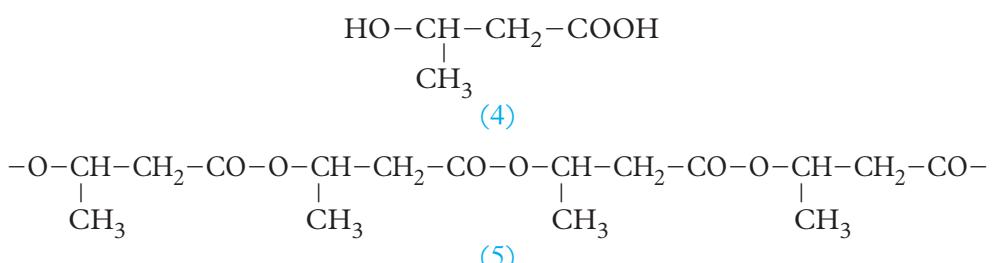
There is a range of microorganisms (for example from the *Alcaligenes*, *Clostridium*, *Rhizobium* and *Streptomyces* genera (groups)) that under suitable conditions can make polymers that have similar properties to polypropylene with the important exception that they are biodegradable (polypropylene is not). The biopolymer formed is a poly(3-hydroxyalkanoate) or PHA. Some explanations about naming are shown in Table 1.4.

The simplest PHA is PHB, poly(3-hydroxybutanoate): the 3 means that the hydroxy group is on the third carbon counting from the carboxylic acid group. The monomer, 3-hydroxybutanoic acid, sometimes called  $\beta$ -hydroxybutanoic acid, has structure (4) and the polymer structure (5).

**TABLE 1.4 Some general classes of carbon compounds**

Class of compound	General formula <sup>a</sup>	Example
alkane	R—H	CH <sub>3</sub> —CH <sub>2</sub> —CH <sub>3</sub> propane
alkanol (alcohol)	R—OH	CH <sub>3</sub> —CH <sub>2</sub> —OH ethanol
alkanoic acid (carboxylic acid)	R—COOH	CH <sub>3</sub> —COOH acetic acid
	or 	
alkanoate (ester) (acid combined with alcohol)	R—COO—R'	CH <sub>3</sub> —COO—CH <sub>2</sub> —CH <sub>3</sub> ethyl ethanoate
	or 	

a  $R$  is any alkyl group (Table 1.1);  $R'$  is another alkyl group (same as or different from  $R$ ).



The polymer is a polyester (same chemical linkage as in PET, Section 1.12). Although PHB has quite a different chemical structure from polypropylene, its physical and mechanical properties are very similar.

To produce PHB a culture of a microorganism such as *Alcaligenes eutrophus* is placed in a suitable medium and fed appropriate nutrients so that it multiplies rapidly and grows into a large quantity. Then the ‘diet’ is changed to restrict the supply of one particular nutrient (such as nitrogen): under these conditions the organism is no longer able to increase its population but instead begins to make the desired polymer which it stores for later use as an energy source. The amount of PHB that the organism can produce is from 30 to 80% of its own dry weight. The organism is then harvested and the polymer separated out.

PHB is much more expensive to make than oil-based polymers with similar properties. However, there is a slowly growing demand for it where biodegradability is a prime consideration. Such applications include disposable nappies and packaging in the form of bottles, bags and wrapping film, particularly packaging for medical and hospital supplies.

## WEBSITES

For further information about the conversion of cellulose to ethanol and about PHB:

<http://www.kcpc.usyd.edu.au/discovery/Syllabus.html>

(click on *Condensation polymers scenic route*, then *Converting cellulose to ethene*; alternatively click on *Biosynthesis of polymers* for information on PHB)

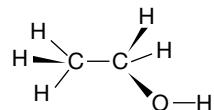
<http://www.personal.psu.edu/users/e/r/erd127/index.htm>

(at the bottom of the page click on any of the named processes for making ethanol from wood (cellulose)).



## 1.16 ETHANOL AS A SOURCE OF ETHYLENE

As explained in Section 1.11, there are good reasons for wanting an alternative source of ethylene for the plastics industry. Ethanol is such a source; it has the structure:



We saw in Section 1.5 that ethanol is an alkanol, meaning that it is an alkane with one H atom replaced by an OH (or alcohol) functional group. The geometrical arrangement of the bonds in the molecule is tetrahedral around each carbon atom and bent around the oxygen atom. This geometry is better shown in the ball-and-stick and space-filling models of ethanol in Figure 1.9. However for printing convenience we generally draw it with bonds at right angles:

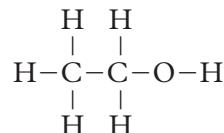
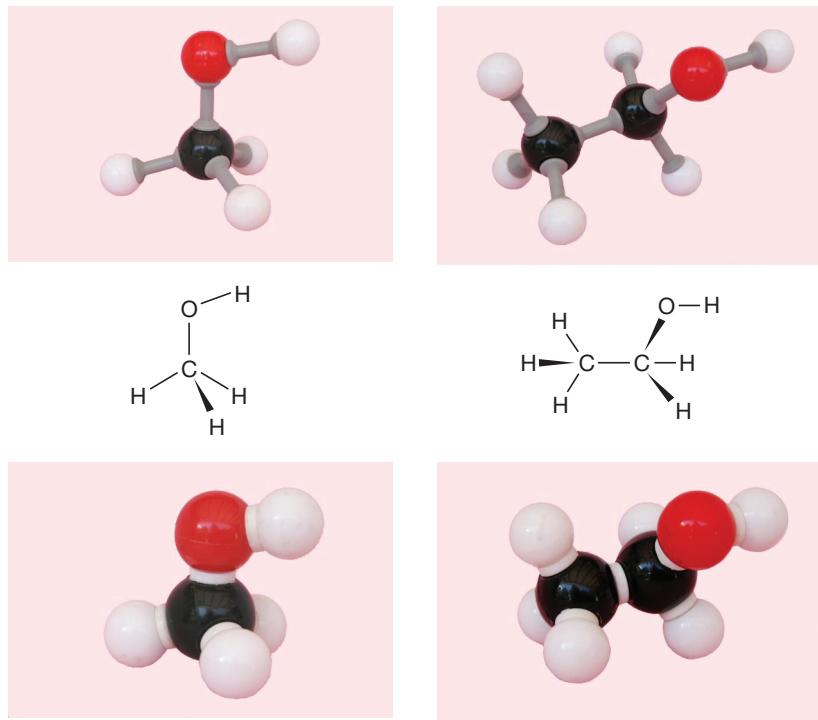


FIGURE 1.9  
Ball-and-stick and space-filling models of methanol (left) and ethanol (right)



Ethylene is made from ethanol by dehydration.

**Dehydration** is a chemical reaction in which water is removed from a compound.

Ethanol is dehydrated by heating it with concentrated sulfuric or phosphoric acid which acts as a catalyst:



The reverse reaction, the addition of water to ethylene, is called *hydration*. It was introduced in Section 1.5. Hydration also needs heat and a catalyst which is generally dilute aqueous sulfuric acid:



These two reactions, *dehydration* and *hydration*, are quite general reactions: they apply to *any* alkanol or alkene respectively. For example 1-pentanol can be dehydrated to 1-pentene and 3-hexene can be hydrated to 3-hexanol. (Naming of alkanols was explained in Section 1.5.)

## 1.17 ETHANOL AS A SOLVENT

As mentioned in Section 1.5 ethanol is widely used as a solvent. In the home it is a common solvent in:

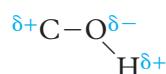
- cosmetics (perfumes, deodorants, after-shaves)
- food colourings and flavourings (cochineal, vanilla essence)
- medicinal preparations (antiseptics)
- some cleaning agents.

It is also widely used as a solvent in industry.



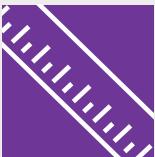
Ethanol is the solvent in many consumer products such as perfumes

Ethanol is a good solvent for both polar and non-polar substances. It dissolves polar substances such as chloroform,  $\text{CHCl}_3$ , and common ether,  $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ , because its OH end is very polar; the C–O and O–H bonds are polar, because O is much more electronegative than C or H (p. 189 CCPC). The partial charges on the ethanol molecule are:



Ethanol is therefore a good solvent for polar substances (p. 199 CCPC). In addition ethanol can form hydrogen bonds with many other substances (pp. 190–2 CCPC) and this increases its ability to dissolve such substances—for example glucose and sucrose, carboxylic acids, amino acids and some proteins. Because of hydrogen bonding ethanol is miscible with water in all proportions (from 100% water through to 100% ethanol).

Because of its alkyl part, the  $\text{CH}_3-\text{CH}_2-$ , which is non-polar, ethanol often dissolves non-polar substances also. Dispersion forces form between this hydrocarbon tail and the non-polar solute. Non-polar iodine readily dissolves in ethanol as do short-chain hydrocarbons such as pentane and heptene.

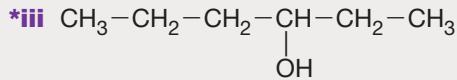
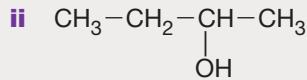
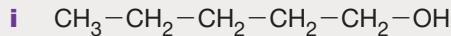


## Exercises

**30 a** Draw structures of the following alkanols:

**i** 2-butanol    **ii** 3-pentanol    **\*iii** 1-hexanol

**b** Name the following compounds:



**31** Explain why ethanol has a much higher boiling point than propane ( $78^\circ\text{C}$  compared with  $-42^\circ\text{C}$ ) despite having similar molecular weights (46 and 44 respectively).

**\*32** Offer an explanation for the fact that iodine is more soluble in ethanol than it is in water.

**33** Urea,  $\text{H}_2\text{N---CO---NH}_2$ , has a much higher solubility in ethanol than heptane does. Offer an explanation: a diagram may help.

**34** The dehydration of ethanol and the hydration of ethylene discussed above are general reactions for all alkanols and alkenes respectively. Hence write equations (using structural formulae) for:

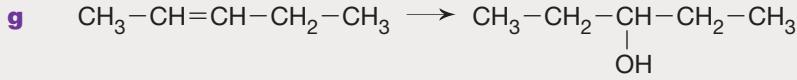
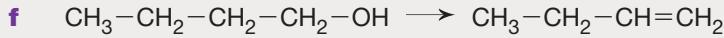
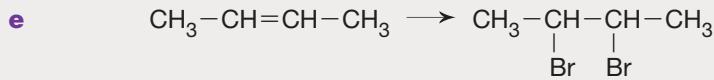
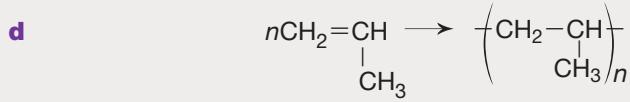
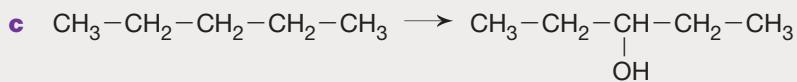
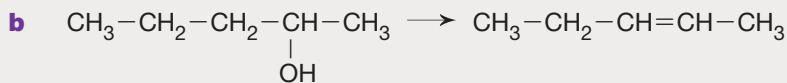
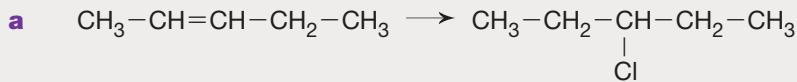
**a** the dehydration of 1-propanol and 2-propanol

**b** the hydration of 2-butene

**\*c** the dehydration of 3-heptanol

**\*d** the hydration of 3-hexene

**35** What type of reaction (substitution, dehydration, addition, hydration, polymerisation) is each of the following?



## 1.18 SYNTHESIS OF ETHANOL FROM PLANT MATERIAL

Until about sixty years ago the major source of ethanol was fermentation of starches and sugars from plant material. With the dramatic increase in use of motor cars after World War II and the rapidly growing demand for high quality petrol for them, the amount of crude oil being refined increased greatly. In addition, processes were developed to increase the yield of petrol from refining (catalytic cracking, Section 1.1). The result was that large supplies of quite cheap ethylene became available as a by-product. In addition this ethylene was available close to the places of greatest demand for ethanol, the industrial cities. Hence it became more economic to produce ethanol from ethylene. Today fermentation provides only a small proportion of industrial alcohol, though it still provides all the beverage alcohol.

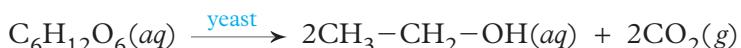
If it becomes necessary to produce ethylene for plastics from ethanol, then fermentation will again become a very important industrial process.

**Fermentation** is a process in which glucose is broken down to ethanol and carbon dioxide by the action of enzymes present in yeast.

For fermentation:

- suitable grain or fruit is mashed up with water
- yeast is added
- air is excluded, and
- the mixture is kept at about blood temperature, 37°C.

Enzymes (biological catalysts) in the mixture first convert any starch or sucrose in the mixture into glucose and/or fructose, then other enzymes convert glucose or fructose into ethanol and carbon dioxide:



Bubbles of carbon dioxide are slowly given off: hence the name, *fermentation*.

Yeast can produce ethanol contents up to about 15%. Alcohol concentrations above this level kill the yeast and stop further fermentation. To produce higher alcohol contents it is necessary to distil the liquid.

If the aqueous mixture from a fermentation process is subjected to fractional distillation (p. 15 CCPC), 95% ethanol can be obtained. This is common industrial or laboratory alcohol. To obtain 100% ethanol more elaborate distillation procedures are needed.

Fermentation and distillation have been used to produce ethanol for centuries. Ethanol was one of the earliest organic compounds to be synthesised and obtained in nearly pure form.

‘*Suitable grain or fruit*’ for fermentation is plant material that has a high content of starch or simple sugars (sucrose, glucose, fructose). Starchy grains (such as wheat, maize or corn, barley), tubers (such as potatoes, cassava or tapioca), and fruits (such as grapes, apples) with high simple-sugar contents are commonly fermented to ethanol.

Molasses, the leftover syrup from sugar milling, is also widely used. Sucrose has a very high solubility in water; this means that

Part of CSR's  
fermentation and  
distillation plant at Sarina  
in North Queensland  
where molasses left over  
from extracting sugar  
from cane is fermented  
into ethanol

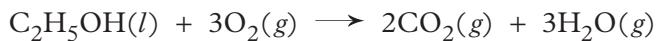


the mother liquor left over after sucrose has been crystallised out still has a high sucrose content, so ethanol can be obtained from an otherwise useless waste product of sugar production. Much of the molasses from the North Queensland sugar industry is used to make ethanol.

The economics of ethanol production change dramatically if sugar cane is grown specifically for conversion to ethanol rather than producing ethanol from a waste product (as Brazil discovered—next section).

## 1.19 ETHANOL AS A FUEL

Ethanol is a liquid which readily burns:



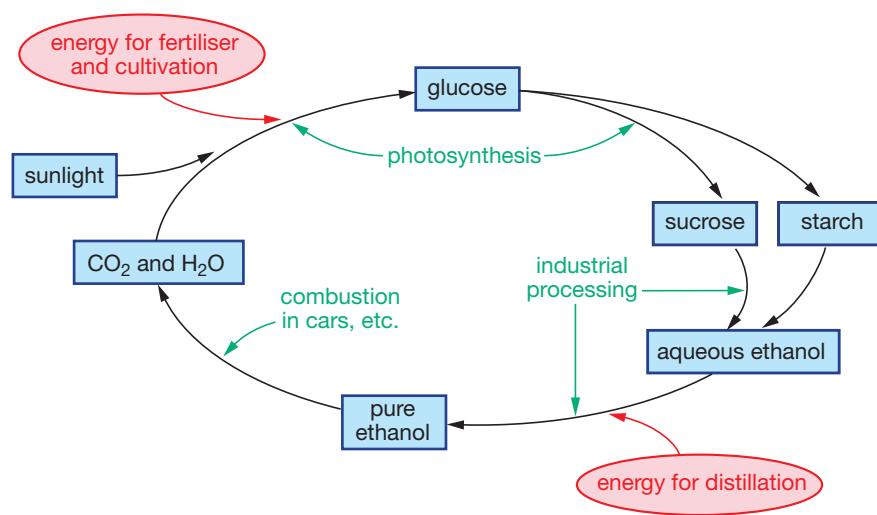
It is also an easily transportable liquid, often used by hikers and campers. Consequently it has often been proposed as a possible alternative liquid fuel for automobiles. It has been used as a ‘petrol extender’ in the past (particularly during World War II) and in a few places in more recent times. One advantage is that petrol containing about 10 to 20% ethanol can be used in ordinary petrol engines without any engine modification. To use 100% ethanol engines need to be modified.

Brazil in the 1970s and '80s adopted ethanol as its major fuel for cars. It grew sugar cane specifically for conversion to ethanol. The purpose was twofold: to reduce consumption of non-renewable crude oil and to address a trade imbalance problem (by replacing expensive oil imports with locally produced fuel). The experiment proved extremely expensive and was virtually abandoned in the 1990s though there are now (2005) moves to re-establish it.

### Ethanol as a renewable resource

Ethanol has been promoted as a fuel for motor cars to supplement or replace petrol on the grounds that it is a renewable resource. Basically it is made from carbon dioxide, water and sunlight (via glucose), and when it is burnt it returns to carbon dioxide and water which can be re-converted to ethanol. The cycle is shown in blue in Figure 1.10.

**FIGURE 1.10**  
The ethanol cycle: the blue cycle is ‘greenhouse neutral’; the red inputs mean that using ethanol as a fuel still contributes significantly to greenhouse emissions



Many people in Australia advocate the addition of ethanol to our petrol to reduce our consumption of crude oil, particularly as local reserves of oil are likely to run out within two or three decades. If we want to make oil supplies last longer or save them for petrochemicals, so the argument goes, then we need to find an alternative, preferably renewable, liquid fuel for our cars.

Ethanol has also been advocated as a fuel on the grounds that it is neutral with respect to the greenhouse effect: the carbon dioxide that it liberates when it burns is just that which was used in its synthesis. However this ignores the other energy inputs in the ethanol cycle. The blue cycle in Figure 1.10 is ‘greenhouse neutral’. However the other energy inputs, shown in red in that diagram, are quite significant—the manufacture of most fertilisers has a large fossil fuel input, and the distillation process (to get 95% ethanol from the 15% fermentation product) requires much energy.

Currently ethanol has potential as a liquid fuel, particularly for transport (cars, trains, planes) when oil runs out provided coal is available for making fertilisers and supplying the energy for distillation, though as technology currently stands this would not be much better than oil from a greenhouse gas viewpoint.

**The advantages of using ethanol** as a fuel are:

- It is a renewable resource and so would reduce the use of non-renewable fossil fuel (provided less fossil fuel was used to make the ethanol than was ‘saved’ by using the ethanol in cars).
- It could reduce greenhouse gas emissions (if the amount of CO<sub>2</sub> not released from oil because of the use of ethanol in cars was greater than the CO<sub>2</sub> released from the fossil fuels used to make the ethanol).

**The disadvantages** are:

- Large areas of agricultural land would need to be devoted to growing suitable crops with consequent environmental problems such as soil erosion, deforestation, fertiliser runoff and salinity.
- Disposal of the large amounts of smelly waste fermentation liquors after removal of ethanol would also present major environmental problems.

## The current situation in Australia

- 1 Ethanol costs more than petrol to produce so the federal government has set up subsidies and excise concessions to encourage the production of ethanol (from crops) to be added to petrol (presumably to reduce oil consumption).
- 2 Car manufacturers accept that up to 10% ethanol in petrol has no detrimental effect on vehicles but have opposed higher concentrations.
- 3 Significant quantities of petrol with 10% ethanol in it are available in some parts of Australia, but there is considerable public suspicion of this blended fuel, largely because of incidents involving some petrol suppliers who put excessive amounts of ethanol in their petrol (to gain from the government subsidies), and because of car manufacturers who have widely claimed that amounts above 10% could damage car engines and may void warranties.
- 4 There are no reliable studies to show whether ethanol as made in Australia from wheat or molasses produces less greenhouse gas in total than does the petrol it replaces.

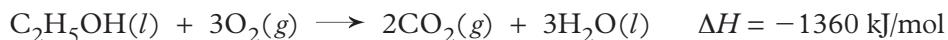
## 1.20 HEAT OF COMBUSTION OF ETHANOL

You will recall from p. 280 CCPC that:

The **molar heat of combustion**<sup>†</sup> of a substance is the heat liberated when one mole of the substance undergoes complete combustion with oxygen at standard atmospheric pressure with the final products being carbon dioxide gas and liquid water.

As thus defined *the molar heat of combustion is minus the enthalpy change for the combustion process* (because enthalpy change,  $\Delta H$ , is always energy absorbed).

In practice, when we burn a fuel the water generally forms as a gas. However the values we tabulate are the ones we would get if the water formed as a liquid. Table 10.1 (p. 281 CCPC) gave molar heats of combustion for some common substances. In particular for ethanol the molar heat of combustion is 1360 kJ mol<sup>-1</sup>. This means that for:



Example 1 illustrates how heats of combustion can be measured in a school laboratory.

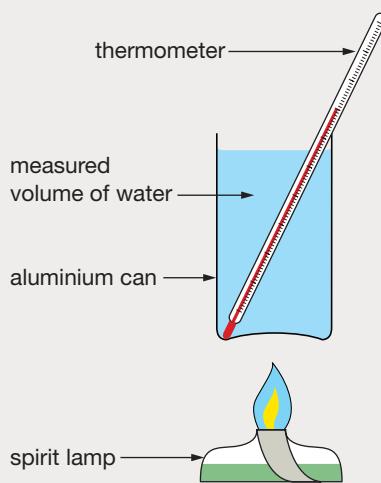
<sup>†</sup> Sometimes this is just called heat of combustion. It is preferable to include the ‘molar’.



### Example 1

The apparatus in Figure 1.11 was used to measure the heat released when ethanol burns in air. Initially the small spirit burner, partly filled with ethanol, had a mass of 155.66 g. The aluminium drink container with its top cut out contained 250 g water at 19.5°C and was suspended above the burner with a clamp in a retort stand. The spirit lamp was lit and used to heat the water in the can (being carefully stirred with a thermometer). When the temperature had risen about 15°C, the flame was extinguished. The maximum temperature that the water reached was 37.3°C. The mass of the spirit burner and its contents at the end of the experiment was 154.75 g. Calculate the heat released per gram of ethanol used, and hence the molar heat of combustion of ethanol. The specific heat capacity of water is 4.18 J K<sup>-1</sup> g<sup>-1</sup>.

FIGURE 1.11  
Apparatus for measuring the heat of reaction for combustion of a liquid



The heat absorbed by a substance when its temperature is increased is given by Equation 8.11 on p. 223 of CCPC, namely:

$$q = m C \Delta T$$

So in this example:

$$\begin{aligned}\text{heat absorbed by the water} &= 250 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (37.3 - 19.5) \text{ K} \\ &= 1.87 \times 10^4 \text{ J} (= 18.7 \text{ kJ})\end{aligned}\quad \dots (1.3)^{\dagger}$$

Let us neglect the heat capacity of the aluminium container and assume that there were no heat losses to the surroundings. On that basis the heat released by the reacting ethanol must be equal to the heat absorbed by the water. That is:

$$\text{heat released by ethanol reacting} = 18.7 \text{ kJ}$$

This is the heat released from burning  $(155.66 - 154.75) = 0.91 \text{ g}$  ethanol.

$$\begin{aligned}\text{So heat released per gram of ethanol} &= \frac{18.7}{0.91} \\ &= 20.5 \text{ kJ/g} \\ &= \mathbf{21 \text{ kJ/g}}\end{aligned}$$

(to two significant figures which is all the accuracy of the experiment justifies)

$$\begin{aligned}\text{The molar mass of ethanol, C}_2\text{H}_5\text{OH} &= 2 \times 12.01 + 6 \times 1.01 + 16.0 \\ &= 46.0 \text{ g/mol}\end{aligned}$$

$$\begin{aligned}\text{Therefore heat released per mole} &= 20.5 \times 46.0 \\ &= 943 \text{ kJ/mol}\end{aligned}$$

That is, molar heat of combustion of ethanol =  **$9.4 \times 10^2 \text{ kJ/mol}$**

While heat of combustion per mole is useful and convenient for chemists, for ordinary citizens who have to buy fuel by the litre or kilogram, heat per litre or per gram is much more useful. Exercises 40 and 41 will highlight this aspect.

#### WEBSITES

<http://www.kcpc.usyd.edu.au/discovery/Syllabus.html>

(click on *Ethanol from plants* for information about the process)

For discussions about using ethanol as a fuel for cars and its greenhouse consequences:

<http://www.canegrowers.com.au/>

(click on *Sugarcane Products* then on *Ethanol*)

<http://www.worldofmolecules.com/fuels/ethanol.htm>

(a more balanced presentation of the energy and greenhouse cases)



## 1.21 OVERVIEW

In this chapter we have seen how crude oil and/or by-products from processing it can be used to make the fibres and plastics that are in widespread use today. We have also seen that oil supplies are likely to run out within a few decades. Ethanol from plant material such as starch and sucrose is a possible alternative source of liquid fuel and of ethylene, the starting substance for many polymers, but there are problems. Cellulose, a much larger fraction of plant material, has not to

† This equation uses the usual value for the specific heat capacity of water, namely  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ . The NSW HSC examination data sheet in recent years has given it as  $4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ . Use of this value in Equation 1.3 would give:  $0.250 \text{ kg} \times 4.18 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} (37.3 - 19.5) \text{ K}$  which of course still gives  $1.87 \times 10^4 \text{ J}$ .

date proved a practical alternative source of petrochemicals though progress is being made.

A major problem with the petroleum-based polymers is their lack of biodegradability. Progress has been made in the development of biodegradable substitutes in the form of biopolymers.

## Exercises

- 36** If 1.00 kg of a 10% solution of glucose in water in apparatus weighing 350 g was completely fermented, and any gas formed allowed to escape, by what amount would the mass of the apparatus and its contents decrease? What percentage decrease does this correspond to?
- 37** The heat of combustion of ethanol is 1360 kJ/mol. What mass of ethanol needs to be burnt to raise the temperature of 350 g water through 77°C if 50% of the heat released by the ethanol is lost to the surroundings? The specific heat capacity of water is 4.2 J K<sup>-1</sup> g<sup>-1</sup>.
- 38** The heat of combustion of each of three different alkanols was measured as follows. Some alkanol was placed in a small spirit burner and the mass determined. The burner was placed under an aluminium container (of mass 21.7 g) filled with 750 g water. The set up was as in Figure 1.11. The temperature of the water was measured then the burner was lit. The water was gently stirred with the thermometer until the temperature had risen by about 20°C. The burner was extinguished and the maximum temperature reached by the water noted. Results from the three alkanols are tabulated below.

Alkanol	Initial mass <sup>a</sup> (g)	Final mass <sup>a</sup> (g)	Initial temperature (°C)	Final temperature (°C)
methanol	124.3	120.6	20.4	41.3
1-propanol	127.8	125.2	19.7	39.4
2-pentanol	122.6	120.2	21.3	41.5

*a* mass of the burner plus alkanol

- a** Write equations for the combustion of the three alkanols.
- b** Calculate the heat of combustion per gram of alkanol and per mole. The specific heat capacity of water is 4.2 J K<sup>-1</sup> g<sup>-1</sup>. Ignore the heat capacity of the aluminium container and any heat losses to the surroundings.
- 39 a** The mass of the aluminium container used in Exercise 38 was 21.7 g. The specific heat capacity of aluminium is 0.89 J K<sup>-1</sup> g<sup>-1</sup>. Show that ignoring the heat capacity of the container in your calculations for Exercise 38 introduced negligible errors.
- b** The values you calculated for the molar heat of combustion of the alkanols in Exercise 38 are much less than those tabulated in books of data. Suggest some reasons why the results of these experiments are low.
- 40** Some heats of combustion are: hydrogen, 285 kJ/mol; propane, 2220 kJ/mol; octane, 5460 kJ/mol; ethanol, 1360 kJ/mol. Calculate the heat released per gram for each of these fuels. For a typical coal the value is 35 kJ/g. Arrange these fuels including coal in decreasing order of heat released per gram of fuel. Why is this a better measure of 'heat efficiency' of fuels than molar heats of combustion?
- 41** The result you obtained in Exercise 40 for the heat per gram for octane is typical of all liquid hydrocarbons. On a mass for mass basis, then, how does ethanol compare as a fuel with the liquid hydrocarbons?

## Important new terms

You should know the meaning of the following terms:

addition polymer (p. 13)  
addition reaction (p. 8)  
alcohol (p. 12)  
alkanol (p. 12)  
alkyl group (p. 9)  
amide link (p. 23)  
amine group (p. 23)  
amino acid (p. 23)  
average molecular weight (p. 15)  
biodegradable (p. 28)  
biomass (p. 26)  
biopolymer (p. 27)  
carboxylic acid group (p. 23)  
cat cracker (p. 6)  
catalytic cracking (p. 6)  
chain branching (p. 13)

chain stiffening (p. 18)  
condensation polymer (p. 22)  
cracking (p. 5)  
cross-linking (p. 19)  
dehydration (p. 30)  
fermentation (p. 33)  
hydration reaction (p. 11)  
molar heat of combustion (p. 36)  
monomer (p. 13)  
peptide link (p. 23)  
polyamide (p. 23)  
polyester (p. 24)  
polymer (p. 13)  
polymerisation (p. 13)  
steam (or thermal) cracking (p. 6)  
substitution reaction (p. 7)  
zeolites (p. 6)  
Ziegler–Natta process (or catalyst) (p. 14)

## Test yourself

- Explain the meaning of each of the items in the ‘Important new terms’ section above.
- Why do oil refineries carry out catalytic cracking? Name the catalyst used and write an equation for a specific example.
- Name two important by-products from catalytic cracking and state their major use.
- What is the difference between catalytic and thermal cracking? How do the experimental conditions differ for the two processes? What is the major purpose of each process?
- Compare the boiling points and solubilities of alkanes and alkenes. Explain why they are so similar or so different. Which members of each class are gases at room temperature?
- What are the two major reactions of alkanes? Write equations for a specific example of each.
- List five addition reactions of alkenes. Write an equation for a specific example of each, using either propene or a butene as the alkene.
- Name and give formulae for the first six alkyl groups.
- Describe a test for distinguishing between alkanes and alkenes.
- How is ethanol made industrially? Include an equation.
- Why does industry need to convert ethylene to vinyl chloride?
- Write an equation for the polymerisation of ethylene. Name the product.
- Name two other addition polymers and draw structures for them.
- What are the systematic names for vinyl chloride and styrene?

- 15** Draw a structure for styrene and give its molecular formula.
- 16** What structural feature is responsible for the difference between low density and high density polyethylene?
- 17** Use the polymers from Questions 12 and 13 to illustrate what is meant by chain stiffening and describe the effect it has on properties.
- 18** Describe the structure of cellulose and give a molecular formula for it.
- 19** What are the major uses of cellulose?
- 20** Name one condensation polymer (not cellulose) and explain how it is formed.
- 21** Describe some biopolymers that are made from cellulose and give some of their uses.
- 22** What is the biopolymer PHB, how is it made, and why is there interest in its commercial development?
- 23** Explain how we could obtain ethylene from ethanol if oil supplies were to run out.
- 24** What types of compounds dissolve in ethanol? Give some specific examples.
- 25** Describe how ethanol is obtained from plant material. What type of plant material is used?
- 26** How would you measure the molar heat of combustion of a liquid such as 1-propanol?
- 27** On a heat per gram basis, how does ethanol compare as a fuel with liquid hydrocarbons?
- 28** Discuss the advantages and disadvantages of using ethanol as a fuel for motor cars.

# Electrochemistry

## IN THIS CHAPTER

Displacement reactions  
Displacement reactions and the activity series  
Valence and oxidation states  
Electricity from redox reactions  
Some technical terms for cells  
Purpose of the salt bridge

Anode and cathode  
Some commercial galvanic cells  
Rechargeable batteries (cells)  
Fuel cells  
Gratzel cell  
Standard electrode potentials  
Calculating EMFs for reactions and cells

Many of the appliances and devices we use in our everyday life need easily portable sources of electricity—batteries, as we call them. Examples range from simple torches, clocks and watches, portable radios and mechanical toys for children to calculators, cameras, cordless drills and shavers and motor car batteries, and more recently to mobile telephones, portable CD players, video cameras and laptop computers. For all of these devices we use batteries. Although there are many different types of battery in use, they all have one feature in common: electricity is generated by chemical reactions.

In this chapter we shall look at how chemical reactions can be made to generate electricity and we shall examine some common batteries in general use.

This area of science that is concerned with the relations between chemistry and electricity is called **electrochemistry**.

We shall begin our study of electrochemistry by looking at the simplest type of chemical reaction that can be used to generate electricity, namely *displacement reactions*.

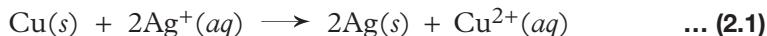
## 2.1 DISPLACEMENT REACTIONS

A **displacement reaction** is a reaction in which a metal converts the ion of another metal to the neutral atom.

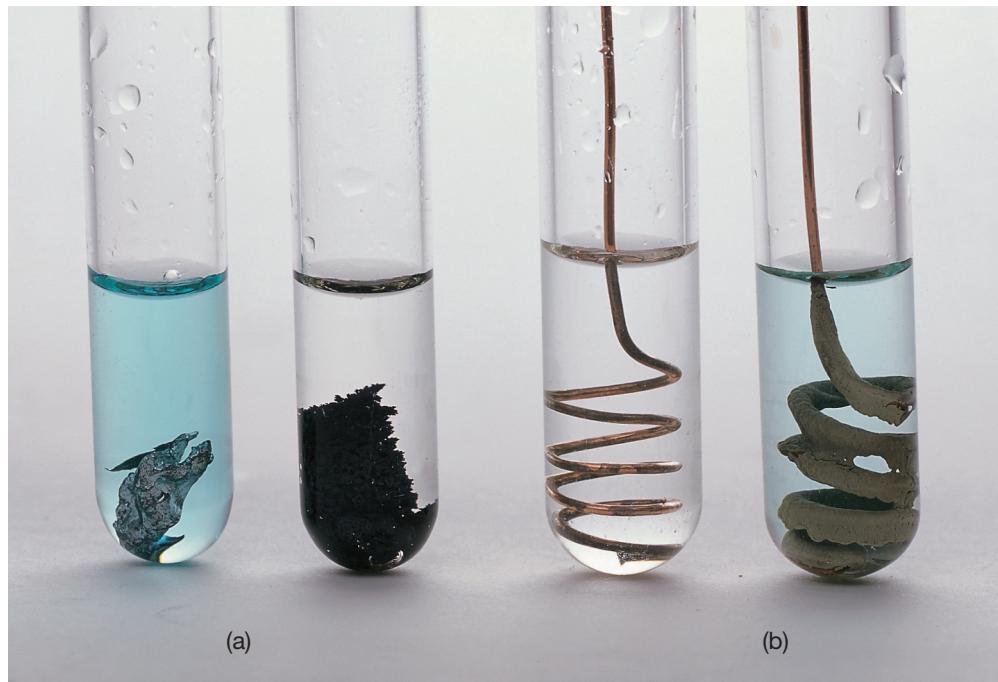
Examples will illustrate.

- When a reddish-brown copper wire is dipped into a colourless solution of silver nitrate, a black deposit of metallic silver forms on the copper (black because the silver is very finely divided). If we let the reaction proceed for

a sufficiently long time, the solution takes on a bluish colour due to copper ions. This is shown in Figure 2.1(b). The reaction is:



**FIGURE 2.1**  
Two displacement reactions: (a) a granule of zinc dropped into a copper sulfate solution; (b) copper wire dipped into a silver nitrate solution. For each case the left-hand test tube shows the metal just after being dropped into the solution: in the right-hand test tube the metal has been in the solution for ten to twenty minutes



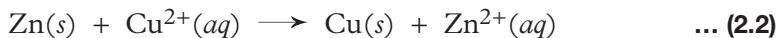
Copper loses two electrons to form  $\text{Cu}^{2+}$  and hence is *oxidised*. Silver ions gain electrons to form Ag and so are *reduced*.

Recall from p. 117 CCPC the definitions:

**Oxidation** is loss of electrons.

**Reduction** is gain of electrons.

- 2 Similarly, when a silvery granule of zinc is dropped into a blue solution of copper sulfate, the zinc gets covered with reddish-brown copper and the blue colour of the solution is discharged (Fig. 2.1(a)) The reaction is:



Zinc metal has been oxidised and copper ions have been reduced.

We can show the oxidation and reduction processes more clearly by writing half reactions (p. 118 CCPC). For Reaction 2.1:



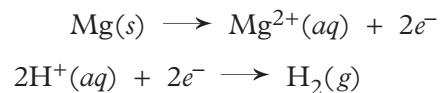
And for Reaction 2.2:



The reaction of metals with dilute acids—that is, with hydrogen ions, (pp. 116–17 CCPC)—can be considered as a special type of displacement reaction. The metal displaces hydrogen gas from a solution of hydrogen ions. For example:



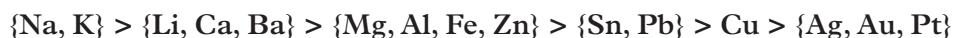
Again we can break this into oxidation and reduction half reactions:



Oxidation–reduction reactions are also called **redox reactions** and **electron transfer reactions**.

## 2.2 DISPLACEMENT REACTIONS AND THE ACTIVITY SERIES

When we were establishing the activity series for metals on p. 119 *CCPC*, we used reactions with oxygen, water and dilute acids to obtain:



where species within curly brackets had equal activities (based on the limited criteria used there).

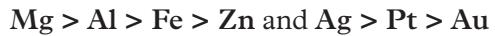
This activity series lists metals, from left to right, in order of increasing difficulty of losing electrons—that is, in order of increasing difficulty of oxidation: *a metal on the left loses electrons more easily than a metal to the right of it.* From the series, lithium and calcium lose electrons more easily (are more easily oxidised) than magnesium and iron; zinc is more easily oxidised than copper or silver.

Displacement reactions also show which of two metals is the more easily oxidised—the one that goes into solution. Reaction 2.1 shows that copper is more easily oxidised than silver (because copper goes into solution), so copper is more active than silver. Similarly Reaction 2.2 shows that zinc is more active than copper. In general, of two metals:

The more reactive metal is the one which will displace the other metal from a solution of its ions.

From Reactions 2.1 and 2.2, copper should be to the left of silver in the activity series and zinc should be to the left of copper, which is consistent with what we already have.

Consequently we can use other displacement reactions to sort out some of the ‘equalities’ in the above interim activity series. By observing experimentally which metal will displace which we can show that in terms of activity:



However displacement reactions do not allow separation of the other two equalities, because of interference of the reaction with water. The measurements on galvanic cells referred to on p. 119 of *CCPC* (and to be discussed in Section 2.14) are needed to arrive at the final activity series (Sequence 4.9 in *CCPC* now to be called 2.3):



† based on measurements from galvanic cells, the sequence for the first five metals would be Li, K, Ba, Ca, Na. The sequence presented here gives greater priority to the vigorousness of the reaction with water: as we saw on pp. 115–16 *CCPC*, K and Na react more vigorously than Li, Ba, and Ca.

Hydrogen has been included in Sequence 2.3 on the basis of reactions of metals with dilute acid. Hydrogen has been placed just to the right of all metals that will react with dilute acid to form hydrogen gas (and so just to the left of those that do not so react).

Once it has been established, we can use this activity series to decide which metal (of a given pair) displaces which from solution:

The metal further to the left in sequence 2.3 will displace the other metal from a solution of its ions.

In other words, the metal further to the left loses electrons more easily or is more easily oxidised. Similarly we can use the series to decide whether or not a metal will react with dilute acid to form hydrogen gas: those to the left of H will do so, those to the right will not.

Oxidation and reduction or electron transfer has some implications for valencies and the way we name certain species.

## 2.3 VALENCE AND OXIDATION STATES

When we were discussing the naming of simple ionic compounds on pp. 76–8 *CCPC*, we talked about the *valence* of various metal ions and of the need with some of these ions to state the valence (in capital Roman numerals) in the name: tin(II) oxide, iron(III) chloride, copper(I) sulfide and the like. What we referred to there as valence is also called the *oxidation state* of the element.

For monatomic ions the **oxidation state** of the element is the charge on the ion (including the sign).

The oxidation state:

- of copper in the oxide  $\text{Cu}_2\text{O}$  ( $2\text{Cu}^+ \text{O}^{2-}$ ) is +1
- of iron in the sulfide  $\text{FeS}$  ( $\text{Fe}^{2+} \text{S}^{2-}$ ) is +2
- of titanium in the chloride  $\text{TiCl}_3$  ( $\text{Ti}^{3+} 3\text{Cl}^-$ ) is +3
- of chlorine in  $\text{MgCl}_2$  ( $\text{Mg}^{2+} 2\text{Cl}^-$ ) is -1
- of sulfur in  $\text{PbS}$  ( $\text{Pb}^{2+} \text{S}^{2-}$ ) is -2.

There are other rules for assigning oxidation states in more complex molecules but they need not concern us at this stage. The only other rule we need is this:

The oxidation state of an element present in its stable elemental state is zero, regardless of the formula of the molecule of the element.

This means, for example, that the oxidation states for elemental zinc, hydrogen, chlorine, phosphorus, sulfur and argon are all zero despite the formulae being  $\text{Zn}$ ,  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{P}_4$ ,  $\text{S}_8$  and  $\text{Ar}$ .

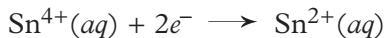
A change in oxidation state of a species corresponds to a loss or gain of electrons:

- An increase in oxidation state corresponds to a loss of electrons and so is oxidation.
- A decrease in oxidation state corresponds to a gain of electrons and so is reduction.

For example the change from iron(II) to iron(III) (+2 to +3) is oxidation (an electron is lost):



while the change from tin(IV) to tin(II) (+4 to +2) is reduction (electrons gained):



The change from bromide to bromine (change of oxidation state from -1 to 0) is oxidation:



while the change from oxygen to oxide (0 to -2) is reduction:



## Exercises

- 1 Write equations for the reactions which occur in the following experiments:
  - a When a granule of zinc is dropped into a clear silver nitrate solution, the zinc becomes covered with a black deposit of metallic silver—black because it forms as extremely small particles.
  - b When a clean iron wire is dipped into a blue copper sulfate solution, a brown deposit forms on the wire and the solution loses its blue colour.
  - \*c When a piece of aluminium foil is dropped into a clear lead nitrate solution, a black deposit of metallic lead forms on the foil.
- 2 Write oxidation and reduction half reactions for each of the reactions in Exercise 1.
- 3 By referring to the Activity series 2.3, select three metals which will displace:
  - a lead from a solution of lead nitrate
  - b iron from a solution of iron(II) sulfate.

Write balanced equations for these reactions.

- 4 a In which direction (left to right or right to left) will the following reactions occur? If no reaction occurs, write NR.

<p>i <math>\text{Sn} + \text{Ag}^+ \longrightarrow \text{Sn}^{2+} + \text{Ag}</math></p> <p>ii <math>\text{Fe} + \text{Mg}^{2+} \longrightarrow \text{Fe}^{2+} + \text{Mg}</math></p>	<p>*iii <math>\text{Cu} + \text{Al}^{3+} \longrightarrow \text{Cu}^{2+} + \text{Al}</math></p> <p>*iv <math>\text{Pb} + \text{Ag}^+ \longrightarrow \text{Ag} + \text{Pb}^{2+}</math></p>
---	---

b Balance the equations in (a), and write them so that they go from left to right.
- 5 For the reactions in Exercise 4, write oxidation and reduction half reactions; write them in the directions in which the reactions actually occur.
- 6 Which of the following metals liberate hydrogen gas from dilute sulfuric acid:

Ca, Ag, Sn, Al, Hg, Cu, Fe?

Write balanced equations for the reactions that occur. Then write the oxidation and reduction half reactions that make up each of your overall reactions.

- 7 a In each of the following compounds the metal exists as a monatomic ion. What is the oxidation state of the metal in each compound?

<p>i <math>\text{CrSO}_4</math></p> <p>ii <math>\text{Cr}_2\text{O}_3</math></p> <p>iii <math>\text{Mn(OH)}_2</math></p>	<p>iv <math>\text{MnO}_2</math></p> <p>v <math>\text{Ce}(\text{SO}_4)_2</math></p> <p>vi <math>\text{V}_2\text{O}_5</math></p>
--	--



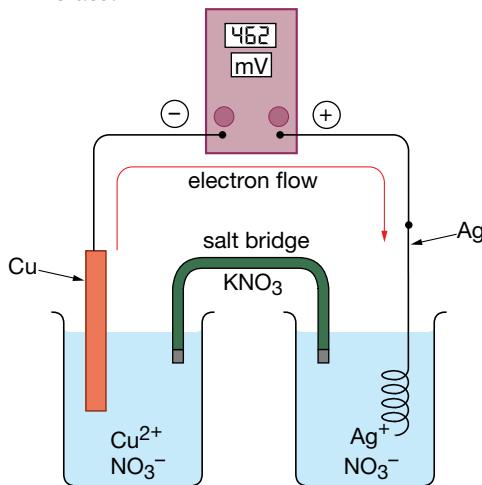
- b** In each of the following compounds the non-metal is present as a monatomic ion. What is the oxidation state of the non-metal in each compound?
- |                             |  |
|-----------------------------|--|
| <b>i</b> KCl                | <b>iv</b> Fe <sub>2</sub> S <sub>3</sub>   |
| <b>ii</b> Na <sub>2</sub> O | <b>v</b> (NH <sub>4</sub> ) <sub>2</sub> S |
| <b>iii</b> AlF <sub>3</sub> | <b>vi</b> PbI <sub>2</sub>                 |
- B** Does each of the following conversions represent oxidation or reduction of the underlined element, or neither? Explain why.
- |  |   |
|--|---|
| <b>a</b> <u>Mn</u> Cl <sub>3</sub> → MnO <sub>2</sub>  | <b>e</b> Fe + S → FeS                                   |
| <b>b</b> Na <u>Br</u> → Br <sub>2</sub>  | * <b>f</b> Ni <u>O</u> (OH) → Ni(OH) <sub>2</sub>       |
| <b>c</b> Fe <u>SO</u> <sub>4</sub> → FeCl <sub>3</sub>   | * <b>g</b> Fe <u>O</u> → Fe <sub>2</sub> O <sub>3</sub> |
| <b>d</b> Cr( <u>NO</u> <sub>3</sub> ) <sub>3</sub> → Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> |   |

## 2.4 ELECTRICITY FROM REDOX REACTIONS

Redox reactions involve transfer of electrons from one reactant to another. An electric current is a flow of electrons through a wire. We can make redox reactions generate electricity by arranging for the oxidation and reduction half reactions to occur at different locations, and by providing a wire for the electrons to flow through. This occurs in all the batteries we use. The following experiment demonstrates the connection between a redox reaction and electricity.

As shown in Figure 2.2, a strip of copper metal is suspended in a beaker of copper nitrate solution, and a spiral of silver wire in a beaker of silver nitrate solution. The two solutions are connected by a U-tube filled with a solution of potassium nitrate held in place by plugs of cotton wool. This U-tube which makes electrical contact between the two solutions is called a **salt bridge**; in order to make electrical contact it must contain some conducting substance such as a solution of potassium nitrate.

FIGURE 2.2  
A simple galvanic cell

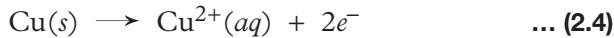


If a voltmeter is now connected across the pieces of metal, it is found that the silver wire is about 0.5 volt positive with respect to the copper; if we connect an ammeter across the terminals, a significant current flows. The electron flow is from the copper through the external circuit (meter and connecting wires) to the silver wire.

If the copper strip and silver wire in Figure 2.2 are connected with a conducting wire, and if the current is allowed to flow for some time, significant chemical change occurs:

- 1 metallic silver deposits on the silver wire—as can be seen by inspection and can be confirmed by weighing
- 2 some of the copper strip dissolves, again as can be confirmed by weighing
- 3 the concentration of silver ions in the right beaker falls appreciably, and
- 4 the concentration of copper ions in the left beaker increases.

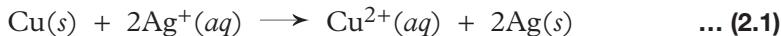
In other words, *electricity has been produced by a chemical reaction*. The voltmeter showed that electrons flowed out of the copper strip into the external circuit then down into the silver wire. The process occurring at the strip of copper metal is therefore:



and the reaction at the silver wire must be:



The overall chemical reaction occurring in our cell is the sum of these two half reactions (with Reaction 2.5 doubled to balance electrons):



This reaction is simply the one that occurred in the test tube in Figure 2.1 when a piece of copper was placed in a solution of silver nitrate; when the reaction occurs in a test tube no electricity is produced.

## 2.5 SOME TECHNICAL TERMS

We use the name **galvanic cell** or **voltaic cell** for a device in which a chemical reaction occurs in such a way that it generates electricity. Motor car batteries, and dry cells for torches and radios, are galvanic cells.

*The conductors of a cell which get connected to the external circuit are called electrodes.* In the present cell we talk about the copper electrode and the silver electrode. *Sometimes the term ‘electrode’ is also used to describe the combination of conductor and associated ion through which electrons enter or leave a cell;* in our example we can talk about the copper electrode and the silver electrode, or more precisely about the  $\text{Cu}^{2+}$ , Cu electrode and the  $\text{Ag}^+$ , Ag electrode.

The solution(s) in a galvanic cell is (are) called *electrolyte* solution(s).

An **electrolyte** is a substance which in solution or molten conducts electricity.

In the cell in Figure 2.2 the copper nitrate, silver nitrate and potassium nitrate solutions are electrolyte solutions.

The chemical reactions occurring at the electrodes are called **electrode processes** or **electrode reactions**. Equations 2.4 and 2.5 are the *electrode reactions* of the cell in Figure 2.2.

## Cell and battery

The device in Figure 2.2 is a galvanic cell. Similarly the ‘batteries’ we put in torches, calculators and radios etc. are galvanic *cells*. Technically a **battery** is several cells joined together in a common outer casing. The common nine volt battery, used for example in smoke detectors, and car batteries are genuinely *batteries*: in both cases they consist of six cells joined together in the one casing. The common 1.5 V dry cell, the alkaline cell and the 1.2 V nickel–cadmium cell are technically cells, not batteries. Although ‘battery’ is commonly used

instead of ‘cell’ in everyday life, we as chemistry students should be aware of the technical distinction.

## 2.6 PURPOSE OF THE SALT BRIDGE

If we remove the **salt bridge**, the voltage falls to zero and no current flows. Hence the salt bridge is necessary to make this and many other galvanic cells operate. What then is its purpose?

If the only changes that occurred were the ones already described, namely Equations 2.4 and 2.5, then the beaker containing copper nitrate would end up with an excess of positive ions (the copper ions produced by the electrode reaction), and the silver nitrate beaker would end up with an excess of negative ions (nitrate ions) because some silver ions have been discharged. Now it is quite impossible to have an imbalance of positive and negative ions in any solution, so some other changes must also be occurring. A closer inspection of the solutions shows that the nitrate concentration in the copper nitrate solution has also increased, and in the silver nitrate solution there has been a decrease in nitrate concentration as well as in silver ion concentration. Electrical neutrality of each solution has in fact been preserved. This implies that there has been a migration of nitrate ions away from the silver nitrate solution through the salt bridge and into the copper nitrate solution.

The purpose of the salt bridge is to allow this migration of ions to occur.

Both positive and negative ions migrate through the salt bridge. In Figure 2.2 not only do nitrate ions migrate from the right-hand beaker into the left-hand one, but also positive ions migrate from left to right. Copper ions move into the salt bridge and ‘push’ potassium ions out into the silver nitrate solution. This migration preserves electrical neutrality in both beakers (half-cells).

The electrolyte used in the salt bridge must be one which does not react with any of the ions in the two solutions it is connecting. Potassium nitrate is a good choice because  $\text{NO}_3^-$  and  $\text{K}^+$  do not form any precipitates with other ions. (See the solubility data in Table 8.1 on p. 205 CCPC.) Sodium chloride is often suitable, but not for solutions containing  $\text{Ag}^+$  because  $\text{AgCl}$  would precipitate.

### When a galvanic cell produces electricity

- 1 One electrode reaction liberates electrons which flow out of the metal of the electrode and into the external circuit.
- 2 These electrons flow through the metallic conductor of the external circuit to the other electrode.
- 3 The reaction at the other electrode consumes these electrons.
- 4 Ions migrate through the solutions and connecting salt bridge to maintain electrical neutrality.

These processes are true of all galvanic cells and are shown diagrammatically in Figure 2.3.

An electric current through a metallic conductor is a flow of electrons. Through a conducting solution it is a *migration of ions*; negative ions move through the solution in the direction that completes the circuit for the electrons: in Figure 2.3 negative ions move from right to left. Positive ions move in the opposite direction. The ‘connection’ between ions and electrons is made by the electrode reactions which occur where the metallic electrode meets the solution.

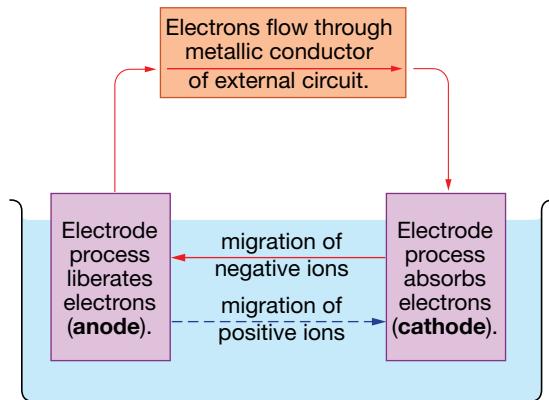


FIGURE 2.3  
Schematic diagram of a galvanic cell

The *negative terminal* of a galvanic cell is by definition the *electrode from which electrons flow out into the external circuit* (torch bulb, calculator, radio). *Oxidation* occurs at this *negative electrode* to provide the electrons for the external circuit. The positive terminal of the battery draws electrons back to the cell from the external circuit. Hence the reaction which occurs at the *positive terminal* to do this is *reduction*.

A galvanic cell is an ‘electron pump’; it pumps electrons out of the negative terminal into the external circuit and ‘sucks’ them back into the positive terminal. It can do this because a redox reaction is occurring in the cell.

## 2.7 ANODE AND CATHODE

Two terms which are frequently used in electrochemistry are anode and cathode. By definition:

The **anode** is the electrode at which oxidation occurs.

The **cathode** is the electrode at which reduction occurs.

An aid to memory is this: **an oxidation** occurs at the anode. In the galvanic cell of Figure 2.2 the copper electrode is the anode (because Cu is being oxidised to  $\text{Cu}^{2+}$  there), and the silver wire is the cathode ( $\text{Ag}^+$  is being reduced to Ag). Hence *in a galvanic cell, the anode is the negative terminal while the cathode is the positive terminal*.

Terms and signs are summarised in Box 2.1.

### BOX 2.1 IN A GALVANIC CELL

Electrode reaction	Name of the electrode	Sign of the electrode
oxidation	anode	negative
reduction	cathode	positive

## 2.8 VARIETY OF GALVANIC CELLS

A great variety of galvanic cells can be made in the laboratory. In addition there is a wide variety of galvanic cells available commercially. Some of these will be discussed in Section 2.9.

In the laboratory we can easily make cells having three different types of electrodes:

- 1 electrodes that consist of a piece of metal dipping into a solution containing the ion of the metal, such as the Cu,  $\text{Cu}^{2+}$  and Ag,  $\text{Ag}^+$  electrodes in Figure 2.2
- 2 electrodes consisting of an inert conductor (a piece of platinum wire or a graphite rod) dipping into a solution containing both an oxidised and a reduced form of the one element, such as a platinum wire dipping into a solution containing both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions (Example 1 below)
- 3 electrodes consisting of a gas bubbling into a solution containing the oxidised or reduced form of the gas with an inert conductor (platinum wire) dipping into the solution, such as a chlorine, chloride electrode (Example 2 below) or a hydrogen, hydrogen ion electrode (Section 2.13).

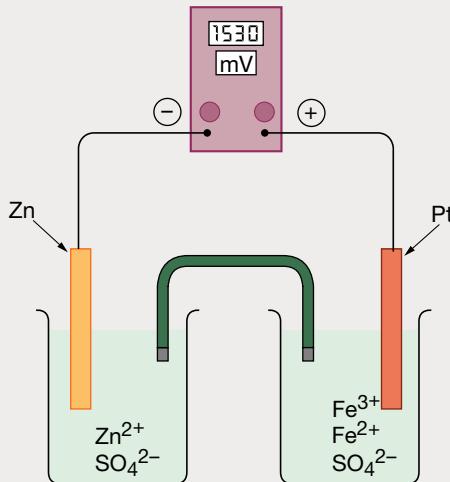
Galvanic cells can be made by combining pairs of electrodes together as the following examples will illustrate.



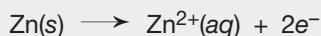
FIGURE 2.4  
The galvanic cell for Example 1

### Example 1

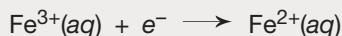
A galvanic cell was made by combining a Zn,  $\text{Zn}^{2+}$  electrode with a  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  electrode as shown in Figure 2.4. As indicated by the voltmeter, the platinum wire (that is, the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  electrode) was positive.



- a What chemical reaction is occurring at each electrode?
  - b What is the overall reaction occurring in this cell as it produces electricity?
  - c In which direction do electrons flow in the external circuit?
  - d In which direction do ions flow within the cell?
  - e Which electrode is the anode?
- a If the platinum wire is positive, the zinc must be the negative electrode, meaning that electrons must be flowing out of the zinc into the external circuit (that's what being the negative electrode of a cell means). So the reaction occurring there must be:



The platinum being positive means that that electrode is absorbing electrons from the external circuit so the reaction must be



- b The overall reaction will be the sum of these two equations, but before we can add them up we need to have the same number of electrons in each half reaction (because

we cannot have free electrons floating around in a balanced overall reaction). Hence we double the Fe half reaction:



then add the two half reactions to get



- c Electrons flow out of the zinc rod through the external circuit (wires and voltmeter) and into the platinum wire.
- d Negative ions flow away from the platinum wire into the salt bridge and into the zinc solution. This is because as  $\text{Fe}^{3+}$  ions are reduced to  $\text{Fe}^{2+}$  there is a decrease in the amount of positive charge near the platinum wire and so there must be a movement of negative charge (ions) away from that region to preserve electrical neutrality. Similarly positive ions move away from the zinc rod into the salt bridge and into the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  solution.
- e Oxidation is occurring at the zinc electrode, so the zinc electrode is the anode (from the definition of anode).

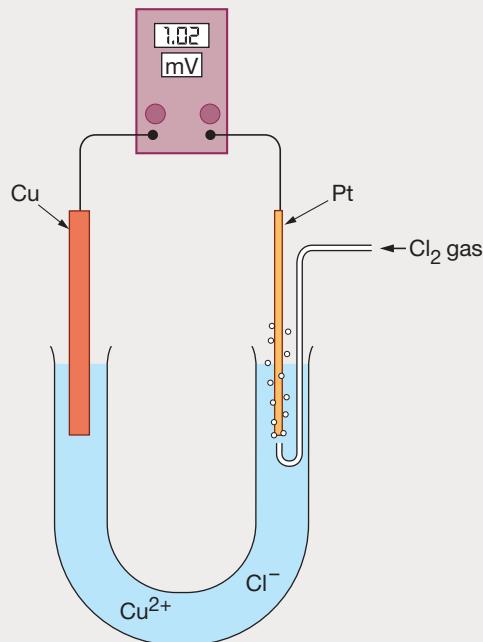
Not all galvanic cells require a salt bridge. Sometimes the one electrolyte can service both electrodes and that makes a salt bridge unnecessary. This is the case in all our commercial cells, but before looking at them let us consider a laboratory example.

### Example 2

A galvanic cell was set up as shown in Figure 2.5 by making a chlorine electrode in the right-hand arm of a U tube containing copper chloride solution and dipping a copper rod into the left-hand arm (to make a Cu,  $\text{Cu}^{2+}$  electrode there). The chlorine electrode consisted of chlorine gas bubbling over a piece of platinum wire immersed in the chloride solution. The platinum wire was positive. What electrode reactions are occurring and what is the overall cell reaction? In which directions do electrons and ions flow as the cell generates electricity? Which electrode is the cathode?



FIGURE 2.5  
A galvanic cell without a salt bridge (Example 2)

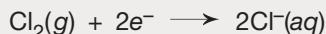


If the platinum wire is positive, the copper wire is negative, so it must be giving up electrons to the external circuit. So the reaction there is:



(In this type of exercise it is best to start with the negative electrode—that's where the electrons come from—and then you can follow them around the complete circuit.)

These electrons flow through the external circuit to the platinum wire where the electrode reaction absorbs them, so the reaction there must be reduction, namely:



The overall reaction will be the sum of the two electrode reactions:



Electrons flow from copper through the external circuit to the platinum. Negative ions flow from the chlorine electrode through the solution to the copper electrode (and so complete the circuit), while positive ions flow from the copper electrode towards the chlorine electrode, in both cases to preserve electrical neutrality in the solution near the electrodes.

Reduction is occurring at the chlorine electrode, so it must be the cathode.

## Exercises

- 9 Write the electrode reactions, and hence the overall reaction, that occur in each of the following galvanic cells as it generates electricity.

**Cell a:** One electrode consists of a piece of cadmium dipping into a cadmium sulfate solution; it is connected by a salt bridge to another electrode which consists of a strip of magnesium metal dipping into a magnesium sulfate solution. The magnesium is the negative electrode.

**Cell b:** One electrode consists of a copper wire dipping into a copper sulfate solution; it is connected by a salt bridge to a solution containing both  $\text{V}^{2+}$  and  $\text{V}^{3+}$  ions (along with sulfate). A piece of platinum wire dips into this solution. The platinum wire is the negative electrode.

- 10 For each of the cells in Exercise 9 what would happen to the voltage if the salt bridge was removed? Explain why.

- 11 a Draw a diagram showing how you would set up each of the cells in Exercise 9 in the laboratory. Include some form of external circuit (such as a torch bulb or voltmeter).  
b On each of your diagrams show the direction of flow of the electrons in the external circuit and the flow of ions within the cell.  
c Label the anode and cathode in each cell.

- 12 Would you expect the cell in Example 2 (Fig. 2.5) to continue to function as a galvanic cell if the copper chloride solution was replaced by a solution of:

- a sodium chloride      b copper sulfate      c sodium sulfate?

Explain why or why not.

- 13 Which of the following reactions could or could not be used as the working reaction in a galvanic cell? Explain.

- a  $\text{Mg(OH)}_2(\text{s}) + 2\text{HCl}(\text{aq}) \longrightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O(l)}$   
b  $\text{Mg(s)} + \text{Pb}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Pb(s)}$   
c  $\text{Fe(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$   
d  $\text{Pb}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq}) \longrightarrow \text{PbBr}_2(\text{s})$

**14** A cell consists of a zinc rod dipping into a beaker of zinc sulfate solution; a salt bridge connects this beaker to a second beaker which contains a solution of iodine and potassium iodide into which dips a platinum wire. Sketch how this cell would look in the laboratory. Measurements with a voltmeter show that the platinum wire is positive with respect to the zinc rod.

- a** What electrode processes are occurring?
- b** What is the overall cell reaction?
- c** What migration of ions (if any) occurs as current flows?
- d** Which electrode is the anode?

**15** Sketch a possible experimental arrangement for each of the following galvanic cells:

- a** a Cu, Cu<sup>2+</sup> electrode joined by a salt bridge to an Fe, Fe<sup>2+</sup> electrode
- b** an Al, Al<sup>3+</sup> electrode connected by a salt bridge to Pb, Pb<sup>2+</sup> electrode.

Use the activity series to decide which electrode would be positive in each cell. Explain your reasoning. Hence write down the electrode reactions and the overall reaction that occur as each cell generates electricity. On your diagrams show the directions of electron flow and ion migration. Also label the anodes and cathodes.

## 2.9 SOME COMMERCIAL GALVANIC CELLS

A wide range of galvanic cells is in everyday use. Some are shown on pp. 2–3.

### The 'ordinary' dry cell

The ordinary **dry cell** is the most common and the cheapest of the commercially available cells. It is widely used in torches, radios and calculators. The technical name for it is the **Leclanché cell**, named after its inventor. Figure 2.6 shows its structure.

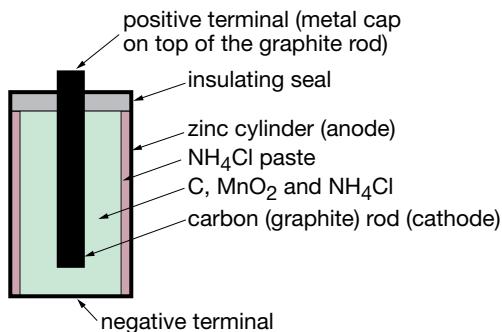
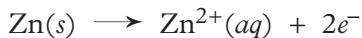
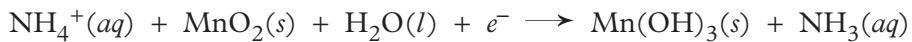


FIGURE 2.6  
The common dry cell  
(Leclanché cell)

It consists of a zinc outer casing, which is the negative electrode (or anode), an aqueous paste of ammonium chloride (so it is not really 'dry'!), and a mixture of powdered carbon, manganese dioxide and ammonium chloride around a carbon rod which is the positive terminal. Initially no zinc chloride is present, but as the cell is used zinc ions are formed and ammonium ions are discharged. At the negative terminal, the half reaction is:



At the carbon rod (the positive electrode), the reduction half reaction is:



Manganese is reduced from an oxidation state of +4 to +3. This cell operates under slightly acid conditions, because as we shall see in Chapter 5 ammonium

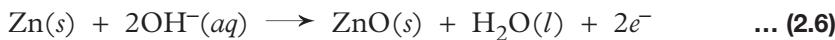
chloride solutions are slightly acidic. This cell initially has a voltage of 1.5 volts but this gradually decreases as the cell is used.

As already stated, this cell is relatively cheap. It was the first commercial battery and therefore had a big impact upon society because it made things such as torches (flashlights), portable radios and battery-operated clocks and toys possible. Today with many other cells available, the Leclanché cell is best used for devices which need only small currents such as radios and liquid-crystal calculators. This dry cell is robust, easy to store and use, and causes minimal environmental problems upon disposal: the manganese(III) is readily oxidised to stable insoluble manganese(IV) oxide and so becomes immobilised, small quantities of zinc are not a problem and ammonium salts and carbon are harmless.

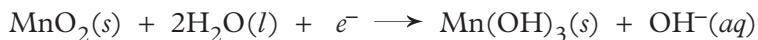
Disadvantages of the cell are that it does not contain a very large amount of electricity for its size, it cannot deliver very high currents and it can develop leaks when it goes flat (the zinc casing gets eaten away during operation).

## The alkaline cell<sup>†</sup>

This cell has a similar appearance to that of the Leclanché cell. However, the electrolyte paste contains potassium hydroxide instead of ammonium chloride so it operates under alkaline conditions instead of slightly acidic ones. The electrode processes are basically the same as in the ordinary dry cell, namely oxidation of zinc to zinc(II) and reduction of manganese(IV) to manganese(III). However, because of the strongly alkaline conditions, the details are different. At the negative electrode:



The reaction at the positive electrode is:



Because these reactions occur so readily under alkaline conditions, this cell is able to delivery *higher currents* than the ordinary dry cell without suffering severe voltage drop. Alkaline cells can deliver a *greater total amount of electricity* than Leclanché cells of the same size. Hence alkaline cells are preferred for appliances requiring high currents (photographic electronic flash units) or high total capacity (tape recorders or children's toys).

Alkaline cells appear more expensive than Leclanché cells but on a cost per unit quantity of electricity basis they are comparable. They are relatively small and robust and very practical to use. Their ability to deliver higher currents and a greater quantity of electricity led to the development of portable higher energy-demanding devices such as portable tape recorders and CD players and more elaborate battery-operated toys.

Leakage problems can be more severe (because of the alkalinity of the electrolyte paste) than with Leclanché cells while disposal problems are similarly minimal.

## Silver oxide cell

The silver oxide cell is a 'button' cell meaning it is small and looks roughly like a button; some are shown in Figure 2.7. It is widely used in miniature appliances

<sup>†</sup> not required for the NSW HSC but is included here because it is such a common battery

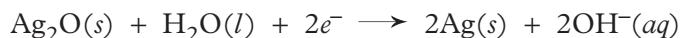
such as watches, hearing aids and calculators. Quite small cells can provide considerable amounts of electricity at a very constant voltage over a long period of time.



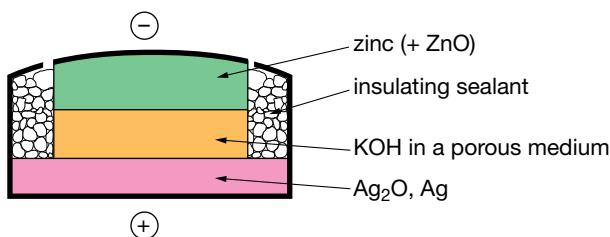
**FIGURE 2.7**  
Silver oxide button cells can be made quite small and are commonly used in cameras, calculators, watches and hearing aids

A typical design is shown in Figure 2.8.

The anode reaction is the same as for the alkaline cell, Equation 2.6. The cathode reaction is:



Addition yields the overall reaction:



**FIGURE 2.8**  
A silver oxide button cell (for watches, calculators and cameras)

This cell delivers a very constant voltage throughout its lifetime, because as it operates there is no change in the concentration of the electrolyte solution (potassium hydroxide).

## Lithium cells

There are many types of lithium cell available commercially; one of the most widely used is the lithium–manganese dioxide cell (generally just called a lithium battery), a use-once-only cell widely used for cameras, watches and electronic devices such as calculators.

Lithium is the ideal metal for making negative electrodes, because it can generate the highest voltage of any metal and, having a low molar mass, it can produce more electrons per gram than any other metal. However it has the disadvantages that it reacts with air and water (p. 115 CCPC) so lithium cells must be water-free and sealed to exclude air.

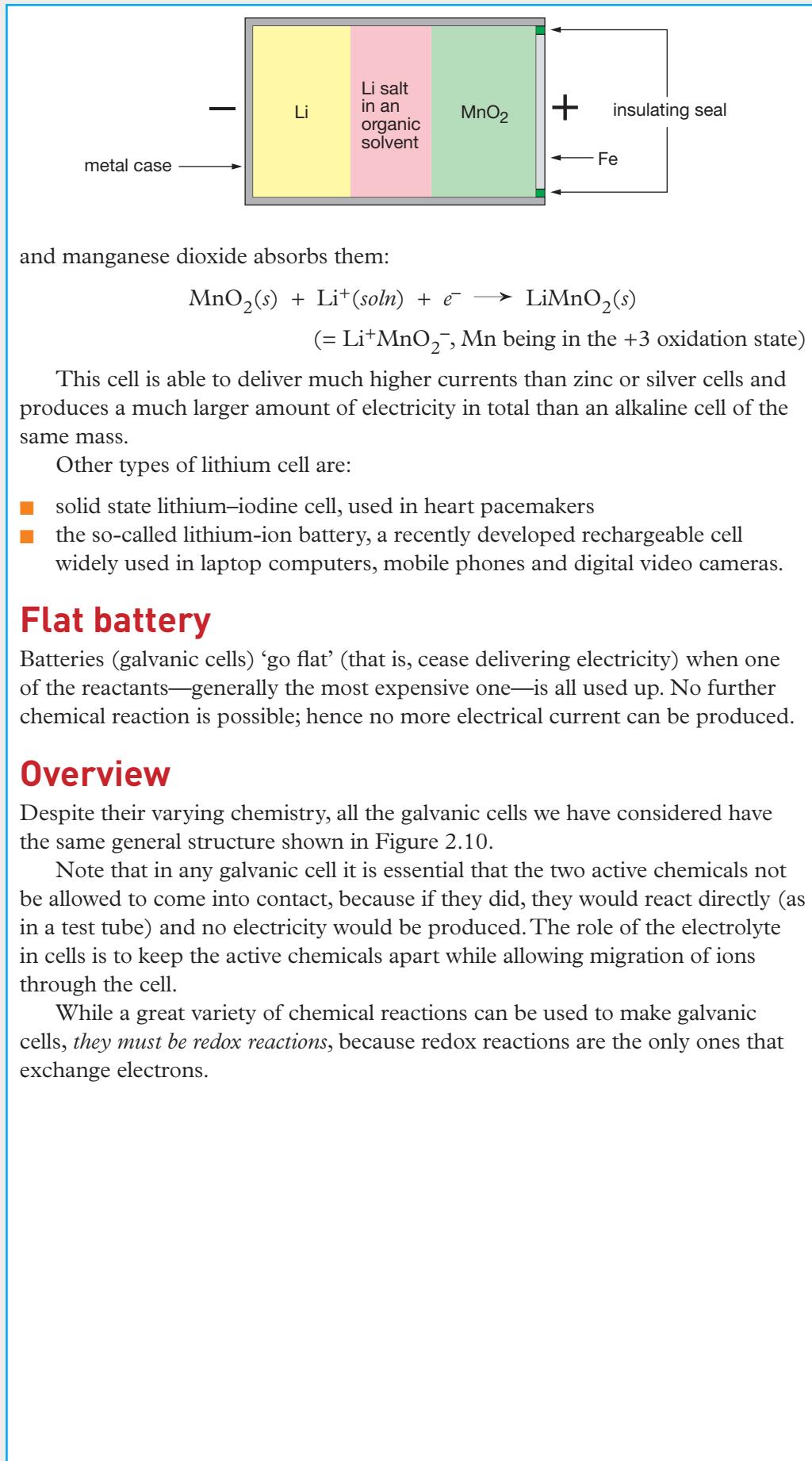
### Lithium–manganese dioxide cell

This cell is shown schematically in Figure 2.9. The negative electrode is lithium while the positive one is manganese dioxide in contact with a metal. Because lithium reacts with water, the electrolyte has to be non-aqueous.

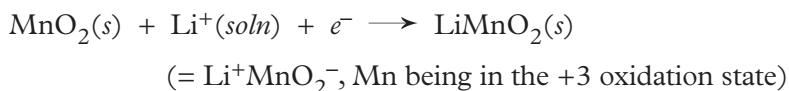
Lithium releases electrons to the external circuit by the reaction



FIGURE 2.9  
Schematic drawing of a lithium–manganese dioxide cell



and manganese dioxide absorbs them:



This cell is able to deliver much higher currents than zinc or silver cells and produces a much larger amount of electricity in total than an alkaline cell of the same mass.

Other types of lithium cell are:

- solid state lithium–iodine cell, used in heart pacemakers
- the so-called lithium-ion battery, a recently developed rechargeable cell widely used in laptop computers, mobile phones and digital video cameras.

## Flat battery

Batteries (galvanic cells) ‘go flat’ (that is, cease delivering electricity) when one of the reactants—generally the most expensive one—is all used up. No further chemical reaction is possible; hence no more electrical current can be produced.

## Overview

Despite their varying chemistry, all the galvanic cells we have considered have the same general structure shown in Figure 2.10.

Note that in any galvanic cell it is essential that the two active chemicals not be allowed to come into contact, because if they did, they would react directly (as in a test tube) and no electricity would be produced. The role of the electrolyte in cells is to keep the active chemicals apart while allowing migration of ions through the cell.

While a great variety of chemical reactions can be used to make galvanic cells, *they must be redox reactions*, because redox reactions are the only ones that exchange electrons.

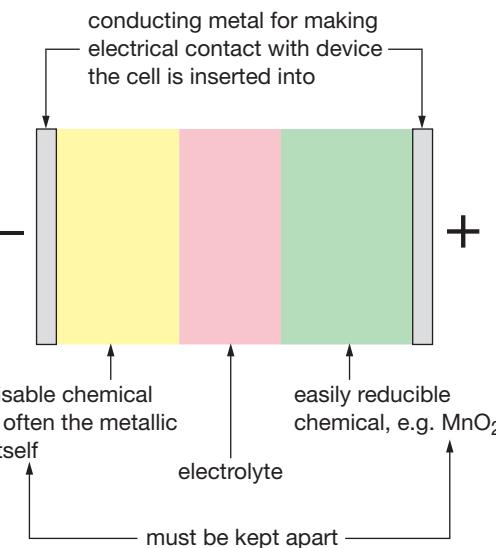


FIGURE 2.10  
The general structure of galvanic cells

The batteries described in this section are ‘use once only and throw away’ type cells. They cannot be recharged. We shall look at the reason for this after we have considered some cells that can be recharged.

## FOR INVESTIGATION

Prepare a table that compares the chemistry of the ordinary dry cell, the alkaline cell, the silver oxide button cell and the lithium–manganese dioxide cell. Then search out information in order to prepare another table in which you compare the relative costs and practicality (including uses), impact on society and environmental impact of these cells.



### WEBSITES

<http://www.powerstream.com/BatteryFAQ.html>

(a good introduction to common types of cells)

<http://www.eveready.com/learning/howbatterieswork.asp>

(general information on commercial batteries with a good simple account of the alkaline battery)



### Exercises

16 Use the information in Section 2.9 to write the overall reaction for the Leclanché cell and for the alkaline cell.



17 The mercury cell is a button cell similar to the silver oxide cell, but with Hg, HgO replacing Ag, Ag<sub>2</sub>O; the mercury electrode is positive. The solid state lithium–iodine cell consists of a lithium anode and a cathode which is a solid solution of iodine in a polymer: the electrodes are separated by a thin film of crystalline lithium iodide.

Write the electrode reactions for these cells. Hence write the overall cell reactions.

18 a Initially an ordinary dry cell consists of an outer zinc cylinder surrounded by a protective wrapping. Explain why this cell has a greater tendency to leak chemicals after it has ‘gone flat’ than when it was new.

b Why would you expect a leaking alkaline battery to cause more damage than a leaking ‘ordinary’ cell?

19 What masses of lithium, zinc and cadmium need to be oxidised to produce a mole of electrons? This highlights an advantage of using lithium as an anode in galvanic cells.

## 2.10 RECHARGEABLE BATTERIES (CELLS)

Some galvanic cells can be recharged by passing an electric current through them in the opposite direction to that in which they delivered current.

Two common rechargeable commercial cells are the lead accumulator (car battery) and the nickel–cadmium cell.

### Lead-acid cell (or lead accumulator)

The **lead-acid cell** or **lead accumulator** is the cell in the common motor car battery; it is shown in Figure 2.11(a). Six such cells are joined together in series to make a car battery as in Figure 2.11(b). In the one cell the positive and negative electrodes each consists of several plates joined together to maximise the area of contact between electrode and electrolyte which allows the cell to deliver a large current. The electrode plates are close together: this also increases the current the cell can deliver.

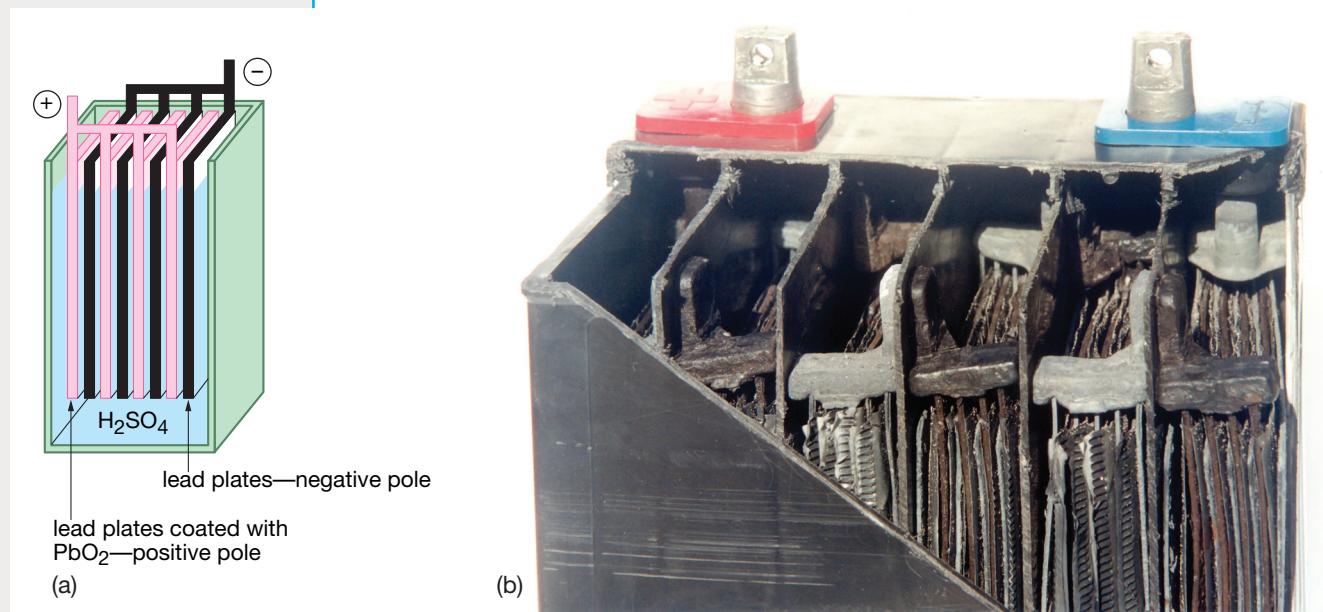
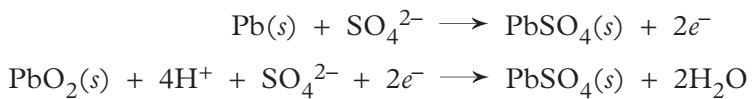
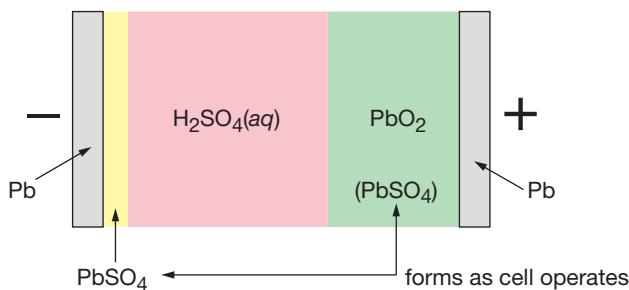


FIGURE 2.11

The lead accumulator: (a) a single 2 V cell, (b) a 12 V car battery which is six such cells joined together. The electrode plates are close together (to generate high currents) and so are separated by thin perforated plastic film (partly cut away in some cells here). As the photo shows, after heavy use the plates buckle with heat and eventually short circuit through the plastic film and so the battery becomes unserviceable.

Figure 2.12 shows the cell schematically. In the charged state the negative electrode is lead while the positive is lead coated with lead(IV) oxide, PbO<sub>2</sub>. The electrolyte is approximately 5 mol/L sulfuric acid. As the cell generates electricity, both electrodes become coated with insoluble lead sulfate, and the concentration of the sulfuric acid solution decreases. The electrode reactions are:





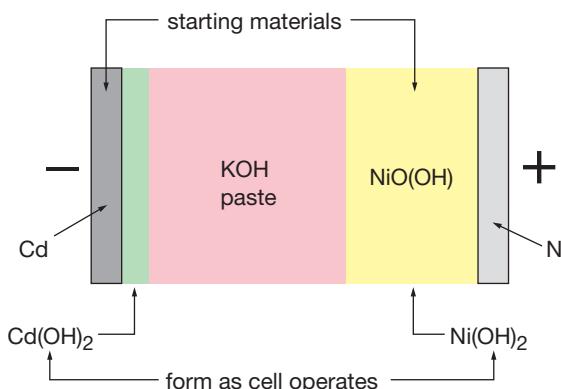
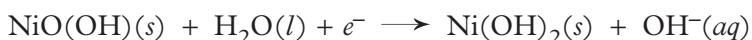
**FIGURE 2.12**  
A schematic diagram of the lead–acid cell

This cell has a voltage of approximately 2 V. To recharge it, a voltage somewhat greater than 2 V is applied, with its positive connected to the positive of the lead–acid cell. This reverses the directions of the above half reactions. The cell is capable of being charged and discharged many times.

Recharging a galvanic cell is simply reversing the spontaneous chemical reaction that occurred when the cell delivered current.

## Nickel–cadmium cell<sup>†</sup>

The nickel–cadmium cell consists of a cadmium, cadmium hydroxide negative electrode and a nickel, nickel oxyhydroxide,  $\text{NiO(OH)}$ , nickel hydroxide,  $\text{Ni(OH)}_2$ , positive electrode, both in contact with an aqueous potassium hydroxide paste as electrolyte as shown schematically in Figure 2.13. Both the cadmium hydroxide and nickel oxyhydroxide are present as (insoluble) solids. The electrode reactions are:



**FIGURE 2.13**  
A schematic drawing of the nickel–cadmium cell

Cadmium is oxidised from the zero to +2 oxidation state while nickel is reduced from the (unusual) +3 oxidation state to the +2 state.

Nickel–cadmium cells are generally designed to look very similar to ordinary cells or alkaline cells (so they can simply replace them). They have a voltage of 1.2 V.

To recharge a nickel–cadmium cell a voltage somewhat greater than 1.2 V is applied, with the positive of the applied voltage connected to the positive (nickel) electrode of the cell. This reverses the above electrode reactions and restores the cell to its original state, ready to be used again.

<sup>†</sup> not required for the NSW HSC but included here because it is such a widely used battery

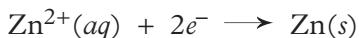
Nickel–cadmium cells are available as general purpose cells of various sizes for direct replacement of dry cells and alkaline cells and also as specially prepared packs for use in specific appliances such as cordless drills ( $8 \times 1.2$  V here) and video cameras ( $5 \times 1.2$  V here)



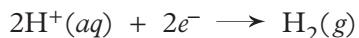
Recharging a galvanic cell is simply reversing the spontaneous chemical reaction that occurred when the cell delivered current.

## Why are some cells non-rechargeable?

Some commercial galvanic cells can be used once only and then have to be thrown away. This is because if we attempt to recharge them, we do not simply reverse the cell reaction but instead bring about a different reaction. For example to recharge the Leclanché cell, we need to bring about:



However when a current is passed through this cell the reaction that occurs is:



This is not only ineffective for recharging the cell, but is quite dangerous (because of the explosive nature of hydrogen).

There are now alkaline cells that are rechargeable. Reaction 2.6 in alkaline solution can be reversed by recharging but there are difficulties of the cell overheating and exploding, so alkaline cells were generally considered to be non-rechargeable. However some alkaline cells are now being made with improved conductivity to overcome the problem, and by using chargers specially built for them (pulsed current at carefully regulated voltages), these alkaline cells can be recharged a limited number of times. Note carefully that only *rechargeable* alkaline cells should be recharged and *only* by using a dedicated recharger.

## 2.11 FUEL CELLS

A **fuel cell** is a type of galvanic cell that can be recharged simply by adding more chemical (fuel) to it.

Fuel cells can operate indefinitely as long as we keep supplying the fuel to them. The reason for this is that fuel cells operate without the electrodes undergoing any change in the electrode reactions. This contrasts with rechargeable

cells, such as the nickel–cadmium cell and the lead–acid cell, where the electrodes undergo changes which have to be reversed in order to recharge those cells.

The *hydrogen–oxygen fuel cell* shown in Figure 2.14 is a typical example. The electrodes are porous carbon with a coating of a catalyst. Hydrogen and oxygen flow slowly across the separate electrodes while there is a potassium hydroxide solution between the electrodes.

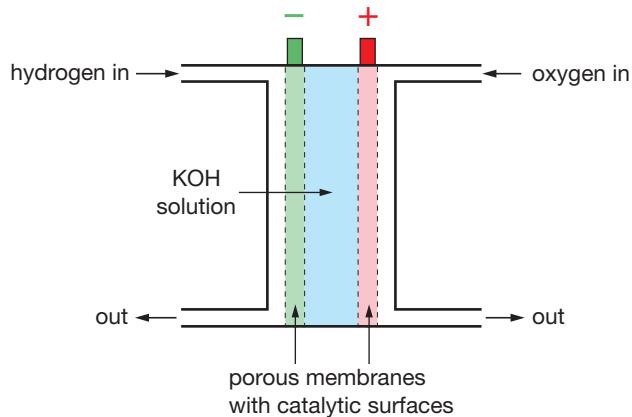


FIGURE 2.14  
A hydrogen–oxygen fuel cell

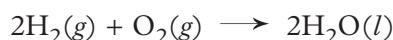
At one electrode, hydrogen is oxidised:



This makes that electrode negative. At the other electrode, oxygen is reduced:



This is therefore the positive electrode. To write the overall reaction, we balance electrons by multiplying Equation 2.8 by 2, then by adding it to Equation 2.9 to get (after cancelling  $2\text{H}_2\text{O}$  on each side):



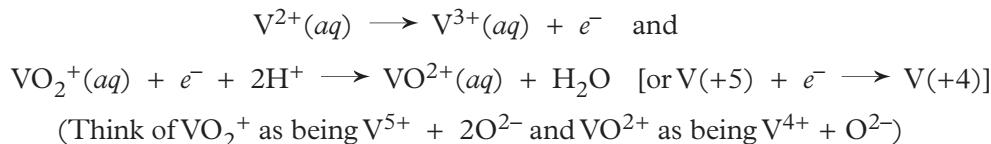
Both hydrogen, which is the fuel, and oxygen have to be supplied continuously to the cell. The product, water, dilutes the KOH electrolyte which therefore has to be slowly replenished during operation. It is because the electrodes undergo no permanent chemical change during cell operation (in contrast to rechargeable cells) that the cell can be operated indefinitely by merely keeping up the supply of fuel and oxygen.

The big advantage of fuel cells is that they provide direct conversion of chemical energy to electrical energy and this can, in principle, be done with 80–100% efficiency. The main problem with fuel cells is developing catalytic electrodes that can provide sufficiently fast electrode reactions for the cells to produce the high currents which are often required. This still remains the main stumbling block to the widespread use of fuel cells.

## Vanadium redox cell

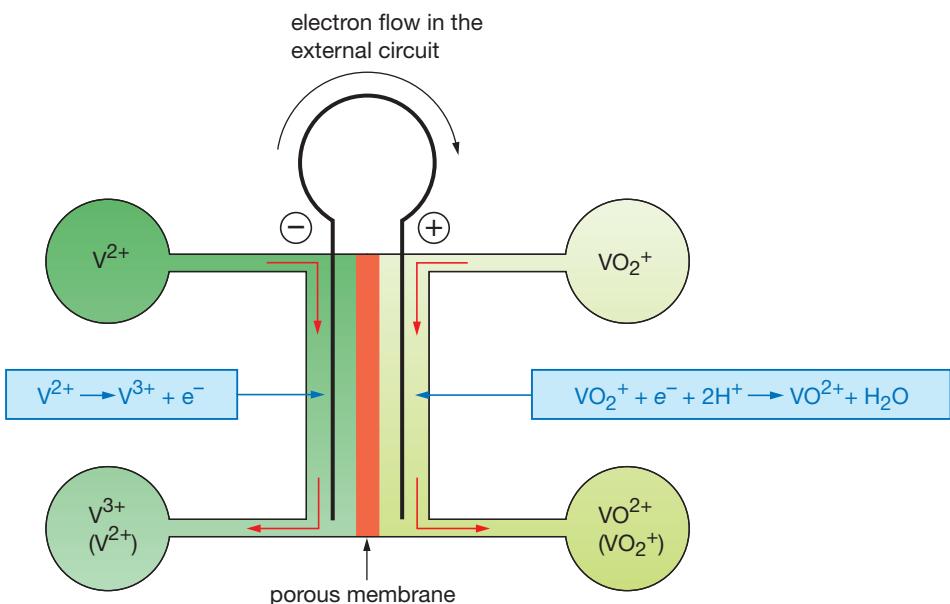
This is a recently developed cell that is showing great potential for the storage of electricity in the form of certain vanadium solutions. The quantities of electricity it can store are in the order of megajoules rather than the kilojoules of the other storage batteries. The electricity can be recovered by using the solutions to operate a galvanic cell.

This cell uses two redox half reactions involving vanadium species in oxidation states 2 and 3 and in 5 and 4 respectively:



The cell is shown schematically in Figure 2.15.

**FIGURE 2.15**  
A schematic drawing of a vanadium redox cell



There are two electrode compartments separated by a porous membrane. A solution of  $\text{VSO}_4$  flows through the anode compartment where  $\text{V}^{2+}$  oxidises to  $\text{V}^{3+}$  releasing electrons to the external circuit. A solution of  $(\text{VO}_2)_2\text{SO}_4$  [i.e.  $\text{V}(+5)$ ] flows through the cathode compartment where  $\text{VO}_2^+$  takes electrons from the electrode and so is reduced to  $\text{VO}^{2+}$  [i.e. to  $\text{V}(+4)$ ]. Sulfate ions migrate through the porous membrane to preserve electrical neutrality.

The cell operates in a flow mode with reactant solutions being recirculated until the concentrations of  $\text{V}^{2+}$  and  $\text{VO}^{2+}$  drop considerably (as  $\text{V}^{3+}$  and  $\text{VO}^{2+}$  are formed).

The cell is recharged by passing an electric current through it (in the reverse direction) and also by reversing the solution flow. This reverses the two half reactions (that is, converts  $\text{V}^{3+}$  back to  $\text{V}^{2+}$  and  $\text{VO}^{2+}$  back to  $\text{VO}_2^+$ ). Because there are no changes to the electrodes during operation, the cell can also be recharged by replacing the spent solutions with fresh ones (with the old ones being regenerated at a more convenient time or place).



### Exercises

- 20** As a lead accumulator discharges, it uses up the sulfuric acid electrolyte. Explain why it is not possible to recharge this cell simply by adding extra sulfuric acid.
- 21 a** A methanol–oxygen fuel cell has been developed. Its construction is similar to the cell in Figure 2.14. The fuel is methanol, the electrolyte is sulfuric acid and oxygen gas (from air) is the other reactant. Deduce the half reactions for this cell (methanol is oxidised to carbon dioxide), and hence the overall reaction.
- b** Suggest an advantage that this cell has over the one in Figure 2.14.
- 22** Is the vanadium redox cell a fuel cell or just a rechargeable cell? Explain.

## 2.12 THE GRATZEL CELL

**Photovoltaic cells** are devices that generate electricity when light falls upon particular surfaces, usually silicon ‘doped’ with small amounts of other elements. They are quite different from galvanic cells. However in recent years a photovoltaic cell has been developed that has some electrochemistry involved in it. It is called the **Gratzel cell**, or more technically, a **liquid junction photovoltaic device**.

The Gratzel cell is shown schematically in Figure 2.16. The photosensitive material is a thin layer of titanium dioxide,  $\text{TiO}_2$  (red in the diagram) on the surface of a thin sheet of glass (green in the diagram); this glass is made electrically conducting by the depositing of platinum on it (black). A thin film of a solution of potassium iodide and iodine separates this ‘electrode’ from another sheet of conducting glass (the other electrode).

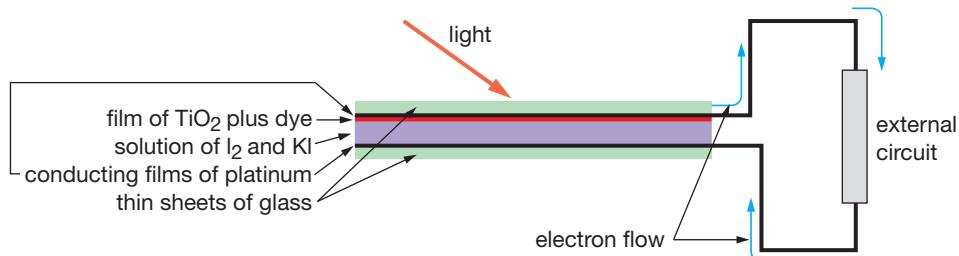
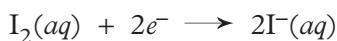


FIGURE 2.16  
The Gratzel cell

When light hits the  $\text{TiO}_2$  an electron is released: it flows through the external circuit to the other sheet of glass. The electron released by the  $\text{TiO}_2$  is replaced by oxidation of iodide:



and so the  $\text{TiO}_2$  can continue emitting electrons as light shines on it. The circuit is completed on the bottom sheet of glass by the iodine absorbing the returning electrons:



Doubling the first equation and adding it to the next two shows that there is no net change to the chemicals involved so the device can operate indefinitely. The only change has been the conversion of light energy into a flow of electricity through the external circuit.

Titanium dioxide is sensitive to only a narrow wavelength range of light so it is usually mixed with a suitable dye to extend its range across most of the solar spectrum.

The layers of material used in this device are extremely thin, so much so that the device is nearly transparent (though darkish looking) and so can be used as watch faces which generate enough power to run the watch. Gratzel cells are also being used as ‘smart windows’—windows that let light into a room but at the same time generate electricity for the house.



## FOR INVESTIGATION

Prepare a table that compares the chemistry of the lead–acid cell, a fuel cell, the vanadium redox cell and the Gratzel cell. Then search out information in order to prepare another table in which you compare the relative costs and practicality (including uses), impact on society and environmental impact of these cells.



### WEBSITES

<http://www.science.org.au/nova/023/023key.htm>

(fuel cells)

<http://www.h2fc.com/technology.html>

(fuel cells)

<http://www.ceic.unsw.edu.au/centers/vrb>

(vanadium redox cell: look in the picture gallery as well as reading the text)

## 2.13 STANDARD ELECTRODE POTENTIALS

Often chemists want to measure and compare voltages of cells and use them to get a measure of the relative activity of metals in cells. To do this it is not necessary to tabulate voltages of all possible cells but rather to assign voltages to electrodes; that is, to list what are called *electrode potentials*. However before doing this we need to clarify the meaning of ‘voltage’.

### Voltage and EMF

As can be verified by anyone who has watched a motor mechanic put a voltmeter across the terminals of a car battery while the starter motor is being operated, the voltage delivered by a galvanic cell is not constant, but depends upon the amount of current being drawn. The greater the current being delivered, the lower the cell voltage. If we are going to compare voltages of cells, we need to standardise the conditions under which they are measured. Hence we introduce a term called electromotive force or EMF.

The **electromotive force** or **EMF** of a galvanic cell is the potential difference (voltage) across the electrodes of the cell when a negligibly small current is being drawn. It is the maximum voltage that the cell can deliver.

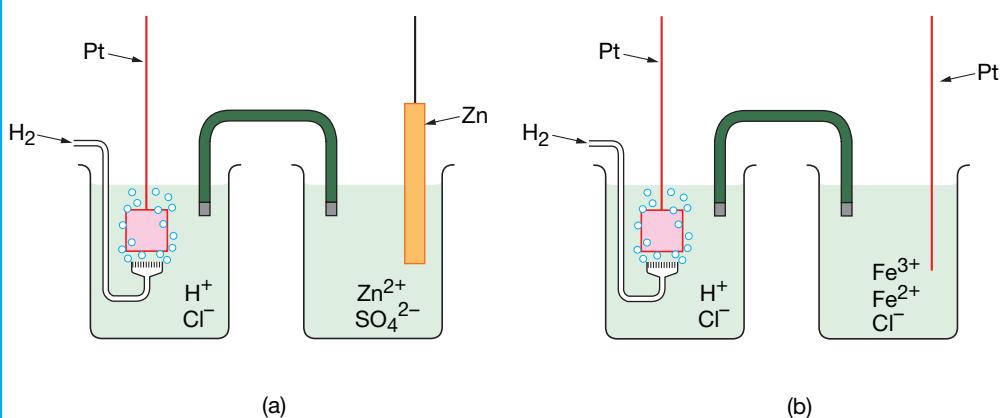
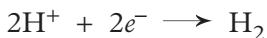
Modern solid-state digital voltmeters are high-resistance devices which measure voltage while drawing a negligibly small current. Hence such voltmeters give a good approximation to the EMF of the cell.

Strictly speaking, for comparative purposes we should talk about the EMFs of galvanic cells rather than just ‘voltages’.

### Standard hydrogen electrode

For reference purposes we tabulate EMFs of electrodes relative to one particular electrode. The chosen reference electrode is the **standard hydrogen electrode**. This consists of a piece of platinum metal immersed in a 1.000 mol/L solution of hydrogen ions (hydrochloric acid) and through which hydrogen gas is bubbled at a pressure of 100.0 kPa. A typical hydrogen electrode is shown in the left-hand

beaker in each of the cells of Figure 2.17. The half reaction associated with this electrode is:



**FIGURE 2.17**  
Cells used for measuring the standard electrode potentials for the  $\text{Zn}^{2+}$ ,  $\text{Zn}$  and  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pt}$  electrodes

We specify a concentration of 1.000 mol/L for hydrogen ion and a pressure of 100.0 kPa for hydrogen gas because cell EMFs depend upon concentration and upon the pressure of any gas involved.

## Measuring standard electrode potentials

Electrode potentials are measured relative to the standard hydrogen electrode.

Each of the other electrodes we are interested in is connected in turn to this standard hydrogen electrode, via a salt bridge, to make a cell as shown in Figure 2.17, and the cell voltage (EMF), including its sign, is measured.

As cell EMF depends upon electrolyte concentration and gas pressure, we also require that the ion associated with the electrode be present at a concentration of 1.000 mol/L and any gas involved be present at a pressure of 100.0 kPa for consistency in tabulated data. These conditions, 1.000 mol/L for solutes and 100.0 kPa for gases comprise, what we call the **standard state**.<sup>†</sup> EMFs of such cells are called standard electrode potentials.

The **standard electrode potential**,  $E^\circ$ , of an electrode is the potential of that electrode in its standard state relative to the standard hydrogen electrode.

$E^\circ$  is the EMF of the cell formed by combining the electrode with a standard hydrogen electrode, and its sign is the sign of the electrode relative to the hydrogen electrode. We use the superscript  $^\circ$  of  $E^\circ$  to denote that the value refers to the standard state.<sup>‡</sup>

Standard electrode potentials are sometimes called *standard redox potentials* or *standard reduction potentials*.

If conditions are not those of the standard state, we just use the term **electrode potential**. Its value would be different from the standard electrode potential.

<sup>†</sup> Defining the standard state for solutes as 1.000 mol/L is not strictly correct, but it suffices for present purposes.

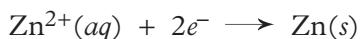
<sup>‡</sup> An older standard state is still in widespread use. It is based on a pressure of 1.000 atmosphere which is a non-systematic unit of pressure that is gradually being phased out:

1 atmosphere = 101.3 kPa. A superscript o is used to denote that older standard state.  $E^\circ$  is the standard electrode potential based on a standard state of 101.3 kPa, while  $E^{\circ\circ}$  refers to the newer standard state (100.0 kPa). You will see  $E^\circ$  in many texts. The numerical value, to the accuracy used in elementary texts such as this one, is the same for both standard states.

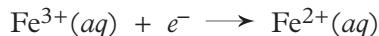
The cell shown in Figure 2.17(a) has an EMF of 0.76 volt with the zinc rod being negative with respect to the platinum of the hydrogen electrode. Hence we say that the  $\text{Zn}^{2+}$ ,  $\text{Zn}$  electrode has a standard electrode potential of  $-0.76$  volt. The cell in Figure 2.17(b) has an EMF of 0.77 volt, with the platinum wire dipping into the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  solution being positive relative to the wire of the hydrogen electrode; hence the standard electrode potential of the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  electrode is  $+0.77$  volt (V).

Standard electrode potentials are assigned not only to the electrodes but also to the *reduction* half reactions associated with the electrodes.

Not only do we say that the  $\text{Zn}^{2+}$ ,  $\text{Zn}$  electrode has a standard electrode potential of  $-0.76$  V, but we also say that the reduction half reaction:

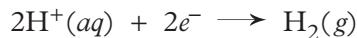


has a standard electrode potential of  $-0.76$  V. Similarly, the reduction half reaction associated with the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  electrode:



has a standard electrode potential of  $+0.77$  V.

Because of the way standard electrode potentials are defined, the  $\text{H}^+$ ,  $\text{H}_2$  electrode has a standard electrode potential of zero; similarly the associated reduction half reaction:



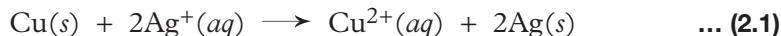
also has a standard electrode potential of zero.

It is important to note that electrode potentials or redox potentials refer to *reduction* half reactions only (and not to oxidation half reactions). We can talk about voltage (or EMF) of an oxidation half reaction but we must *never* call it an electrode potential; that term is reserved for reduction half reactions.

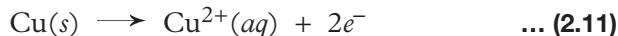
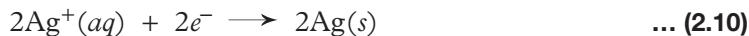
Standard electrode potentials for some common electrodes (or electrode reactions) are given in Table 2.1. Such a table of standard electrode potentials can be used to calculate EMFs of redox reactions or of cells and to determine the relative oxidising or reducing strengths of different substances.

## 2.14 CALCULATING EMFs FOR REDOX REACTIONS AND CELLS

Just as half reactions can be added to form complete redox reactions, so too standard electrode potentials can be combined to calculate EMFs of complete reactions. As an illustration, let us calculate the EMF of the first reaction we discussed in Section 2.1:



We first break it into its half reactions:



Since the required reaction (Equation 2.1) is made by adding these half reactions, it follows that:

**TABLE 2.1 Standard electrode potentials at 25°C<sup>a</sup>**

Oxidised form + ne <sup>-</sup>	→	Reduced form	E <sup>o</sup> (V)
F <sub>2</sub> + 2e <sup>-</sup>	→	2F <sup>-</sup>	+2.87
H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup>	→	2H <sub>2</sub> O	+1.78
Au <sup>+</sup> + e <sup>-</sup>	→	Au	+1.69
MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup>	→	Mn <sup>2+</sup> + 4H <sub>2</sub> O	+1.51
PbO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup>	→	Pb <sup>2+</sup> + 2H <sub>2</sub> O	+1.46
Cl <sub>2</sub> + 2e <sup>-</sup>	→	2Cl <sup>-</sup>	+1.36
O <sub>3</sub> + H <sub>2</sub> O + 2e <sup>-</sup>	→	O <sub>2</sub> + 2OH <sup>-</sup>	+1.24
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup> + 6e <sup>-</sup>	→	2Cr <sup>3+</sup> + 7H <sub>2</sub> O	+1.23
O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup>	→	2H <sub>2</sub> O	+1.23
MnO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup>	→	Mn <sup>2+</sup> + 2H <sub>2</sub> O	+1.22
Ag <sub>2</sub> O + 2H <sup>+</sup> + 2e <sup>-</sup>	→	2Ag + H <sub>2</sub> O	+1.17
Br <sub>2</sub> + 2e <sup>-</sup>	→	2Br <sup>-</sup>	+1.09
NO <sub>3</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup>	→	NO + 2H <sub>2</sub> O	+0.96
NO <sub>3</sub> <sup>-</sup> + 3H <sup>+</sup> + 2e <sup>-</sup>	→	HNO <sub>2</sub> + H <sub>2</sub> O	+0.93
2Hg <sup>2+</sup> + 2e <sup>-</sup>	→	Hg <sub>2</sub> <sup>2+</sup>	+0.92
Hg <sup>2+</sup> + 2e <sup>-</sup>	→	Hg	+0.85
NO <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup> + e <sup>-</sup>	→	NO <sub>2</sub> + H <sub>2</sub> O	+0.80
Ag <sup>+</sup> + e <sup>-</sup>	→	Ag	+0.80
Fe <sup>3+</sup> + e <sup>-</sup>	→	Fe <sup>2+</sup>	+0.77
O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>2</sub> O <sub>2</sub>	+0.70
MnO <sub>4</sub> <sup>-</sup> + 2H <sub>2</sub> O + 3e <sup>-</sup>	→	MnO <sub>2</sub> + 4OH <sup>-</sup>	+0.60
I <sub>2</sub> + 2e <sup>-</sup>	→	2I <sup>-</sup>	+0.54
O <sub>2</sub> + 2H <sub>2</sub> O + 4e <sup>-</sup>	→	4OH <sup>-</sup>	+0.40
Ag <sub>2</sub> O + H <sub>2</sub> O + 2e <sup>-</sup>	→	2Ag + 2OH <sup>-</sup>	+0.34
Cu <sup>2+</sup> + 2e <sup>-</sup>	→	Cu	+0.34
SO <sub>4</sub> <sup>2-</sup> + 4H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>2</sub> SO <sub>3</sub> + H <sub>2</sub> O	+0.17
Sn <sup>4+</sup> + 2e <sup>-</sup>	→	Sn <sup>2+</sup>	+0.15
S + 2H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>2</sub> S	+0.14
S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> + 2e <sup>-</sup>	→	2S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	+0.08
2H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>2</sub>	0.00
Pb <sup>2+</sup> + 2e <sup>-</sup>	→	Pb	-0.13
Sn <sup>2+</sup> + 2e <sup>-</sup>	→	Sn	-0.14
Ni <sup>2+</sup> + 2e <sup>-</sup>	→	Ni	-0.26
Co <sup>2+</sup> + 2e <sup>-</sup>	→	Co	-0.28
PbSO <sub>4</sub> + 2e <sup>-</sup>	→	Pb + SO <sub>4</sub> <sup>2-</sup>	-0.36
Cd <sup>2+</sup> + 2e <sup>-</sup>	→	Cd	-0.40
Fe <sup>2+</sup> + 2e <sup>-</sup>	→	Fe	-0.45
2CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup>	→	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	-0.49
Zn <sup>2+</sup> + 2e <sup>-</sup>	→	Zn	-0.76
2H <sub>2</sub> O + 2e <sup>-</sup>	→	H <sub>2</sub> + 2OH <sup>-</sup>	-0.83
Al <sup>3+</sup> + 3e <sup>-</sup>	→	Al	-1.66
Mg <sup>2+</sup> + 2e <sup>-</sup>	→	Mg	-2.37
Na <sup>+</sup> + e <sup>-</sup>	→	Na	-2.71
Ca <sup>2+</sup> + 2e <sup>-</sup>	→	Ca	-2.87
Ba <sup>2+</sup> + 2e <sup>-</sup>	→	Ba	-2.91
K <sup>+</sup> + e <sup>-</sup>	→	K	-2.93
Li <sup>+</sup> + e <sup>-</sup>	→	Li	-3.04

oxidising strength increases

reducing strength increases

On the large, side arrows, ‘oxidising strength’ refers to the oxidised form of the redox half reaction and ‘reducing strength’ refers to the reduced form.

a State symbols (phase descriptors) have been omitted in order not to clutter up what is already a complex table. All ions are present as aqueous solutions; other substances are present in their stable pure forms at 25°C and 100 kPa.

$$\left\{ \begin{array}{l} \text{Standard EMF} \\ \text{of the complete} \\ \text{reaction} \end{array} \right\} = \left\{ \begin{array}{l} \text{Standard EMF} \\ \text{of the reduction} \\ \text{half reaction} \end{array} \right\} + \left\{ \begin{array}{l} \text{Standard EMF} \\ \text{of the oxidation} \\ \text{half reaction} \end{array} \right\} \dots (2.12a)$$

or in symbols:

$$\text{EMF}^{\circ}(\text{total}) = \text{EMF}^{\circ}(\text{red}) + \text{EMF}^{\circ}(\text{oxid}) \dots (2.12b)$$

Now the standard EMF of the reduction half reaction in Equation 2.10 is simply the standard electrode potential of the  $\text{Ag}^+$ ,  $\text{Ag}$  electrode,  $E^{\circ}_{\text{Ag}}$ , which is  $+0.80\text{ V}$ . Because the oxidation half reaction is the reverse of the reduction half reaction, the EMF of the oxidation half reaction is *minus* the standard electrode potential of the corresponding reduction half reaction. Hence in our particular case:

$$\text{EMF}^{\circ}(\text{oxid}) = -E^{\circ}_{\text{Cu}} = -(+0.34\text{ V}) \quad (\text{from Table 2.1})$$

$$\begin{aligned} \text{Hence } \text{EMF}^{\circ}(\text{total}) &= E^{\circ}_{\text{Ag}} + (-E^{\circ}_{\text{Cu}}) \\ &= 0.80 - 0.34\text{ V} \\ &= 0.46\text{ V} \end{aligned}$$

Reaction 2.10 is actually *twice* the reaction written in Table 2.1. Note carefully that

doubling the half reaction does not alter  $E^{\circ}$ .

This contrasts with  $\Delta H^{\circ}$ 's (p. 277 CCPC). The reason is that  $E^{\circ}$  is a type of *energy per electron*. It does not matter how many electrons are in the reaction written—the energy per electron is unaltered. Changing the direction of the half reaction does change the sign of its  $\text{EMF}^{\circ}$ . In this regard  $\text{EMF}^{\circ}$  behaves like  $\Delta H$ .



### Example 3

Using standard electrode potentials from Table 2.1, calculate the standard EMF of the reaction:



This reaction is made up of the following half reactions:

$$\begin{aligned} \text{Ni(s)} &\longrightarrow \text{Ni}^{2+}(\text{aq}) + 2e^- \quad \text{EMF}^{\circ} = -E^{\circ}_{\text{Ni}} \\ &= -(-0.26)\text{ V} = +0.26\text{ V} \end{aligned}$$

$$\begin{aligned} \text{Cl}_2(\text{g}) + 2e^- &\longrightarrow 2\text{Cl}^-(\text{aq}) \quad \text{EMF}^{\circ} = E^{\circ}_{\text{Cl}} \\ &= +1.36\text{ V} \end{aligned}$$

By Equation 2.12:

$$\begin{aligned} \text{EMF}^{\circ}(\text{total}) &= +0.26 + 1.36 \\ &= \mathbf{1.62\text{ V}} \end{aligned}$$

In summary: to calculate the EMF of a redox reaction, we use Equation 2.12 together with the fact that the EMF of an oxidation half reaction is *minus* the electrode potential of the corresponding reduction half reaction.

Having seen how to calculate the EMF of a redox reaction, we need to explore exactly what it means. While chemists often talk about the EMF of a

reaction, what they really mean is ‘the EMF of the galvanic cell in which that reaction occurs’. The EMF of Reaction 2.1 is really the EMF of the cell shown in Figure 2.2. *With regard to sign, it is the voltage of the piece of metal where the reduction half reaction is occurring relative to the other electrode*—in this case, the voltage of the silver wire *relative* to the copper wire.

For Reaction 2.13 the galvanic cell it refers to would be like the one in Figure 2.5 with a piece of nickel and a nickel chloride solution replacing the copper and copper chloride solution respectively. Our calculation shows us that the chlorine electrode (the piece of platinum wire) is positive relative to the piece of nickel.

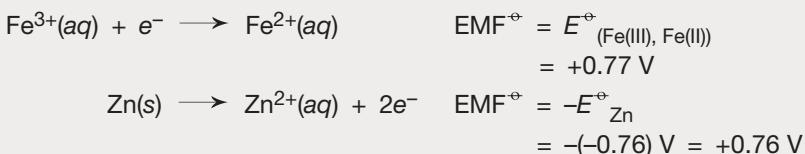
### To calculate the emf of a galvanic cell

We first write the redox half reactions associated with the cell, then follow the above procedure. If we are told which electrode is positive, we write a reduction half reaction for that electrode (*and oxidation for the other*) and proceed as above. Alternatively, we write reduction at the electrode with the higher electrode potential.

### Example 4

Calculate the standard EMF of the galvanic cell in Figure 2.4.

We are told that the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  electrode is positive, so we write the half reactions:



By Equation 2.12:

$$\begin{aligned} \text{EMF}^\ominus_{(\text{cell})} &= 0.77 + 0.76 \\ &= \mathbf{1.53 \text{ V}} \end{aligned}$$

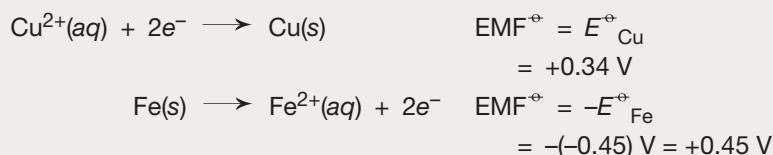
(with the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  electrode, the Pt wire, being positive relative to the Zn)

### Example 5

Calculate the EMF of a cell made by connecting a Cu,  $\text{Cu}^{2+}$  electrode to a Fe,  $\text{Fe}^{2+}$  electrode.



Since we are not told which electrode is positive and hence at which electrode reduction is occurring, we use the suggestion above of writing reduction at the electrode with the higher electrode potential. From Table 2.1 copper has the higher electrode potential (+0.34 V compared with –0.45 V), so we write:



By Equation 2.12:

$$\begin{aligned} \text{EMF}^\ominus_{(\text{cell})} &= 0.34 + 0.45 \\ &= \mathbf{0.79 \text{ V}} \end{aligned}$$

(with the copper wire being positive relative to the iron one)

This example shows that when considering a galvanic cell with electrodes A and B, Equation 2.12(a) can be written as:

$$\text{EMF}^{\circ}_{\text{(cell)}} = \left\{ \begin{array}{l} \text{standard electrode} \\ \text{potential of} \\ \text{electrode A} \end{array} \right\} - \left\{ \begin{array}{l} \text{standard electrode} \\ \text{potential of} \\ \text{electrode B} \end{array} \right\} \dots (2.14)$$

where  $\text{EMF}^{\circ}_{\text{(cell)}}$  is the voltage of electrode A relative to electrode B. If we know the values of the two electrode potentials, it is convenient (though not essential) to make A the more positive electrode.

This equation is particularly useful when we want to calculate an electrode potential from a measured cell EMF and a known electrode potential as in Exercise 28(b) below.

Finally, concerning the significance of the sign of the calculated EMF of the reaction (or of the cell):

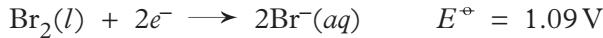
If the EMF of a redox reaction calculated by Equation 2.12 is positive, then the reaction occurs as written; if the calculated EMF turns out to be negative, then the reaction does not occur as written, but rather occurs in the reverse direction.

## A consequence

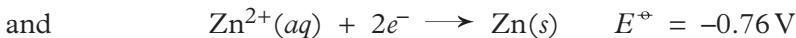
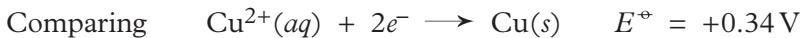
A consequence of that last calculation is this:

When comparing two reduction half reactions, the one with the larger standard electrode potential has the greater tendency to occur. As it occurs it drives the other half reaction in the reverse direction.

For example,



The first half reaction (with the higher  $E^{\circ}$ ) occurs as written and drives the other one in the reverse direction:  $\text{Cl}_2$  oxidises  $\text{Br}^-$  to  $\text{Br}_2$  (and is itself reduced to  $\text{Cl}^-$ ).



the first half reaction goes as written and drives the second one in the reverse direction:  $\text{Cu}^{2+}$  oxidises  $\text{Zn}$  to  $\text{Zn}^{2+}$  (and the  $\text{Cu}^{2+}$  is itself reduced to  $\text{Cu}$ ) or, stated differently,  $\text{Zn}$  reduces  $\text{Cu}^{2+}$  to  $\text{Cu}$  and is itself oxidised to  $\text{Zn}^{2+}$ .

We can generalise from these examples:

*The greater the standard electrode potential, the greater is the oxidising strength of the oxidised form (left-hand side) of the redox half reaction.*

*Alternatively, the algebraically smaller the standard electrode potential, the greater is the reducing strength of the reduced form (right-hand side) of the redox half reaction.*

These trends are shown by the red arrows in Table 2.1.

## Exercises



**23** Three galvanic cells were set up, each having a standard hydrogen electrode as one of its electrodes with the other electrode being:

- i** gold in contact with a  $\text{Au}^{3+}$  solution
- ii** cadmium in contact with a  $\text{Cd}^{2+}$  solution
- iii** a chlorine electrode ( $\text{Cl}_2$ ,  $\text{Cl}^-$  in contact with a platinum wire).

In all these cells solutes were present at a concentration of 1.00 mol/L and any gases were present at pressures of 100.0 kPa. The standard EMFs of these cells were **i** 1.99 V (gold positive) **ii** 0.40 V (hydrogen electrode positive) **iii** 1.36 V (chlorine electrode positive).

- a** Use these results to calculate the standard electrode potentials of the three electrodes.
  - b** Write the half reactions these standard electrode potentials refer to.
- 24 \*a** What are the two different meanings of the word *electrode*? (Section 2.5)
- b** Many electrodes are of the types *metal conductor, metal ion solution*. Give six examples of such electrodes.
  - c** Some electrodes are of the type *inert conductor (platinum or graphite) in contact with a solution containing both oxidised and reduced forms of a redox couple*. List three such electrodes. For each give its electrode (reduction) reaction.

**25 a** For each of the reactions below, calculate the standard EMF:

- i**  $\text{Cu}^{2+} + \text{Ni} \rightarrow \text{Ni}^{2+} + \text{Cu}$
- ii**  $\text{Cd} + 2\text{H}^+ \rightarrow \text{H}_2 + \text{Cd}^{2+}$
- iii**  $\text{Pb} + \text{Mg}^{2+} \rightarrow \text{Pb}^{2+} + \text{Mg}$
- iv**  $\text{Al}^{3+} + \text{Br}^- \rightarrow \text{Al} + \text{Br}_2$
- v**  $\text{Ag}_2\text{O} + \text{H}^+ + \text{Sn} \rightarrow \text{Ag} + \text{Sn}^{2+} + \text{H}_2\text{O}$
- vi**  $\text{Fe}^{3+} + \text{Br}^- \rightarrow \text{Fe}^{2+} + \text{Br}_2$

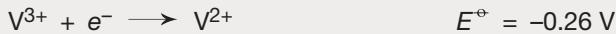
- b** Balance any of the above equations that are not already balanced.
- c** In which direction (left to right or right to left) does each of these reactions go?

**26** Use Table 2.1 to calculate the standard EMF of each of the following cells; state clearly which electrode is positive:

- a** a nickel, nickel ion electrode connected with a salt bridge to a silver, silver ion electrode
- b** an aluminium, aluminium ion electrode connected to a silver, silver ion electrode
- c** an  $\text{Fe}^{3+}, \text{Fe}^{2+}$  electrode connected to a chlorine, chloride electrode

**27 a** Sketch what each of the cells in Exercise 26 would look like in the laboratory.  
**b** Write the overall reaction that occurs in each of these cells as it generates electricity.

**28 a** Calculate the standard EMFs for the silver oxide cell, the lead–acid cell and the vanadium redox cell using Table 2.1 and the following:



- b** The nickel–cadmium cell has an EMF of 1.25 V. The electrode potential for the cadmium, cadmium hydroxide electrode is –0.76 V. Calculate the electrode potential for the nickel hydroxide, oxyhydroxide electrode.

## Important new terms

You should know the meaning of the following terms.

anode (p. 49)	galvanic cell (p. 47)
battery (p. 47)	Gratzel cell (p. 63)
cathode (p. 49)	lead–acid cell (lead accumulator) (p. 58)
displacement reaction (p. 41)	Leclanché cell (p. 53)
dry cell (p. 53)	liquid junction photovoltaic device (p. 63)
electrochemistry (p. 41)	oxidation <sup>†</sup> (p. 42)
electrode (p. 47)	oxidation state (p. 44)
electrode potential (p. 65)	photovoltaic cell (p. 63)
electrode reaction (process) (p. 47)	redox reaction <sup>†</sup> (p. 43)
electrolyte (p. 47)	reduction <sup>†</sup> (p. 42)
electromotive force (EMF) (p. 64)	salt bridge (p. 46)
electron transfer reaction (p. 43)	standard electrode potential (p. 65)
fuel cell (p. 60)	standard hydrogen electrode (p. 64)
	standard state (p. 65)
	voltaic cell (p. 47)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Write equations for three displacement reactions involving metals and metal ions.
- 3 Write oxidation and reduction half equations for the complete equations you wrote in Question 2.
- 4 Why do oxidation and reduction always occur together in the one chemical reaction?
- 5 How can you use the Activity Series 2.3 to decide which metal will displace which other metal from solution?
- 6 Name three metals that will displace copper from a copper sulfate solution, and four metals which will displace silver from silver nitrate solution.
- 7 What is the oxidation state of **(a)** chromium in  $\text{Cr}_2\text{O}_3$  **(b)** titanium in  $\text{TiCl}_4$  and **(c)** iodine in  $\text{MgI}_2$ ?
- 8 When tin(IV) is converted to tin(II) is the process oxidation or reduction or neither? Explain why.
- 9 What type of reaction can be used to make a galvanic cell? Why not other types?
- 10 Sketch a simple laboratory galvanic cell. Show the electrode reactions, the flow of electrons, the flow of ions, and identify the anode and cathode.
- 11 What is the purpose of a salt bridge in a galvanic cell?
- 12 Describe the structure of an ordinary dry cell (Leclanché cell) and explain its chemistry.
- 13 Sketch a silver oxide button cell and write the electrode reactions for it.

<sup>†</sup> These terms were introduced on pp. 117–18 CCPC: they are repeated here because they were not strictly part of the *Preliminary Course* syllabus.

- 14** How do we recharge certain galvanic cells? Name two everyday rechargeable cells.
- 15** Why do we use the term ‘EMF’ instead of ‘cell voltage’?
- 16** What is a standard hydrogen electrode? Draw a diagram of one.
- 17** Describe how you would measure the standard electrode potential of the  $\text{Ag}^+$ , Ag electrode.
- 18** Standard electrode potentials are assigned to which type of half reaction—oxidation or reduction or both?
- 19** How do we calculate the standard EMF of a redox reaction from standard electrode potentials?
- 20** How do we use the EMF of a reaction to decide in which direction the reaction goes?
- 21** Explain how we calculate the standard EMF of a galvanic cell from electrode potentials. The calculated EMF is the voltage of which electrode (relative to the other)? If the calculated EMF for a cell is negative, what does this mean for the half reactions we wrote?

# CHAPTER 3

# Nuclear chemistry

## IN THIS CHAPTER

Radioactivity  
Isotopes and symbols for them  
Stable and unstable isotopes  
Types of radiation emitted  
Alpha-emitting radioisotopes  
Beta-emitting radioisotopes  
Nuclear fission and nuclear reactors

Transuranic elements  
Half-life  
Preparation of commercially useful isotopes  
Detection of radiation  
Uses of radioisotopes

Continuing with the theme of using chemistry to make new materials that are useful to human society, we now turn to what are called radioactive materials. These are particularly useful in medicine (for diagnosis and therapy) and in industry (as tools for monitoring processes).

### 3.1 RADIOACTIVITY

In 1896 the French physicist, Becquerel, discovered that uranium compounds could darken photographic plates even when the plates were protected by the usual opaque paper. All compounds of uranium had this effect, so it was concluded that it was *atoms* of uranium which were emitting some form of radiation. Several other elements—radium, polonium and thorium—were soon found which had this same property. These elements were called *radioactive*, as they actively emitted radiation. This spontaneous emission of radiation by certain elements is called **radioactivity**.

For some elements *all* isotopes are radioactive, while for others only *one* or *some* isotopes are radioactive. For example, all isotopes of uranium, U, and radium, Ra, are radioactive while rubidium, Rb, and rhenium, Re, each have two isotopes, only one of which is radioactive. Hence we talk about **radioactive isotopes** or **radioisotopes** rather than radioactive elements. Furthermore the radioactive emission comes from the nucleus of the isotope, so scientists talk about **unstable nuclei** (ones that are radioactive) and **stable nuclei** (not radioactive).

Before delving too far into radioactivity, let us recall and extend some of our basic knowledge about atomic structure (from pp. 40–2 and p. 131 CCPC).

## 3.2 ISOTOPES AND SYMBOLS FOR THEM

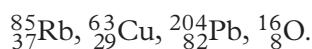
On p. 131 *CCPC* it was explained that **isotopes** are atoms of the one element that differ by having different numbers of neutrons in their nuclei. On p. 42 *CCPC* **atomic number**,  $Z$ , of an atom was defined as the number of protons in the nucleus of an atom of the element. **Mass number**,  $A$ , was defined as the number of protons plus neutrons in the nucleus of the species concerned.

Isotopes of the one element, then, have the same atomic number but different mass numbers. For example, the stable isotope of rubidium has an atomic number of 37 (37 protons) and a mass number of 85 (37 protons plus 48 neutrons); the radioactive isotope has an atomic number of 37 (otherwise it would not be rubidium) and a mass number of 87 (37 protons plus 50 neutrons).

Isotopes are generally named by their mass number. We talk about rubidium-85 and rubidium-87 or chlorine-35 and chlorine-37. In addition we often use a special symbol for isotopes:



where  $M$  is the chemical symbol for the element,  $A$  is the mass number and  $Z$  is the atomic number. Some examples are



## 3.3 STABLE AND UNSTABLE ISOTOPES

If we plot the number of neutrons against the number of protons in the nucleus for isotopes that are stable we find, as shown in Figure 3.1, all the points lie in a narrow band—the red shaded area. We say that they all lie in a **zone (or band) of stability**.

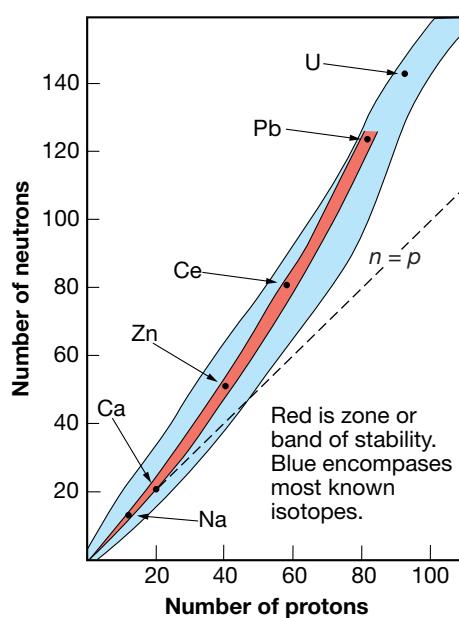


FIGURE 3.1  
A graph of number of neutrons versus number of protons for all known isotopes (blue area): the red shaded area is the zone of stability

For light elements ( $Z$  less than 20) stable isotopes have a ratio of neutrons to protons of about 1.0. As atomic number increases, this stability ratio of neutrons to protons increases: at  $Z = 50$  the ratio is about 1.3 and at  $Z = 80$  it is about 1.5. Points for unstable nuclei lie outside this zone of stability. In addition we find that there are no stable isotopes with atomic numbers greater than 83 (bismuth).

In summary:

An isotope is unstable

- if its atomic number is greater than 83, or
- if its ratio of neutrons to protons places it outside the zone of stability of Figure 3.1.

In unstable nuclei the number of neutrons can be greater or less than the value that gives stability.

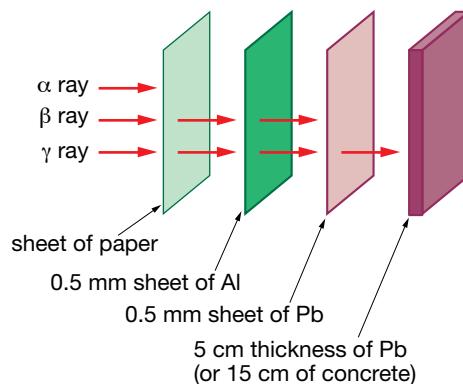
We have said that unstable nuclei undergo radioactive decay. Just what does this mean?

## 3.4 TYPES OF RADIATION EMITTED

It was found that the various radioactive substances could produce three different types of radiation which were originally called alpha ( $\alpha$ ), beta ( $\beta$ ) and gamma ( $\gamma$ ) rays because their true identities were unknown.

**Alpha rays or particles** were relatively heavy positively charged particles which had low penetrating power; a sheet of paper could stop them. **Beta rays or particles** were much lighter negatively charged particles with greater penetrating power; they could pass through a sheet of paper and even through 0.5 mm of aluminium but could not penetrate a 0.5 mm thickness of lead. **Gamma rays** were like X-rays in that they seemed to be genuine radiation rather than particles. They carried no charge and were extremely penetrating; they could be stopped only by several centimetres of lead or many centimetres of concrete. The relative penetrating power of  $\alpha$ ,  $\beta$  and  $\gamma$  rays is shown in Figure 3.2.

FIGURE 3.2  
Relative penetrating power of  $\alpha$ ,  $\beta$  and  $\gamma$  rays



Eventually it was discovered that *alpha rays or alpha particles are helium nuclei* (2 protons and 2 neutrons stuck together), and that *beta particles (rays) are simply electrons*. *Gamma rays are a type of electromagnetic radiation* like radio waves, light and X-rays. Gamma rays have shorter wavelengths than the other forms of this radiation and therefore carry large amounts of energy. The properties of these particles are summarised in Table 3.1.

## 3.5 ALPHA-EMITTING RADIOISOTOPES

The common radioisotopes of uranium and radium are alpha emitters.



An important question is: what has happened to the uranium nucleus after it has lost a helium nucleus? The uranium nucleus originally contained 92 protons

**TABLE 3.1 Types of radioactive emissions**

Name	Symbols	Identity	Relative charge <sup>a</sup>	Relative mass <sup>b</sup>	Penetrating power
alpha	$\alpha$ , ${}_2^4\text{He}$	helium nucleus	+2	4	low
beta	$\beta$ , ${}_{-1}^0e$	electron	-1	1/2000	moderate
gamma	$\gamma$	electromagnetic radiation	0	0	high

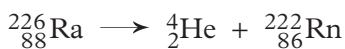
<sup>a</sup> relative to the charge on a proton taken as +1<sup>b</sup> on the relative atomic mass scale (pp. 130–2 CCPC)

and 146 neutrons. If it loses 2 protons and 2 neutrons, we have left a nucleus with 90 protons and 144 neutrons. Now, the number of protons determines what element it is (p. 41 CCPC). From the Periodic Table we see that 90 protons in the nucleus (i.e. atomic number 90) means that the substance is now thorium. At last then we have achieved the medieval alchemists' dream of transmuting one element into another! As uranium disintegrates (spits out a helium nucleus), it is transformed into thorium. Hence we can complete our **nuclear equation** by writing:



*In these nuclear equations we write the atomic number as a subscript on the left of the symbol and the mass number as a superscript, also on the left* (Section 3.2). In such equations the atomic and mass numbers must balance, as they represent numbers of protons and neutrons. That is the reason we wrote thorium-234 above: there are several other isotopes of thorium but when uranium-238 disintegrates it can only form thorium-234 because the mass numbers must balance.

Similarly for alpha emission from radium: it will form a nucleus with  $88 - 2 = 86$  protons. From the Periodic Table, this is radon, Rn. The particular isotope formed is the one with mass number  $226 - 4 = 222$ .



This type of radioactive disintegration, alpha emission, is shown in Figure 3.3(a).

Radioisotopes that emit alpha particles often emit gamma rays as well. These gamma rays carry away the excess energy from the reaction. Most of the heavy elements have alpha-emitting radioisotopes—thorium, radon, polonium, plutonium.

## 3.6 BETA-EMITTING RADIOISOTOPES

Just as alpha particles come from the nucleus in radioactive decay, so too do beta particles (electrons) come from the nucleus and *not* from the electron cloud surrounding the nucleus. It at first seems puzzling that a nucleus which contains only protons and neutrons can emit electrons! However this happens because a neutron 'decomposes' into a proton and an electron:



Putting the atomic and mass numbers on the symbols we have:

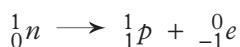
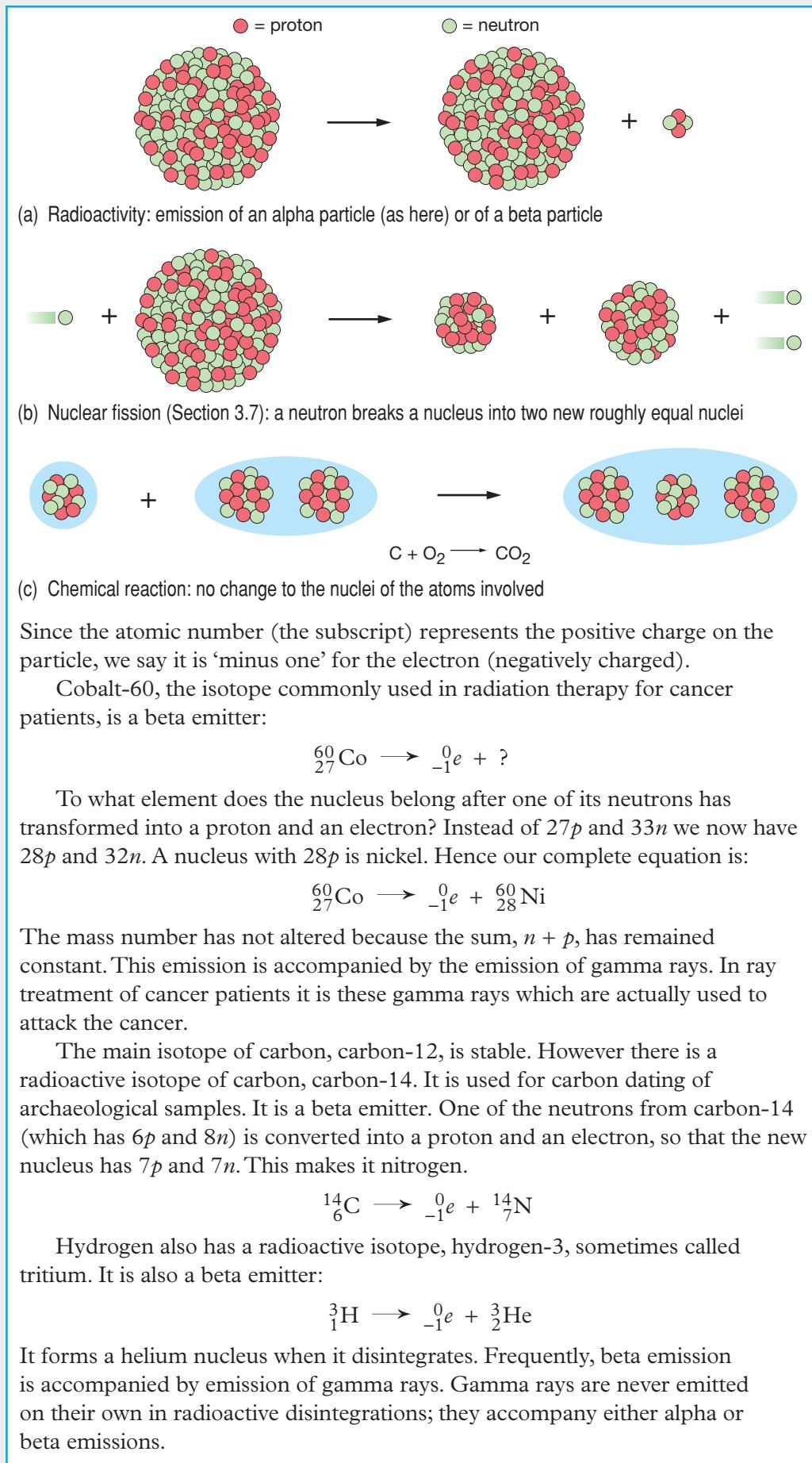


FIGURE 3.3

The difference between nuclear reactions (a) and (b) and a chemical reaction (c). The electron clouds are not shown in the nuclear reactions



## FOR INVESTIGATION<sup>†</sup>

Alpha and beta emissions are the only two decay processes for *natural* radioactive nuclei. Some artificial radioactive isotopes decay by positron emission and electron capture. Search out what these two processes are, including the ultimate fate of the positron.



† not required for NSW HSC

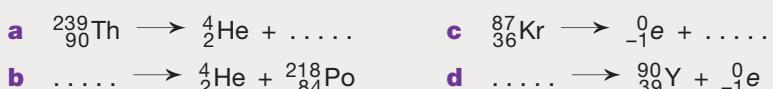
A reaction in which a change occurs to the nucleus of an atom is called a **nuclear reaction**.

Alpha and beta emissions are nuclear reactions. In ordinary *chemical reactions* there are no changes to the nuclei of the atoms involved, just rearrangement of ions or of electrons (for example, as in precipitation and redox reactions). This is illustrated in Figure 3.3.

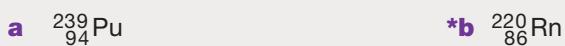
### Exercises

- 1 Write the symbol of the type  ${}^A_ZM$  for each of the following isotopes:
- a C (6 protons, 6 neutrons)
  - b S (16 protons, 16 neutrons)
  - c Cl (17 protons, 20 neutrons)
  - d iodine-127 (53 protons)
  - \*e zinc (30 electrons, mass number 65)
  - \*f radium-226 (88 electrons)

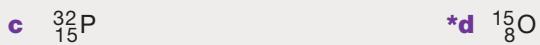
- 2 Complete the following equations for radioactive disintegrations:



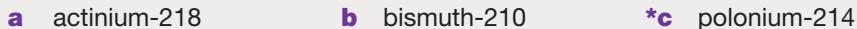
- 3 Write equations for radioactive disintegration of the  $\alpha$ -emitters:



and of the  $\beta$ -emitters:



- 4 Use a Periodic Table to decide what element is formed when each of the following undergoes  $\alpha$ -decay.



What element is formed when each of the following undergoes  $\beta$ -decay?



- 5 How do you expect alpha, beta and gamma particles to be affected by an electric field? Draw a diagram.

- 6 How does (a) a beta emission and (b) an alpha emission affect the neutrons to protons ratio in a nucleus? Explain, using a specific example for each.

- 7 By comparing each of the following isotopes with data for the element in the Periodic Table, decide whether you would expect it to be stable or not. Give your reason. Which, if any, would you expect to be beta emitters?

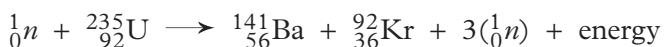


## 3.7 NUCLEAR FISSION AND NUCLEAR REACTORS

Radioactive disintegration is one type of nuclear reaction: it involves the splitting off of a small fragment (alpha or beta particle) from certain nuclei. Another type of nuclear reaction is nuclear fission.

**Nuclear fission** is the process in which neutrons bombard atoms and cause them to split into two roughly equal fragments. Nuclear fission is sometimes referred to as *splitting the atom*. It is illustrated in Figure 3.3(b).

Uranium-235 provides the commonest example of nuclear fission:



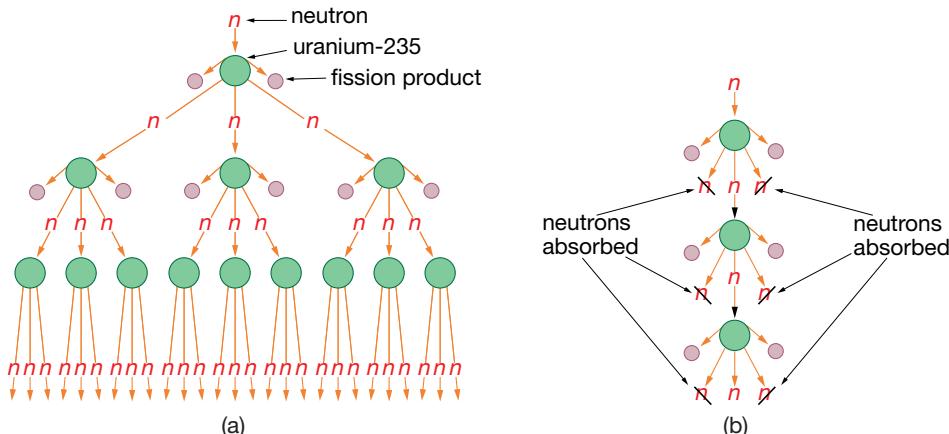
Nuclear fission is the basis of both atomic bombs and nuclear power stations. The amount of energy released per gram of uranium is enormous—far, far greater than is released in normal chemical reactions such as burning a gram of coal or petrol.

If all of the neutrons formed in the above fission reactions are allowed to hit further uranium atoms, the number of neutrons builds up rapidly so that the rate of energy release accelerates dramatically and an enormous explosion results: this is an *atomic bomb*. It is illustrated in part (a) of Figure 3.4.

However if all but one of the neutrons released is absorbed by some other material, so that only this one neutron is allowed to carry on the reaction, then we get a steady and controlled rate of reaction. This constitutes a *nuclear reactor* and is shown in part (b) of Figure 3.4.

FIGURE 3.4

Nuclear reactions: (a) as in atomic bombs where all neutrons released can initiate further fission reactions, (b) as in nuclear reactors where all but one of the emitted neutrons are captured so that a steady reaction proceeds



A **nuclear reactor** is a structure in which controlled nuclear fission occurs. It can be used to generate electricity (as done in many countries such as several European ones, Japan and the USA) or to produce radioactive isotopes for medical and industrial uses (so used in most countries including Australia).

Nuclear reactors have produced several new elements and can be used to make new isotopes of naturally occurring elements.

## 3.8 TRANSURANIC ELEMENTS

Some isotopes such as  ${}^{235}\text{U}$  when hit by neutrons undergo fission. Others however undergo nuclear reactions that produce new elements. For example



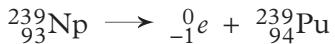
LEFT An atomic bomb blast

ABOVE The nuclear power station and reprocessing plant at Sellafield in the UK

$^{238}\text{U}$  is not **fissionable** (or not **fissile**), meaning that it does not split when hit by a neutron. Instead it forms a new element neptunium, Np:



Neptunium rapidly decays to plutonium Pu which is much more stable:



Neither neptunium nor plutonium exist in nature. They are artificial elements which are made in nuclear reactors.

Most of the new elements that have been made have atomic numbers greater than that of uranium (92) which has the largest value of the naturally occurring elements. These artificial elements with atomic numbers greater than 92 are called **transuranic elements**. One transuranic element is americium, the isotope that is used in domestic smoke alarms. It is made by bombarding plutonium with neutrons:



Scientists have been able to produce about 23 transuranic elements with atomic numbers up to 118. The first few were made by bombardment of other nuclei with neutrons in nuclear reactors as just described. Later ones were made by bombarding heavy nuclei with high speed positive particles such as helium or carbon nuclei; for example californium was made by bombarding uranium-238 with carbon:

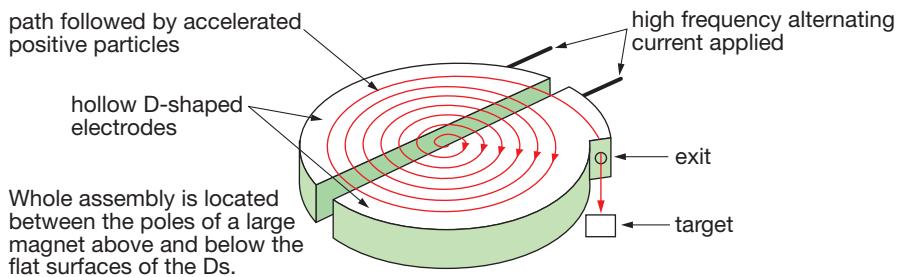


High speed positive particles are produced in machines called *linear accelerators* and *cyclotrons*.

In a **linear accelerator** positive particles are accelerated in a straight line along the axes of a series of cylinders made alternatively positive and negative so the particles are always being pushed from behind by a positive cylinder and pulled from in front by a negative one. This means that linear accelerators are often more than a kilometre in length.

**Cyclotrons** also accelerate positive particles by passing them through alternating positive and negative fields, but they use in addition a strong magnetic field to constrain the particles to a spiral path as shown in Figure 3.5. This makes the machine more compact. There are cyclotrons in major hospitals in Sydney, Melbourne and Brisbane; they are used to produce short-lived isotopes for medical diagnosis (Section 3.12 and Table 3.3).

FIGURE 3.5  
Basic design of a cyclotron



The first of the transuranic elements were made in the 1940s (in nuclear reactors) with others (up to 105) being made, often from high speed positive particles, in the 1950s and '60s. Element 106 was made in 1974 almost simultaneously by Russian and US teams of scientists. Elements 107, 108 and 109 were made in the 1980s, 110 and 111 in 1994, 112 in 1996 and 114, 116 and 118 in 1999.



#### WEBSITE

<http://www.webelements.com>

(for information on transuranic elements including how each was made, just click on the required element in the Periodic Table)



#### Exercises

- 8** When uranium-235 undergoes fission, some groups of products which are formed (in addition to those mentioned in Section 3.7) are:
- a** cerium-144, selenium and 4 neutrons ( $4n$ )
  - b** ruthenium-112, cadmium and  $3n$
  - \*c** iodine-131, yttrium and  $2n$
  - \*d** molybdenum-99, tin and  $4n$ .

Write balanced nuclear equations for these fission reactions.

- 9** Some transuranic elements can be made as follows:
- a** curium-242, by bombarding plutonium-239 with helium nuclei
  - b** californium-245, by bombarding curium-242 with alpha particles: a neutron is emitted
  - c** seaborgium-263, Sg, by bombarding californium-249 with oxygen nuclei: several neutrons are released in the process.

Write nuclear equations for these processes.

- 10 Chadwick discovered neutrons by bombarding beryllium with alpha particles. Write a nuclear equation for the reaction that occurred.
- 11 Suggest a reason for nuclei such as helium and carbon having to be accelerated to high speeds to bring about nuclear transformations whereas neutrons do not need to be so accelerated.

## 3.9 HALF-LIFE<sup>†</sup>

An important property of radioisotopes is their stability, or in other words how long they survive before completely decaying to other isotopes. This is measured by what is called their *half-life*.

Radioisotopes differ greatly in the rate at which they disintegrate. Some, such as sodium-24, will completely disintegrate in a few days, while others, like cobalt-60, take many years. Others, like plutonium-239 (a by-product of nuclear reactors), take tens of thousands of years. Some such as uranium-238 and 235 take billions of years. We use the term ‘half-life’ to characterise the rate at which radioisotopes disintegrate.

The **half-life** of a radioisotope is the time required for half the atoms in a given sample to undergo radioactive decay; for any particular radioisotope, the half-life is independent of the initial amount of the isotope present.

The half-life of iodine-131 is 8 days. If we start with 1 g of iodine-131, then after 8 days we will have only 0.5 g left (the other half gram will have decayed into xenon). After a further 8 days, half of this 0.5 g will have decayed, leaving us with only 0.25 g. After a further 8 days, the amount of iodine-131 left will be 0.125 g. After a total of 40 days (five half-lives), of our original 1 g, there will be only 0.031 g left.

The half-lives of some common isotopes are given in Table 3.2.

**TABLE 3.2 Common isotopes, the radiation they emit and their half-lives<sup>a</sup>**

Name	Radiation emitted	Half-life
*carbon-14	$\beta$	$5.7 \times 10^3$ years
fluorine-20	$\beta, \gamma$	11 seconds
*hydrogen-3 (tritium)	$\beta$	12.3 years
molybdenum-99	$\beta, \gamma$	2.7 days
phosphorus-32	$\beta$	14 days
*plutonium-239	$\alpha, \gamma$	$2.4 \times 10^4$ years
*potassium-40	$\beta$	$1.3 \times 10^9$ years
*radium-226	$\alpha, \gamma$	$1.6 \times 10^3$ years
sodium-24	$\beta, \gamma$	15 hours
strontium-90	$\beta$	28 years
sulfur-35	$\beta$	87 days
*uranium-238	$\alpha, \gamma$	$4.5 \times 10^9$ years

\* denotes a naturally occurring isotope

a Other isotopes are listed in Table 3.3

† Half-life is not mentioned in the NSW HSC syllabus, but it is hard to appreciate why different isotopes are used for different purposes (Section 3.12 and Table 3.3) without some understanding of the term: hence its inclusion here.

## 3.10 PREPARATION OF COMMERCIALLY USEFUL ISOTOPES

There are only about 50 naturally occurring radioactive isotopes. However about 2000 radioisotopes have been created, mostly in the normal operation of nuclear reactors. Most synthetic radioisotopes have quite short half-lives (hours to seconds) and are either annoying by-products that have to be managed or just laboratory curiosities. However, about twenty radioisotopes have found widespread use in medicine and industry. There are two common methods for producing radioisotopes: (1) from nuclear reactors and (2) in cyclotrons.

### Radioisotopes from nuclear reactors

Nuclear reactors are convenient sources of neutrons (Section 3.8), and so are used to make radioisotopes that can be prepared by neutron bombardment. Suitable target nuclei are placed in the reactor core where they are bombarded by neutrons to produce the required isotope. For example cobalt-60, which is used for cancer treatment, is made by placing normal cobalt-59 in a reactor where it captures a neutron.

Sometimes the required isotope is a direct product of uranium fission as in the case of the precursor of technetium-99*m*.

### Technetium-99*m*

Technetium-99*m*<sup>†</sup> is widely used in medicine for diagnosis. Its half-life is only 6 hours. Consequently it has to be produced at the hospital needing it rather than transported from a nuclear reactor. Technetium-99*m* is formed by the radioactive decay of molybdenum-99 which is a fission product of uranium-235. Molybdenum-99 has a half-life of 66 hours: this is long enough for it to be transported from the Lucas Heights reactor (south of Sydney) to all major hospitals in Australia.

Molybdenum-99 is prepared by placing special pellets of UO<sub>2</sub> in the reactor core for about a week. The UO<sub>2</sub> contains about 2% <sup>235</sup>U: some of this undergoes fission to <sup>99</sup>Mo. This molybdenum is extracted, adsorbed onto alumina and packaged into small glass tubes about the size of a person's thumb for despatch to hospitals. <sup>99</sup>Mo decays to <sup>99m</sup>Tc continuously. At the hospital <sup>99m</sup>Tc is extracted from the alumina by flowing normal saline solution through it. The <sup>99m</sup>Tc is then chemically bound to biologically significant molecules for the diagnostic test to be performed.

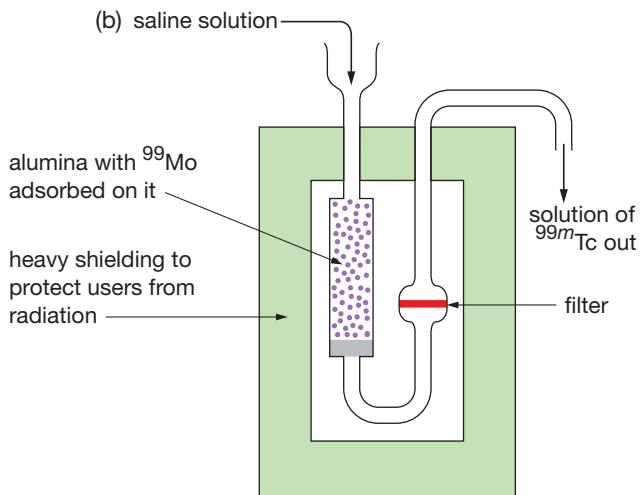
The <sup>99</sup>Mo parent or 'cow' is eluted or 'milked' every day for about a week by which time its activity has become too low for practical use.

Figure 3.6 shows a technetium-99*m* generator.

### Radioisotopes from cyclotrons

Some radioisotopes for medical use have to be prepared in a cyclotron (Fig. 3.5). That means they are prepared by bombarding a suitable target nucleus with a small positive particle such as a helium or carbon nucleus. Fluorine-18 is

<sup>†</sup> The *m* denotes that it is an unstable form of the isotope which decays to a more stable form. It is this unstable form that is used in medical diagnosis.



**FIGURE 3.6**  
 (a) A technetium-99m generator: it is heavily shielded to protect users from the radiation emitted by the molybdenum-99 it contains. (b) shows schematically how the technetium-99m is eluted without removing the molybdenum source from its shielded container

prepared by bombarding nitrogen with helium nuclei:



Iodine-123 is also prepared in a cyclotron.

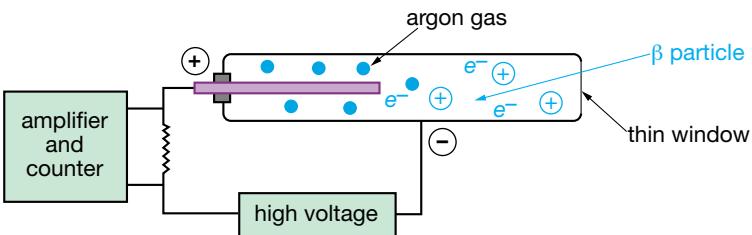
Some commercial radioisotopes and their uses are listed in Table 3.3.

## 3.11 DETECTION OF RADIATION

Emissions from radioisotopes can be detected and measured by the following devices:

- 1 **Photographic film.** Darkening of such film was the way radioactivity was first detected. The method is still used today in some *radiation badges* worn by laboratory workers handling radioactive substances; the amount of darkening of the film is a measure of the amount of radiation that the worker has received.
- 2 **Cloud chamber.** This is an instrument which contains a supersaturated vapour of water or alcohol. When radiation passes through it, it ionises some of the air; the ions formed act as nuclei upon which droplets of liquid form. In this way the path of the radiation is made visible. Alpha particles form straight dense tracks; beta particles form less dense zig-zag tracks while gamma rays generate even fainter tracks.
- 3 **Geiger-Müller counter.** This device also uses ionising properties of radiation. It is particularly good for measuring beta particles, though it can be made to work for alpha and gamma rays too. The beta ray enters through the thin end window of the Geiger tube, Figure 3.7, hits a gas molecule (generally argon) and ionises it by knocking an electron out of it. The high voltage accelerates this electron towards the central electrode and as it gains speed (energy) it ionises more argon atoms in its path, so that there is a cascade of electrons reaching that electrode. This constitutes an electrical pulse which is amplified and measured either by generating clicks in an audio amplifier or by operating an electronic digital counter. The positive argon ions move more slowly towards the negative case to complete the circuit.
- 4 **Scintillation counter.** This instrument uses the fact that when certain substances are irradiated with alpha, beta or gamma rays (different substances for each type of radiation), they emit a flash of light which can be

FIGURE 3.7  
A Geiger-Müller counter



collected and amplified in a photomultiplier. The electrical signal generated then operates an electronic counter.

## 3.12 USES OF RADIOISOTOPES

Radioisotopes are widely used in medicine and industry.

### Medical uses

**1 Cancer treatment.** One method of treating cancer is to irradiate the affected areas of the body with gamma rays which kill cancer cells (along with some 'good' cells as well). As mentioned in Section 3.6 the common source for this radiation therapy is cobalt-60. This isotope is made by neutron bombardment of normal cobalt-59; it disintegrates by beta emission to form nickel-60: it is the gamma rays that accompany this beta emission that attack the cancer because they are able to penetrate quite deeply into body tissue.

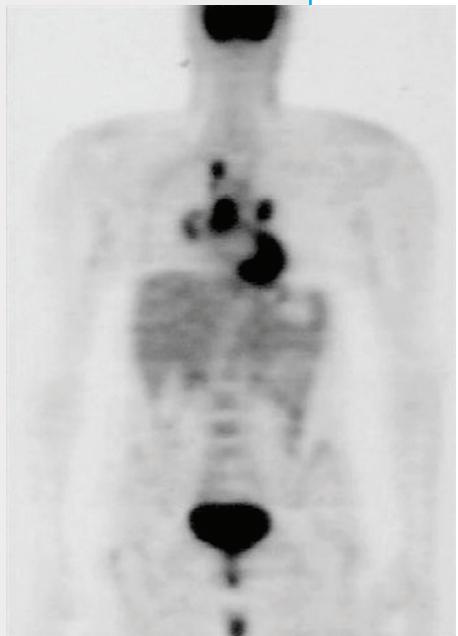
Cobalt-60 is used because the gamma rays carry a suitable amount of energy to destroy certain biological molecules, and because cobalt-60 has a suitable half-life: it is sufficiently long for the radiation source to have a reasonable lifetime in the equipment (about 4 to 6 years) but short enough for the source to emit a reasonable intensity of radiation.

A more recent development in cancer treatment is *in situ* radiation in which a radioactive source, often iridium-192, encased in a thin sealed container is surgically implanted beside the affected organ for a period of time; this technique concentrates the radiation on the cancer and minimises damage to other tissue.

**2 Diagnosis.** Several radioisotopes are used for medical diagnosis. A widely used one is technetium- $99m$  (Table 3.3). If incorporated into some blood serum and injected into a patient's bloodstream, its distribution throughout the body can be measured with a scintillation counter and used to detect blood clots, constrictions and other circulation disorders. In a different form it can be taken up by heart tissue and so used to assess damage after a heart attack. It can also be used to detect brain tumours.

A property of technetium- $99m$  which makes it particularly suitable for medical diagnosis is its short half-life of 6 hours: it rapidly decays and so causes minimal damage to the patient.

Technetium- $99m$  is also used to diagnose thyroid abnormalities. One method of treating over-active thyroid glands is to have the patient ingest some iodine-131 which accumulates in the gland and being a beta emitter irradiates and so destroys some of the gland.



Positron emission tomography (PET) using  $^{18}\text{F}$  bonded to glucose can be used for the early detection of secondary cancers (black spots) after removal of a melanoma (skin cancer)

**TABLE 3.3 Some radioisotopes produced by the Australian Nuclear Science and Technology Organisation (ANSTO)<sup>a</sup>**

Radioisotope	Radiation emitted	Half-life	Uses
technetium-99m	$\gamma$	6 h	medical diagnosis for heart, bone, lung, brain, thyroid, blood flow
iodine-131	$\beta, \gamma$	8 d	treatment of diseases of the thyroid
iridium-192	$\beta, \gamma$	74 d	used as an internal radiotherapy source
fluorine-18	$\beta^+ b$	1.8 h	positron emission tomography (PET) to study brain function and to diagnose epilepsy, heart diseases and certain types of cancer
iodine-123	E.C. <sup>b</sup> , $\gamma$	13.2 h	diagnosis of thyroid diseases and some cancers
cobalt-60	$\beta, \gamma$	5.3 y	gamma radiation for cancer treatment
caesium-137	$\beta, \gamma$	30 y	thickness gauges in industry radiography of machinery and welds irradiation of food (not in Australia—yet)
americium-241 <sup>c</sup>	$\alpha$	432 y	smoke detectors
gold-198	$\beta, \gamma$	2.7 d	radio-tracer to follow movements of sewage and other wastes through waterways movement of sand in river beds and ocean floors (erosion)
zinc-65 and manganese-54 (produced together)	$\beta^+ b$ E.C. <sup>b</sup>	244 d 312 d	follow heavy metals in waste water from mining

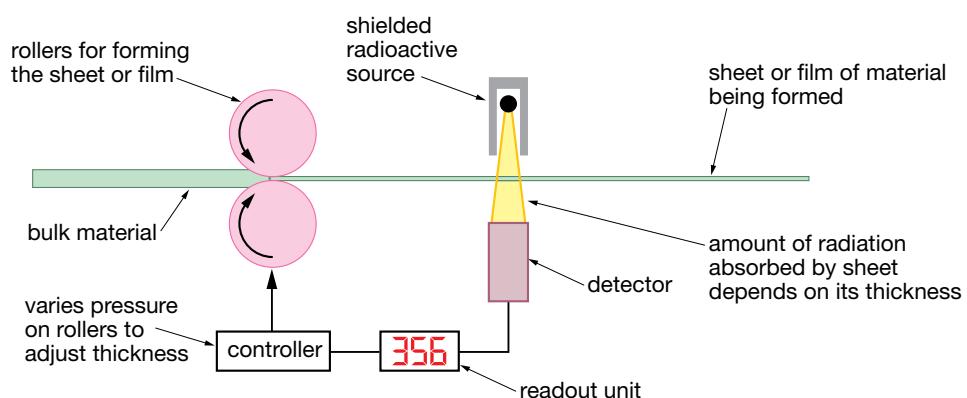
*a*  $^{18}\text{F}$  and  $^{123}\text{I}$  are produced at the National Medical Cyclotron near Royal Prince Alfred Hospital, Sydney; the others are made at the Lucas Heights reactor by placing suitable substances in the reactor core.

*b*  $\beta^+$  is positron emission; E.C. is electron capture. See For Investigation in Section 3.6.

*c* distributed but not made by ANSTO

## Industrial uses

- 1 Thickness gauges.** A radioactive source and a detector arranged as in Figure 3.8 can be used to monitor and control the thickness of materials such as steel sheets, paper, aluminium foil and plastic film in factories. With fixed geometry for the source and detector and the same material passing between them, the amount of radiation received by the detector depends upon the thickness of the material: thicker material absorbs more radiation and so the signal drops. This can be built into a feed-back loop to control the manufacturing process.



**FIGURE 3.8**  
Thickness gauges using radioactive sources are widely used in industry to monitor and control the thickness of materials ranging from paper to plastics to steel

For this purpose an isotope with a fairly low energy emission but a long half-life is used—low energy because we want the thin film to be able to absorb a significant proportion of it, and long half-life so we do not have to replace the source too frequently. Low energy emissions also mean that safety precautions are minimal. Strontium-90 (half-life 28 years), caesium-137 (half-life 30 years) and cobalt-60 (half-life 5.3 years) are often used.



## FOR INVESTIGATION

Select one use of a radioisotope in each of medicine and industry. Collect information on how the isotope is used and how its use relates to its properties. Find information to analyse the benefits of using the isotope for that purpose and to discuss problems (including safety and environmental consequences) associated with that use.

- 2 Leak detectors.** Leaks can be detected in water pipes or underground oil pipelines by adding a suitable radio tracer to the liquid and scanning along the pipe. No radiation will be detected from the isotope inside the pipe, but if the tracer leaks into the soil surrounding the pipe it can be detected and the leak located. For this use a short-lived isotope is needed, so that after the leak has been found the radioactivity quickly decays, the water or oil becomes safe to use again and the environment is quickly decontaminated. Sodium-24 with a half-life of 15 hours is widely used.
- 3 Irradiation of medical supplies and food.** Because gamma radiation is particularly effective in destroying large biological molecules such as DNA, it has been widely (and successfully) used for several decades to kill bacteria and so sterilise medical supplies such as dressings and bandages. In more recent years there have been moves to irradiate food in order to destroy micro-organisms and so minimise spoilage and extend shelf life. Many countries have approved irradiation of specified foods: Australia (as at early 2005) has approved the irradiation of only herbs, spices and certain herbal infusions (but not tea).

Arguments in favour of irradiating food are that by destroying bacteria and moulds it makes food safer and it keeps food ‘fresher’ for longer and so reduces wastage. Arguments against are that it does not necessarily kill all dangerous organisms, it destroys some of the vitamin content of the food, it may lead to the formation of harmful compounds in the food, and it can lead to laxity with food hygiene standards.

Food irradiation requires gamma rays of sufficient energy to destroy bacteria but not enough energy to make the food radioactive (carbon-12 and oxygen-16 are easily converted to radioactive isotopes), and the source must have a reasonably long half-life (to minimise replacement). Caesium-137 and cobalt-60 are widely used.

## Domestic smoke alarms<sup>†</sup>

Simple domestic smoke alarms contain a small source of alpha particles (often americium-241). These alpha particles ionise air, the ions are collected by an

<sup>†</sup> not required for the NSW HSC

electrode and the resulting electrical current measured. When smoke (small solid particles) is present in the air, it prevents ions reaching the electrode causing a reduction in the electrical current which triggers an alarm.

#### WEBSITES

<http://www.ansto.gov.au>

(a variety of information about many aspects of nuclear science. For information about industrial and medical uses move your mouse over *Publications and media* to highlight it, click on *Brochures, fact sheets and links*, then scroll down either to *Brochures* (and click on *Medical and Industrial Isotopes (PDF)(html)*) or to *Information* (and click on *Nuclear Medicine (html)*). You can get to this latter site directly from [www.ansto.gov.au/info/reports/radboyd.html](http://www.ansto.gov.au/info/reports/radboyd.html).)

<http://www.uic.com.au/nip26.htm>

(nuclear medicine)

<http://www.uic.com.au/nip27.htm>

(industrial uses)

<http://education.jlab.org/glossary/cyclotron.html>

(simple account of a cyclotron)



## 3.13 BENEFITS AND PROBLEMS

There are both benefits and problems associated with the use of radioisotopes in industry and medicine.

The *benefits for industry* include the ability to make monitoring equipment that is more sensitive, precise and reliable than earlier equipment, to do things more efficiently and reliably (such as sterilisation of medical supplies) and to do things that were not otherwise possible (such as examine buildings and machinery for weld and structural faults).

The *benefits for medicine* are that radioisotopes have opened up a wide range of non-invasive diagnostic procedures that otherwise would not be possible (on organs such as heart, brain, kidney, thyroid) and have allowed the introduction of radiation therapy for treating many forms of cancer; in many cases this has proved the most effective treatment.

### Problems

The problems with using radioisotopes are the same for industry and medicine. They arise from the fact that *radiation from radioisotopes is harmful to people* (and all other life forms). Alpha, beta and gamma radiation from radioactive substances can cause undesirable reactions in living tissue and so upset the delicate balance that exists among the numerous complex chemical reactions that are always occurring in living cells. Such radiation can cause:

- *tissue damage* (which is immediate and can show up as skin burns and/or nausea, if exposure is mild, or as radiation sickness that can lead to death if exposure is high)

A simple domestic smoke alarm that uses americium-241

- *cancer* (particular leukaemia and lung cancer) which generally does not show up until ten to twenty years after exposure, and
- *genetic damage* which leads to deformities in offspring.

To avoid the harmful effects of radiation people working with radioisotopes must observe a set of stringent safety precautions.

## Safety precautions

The following are some of the safety precautions that must be observed when handling radioactive materials:

- 1 Radioactive materials must always be stored in well-shielded containers.
- 2 Equipment that uses radioactive materials must be designed to ensure that radiation is directed only where it is required and that there is no stray radiation escaping from it.
- 3 People using such equipment or materials must be well trained to handle such things in a safe manner.
- 4 Such people must always wear appropriate safety clothing which depending on the radioisotope in use may vary from gloves and face mask to specially laundered laboratory coats and overshoes, lead-lined aprons and, in the extreme, full protective body suits.
- 5 People working in and around radiation facilities must wear radiation monitors (badges) that record the cumulative amount of radiation they have received.
- 6 Proper procedures for safe storage and disposal of radioactive wastes must be established along with stringent accounting of quantities received and despatched.
- 7 Clear and unambiguous signs must be displayed in any location where radiation equipment or materials are being used or stored.

This is the international radiation hazard sign.  
It must be displayed in any location where radioisotopes are used.



## Exercises

- 12 After some nuclear testing in the Pacific Ocean, certain North Queensland pastures (and consequently the milk of cattle which grazed on them) became contaminated with iodine-131. If the levels of activity were 64 times greater than was acceptable, how long did the dairy farmers have to wait before they could safely market their milk again? The half-life of iodine-131 is 8 days.
- 13 After reprocessing a nuclear fuel, scientists had samples of two radioactive isotopes to look after. Isotope A had an activity of 1000 disintegrations per second (dps) and a half-life of 30 s. Isotope B had an activity of 10 dps and a half-life of 1500 years. An activity of 1 dps was considered safe. Which isotope would present the greater problem for long-term storage? Explain.

- 14** Why is it necessary to produce technetium-99*m* at or close to the hospital using it?
- 15** When using a Geiger–Müller counter, why is it necessary to maintain a fixed geometrical arrangement between sample and detector in order for measurements to be comparable?
- 16** Write nuclear equations for:
- the conversion of cobalt-59 to cobalt-60 by neutron bombardment
  - the decay of cobalt-60 by beta ray emission
  - the fission of a uranium-235 nucleus into a molybdenum-99 nucleus and another nucleus and three neutrons
- 17** Why is iodine-123 preferred over iodine-131 for diagnosis of possible problems with the thyroid gland whereas iodine-131 is preferred for irradiation of an overactive thyroid?

## Important new terms

You should know the meaning of the following terms:

alpha rays (particles) (p. 76)  
atomic number<sup>†</sup> (p. 75)  
band of stability (p. 75)  
beta rays (particles) (p. 76)  
cloud chamber (p. 85)  
cyclotrons (p. 82)  
fissile (fissionable) (p. 81)  
gamma rays (p. 76)  
Geiger–Müller counter (p. 85)  
half-life (p. 83)  
isotope (p. 75)

linear accelerator (p. 82)  
mass number<sup>†</sup> (p. 75)  
nuclear equation (p. 77)  
nuclear fission (p. 80)  
nuclear reaction (p. 79)  
nuclear reactor (p. 80)  
radioactive isotopes (p. 74)  
radioactivity (p. 74)  
radioisotope (p. 74)  
scintillation counter (p. 86)  
stable nuclei (p. 74)  
transuranic elements (p. 81)  
unstable nuclei (p. 74)  
zone of stability (p. 75)

## Test yourself

- Explain the meaning of each of the items in the ‘Important new terms’ section above.
- Give the isotopic symbol for the chlorine isotope that has 17 protons and 20 neutrons in its nucleus.
- Explain how you can predict whether a particular isotope is likely to be stable or radioactive.
- Describe the nature and relative penetrating powers of alpha, beta and gamma particles (rays).
- Why do we talk of radioisotopes and not just radioactive elements?
- Write nuclear equations for the emission of  $\alpha$ -particles from  $^{235}_{92}\text{U}$  and  $^{226}_{88}\text{Ra}$ .
- How does a nucleus which contains only protons and neutrons emit an electron?

CHAPTER  
**3**

<sup>†</sup> These terms were introduced in CCPC but are listed here because it is important that you know their meanings.

- 8** Write nuclear equations for the emission of a  $\beta$ -particle from  $^{60}_{27}\text{Co}$  and  $^{14}_{6}\text{C}$ .
- 9** Explain what is meant by nuclear fission. Give at least one equation to illustrate it.
- 10** What is the essential difference between a nuclear reactor for generating electricity and an atomic bomb?
- 11** Describe two methods for preparing transuranic elements.
- 12** List four practical applications of radioisotopes, two medical and two industrial.
- 13** What properties of particular isotopes make them suited to each of the uses you listed in Question 12?

# EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 1

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination: they use the HSC list of verbs (such as **account** for, **analyse**, **assess**, **compare**, **contrast**, **demonstrate**, **describe**, **discuss**, **evaluate**, **explain**, **identify**, **justify**, **outline**, **propose**, **summarise**) and relate closely to items in the syllabus document. They place heavy emphasis upon recall of learnt information. Practice is the best way of developing skill in answering this type of exam question.

The actual HSC exam will be a mixture of this type of question and ones similar to the problem-solving exercises located within the chapters of Conquering Chemistry. The Revision Tests that follow these sets of questions at the end of the modules are similar mixes.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

	MARKS
1 Outline the importance of the cracking of hydrocarbons to our industrialised society.	4
2 Demonstrate that displacement reactions are electron transfer reactions.	4
3 Distinguish between stable and unstable (radioactive) isotopes and outline the way scientists decide whether a particular isotope will be stable or not.	5
4 Outline the structure, sources and uses of cellulose and assess its potential as a source of chemicals that we currently obtain from oil.	7
5 Discuss the advantages and disadvantages of using ethanol as a fuel or fuel additive for motor cars.	5
6 Demonstrate the usefulness of radioisotopes in industry and in medicine.	5
7 Describe, with a diagram, a galvanic cell that you have set up in the laboratory and explain the flow of electrons and ions through it; identify its anode and cathode.	6
8 Compare and contrast the physical and chemical properties of alkanes and alkenes.	7
9 Assess the need for alternative sources of chemical compounds presently obtained from oil.	4
10 Compare and contrast the chemistry of either the vanadium redox cell or some other fuel cell with that of the lead–acid cell.	6
11 Outline the use of one radioisotope in medicine or industry and describe the properties that make it particularly suited for that use.	4
12 Explain, with an example, how oxidation states allow chemists to decide whether or not a reaction involves electron transfer.	3
13 Describe the method of production and uses of a biopolymer that has come into commercial use in only the last twenty years and evaluate its significance for society.	7

- |   |          |
|---|----------|
| <b>14</b> Describe an experiment you have performed to measure and compare the heats of combustion of three alkanols. List the major sources of error in your experiment and outline steps you took to minimise them. | <b>7</b> |
| <b>15</b> Use two specific examples to demonstrate how the use of a particular polymer for a particular purpose depends upon its properties which in turn depend upon its chemical structure.                         | <b>4</b> |
| <b>16</b> Demonstrate the importance of ethylene as an industrial chemical.   | <b>4</b> |
| <b>17</b> Discuss the benefits and problems associated with the use of radioisotopes in medicine.   | <b>5</b> |
| <b>18</b> Describe the chemical structure and uses of three addition polymers.  | <b>6</b> |
| <b>19</b> Describe the structure and chemistry of the ordinary dry cell and assess its importance to society over the last hundred years or so.   | <b>5</b> |
| <b>20</b> Evaluate the claim that ethanol is a renewable fuel.  | <b>5</b> |

# REVISION TEST FOR MODULE 1

MODULE  
**1**

**Total marks: 50 Suggested time: 90 minutes**

Table 2.1 on p. 67 may be used if needed

## MULTIPLE CHOICE QUESTIONS (1 mark each)

Select the alternative **a**, **b**, **c**, or **d** which best answers the question.

- 1 For the galvanic cell consisting of a zinc, zinc ion electrode connected by a salt bridge to a nickel, nickel ion electrode, the standard EMF (voltage) is:  
**a** 0.50 V with the Ni positive      **c** 1.02 V with the Ni positive  
**b** 0.50 V with the Zn positive      **d** 1.02 V with the Zn positive
- 2 The compound which could *not* be the monomer for making a polymer is:  
**a**  $\text{CH}_2=\text{CH}-\text{CN}$       **c**  $\text{CF}_2=\text{CF}_2$   
**b**  $\text{CH}_3-\text{CH}_2-\text{COOH}$       **d**  $\text{Cl}-\text{CH}=\text{CH}-\text{Cl}$
- 3 The property of beta particles that is used to detect them in a Geiger–Müller counter is:  
**a** a flow of beta particles constitutes an electric current  
**b** their great penetrating power  
**c** they darken photographic plates  
**d** they ionise argon gas at low pressure
- 4 The compound  $\begin{array}{c} \text{H} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ | \\ \text{Cl} \end{array}$  can be prepared by reacting:  
**a** propene with chlorine  
**b** propane with chlorine in the dark  
**c** propene with hydrogen chloride  
**d** 2-propanol with chlorine
- 5 The reaction that goes in the direction shown is:  
**a**  $2\text{Ag}(s) + \text{Sn}^{2+}(aq) \rightarrow 2\text{Ag}^+(aq) + \text{Sn}(s)$   
**b**  $\text{Pb}(s) + \text{Fe}^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{Fe}(s)$   
**c**  $\text{Mg}^{2+}(aq) + \text{Fe}(s) \rightarrow \text{Mg}(s) + \text{Fe}^{2+}(aq)$   
**d**  $\text{Fe}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Cu}(s)$
- 6 In the following nuclear equation:  
$${}_{86}^{222}\text{Rn} \rightarrow {}_2^4\text{He} + {}_y^z\text{X}$$
  
**a**  $z = 218$  and  $y = 88$       **c**  $z = 226$  and  $y = 84$   
**b**  $z = 218$  and  $y = 84$       **d**  $z = 226$  and  $y = 86$
- 7 The heat of combustion of 2-propanol is 33.5 kJ/g. The enthalpy change for the combustion reaction is:  
**a**  $-1.54 \times 10^3 \text{ kJ/mol}$       **c**  $-2.01 \times 10^3 \text{ kJ/mol}$   
**b**  $+2.01 \times 10^3 \text{ kJ/mol}$       **d**  $+1.54 \times 10^3 \text{ kJ/mol}$

- 8** The substance that ethylene cannot easily be converted to is:
- a** ethylene glycol
  - c** propylene (propene)
  - b** ethanol
  - d** chloroethane
- 9** Some isotopes of lead and strontium are  $^{206}\text{Pb}$ ,  $^{212}\text{Pb}$ ,  $^{214}\text{Pb}$ ,  $^{88}\text{Sr}$ ,  $^{90}\text{Sr}$  and  $^{94}\text{Sr}$ . The *least* stable of these isotopes for each element are:
- a**  $^{214}\text{Pb}$  and  $^{94}\text{Sr}$
  - c**  $^{206}\text{Pb}$  and  $^{88}\text{Sr}$
  - b**  $^{214}\text{Pb}$  and  $^{90}\text{Sr}$
  - d**  $^{212}\text{Pb}$  and  $^{94}\text{Sr}$
- 10** Ethanol would be a good replacement for petrol as a liquid fuel for cars because:
- a** it is easily made from cellulose which is a major component of plant material
  - b** it can be used in current petrol engines after suitable modification to the engines
  - c** its formation by fermentation is a natural process which produces a concentrated solution from which pure ethanol is separated with little expenditure of energy
  - d** its large-scale production would cause far less environmental damage than does extraction and refining of crude oil

#### SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

The number of marks for each part of each question is shown at the right-hand end of the question. Marks allocated are based on the HSC scale of 1 mark per 1.8 minutes.

- |   | MARKS    |
|---|----------|
| <b>11</b> Demonstrate the difference between addition and condensation polymers.  | <b>4</b> |
| <b>12</b> <b>a</b> The mass of ethanol that had to be burnt in air to heat 575 g of water from $18.6^\circ\text{C}$ to $31.2^\circ\text{C}$ was 1.65 g. The specific heat capacity of water is $4.2 \text{ J K}^{-1} \text{ g}^{-1}$ . Calculate the molar heat of combustion of ethanol.   | <b>2</b> |
| <b>b</b> The value obtained in (a) is much lower than tabulated values. Suggest two possible reasons for this.  | <b>2</b> |
| <b>13</b> Describe an experiment you have performed to measure the voltage (EMF) of a cell made up of two metal, metal ion electrodes. On a diagram of your cell show the directions of electron and ion flows and label the anode and cathode. Suggest reasons why your measured voltage differed from that calculated from standard electrode potentials. | <b>6</b> |
| <b>14</b> <b>a</b> Industrial ethanol is generally made from ethylene. It is also possible to make ethylene from ethanol. Write equations for these two reactions and give the experimental conditions needed for each of them. Which catalyst, if any, is required for each reaction?  | <b>2</b> |
| <b>b</b> To which general classes of reaction do the reactions in (a) belong? For one of these classes give another example <i>not</i> involving any of the reactants or products of the reactions in (a).  | <b>2</b> |
| <b>15</b> Describe, with examples, how commercial radioisotopes are produced.   | <b>4</b> |
| <b>16</b> <b>a</b> Two current or future concerns about the synthetic polymers in widespread use today are <b>(i)</b> uncertainty about future sources of raw   |          |

materials and (ii) disposal problems. Explain what these problems are and how they arise. **2**

- b** Discuss one recent development in polymer science that has potential for alleviating both of these concerns. Refer to at least one specific substance and include details of how it can be made. **4**
- 17** Outline the structure and operating principle of one instrument used to measure radiation from radioactive sources. **3**
- 18** Describe an experiment you have performed to distinguish between alkanes and alkenes. Include at least one chemical equation. **3**
- 19** Compare and contrast the chemistry, uses and environmental impacts of either the common dry cell or the lead–acid cell with one other commercial galvanic cell you have studied. **6**

# MODULE 1 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 1 of the New South Wales Higher School Certificate HSC Course.

## Syllabus content

The following table lists (for Module 1) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

### Location of HSC Course material in *Conquering Chemistry* for Module 1

Syllabus reference	Sections where found in CCHSC
Students learn to	
<b>9.2.1 Fossil fuels provide both energy and raw materials such as ethylene, for the production of other substances</b>	
■ identify the industrial source of ethylene from the cracking of some of the fractions from the refining of petroleum	1.1
■ identify that ethylene, because of the high reactivity of its double bond, is readily transformed into many useful products	1.4, 1.5
■ identify that ethylene serves as a monomer from which polymers are made	1.6
■ identify polyethylene as an addition polymer and explain the meaning of this term	1.6
■ outline the steps in the production of polyethylene as an example of a commercially and industrially important polymer	1.6
■ identify the following as commercially significant monomers: – vinyl chloride – styrene by both their systematic and common names	1.8
■ describe the uses of the polymers made from the above monomers in terms of their properties	1.9, 1.10
<b>9.2.2 Some scientists research the extraction of materials and energy from biomass to reduce our dependence on fossil fuels</b>	
■ discuss the need for alternative sources of the compounds presently obtained from the petrochemical industry	1.11
■ explain what is meant by a condensation polymer	1.12
■ describe the reaction involved when a condensation polymer is formed	1.12
■ describe the structure of cellulose and identify it as an example of a condensation polymer found as a major component of biomass	1.12, 1.13
■ identify that cellulose contains the basic carbon-chain structures needed to build petrochemicals and discuss its potential as a raw material	1.13

Syllabus reference	Sections where found in CCHSC
Students learn to	
<b>9.2.3 Other resources, such as ethanol, are readily available from renewable resources such as plants</b>	
■ describe the dehydration of ethanol to ethylene and identify the need for a catalyst in this process and the catalyst used	1.16
■ describe the addition of water to ethylene resulting in the production of ethanol and identify the need for a catalyst in this process and the catalyst used	1.16
■ describe and account for the many uses of ethanol as a solvent for polar and non-polar substances	1.17
■ outline the use of ethanol as a fuel and explain why it can be called a renewable resource	1.19
■ describe conditions under which fermentation of sugars is promoted	1.18
■ summarise the chemistry of the fermentation process	1.18
■ define the molar heat of combustion of a compound and calculate the value for ethanol from first-hand data	1.20
■ assess the potential of ethanol as an alternative fuel and discuss the advantages and disadvantages of its use	1.19
■ identify the IUPAC nomenclature for straight-chained alkanols from C1 to C8	1.5
<b>9.2.4 Oxidation-reduction reactions are increasingly important as a source of energy</b>	
■ explain the displacement of metals from solution in terms of transfer of electrons	2.1
■ identify the relationship between displacement of metal ions in solution by other metals to the relative activity of metals	2.2
■ account for changes in the oxidation state of species in terms of their loss or gain of electrons	2.3
■ describe and explain galvanic cells in terms of oxidation-reduction reactions	2.4, 2.6
■ outline the construction of galvanic cells and trace the direction of electron flow	2.4, 2.6
■ define the terms anode, cathode, electrode and electrolyte to describe galvanic cells	2.5, 2.7
<b>9.2.5 Nuclear chemistry provides a range of materials</b>	
■ distinguish between stable and radioactive isotopes and describe the conditions under which a nucleus is unstable	3.1, 3.3
■ describe how transuranic elements are produced	3.7, 3.8
■ describe how commercial radioisotopes are produced	3.10
■ identify instruments and processes that can be used to detect radiation	3.11

Syllabus reference	Sections where found in CCHSC
Students learn to	
<ul style="list-style-type: none"> <li>■ identify one use of a named radioisotope:           <ul style="list-style-type: none"> <li>– in industry</li> <li>– in medicine</li> </ul> </li>   <li>■ describe the way in which the above named radioisotope is used and explain its use in terms of its chemical properties</li> </ul>	3.12  3.12

## Compulsory experiments

The table below lists the compulsory experiments (from the right-hand column of the syllabus), along with places where you can find procedures for these experiments (in *CCHSC BLM*) and the location of relevant information in *CCHSC*.

*CCHSC* is an abbreviation for this book *Conquering Chemistry HSC Course*.

*CCHSC BLM* is *Conquering Chemistry HSC Course Blackline Masters* by Debra Smith, Cengage Learning Australia.

### Information about compulsory experiments for Module 1

Experiment	Location in CCHSC BLM	Related material in CCHSC <sup>a</sup>
1 Plan and perform an experiment to compare the reactivities of alkenes and the corresponding alkanes with bromine water.	Module 1 Worksheet 2 (p. 6)	Section 1.4 Chapter 1 Exercise 14 Revision Test Question 18
2 Plan and perform an experiment to ferment glucose and monitor mass changes.	Module 1 Worksheet 7 (p. 21)	Section 1.18 Chapter 1 Exercise 36
3 Determine and compare the heats of combustion of three liquid alkanols.	Module 1 Worksheet 8 (p. 23)	Example 1 in Section 1.20 Chapter 1 Exercises 38, 39 Exam-style Question 14
4 Identify the simplest conditions under which a galvanic cell can be produced.	Module 1 Worksheet 9 (p. 25)	Sections 2.4 and 2.6 and Figure 2.11 may help.
5 Measure cell voltages (EMFs) for several galvanic cells made from metal, metal ion solution electrodes.	Module 1 Worksheet 11 (p. 31)	Revision Test Question 13
<sup>a</sup> Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.		

## Other items in the student activity (right-hand) column

The table below lists (in abbreviated form) the non-experimental items in the student activity (right-hand) column of the syllabus and indicates where in *Conquering Chemistry* relevant information is located.

## Location of material for other Module 1 activities

Syllabus item	Relevant material in CCHSC
<b>9.2.1</b>	<ul style="list-style-type: none"> <li>■ ... write equations to represent all chemical reactions encountered ...</li> <li>■ Experiment 1 (see above)</li> <li>■ analyse information ... to model the polymerisation process</li> </ul>
<b>9.2.2</b>	<ul style="list-style-type: none"> <li>■ use available evidence ... development and use of a named biopolymer ...</li> </ul>
<b>9.2.3</b>	<ul style="list-style-type: none"> <li>■ process information ... to model ... addition of water to ethylene ... dehydration of ethanol</li> <li>■ process information ... industrial production of ethanol from sugar cane</li> <li>■ process information ... use of ethanol as an alternative car fuel ... success of current usage</li> <li>■ Experiment 2 (see above)</li> <li>■ present information ... balanced equation for fermentation of glucose ...</li> <li>■ Experiment 3 (see above)</li> </ul>
<b>9.2.4</b>	<ul style="list-style-type: none"> <li>■ Experiment 4 (see above)</li> <li>■ Experiment 5 (see above)</li> <li>■ gather ... structure and chemistry of a dry cell or lead-acid cell and evaluate it ... in comparison to ... in terms of ...</li> <li>■ solve problems ... to calculate the potential <math>E^\ominus</math> requirement of named electrochemical processes ...</li> </ul>
<b>9.2.5</b>	<ul style="list-style-type: none"> <li>■ process information ... to describe recent discoveries of elements</li> <li>■ use available evidence ... benefits and problems ... use of radioactive isotopes</li> </ul>

## Prescribed focus areas

The five prescribed focus areas of the syllabus are:

- 1** the history of chemistry
- 2** the nature and practice of chemistry
- 3** applications and uses of chemistry
- 4** implications for society and the environment
- 5** current issues, research and development.

As with most modules, the material of Module 1 (in this book and in the syllabus) relates strongly to focus areas 2 and 3. However there are many opportunities in Module 1 for involving areas 4 and 5.

For area 4, implications for society and the environment, there are:

- plastics with issues of resource depletion and environmental contamination
- ethanol as a fuel and its economic and environmental consequences
- environmentally safe disposal of commercial galvanic cells
- the environmental problems associated with the manufacture, use and disposal of the radioisotopes widely being used in industry and medicine.

For area 5, current issues, research and development, there are:

- the development of new biodegradable biopolymers
- current controversies over the addition of ethanol to petrol
- production of newer types of galvanic cells such as lithium batteries, vanadium redox cells and the Gratzel cell, and
- controversies about the nuclear reactor being built in Sydney's far-south suburbs (needed to produce some of the radioisotopes required by industry and medicine).

There is little scope in this module for discussing area 1, history of chemistry.

# MODULE 2

## The acidic environment

Acids have been known to chemists for well over 200 years. They are widely involved in natural processes such as the functioning of our respiratory and digestive systems, and the control of acidity is an important factor in creating hospitable environments for a wide range of living organisms.

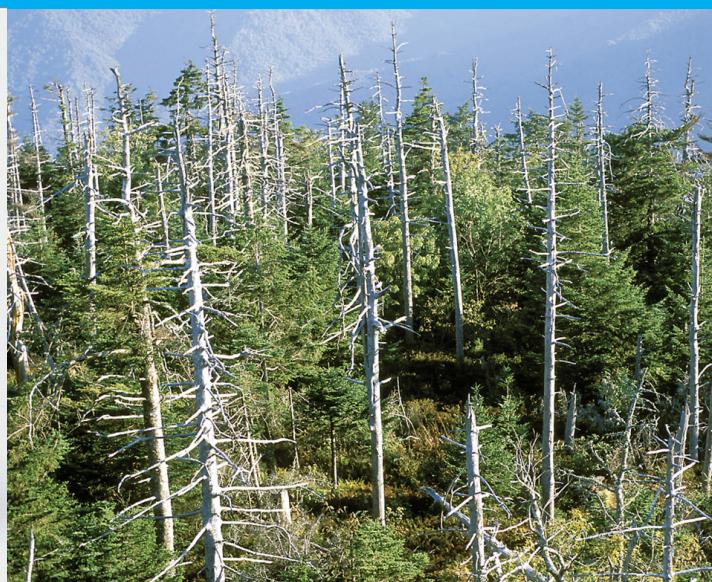
Acids and their partners in reactivity, bases, are widely used in industry. While we, as ordinary consumers, come into contact with some acids and bases—such as the products shown below—much larger quantities of acids and bases are used industrially to extract common metals and to manufacture other products that we are more familiar with, such as fertilisers, detergents, explosives, paints, plastics, synthetic fibres, glass, dyes, insecticides and pharmaceuticals. Apart from sulfuric acid in car batteries and sodium hydroxide in oven and drain cleaners, consumers have little contact with the major acids and bases of industry despite the fact that sulfuric and nitric acids, sodium hydroxide and calcium oxide rank in the top dozen manufactured chemicals in terms of quantities produced worldwide per year.

Because acids are involved in our natural environment and in the making of many of the products we use in our everyday lives, and because there is growing concern about the way that acidic and basic discharges are affecting the environment, we shall undertake a study of them in this module. This will help us handle these substances safely.



Chapter 4 will begin with a general introduction to acids, bases, neutralisation and salts then turn to acidic and basic oxides. This leads into a discussion of the equilibrium between carbon dioxide and its aqueous solution and to the introduction of an important chemical concept, Le Chatelier's principle. We then look at acidic oxides in the atmosphere—how they get there, their detrimental effects and how they are removed: this leads into a discussion of acid rain. Attention then turns to some common acids in everyday life, to the concept of pH, and to explanations of the terms weak and strong, concentrated and dilute. Calculations involving volumes of gases are also treated here.

In Chapter 5 we will look at the way that the concepts of acids and bases have developed over time, paying particular attention to the Brönsted–Lowry concept and its applications. This leads to an account of the use of acid–base reactions in volumetric analysis, and to a discussion of what are called buffers and how they control acidity, particularly in natural systems. The chapter will end with a discussion of alkanols and a particular type of acid called alkanoic acids and of the compounds (called esters) that form by reaction between alkanols and alkanoic acids.



## ACIDS AND BASES AND THEIR EFFECTS ARE ALL AROUND US

Many everyday products such as the ones in these photographs are, or contain, acids and bases. We often determine acidity or basicity by using indicator solutions or papers. One detrimental effect of our discharge of acidic oxides such as nitrogen dioxide and sulfur dioxide into the atmosphere is acid rain which has caused damage to pine forests in parts of Europe and North America.



# Acids and bases in everyday life

## IN THIS CHAPTER

Simple definitions of acids and bases

Indicators for determining acidity and basicity of solutions

Acid-base reactions

Common acids and names for salts

Acidic and basic oxides

The carbon dioxide–water equilibrium

Le Chatelier's principle

Le Chatelier's principle and the  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$  equilibrium

Acidic oxides in the atmosphere

Properties of oxides of sulfur and nitrogen

The 'fate' of oxides of sulfur and nitrogen in the atmosphere

Acid rain

Calculations involving volumes of gases

Some common acids and bases

Meaning of pH

Self-ionisation of water

pH of alkaline solutions

Neutral, acidic and alkaline solutions

Measuring pH of solutions

Weak and strong acids

Many of the substances we deal with in our everyday lives are classed as acids or bases. Common substances that contain acids were shown on page 104: vinegar (contains acetic acid), lemon juice (contains citric acid), aspirin (acetyl salicylic acid) and vitamin C (ascorbic acid). In addition car batteries and rust converters contain sulfuric and phosphoric acids respectively.

Some household substances that contain bases were shown on page 105: cloudy ammonia, for cleaning, washing soda (sodium carbonate), antacid tablets (contain calcium carbonate and/or magnesium hydroxide) and oven and drain cleaners (contain sodium hydroxide). Others are lime for making mortar (calcium hydroxide) and garden lime (calcium carbonate).

This chapter will survey some of the ways that acids and bases impact upon our lives.

## 4.1 SIMPLE DEFINITIONS OF ACID AND BASE

In Chapter 5 we shall look at the way that the concepts of acids and bases have developed over the centuries. For present purposes we will use the following definitions.

An **acid** is a substance which in solution produces hydrogen ions,  $\text{H}^+$  or more strictly  $\text{H}_3\text{O}^+$ , sometimes called **hydronium ions**.

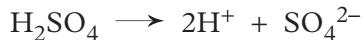
A **base** is a substance which either contains the oxide  $O^{2-}$  or hydroxide ion  $OH^-$  or which in solution produces the hydroxide ion.

A soluble base is called an **alkali**.

Compounds that contain the oxide ion are either insoluble in water ( $CuO$ ,  $MgO$ ,  $Fe_2O_3$ ) or they react with water to form hydroxide ions ( $Na_2O$ ,  $CaO$ ). Therefore alkalis are compounds which contain, or in aqueous solution produce, hydroxide ions.

Common acids are hydrochloric acid,  $HCl$ , sulfuric acid,  $H_2SO_4$ , and nitric acid,  $HNO_3$ .

In solution, for example:



Other acids are shown in Table 4.2 (on page 114).

Common bases are sodium hydroxide,  $NaOH$ ; barium hydroxide,  $Ba(OH)_2$ ; potassium oxide,  $K_2O$ ; magnesium oxide,  $MgO$ ; iron(III) oxide,  $Fe_2O_3$ ; copper hydroxide,  $Cu(OH)_2$ ; ammonia,  $NH_3$ . Of these seven substances only the first three and ammonia are alkalis (soluble in water).

### Common properties of all acids

- 1 Acids have a *sour taste* (but you must *never* taste chemicals in the laboratory).
- 2 Acids *sting* or *burn* the skin.
- 3 In solution, acids *conduct electricity*.
- 4 Acids *turn blue litmus* (a vegetable dye) *red*. (Blue in Acid goes Red—BAR.)

These common properties arise because all acids produce hydrogen ions.

### Common properties of alkalis

- 1 Alkalies have a *soapy feel*.
- 2 Alkalies have a *bitter taste* (though as with acids you should *never* taste them).
- 3 In solution, alkalies are *good conductors of electricity*.
- 4 Alkalies turn *red litmus blue*.

It was their effects upon vegetable dyes such as litmus that were first used to classify substances as acids or bases.

## 4.2 INDICATORS

*Litmus* is a dye that is extracted from lichens which are mixed algae-fungi organisms that grow on rocks and trees. In the eighteenth century it was discovered that certain substances could change the colour of litmus solution. Hence this colour change was used to classify substances as acids or bases. In addition if a substance did not change the colour of litmus (it left blue litmus blue, and red litmus red) it was classed as neutral: that is, it was neither an acid nor a base. The terms, **acidic**, **basic** (or **alkaline**)<sup>†</sup> and **neutral** are used to describe solutions that contain acid, base or neither respectively. We call litmus an indicator.

<sup>†</sup> Note that while the terms *base* and *alkali* have different meanings (alkalis are a sub-group of bases), the terms *basic* and *alkaline* when used to describe solutions have exactly the same meaning.

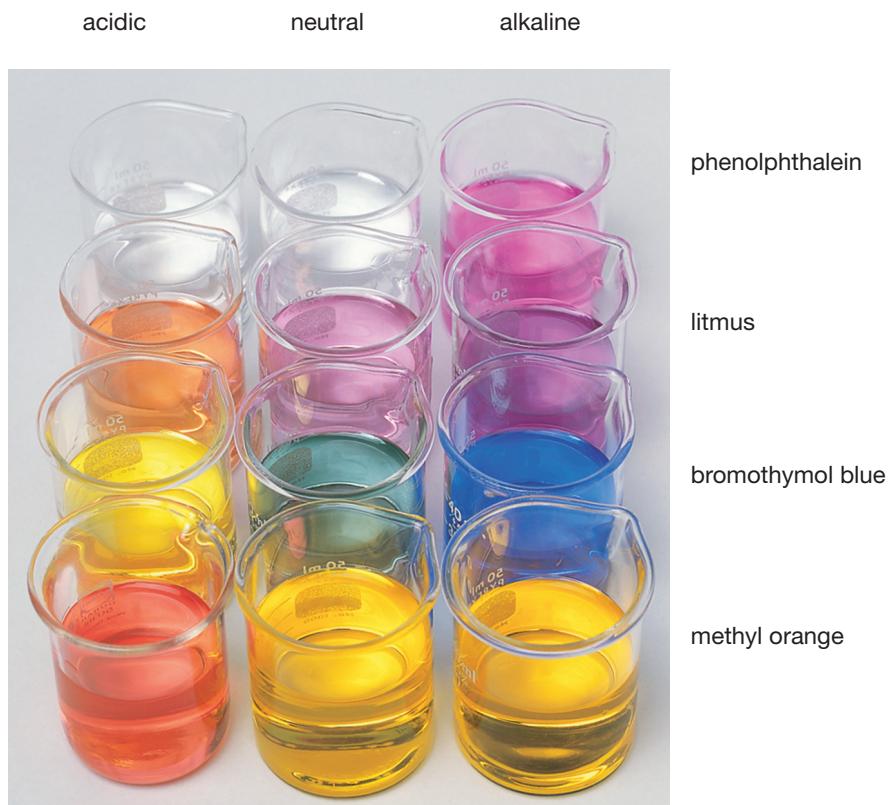
An **indicator** is a substance (usually a vegetable dye) that in solution changes colour depending on whether the solution is acidic or alkaline.

Many other vegetable dyes have this same property of changing colour when added to acidic or alkaline solutions. For example if red cabbage leaves are crushed up and extracted with methanol, the red solution obtained is an indicator. In acid solution it is red: as the hydrogen ion concentration is decreased, the colour changes to purple and then to green: if placed in a hydroxide ion solution this dye goes yellow.

The actual range of acidity or alkalinity over which indicators change colour varies from one indicator to another. Some indicators such as litmus and bromothymol blue have one colour in acid solution and a different one in alkaline solution. Others change colour as the solution changes from highly acidic to slightly acidic or from highly alkaline to slightly alkaline. Some common indicators and their colour changes are shown in Table 4.1 and illustrated in Figure 4.1.

**TABLE 4.1 Common indicators and their acidity/alkalinity ranges**

Indicator	Colour change				
	Highly acidic	Slightly acidic	Neutral	Slightly alkaline	Highly alkaline
methyl orange	red → yellow		yellow	yellow	yellow
bromothymol blue	yellow	yellow → blue		blue	blue
litmus	red → blue	red		blue	blue
phenolphthalein	colourless	colourless	colourless	colourless → red	



**FIGURE 4.1**  
Common indicators in acidic, neutral and alkaline solutions



## Example 1

Five solutions, A, B, C, D and E, were tested with indicators: the results are tabulated below. Using Table 4.1 deduce whether the solutions are acidic, neutral or alkaline, and if not neutral, decide whether they are highly or slightly acidic or alkaline. For Solution E describe any further test you would need to perform to answer these questions completely.

	A	B	C	D	E
litmus		purple <sup>a</sup>	red		
bromothymol blue		yellow		blue	
methyl orange	red		yellow	yellow	
phenolphthalein				red	colourless

a Purple is an equal mixture of blue and red.

**Solution A:** The yellow colour of bromothymol blue tells us that this solution is acidic; the red colour with methyl orange tells us that it is *highly acidic*.

**Solution B:** The litmus colour is halfway between red and blue: this means that the solution is *neutral*. The methyl orange colour shows that this solution is not highly acidic which is consistent with the litmus result.

**Solution C:** The red litmus colour shows that this solution is acidic; the yellow colour with methyl orange shows that it is only *slightly acidic*.

**Solution D:** The blue colour with bromothymol blue shows that this solution is alkaline; the red phenolphthalein colour tells us that it is *highly alkaline*.

**Solution E:** All the phenolphthalein test tells us is that this solution is not highly alkaline. If we tested this solution with litmus, a blue colour would tell us that it is alkaline (and therefore slightly alkaline since it cannot be highly alkaline), a purple colour (mixed blue and red) would mean that it was neutral, and a red colour would show that it was acidic. In this last case we would then need to use methyl orange to decide whether it was highly or slightly acidic.

We can use litmus or bromothymol blue to decide whether a solution is acidic, neutral or basic (alkaline) and then we can use methyl orange or phenolphthalein to decide whether the solution is highly or slightly acidic or alkaline respectively.

## Practical uses of indicators

Indicators provide a cheap and convenient way of determining the acidity or alkalinity of substances. Some everyday uses of indicators are:

- testing the acidity or alkalinity of soils (because some plants need an acidic soil—azaleas and camellias—while others need an alkaline or near neutral soil—most annual flowers and vegetables)
- testing home swimming pools (these need to be approximately neutral, though adding chemicals to sanitise the water can change its acid–alkali balance)
- monitoring wastes from laboratories that process photographic film (discharges to the sewerage system must be nearly neutral: photographic solutions are often highly alkaline).



A simple kit that is commercially available for measuring soil pH (using a universal indicator)

## Exercises

- 1** Use Table 4.1 and the results in the table below to decide whether the solutions listed are acidic, neutral or alkaline (basic). If for any solution the result is inconclusive, describe what additional test you would perform and explain how this would clarify the uncertainty.



Solution	Z	Y	X	W	U	M	N
Indicator <sup>a</sup>	btb	litmus	meth	btb	phth	litmus	meth
Colour	yellow	blue	red	green <sup>b</sup>	red	purple <sup>c</sup>	yellow

a btb = bromothymol blue, meth = methyl orange, phth = phenolphthalein

b Green is an equal mixture of yellow and blue.

c Purple is an equal mixture of blue and red.

- 2** The table below shows the results of some indicator tests on six different solutions. Decide whether the solutions are neutral or highly or slightly acidic or alkaline. If the results for any particular solution are not conclusive, describe any additional test(s) that you would perform and explain how it or they would resolve the situation.

	P	Q	R	S	T	V
litmus			blue			
bromothymol blue			yellow		green <sup>a</sup>	
methyl orange	red		yellow	yellow		yellow
phenolphthalein				red	colourless	colourless

a Green is an equal mixture of yellow and blue.

- 3** Which solute ions would be present in aqueous solutions of each of

- a** the following acids:
  - i** hydrobromic acid
  - ii** nitric acid
- b** the following alkalis:
  - i** barium hydroxide
  - ii** sodium oxide

## 4.3 ACID-BASE REACTIONS

Acids react with bases in what are called *neutralisation* reactions to form compounds called *salts*.

Typical acid-base reactions are:

- the reaction of the base (alkali) sodium hydroxide with hydrochloric acid to form the salt sodium chloride and water:



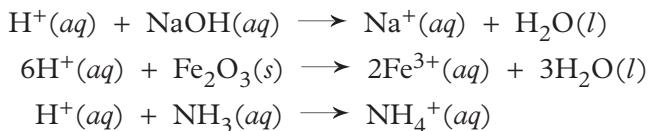
- the reaction of nitric acid with the base iron(III) oxide to form the salt iron(III) nitrate and water:



- the reaction of sulfuric acid with the alkali ammonia to form ammonium sulfate:

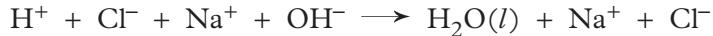


The aqueous acid solutions in the above three equations all contain  $\text{H}^+$  ions (along with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions respectively). The bases actually react with these  $\text{H}^+$  ions. The anions are still present in solution, unaltered, at the end of the reaction. Hence we often write these equations as:



Because the anions,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , are not actually involved in the reactions, we call them *spectator ions* as we did in similar situations on p. 117 CCPC.

Equation 4.2 can be written in a complete ionic form (as on pp. 116–17 CCPC):



This shows that  $\text{Na}^+$  as well as  $\text{Cl}^-$  is a spectator ion. The net ionic equation is therefore just

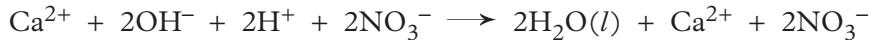


This is the net ionic equation for many acid–alkali reactions: for example for the reaction between calcium hydroxide solution and nitric acid:

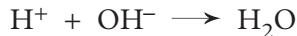
*Neutral species equation:*



*Complete ionic equation:*



*Net ionic equation:*



To define terms:

**Neutralisation** is the reaction of an acid with a base.

A **salt** is an ionic compound formed when a base (alkali) reacts with an acid.

Or a salt is a compound formed when the hydrogen of an acid is replaced by a metal ion. In general:



Neutralisation reactions generally produce water as well as salts, but there are exceptions: see Reaction 4.3 above.

The salts sodium chloride, iron(III) nitrate, ammonium sulfate and calcium nitrate were formed in the reactions above. Other common salts are:

potassium nitrate	$\text{KNO}_3$	$(\text{K}^+ \text{NO}_3^-)$
copper sulfate	$\text{CuSO}_4$	$(\text{Cu}^{2+} \text{SO}_4^{2-})$
zinc chloride	$\text{ZnCl}_2$	$(\text{Zn}^{2+} 2\text{Cl}^-)$
aluminium nitrate	$\text{Al}(\text{NO}_3)_3$	$(\text{Al}^{3+} 3\text{NO}_3^-)$
ammonium phosphate	$(\text{NH}_4)_3\text{PO}_4$	$(3\text{NH}_4^+ \text{PO}_4^{3-})$

## 4.4 COMMON ACIDS AND NAMES FOR SALTS

Salts are named in a similar way to that used for binary ionic compounds on pp. 77–8 CCPC: several salts were named on p. 79 CCPC.

The metal ion (or cation) is named first with the name for the anion being derived from the name of the acid.

The hydrohalic acids—hydrochloric acid ( $\text{HCl}$ ), hydrobromic acid ( $\text{HBr}$ ), hydroiodic acid ( $\text{HI}$ )—lead to salts called **halides**—chlorides, bromides and iodides. Hence we have the salts magnesium chloride,  $\text{MgCl}_2$ ; potassium bromide,  $\text{KBr}$ ; silver iodide,  $\text{AgI}$ . These names follow from the way we named binary compounds on pp. 77–8 CCPC.

Most of our common acids are what are called **oxyacids**: they have oxygen attached to an element such as sulfur, nitrogen, phosphorus, chlorine or carbon. When the name of the oxyacid ends in ‘-ic’, the salt takes a similar name but with the ending ‘-ate’. Sulfuric acid forms sulfates; nitric acid forms nitrates; phosphoric acid, phosphates; carbonic acid, carbonates. Hence we have the salts aluminium sulfate,  $\text{Al}_2(\text{SO}_4)_3$ ; lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ ; sodium phosphate,  $\text{Na}_3\text{PO}_4$ ; and calcium carbonate,  $\text{CaCO}_3$ .

Two other common acids are nitrous acid,  $\text{HNO}_2$ , and sulfurous acid,  $\text{H}_2\text{SO}_3$ . When the name of the acid ends in ‘-ous’, the name of the salt ends in ‘-ite’: nitrous acid forms nitrites such as sodium nitrite,  $\text{NaNO}_2$ ; sulfurous acid forms sulfites such as potassium sulfite,  $\text{K}_2\text{SO}_3$ .

Anions formed from oxyacids are called **oxyanions**. Nitrate,  $\text{NO}_3^-$ , sulfate,  $\text{SO}_4^{2-}$ , carbonate,  $\text{CO}_3^{2-}$ , nitrite,  $\text{NO}_2^-$ , are all oxyanions.

Names of common acids and of the salts they form are given in Table 4.2. It is essential that you know the names of the acids and anions in this table and are able to write formulae for salts formed from them.

The formulae of the acids should be memorised; the negative charge on the anion formed (that is, the valence of the anion) can be worked out from the number of  $\text{H}^+$  ions lost. Knowing this and knowing the positive charge (valence) of the metal ion involved, we can deduce the formula of any salt. This is because, as on pp. 76–7 CCPC, the ions are present in ratios such that the total number of positive charges equals the total number of negative charges.

To deduce the formula of potassium sulfate, we start with the knowledge that potassium forms a singly charged ion,  $K^+$ , and that sulfuric acid is  $H_2SO_4$ , so sulfate is  $SO_4^{2-}$ . Hence potassium sulfate is  $K_2SO_4$ , because  $2 \times (1+)$  in magnitude equals  $1 \times (2-)$ . Similarly for aluminium nitrate: knowing that aluminium forms the  $Al^{3+}$  ion and that nitric acid is  $HNO_3$ , we deduce that the nitrate ion is singly charged,  $NO_3^-$ , and so aluminium nitrate is  $Al(NO_3)_3$ , because  $1 \times (3+)$  in magnitude equals  $3 \times (1-)$ .

**TABLE 4.2 Common acids and the anions they form**

Acid		Anion		Typical salt
hydrofluoric	HF	$F^-$	fluoride	$CaF_2$
hydrochloric	HCl	$Cl^-$	chloride	$NaCl$
hydrobromic	HBr	$Br^-$	bromide	$KBr$
hydroiodic	HI	$I^-$	iodide	$Agl$
sulfuric	$H_2SO_4$	$SO_4^{2-}$	sulfate	$K_2SO_4$
sulfurous	$H_2SO_3$	$SO_3^{2-}$	sulfite	$Na_2SO_3$
nitric	$HNO_3$	$NO_3^-$	nitrate	$Pb(NO_3)_2$
nitrous	$HNO_2$	$NO_2^-$	nitrite	$NaNO_2$
carbonic	$H_2CO_3$	$CO_3^{2-}$	carbonate	$CaCO_3$
phosphoric	$H_3PO_4$	$PO_4^{3-}$	phosphate	$Na_3PO_4$
formic (methanoic)	HCOOH	$HCOO^-$	formate (methanoate)	$Mg(HCOO)_2$
acetic (ethanoic)	$CH_3COOH$	$CH_3COO^-$	acetate (ethanoate)	$Ag(CH_3COO)$
hydrocyanic	HCN	$CN^-$	cyanide	$KCN$
hydrogen sulfide	$H_2S$	$S^{2-}$	sulfide	$ZnS$

As pointed out on p. 76 CCPC we need to memorise the charges of the common metal ions in Table 3.2 on p. 77 CCPC. There is no need to memorise formulae of individual salts—there are far too many of them for that—but we must be able to work out formulae for salts very quickly.

## Exercises

- 4 Write equations for the reactions of each of:
- a** nitric acid      **b** sulfuric acid      **\*c** hydroiodic acid  
 with each of: **(i)** sodium hydroxide **(ii)** zinc oxide **(iii)** ammonia.
- 5 Write equations for the reaction of any acid (that is, of  $H^+$ ) with:
- a** potassium oxide      **c** sodium hydroxide      **\*e** iron(III) hydroxide  
**b** aluminium oxide      **d** magnesium hydroxide      **f** ammonia
- 6 Write equations for the reaction of the hydroxide ion with:
- a** nitric acid      **b** carbonic acid      **c** phosphoric acid

Name the anion formed in each case.

7 Give the formulae of:

- |                     |                      |                        |
|---------------------|----------------------|------------------------|
| a potassium iodide  | e aluminium chloride | *i ammonium carbonate  |
| b barium sulfate    | f zinc nitrate       | *j potassium phosphate |
| c sodium acetate    | *g barium bromide    | *k ammonium nitrite    |
| d potassium sulfite | *h sodium sulfide    | *l aluminium sulfate   |

8 a Name the salts in the right-hand column of Table 4.2.

b Give the names of:

- |  |                                   |  |
|--|-----------------------------------|--|
| i AgBr   | iv MgF <sub>2</sub>               | *vii Al(NO <sub>3</sub> ) <sub>3</sub>   |
| ii (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> | v KNO <sub>2</sub>                | *viii FeCl <sub>2</sub>                  |
| iii Na <sub>2</sub> SO <sub>3</sub>                | vi K <sub>3</sub> PO <sub>4</sub> | *ix Ca(CH <sub>3</sub> COO) <sub>2</sub> |

9 a Describe one method of preparing each of the salts in Exercise 7 (e) and (f) and in Exercise 8 (b) (iv) and (ix).

b For each of the reactions you used to prepare the salts in Exercises 7 (e) and 8 (b) (iv) write neutral species, complete ionic and net ionic equations.

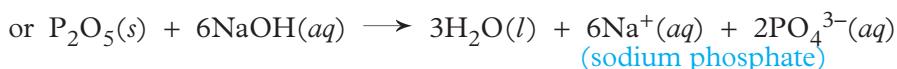
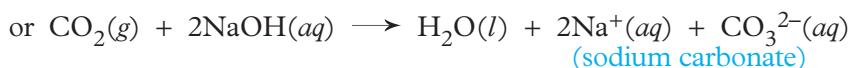
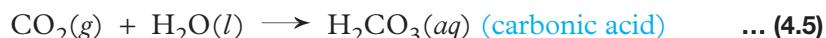
## 4.5 ACIDIC AND BASIC OXIDES

Oxides are a class of compound that often displays acidic or basic properties.

An **acidic oxide** is one which either:

- reacts with water to form an acid or
- reacts with bases to form salts (or does both).

Common acidic oxides are carbon dioxide, CO<sub>2</sub>, and diphosphorous pentoxide, P<sub>2</sub>O<sub>5</sub>, because



A **basic oxide** is one that:

- reacts with acids to form salts but
- does not react with alkali solutions (such as NaOH or KOH).

Common basic oxides are copper oxide, CuO, and iron(III) oxide, Fe<sub>2</sub>O<sub>3</sub>, because:



There are some oxides, such as ZnO, PbO and Al<sub>2</sub>O<sub>3</sub>, that react with acids to form salts, but which also react with alkalis. These are called **amphoteric oxides**.

There is another group of oxides that do not react with either acids or bases. These are called **neutral oxides**. Common neutral oxides are carbon monoxide, CO, nitrous oxide, N<sub>2</sub>O, and nitric oxide, NO.

Examples of the four types of oxide are listed in Table 4.3.

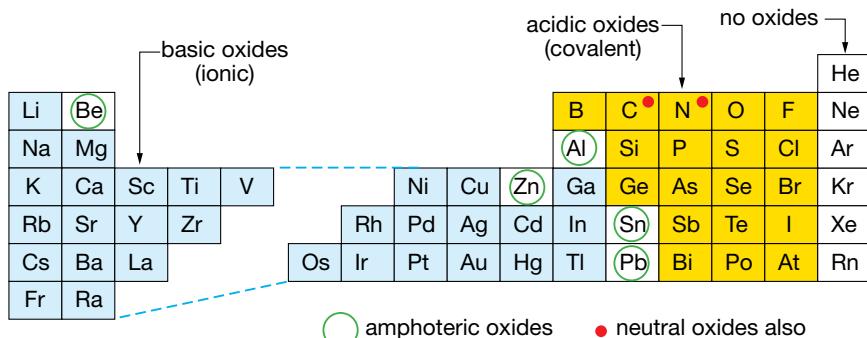
**TABLE 4.3 Common acidic, basic, amphoteric and neutral oxides**

Acidic oxides	Basic oxides	Amphoteric oxides	Neutral oxides
$\text{CO}_2$	$\text{Na}_2\text{O}$	$\text{ZnO}$	$\text{CO}$
$\text{NO}_2$	$\text{K}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{NO}$
$\text{P}_2\text{O}_3$	$\text{MgO}$	$\text{PbO}$	$\text{N}_2\text{O}$
$\text{P}_2\text{O}_5$	$\text{CaO}$	$\text{SnO}$	
$\text{SO}_2$	$\text{CuO}$		
$\text{SO}_3$	$\text{Fe}_2\text{O}_3$		
$\text{Cl}_2\text{O}$	$\text{Ag}_2\text{O}$		

Acidic oxides are generally oxides of non-metals. They are all covalent compounds. Elements that have acidic oxides occur towards the right and top of the Periodic Table as shown in Figure 4.2.

Basic oxides are oxides of metals. They are ionic compounds. Elements that form basic oxides occur towards the left of the Periodic Table (Figure 4.2).

**FIGURE 4.2**  
Location of different types of oxides in the Periodic Table



## Exercises

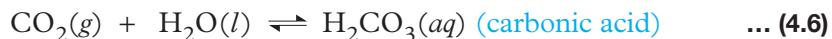
- 10 a** The following oxides are all acidic:  $\text{B}_2\text{O}_3$ ,  $\text{N}_2\text{O}_3$ ,  $\text{P}_2\text{O}_3$ ,  $\text{SO}_3$ ,  $\text{Cl}_2\text{O}$ . In water they form (respectively) boric acid,  $\text{H}_3\text{BO}_3$ , nitrous acid,  $\text{HNO}_2$ , phosphorous acid,  $\text{H}_3\text{PO}_3$ , sulfuric acid,  $\text{H}_2\text{SO}_4$ , and hypochlorous acid,  $\text{HOCl}$ . Write equations for these reactions.
- b** Write equations for the reaction of sodium hydroxide with carbon dioxide, sulfur trioxide and \*dichlorine monoxide.
- 11** Acidic oxides react with basic oxides to form salts. Write equations for the reaction of:
- a** carbon dioxide with calcium oxide
  - b** sulfur dioxide with sodium oxide
  - \*c** sulfur trioxide with copper oxide.

## 4.6 THE CARBON DIOXIDE-WATER EQUILIBRIUM

The reaction between carbon dioxide and water, Equation 4.5, is of great practical significance. It is involved in the removal of carbon dioxide from our

bodies, the transport of carbon dioxide in photosynthesis, the removal of carbon dioxide from the atmosphere and in the preparation of aerated drinks.

This reaction between carbon dioxide and water does not go to completion. Rather it is an equilibrium reaction: Equation 4.5 is more correctly written as:



The concept of chemical equilibrium was introduced on pp. 208–10 CCPC.

Another way of looking at this reaction is to regard it as the solubility of carbon dioxide in water. We find that this solubility increases as the pressure of carbon dioxide above the solution increases. If we maintain standard atmospheric pressure<sup>†</sup> of carbon dioxide above a solution of  $\text{CO}_2$  in water at  $25^\circ\text{C}$ , the concentration of carbon dioxide (or of carbonic acid) in the solution is 0.033 mol/L. If we increase the pressure by a factor of three, the solubility increases to about 0.10 mol/L. If the pressure of  $\text{CO}_2$  above the solution falls to the normal  $\text{CO}_2$  pressure in the atmosphere ( $35 \text{ Pa}^{\dagger}$ ), the solubility falls to  $1.2 \times 10^{-5} \text{ mol/L}$ .

The solubility of carbon dioxide decreases as the temperature increases. This is shown in Figure 4.3. With solids and liquids solubility generally increases as temperature increases, but with gases solubility *decreases* as temperature increases.

These effects of changing pressure and temperature can be regarded as moving the position of equilibrium for Reaction 4.6. **Position of equilibrium**, or **equilibrium position**, means the extent to which the reaction has gone in the forward or reverse direction. If we say that the position of equilibrium lies well to the right, we mean that at equilibrium most of the reactant has been converted to product. If it lies well to the left, then at equilibrium most of the reactant is still present with only a small proportion of it having been converted to product.

There is a general principle that can be used to predict the effect on the position of equilibrium of changing the conditions.

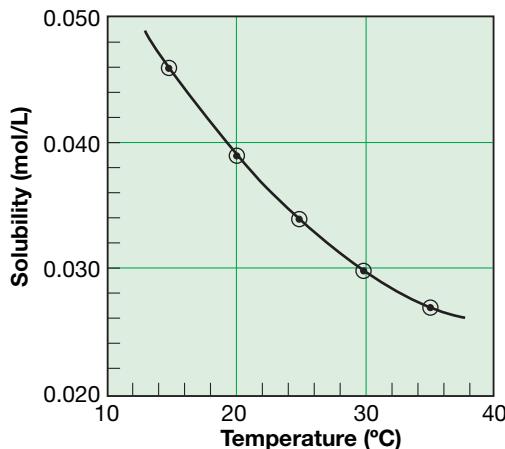


FIGURE 4.3  
Solubility of carbon dioxide in water as a function of temperature (with 100 kPa pressure of  $\text{CO}_2$  above the solution)

## 4.7 LE CHATELIER'S PRINCIPLE

In 1885, Le Chatelier formulated a simple generalisation for predicting how an equilibrium will respond to a disturbance; it is known as **Le Chatelier's principle**.

If a system at equilibrium is disturbed, then the system adjusts itself so as to minimise the disturbance.

<sup>†</sup> standard atmospheric pressure = 101.3 kPa; kPa is kilopascal; Pa, pascal, is the systematic unit of pressure

In this context, an equilibrium is ‘disturbed’:

- if the *concentration* (or *pressure*) of one or more of the species involved is changed
- if the *total pressure* acting upon a reaction that involves gases is changed, or
- if the *temperature* is altered.

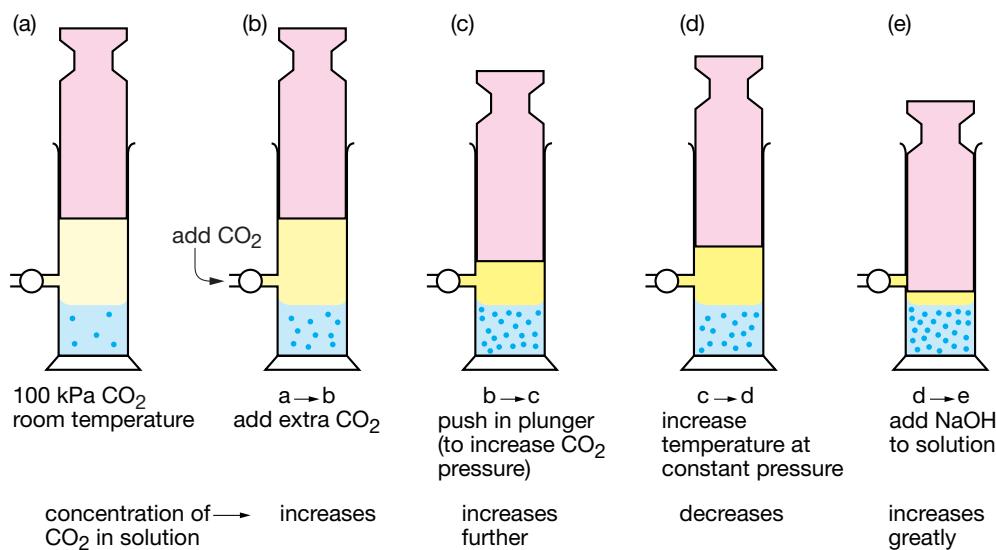
## 4.8 LE CHATELIER’S PRINCIPLE AND THE $\text{CO}_2$ , $\text{H}_2\text{CO}_3$ EQUILIBRIUM

We can illustrate the three ways of disturbing an equilibrium with our  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$  reaction:

- 1 If the pressure of  $\text{CO}_2$  is increased (for example, by pumping more  $\text{CO}_2$  into the reaction vessel, (b) in Fig. 4.4), then some  $\text{CO}_2$  goes into solution as  $\text{H}_2\text{CO}_3$  to try to counteract the increase; we say that the equilibrium, Equation 4.6, *moves to the right*. If the pressure of  $\text{CO}_2$  is decreased (for example by sucking some of it out of the reaction vessel), then some  $\text{H}_2\text{CO}_3$  decomposes to  $\text{CO}_2$  and comes out of solution to try to counteract the decrease. We say that the equilibrium moves to the left.
- 2 If the total pressure on the reaction system is increased (for example by pushing in a plunger as in Fig. 4.4(c)), the equilibrium moves in the direction that tends to reduce pressure. That is, some  $\text{CO}_2$  dissolves: the equilibrium moves to the right.
- 3 Reaction 4.6 is exothermic. This means that as it proceeds from left to right, heat is liberated, and conversely as it goes from right to left, heat is absorbed. If we increase the temperature of a  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$  equilibrium mixture at constant pressure, the equilibrium moves to the left, because that is the direction that absorbs heat and so tends to counteract the temperature increase. In Figure 4.4(d), in order to maintain a constant pressure we would need to draw the piston back as  $\text{CO}_2$  came out of solution.

FIGURE 4.4

How the  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$  equilibrium changes as conditions are changed



A word of caution is needed about the effect of increasing the total pressure. If we had increased the total pressure by pumping some nitrogen or argon into the vessel (instead of decreasing the volume as in Figure 4.4(c)), this would have had no affect upon the equilibrium because it would not have changed the pressure of CO<sub>2</sub>.

Another way of increasing the solubility of carbon dioxide in water is to make the solution alkaline. If there is OH<sup>-</sup> in the solution, then carbonic acid reacts with it:



This effectively removes the product from Reaction 4.6. The equilibrium then moves to try to counteract this, so more CO<sub>2</sub> dissolves to form more H<sub>2</sub>CO<sub>3</sub> which in turn reacts with OH<sup>-</sup> and so on (Fig. 4.4(e)). This illustrates an effective method of forcing an equilibrium reaction to completion—remove the product as it forms.

## The CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub> equilibrium and aerated drinks

Aerated ('fizzy') drinks contain carbon dioxide. To make such drinks the solution is exposed to a high pressure of carbon dioxide. This causes a significant concentration of CO<sub>2</sub> to dissolve; the bottle or can is then sealed. The gas space above the solution (drink) still contains a high pressure of carbon dioxide. When the bottle or can is opened, the high pressure of CO<sub>2</sub> escapes. The reactant concentration (pressure) of Equation 4.6 has been greatly lowered and so the equilibrium moves to the left: CO<sub>2</sub> comes out of solution, forming the bubbles we see in the drink. If we leave the drink in a glass exposed to the atmosphere, then the pressure of CO<sub>2</sub> above the solution soon falls to normal carbon dioxide-in-air pressure (35 Pa) and the CO<sub>2</sub> concentration in the solution falls to about 1.2 × 10<sup>-5</sup> mol/L. The drink has 'gone flat'.

If we open a warm container of fizzy drink, it produces bubbles more rapidly. This is partly because the equilibrium concentration of dissolved CO<sub>2</sub> at the higher temperature is lower and so more carbon dioxide has to escape, and partly because chemical reactions usually go faster at higher temperatures (p. 291 *CCPC*).

Shaking the bottle of drink when the cap is removed speeds up the release of carbon dioxide and so the drink froths up and shoots everywhere; equilibrium is reached more rapidly.

It is dangerous to put bottles of aerated drinks in a freezer, because as the temperature falls, pure ice freezes out of the drink. This means that all the CO<sub>2</sub> originally dissolved in the drink is forced as gas into the small gas space. This builds up an excessive pressure and the bottle may explode. In other words carbon dioxide has a very low solubility in solid ice.

Removing the cap from a bottle of lemonade causes CO<sub>2</sub> bubbles to be released





## Exercises

**12** The table below gives the solubility of carbon dioxide as a function of the pressure of carbon dioxide above the solution at 25°C.

- a Show graphically that solubility is proportional to the partial pressure of the gas above the solution. Hence calculate the constant  $k$  in the equation:

$$\text{Solubility} = k \times (\text{pressure of CO}_2)$$

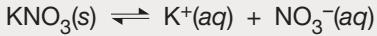
Pressure of CO <sub>2</sub> (kPa)	10	30	50	80	130
Solubility (mol/L)	0.0031	0.0097	0.165	0.0260	0.042

- b From your graph calculate (i) the solubility when the pressure of CO<sub>2</sub> is 65 kPa, and (ii) the pressure of CO<sub>2</sub> needed to produce a solubility of 0.030 mol/L.  
c Use either your graph or the equation in (a) to calculate (i) the solubility at a CO<sub>2</sub> pressure of 250 kPa, and (ii) the pressure of CO<sub>2</sub> needed to produce a solubility of 0.055 mol/L.

**13** A bottle of soft drink is opened and half of the contents consumed, then the cap is screwed back on the bottle. Some time later the bottle is opened and the rest of the drink consumed. This portion of the drink tastes significantly ‘flatter’ than the original; that is, there is less ‘fizz’ in the drink. Explain why this is so.

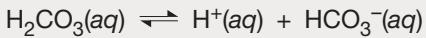
**14 a** The process liquid  $\rightleftharpoons$  vapour is reversible and is endothermic. Use Le Chatelier’s principle to decide whether vapour pressure increases or decreases as temperature increases. Explain your reasoning.

- \*b Dissolution of potassium nitrate in water is a reversible process:



The solubility of KNO<sub>3</sub> increases as temperature increases. Use Le Chatelier’s principle to decide whether the process is exothermic or endothermic. Explain your reasoning.

**15 a** In home swimming pools one equilibrium reaction that occurs is:



Use Le Chatelier’s principle to determine the effect on hydrogen ion concentration of adding sodium hydrogen carbonate to the pool water.

b When home swimming pools are sterilised by adding so-called ‘solid’ chlorine (calcium hypochlorite, Ca(OCl)<sub>2</sub>) or ‘liquid’ chlorine (solution of sodium hypochlorite, NaOCl), another equilibrium involved is:



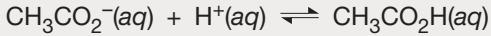
The species which is best at destroying bacteria and at resisting decomposition by sunlight is HOCl, not OCl<sup>-</sup>. How can you ‘force’ this equilibrium to the right?

**16** The salt silver acetate, CH<sub>3</sub>CO<sub>2</sub>Ag, is sparingly soluble in water (almost insoluble).

- a Write the equation for the equilibrium involved.

b If sodium acetate solution was added to a silver nitrate solution to precipitate silver acetate, how would you maximise the amount of silver ion precipitated as acetate (i.e. how would you drive this equilibrium to the right)?

- c The acetate ion is also involved in the equilibrium:



This equilibrium lies well to the right. When hydrochloric acid is added to the mixture of precipitate and solution in (b), the precipitate redissolves. Use Le Chatelier’s principle along with the two equilibria involved to explain why this happens.

## 4.9 ACIDIC OXIDES IN THE ATMOSPHERE

Three acidic oxides are minor constituents of the atmosphere:

- carbon dioxide,  $\text{CO}_2$ , 360 ppm
- sulfur dioxide,  $\text{SO}_2$ , 0.001 ppm
- nitrogen dioxide,  $\text{NO}_2$ , 0.001 ppm

ppm means parts per million. The values given are for unpolluted dry air.

Figure 4.5 shows models of these three oxides along with the two neutral oxides of nitrogen.

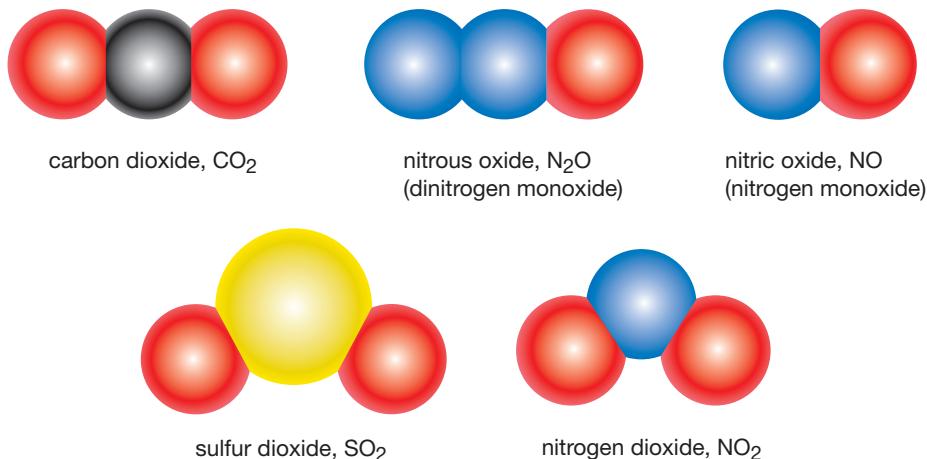


FIGURE 4.5  
Models of some oxides of carbon, nitrogen and sulfur. Black is C, blue N, yellow S and red O. For  $\text{N}_2\text{O}$  and NO the systematic names are given in brackets, though these names are not widely used; for the other three oxides the common names are the systematic names (p. 81 CCPC)

In gaseous contexts **parts per million** has a different meaning from that in solution contexts (p. 213 CCPC). In gases parts per million means number of *molecules* of the particular species per million molecules of the mixture. As we will see in Section 4.12, this also means parts per million by *volume*. 360 ppm carbon dioxide means 360  $\text{CO}_2$  molecules per million molecules of air or 360 mL  $\text{CO}_2$  in one million mL of air.

### Carbon dioxide

Carbon dioxide in the atmosphere is part of the natural carbon cycle in which carbon moves through plants, animals, oceans and rivers, carbonate rocks and the atmosphere. However in the past 150 years human activity in the form of combustion of fossil fuels has led to a 30% increase in the concentration of carbon dioxide in the atmosphere—from about 280 ppm at the start of the industrial revolution to 360 ppm today.

This increase is of considerable concern because it is the major factor in the enhanced greenhouse effect (p. 288 CCPC).

### Sulfur dioxide

About two-thirds of the sulfur dioxide released to the atmosphere worldwide comes from natural sources such as *geothermal hot springs* and *volcanoes*. Because volcanic activity varies greatly from year to year, atmospheric concentrations of sulfur dioxide also vary quite widely.

The main human activities that release sulfur dioxide to the atmosphere are:

- processing or burning fossil fuels
- extracting metals from sulfide ores.

Coal generally contains from 0.5 to 6% sulfur, mainly as metallic sulfides and sulfur in carbon-containing compounds. It is not practical to extract sulfur from coal before burning it, so in the combustion process most of the sulfur is converted to sulfur dioxide:



Although some coal-burning power stations remove most of the sulfur dioxide from their effluent gases (particularly in heavily industrialised parts of Europe and North America), the alternative of using low-sulfur coal (without any clean-up) is still widely favoured. Australian coals are generally low in sulfur (0.5 to 2%) which is why they are in strong demand.

Crude oil and sometimes natural gas contain a variety of sulfur compounds. Most of these are extracted at oil refineries or gas processing plants as elemental sulfur which is sold to sulfuric acid manufacturers. However there is some release of sulfur dioxide by refineries. In addition sometimes a small amount of sulfur remains (as compounds) in refined petrol and is also released to the atmosphere, generally as  $\text{SO}_2$  but under some conditions as hydrogen sulfide.

Many metals occur as sulfides (e.g. copper, lead, zinc, silver, nickel) and the first step in extracting the metal is to roast the sulfide ore in air. This produces sulfur dioxide along with the metal or metal oxide. The extraction of copper was discussed on pp. 111–12 CCPC. For zinc the reaction is:



Depending on the location of the processing plant, the sulfur dioxide may be collected or just released to the atmosphere for dispersal over large tracts of sparsely populated land.

## Oxides of nitrogen

There are three common oxides of nitrogen, nitrous oxide,  $\text{N}_2\text{O}$ , nitric oxide,  $\text{NO}$ , and nitrogen dioxide,  $\text{NO}_2$ .  $\text{NO}_2$  is acidic: the other two are neutral.

### Nitric oxide and nitrogen dioxide

The major natural source of *nitric oxide* is *lightning*. At the very high localised temperatures generated by lightning, atmospheric oxygen and nitrogen gases combine to form nitric oxide:



Nitric oxide slowly reacts with oxygen to form *nitrogen dioxide*:



This is the major natural source of nitrogen dioxide.

The human activity that generates large amounts of nitric oxide and nitrogen dioxide is *combustion*, both in stationary sources (power stations) and moving ones (cars and trucks). At the high temperatures in the combustion chambers, oxygen and nitrogen from air combine to form nitric oxide (as they do in lightning, Equation 4.7). And again nitric oxide is slowly converted to nitrogen dioxide (Equation 4.8). Exhausts from power stations and vehicles generally have NO and  $\text{NO}_2$  in the ratio of about 4:1, though additional reactions in the atmosphere gradually convert most of the NO to  $\text{NO}_2$ .

The mixture, NO plus  $\text{NO}_2$ , is often referred to as  $\text{NO}_x$  or  $\text{NOx}$ .

Combustion processes that use a high ratio of air to fuel (power stations and diesel engines) produce proportionately more  $\text{NO}_x$  than do petrol engines (which have a relatively low air to fuel ratio).

## Nitrous oxide

*Nitrous oxide* is formed naturally by the action of certain *bacteria on nitrogenous material in soils*. Human activity has increased the release of nitrous oxide to the atmosphere through the increased use of nitrogenous fertiliser which provides more raw material for the bacteria. This is of considerable concern because nitrous oxide contributes to the enhanced greenhouse effect (p. 288 CCPC).

## Health effects

*Sulfur dioxide* irritates the respiratory system and causes breathing difficulties at concentrations as low as 1 ppm. People suffering from asthma and emphysema are particularly susceptible. The effects of sulfur dioxide are magnified if particulates are present also.

*Nitrogen dioxide* irritates the respiratory tract and causes breathing discomfort at concentrations above about 3 to 5 ppm and at higher concentrations does extensive tissue damage. Concentrations above 3 ppm have rarely been reached even in heavily polluted cities. The main problem with  $\text{NO}_2$  is that it leads to the formation of ozone in what is called **photochemical smog**. This is a form of air pollution in which sunlight acts upon nitrogen dioxide in the presence of hydrocarbons and oxygen to form ozone, other pollutants called peroxyacetyl nitrates (PANS) and haze, which is poor visibility due to small particles in the air. It will be discussed in Section 7.5. Ozone has harmful effects at concentrations as low as 0.1 ppm.

## Environmental effects

The major environmental effects of emissions of oxides of sulfur and nitrogen to the atmosphere are those coming from the acid rain that these oxides eventually lead to (discussed in the next section).

Releases of sulfur dioxide to the atmosphere in industrialised cities up until the middle of the twentieth century and in mining and smelting areas until much more recently produced air that often had an unpleasant odour and which was detrimental to health, particularly for aged people and those with respiratory weaknesses.

Releases of oxides of nitrogen leads to formation of photochemical smog (above) which is both visually unattractive and a health hazard.

These matters will be considered further in the next section.

Information about the gaseous oxides discussed in this section is summarised in Table 4.4.

## 4.10 THE 'FATE' OF OXIDES OF SULFUR AND NITROGEN IN THE ATMOSPHERE

Sulfur dioxide and  $\text{NO}_x$  are pollutants that form in localised industrial areas such as big cities (with industry, power generation and many vehicles) and mining towns ( $\text{SO}_2$  from roasting ores). They do not spread out globally because natural processes remove them from the air.

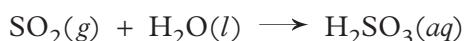
**TABLE 4.4 Some gaseous oxides of atmospheric importance**

	<b>Carbon dioxide CO<sub>2</sub></b>	<b>Sulfur dioxide SO<sub>2</sub></b>	<b>Nitrous oxide N<sub>2</sub>O</b>	<b>Nitric oxide NO</b>	<b>Nitrogen dioxide NO<sub>2</sub></b>
colour	colourless	colourless	colourless	colourless	reddish-brown
odour	odourless	pungent odour	slightly sweet	cannot be smelt <sup>b</sup>	choking odour
solubility in water	soluble	soluble	insoluble	insoluble	soluble
adverse health effects	none <sup>c</sup>	respiratory problems	none <sup>d</sup>	converts to NO <sub>2</sub>	respiratory problems <sup>e</sup>
concentration in clean air <sup>a</sup>	360	0.001 <sup>f</sup>	0.31	<0.001	0.001
natural sources	carbon cycle	volcanoes, geothermal springs	bacteria in soils	lightning	from NO + O <sub>2</sub>
human activities that produce it	burning fossil fuels	extracting metals, burning fuels	use of nitrogen fertilisers	combustion	from NO from combustion
concentrations <sup>a</sup> in urban areas	same as global	0.01 <sup>g</sup>	same as global	0.01	0.01
changes to global concentrations	increasing (30% in last 150 years)	not changing	increasing (15% in last 150 years)	not changing	not changing
maximum allowed concentrations <sup>a, h</sup>	no limit set	0.02 (1 year) 0.08 (1 day)	no limit set		0.03 (1 year) 0.12 (1 hour)

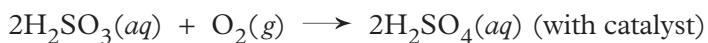
<sup>a</sup> ppm<sup>b</sup> because it is quickly converted to NO<sub>2</sub><sup>c</sup> though it can cause suffocation at high concentrations<sup>d</sup> used as an anaesthetic, so prolonged exposure is dangerous<sup>e</sup> above 3 to 5 ppm, which is rarely reached in the atmosphere; tissue damage at even higher concentrations<sup>f</sup> can fluctuate significantly with volcanic activity<sup>g</sup> but can be up to 1.0 ppm in some mining locations<sup>h</sup> set by the National Environmental Protection Council in 1998<sup>j</sup> means that the average over a year must not exceed 0.02 ppm, though a one-day average of up to 0.08 is acceptable

When these oxides disperse through larger volumes of air, they dissolve in water droplets (rain) and so are washed out of the atmosphere by rain.

Sulfur dioxide reacts to form sulfurous acid:



In water droplets various other impurities in air catalyse the conversion of sulfurous acid to sulfuric acid:

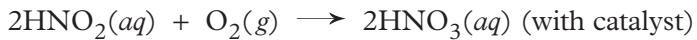


Sulfuric acid is also soluble in water and so it is removed from the atmosphere by rain.

Similarly, nitrogen dioxide reacts with water to form a mixture of nitrous and nitric acids:



Nitrous acid in solution is catalytically oxidised to nitric acid:



Again nitric acid is soluble in water and so is washed out of the atmosphere by rain.

## **SO<sub>2</sub> and NO<sub>x</sub> concentrations in industrialised areas**

After the Industrial Revolution of the early 1800s there was a great increase in emissions of sulfur dioxide (and particulates) to the air in the growing industrial cities (mainly from burning coal and extracting metals). Air quality deteriorated significantly until about the 1950s and '60s when a series of nasty pollution episodes in London and the north-east of the USA caused many deaths. This led to the introduction of regulations to control emissions from factories and these caused a dramatic improvement in air quality, particularly with respect to SO<sub>2</sub> and particulates. Today although the annual average concentration of sulfur dioxide in cities and mining areas is significantly greater than in 'pure' air, it is generally below the upper limits for safety recommended by health authorities.

Serious pollution from NO<sub>x</sub> did not develop until the twentieth century as electricity generation and use of motor cars expanded dramatically (since it is high temperature combustion that produces NO). Photochemical smog (ozone in the air formed from NO<sub>x</sub> and sunlight) first became a problem in the 1960s (first in Los Angeles, then in many other sunny cities). This led to the introduction of emission controls on motor cars (and some restrictions on power station emissions also). Consequently there was considerable improvement in air quality for about two decades.

However increasing city populations and increasing vehicle-kilometres being driven have to a large extent cancelled out further benefits of increasingly stringent emission controls. In most major cities air quality has probably not deteriorated in the past decade but it has not been improving either.

The annual average concentration of SO<sub>2</sub> and NO<sub>2</sub> in most large cities around the world is about 0.01 ppm for each gas. This is about ten times the value for clean air, though a concentration of 0.01 ppm of either gas is not harmful. Of more concern for the health of people is the number of days per year on which the concentration of one of these pollutants exceeds what health authorities generally regard as safe. In Sydney and Melbourne while the annual concentrations of these gases are suitably low, there is some concern about the number of days per year that safe levels are exceeded.

Ambient air quality standards are generally written in terms of both an annual average that should not be exceeded and a short-term average (over an hour or a few hours or a day) which also should not be exceeded more than a certain number of times per year. The last row in Table 4.4 shows the Australian standards: the short-term averages should not be exceeded more than once per year.

While the air quality in Australia's major cities generally meets the SO<sub>2</sub> and NO<sub>2</sub> standards, there are some mineral-processing areas which frequently exceed the sulfur dioxide limits, notably Port Pirie in SA, Mt Isa in Qld and Kalgoorlie in WA; these places process sulfide ores. Improved operating procedures, including trapping sulfur dioxide from flue gases, have resulted in steady improvement in air quality in these locations in recent years. High sulfur dioxide concentrations used to be regularly observed in the Port Kembla area (a copper smelter is there), but after the smelter was rebuilt in 2000 with the sulfur dioxide being trapped and used to make sulfuric acid, SO<sub>2</sub> levels have only rarely exceeded the safety standards.

## **SO<sub>2</sub> and NO<sub>x</sub> concentrations in the atmosphere globally**

Because SO<sub>2</sub> and NO<sub>2</sub> are washed out of the atmosphere by rain, there appears not to have been any significant build-up of their concentrations over the last century or so. This contrasts with the significant increases that have occurred for carbon dioxide and nitrous oxide. Carbon dioxide concentration has increased by about 30% over the last 150 years to about 360 ppm at the present, while nitrous oxide concentration has increased by about 15% over the same time period (to about 0.31 ppm). However it is difficult to be sure about SO<sub>2</sub> and NO<sub>2</sub>, because there is a lack of reliable data for periods before about 1950. It has only been in the last few decades that we have been able to measure concentrations of these gases below 0.1 ppm with sufficient accuracy to follow changes in them.

### **4.11 ACID RAIN**

High emissions of sulfur and nitrogen dioxides to the atmosphere lead to rain being somewhat acidic, because as we have just seen these pollutants are converted to sulfuric and nitric acids which dissolve in the rain.

**Acid rain** is rain that has a higher hydrogen ion concentration than normal—higher than about  $10^{-5}$  mol/L.

The acids generally present in acid rain are sulfuric and nitric acids.

Rain that is unaffected by any pollutants is slightly acidic because of dissolved carbon dioxide which forms carbonic acid (Equation 4.6). This leads to the rain having a hydrogen ion concentration of between  $10^{-5}$  and  $10^{-6}$  mol/L. (We will see in Section 4.18 that in neutral solution the hydrogen ion concentration is  $10^{-7}$  mol/L.) However when rain is affected by industrial emissions of sulfur and nitrogen dioxides, it can have a hydrogen ion concentration between  $10^{-3}$  and  $10^{-5}$  mol/L.

### **Effects of acid rain**

Effects of acid rain include:

- *increasing acidity of lakes* which has a detrimental effect upon fish populations; such effects have been observed in many lakes of Scandinavia (partly from British and Central European emissions) and North America
- *damage to pine forests* in parts of Europe and North America (as shown in the photo on p. 105)
- *erosion of the marble and limestone of building surfaces and decorations*, because such materials contain carbonates, particularly calcium carbonate, and these readily react with acids; in parts of Europe acid rain over the past fifty years has done more damage to priceless statuary than the weathering of the previous 500 years.
- *severe damage to vegetation* around mine and smelter sites, particularly when they are located in high-rainfall areas such as Queenstown in Tasmania; this problem is less severe today than it was 50 to 150 years ago, when there were no controls on what could be released from mining and smelting operations.

While the last effect occurs quite close to the source of the pollution, the first three are often experienced in very diverse locations quite remote from the primary sources of the pollution.

The only way to prevent acid rain is to stop emitting  $\text{SO}_2$  and  $\text{NO}_2$  to the atmosphere. In most countries there are now legal limits on the amounts of these two pollutants that factories and power stations can emit.



This statue at St Alfege's Church, Greenwich, London has suffered more damage from acid rain in the past fifty years than from all atmospheric sources in the previous 500 years

## Exercises

- 17 What are the systematic names for nitrous oxide, nitric oxide and nitrogen dioxide?
- 18 Some coals contain iron(II) sulfide. During combustion this is converted to iron(II) oxide and sulfur dioxide. Write an equation for the reaction.
- 19 A small proportion of the sulfur dioxide in polluted air is photolytically oxidised to sulfur trioxide in the gas phase with the sulfur trioxide so formed dissolving in water droplets. Write equations for these reactions.
- 20 In industrial areas a significant amount of ammonia is released to the atmosphere. This generally precipitates out as ammonium sulfate. Explain, with equations, how this substance forms. Could any ammonium carbonate be formed? If so, explain how.
- 21 One method of removing sulfur dioxide from the effluent gases from power stations is to pass the gas over calcium oxide. What would you expect to be the product of this reaction? Write an equation.
- 22 Write equations for the reactions of the main two components of acid rain with calcium carbonate, a major constituent of marble, and explain why this caused deterioration of marble statues.
- 23 1.00 L of air at 25°C and standard atmospheric pressure contains 0.041 moles of gas. If the concentrations of carbon dioxide and sulfur dioxide in this air are 360 ppm and 0.02 ppm respectively, what would be their concentrations in moles per litre?





## WEBSITES

For air quality standards:

<http://www.ephc.gov.au>

(click on *NEPMs* then *Ambient Air Quality*; there is also other useful information about air quality on this site)

For SO<sub>2</sub> and NO<sub>x</sub> in the atmosphere:

<http://www.deh.gov.au/soe/2001/atmosphere.html>

(click on *Key issues*, then on *Urban air quality* or *Regional air quality*; alternatively, scroll down the page to the relevant bits)

For acid rain:

<http://www.ausetute.com.au/acidrain.html> and <http://www.epa.gov/airmarkets/acidrain>

(both are good simple introductions to the topic)

## 4.12 CALCULATIONS INVOLVING VOLUMES OF GASES

We often want to calculate quantities of gases involved in chemical reactions. On pp. 142–5 *CCPC* we saw how to calculate masses in reactions. However with gases it is generally more convenient to work in terms of volumes. Let us see how this can be done.

On p. 150 *CCPC* Avogadro's hypothesis was stated as:

When measured at the same temperature and pressure, equal volumes of gases contain the same number of molecules.

This can be rearranged into:

Equal numbers of molecules of different gases occupy the same volume  
(at the same temperature and pressure). ... (4.9)

Since a mole is a fixed number of molecules ( $6.02 \times 10^{23}$ ), a mole of any gas has the same volume as a mole of any other gas (at the same temperature and pressure). This volume is called the **molar volume** of a gas—the volume of one mole.

Because the volume of a gas changes quite significantly as its temperature and the pressure acting upon it change, we must always state the temperature and pressure when we give the volume of a gas. The two temperatures commonly used for the molar volume of a gas are 0°C and 25°C.

The common pressure used for both temperatures has been the *atmosphere*<sup>†</sup>. However the atmosphere is not part of the International System of Units (SI Units) and so its use is being phased out. The SI Unit for pressure is the pascal (Pa) which is a force of 1 newton per square metre, N m<sup>-2</sup>. Standard atmospheric pressure (or 1 atmosphere) is 101.3 kPa (kilopascals). In nearly all chemistry books the molar volume of a gas is given for this pressure (101.3 kPa). However the NSW HSC examiners require that molar volume be given for a pressure of 100 kPa (more correctly 100.0 kPa, because it is not possible to tell whether 100 has one or three significant figures). Hence:

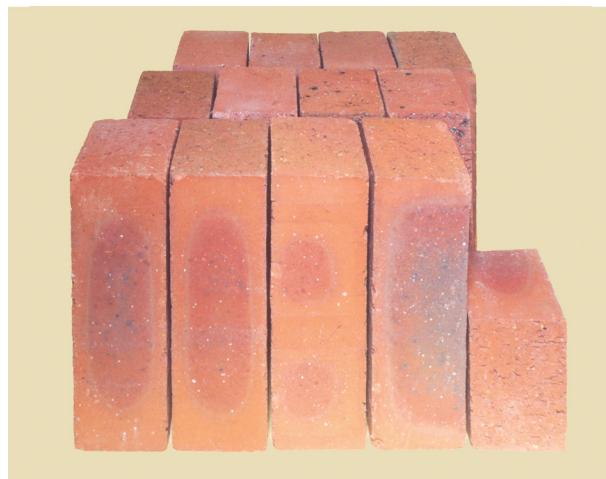
<sup>†</sup> As a unit of pressure the *atmosphere* is defined as being equal to standard atmospheric pressure, which is sea-level pressure averaged over time and space around the globe: it is 101.3 kPa. That is 1.000 atmosphere = 101.3 kPa. However, despite its convenience, we shall not be using the *atmosphere* as a unit of pressure in this book.

At 0°C and 100.0 kPa, the molar volume of all gases is 22.71 L. ... (4.10)

At 25°C and 100.0 kPa, the molar volume of all gases is 24.79 L. ... (4.11)

Figure 4.6 illustrates the size of a mole of gas. Examples will illustrate how to interconvert volumes and masses using the molar volume of a gas. In many ways the calculations are similar to the mass–mass calculations on pp. 143–5 CCP.

FIGURE 4.6  
A mole of any gas at 25°C and 100 kPa has the volume of about twelve house bricks or of about twelve 2-litre milk bottles



### Example 2

What mass of gas is present in a 515 mL flask containing carbon dioxide at 25°C and at a pressure of 100.0 kPa?

Using the molar volume of a gas at 25°C and 100.0 kPa:



$$\text{Number of moles of CO}_2 \text{ present} = \frac{0.515 \text{ L}}{24.79 \text{ L/mol}}$$
$$= 0.0208 \text{ mol}$$

$$\text{Molar mass of CO}_2 = 12.0 + 2 \times 16.0$$
$$= 44.0 \text{ g/mol}$$

$$\text{Mass of CO}_2 = 0.0208 \times 44.0$$
$$= \mathbf{0.914 \text{ g}}$$

### Example 3

What volume is needed to store 3.11 g ethane at 100 kPa and 0°C?

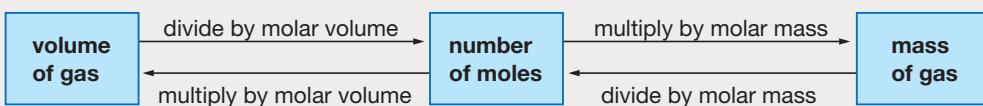


$$\text{Molar mass of ethane, C}_2\text{H}_6 = 2 \times 12.0 + 6 \times 1.01$$
$$= 30.1 \text{ g/mol}$$

$$\text{Number of moles of ethane} = \frac{3.11 \text{ g}}{30.1 \text{ g/mol}}$$
$$= 0.103 \text{ mol}$$

$$\text{Volume this will occupy} = 0.103 \times 22.71$$
$$= \mathbf{2.35 \text{ L}}$$

The method for doing these calculations can be shown schematically:



When a chemical reaction is involved, there is an additional step—using the chemical equation to convert from moles of given substance to moles of required substance. In many ways the calculations are similar to the mass–mass calculations on pp. 144–5 of *CCPC* as the following examples will illustrate.



### Example 4

Calculate the volume of hydrogen produced at 0°C and 100.0 kPa when 2.5 g sodium reacts with excess water. The balanced equation is:



$$\text{Molar mass of Na} = 23 \text{ g/mol}$$

$$\therefore \text{number of moles of Na used} = \frac{2.5}{23} \\ = 0.109 \text{ mol}$$

From the chemical equation:

$$\frac{\text{number of moles of H}_2 \text{ produced}}{\text{number of moles of sodium used}} = \frac{1}{2}$$

$$\text{So number of moles of H}_2 \text{ produced} = \frac{1}{2} \times 0.109 \\ = 0.054 \text{ mol}$$

Molar volume of a gas

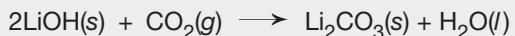
$$\text{at } 0^\circ\text{C and } 100.0 \text{ kPa} = 22.71 \text{ L}$$

$$\text{Hence volume of H}_2 \text{ produced} = 0.054 \times 22.7 \\ = \mathbf{1.2 \text{ L}}$$



### Example 5

Lithium hydroxide has been commonly used in space craft to absorb carbon dioxide from the air. The reaction is:



Calculate the mass of lithium hydroxide needed to absorb 250.0 L carbon dioxide at 25°C and 100.0 kPa pressure.

The molar volume of a gas at 25°C and 100.0 kPa is 24.8 L.

$$\therefore \text{number of moles of CO}_2 \text{ to absorb} = \frac{250}{24.79} \\ = 10.1 \text{ mol}$$

From the chemical equation:

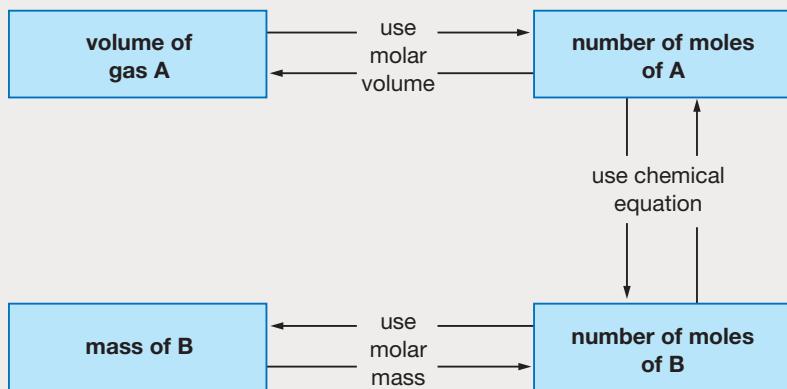
$$\frac{\text{number of moles of LiOH needed}}{\text{number of moles of CO}_2 \text{ to absorb}} = \frac{2}{1}$$

$$\text{So number of moles of LiOH needed} = 2 \times 10.1 \\ = 20.2 \text{ mol}$$

$$\text{Molar mass of LiOH} = 6.9 + 16.0 + 1.0 \\ = 23.9 \text{ g/mol}$$

$$\therefore \text{mass of LiOH needed} = 23.9 \times 20.2 \\ = \mathbf{483 \text{ g}}$$

Again the method for doing these calculations can be shown schematically as in Figure 4.7.



**FIGURE 4.7**  
The method for doing mass–volume calculations involving chemical reactions

## Exercises

- 24 a** A 2.042 L flask contains chlorine gas at 0°C and 100.0 kPa. What mass of gas is in the flask?
- b** What volume would 1.32 g carbon dioxide occupy at 25°C and 100.0 kPa pressure?
- 25** When 1.0 g magnesium is dissolved in excess hydrochloric acid, what volume of hydrogen (measured at 0°C and 100.0 kPa pressure) is formed?
- 26** What volume of carbon dioxide, measured at 25°C and 100.0 kPa, is formed when 0.33 g calcium carbonate is decomposed to form calcium oxide and carbon dioxide?
- 27** Sodium hydroxide reacts with carbon dioxide to form sodium carbonate and water. What volume of carbon dioxide (measured at 0°C and 100.0 kPa) will 100 mL of 1.35 mol/L solution of sodium hydroxide absorb?
- 28** As mentioned in Exercise 21, sulfur dioxide can be removed from the exhaust gas of power stations by reacting it with calcium oxide. What mass of calcium oxide is needed to absorb  $1.00 \times 10^3$  L sulfur dioxide (at 25°C and 100.0 kPa)?



## 4.13 SOME COMMON ACIDS AND BASES

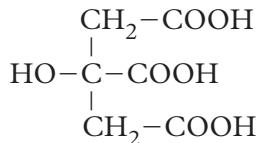
Some of the common acids that are involved in our everyday lives, either directly or indirectly, are the naturally occurring ones, hydrochloric, acetic and citric acids and the synthetic ones, sulfuric and nitric acids.

### Naturally occurring acids

- **Hydrochloric acid, HCl.** This is produced by glands in the lining of our stomachs to form an acidic environment for the efficient operation of the enzymes that break some complex food molecules into easily transportable small molecules that are absorbed into the blood stream when they pass into the intestine.  
Hydrochloric acid is also made commercially in very large quantities; it has many industrial uses such as cleaning metals before galvanising or soldering, cleaning brickwork, neutralising bases in manufacturing processes and adjusting acidity in swimming pools.
- **Acetic acid,  $\text{CH}_3\text{—COOH}$**  (systematic name ethanoic acid). The carboxylic acid functional group —COOH was introduced in Section 1.12 and will be discussed more fully in Section 5.19. Acetic acid is present in vinegar which is commonly made from wine by oxidation of the ethanol.

Acetic acid is also made industrially and used to make a wide range of organic chemicals.

- **Citric acid** (systematic name 2-hydroxypropane-1,2,3-tricarboxylic acid). This occurs in citrus fruit. It is also made industrially and widely used as a food additive (for flavour and as a preservative). The molecular formula of citric acid is  $C_6H_8O_7$ . Its structure is:



- **Vitamin C** (ascorbic acid). This acid occurs widely in fruit and vegetables and is essential to our health and wellbeing. Its molecular formula is  $C_6H_8O_6$ .

## Synthetic acids

- **Sulfuric acid,  $H_2SO_4$** . More sulfuric acid is manufactured worldwide than any other chemical. It is used to make fertilisers, synthetic fibres, industrial ethanol, detergents and car batteries. Its synthesis and uses are discussed in Chapter 9.
- **Nitric acid,  $HNO_3$** . This acid is synthesised in huge quantities for the manufacture of fertilisers and explosives and numerous other chemicals.

## Naturally occurring bases

- **Ammonia,  $NH_3$** . This is present in the stale urine of humans and other animals. It has a sharp penetrating odour. Ammonia is also formed by *anaerobic decay* (decay without oxygen) of organic matter.  
Ammonia is manufactured in huge quantities for the production of fertilisers, nitric acid and many other chemicals. It is often used in the home as a cleaning agent as it is good at removing waxes, particularly from floors.
- **Amines**. These are compounds with some other group such as an alkyl replacing one or more of the H atoms of ammonia (see Section 1.12). They have a strong fishy smell and are weak bases; they also are formed during the anaerobic decomposition of organic matter.
- **Metallic oxides** such as iron(III) oxide, copper oxide and titanium oxide. Metals are often extracted from such insoluble bases.
- **Carbonates** such as soluble sodium carbonate (in the mineral trona,  $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ ), and insoluble calcium carbonate (limestone) and magnesium carbonate. The insoluble carbonates do not conform to our interim definition of bases in Section 4.1, but are bases in terms of the broader definition to be introduced in Section 5.2.

Sodium carbonate is synthesised industrially in large quantities (Sections 10.17 to 10.19) for use in making glass, paper and soaps and detergents, for treating water and as a cheap base for neutralising acids.

## Synthetic bases

- **Sodium hydroxide**. This is made from common salt (Sections 10.4 to 10.7). It is widely used for making soap and detergents, rayon and other synthetic fibres and for extracting alumina from bauxite (the first step in producing aluminium). Domestically it is used in oven cleaners and for clearing blocked

drains (though its extremely corrosive nature requires that it be handled very carefully).

■ **Calcium oxide, CaO** (quick lime) and **hydroxide Ca(OH)<sub>2</sub>** (slaked lime).

Calcium oxide is made by heating limestone (calcium carbonate), and then hydroxide is made by reacting the oxide with water. Quicklime is used to make cement while slaked lime is used in some mortars and plasters and as whitewash. Agricultural lime is finely ground calcium carbonate.

## Acids as food additives

Acids are frequently added to food in order to:

- *improve the taste*, by giving the food a certain tartness (for example in drinks and sweets)
- *preserve the food* by increasing its acidity (for example in canned fruits and vegetables and in pickles and chutneys), because many bacteria cannot survive in acid conditions.

The common acids added are acetic acid (vinegar) and citric acid, with phosphoric acid occasionally being used. Propanoic acid (propionic acid) is often used as a preservative in bread.

Ascorbic acid (vitamin C) is often added to foods but this is done because it is a vitamin (essential dietary ingredient), not specifically because it is an acid. Potassium hydrogen tartrate (cream of tartar) is often added to food along with sodium hydrogen carbonate as baking powder to make cakes rise as they cook.

### WEBSITE

About food additives:

<http://www.foodstandards.gov.au/whatsinfood/foodadditives.cfm>

(scroll through the page for general information about additives; click on *Food Additives List—Alphabetical* to see a listing of allowed additives and their purposes)



## 4.14 ACIDS—A CLOSER LOOK

In Section 4.1 we said that an acid was a substance that in solution produces hydrogen ions, H<sup>+</sup>. As was explained on p. 198 CCPC, it is often convenient to write the hydrogen ion as H<sup>+</sup>, but it is more accurately described as H<sub>3</sub>O<sup>+</sup>—an H<sup>+</sup> attached to a water molecule. Free H<sup>+</sup> does not exist in aqueous solution. When our common acids dissolve in water, they actually react with the water to form these H<sub>3</sub>O<sup>+</sup> ions. For nitric acid the reaction is:



This equation reads: liquid nitric acid reacts with liquid water to form an aqueous solution containing hydrogen ions and nitrate ions. We call this an **ionisation reaction**: the nitric acid has ionised to form H<sub>3</sub>O<sup>+</sup> and NO<sub>3</sub><sup>-</sup>. The H<sub>3</sub>O<sup>+</sup> ion is sometimes called the *hydronium ion*. Sometimes for brevity we write the ionisation reaction simply as:



Pure HCl is a covalent gas called hydrogen chloride. When it dissolves in water, it reacts with the water:



This aqueous solution of hydrogen and chloride ions is called hydrochloric acid. Again for convenience we often write this as:



A term that is often used in acid–base contexts is pH.

## 4.15 MEANING OF pH

Because hydrogen ion concentration is frequently referred to, and since its values can cover such a wide range—from 10 mol/L to  $10^{-13}$  mol/L—chemists have introduced a more convenient scale for its measurement, called the pH scale.

The **pH** of a solution is defined as the negative of the logarithm (to base 10) of the hydrogen ion concentration:<sup>†</sup>

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] \quad \dots (4.12)$$

where square brackets around a species mean *concentration of*.

For a solution in which  $[\text{H}_3\text{O}^+] = 0.01$  mol/L (that is,  $10^{-2}$  mol/L), the pH is 2.0. If  $[\text{H}_3\text{O}^+] = 10^{-7}$  mol/L, then pH = 7.0.

Most calculators have a ‘log to base ten’ key, usually labelled just ‘LOG’ (not to be confused with the ‘LN’ key which calculates the logarithm to the base  $e$ ). Therefore, calculation of pH is a simple operation.

### To calculate the pH

For a solution in which  $[\text{H}_3\text{O}^+] = 0.042$  mol/L:

- use your calculator to find the LOG (to base 10) of this number: **-1.377**
- change the sign: **+1.377**
- adjust to the correct number of significant figures and write: **pH = 1.38**.

The *rule for significant figures* in converting between  $[\text{H}_3\text{O}^+]$  and pH is this: the number of *decimal places* in the value for pH should equal the number of *significant figures* in the value for  $[\text{H}_3\text{O}^+]$ . In the above example  $[\text{H}_3\text{O}^+]$  had two significant figures so pH had two decimal places, 1.38.

From Equation 4.12, it follows that:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \quad \dots (4.13)$$

Hence if a solution has a pH of 2.0, then  $[\text{H}_3\text{O}^+] = 10^{-2}$  mol/L = 0.01 mol/L. If the pH is 5.0, then  $[\text{H}_3\text{O}^+] = 10^{-5}$  mol/L.

To calculate  $[\text{H}_3\text{O}^+]$  from pH when pH is not a whole number, we again need our calculators. Most calculators have a key labelled ‘SHIFT’, ‘INV’ or ‘2nd F’ (second function) which, when used with the LOG key, calculates 10 raised to the power keyed in. Generally the LOG key carries the secondary label,  $10^x$ .

If the pH of a solution is 4.63, then to calculate the hydrogen ion concentration, we need to calculate  $10^{-4.63}$ .

<sup>†</sup> The logarithm to base 10 of a number is the power to which the base 10 must be raised to give the number. If  $\log_{10} Z = Y$ , then  $Z = 10^Y$ .

## To calculate $[H_3O^+]$ from pH

When pH = 4.63:

- change the sign of the pH: **-4.63**
- use your calculator to find the ANTILOG of this number (SHIFT, LOG or INV, LOG or 2nd F, LOG): **0.00002344** or  **$2.344 \times 10^{-5}$**
- adjust to the correct number of significant figures and add units:  
 $[H^+] = 2.3 \times 10^{-5}$  mol/L (two decimal places in pH give two significant figures in  $[H^+]$ ).

Similarly, if pH = 8.95,  $[H_3O^+] = 1.1 \times 10^{-9}$  mol/L by the same sequence (try it!).

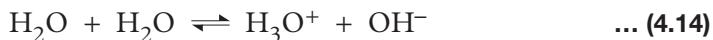
Because of the way that pH is defined,

a change in pH of one unit corresponds to a tenfold change in  $[H_3O^+]$ .

pH is also used for alkaline solutions. To see how this can be done we need to take a closer look at water.

## 4.16 SELF-IONISATION OF WATER

Although water is a covalent liquid, its electrical conductivity is significantly higher than that of other covalent liquids such as hexane or chloroform. This and other evidence shows that water undergoes a self-ionisation reaction to a small but significant extent:



This is called the **self-ionisation of water**. It is an equilibrium reaction that lies well to the left. At equilibrium in pure water only one molecule in four billion has ionised (formed a hydrogen ion). This self-ionisation of water occurs not just in pure water but in all aqueous solutions also.

In addition we find that there is always a relationship between the concentrations of hydrogen ions and hydroxide ions: the product of these concentrations is always constant at constant temperature; that is:

$$[H_3O^+][OH^-] = K_w \quad \dots (4.15)$$

where  $K_w$  is a constant at constant temperature.  $K_w$  is called the **ionic product constant for water**. At 298 K its value is  $1.00 \times 10^{-14}$  (mol/L)<sup>2</sup>. Therefore:

$$\text{At 298 K} \quad [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ (mol/L)}^2 \quad \dots (4.16)$$

Although the more correct formula for the hydrogen ion (or hydronium ion) is  $H_3O^+$ , it is often written as  $H^+$  for convenience. It is acceptable to use  $H^+$  provided you understand clearly that it is just an abbreviation for the more correct form,  $H_3O^+$ .

Consequently you may see Equations 4.12, 4.14 and 4.16 written as:

$$pH = -\log_{10} [H^+]$$



$$\text{At 298 K} \quad [H^+][OH^-] = 1.00 \times 10^{-14} \text{ (mol/L)}^2$$

A consequence of Equation 4.15 (or 4.16) is that we can talk about the

hydrogen ion concentration in an alkaline solution and hence about the pH of an alkaline solution.

## 4.17 pH OF ALKALINE SOLUTIONS

If we know the hydroxide ion concentration in an alkaline solution at 298 K, we can use Equation 4.16 to calculate the hydrogen ion concentration and hence get pH. For example if  $[\text{OH}^-]$  is  $1 \times 10^{-3}$  mol/L, then:

$$\begin{aligned}\text{from Equation 4.16} \quad [\text{H}_3\text{O}^+] &= \frac{1.00 \times 10^{-14}}{1 \times 10^{-3}} \\ &= 1 \times 10^{-11} \\ \text{and so} \quad \text{pH} &= -\log_{10}(1 \times 10^{-11}) \\ &= 11.0\end{aligned}$$

This means that we can use pH for alkaline solutions as well as for acidic ones. Table 4.5 shows the hydrogen and hydroxide ion concentrations corresponding to various pHs.

**TABLE 4.5 Hydronium and hydroxide ion concentrations for various pHs**

pH	1.0	3.0	5.0	7.0	9.0	11.0	13.0
$[\text{H}_3\text{O}^+]$	$10^{-1}$	$10^{-3}$	$10^{-5}$	$10^{-7}$	$10^{-9}$	$10^{-11}$	$10^{-13}$
$[\text{OH}^-]$	$10^{-13}$	$10^{-11}$	$10^{-9}$	$10^{-7}$	$10^{-5}$	$10^{-3}$	$10^{-1}$

In Section 4.1 we said that a neutral solution was one that was neither acidic nor alkaline. Let us review this in the light of the self-ionisation of water.

## 4.18 NEUTRAL, ACIDIC AND ALKALINE SOLUTIONS

A **neutral solution** is defined as one in which the concentrations of hydrogen ions and hydroxide ions are equal.

That is:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

Putting this equality into Equation 4.16 gives at 25°C:

$$[\text{H}_3\text{O}^+]^2 = 1.00 \times 10^{-14} \text{ (mol/L)}^2$$

or

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-7} \text{ mol/L}$$

Hence at 25°C, a neutral solution is one in which the hydrogen ion concentration is  $1.00 \times 10^{-7}$  mol/L.

If  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ , we say the solution is acidic. This means that at 25°C, a solution is acidic if  $[\text{H}_3\text{O}^+]$  is greater than  $10^{-7}$  mol/L.

If  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ , we say that the solution is alkaline (or basic). This means that at 25°C, a solution is alkaline if  $[\text{H}_3\text{O}^+]$  is less than  $10^{-7}$  mol/L. Alternatively, a solution is alkaline if  $[\text{OH}^-] > 10^{-7}$  mol/L (since by Equation 4.16 the only way  $[\text{H}_3\text{O}^+]$  can be less than  $10^{-7}$  is if  $[\text{OH}^-]$  is greater than  $10^{-7}$  mol/L).

## In terms of pH

- a neutral solution has pH = 7.00
- an acidic solution has pH < 7
- an alkaline solution has pH > 7

Table 4.6 shows the pH and hydrogen ion concentration of some common acidic and alkaline substances.

**TABLE 4.6 pH of some common substances<sup>a</sup>**

[H <sub>3</sub> O <sup>+</sup> ]	pH	Substance	
10	-1	concentrated hydrochloric acid,	ACID
1	0	car battery acid 1 mol/L hydrochloric acid	
10 <sup>-1</sup>	1	0.1 mol/L hydrochloric acid	
10 <sup>-2</sup>	2	stomach acid	
10 <sup>-3</sup>	3	vinegar lemon juice	
10 <sup>-4</sup>	4	soft drinks soda water	
10 <sup>-5</sup>	5	wine black coffee	
10 <sup>-6</sup>	6	rain water milk, saliva	
10 <sup>-7</sup>	7	very pure water	NEUTRAL
10 <sup>-8</sup>	8	blood sea water	
10 <sup>-9</sup>	9	bore water baking soda solution	
10 <sup>-10</sup>	10	toilet soap	
10 <sup>-11</sup>	11	laundry detergents	ALKALINE
10 <sup>-12</sup>	12	household ammonia dishwashing machine powders	
10 <sup>-13</sup>	13	chlorine bleach solutions	
10 <sup>-14</sup>	14	oven cleaners 1.0 mol/L sodium hydroxide	

<sup>a</sup> The colour strip at the left shows the changes universal indicator undergoes as pH changes.



## Exercises

29 Calculate the pH of solutions in which  $[\text{H}_3\text{O}^+]$  is:

- |                            |                               |                              |
|----------------------------|-------------------------------|------------------------------|
| a $1 \times 10^{-4}$ mol/L | c 0.00255 mol/L               | e $5.8 \times 10^{-5}$ mol/L |
| b 0.017 mol/L              | d $4.33 \times 10^{-4}$ mol/L | f 1.3 mol/L                  |

30 Calculate the hydrogen ion concentration in solutions having pHs of:

- |         |        |         |
|---------|--------|---------|
| a 3.00  | d 1.44 | g 9.4   |
| b 3.86  | e 12.5 | h 0.35  |
| c 10.60 | f 5.82 | i -0.70 |

31 Show that a change in pH from 4.75 to 3.75 corresponds to a tenfold increase in hydrogen ion concentration.

## 4.19 MEASURING pH OF SOLUTIONS

**pH meters** are instruments that measure pH directly. The sensing device, shown in Figure 4.8, consists of a pair of electrodes (often mounted concentrically in the one unit). The measuring electrode, called a **glass electrode**, consists of a very thin and fragile membrane made out of a special kind of glass. This develops an electrical potential which depends upon pH. The other electrode is a reference electrode. When this sensing unit is immersed in the solution to be tested, it forms a galvanic cell (Section 2.5); the accompanying electronics unit simply measures the voltage (EMF) of this cell and converts it into a pH reading. A big advantage of a pH meter is that in measuring the pH of a solution, it does not alter the pH of the solution in any way; it does not disturb any chemical equilibria involved.

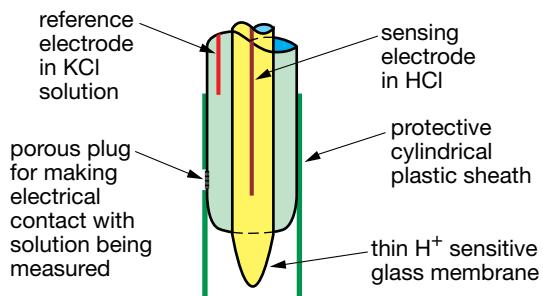


FIGURE 4.8  
A pH meter in use. The diagram at the right shows the sensing (glass) electrode and the reference electrode mounted concentrically in one unit

pH meters give fairly accurate pH values, but they are relatively expensive. A cheaper way of estimating the pH of solutions is to use indicators. The use of a few indicators for determining whether solutions were acidic or basic was described in Section 4.2. Indicators change colours over fairly narrow pH ranges so they can be used to measure approximate pHs. Table 4.7 presents the ranges of pH over which several indicators change colour. Some of these changes are shown in Figure 4.9.

### Using indicators to measure pH

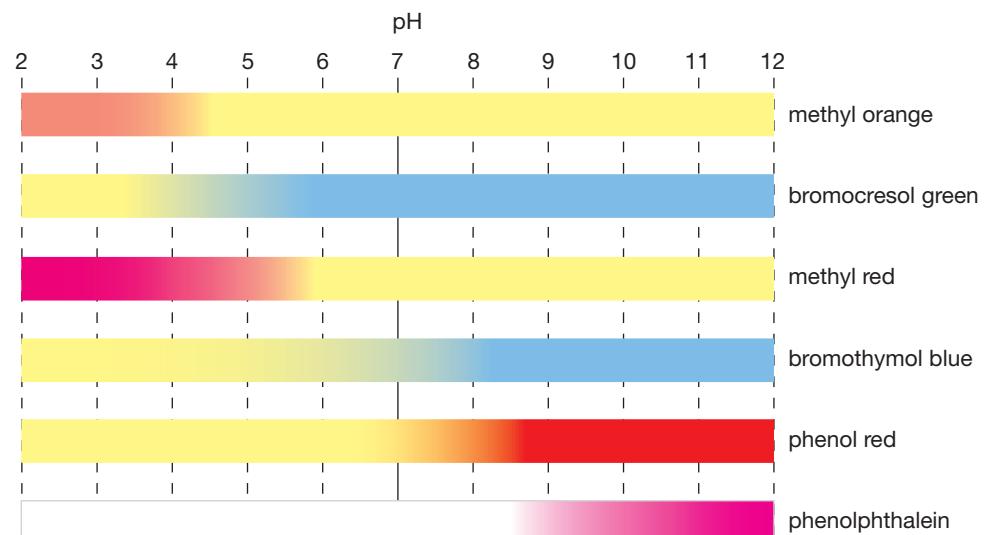
There are several ways of using indicators to estimate the pH of a solution.

**TABLE 4.7 Common indicators and their pH ranges**

Indicator	Colour change <sup>a</sup>	pH range
methyl orange	red – yellow	3.1–4.4
bromophenol blue	yellow – blue	3.0–4.6
bromocresol green	yellow – blue	3.8–5.4
methyl red	pink – yellow	4.4–6.0
litmus	red – blue	5.0–8.0
bromothymol blue	yellow – blue	6.2–7.6
phenol red	yellow – red	6.8–8.4
thymol blue	yellow – blue	8.0–9.6
phenolphthalein	colourless – red	8.3–10.0

*a low pH colour – high pH colour*

- 1 We can use the overall colour changes in Table 4.7 of two or more indicators to determine the approximate pH of a solution. Example 6 illustrates this.
- 2 We can use the changing colour of one indicator to estimate the pH over a narrow range. This can be done by preparing suitable standard solutions and comparing the colour of the unknown solution with these. However this is more commonly done by using indicator papers. An indicator paper is impregnated with one indicator; a piece of the paper is dipped into the solution to be tested and the pH is determined by comparing the colour of the paper with standard colours shown on the package the paper came in.
- 3 We can use what is called a **universal indicator**. This is indicator solution that passes through a variety of colours (shown in Table 4.6) as pH changes from about 1 to 11. Again by comparing the colour of the test solution with colours printed on the label of the bottle a quick estimate of pH can be obtained (to about  $\pm 1$  pH unit). Universal indicator is actually a mixture of several ordinary indicators. Universal indicator is also available as indicator paper.

**FIGURE 4.9**  
Colours of common  
indicators over ranges  
of pH



## Example 6

To estimate the pH of two solutions labelled A and B a student added drops of different indicators to separate samples of the solutions. The results were:

Solution A		Solution B	
Indicator	Colour	Indicator	Colour
methyl red	pink	thymol blue	yellow
methyl orange	yellow	bromothymol blue	blue

Using Table 4.6:

- For solution A, methyl red colour tells us that  $\text{pH} \leq 4.4$  and methyl orange tells us that  $\text{pH} \geq 4.4$ . Therefore solution A has a pH of 4.4.
- For solution B, thymol blue tells us that  $\text{pH} \leq 8.0$  and bromothymol blue tells us that  $\text{pH} \geq 7.6$ . Hence solution B has a pH of between 7.6 and 8.0.

## 4.20 WEAK AND STRONG ACIDS

Further insight into the nature of acids can be obtained by measuring the pH of solutions of equal concentration of several acids. Some such results are shown in Table 4.8.

TABLE 4.8 pH of 0.100 mol/L solutions of several acids

Acid	hydrochloric acid	acetic acid	citric acid	boric acid
pH	1.0	2.9	2.1	5.1

In the 0.10 mol/L hydrochloric acid solution, the pH value tells us that:

$$[\text{H}_3\text{O}^+] = 10^{-1.0} = 0.1 \text{ mol/L}$$

However the pH of the 0.10 mol/L acetic acid solution shows that:

$$[\text{H}_3\text{O}^+] = 10^{-2.9} = 1 \times 10^{-3} \text{ mol/L.}$$

These  $[\text{H}_3\text{O}^+]$  values show that *all* the hydrochloric acid is present as ions but that in the acetic acid solution only *some* of the acetic acid molecules have ionised into hydrogen and acetate ions.

This leads us to the idea of weak and strong acids.

A **strong acid** is one in which all the acid present in solution has ionised to hydrogen ions: there are no neutral acid molecules present.

A **weak acid** is one in which only some of the acid molecules present in the solution have ionised to form hydrogen ions.

Hydrochloric acid is a strong acid. This means that when we dissolve hydrogen chloride gas in aqueous solution *all* the HCl molecules react with water to form hydrogen ions:



For a strong acid the ionisation reaction with water goes to completion.

On the other hand acetic acid is a weak acid, because when pure covalent acetic acid is dissolved in aqueous solution, only *some* of the acetic acid molecules actually react with water to form hydrogen ions; we write this as:



This reaction is an equilibrium one: it does not go to completion.

The pH measurement in Table 4.8 allows us to calculate the fraction of the acetic acid molecules that have ionised:

Total concentration of acetic acid in the solution = 0.10 mol/L

Concentration of hydrogen ions in the solution = 0.001 mol/L (from the pH value)

$$\begin{aligned}\text{So fraction of the molecules that have ionised} &= \frac{0.001}{0.10} \\ &= 0.01 \text{ (or } 1\%) \end{aligned}$$

The other 99% are still present as neutral  $\text{CH}_3\text{COOH}$  molecules.

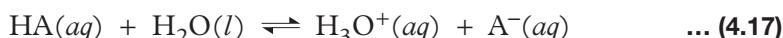
The fraction of the molecules that has ionised is called the **degree of ionisation**.

For the citric acid solution,  $[\text{H}_3\text{O}^+] = 10^{-2.1} = 8 \times 10^{-3}$  mol/L so the degree of ionisation is  $8 \times 10^{-3}/0.10 = 0.08$  or 8%. For boric acid the degree of ionisation is only  $8 \times 10^{-5}$ .

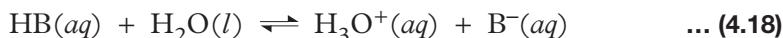
The pH measurements in Table 4.8 allow us to rank the weak acids in order of strength.

## Relative strengths of weak acids

We say that acid HA is stronger than acid HB if the equilibrium

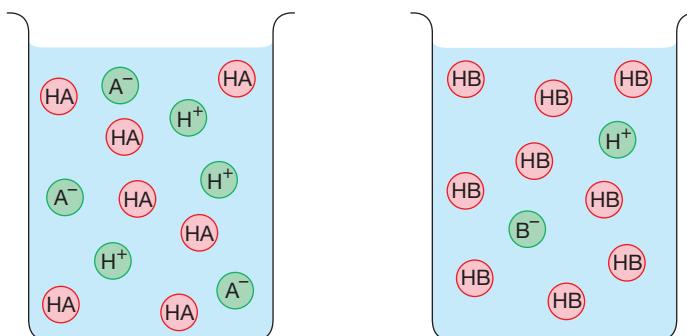


lies further to the right than does



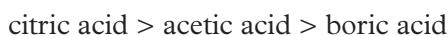
That is, the *degree of ionisation* of HA is greater than that of HB. Figure 4.10 illustrates this.

Therefore if we use solutions of equal concentration, HA will be a stronger acid than HB if the  $[\text{H}_3\text{O}^+]$  in the solution of HA is greater than in the HB solution, which means the pH of the HA solution is *less* than that of the HB solution.



**FIGURE 4.10**  
Illustrating the relative strengths of two weak acids: HB is a weaker acid than HA, because fewer HB molecules are ionised than HA molecules (one as opposed to three out of a total of ten molecules for each acid)

Hence from Table 4.8 we can deduce that the order of decreasing strength of the three weak acids is



because this is the order of *increasing* pH.

While we can talk about degrees of weakness of weak acids—moderately weak, extremely weak and the like—note carefully that:

*there are no degrees of strongness for strong acids,*

because if an acid is strong, it is completely ionised: end of story. If an acid is not completely ionised, it is not strong: it is weak.

In school laboratories the common strong acids are hydrochloric, hydrobromic, hydroiodic, nitric and the first step of sulfuric. All other common acids are weak.

## Concentrated and dilute

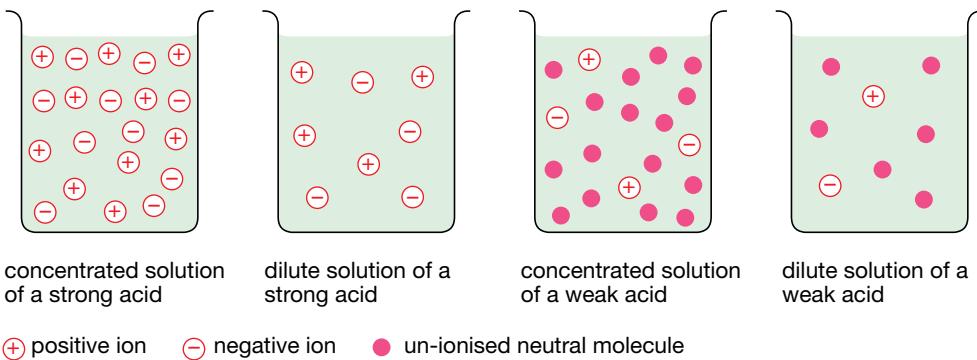
Concentrated and dilute are other terms that are used to describe acid and alkali solutions.

A **concentrated solution** is one in which the total concentration of solute species is high—say, above about 5 mol/L.

A **dilute solution** is one in which the total concentration of solute species is low—say, less than about 2 mol/L.

We can therefore have a concentrated solution of a weak acid or a dilute solution of a strong acid: the terms ‘strong’ and ‘weak’, and ‘concentrated’ and ‘dilute’, have completely independent meanings. Figure 4.11 illustrates this.

FIGURE 4.11  
Concentrated and dilute  
solutions of a weak and  
strong acid



If we know the concentration of a strong acid solution, we can calculate its pH because the acid is completely ionised into hydrogen ions.

## Exercises

- 32 When drops of indicators were added to samples of solutions A, B and C, the colours were as shown below. What is the pH of each solution? You may have to give a range within which the pH lies.

Solution	A	B	C
Indicator: colour	mr: yellow	bcg: yellow	btb: blue
	btb: yellow	bpb: green <sup>a</sup>	tb: yellow

bpb: bromophenol blue; bcg: bromocresol green; mr: methyl red; btb: bromothymol blue; tb: thymol blue  
<sup>a</sup> green = yellow + blue

- 33** Estimate the pH of the solutions in Exercise 2, in terms such as less than or greater than a particular value or within a particular range.
- 34 a** Pure sulfuric acid is a covalent liquid; it dissolves in water to form a strong acid solution. Hydrogen fluoride is a covalent gas; it dissolves in water to form hydrofluoric acid, a weak acid. Write equations for the ionisation of these two substances.
- b** Perchloric acid,  $\text{HClO}_4$ , is a strong acid, while chlorous acid,  $\text{HClO}_2$ , is weak. For the ionisation reactions of these acids in water write equations that reflect these strengths.
- 35 a** Calculate the pH of a 0.065 mol/L solution of hydrobromic acid, a strong acid.
- b** The pH of a 0.037 mol/L solution of hydrofluoric acid is 2.32. Calculate the degree of ionisation of the acid in this solution.
- 36** 0.015 mol/L solutions of five acids, A, B, C, D and E, have pHs of 3.6, 2.5, 1.82, 5.8 and 4.3 respectively. Arrange them in order of increasing acid strength (weakest first, strongest last). Which, if any, would you class as a strong acid?
- 37 a** A  $2.3 \times 10^{-4}$  mol/L solution of sulfuric acid is completely dissociated. Calculate its pH.
- b** The pH of an 0.020 mol/L solution of sulfuric acid was 1.58. What can you deduce about the extent of ionisation of the  $\text{HSO}_4^-$  ion in this solution?

## Important new terms

You should know the meaning of the following terms:

acid (p. 107)  
acid rain (p. 126)  
acidic (p. 108)  
acidic oxide (p. 115)  
alkali (p. 108)  
alkaline (p. 108)  
amphoteric oxide (p. 115)  
base (p. 108)  
basic (p. 108)  
basic oxide (p. 115)  
concentrated solution (p. 142)  
degree of ionisation (p. 141)  
dilute solution (p. 142)  
equilibrium position (p. 117)  
glass electrode (p. 138)  
halide (p. 113)  
hydronium ion (p. 107)  
indicator (p. 109)

ionic product constant of water,  $K_w$  (p. 135)  
ionisation reaction (p. 133)  
Le Chatelier's principle (p. 117)  
molar volume (p. 128)  
neutral (p. 108)  
neutral oxide (p. 115)  
neutral solution (p. 136)  
neutralisation (p. 112)  
oxyacid (p. 113)  
oxyanion (p. 113)  
parts per million (ppm) in gases (p. 121)  
pH (p. 134)  
pH meter (p. 138)  
photochemical smog (p. 123)  
position of equilibrium (p. 117)  
salt (p. 113)  
self-ionisation of water (p. 135)  
strong acid (p. 140)  
universal indicator (p. 139)  
weak acid (p. 140)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Give the names and formulae of five common acids.
- 3 List four common properties of acids.
- 4 Give names and formulae of three alkalis. Name three bases that are not alkalis.
- 5 List four common properties of alkalis.
- 6 Name four indicators that can be used to measure the acidity or alkalinity of solutions. Explain how you would use them to do this.
- 7 Write equations for three acid–base reactions.
- 8 Write the equation for the reaction between barium hydroxide and hydrochloric acid in three different ways—neutral species, complete ionic, and net ionic forms.
- 9 Write equations for two other neutralisation reactions. Give a general equation for neutralisation involving the hydroxide ion.
- 10 Name and give formulae for five salts.
- 11 Write a chemical equation that involves spectator ions.
- 12 Give the name and formula of an oxyacid of each of carbon, nitrogen, sulfur and phosphorus.
- 13 Give names and formulae for four acidic, four basic and two neutral oxides.
- 14 Name and give the formulae for two amphoteric oxides.
- 15 Write equations to demonstrate the acidic nature of the oxides you classed as acidic in Question 13.
- 16 Write an equation for a reaction between an acidic oxide and a basic oxide.
- 17 How do basic–acidic properties of oxides change in going across the Periodic Table from left to right?
- 18 How does the solubility of carbon dioxide in water depend upon the pressure of carbon dioxide above the solution and upon temperature? Write an equation for the dissolution reaction (which is exothermic) and show how Le Chatelier’s principle explains these solubility changes.
- 19 List three acidic oxides that are present in the atmosphere and explain how they get there.
- 20 Describe the detrimental effects (if any) of these oxides being in the atmosphere and explain how they are removed from the atmosphere.
- 21 What is acid rain and why is it detrimental to the environment? Name two pollutants which cause it. Give equations to illustrate.
- 22 What volume of hydrogen gas is produced at 100 kPa pressure and 25°C when 0.15 mol zinc reacts with excess hydrochloric acid?
- 23 Name three acids that are common food additives and give their formula or structure.
- 24 Many acids are covalent molecular substances which ionise when dissolved in water. Write two equations to illustrate this.
- 25 Write an equation which gives  $[H_3O^+]$  in terms of pH.

- 26** What is  $[\text{H}_3\text{O}^+]$  in solutions of pH 5 and 10?
- 27** What relation exists between  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  in aqueous solution?
- 28** What is the numerical value of the ionic product constant of water at 298 K?
- 29** In terms of pH, what is:
- a** a neutral solution
  - b** an acidic solution
  - c** an alkaline solution?
- 30** How would you decide experimentally whether an acid was strong or weak?
- 31** Name the three most common strong acids.
- 32** Name three weak acids. Give formulae for them.
- 33** 0.1 mol/L solutions of acids HX and HY have pHs of 1.0 and 3.0 respectively. Are acids HX and HY strong or weak? Explain.
- 34** What is the difference between a *strong* acid and a *concentrated* acid?

# CHAPTER 5

# Acids—changing concepts, use in analysis and making esters from

## IN THIS CHAPTER

Some history of the concept of acids  
Brönsted–Lowry concept of acids and bases  
Conjugates  
Importance of each definition of acids  
Mono-, di- and triprotic acids  
Salts as acids and bases  
Amphiprotic substances  
Neutralisation  
Volumetric analysis  
Primary standards and standard solutions

Preparing a standard solution  
Using volumetric glassware  
Choice of indicator  
Buffer solutions  
Buffers in nature  
Neutralisation and safety  
Alkanols and alkanoic acids  
Their melting and boiling points  
Esters  
Occurrence and uses of esters

The concept of an acid, like all concepts in science, has developed as our knowledge has increased. Let us briefly review this development.

### 5.1 SOME HISTORY

Originally, an acid was a substance that had a sour taste (vinegar, lemon juice) and which reacted with certain metals (such as zinc and iron).

Antoine Lavoisier, in about 1780, proposed that *acids were substances that contained oxygen*; in fact the name ‘oxygen’ derives from Greek words meaning ‘produces sour taste’. However this theory was soon disproved: many oxygen-containing substances were basic (such as sodium and calcium oxides) and some acidic substances (such as hydrochloric acid—called muriatic acid at that time) were distinctly acidic but contained no oxygen.

Humphry Davy in 1815 suggested that *acids were substances that contained replaceable hydrogen*—hydrogen that could be partly or totally replaced by metals. When acids reacted with metals they formed *salts* (such as  $\text{ZnCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{NaNO}_3$ ). *Bases* were substances that reacted with acids to form salts and water. These definitions worked quite well for most of that century.

Svante Arrhenius in 1884 proposed that *acids were substances that ionised in solution to produce hydrogen ions*: acids were strong if they ionised completely (hydrochloric, nitric), and weak if they ionised only slightly (acetic, formic). It was the Arrhenius definition of acids that was presented in Section 4.1. Arrhenius defined a base as a substance that in solution produced hydroxide



Antoine Lavoisier (1743–1794), centre, in black, was a great pioneering chemist, though he was wrong about acids

ions. This definition is somewhat narrow in that it excludes metallic oxides that are distinctly basic.

However there are some inadequacies with the Arrhenius definition of an acid. First, it does not give due recognition to the role of the solvent. Ionisation of an acid is not something the acid does in isolation: rather it is a reaction between the acid molecule and the solvent. Whether an acid is strong or weak depends not only upon the nature of the acid itself, but also upon the nature of the solvent it is dissolved in: hydrochloric acid in water is a strong acid, but when dissolved in diethyl ether it is quite weak. Second, acid–base reactions often occur in solvents in which the ‘acid’ is not ionised at all: hydrochloric acid, when dissolved in benzene, is not ionised yet it still reacts with ammonia to form ammonium chloride. Hydrochloric acid is still reacting with a base to form a salt, although the acid does not ionise in that solvent.

In 1923 two chemists, Brönsted from Denmark and Lowry from Britain, independently proposed new definitions for acids and bases in terms of proton donors and acceptors: these definitions overcome the difficulties, and are the most widely used definitions today.

Because of their relevance to chemical analysis, we shall consider the Brönsted–Lowry definitions and their consequences in detail.

## 5.2 THE BRÖNSTED–LOWRY CONCEPT OF ACIDS AND BASES

An **acid** is a substance that, in solution, tends to give up protons (hydrogen ions), and a **base** is a substance that tends to accept protons; or more briefly:

An acid is a proton donor.

A base is a proton acceptor.



Humphry Davy (1778–1829), among many scientific achievements, including the Davy safety lamp for miners, provided the first successful working definition of an acid

If a substance, HA, has a greater tendency to give up protons than the solvent, then that substance in that solvent will be an acid. If the solvent is water, then:



Remember from p. 198 *CCPC* and Section 4.14 of this book the hydrogen ion is more correctly written as  $\text{H}_3\text{O}^+$  rather than just  $\text{H}^+$ .

Similarly, if substance B has a greater tendency to accept protons than the solvent has, then B will be a base in that solvent. If the solvent is water, then:

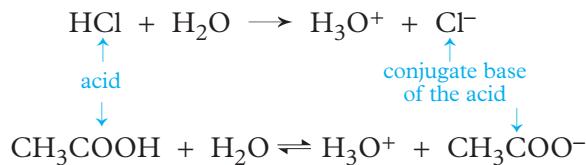


In this way, the Brönsted–Lowry concept necessarily relates acidity and basicity to the structure of both the substance *and* the solvent; production of hydrogen ions is seen to be due not solely to the properties of the acid, but rather to the properties of the acid *relative to those of the solvent*.

The Brönsted–Lowry definitions bring with them the idea of conjugates.

## Conjugates

An acid gives up a proton to form what is called its **conjugate base**:



That is:

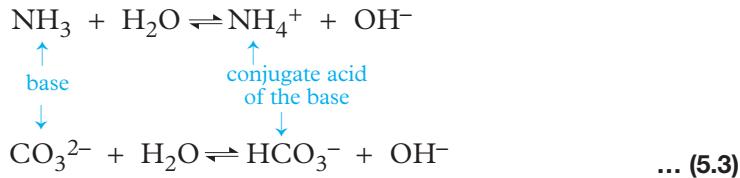


The reaction product is called a conjugate *base* because in solution it tends to gain (accept) a proton:



The acetate ion is acting here as a base. ‘Conjugate’ means ‘linked with’—linked with the acid in question, acetic acid.

Similarly, a base accepts a proton to form what is called its **conjugate acid**:



That is:



The reaction product is called a conjugate *acid* because in solution it tends to give up (donate) a proton:



The ammonium ion is acting here as an acid.

Some common acids with their conjugate bases, and some common bases with their conjugate acids, are shown in Table 5.1. By the Brönsted–Lowry

definitions, anions and cations as well as neutral molecules can be acids and bases.

**TABLE 5.1 Some common acids and bases and their conjugates**

Acid	Conjugate base	Base	Conjugate acid
HCl	Cl <sup>-</sup>	OH <sup>-</sup>	H <sub>2</sub> O
HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	C <sub>5</sub> H <sub>5</sub> N <sup>a</sup>	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup>
HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CN <sup>-</sup>	HCN
NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	H <sub>2</sub> CO <sub>3</sub>
H <sub>2</sub> O	OH <sup>-</sup>	S <sup>2-</sup>	HS <sup>-</sup>
H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>

<sup>a</sup> pyridine, a weak base

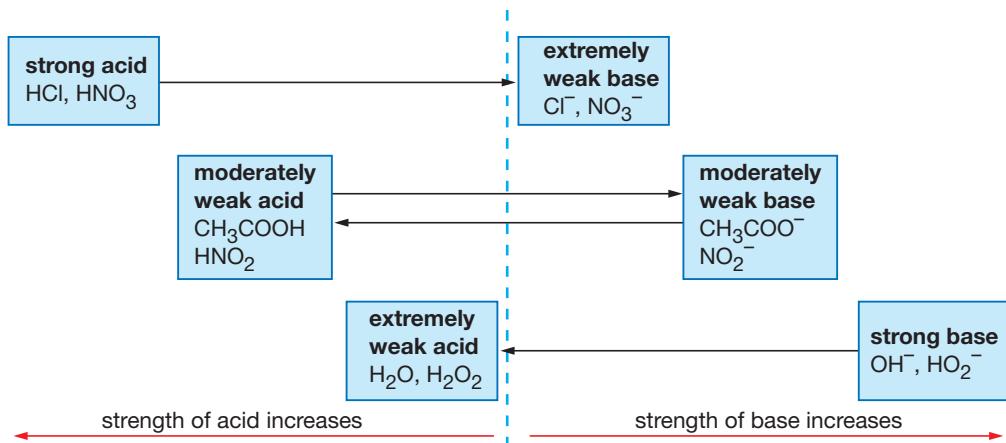
## Relative strengths of acid–base conjugates

The conjugate base of a strong acid is an extremely weak base; this means that the base reacts with water to only a minute (usually negligible) extent. The strong acids, HCl and HNO<sub>3</sub>, react completely with water (to form Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>); consequently the conjugate bases, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, do not react significantly with water. This is important for explaining pH of salt solutions (Section 5.5).

The conjugate base of a weak acid is a weak base, so both acid and base react with water to a significant extent (as Equation 5.2 shows).

The conjugate acid of a strong base is an extremely weak acid; this means that the acid reacts with water to only a minute (usually negligible<sup>†</sup>) extent.

Figure 5.1 shows the relation between the strengths of the acid and base in conjugate pairs.



**FIGURE 5.1**  
Relative strengths of the members of acid–base conjugate pairs

<sup>†</sup> However the minute extent to which the acid, water (conjugate acid of the base OH<sup>-</sup>) reacts with water (its self-ionisation, Section 4.16)—about one molecule in four billion—is of considerable significance for the pH of aqueous solutions (Sections 4.16 to 4.18).



## Exercises

- 1 Write equations showing the acidic nature of the following substances in aqueous solution:

<b>a</b> $\text{HClO}_2$	<b>*c</b> $\text{HAsO}_2^-$	<b>*e</b> $\text{H}_3\text{PO}_3$
<b>b</b> $\text{HOBr}$	<b>*d</b> $\text{H}_2\text{S}$	<b>f</b> $\text{NaHSO}_4$
- 2 Write equations showing the basic nature of the following substances in aqueous solution:

<b>a</b> methylamine, $\text{CH}_3\text{NH}_2$	<b>*d</b> hypochlorite ion, $\text{ClO}^-$
<b>b</b> hydrazine, $\text{N}_2\text{H}_4$	<b>*e</b> potassium sulfide, $\text{K}_2\text{S}$
<b>c</b> cyanide ion, $\text{CN}^-$	<b>*f</b> sodium hydrogen sulfite, $\text{NaHSO}_3$
- 3 Give the conjugate bases of the acids in Exercise 1, and the conjugate acids of the bases in Exercise 2.
- 4 **a** Give the conjugate bases of the acids  $\text{HCOOH}$ ,  $\text{HOCN}$ ,  $\text{HNO}_2$ ,  $^*\text{HOI}$ ,  $^*\text{H}_3\text{AsO}_4$ ,  $^*\text{H}_2\text{CrO}_4$ ,  $\text{HSO}_4^-$ ,  $^*\text{H}_2\text{PO}_3^-$  and  $^*\text{HPO}_4^{2-}$ .  
**b** Give the conjugate acids of the bases aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ ; pyridine,  $\text{C}_5\text{H}_5\text{N}$ ; hydroxylamine,  $\text{NH}_2\text{OH}$ ;  $^*\text{HS}^-$ ;  $^*\text{HCOO}^-$ ;  $\text{H}_2\text{PO}_4^-$ ;  $^*\text{CO}_3^{2-}$ ;  $^*\text{SO}_4^{2-}$ ; oxide,  $\text{O}^{2-}$ .
- 5 **a** In each of the following reactions which reactant is an acid? What is its conjugate base?
  - i**  $\text{NH}_4^+ + \text{HCOO}^- \rightleftharpoons \text{NH}_3 + \text{HCOOH}$
  - ii**  $\text{CO}_3^{2-} + \text{HCN} \rightleftharpoons \text{HCO}_3^- + \text{CN}^-$
  - \*iii**  $\text{H}_2\text{O}_2 + \text{HS}^- \rightleftharpoons \text{H}_2\text{S} + \text{HO}_2^-$**b** In each of the following reactions which reactant is a base? What is its conjugate acid?
  - i**  $\text{HNO}_2 + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NO}_2^-$
  - ii**  $\text{CH}_3\text{O}^- + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{OH} + \text{NH}_2^-$
  - \*iii**  $\text{N}_2\text{H}_4 + \text{HOCl} \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OCl}^-$

## 5.3 IMPORTANCE OF EACH DEFINITION OF AN ACID

We have looked at four definitions of acids—those by Lavoisier, Davy, Arrhenius and Brönsted–Lowry (Sections 5.1 and 5.2). Some comment about the importance of each definition is warranted.

Lavoisier's definition was wrong. However it did stimulate a lot of research into the composition of acids and created awareness of the need to define an acid.

The Davy definition defined an acid in terms of its properties and reactions; it helped *classify* substances without trying to *interpret* properties.

The Arrhenius definition increased our understanding of acids by *interpreting* acid properties in terms of the hydrogen ions they produced, and explained weak and strong acids in terms of the extent to which the ionisation reaction proceeded. This increased our understanding considerably. Arrhenius's work was a big step forward in developing the concept of an acid. Unfortunately his definition of a base was much less successful in that it was very restrictive (a substance that produced hydroxide ions in solution);

chemists even at that time generally recognised insoluble oxides and carbonates as bases though being insoluble they could not produce hydroxide ions in solution.

The Brönsted–Lowry definition increased our understanding further by showing that acidity depends not just upon the structure of the substance itself but rather on its properties relative to those of the solvent or other reactant present in the solution. It showed that neutralisation did not need to involve ionisation to  $\text{H}^+$  and  $\text{OH}^-$  ions but could proceed directly by proton transfer (as in  $\text{NH}_3 + \text{HCl}$  in benzene solution). In addition the Brönsted–Lowry concept showed that the hydrolysis of salts (reaction with water, Section 5.5) to produce pHs significantly different from 7.0 was nothing more than simple acid or base reactions. The Brönsted–Lowry concept also provided a sound basis for the quantitative treatment of acid–base equilibria and pH calculations.

## 5.4 MONOPROTIC, DIPROTIC AND TRIPROTIC ACIDS

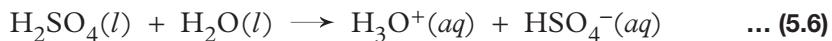
Some acids, such as hydrochloric,  $\text{HCl}$ , and nitric,  $\text{HNO}_3$ , are able to give up only one proton (hydrogen ion) per molecule of acid. These acids are called *monoprotic*, meaning one proton.

A **monoprotic acid** is one that forms one proton (hydrogen ion) per molecule.

Other acids, such as sulfuric,  $\text{H}_2\text{SO}_4$ , and carbonic,  $\text{H}_2\text{CO}_3$ , are able to give up two protons (hydrogen ions) per molecule of acid:



Such acids are called **diprotic**. The ionisation of a diprotic acid occurs in a stepwise fashion:



In Brönsted–Lowry terms,  $\text{HSO}_4^-$  is the conjugate base of  $\text{H}_2\text{SO}_4$ . However  $\text{HSO}_4^-$  is itself an acid (because it can undergo Reaction 5.7):  $\text{SO}_4^{2-}$  is the conjugate base of the acid  $\text{HSO}_4^-$ .  $\text{H}_2\text{SO}_4$  is a strong acid (completely ionised) while  $\text{HSO}_4^-$  is a weak acid (not completely ionised).

A consequence of the stepwise ionisation of diprotic acids such as sulfuric is that such acids can form two series of salts—the normal ones such as sulfates, for example  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$ , and another set which we call **hydrogen salts** or **acid salts**, for example sodium hydrogen sulfate,  $\text{NaHSO}_4$ , sometimes called sodium bisulfate. Similarly, carbonic acid forms carbonates, e.g. calcium carbonate,  $\text{CaCO}_3$ , and also forms *hydrogen carbonates*, such as sodium hydrogen carbonate,  $\text{NaHCO}_3$  (sodium bicarbonate, or to cooks and those who overeat, bicarbonate of soda).

Phosphoric acid,  $\text{H}_3\text{PO}_4$ , is a **triprotic acid**. It can form three series of salts: ordinary phosphates, such as sodium phosphate,  $\text{Na}_3\text{PO}_4$ ; hydrogen phosphates, such as potassium hydrogen phosphate,  $\text{K}_2\text{HPO}_4$ ; and dihydrogen phosphates, such as calcium dihydrogen phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  (the active constituent of superphosphate fertiliser).

Common diprotic and triprotic acids and the salts they form are shown in Table 5.2.

**TABLE 5.2 Diprotic and triprotic acids and the anions they form**

Acid		Anions formed		Typical salt
sulfuric acid	$\text{H}_2\text{SO}_4$	sulfate hydrogen sulfate	$\text{SO}_4^{2-}$ $\text{HSO}_4^-$	$\text{Na}_2\text{SO}_4$ $\text{KHSO}_4$
carbonic acid	$\text{H}_2\text{CO}_3$	carbonate hydrogen carbonate	$\text{CO}_3^{2-}$ $\text{HCO}_3^-$	$\text{CaCO}_3$ $\text{NaHCO}_3$
sulfurous acid	$\text{H}_2\text{SO}_3$	sulfite hydrogen sulfite	$\text{SO}_3^{2-}$ $\text{HSO}_3^-$	$\text{MgSO}_3$ $\text{KHSO}_3$
phosphoric acid	$\text{H}_3\text{PO}_4$	phosphate hydrogen phosphate dihydrogen phosphate	$\text{PO}_4^{3-}$ $\text{HPO}_4^{2-}$ $\text{H}_2\text{PO}_4^-$	$\text{Na}_3\text{PO}_4$ $\text{K}_2\text{HPO}_4$ $\text{NaH}_2\text{PO}_4$



## Exercises

6 Write the formulae for:

- a potassium hydrogen carbonate
- b ammonium hydrogen sulfate
- \*c sodium hydrogen sulfite

- \*d sodium dihydrogen phosphate
- e lithium hydrogen phosphate
- \*f calcium hydrogen sulfide

7 Name the following salts:

- a  $\text{LiHCO}_3$
- b  $\text{Zn}(\text{HSO}_4)_2$
- \*c  $\text{Cu}(\text{HCO}_3)_2$

- d  $(\text{NH}_4)_2\text{HPO}_4$
- \*e  $\text{NH}_4\text{HS}$
- f  $\text{KH}_2\text{PO}_4$

8 Write equations for the stepwise ionisation of:

- a carbonic acid
- \*b sulfurous acid
- \*c phosphoric acid

## 5.5 SALTS AS ACIDS AND BASES

In Section 4.3 a salt was defined as a compound formed when an acid was neutralised by a base. This may give the impression that solutions of salts are neutral ( $\text{pH} = 7$ ). However as Table 5.3 shows salts may be acidic, basic or neutral.

The reason why the pH of aqueous solutions of many salts is different from 7.0 is that many anions and cations can act as acids or bases.

### Salt solutions with pH greater than 7.0

These contain an anion that is a weak base. The nitrite ion,  $\text{NO}_2^-$ , is the conjugate base of nitrous acid,  $\text{HNO}_2$ :



The nitrite ion therefore accepts a proton from water and so hydroxide ion is formed and pH is greater than 7.0:



As we saw in Section 5.2 the acetate ion is the conjugate base of acetic acid and so it reacts to some extent with water to form hydroxide ion: this makes the

**TABLE 5.3 pH of 0.25 mol/L aqueous solutions of some common salts**

Salt	pH
sodium chloride, NaCl	7.0 <sup>a</sup>
potassium nitrate, KNO <sub>3</sub>	7.0 <sup>a</sup>
sodium sulfate, Na <sub>2</sub> SO <sub>4</sub>	7.0 <sup>a</sup>
sodium hydrogen sulfate, NaHSO <sub>4</sub>	1.3
potassium hydrogen oxalate, KHC <sub>2</sub> O <sub>4</sub>	2.4
ammonium nitrate, NH <sub>4</sub> NO <sub>3</sub>	4.8
potassium nitrite, KNO <sub>2</sub>	8.3
sodium hydrogen carbonate, NaHCO <sub>3</sub>	8.3
sodium acetate, CH <sub>3</sub> COONa	9.1
potassium cyanide, KCN	11.3
sodium carbonate, Na <sub>2</sub> CO <sub>3</sub>	11.8
ammonium acetate, CH <sub>3</sub> COONH <sub>4</sub>	7.0

*a Great care is needed to exclude CO<sub>2</sub> from these solutions to obtain these values.*

solution of sodium acetate alkaline (pH > 7.0).

These two examples illustrate a general situation:

In a salt formed from a weak acid and a strong base (e.g. sodium acetate from acetic acid and sodium hydroxide), the anion is a weak base and so the salt in aqueous solution has a pH greater than 7.

## Salt solutions with pH less than 7.0

These solutions contain an ion that is a weak acid. In sodium hydrogen sulfate, the HSO<sub>4</sub><sup>-</sup> ion, as we saw in Equation 5.7, is a weak acid: it produces H<sub>3</sub>O<sup>+</sup> ions and so the pH is less than 7. The hydrogen oxalate ion, HC<sub>2</sub>O<sub>4</sub><sup>-</sup>, is similarly a weak acid and so it also produces a pH of less than 7.

However not all acid salts produce acidic solutions as sodium hydrogen carbonate in Table 5.3 shows: we will discuss this salt in the next section.

In ammonium nitrate the ammonium ion, NH<sub>4</sub><sup>+</sup>, is the conjugate acid of the weak base ammonia (Equation 5.3), so in solution the NH<sub>4</sub><sup>+</sup> ion produces H<sub>3</sub>O<sup>+</sup> ions (Equation 5.5) which makes the pH of the solution less than 7. It is this acidic nature of the ammonium ion that means gardeners have to add lime to their lawns occasionally if they regularly use ammonium sulfate fertiliser.

Ammonium nitrate illustrates another general situation:

In a salt formed from a weak base and strong acid (e.g. ammonium nitrate from ammonia and nitric acid), the cation is a weak acid and so the salt in aqueous solution has a pH less than 7.

## A salt formed from a strong acid and a strong base

This salt has a pH close to 7.0. This is because (1) as explained in Section 5.2, the conjugate base of a strong acid (e.g. Cl<sup>-</sup> from HCl) does not react with water to any significant extent and so it does not alter the pH, and (2) because by similar arguments the conjugate acid of a strong base (H<sub>2</sub>O from OH<sup>-</sup>) does not react with water sufficiently to alter its pH. Hence the pH of such salts is just the pH of pure water, 7.0.

## A salt formed from a weak acid and a weak base

Such a salt, (for example, ammonium acetate from ammonia and acetic acid) also has a pH close to 7.0, because both the anion and the cation react with water to small extents and so approximately cancel each other.

The pHs of solutions of these different categories of salts are summarised in Table 5.4.

Basically, what we have been considering in this section is the reaction of salts with water, which is called *hydrolysis of salts*.

**Hydrolysis** is a chemical reaction in which a substance reacts with water.<sup>†</sup>

**TABLE 5.4 pH of solutions of salts formed from different types of acids and bases**

	<b>Strong base (NaOH, KOH)</b>	<b>Weak base (<math>\text{NH}_3</math>)</b>
<b>Strong acid (<math>\text{HCl}</math>, <math>\text{HNO}_3</math>)</b>	pH = 7 ( $\text{NaCl}$ , $\text{KNO}_3$ )	pH < 7 ( $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{NO}_3$ )
<b>Weak acid (<math>\text{CH}_3\text{COOH}</math>, <math>\text{HNO}_2</math>)</b>	pH > 7 ( $\text{CH}_3\text{COONa}$ , $\text{KNO}_2$ )	pH = 7 ( $\text{CH}_3\text{COONH}_4$ )

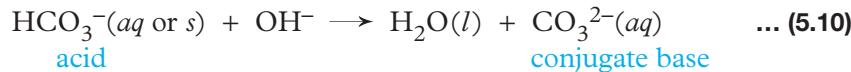
## 5.6 AMPHIPROTIC SUBSTANCES

A substance that can act both as a proton donor and as a proton acceptor is called an **amphiprotic** substance (*amphi* means ‘both’).

The hydrogen carbonate ion is amphiprotic, because in aqueous solution it reacts with water in two ways:



In the first equation  $\text{HCO}_3^-$  is a proton donor (acid), while in the second it is a proton acceptor (base). Both of these reactions occur simultaneously when sodium hydrogen carbonate is dissolved in water but to only small extents (hence the reversible arrows  $\rightleftharpoons$ ). However if placed in alkaline (basic) solution, hydrogen carbonate acts as an acid:



If placed in acid solution hydrogen carbonate acts as a base:



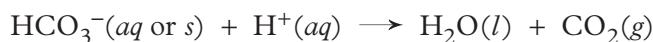
and in both cases the reactions go to completion (hence the one-way arrows  $\longrightarrow$ ). We looked at the equilibrium between carbonic acid,  $\text{H}_2\text{CO}_3$ ,

<sup>†</sup> The distinction between *hydrolysis* and *hydration* (Section 1.5) is this: hydration is the addition of a molecule of water to another molecule to form a new molecule as in hydration of ethylene to form ethanol. It is just one type of hydrolysis reaction. Here we have been considering hydrolysis in which one species reacts with water to form two different species as in  $\text{NO}_2^-$  reacting with water to form  $\text{HNO}_2$  and  $\text{OH}^-$ .

and carbon dioxide gas in Sections 4.6 and 4.8. Because carbon dioxide does not have a very high solubility in water, the carbonic acid breaks up to release carbon dioxide:



As we saw previously this equilibrium lies well towards the  $\text{CO}_2(g)$  side, so  $\text{CO}_2$  comes out of solution. When we add hydrogen carbonate to acid solution, we observe rapid evolution of gas. The overall reaction is often written as:



When hydrogen carbonate is dissolved in pure water, Reactions 5.8 and 5.9 go to only a small extent. When  $\text{HCO}_3^-$  is added to acidic or basic solution, Reaction 5.10 or 5.11 (respectively) goes to completion.

The hydrogen sulfite ion,  $\text{HSO}_3^-$ , is also amphiprotic. It reacts with basic and acidic solutions in the same way as hydrogen carbonate does; in acid solution it releases sulfur dioxide which has a distinctively sharp or choking smell.

Another amphiprotic substance is water. This can be seen from Equations 5.1 and 5.2. In Equation 5.1 the solvent, water, is acting as a proton acceptor, and hence as a base;  $\text{H}_3\text{O}^+$  is the conjugate acid of the base,  $\text{H}_2\text{O}$ . In Equation 5.2 the solvent, water, is acting as a proton donor and therefore as an acid;  $\text{OH}^-$  is the conjugate base of the acid,  $\text{H}_2\text{O}$ .

The solvent, water, can act both as an acid and as a base. If a substance (for example HCl) has a greater tendency to lose protons than water has, then that substance (HCl) is an acid in aqueous solution, and the water acts as a base. If a substance (for example ammonia) has a lesser tendency to lose protons than the solvent has, then that substance ( $\text{NH}_3$ ) in aqueous solution is a base, and the water acts as an acid.

## Exercises

- 9 For each of the salts below, give the formula and state whether you would expect 0.1 mol/L aqueous solutions to have a pH of about 7, less than 7 or greater than 7. Explain why, giving equations where necessary.

- |                  |                    |                      |
|------------------|--------------------|----------------------|
| a barium nitrate | c sodium carbonate | *f potassium bromide |
| b sodium formate | d ammonium nitrate | g sodium cyanide     |
| (methanoate)     | *e sodium sulfite  | *h potassium sulfate |

- 10 The following substances are amphiprotic:

- |                    |  |
|--------------------|--|
| a $\text{HSO}_3^-$ | c $\text{H}_2\text{PO}_4^-$                                |
| *b $\text{HS}^-$   | *d glycine, $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ . |

Write equations for the reactions of each of them with

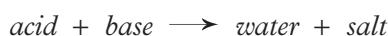
- |         |                      |                       |
|---------|----------------------|-----------------------|
| i water | ii hydrochloric acid | iii sodium hydroxide. |
|---------|----------------------|-----------------------|

Take care to use the correct arrow,  $\rightarrow$  or  $\rightleftharpoons$ , in each equation.



## 5.7 NEUTRALISATION

In Section 4.3, neutralisation was the reaction:



For example:

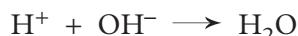


or



Neutralisation reactions are **proton transfer reactions**: in Reaction 5.12 the acid HCl transfers a proton to the base OH<sup>-</sup> (to form H<sub>2</sub>O).

In Section 4.3 we saw that the net ionic reactions for many (but not all) neutralisation reactions was:



or using the more accurate formula for the hydrogen ion,



This shows neutralisation as a proton transfer from the H<sub>3</sub>O<sup>+</sup> ion to the OH<sup>-</sup> ion. There are other forms for neutralisation reactions but they still involve a proton transfer.

In the neutralisation of ammonia by nitric acid:



or in net ionic form (since HNO<sub>3</sub> is completely ionised):



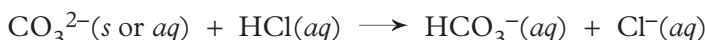
the acid transfers a proton to ammonia (to form the NH<sub>4</sub><sup>+</sup> ion).

Similarly when sodium hydroxide solution neutralises acetic acid:



a proton is transferred from the acetic acid to the base, OH<sup>-</sup> (to form H<sub>2</sub>O).

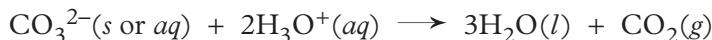
Sodium carbonate reacts with hydrochloric acid: we can consider this as a three-step process:



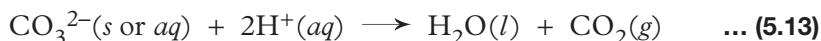
or write it as one overall reaction:



In either case, it is a reaction in which protons are transferred from HCl to the base, CO<sub>3</sub><sup>2-</sup>, and so it is neutralisation. We can write this reaction without the spectator ion, Cl<sup>-</sup>:



or just as



We tend to write equations in terms of H<sub>3</sub>O<sup>+</sup> when we are focusing on the proton transfer aspect of the reaction. When we are using equations for calculating quantities involved in a reaction (Sections 5.8, 5.9) we tend to write them in terms of H<sup>+</sup> because that makes the equations simpler.

## Heat of reaction

Neutralisation is an exothermic reaction (p. 275 CCPC), meaning that heat is liberated as it occurs and that the enthalpy change,  $\Delta H$ , for the reaction is negative. The enthalpy change,  $\Delta H$ , for neutralisation reactions is approximately  $-56 \text{ kJ/mol}$ . It varies by a few  $\text{kJ/mol}$  depending upon whether the acid or base involved is weak or strong and upon the concentration of the solutions involved. It can be measured in the same way as in Example 3 on pp. 278–9 CCPC and summarised in Box 10.1 on p. 279 CCPC.

### Exercises

11 Three common neutralisation reactions are

- a the reaction of hydrochloric acid with calcium oxide
- b the reaction of sulfuric acid with copper hydroxide
- c the reaction of nitric acid with ammonia solution.

Write equations for these reactions and identify the proton transfer that is occurring in each.

12 Sodium sulfite reacts with hydrochloric acid. Write an equation for the reaction. If the reaction mixture is heated a gas with a choking smell is formed. What is this gas? Write an equation for its formation. Would you expect to form the same gas by adding hydrochloric acid to potassium hydrogen sulfite? If yes, write an equation.

13 Nitrous acid reacts with sodium cyanide:



Would you consider this a neutralisation reaction? Explain why or why not.

14 When 25 mL of a solution at  $23.2^\circ\text{C}$  containing  $5.00 \times 10^{-3} \text{ mol}$  sodium hydroxide was mixed with 50 mL of a solution also at  $23.2^\circ\text{C}$  that contained  $6.00 \times 10^{-3} \text{ mol}$  hydrochloric acid in a light plastic beaker, the final temperature of the mixture was  $24.1^\circ\text{C}$ . Calculate the heat released and hence the enthalpy change per mole for the neutralisation reaction. Take the density and specific heat capacity of all solutions involved as  $1.00 \text{ g/mL}$  and  $4.2 \text{ J K}^{-1} \text{ g}^{-1}$  respectively, assume that the container had negligible heat capacity and that heat losses to the surroundings were negligible.

15 50 mL of a  $0.28 \text{ mol/L}$  solution of ammonia at  $19.6^\circ\text{C}$  was added to 100 mL of a  $0.14 \text{ mol/L}$  solution of nitric acid also at  $19.6^\circ\text{C}$ . The final temperature was  $20.7^\circ\text{C}$ . Write a net ionic equation for the reaction that occurred. Making the same assumptions and using the same values for density and heat capacity as in Exercise 14, calculate the enthalpy change for this reaction.



## 5.8 VOLUMETRIC ANALYSIS

Neutralisation reactions are widely used in what is called volumetric analysis.

**Volumetric analysis** is a form of chemical analysis in which the concentration (or amount) of a substance A is determined by measuring the volume of a solution of known concentration of another substance B which is just sufficient to react with all of the sample of A.

The process of determining the ‘just sufficient’ volume is called **titration**. For a titration to work we need to be able to detect what is called the equivalence point of the reaction.

## Equivalence point

The **equivalence point** of a chemical reaction is the point at which the amounts of the two reactants are just sufficient to cause complete consumption of both reactants.

The equivalence point is sometimes called the **end point**.

Suppose we are adding sulfuric acid to sodium hydroxide. If we have, say, 0.10 mole of sodium hydroxide, then the equivalence point is when 0.050 mole of sulfuric acid has been added, because the equation for the reaction is:



We detect the equivalence point of a titration by using an indicator. We saw in Section 4.19 (Table 4.7) that indicators change colours over fairly narrow pH ranges. During an acid–base titration the pH changes quite suddenly at the equivalence point—as the solution in the flask changes from slightly alkaline to slightly acidic (or *vice versa*). This means that a suitable indicator in the solution in the flask will change colour quite sharply at the equivalence point.

## Acid–base titrations

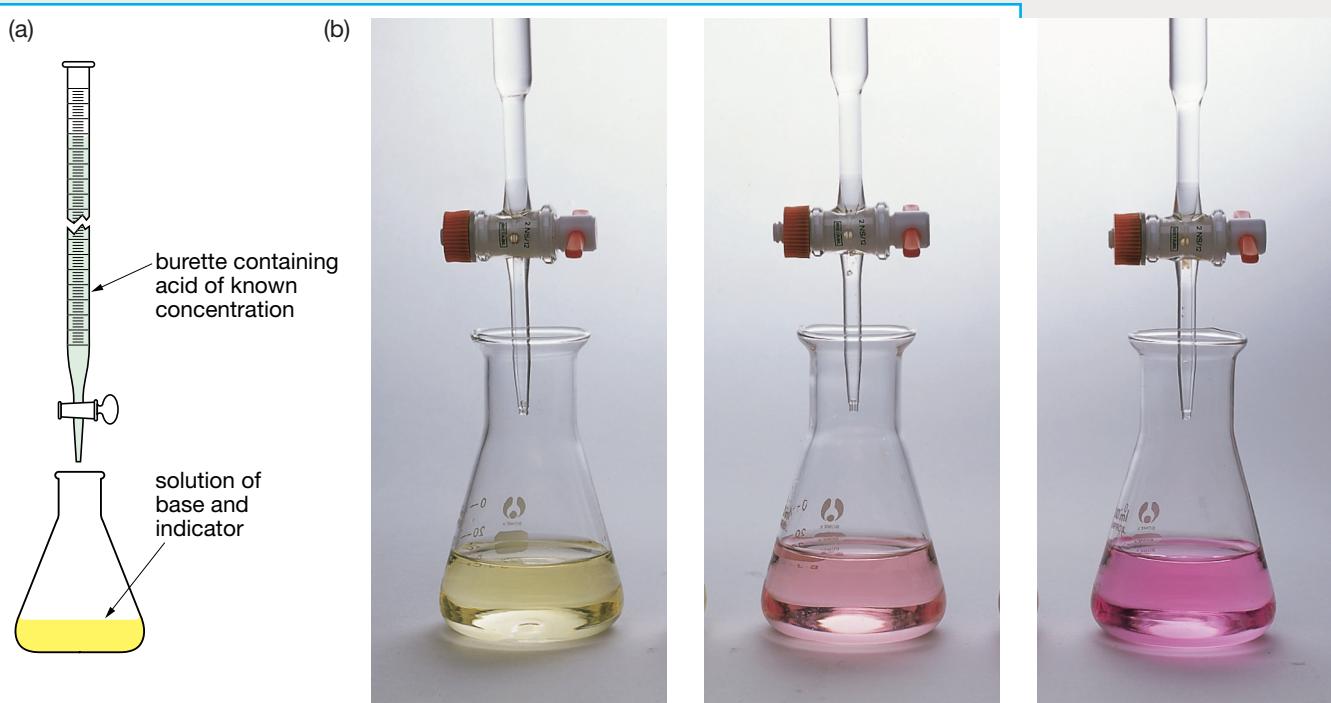
The basic steps for performing an acid–base titration are:

- Fill a *burette* (Figure 8.5 on p. 215 CCPC) with a solution of known concentration (for example sulfuric acid) and adjust the solution level in the burette to the zero mark<sup>†</sup>; the solution in the burette is called the **titrant**.
- Place a solution of the sample to be analysed (for example sodium hydroxide) in a flask under the burette.
- Add one or two drops of a suitable indicator to the flask.
- Place a white tile or card under the flask to make it easier to detect the colour change in the indicator without overshooting the equivalence point.
- Slowly run solution from the burette into the flask with continuous swirling until the indicator just changes colour; near the equivalence point add the titrant slowly, one drop at the time.
- Read the volume delivered by the burette as accurately as possible.
- Repeat the titration several times until a consistent volume of titrant is obtained (volumes differing by no more than about  $\pm 0.1$  or  $\pm 0.2$  mL); often the first titration will overshoot the equivalence point, because we do not know at what approximate volume it will occur.
- Calculate the required concentration or amount of the unknown using the basic principles of molarity calculations explained on pp. 218–20 CCPC.

A typical arrangement for performing a titration is shown in Figure 5.2(a), while (b) shows the colour change for methyl red at the equivalence point.

For volumetric analysis we need solutions of known concentration to use in titrations of the unknown solutions. This means that we need some substances of high purity that we can use as primary standards.

<sup>†</sup> Alternatively, accurately read *and record* the solution level in the burette, then when the equivalence point is reached, read the final level of the solution; the difference between the final and initial levels in the burette is the volume of titrant used (called the *titre*).



**FIGURE 5.1**  
 (a) A typical set-up for performing a titration;  
 (b) methyl red indicator just before, at, and just after the equivalence point as acid is added from the burette to alkali in the flask

## 5.9 PRIMARY STANDARDS AND STANDARD SOLUTIONS

We cannot make solutions of precisely known concentration of our common acids, HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, by accurate dilution of concentrated acids because the concentration of these acids changes with time. This is due to volatilisation of HCl and HNO<sub>3</sub> and to absorption of water by H<sub>2</sub>SO<sub>4</sub> on standing. Similarly, we cannot prepare accurately known solutions of NaOH or KOH because both of them absorb moisture from the air and also react with carbon dioxide from the air (to form Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>). Even if we could dry out the solid, we could not be sure it was pure hydroxide.

Hence it is necessary to choose a pure stable substance with which to make up a first accurately known solution for use in titrations. Such a substance is called a primary standard.

A **primary standard** in volumetric analysis is a substance of sufficiently high purity and stability that a solution of it, of accurately known concentration, can be prepared by weighing out the desired mass, dissolving it in water, and making the volume up to an accurately known value.

The resulting solution is known as a **standard solution**—a solution of accurately known concentration. A standard solution is made up in a *volumetric flask* (p. 215 CCPC).

For acid–base titrations, sodium carbonate and sodium hydrogen carbonate are suitable primary standards. Both chemicals, after drying, have high purity and can be accurately weighed out, dissolved in water and made up to the required volume.

Such a standard solution can be used in a titration with an acid solution in order to *standardise* (measure the concentration of) the acid solution. The acid solution can then be used to determine the concentrations of other solutions.

## Key equations

The key equations for calculating results from a volumetric analysis are Equations 5.1 and 8.9 from pp. 136 and 217 *CCPC*, namely:

$$\text{Number of moles} = \frac{\text{mass}}{\text{molar mass}} \quad \dots (5.14)$$

$$\text{Molarity} = \frac{\text{number of moles}}{\text{volume of solution in litres}} \quad \dots (5.15)$$

Examples 1 and 2 will illustrate the general procedure.



### Example 1

15.922 g sodium carbonate was dissolved in water and made up to 500 mL in a volumetric flask. Calculate the molarity of this solution.

We calculate the molarity of the sodium carbonate solution using Equations 5.14 and 5.15.

$$\begin{aligned}\text{Molar mass of } \text{Na}_2\text{CO}_3 &= 2 \times 23.0 + 12.0 + 3 \times 16.0 \\ &= 106.0 \text{ g/mol}\end{aligned}$$

From Equation 5.14:

$$\begin{aligned}\text{number of moles of } \text{Na}_2\text{CO}_3 \text{ taken} &= \frac{15.922}{106.0} \\ &= 0.1502 \text{ mol}\end{aligned}$$

From Equation 5.15:

$$\begin{aligned}\text{molarity} &= \frac{0.1502}{0.500} \\ &= 0.3004 \text{ mol/L}\end{aligned}$$



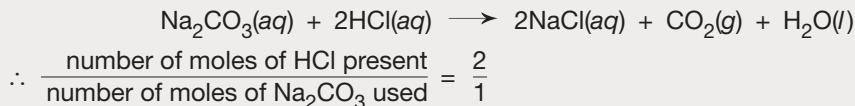
### Example 2

To standardise a roughly 0.4 mol/L hydrochloric acid solution, 25.0 mL of the sodium carbonate solution from Example 1 was titrated with this hydrochloric acid. It required 38.2 mL of the acid to reach the equivalence point. Calculate the accurate molarity of the hydrochloric acid solution.

From the titration, using Equation 5.15 rearranged,

$$\begin{aligned}\text{number of moles of } \text{Na}_2\text{CO}_3 \text{ used} &= \frac{0.3004 \times 25}{1000} \\ &= 7.51 \times 10^{-3} \text{ mol}\end{aligned}$$

The equation for the titration is:



$$\begin{aligned}\text{So number of moles of HCl present} &= 2 \times (\text{number of moles of } \text{Na}_2\text{CO}_3 \text{ used}) \\ &= 2 \times 7.51 \times 10^{-3} \\ &= 0.0150 \text{ mol}\end{aligned}$$

This amount of HCl was present in 38.2 mL ( $= 0.0382 \text{ L}$ )

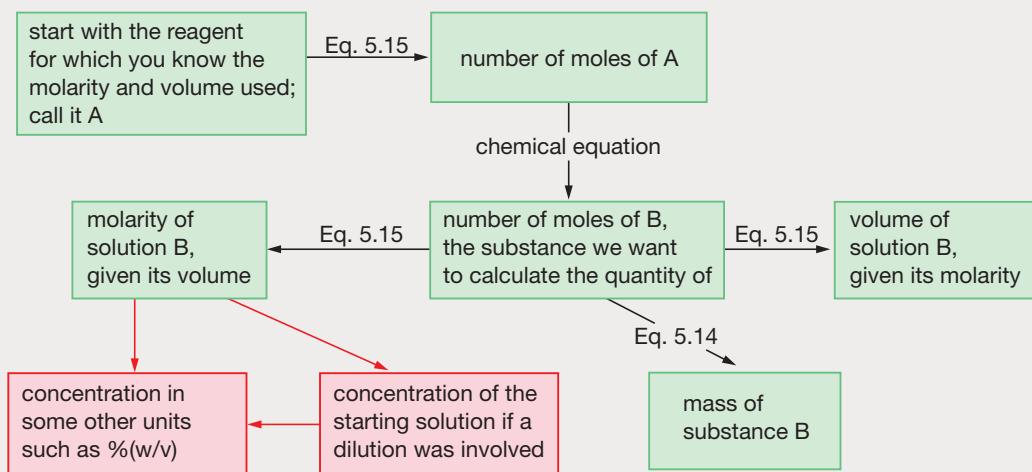
$\therefore$  by Equation 5.15

$$\begin{aligned}\text{molarity of HCl solution} &= \frac{0.0150}{0.0382} \\ &= 0.393 \text{ mol/L}\end{aligned}$$

The accurate concentration of the ‘roughly 0.4 mol/L’ hydrochloric acid is **0.393 mol/L**.

The steps involved in a typical volumetric analysis calculation are shown in Figure 5.3

FIGURE 5.3  
The steps in a volumetric analysis calculation



In volumetric analysis samples to be analysed are often quantitatively diluted so that the volume of titrant they require is within the accuracy range of the burette, say between 15 and 50 mL for a 50 mL burette. The method of calculating concentration after dilution was described on p. 215 CCPC. The following example illustrates a typical volumetric analysis using a quantitative dilution.

### Example 3

In order to determine the concentration of acetic acid in a particular brand of vinegar, a chemist first diluted 10 mL of the vinegar to exactly 100 mL, then took 25 mL of the dilute solution and titrated it with 0.105 mol/L sodium hydroxide. 15.9 mL of the sodium hydroxide solution was needed. Calculate the molarity and the percentage (w/v) of acetic acid in the original vinegar.



$$\begin{aligned} \text{Number of moles of NaOH used in the titration} &= 0.0159 \times 0.105 \\ &= 1.67 \times 10^{-3} \text{ mol} \end{aligned}$$

The chemical equation for the titration reaction is:



From this equation:

$$\begin{aligned} \text{number of moles of acetic acid present in the titrated sample} &= \text{number of moles of NaOH used} \\ &= 1.67 \times 10^{-3} \end{aligned}$$

This amount of acetic acid was in 25 mL (= 0.025 L) of the dilute solution

$$\begin{aligned} \text{so molarity of dilute solution} &= \frac{1.67 \times 10^{-3}}{0.025} \\ &= 0.0668 \text{ mol/L} \end{aligned}$$

This is the molarity of acetic acid in the *diluted* vinegar. To calculate the molarity of the concentrated solution ( $Z_1$ , say), we note (as explained on p. 215 CCPC) that:

$$\text{number of moles of acetic acid in 10 mL concentrated solution} = \frac{\text{number of moles of acetic acid in 100 mL dilute solution}}{10}$$

Therefore

$$\frac{Z_1 \times 10}{1000} = \frac{0.0668 \times 100}{1000}$$

giving

molarity of acetic acid  
in the original vinegar,  $Z_1 = 0.668 \text{ mol/L}$

The percentage (w/v) is the mass of acetic acid per 100 mL of solution. From the molarity we have 0.0668 mol per 100 mL.

$$\begin{aligned}\text{Molar mass of acetic acid, } \text{CH}_3\text{COOH} &= 2 \times 12.0 + 4 \times 1.01 + 2 \times 16.0 \\ &= 60.0 \text{ g/mol} \\ \text{so } 0.0668 \text{ mol/100 mL} &= 0.0668 \times 60.0 \\ &= 4.01 \text{ g/100 mL}\end{aligned}$$

Therefore the percentage of acetic acid in the original vinegar is **4.01% (w/v)**.

In performing such calculations we must ensure that the answer is given to the correct number of *significant figures*. In Example 3 both the concentration of the sodium hydroxide solution (0.105 mol/L) and the volume of sodium carbonate solution needed (15.9 mL) had three significant figures, so the answer must have three significant figures, 0.668 mol/L and 4.01%. This would be a good time to revise the use of significant figures in the appendix on pp. 310–11 CCPC.

The vinegar and the equipment used to analyse it in Example 3



For volumetric analysis to be accurate, we must pay attention to some practical details, first to ensure that the standard solutions we make have precisely the concentrations we expect, and secondly to ensure that we reach the exact equivalence point in the titration.

## 5.10 PREPARING A STANDARD SOLUTION

The accuracy of any volumetric analysis depends upon the care taken in preparing the solution of the primary standard (Section 5.9) upon which the analysis is based. Hence it is essential to ensure:

- 1 that the substance being used as the primary standard is as *pure as possible*, and particularly that it is *free of moisture*: drying in an oven and cooling in a desiccator are the usual precautions in this regard

- 2** that it is weighed as accurately as possible
- 3** that the volumetric flask has been thoroughly cleaned (though it may be left wet with pure water since water will be added in making up the solution)
- 4** that care is taken to transfer *all* of the solute from the beaker used for weighing into the volumetric flask
- 5** that the solute is completely dissolved in water before making the volume up to the graduation mark
- 6** that the volume of solution is made accurately to the graduation mark on the flask (bottom of meniscus sitting exactly on the mark), preferably using a Pasteur pipette for adding the last few millilitres
- 7** that pure water, either distilled or de-ionised (demineralised), is used for preparation of all solutions and for final rinsing of all glassware
- 8** that after the solution is made up to the mark it is well shaken to ensure uniform mixing before any of it is withdrawn from the flask.

## 5.11 USING VOLUMETRIC GLASSWARE

Before use all volumetric glassware must be thoroughly cleaned and rinsed several times with distilled or de-ionised water. Volumetric flasks and titration flasks may be left wet with water. However *pipettes and burettes must finally be rinsed with a portion of the solution to be measured*. This final rinsing is to prevent dilution of the solution by a film of water remaining on the inside surfaces.

### Using a pipette

To fill a pipette (after rinsing it with some of the solution first), the solution is drawn in, using some type of pipette filler (for hygiene and safety), until the solution is well above the graduation mark, then the solution is carefully run out until the meniscus sits exactly on the mark. To do this it is essential to hold the pipette at eye level to avoid parallax errors. It also helps if a white or plain wall can be used as background to sharpen up the appearance of the meniscus.

The solution is then let run out of the pipette into the required flask by gravity (never blown out) and finally, the pipette is held with its tip in contact with the wall of the receiving flask or beaker for the specified draining time (typically 20 s). The portion of liquid remaining in the tip of the pipette must *not* be blown out, because the pipette has been calibrated on the basis that the remaining portion of liquid stays there. In all operations, the pipette is held vertically.

### Using a burette

Before filling a burette, it is rinsed with a portion of the solution to be dispensed. It is then overfilled, and the excess run out. During this procedure, care is taken to ensure that all air bubbles are removed from the section of the burette between the stopcock and the tip. To do this, it may be necessary to hold the burette at an angle to the vertical. Once any such air bubbles have been removed, the burette is clamped vertically and the liquid level lowered until the meniscus sits exactly on the zero mark. Reading most burettes is facilitated by holding a piece of white card behind the burette; this ‘sharpens up’ the appearance of the meniscus. Burettes are usually marked with 0.1 mL graduations. By estimating the fraction of a division (for example  $\frac{1}{3}$ ,  $\frac{1}{2}$  or  $\frac{2}{3}$ ), it is possible to read a burette to  $\pm 0.03$  mL. Near the end-point of a titration, fractions of a drop can be dispensed by

allowing a portion of a drop to build up on the tip, then washing it into the titration flask with a wash bottle.

When we need to know the volume of a solution accurately, a measuring cylinder must *not* be used, because it is not accurate enough (p. 214 *CCPC*). Its accuracy is only about  $\pm 5\%$  whereas for volumetric analysis we need to measure volumes to  $\pm 0.5\%$  or better.

## 5.12 CHOICE OF INDICATOR

It is important to choose an indicator that will undergo a sharp colour change at the exact equivalence point of the titration. The pH change is slightly different for different strengths of acid and base so different indicators should be used. Table 5.5 lists suitable indicators for the common types of acid–base titration.

**TABLE 5.5 Indicators for different acid–base titrations**

Titration	Suitable indicator	Colour change <sup>a</sup>	pH range
strong acid–weak base	methyl orange	red–yellow	3.1–4.4
	bromophenol blue	yellow–blue	3.0–4.6
	bromocresol green	yellow–blue	3.8–5.4
	methyl red	pink–yellow	4.4–6.0
strong acid–strong base	litmus	red–blue	6–8
	bromothymol blue	yellow–blue	6.2–7.6
	phenol red	yellow–red	6.8–8.4
weak acid–strong base	thymol blue phenolphthalein	yellow–blue colourless–red	8.0–9.6 8.3–10.0

*a* acid colour–base colour

We generally do not perform weak acid–weak base titrations (hence no entry in Table 5.5), because the pH change around the equivalence point of such titrations is not very large. Consequently we do not get a sharp colour change with any indicator; rather the change occurs over several drops, say over about 0.2 mL to 0.5 mL, and so it is not possible to determine the equivalence point accurately.

## Why use different indicators?

The reason for using different indicators for different titrations (as in Table 5.5) is that we want the indicator to change colour at the equivalence point of the reaction and the pH of the equivalence point can vary from one type of titration to another as the following examples illustrate:

- When we titrate an ammonia solution with hydrochloric acid (strong acid–weak base), at the equivalence point we have a solution of ammonium chloride:



As we saw in Section 5.5 a solution of ammonium chloride has a pH < 7 (because  $\text{NH}_4^+$  is a weak acid and so produces some  $\text{H}^+$  ions), so we need an indicator that changes colour at pH < 7, meaning any one of the four in the first row of Table 5.5.

- When we titrate a solution of acetic acid with sodium hydroxide solution

(weak acid-strong base), at the equivalence point we have a solution of sodium acetate:



As we saw in Section 5.5, a solution of sodium acetate has a pH > 7 (because the acetate ion is a weak base that reacts with water to a small extent to produce some OH<sup>-</sup> ions) and so we need an indicator that changes colour at pH > 7.

### To determine which indicator to use for an acid-base titration

- Decide what salt is present at the equivalence point.
- Determine whether either ion of that salt is a weak acid or a weak base or neither.
- Hence decide whether the pH of its solution will be greater than, approximately equal to or less than 7.
- Select an indicator that changes colour in that pH region (less than, around about or greater than 7).

### Exercises

- 16 5.267 g anhydrous sodium carbonate was dissolved in water in a volumetric flask and the volume made up to 250 mL. 10 mL of this solution was pipetted into a conical flask and titrated with hydrochloric acid. 21.3 mL was needed to reach the equivalence point. Calculate the molarity of the hydrochloric acid solution.

This solution was then used to determine the concentration of an unknown barium hydroxide solution. 25 mL of the barium hydroxide solution required 27.1 mL hydrochloric acid solution for exact neutralisation. Calculate the molarity of the barium hydroxide solution. In addition, calculate its concentration in grams per litre.

- 17 Phthalic acid is a weak diprotic acid for which we can write the formula as H<sub>2</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>). Potassium hydrogen phthalate, KH(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>), is a good primary standard for standardising alkali solutions. It contains one acidic hydrogen per formula unit. 0.917 g potassium hydrogen phthalate was dissolved in water and titrated with an approximately 0.2 mol/L sodium hydroxide solution; 27.2 mL hydroxide solution was needed to reach the end point. Calculate the accurate molarity of the hydroxide solution.

- 18 What indicator would you use for each of the three titrations in Exercises 16 and 17? Justify your choice.

- 19 The standard sodium hydroxide solution from Exercise 17 was used to determine the concentration of acetic acid in a particular brand of vinegar. 50 mL of the vinegar (by pipette) was accurately diluted to 250 mL (volumetric flask), and then 25 mL aliquots of this diluted solution were titrated with the sodium hydroxide solution. The results of successive titrations were 21.95, 21.60, 21.55 and 21.60 mL. Calculate the molarity and % (w/v) of acetic acid in the original vinegar.

- 20 List the precautions you would take to ensure the accuracy of the analysis in Exercise 19.

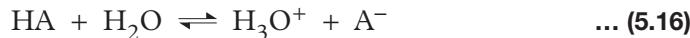
- 21 ‘Cloudy ammonia’ is often used in the home as a cleaning agent. To determine the concentration of ammonia in the solution, a chemist first accurately diluted 25 mL (by pipette) to 500 mL (volumetric flask), then titrated 25 mL (by pipette) of the diluted solution with 0.151 mol/L nitric acid solution; it required 27.2 mL. Calculate the molarity of the original ammonia solution.



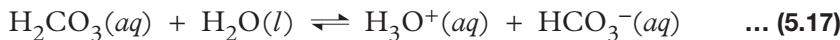
- 22** 25 mL of sulfuric acid from a car battery was accurately diluted to 500 mL. 25 mL of the diluted solution was titrated with 0.206 mol/L sodium hydroxide. It required 38.8 mL. Calculate the molarity of the original battery acid and its concentration in grams per litre. If 50 mL of this acid were spilt on the bench, how much anhydrous sodium carbonate would be needed to neutralise it?
- 23** The acidity of a particular white wine was determined by titrating 25 mL of the wine with 0.0511 mol/L sodium hydroxide solution; 8.7 mL was required. Calculate the molarity of hydrogen ions in the wine. Assume that the hydrogen ions come entirely from diprotic tartaric acid,  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , and calculate the concentration of tartaric acid in the wine in grams per 100 mL.
- \*24** Suppose you wanted to determine the percentage purity of a sample of washing soda, sodium carbonate decahydrate, that you had just purchased. Your laboratory has a solution of hydrochloric acid labelled 0.25 mol/L. It also has the usual range of pure chemicals and indicator solutions, an accurate mass balance and a full range of volumetric glassware. Explain fully how you would accurately determine the percentage purity of the washing soda. Include at least one diagram and give all experimental details. Name the indicator you would use and explain why.
- 25** Which indicator would you use for each of the following titrations? Explain why.
- formic (methanoic) acid with sodium hydroxide
  - ammonia with nitric acid
  - sulfuric acid with potassium hydroxide
  - \*d** nitric acid with sodium hydrogen carbonate
  - \*e** nitrous acid with sodium hydroxide
- 26 a** Oxalic acid dihydrate,  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ , can be used as a primary standard for standardising alkali solutions. 0.291 g diprotic oxalic acid required 18.2 mL of a potassium hydroxide solution for exact neutralisation. Calculate the molarity of the hydroxide solution.
- b** This hydroxide solution was used to determine the concentration of acetic acid in a particular type of vinegar. 10 mL aliquots (by pipette) were titrated with the hydroxide solution. The volumes of hydroxide solution in successive titrations were 24.90, 24.35, 24.45 and 24.40 mL. Calculate the molarity of acid in the vinegar. Assuming that acetic acid is the only acid present in the vinegar, calculate the percentage (w/v) of it in the vinegar.
- c** A student suggested that a more direct way of determining the concentration of acid in the vinegar would be to prepare a standard solution of sodium hydrogen carbonate (a good primary standard) and use it to titrate the vinegar directly. Why is this not a good way of accurately determining the acid concentration in the vinegar?

## 5.13 BUFFER SOLUTIONS

A solution containing comparable amounts of a weak acid and its conjugate base (for example carbonic acid and sodium hydrogen carbonate) is very good at maintaining an approximately constant pH even when strong acid or alkali is added. The equilibrium involved is:



where HA is the weak acid and A<sup>-</sup> its conjugate base; for example



If hydrogen ion (a product) is added to this solution, then by Le Chatelier's principle (Section 4.7) the equilibrium in Equation 5.16 will move to the left:

the base  $A^-$  will combine with much of the added  $H_3O^+$  to form HA in order to minimise the change in  $[H_3O^+]$ .<sup>†</sup> If instead hydroxide ion had been added, it would react with the  $H_3O^+$  and cause pH to rise, but again (by Le Chatelier's principle) the equilibrium in Equation 5.16 will move to the right to try to minimise the change: HA will ionise to produce more  $A^-$ . Because of its ability to maintain an approximately constant pH, such a solution is called a *buffer solution*: it acts as a 'buffer' against change in pH.

A **buffer solution** is a solution that contains comparable amounts of a weak acid and its conjugate base and which is therefore able to maintain an approximately constant pH even when significant amounts of strong acid or strong base are added to it.

Some common buffer solutions are listed in Table 5.6 along with the pH around which they are effective.

**TABLE 5.6 Some common buffer solutions and the pH around which they are effective**

Buffer	pH <sup>a</sup>
acetic acid and sodium acetate: $CH_3COOH$ , $CH_3COONa$	4.6
carbon dioxide (carbonic acid) and hydrogen carbonate: $H_2CO_3$ , $HCO_3^-$	6.4 <sup>b</sup>
sodium dihydrogen phosphate and hydrogen phosphate: $H_2PO_4^-$ , $HPO_4^{2-}$	7.2
ammonium chloride and ammonia: $NH_4^+$ , $NH_3$	9.3
sodium carbonate and hydrogen carbonate: $CO_3^{2-}$ , $HCO_3^-$	10.3

*a* of equimolar mixtures of the acid and its conjugate base.

*b* because of the low solubility of carbon dioxide in water, in nature this buffer works around a pH of 7.

## 5.14 BUFFERS IN NATURE

Because many processes in nature require carefully controlled pH, there are many natural buffer systems. The simplest is the one in Equation 5.17 which involves carbon dioxide from the air (which dissolves as carbonic acid) and hydrogen carbonate (formed from small amounts of dissolved carbonate). It occurs in freshwater lakes and rivers.

In rain water (where there is no source of  $HCO_3^-$  other than  $CO_2$  from the air) this equilibrium produces a pH of about 5.7 to 6.0. In rivers or lakes where some  $HCO_3^-$  comes from dissolving salts out of the rocks around the rivers and lakes, this added  $HCO_3^-$  pushes Equilibrium 5.17 to the left and so raises pH to between 6.5 and 7.5. Rain water is a dilute solution of  $H_2CO_3$ ; this is *not* a buffer solution, because the only source of  $HCO_3^-$  is the ionisation of  $H_2CO_3$  and this provides too little to let the solution act as a buffer. To be a buffer there must be *comparable amounts* of  $H_2CO_3$  and  $HCO_3^-$  in the solution and this means that there must be a source of  $HCO_3^-$  apart from dissolved  $CO_2$ . Hence lakes and rivers are only buffered if there are carbonate rocks available from which  $HCO_3^-$  can be formed.

It was the absence of this buffering action in lakes in Scandinavia that resulted in the first detection of falling pH from acid rain (Section 4.11): the

<sup>†</sup> Remember, square brackets around a chemical formula means concentration of that species (Section 4.15).



Some test kits for home swimming pools measure 'total alkalinity' meaning buffer capacity as well as pH and chlorine (for sterilisation) content

rocks from which the lakes had been carved contained no carbonate to provide  $\text{HCO}_3^-$  to make the buffer.

This  $\text{H}_2\text{CO}_3-\text{HCO}_3^-$  buffer is also used in home swimming pools. If pH is proving difficult to control in the desired range of 7.2 to 7.4, sodium hydrogen carbonate is added to increase the buffering capacity of Equation 5.17. Pool test kits often measure 'total alkalinity' of pool water meaning  $\text{OH}^-$  and  $\text{HCO}_3^-$ . This test is really measuring the buffering capacity of the water: if it is low, sodium hydrogen carbonate needs to be added.

Many of the complex processes occurring in the human body require carefully controlled pH for their proper functioning, because the enzymes involved only operate over narrow pH ranges. This same  $\text{H}_2\text{CO}_3-\text{HCO}_3^-$  buffer controls the pH in many parts of the human body. However it cannot buffer against changing acidity due to changing concentrations of carbon dioxide. Therefore in blood other buffers are involved, most notably haemoglobin which is

itself a weak base (strictly it is amphiprotic), so can act as a buffer; writing Hb for haemoglobin:



Our kidneys purify blood by removing metabolic waste products, many of which are acids. Because the kidneys have to dispose of these acidic wastes without producing an excessively low pH, they too involve buffers. Many acidic wastes are excreted as dihydrogen phosphates which accounts for urine having a pH of about 6.0.

## 5.15 NEUTRALISATION AND SAFETY

Neutralisation reactions are widely used for safety in laboratories and factories where acids or bases are used. Because many acids and alkalis are very corrosive, it is important to neutralise any spills of these substances quickly. In addition sewage authorities put strict limits on the pH of factory and laboratory effluents discharged to sewers (so as not to upset bacterial breakdown). Neutralisation reactions are widely used to ensure that effluents from such places are neither acidic nor alkaline.

Sodium carbonate is widely used to neutralise acidic spills or effluents because:

- it is a stable solid which is easily and safely handled and stored
- it is the cheapest alkali available and
- if too much of it is used there is less danger than from excess sodium hydroxide or lime (calcium hydroxide).

For the controlled neutralisation of alkaline wastes hydrochloric or sulfuric acid is used but as a safety chemical to have readily available for neutralising spills sodium hydrogen carbonate is preferred: it is safe and easy to handle itself and there is no great problem if excess is used. In fact, because it is amphiprotic, it can be used for acid spills as well. Many laboratories have bottles of powdered

sodium hydrogen carbonate conveniently located on shelves and benches for easy access and use in case of spills of acid or alkali.

These examples illustrate the factors that need to be considered in choosing a substance to neutralise acid or alkali spills in factories or laboratories, namely:

- the speed of the reaction for neutralising the spilt material
- the need for a reagent that will not have any harmful effect if an excess of it is used (since it is hard to determine exact quantities for neutralising spills)
- the safety in handling and storing the reagent
- the cost of the reagent
- the possibility of the one reagent being able to neutralise both acid and alkali spills.

## Exercises

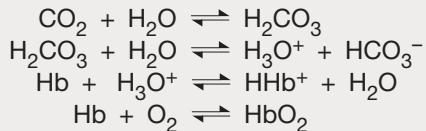
**27** A mixture of sodium dihydrogen phosphate and sodium hydrogen phosphate is widely used in laboratories to buffer solutions at pHs of around 7. Explain how this combination of salts maintains approximately constant pH even when small amounts of HCl or NaOH are added to the solution.



**28** Would 1 L of aqueous solution containing each of the following pairs of substances be a buffer solution or not? Explain why (or why not). Use an equation where appropriate.

- a 0.3 mol ammonia and 0.3 mol ammonium chloride
- \*b 0.2 mol nitrous acid and 0.2 mol sodium nitrite
- c 0.2 mol nitric acid and 0.2 mol sodium nitrate
- \*d 0.25 mol methanoic (formic) acid and 0.25 mol sodium methanoate

**\*29** Some equilibria involved in blood are:



where Hb is haemoglobin, HHb<sup>+</sup> is its conjugate acid and HbO<sub>2</sub> is oxyhaemoglobin. Use Le Chatelier's principle to describe:

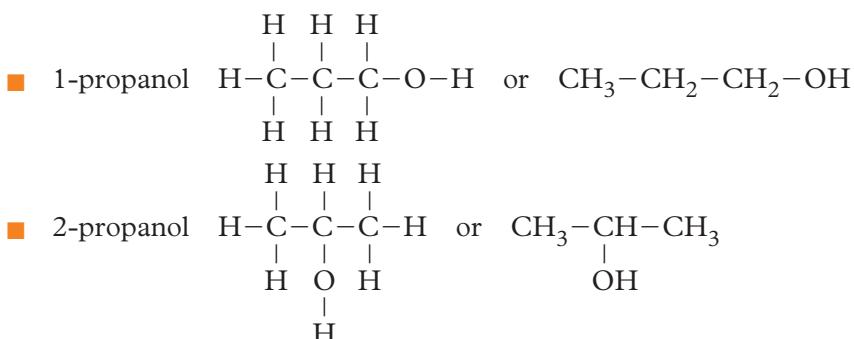
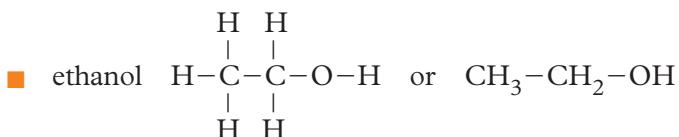
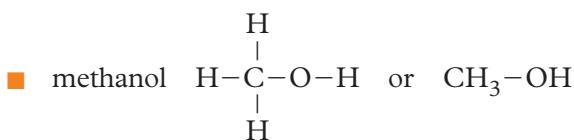
- a how each of these equilibria moves as CO<sub>2</sub> diffuses from tissue cells into the blood stream: in particular, explain how diffusion of CO<sub>2</sub> into the blood facilitates release of oxygen to tissue cells.
  - b how uptake of oxygen by haemoglobin in the lungs facilitates the release of CO<sub>2</sub> from the blood.
- 30** Two neighbouring factories produce large quantities of effluent that they have to dispose of safely. One effluent is acidic and the other is basic. 25.0 mL of one effluent required 29.5 mL 0.233 mol/L sulfuric acid for exact neutralisation. 25.0 mL of the other required 32.8 mL 0.274 mol/L sodium hydroxide for exact neutralisation. What volume of the first effluent should be mixed with 100 L of the second in order to produce neutral effluent?

The dominant reaction so far in this chapter has been neutralisation. For one important class of acids, the so-called *carboxylic acids*, there is another important reaction called *esterification*. To understand this we first need to look at the structure of alkanols and alkanoic acids.

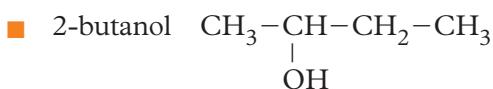
## 5.16 ALKANOLS AND ALKANOIC ACIDS

We saw in Section 1.5 that *alkanols* were compounds formed by replacing an H atom of an alkane with an OH group and that they are named by replacing the final *e* of the parent alkane with *-ol* and using a number prefix to denote the position of the OH group:

### Some simple alkanols



and just in condensed form:



Molecular models of methanol and ethanol and of 1- and 2-propanol are shown in Figures 5.4 and 5.5.

1-propanol and 2-propanol are *isomers*, because they are different compounds having the same molecular formula,  $\text{C}_3\text{H}_8\text{O}$ . Similarly 1- and 2-butanol are isomers, having the molecular formula,  $\text{C}_4\text{H}_{10}\text{O}$ .

The alkanols form an *homologous series* having the general formula,  $\text{C}_n\text{H}_{2n+2}\text{O}$  or  $\text{C}_n\text{H}_{2n+1}\text{OH}$ .

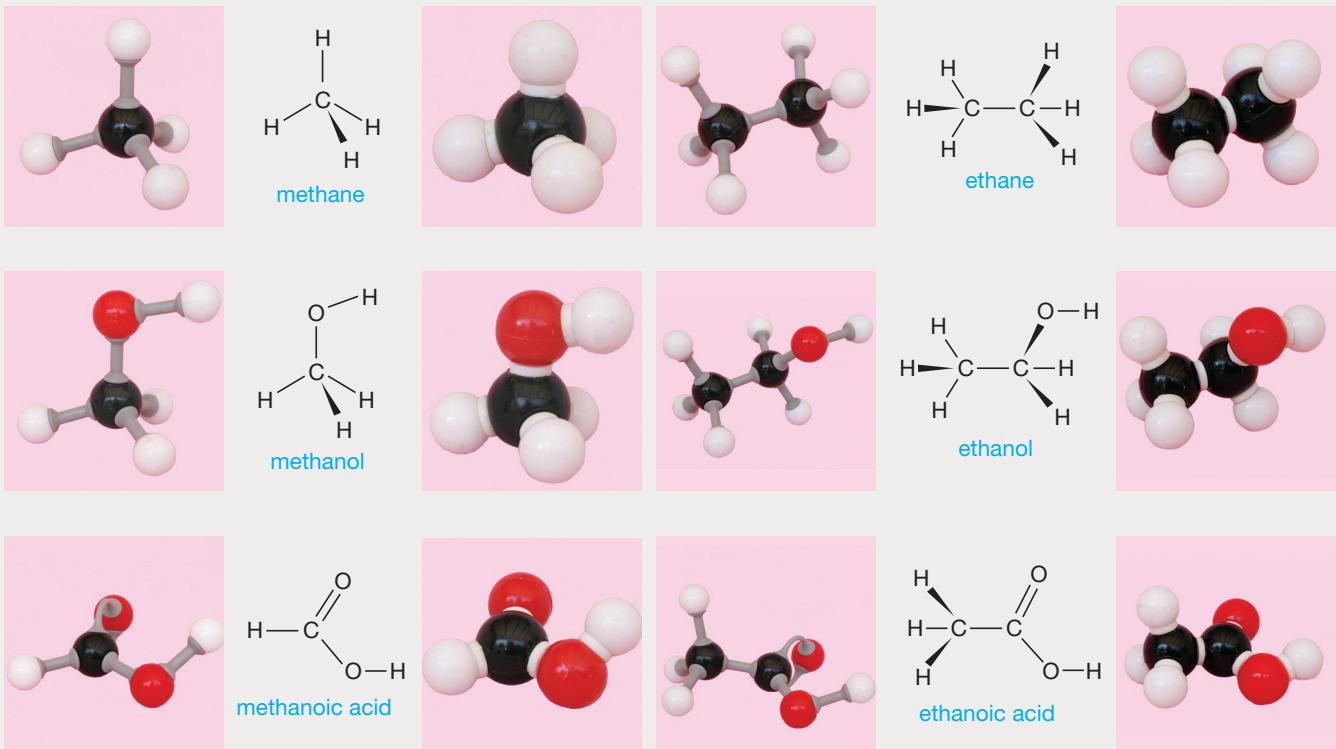
Alkanols are a subset of a larger class of compounds called *alcohols*.

An **alcohol** is a compound which contains an OH group attached to a C atom that only has C or H atoms attached to it, regardless of what else is in the molecule.

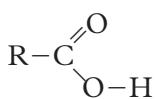
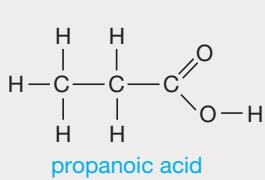
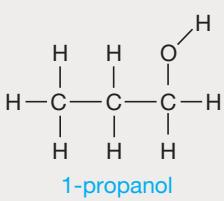
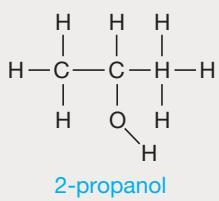
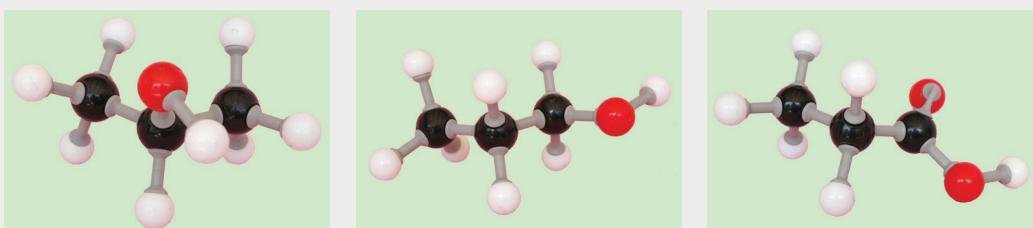
Both of the compounds,  $\text{CH}_3-\text{CH}_2-\text{OH}$  and  $\text{CCl}_3-\text{CH}_2-\text{OH}$ , are alcohols, but only  $\text{CH}_3-\text{CH}_2-\text{OH}$  is an alkanol. The OH group is commonly called the **alcohol group**.

### Alkanoic acids

An **alkanoic acid** is a compound which has the general structure:

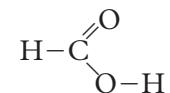


**FIGURE 5.4** (above)  
Ball-and-stick and  
space-filling models  
for the simplest  
alkanes, alkanols and  
alkanoic acids

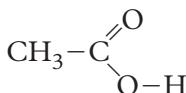


where R is an alkyl group (Section 1.4) or an H atom. The simplest alkanoic acids are:

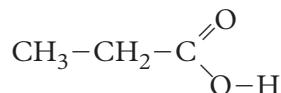
**FIGURE 5.5 (left)**  
Ball-and-stick and space-filling models of 2- and 1-propanol and propanoic acid



methanoic acid  
(formic acid)

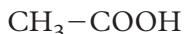


ethanoic acid  
(acetic acid)



propanoic acid

For convenience we often write these structures as:



The homologous series called alkanoic acids has the general formula  $\text{C}_n\text{H}_{2n}\text{O}_2$  with  $n > 0$  or  $\text{C}_n\text{H}_{2n+1}\text{COOH}$  with  $n \geq 0$ .

Models of the simplest alkanoic acids, along with the alkanes and alkanols they come from, are shown in Figures 5.4 and 5.5.

### Names of alkanoic acids

These are derived by dropping the final *e* from the parent alkane and adding the suffix *-oic* and the word ‘acid’; methanoic, ethanoic and propanoic acids for the examples above.  $\text{C}_5\text{H}_{10}\text{O}_2$  or  $\text{C}_4\text{H}_9\text{COOH}$  is pentanoic acid, and  $\text{C}_8\text{H}_{16}\text{O}_2$  or  $\text{C}_7\text{H}_{15}\text{COOH}$  is octanoic acid. However, formic acid and acetic acid are the IUPAC-preferred names for methanoic and ethanoic acids†.

Because the  $-\text{COOH}$  group has only one free carbon valence, it must always be at the end of a carbon chain. Hence no number is needed to signify its location.

Methanoic (formic) acid is present in ant stings, while ethanoic (acetic) acid is the key constituent of vinegar. Butanoic acid gives rancid butter its unpleasant odour.

The  $-\text{COOH}$  group is called the **carboxylic acid group**. **Carboxylic acids** are compounds which contain this group, regardless of what is attached to it.  $\text{CH}_3-\text{COOH}$  and  $\text{Cl}-\text{CH}_2-\text{COOH}$  are both carboxylic acids;  $\text{CH}_3\text{COOH}$  is an alkanoic acid, but  $\text{Cl}-\text{CH}_2-\text{COOH}$  is not.

*Alkanoic acids are weak acids* and undergo the usual reactions of such acids, such as dissolving in sodium hydroxide solution to form soluble sodium salts and reacting with sodium carbonate to form bubbles of carbon dioxide.

## 5.17 MELTING AND BOILING POINTS OF ALKANOLS AND ALKANOIC ACIDS

Both the C–O and the O–H bonds are polar. This means that alkanols are polar molecules. The C=O bond is also polar, so with these three polar bonds alkanoic acids are even more polar. In addition to simple polarity, O–H bonds are able to form hydrogen bonds. Consequently *there are strong intermolecular forces in alkanols and in alkanoic acids*. Therefore they have much higher melting and boiling points than alkanes of similar molecular weight as shown in Table 5.7. They also have quite high solubilities in water. To show the effect of polarity and/or hydrogen bonding on physical properties we generally compare compounds with similar molecular weights, because the dispersion forces will be roughly similar in such compounds. This is because the strength of dispersion forces increases as the number of electrons in the molecule increases, and the

† See pp. 261–2 CCPC for an explanation of the use of systematic versus trivial names.

number of electrons generally increases as molecular weight increases, at least in compounds of similar structure.

**TABLE 5.7 Boiling points for alkanes, alkanols and alkanoic acids of similar molecular weights**

Molecular weights <sup>a</sup>	Alkane	Boiling point (°C)	Alkanol	Boiling point (°C)	Alkanoic acid	Boiling point (°C)
16	methane	-162				
30, 32	ethane	-89	methanol	65		
44, 46	propane	-42	ethanol	78	methanoic	100
58, 60	butane	-0.5	1-propanol	97	ethanoic	118
72, 74	pentane	36	1-butanol	117	propanoic	141
86, 88	hexane	69	1-pentanol	138	butanoic	164
100, 102	heptane	98	1-hexanol	157	pentanoic	186

a The first value is for the alkane; the second is for both the alkanol and the alkanoic acid.

Alkanols and alkanoic acids react to form compounds called *esters*.

## Exercises

**31** Draw structural formulae for:

- |                        |                        |
|------------------------|------------------------|
| <b>a</b> 2-pentanol    | <b>c</b> 3-heptanol    |
| <b>b</b> butanoic acid | <b>d</b> hexanoic acid |

**32** Name the following compounds

- |   |   |
|---|---|
| <b>a</b> $\text{CH}_3-\text{CH}_2-\underset{\text{OH}}{\overset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$ | <b>c</b> $\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3-\text{CH}_2}{\overset{ }{\text{CH}_2}}-\text{CH}-\text{OH}$ |
| <b>b</b> $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$                                  | <b>d</b> $\text{CH}_3-(\text{CH}_2)_6-\text{COOH}$  |

**33 a** Using data in Table 5.7 and just the one set of axes, draw graphs of boiling points of

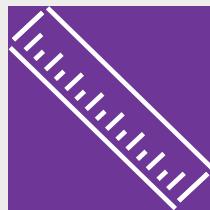
- i** alkanols      **ii** alkanoic acids

against number of carbon atoms per molecule. Draw suitable curves or lines through the points and summarise how boiling point depends upon number of carbon atoms in the molecule. Offer an explanation for any trends that you observe. In addition explain why the curves for the two sets of compounds are separated from each other.

**b** Use your graphs to estimate the boiling points of:

- i** 1-heptanol      **ii** hexanoic acid

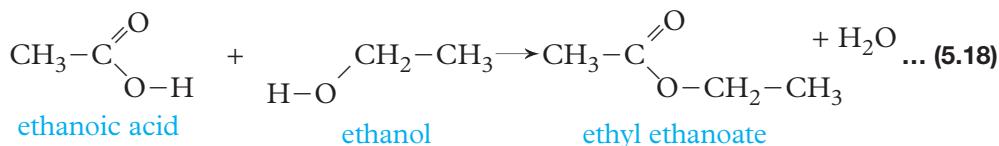
Assess the accuracy of your estimates: that is, give your estimates as  $(x \pm y)^\circ\text{C}$ . Keep your graph for Exercise 41 below.



## 5.18 ESTERS

**Esters** are compounds formed when alkanoic acids react with alkanols, or more generally, when carboxylic acids combine with alcohols.

When ethanoic (acetic) acid and ethanol are heated with a few drops of concentrated sulfuric acid, the ester, ethyl ethanoate (ethyl acetate) is formed:



Esters contain the structural unit



Table 5.8 presents structures and properties for some common esters. Models of the most widely used ester, ethyl acetate, are shown in Figure 5.6.

**TABLE 5.8 Formulae and properties of common esters**

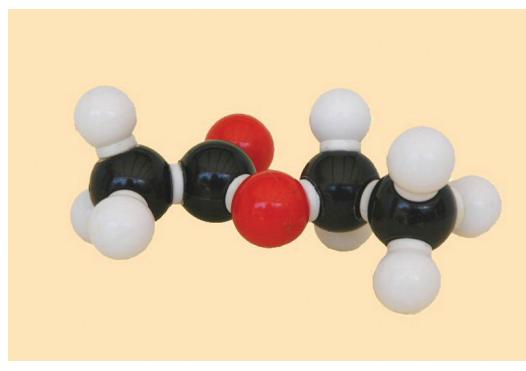
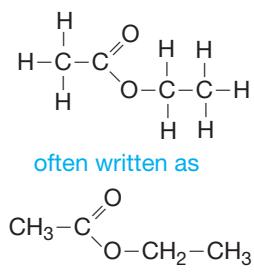
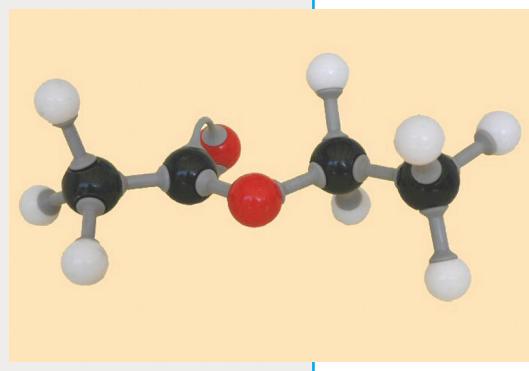
Name <sup>a</sup>	Formula	Molecular weight	Boiling point (°C)	Solubility in water <sup>b</sup>
methyl methanoate (formate)	$\text{H}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	60	32	24
methyl ethanoate (acetate)	$\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	74	57	6.7
methyl propanoate	$\text{CH}_3-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_3$	88	80	7.3
ethyl ethanoate (acetate)	$\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_3$	88	77	7.5
propyl ethanoate (acetate)	$\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	102	102	2

a Formate and acetate are the IUPAC-preferred names, although the systematic names are methanoate and ethanoate.

*b* grams of solute per 100 g water

FIGURE 5.6

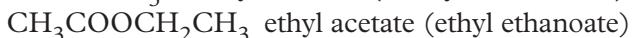
## Ball-and-stick and space-filling models of the ester ethyl acetate (ethyl ethanoate)



## Naming esters<sup>†</sup>

Esters from alkanols and alkanoic acid are named as *alkyl alkanoates*: the alkyl part of the name comes from the alcohol from which the ester was formed, and the alkanoate from the alkanoic acid. The first three esters of Table 15.8 are all methyl esters (because they come from methanol); the acids they were formed from are methanoic, ethanoic and propanoic acids. So their systematic names are methyl methanoate, methyl ethanoate and methyl propanoate. However because the IUPAC-preferred names for the first two acids are formic and acetic acids, the preferred names for the first two of these esters are methyl formate and methyl acetate.

For ease of printing, esters are often written as:



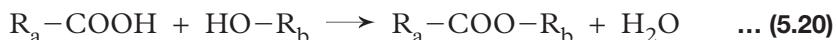
but it must be clearly understood that the  $-\text{COOC}-$  means the arrangement of bonds shown in Structure 5.19.

## Properties and synthesis

The C=O and C–O bonds make esters *polar substances*. However the lack of hydrogen bonding means that esters have much lower boiling points than acids or alkanols of the same molecular weight (compare Tables 5.7 and 5.8). They are also much less soluble in water.

The reaction between an alkanol and an alkanoic acid is called **esterification**.

In general terms it can be written as:

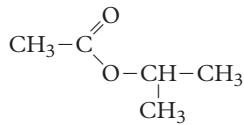


where  $\text{R}_a$  and  $\text{R}_b$  are alkyl groups.  $\text{R}_a$  and  $\text{R}_b$  may be the same group or different ones;  $\text{R}_a$  (but not  $\text{R}_b$ ) may be a hydrogen atom (in which case the ester is a methanoate).

Esterification is moderately slow at room temperature and the reaction does not go to completion: it comes to equilibrium. To speed up the reaction *concentrated sulfuric acid is used as a catalyst*; it also absorbs the product water and so forces the equilibrium to the right. In addition the reaction is often carried out at temperatures near the boiling point of the alcohol. In order to prevent the alcohol being lost by vaporisation, the reaction flask is usually fitted with a water-cooled condenser as shown in Figure 5.7. This causes any alcohol vapour which rises from the hot reaction mixture to be condensed and to run back into the reaction vessel. This process is called *refluxing*.

† The naming rule given here does not address the question of which carbon atom of the alkyl group is attached to the O of the ester group. However for the NSW HSC, students are required to consider only esters with the end carbon atom of the alkyl group attached to the O, esters from so-called primary alkanols. No numbering is needed for these esters though for all other esters a number must be given to indicate which of the C atoms of the alkyl group is attached to the O of the ester group.

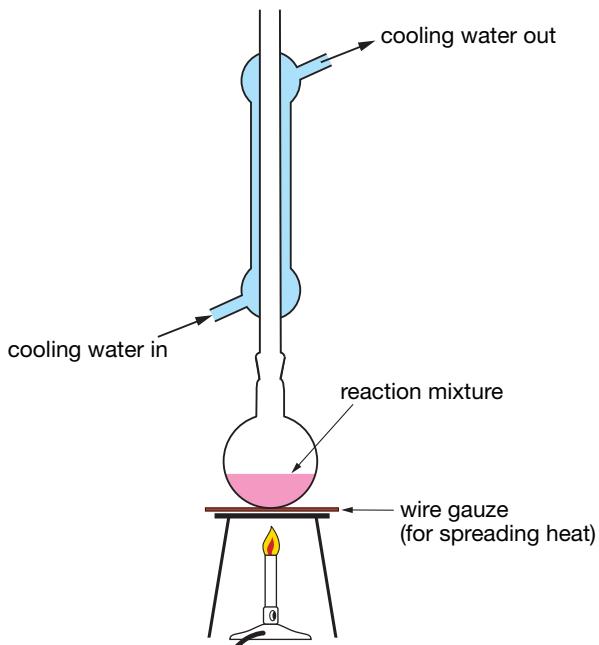
Hence 2-propyl acetate for



but just propyl acetate for the last entry in Table 5.8.

**Refluxing** is the process of heating a reaction mixture in a vessel with a cooling condenser attached in order to prevent loss of any volatile reactant or product.

FIGURE 5.7  
Simple apparatus for refluxing



It allows the reaction to be brought about at a higher temperature than would otherwise be possible. The alternative of performing the reaction in a closed vessel could lead to a dangerous build-up of pressure and the possibility of an explosion.

## 5.19 OCCURRENCE AND USES OF ESTERS

Esters have pleasant, fruity odours and occur widely in nature as perfumes and flavouring agents. While the characteristic smells or flavours of many plants and fruits usually arise from a complex mixture of substances, often one ester can be identified as the major ingredient of the smell or flavour. Some such esters are listed in Table 5.9.

TABLE 5.9 Esters in some common natural flavours<sup>a</sup>

Flavour	Main ester(s) present
apple	methyl butanoate and iso-pentyl pentanoate <sup>b</sup>
banana	iso-pentyl ethanoate <sup>b</sup>
grape	ethyl methanoate and ethyl heptanoate
orange	octyl thanoate
pear	pentyl ethanoate
raspberry	butyl ethanoate
rum	ethyl methanoate
jasmine	benzyl ethanoate

*a* Each natural flavour results from a complex mixture of many esters. These are just the main ones in the flavours listed.

*b* iso-pentyl is  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ . The systematic names for these esters are 3-methyl-1-butyl pentanoate or 3-methyl-1-butyl ethanoate, though the -1- is often omitted.

What we mean by flavour is really a combination of crude taste (sweet, sour, salt, bitter) and odour; it is the odour of esters that contributes to flavours. There is now a substantial industry for developing and manufacturing synthetic flavours and perfumes. The first step is often to identify the constituents of the natural flavour and then to synthesise similar mixtures of esters which reproduce this flavour. Such artificial flavours are often cheaper than natural extracts, and provided they contain only substances that occur in the natural flavours, they represent little health hazard. Esters for such flavours are synthesised as described above using Equation 5.20.

Ethyl acetate (ethanoate) is widely used as a solvent in industry. It is also the common solvent in nail polish remover. It is manufactured on a large scale from acetic acid and ethanol (Equation 5.18), using in principle the same process as is used in the laboratory. High molecular weight (i.e. non-volatile) esters such as dialkyl phthalates are used as plasticisers in some plastics such as PVC: they make the materials soft and pliable. Again they are synthesised by using Equation 5.20.



Some everyday substances that contain esters—perfume, nail polish remover and food flavourings

## Functional groups

Recall from p. 267 CCPC that a *functional group* is a *centre of reactivity* in a carbon compound. This account of alkanols, alkanoic acids and esters has introduced three functional groups:

- the *alcohol* functional group  $\text{---}\overset{\text{l}}{\underset{|}{\text{C}}}\text{---O---H}$
- the *carboxylic acid* functional group  $\text{---}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{---O---H}$
- the *ester* functional group  $\text{---}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{---O---}\overset{\text{l}}{\underset{|}{\text{C}}}\text{---}$

## Exercises

**34** Name the following compounds:

- |   |   |
|---|---|
| <b>a</b> $\text{H---C}=\text{O---CH}_2\text{---CH}_3$               | <b>c</b> $\text{CH}_3\text{---CH}_2\text{---C}=\text{O---CH}_2\text{---CH}_2\text{---CH}_3$ |
| <b>b</b> $\text{CH}_3\text{---CH}_2\text{---O---C}=\text{O---CH}_3$ | <b>d</b> $\text{CH}_3\text{---O---C}=\text{O---CH}_2\text{---CH}_2\text{---CH}_3$           |

**35** Draw structural formulae for:

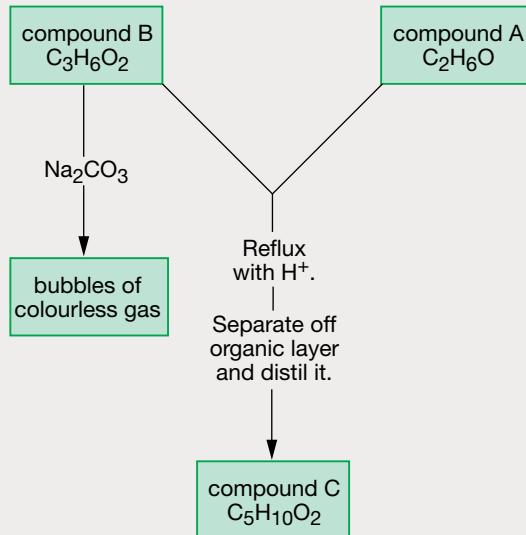
- |                            |                          |                         |
|----------------------------|--------------------------|-------------------------|
| <b>a</b> methyl propanoate | <b>c</b> butyl hexanoate | <b>e</b> ethyl formate  |
| <b>b</b> propyl methanoate | <b>d</b> hexyl butanoate | <b>f</b> pentyl acetate |

**36** Draw structural formulae for three esters of molecular formula  $\text{C}_4\text{H}_8\text{O}_2$ . Name them.

**37** Write equations for the formation of the esters in Exercises 35 and \*36. Describe with full experimental detail how you would prepare one of these esters in the laboratory.



- 38 a** Explain why methyl acetate has a much lower boiling point than ethanoic acid ( $57^{\circ}\text{C}$  compared with  $118^{\circ}\text{C}$ ), despite having a higher molecular weight.
- b** Explain why acetic acid has a much greater solubility in water than methyl formate.
- 39** Explain why the solubility of esters in water decreases as molecular weight increases (Table 5.9).
- 40** Consider the following reaction scheme:



Tests show that compound A is an alkanol.

- a** Deduce the structures of compounds B and C and name them.
- b** Write equations for the two reactions involved.
- c** Draw diagrams of the apparatus used to ‘reflux’ and ‘distil’ on the chart, and explain what these processes do.
- 41 \*a** On the graph you drew in Exercise 33, plot boiling points of methyl esters against the number of carbon atoms in the alkanoate part of the molecule and draw a suitable curve or line through the points. Some boiling points are in Table 5.8: others are methyl butanoate,  $102^{\circ}\text{C}$ ; methyl pentanoate,  $126.5^{\circ}\text{C}$ .
- b** How does boiling point of these esters vary with number of carbon atoms in the alkanoate part of the molecule? How does the boiling point of a methyl ester compare with that of the parent alcanoic acid? Offer an explanation for this.
- 42 a** A sample of octyl ethanoate (which is insoluble in water) was contaminated with a small amount of ethanoic acid (which is soluble in water). Explain how you would use water and a separating funnel to purify the octyl ethanoate. Sketch the separating funnel.
- b** Another sample of octyl ethanoate was contaminated with a small amount of pentanoic acid, which is soluble in the octyl ethanoate but insoluble in water. Explain how you would use an aqueous solution of sodium carbonate and a separating funnel to purify this octyl ethanoate.
- 43** Compound X was prepared by the following procedure.
- 0.20 mol acetic (ethanoic) acid, 0.15 mol 1-propanol and 1 mL concentrated sulfuric acid were refluxed for 15 min. After cooling the reaction mixture was poured into 20 mL water, shaken vigorously, then allowed to settle. Two layers formed. The two layers were separated using a separating funnel and the aqueous layer was discarded. Small quantities of sodium carbonate solution were added to the organic layer until effervescence ceased. Another 10 mL water was added, the mixture shaken then allowed to settle. Again the two layers were separated and the aqueous layer discarded. The organic layer was dried by allowing it to stand over granular anhydrous calcium chloride for 15 min. The drying agent was filtered off and the remaining liquid

distilled. The first 1 mL of the distillate was discarded and the distillation was stopped when about 1 mL remained in the distillation flask.

- a What is the name of the compound X being prepared? Write an equation for the chemical reaction.
  - b Which reactant was used in excess and how was the excess removed before distillation? Why did the first extraction with water not remove all of the excess reagent? How would you determine experimentally that, after settling, the bottom layer was the aqueous one? Smell is not acceptable (why?). Why was sodium carbonate added before the second extraction with water?
  - c Draw fully labelled diagrams for:
    - i the refluxing process
    - ii the distillation
- Why were the first and last 1 mL portions discarded in the distillation?
- d Why is compound X much less soluble in water than either of the reactants?

## Important new terms

You should know the meaning of the following terms.

acid (Brönsted–Lowry) (p. 147)  
acid salts (p. 151)  
alcohol (p. 170)  
alcohol group (p. 170)  
alkanoic acid (p. 170)  
amphiprotic (p. 154)  
base (Brönsted–Lowry) (p. 147)  
Brönsted–Lowry definitions of acids and bases (p. 147)  
buffer solution (p. 167)  
carboxylic acid (p. 172)  
carboxylic acid group (p. 172)  
conjugate acid (p. 148)  
conjugate base (p. 148)

diprotic acid (p. 151)  
end point (p. 158)  
equivalence point (p. 158)  
ester (p. 173)  
esterification (p. 175)  
hydrogen salts (p. 151)  
hydrolysis (p. 154)  
monoprotic acid (p. 151)  
primary standard (p. 159)  
proton transfer reaction (p. 156)  
refluxing (p. 176)  
standard solution (p. 159)  
titrant (p. 158)  
titration (p. 157)  
triprotic acid (p. 151)  
volumetric analysis (p. 157)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 Describe the nature of the hydrogen ion in aqueous solution.
- 3 Why is the Arrhenius definition of an acid not entirely satisfactory?
- 4 What are the conjugate bases of HCl, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH?
- 5 What are the conjugate acids of N<sub>2</sub>H<sub>4</sub> (hydrazine), OH<sup>−</sup> and CO<sub>3</sub><sup>2−</sup>?
- 6 Give the names and formulae of two diprotic acids and one triprotic acid and of the three different potassium salts that can be formed from the triprotic acid.
- 7 Name three salts that, in aqueous solution, you would expect to have a pH
  - a of approximately 7
  - b significantly less than 7
  - c significantly greater than 7.

- 8** Explain why your salts have these pHs.
- 9** Give two examples of amphiprotic substances and illustrate their amphiprotism by writing equations.
- 10** Write equations for two neutralisation reactions. Use these to explain why neutralisation is considered a proton-transfer reaction.
- 11** Name one primary standard for acid–base analysis and explain why it is suitable for this purpose.
- 12** Describe, with full experimental detail, how you would prepare a standard solution of this primary standard.
- 13** Describe, with full experimental detail, how you would use a burette and pipette to determine the concentration of an acid solution by using an alkali solution of accurately known concentration.
- 14** Explain how a buffer solution works. Give a specific example.
- 15** Describe two situations in nature where buffers are involved and explain how they function.
- 16** What is the general formula for the homologous series of alkanols?
- 17** Give the names and structural formulae of the first six alkanols.
- 18** Draw the structures and give the names of the first five alkanoic acids.
- 19** Give the full structure of the carboxylic group, –COOH.
- 20** What is the difference between the two terms
  - a** alcohol and alkanol
  - b** carboxylic acid and alkanoic acid?
- 21** Explain why alkanols and alkanoic acids have polar molecules, and give three consequences of this polarity.
- 22** Give names and structural formulae for four esters.
- 23** How are esters prepared? Give two examples, including equations.
- 24** Describe, with full practical details, how you would carry out an esterification.
- 25** What is meant by *refluxing* in chemical contexts? Sketch a simple set of apparatus for carrying out this procedure.
- 26** Sketch apparatus for carrying out a simple distillation.
- 27** Why are esters more volatile than the carboxylic acids they are derived from, despite having higher molecular weights?
- 28** Where do esters occur in nature? What are some practical uses of esters?
- 29** Draw the structures of the alcohol, carboxylic acid and ester functional groups.

# EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 2

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination; for more information see p. 93.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

## MARKS

- |    |   |   |
|----|---|---|
| 1  | The solubility of carbon dioxide in water depends upon the pressure of carbon dioxide gas above the solution and upon the pH of the solution. Use these facts to demonstrate the usefulness of Le Chatelier's principle.  | 5 |
| 2  | Explain why a solution of sodium acetate (ethanoate) is alkaline and a solution of ammonium nitrate is acidic, while solutions of sodium iodide and potassium nitrate are neutral.  | 5 |
| 3  | Describe an experiment you have performed to prepare and test a natural indicator. List at least three everyday substances whose acidity you tested with this indicator and include the results you obtained for each.  | 4 |
| 4  | Outline the human activities, using chemical equations where appropriate, that release oxides of nitrogen and sulfur to the atmosphere. Indicate whether or not these releases are leading to increases in the overall global concentrations of these gases in the atmosphere and explain why this is so. | 6 |
| 5  | Assess the usefulness of the pH scale to chemistry and the world at large.  | 4 |
| 6  | Explain how a buffer works, using a specific example from a natural system.   | 5 |
| 7  | Evaluate the use of a set of indicators (as opposed to an electronic pH meter) for determining the approximate pH of a solution. Mention at least one everyday example of this use.   | 4 |
| 8  | Compare the melting and boiling points of alkanols, alkanoic acids and esters, and explain any similarities and differences.  | 5 |
| 9  | Discuss the evidence for and against increases in atmospheric concentrations of oxides of sulfur and nitrogen.  | 7 |
| 10 | Summarise the causes and effects of acid rain and explain the role of natural buffers in minimising the effects.  | 6 |
| 11 | Explain with examples why acids are added to many foods.  | 4 |
| 12 | Contrast, with examples, the meanings of the terms 'weak', 'strong', 'concentrated' and 'dilute' as applied to acids and bases.   | 4 |
| 13 | Outline the way that the concept of an acid has developed from the time of Humphry Davy in the early 1800s to the work of Johannes Brönsted and Thomas Lowry in the 1920s.  | 6 |
| 14 | Evaluate the effectiveness of placing containers of powdered sodium hydrogen carbonate around a chemical laboratory as a safety measure.  | 4 |
| 15 | Explain the concept of conjugates for acids and bases and assess its usefulness.  | 5 |

- 16** Describe an experiment you have performed to determine the concentration of a domestic acidic substance. Outline the measures you took to ensure that your results were accurate. **7**
- 17** A pair of students who performed the experiment described in Question 16 obtained results that were very reproducible but not accurate. What does ‘very reproducible but not accurate’ mean? Propose reasons for the students getting such results. **4**
- 18** Describe an experiment you have performed to measure the pH of a range of salt solutions. Mention the precautions you took to ensure the accuracy of your results. For three of the salts used explain why their pHs were different from 7. **7**
- 19** Contrast the two processes, refluxing and distillation. **4**
- 20** Classify each of the following oxides as acidic, basic or neutral and, for each, give an equation or reason for your classification: magnesium oxide, diphosphorus pentoxide, nitric oxide, nitrogen dioxide and copper oxide. **5**

# REVISION TEST FOR MODULE 2

# MODULE 2

**Total marks: 50 Suggested time: 90 minutes**

At a pressure of 100.0 kPa the molar volume of a gas is 22.7 L at 0°C and 24.8 L at 25°C. The ionic product constant for water,  $K_w$  at 25°C is  $1.0 \times 10^{-14}$ . Table 5.5 on p. 164 may be used if necessary.

Table 5.5 on p. 164 may be used if necessary.

## **MULTIPLE CHOICE QUESTIONS (1 mark each)**

Select the alternative **a**, **b**, **c**, or **d** which best answer the question.

- 1** The conjugate base of the acid  $\text{HCrO}_4^-$  is:

**a**  $\text{H}_2\text{CrO}_4$       **c**  $\text{CrO}_4^{2-}$   
**b**  $\text{H}_2\text{CrO}_4^-$       **d**  $\text{CrO}_4^-$

**2** The list which contains only acidic oxides is:

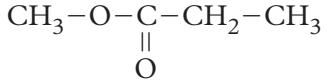
**a**  $\text{CO}, \text{CO}_2, \text{B}_2\text{O}_3, \text{SO}_3$       **c**  $\text{P}_2\text{O}_3, \text{NO}, \text{SO}_2, \text{Cl}_2\text{O}$   
**b**  $\text{Cl}_2\text{O}, \text{P}_2\text{O}_5, \text{NO}_2, \text{SO}_2$       **d**  $\text{N}_2\text{O}, \text{NO}_2, \text{CO}_2, \text{SO}_3$

**3** The correct name for the compound having the following structure is:

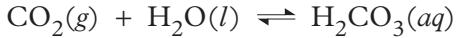
$$\begin{array}{c} \text{CH}_3-\text{O}-\text{C}-\text{CH}_2-\text{CH}_3 \\ || \\ \text{O} \end{array}$$

**a** methyl acetate      **c** methyl ethanoate  
**b** ethyl methanoate      **d** methyl propanoate

**4** The dissolution of carbon dioxide in water is an exothermic equilibrium reaction:



- |          |                  |          |                   |
|----------|------------------|----------|-------------------|
| <b>a</b> | methyl acetate   | <b>c</b> | methyl ethanoate  |
| <b>b</b> | ethyl methanoate | <b>d</b> | methyl propanoate |



The solubility of carbon dioxide can be increased (that is, this reaction driven towards the right) by:

- 5** The boiling points for methyl propanoate, butanoic acid and 1-pentanol in that order are:

**a** 138°C, 80°C, 164°C      **c** 164°C, 138°C, 80°C  
**b** 80°C, 138°C, 164°C      **d** 80°C, 164°C, 138°C

**6** The volume of carbon dioxide measured at 0°C and 100.0 kPa pressure that can be absorbed by 0.30 mol potassium hydroxide is:

**a** 3.41 L      **c** 13.6 L  
**b** 6.81 L      **d** 3.72 L

**7** The pH of a solution of completely ionised sulfuric acid was 3.40. This means that in that solution the sulfate ion concentration in moles per litre was:

**a**  $4.0 \times 10^{-4}$       **c**  $8.0 \times 10^{-4}$   
**b**  $2.0 \times 10^{-4}$       **d**  $2.0 \times 10^{-3}$

**8** When 25 mL 0.0858 mol/L sodium carbonate solution was titrated with a solution of hydrochloric acid, the volume of acid needed to reach the equivalence point was 37.8 mL. The concentration of the hydrochloric acid solution in moles per litre is:

**a** 0.0567      **c** 0.130  
**b** 0.0284      **d** 0.113

- 9** For a titration of ammonia solution with a nitric acid solution, a suitable indicator, with a correct reason for choosing it, is:
- phenolphthalein, because it changes colour at pH > 7 and at the equivalence point of this titration the pH is greater than 7
  - litmus, because it changes colour around pH 7 and for a neutralisation reaction the equivalence point occurs at pH 7
  - methyl orange because it changes colour at pH < 7 and at the equivalence point of this titration the pH is less than 7
  - any one of the above three indicators, because for a neutralisation reaction the equivalence point occurs at pH 7
- 10** The list which contains oxides whose concentrations in the atmosphere have all been increasing significantly over the past 100 years is:
- CO<sub>2</sub> and N<sub>2</sub>O
  - CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>2</sub>
  - CO, SO<sub>2</sub> and NO
  - CO<sub>2</sub> and NO<sub>2</sub>

#### SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

The number of marks for each part of each question is shown at the right-hand end of the question. Marks allocated are based on the HSC scale of 1 mark per 1.8 minutes.

- |  |              |
|--|--------------|
|  | <b>MARKS</b> |
|--|--------------|
- 11 a** When drops of indicators were added to samples of Solutions P, Q, R, S, the colours were as shown below. Use Table 5.5 on page 164 to determine the pH of each solution. You may have to give a range within which the pH lies. 2
- | Solution          | P          | Q                      | R         | S                       |
|-------------------|------------|------------------------|-----------|-------------------------|
| Indicator: colour | bcg: blue  | pr: red                | pr: red   | mo: orange <sup>b</sup> |
|                   | pr: yellow | tb: green <sup>a</sup> | phth: red | bcg: yellow             |
- bcg: bromocresol green; mo: methyl orange; phth: phenolphthalein; pr: phenol red; tb: thymol blue*  
*a green = yellow + blue*  
*b orange = red + yellow*
- b** The pHs of two solutions A and B are 4.0 and 5.3 respectively. In which solution is the hydrogen ion the greater? How many times greater is it in this solution than in the other one? 1
- 12** Many fresh water lakes are buffered by a mixture of carbonic acid from rain and hydrogen carbonate (leached from rocks and soils). Explain what ‘buffered’ means. Illustrate by writing equations for what happens when acid or alkali is added to such water. Include mention of Le Chatelier’s principle in your explanation. 2
- 13** Outline an experiment you have performed to prepare an ester. Include a diagram and an equation. Which reactant did you use in excess and why? 7
- 14** Naturally occurring citric acid has the molecular formula C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>. Like all acids it reacts with carbonate solution to form carbon dioxide gas. When 1.537 g citric acid was added to a solution containing excess sodium carbonate, 299 mL carbon dioxide (measured at 25°C and 100.0 kPa pressure) was formed.

- a** How many moles of carbon dioxide were formed? **1**
- b** Write an equation for the reaction of hydrogen ions with carbonate ions. Therefore, how many moles of hydrogen ion did the 1.537 g citric acid produce? **1**
- c** Hence determine whether citric acid is mono-, di- or triprotic. Explain your reasoning. **1**
- 15 a** Name the following compounds:
- i**  $\text{CH}_3-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$
- ii**  $\text{CH}_3-\text{CH}_2-\underset{\text{O}-\text{H}}{\overset{\text{O}}{\text{C}}}$
- iii**  $\text{CH}_3-\underset{\text{O}-\text{CH}_3}{\overset{\text{O}}{\text{C}}}$  **2**
- b** Which, if any, of these compounds is(are) isomers? Explain why. **1**
- 16** Demonstrate that oxides of elements on the left-hand side of the Periodic Table are basic while those of elements on the right-hand side are acidic. Include chemical equations. **4**
- 17** Oxalic acid dihydrate,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , a diprotic acid, is sometimes used to standardise sodium hydroxide solutions. For one particular experiment, 0.495 g oxalic acid dihydrate was measured out and dissolved in about 50 mL of water. One drop of phenolphthalein indicator was added and the solution titrated with the sodium hydroxide solution that was required to be standardised. 38.7 mL was needed to reach the equivalence point.
- a** Give two reasons why sodium hydroxide solutions need to be standardised. **1**
- b** Give two properties or characteristics which oxalic acid dihydrate must have if it is suitable for use to standardise hydroxide solutions. **1**
- c** Describe the steps you would take to prepare the burette for dispensing the sodium hydroxide solution in order to make the titration as accurate as possible. **1**
- d** Calculate the molarity of the sodium hydroxide solution. **1**
- 18** 0.050 mol/L aqueous solutions of two acids, HP and HQ, were prepared. The solutions of HP and HQ had pHs of 3.30 and 1.30 respectively.
- a** Calculate the hydrogen ion concentrations in these solutions. **1**
- b** Classify HP and HQ as weak or strong acids, giving your reason. **1**
- c** If either of, or both, acids is(are) weak, calculate its (their) degree of ionisation. **3**
- 19** Justify the claim that for all strong and weak acids and bases neutralisation is a proton-transfer reaction. **4**
- 20** Assess the impact of human sources of oxides of sulfur and nitrogen upon the environment, using chemical equations where appropriate. **7**

## MODULE 2 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 2 of the New South Wales Higher School Certificate Course.

### Syllabus content

The following table lists (for Module 2) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

#### Location of HSC Course material in *Conquering Chemistry* for Module 2

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.3.1 Indicators were identified with the observation that the colour of some flowers depends on soil composition</b>	
■ classify common substances as acidic, basic or neutral	4.1, 4.13
■ identify that indicators such as litmus, phenolphthalein, methyl orange and bromothymol blue can be used to determine the acidic or basic nature of a material over a range, and that the range is identified by change in indicator colour	4.2
■ identify and describe some everyday uses of indicators including the testing of soil acidity/basicity	4.2
<b>9.3.2 While we usually think of the air around us as neutral, the atmosphere naturally contains acidic oxides of carbon, nitrogen and sulfur. The concentrations of these acidic oxides have been increasing since the Industrial Revolution</b>	
■ identify oxides of non-metals which act as acids and describe the conditions under which they act as acids	4.5
■ analyse the position of these non-metals in the Periodic Table and outline the relationship between position of elements in the Periodic Table and acidity/basicity of oxides	4.5
■ define Le Chatelier's principle	4.7
■ identify factors which can affect the equilibrium in a reversible reaction	4.7
■ describe the solubility of carbon dioxide in water under various conditions as an equilibrium process and explain in terms of Le Chatelier's principle	4.6, 4.8
■ identify natural and industrial sources of sulfur dioxide and oxides of nitrogen	4.9
■ describe, using equations, examples of chemical reactions which release sulfur dioxide and chemical reactions which release oxides of nitrogen	4.9
■ assess the evidence which indicates increases in atmospheric concentration of oxides of sulfur and nitrogen	4.10

Syllabus reference	Sections where found in CCHSC
Students learn to	
■ calculate volumes of gases given masses of some substances in reactions, and calculate masses of substances given gaseous volumes, in reactions involving gases at 0°C and 100 kPa or 25°C and 100 kPa	4.12
■ explain the formation and effects of acid rain	4.11
<b>9.3.3 Acids occur in many foods, drinks and even within our stomachs</b>	
■ define acids as proton donors and describe the ionisation of acids in water	5.2, 4.14
■ identify acids including acetic (ethanoic), citric (2-hydroxypropane-1,2,3-tricarboxylic), hydrochloric and sulfuric acid	4.13
■ describe the use of the pH scale in comparing acids and bases	4.15 to 4.18
■ describe acids and their solutions with the appropriate use of the terms strong, weak, concentrated and dilute	4.20
■ identify pH as $-\log_{10}[\text{H}^+]$ and explain that a change in pH of 1 means a tenfold change in $[\text{H}^+]$	4.15
■ compare the relative strengths of equal concentrations of citric, acetic and hydrochloric acids and explain in terms of the degree of ionisation of their molecules	4.20
■ describe the difference between a strong and a weak acid in terms of an equilibrium between the intact molecule and its ions	4.20
<b>9.3.4 Because of the prevalence and importance of acids, they have been used and studied for hundreds of years. Over time the definitions of acid and base have been refined</b>	
■ outline the historical development of ideas about acids including those of	5.1
– Lavoisier	
– Davy	
– Arrhenius	
■ outline the Brönsted–Lowry theory of acids and bases	5.2
■ describe the relationship between an acid and its conjugate base and a base and its conjugate acid	5.2
■ identify a range of salts that form acidic, basic or neutral solutions and explain their acidic, neutral or basic nature	5.5
■ identify conjugate acid/base pairs	5.2
■ identify amphiprotic substances and construct equations to describe their behaviour in acidic and basic solutions	5.6
■ identify neutralisation as a proton transfer reaction which is exothermic	5.7
■ describe the correct technique for conducting titrations and preparation of standard solutions	5.8 to 5.12
■ qualitatively describe the effect of buffers with reference to a specific example in a natural system	5.13, 5.14

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.3.5 Esterification is a naturally occurring process which can be performed in the laboratory</b>	
■ describe the differences between the alkanol and alkanoic acid functional groups in carbon compounds	5.16
■ identify the IUPAC nomenclature for describing the esters produced by reactions of straight-chained alkanoic acids from C1 to C8 and straight-chained primary alkanols from C1 to C8	5.18
■ explain the difference in melting point and boiling point caused by straight-chained alkanoic acid and straight-chained primary alkanol structures	5.17
■ identify esterification as the reaction between an acid and an alkanol and describe, using equations, examples of esterification	5.18
■ describe the purpose of using acid in esterification for catalysis	5.18
■ explain the need for refluxing during esterification	5.18
■ outline some examples of the occurrence, production and uses of esters	5.19

## Compulsory experiments

The table below lists the compulsory experiments (from the right-hand column of the syllabus), along with places where you can find procedures for these experiments (in *CCHSC BLM*) and the location of relevant information in *CCHSC*.

*CCHSC* is an abbreviation for this book *Conquering Chemistry HSC Course*.

*CCHSC BLM* is *Conquering Chemistry HSC Course Blackline Masters* by Debra Smith, Cengage Learning Australia.

### Information about compulsory experiments for Module 2

Experiment	Location in CCHSC BLM	Related material in CCHSC <sup>a</sup>
1 Prepare and test a natural indicator.	Module 2 Worksheet 2 (p. 53)	Section 4.2 Exam-style Question 3
2 Decarbonate soft drink and gather data to calculate the mass changes involved and calculate the volume of gas released at 25°C and 100 kPa.	Module 2 Worksheet 5 (p. 63)	Sections 4.6 to 4.8 and 4.12 Chapter 4 Exercise 24(b)
3 Use pH meters/probes and indicators to distinguish between acidic, basic and neutral chemicals.	Module 2 Worksheet 7 (p. 69)	Section 4.19 including Example 6 Chapter 4 Exercises 32, 33 Revision Test Question 11(a)
4 Measure the pH of identical concentrations of strong and weak acids.	Module 2 Worksheet 9 (p. 78)	Section 4.20 Chapter 4 Exercises 35, 36 Revision Test Question 18
5 Determine the pH of a range of salt solutions.	Module 2 Worksheet 11 (p. 85)	Section 5.5 Exam-style Question 18

<b>Experiment</b>	<b>Location in CCHSC BLM</b>	<b>Related material in CCHSC<sup>a</sup></b>
<b>6</b> Carry out titrations, including the preparation of standard solutions and the calculation of results.	Module 2 Worksheet 13 (p. 94)	Sections 5.8 to 5.12 Chapter 5 Exercises 16 to 24 Revision Test Question 17
<b>7</b> Determine the concentration of a domestic acidic substance.	Module 2 Worksheet 14 (p. 98)	Sections 5.8 to 5.12 Chapter 5 Exercises 19, 23, 26
<b>8</b> Prepare an ester using reflux.	Module 2 Worksheet 17 (p. 111)	Section 5.18 Chapter 5 Exercise 43 Revision Test Question 13

<sup>a</sup> Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.

## Other items in the student activity (right-hand) column

The table below lists (in abbreviated form) the non-experimental items in the student activity (right-hand) column of the syllabus and indicates where in *Conquering Chemistry* relevant information is located.

### Location of material for other Module 2 activities

<b>Syllabus item</b>	<b>Relevant material in CCHSC</b>
<b>9.3.1</b>	<ul style="list-style-type: none"> <li>■ Experiment 1 (see previous table)</li> <li>■ identify data ... about the colour changes of ... indicators</li> <li>■ solve problems ... indicators ... to classify some household substances as acidic, neutral or basic</li> </ul>
<b>9.3.2</b>	<ul style="list-style-type: none"> <li>■ Experiment 2 (see previous table)</li> <li>■ analyse information ... industrial origins of [SO<sub>2</sub> and NO<sub>x</sub>]... and evaluate reasons for concern about their release into the environment</li> </ul>
<b>9.3.3</b>	<ul style="list-style-type: none"> <li>■ Experiment 3 (see previous table)</li> <li>■ Experiment 4 (see previous table)</li> <li>■ gather ... information ... to write ionic equations ... ionisation of acids</li> <li>■ ... model the molecular nature of acids and ... ionisation of strong and weak acids</li> <li>■ gather ... information ..., to explain the use of acids as food additives</li> <li>■ identify data ... examples of naturally occurring acids and bases and their chemical composition</li> <li>■ process information ... to calculate the pH of strong acids ...</li> </ul>
<b>9.3.4</b>	<ul style="list-style-type: none"> <li>■ gather ... information ... to trace developments in understanding ... acid/base reactions</li> </ul>

Syllabus item	Relevant material in CCHSC
■ Experiment 5 (see previous table)	
■ Experiment 6 (see previous table)	
■ Experiment 7 (see previous table)	
■ analyse information ... use of neutralisation reactions as a safety measure ...	Section 5.15 Exam-style Question 14
9.3.5 ■ Experiment 8 (see previous table)	
■ process information ... uses of esters as flavours and perfumes ...	Section 5.19

### Prescribed focus areas

The five prescribed focus areas of the syllabus are listed on p. 101.

As with most modules, the material of Module 2 (in this book and in the syllabus) relates strongly to focus areas 2 and 3, the nature and practice of chemistry, and applications and use. However there are several opportunities in Module 2 for involving areas 1 and 4.

For area 1, the history of chemistry, there is the development of the concept of an acid from Lavoisier to Brönsted and Lowry. On a different level there is the move away from indicators to pH meters for measuring pH as the latter have become increasingly cheaper (relatively). Or more speculatively, the future of the concept of pH now that electronic calculators have made logarithms virtually redundant (at least for calculation purposes).

For area 4, implications for society and the environment, there is considerable scope on the environmental side, particularly in discussing oxides of sulfur and nitrogen in the atmosphere and acid rain and possibly the enhanced greenhouse effect, though that issue is not specifically mentioned in the syllabus. Implications for society could become involved if discussions of acids as food additives were allowed to expand into the question of food additives generally and the questions of what is ‘natural’ and what is not, and of the desirability of the former over the latter.

Module 2 does not offer much opportunity to treat area 5, current issues, research and development.

MODULE 3

# Chemical monitoring and management

Industrialised societies today manufacture many substances and discard large amounts of wastes into the environment. Careful monitoring and management are essential if we are to produce substances efficiently with a minimum of waste, and if we are to protect the environment from the harmful effects of those industrial wastes and of the numerous other wastes we generate in our consumer-oriented society.

In this module, then, we shall look at several aspects of chemical monitoring and management.

We shall start with a survey of what chemists do in industry. This will involve a close look at one industrial process, the synthesis of ammonia (which is made in huge quantities worldwide, largely for fertiliser production). The discussion will show that careful monitoring and management improve the efficiency of the process (in materials, energy and dollar terms). This discussion will also let us explore further the nature of chemical equilibrium and the importance of reaction rates.

Monitoring chemical processes is only part of the job: the starting materials and the products of manufacturing must be analysed to ensure that they meet quality standards (i.e. are sufficiently pure and free from harmful contaminants).



Attention will therefore turn to analysing (both qualitatively and quantitatively) for ions in various products or mixtures. This monitoring of processes and products constitutes Chapter 6.

Many of the products of chemical industry either directly or indirectly end up in the environment, causing considerable harm. Therefore we shall turn to the question of monitoring and managing pollution of the atmosphere and of water.

To understand the effects and fates of chemicals released into the air, we need knowledge of the structure and functioning of the atmosphere and of the structure and properties of the chemicals involved. So in Chapter 7 we shall survey the atmosphere generally then look at several forms of air pollution and their sources. Particular attention will focus on the so-called ozone hole, the destruction of stratospheric ozone over the Antarctic in spring: the chemistry involved and the strategy for overcoming the problem will be discussed.

In Chapter 8 we shall consider monitoring water in the environment. The main criteria for assessing water quality will be described and several forms of water pollution will be discussed. We shall explore the variety of ways in which ions get into waterways, and the chapter will finish with a discussion of methods of treating and sanitising water for town and city supplies.



## BOTH MANUFACTURING AND THE ENVIRONMENT NEED CHEMICAL MONITORING

The efficient operation of large factories requires careful monitoring which is often done in separate chemical laboratories. One common side effect of manufacturing and other human activities is air pollution such as the Sydney smog in the photograph. Close monitoring of the environment is necessary in order to control and manage our pollution problems.



# Monitoring and management in the chemical industry

## IN THIS CHAPTER

What chemists in industry do  
The job of one particular chemist  
Branches of chemistry  
Need for collaboration  
Need for monitoring  
Uses of ammonia  
Industrial synthesis of ammonia  
Monitoring manufactured products  
Identification of cations in solution  
Procedure when only one cation is present

Identifying cations in mixtures  
Identification of anions in solutions  
Identifying anions in mixtures  
Flame tests  
Why monitor cations and anions?  
An example of gravimetric analysis  
Atomic emission spectroscopy  
Atomic absorption spectroscopy (AAS)  
AAS and trace elements

In this chapter we shall look at some of the ways that chemists monitor and manage chemicals and chemical processes in industry. But first let us survey the roles of chemists in industry.

### 6.1 WHAT CHEMISTS IN INDUSTRY DO

In industry chemists mainly monitor and manage industrial processes. The main reasons for such monitoring and managing are to ensure that:

- chemical reactions proceed efficiently in terms of speed and yield
- the products are sufficiently pure and free from dangerous contaminants
- the raw materials meet specifications (i.e. that they do not contain impurities that would upset the process or pass through to the final product)
- the workplace remains safe and healthy
- gaseous and aqueous effluents and solid wastes from the factory meet statutory requirements in terms of not exceeding allowable amounts of pollutants.

The more highly qualified chemists are also involved in research and development as it relates to the chemicals and processes used in their particular manufacturing plant.

The job of one particular chemist will further illustrate the role of chemists.

## 6.2 THE JOB OF ONE PARTICULAR CHEMIST

Luke (not his real name) is a plant chemist at a major Australian chemical manufacturing company that makes ethylene from ethane, then polymerises it to polyethylene as described in Sections 1.1 and 1.6. This company is part of the chemicals and plastics manufacturing industry. It sells some of its ethylene to another company that uses it to make ethylene oxide and ethylene glycol (Section 1.5), non-ionic surfactants (Section 10.14) and starting materials for making other plastics (polymers).

### Components of Luke's job

- Monitoring the quality of the ethylene produced by the plant to ensure that it meets the requirements for the next stage of manufacture: in particular determining the nature and amount of any impurities present
- Monitoring waste water from the plant to ensure that it meets environmental requirements (such as pH, suspended solids, sulfate, grease, hydrocarbons) before it is discharged
- Monitoring gaseous emissions to the atmosphere to ensure that they do not contain particulates (solid particles plus small droplets of liquid) or polluting chemicals above what the statutory authorities allow, and
- Collaborating with process engineers at the cracking furnace (ethane to ethylene) to adjust operating conditions in order to optimise product yields.

As a chemist in the central laboratory, Luke is not so much concerned with the hour-by-hour monitoring of products and water wastes (that is done by shift workers); rather his job is to check that the equipment operates properly, to calibrate instruments from time to time, train shift workers in the use of the instruments, carry out occasional analyses to ensure the reliability of results, solve problems that arise and generally look out for ways of improving the overall monitoring process.

The efficient operation of plants as complex as this one requires regular routine monitoring. In addition there needs to be skilled chemists available to oversee this routine work, check on its reliability, solve problems that occur and develop new procedures as circumstances or operating conditions change. Luke is one of those chemists at this plant.

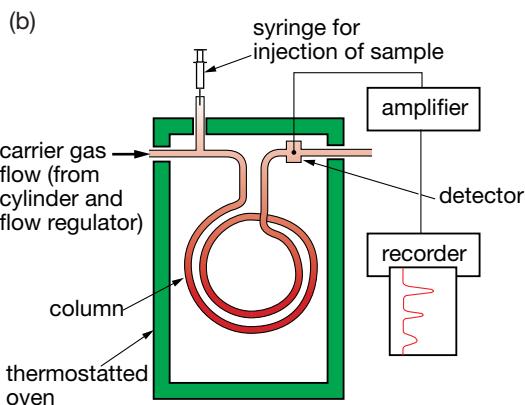
### The branch of chemistry

Luke mainly works in *analytical chemistry*—the part of chemistry concerned with determining what substances (and how much of each) are present in materials.

Many of Luke's analyses use **gas chromatography**. This is a technique in which a liquid or gaseous mixture is vaporised into a stream of helium that flows over a stationary phase which can be a solid, or a liquid coated on the surface of a solid. The stationary phase can be a finely divided solid packed in a long thin tube or column (for example, 0.5 to 2 m long, 3 to 9 mm diameter), called gas–solid chromatography, or it can be a liquid coated on the walls of a long thin glass (silica) capillary tube (10 to 100 m long, 0.1 to 0.5 mm diameter), called gas–liquid chromatography, GLC.

### The chemical principles involved

These are *adsorption* (for gas–solid chromatography) and *solubility* (for GLC).



(a) Our featured chemist setting up one of the gas chromatographs in his laboratory;  
 (b) the essential features of a gas chromatograph

If the stationary phase is a solid, then the components of the mixture injected into the flowing carrier gas adsorb on to it (stick on to its surface) to differing extents and desorb back into the gas phase at different rates, which means that they pass through the column at different rates and so are separated. A device at the end of the column detects each substance as it passes out of the column and measures it quantitatively.

If the stationary phase is a liquid, then the components of the injected mixture dissolve in it and evaporate back out of it at differing rates and so pass through the column at different speeds. The more soluble a substance is in the stationary liquid, then the slower that substance moves through the column (tube). Hence a separation is effected and the detector measures the amount of each component as it emerges from the column. Polarity of molecules is often a key factor in GLC separations: if the stationary phase is a polar liquid, then the more polar a component of the mixture to be analysed, the greater is its solubility and so the more slowly it moves through the column.

## 6.3 BRANCHES OF CHEMISTRY

Chemistry is a very broad subject and for convenience is often broken into several branches such as:

- *analytical chemistry*, the determination of what substances are present in samples (qualitative analysis) and how much of each is present (quantitative analysis)
- *physical chemistry*, the study and measurement of physical aspects of compounds and reactions, such as rates of reactions, energy aspects, structures of compounds and the nature of chemical bonding
- *organic chemistry*, the study of compounds of carbon, compounds that are usually but not exclusively associated with living matter, such as hydrocarbons, alcohols, carboxylic acids, fats, carbohydrates (sugars), amino acids and proteins
- *inorganic chemistry*, the study of compounds that are not organic; that is, compounds in which carbon is not the predominant element. Inorganic chemistry often focuses of metals, their extraction, reactions and compounds.

These have been the traditional branches of chemistry: they are based upon the intrinsic nature of chemistry—how it could most effectively be divided

for purposes of study and research. However in recent decades, as chemistry has become more involved in industrial and everyday activities of human society, further branches have become recognised based upon the uses to which chemistry is being put in the world at large. These newer branches have developed because to study many everyday problems chemists have needed to straddle the traditional boundaries. Some such branches are:

- *environmental chemistry*, concerned with determining how substances interact in the environment and with monitoring concentrations of substances, particularly pollutants, in air, water and soil
- *polymer chemistry*, a branch involved with developing new polymers with particular properties, working out how polymerisation occurs and how it can be made more efficient, and studying the properties of polymers
- *industrial chemistry*, concerned with the chemistry of industrial processes such as the manufacture of ammonia, sulfuric and nitric acids and the thousands of other compounds that are made industrially in modern society
- *food chemistry*, which looks at chemical aspects of the production, preservation and use of foods and chemicals added to food
- *pharmaceutical chemistry*, which involves the discovery, testing, synthesis and commercial development of chemicals for use as medicines
- *nuclear chemistry*, which focuses on the production and use of radioisotopes in medicine and industry as well as studying the fundamental nature of nuclear reactions
- *forensic chemistry*, concerned with the collection of evidence for use in law courts, particularly with identifying and tracing the origins of substances found at crime scenes.

This list of specialist areas of chemistry is by no means exhaustive.

These newer branches of chemistry have developed because the everyday activities they address require chemical inputs that straddle the traditional boundaries of the subject. For example environmental chemists use a lot of analytical chemistry but they also need knowledge of physical chemistry and often organic and inorganic chemistry. Forensic chemists again need analytical chemistry, but often need physical chemistry to master the complex instrumental techniques needed to trace origins of extremely small samples.

## 6.4 NEED FOR COLLABORATION

Chemistry is such a broad discipline that chemists tend to specialise in particular branches of it such as the ones listed above. Such specialisation usually starts during university training of chemists and develops further with professional experience and on-the-job training.

However many chemical problems in the real world require expertise from more than just one branch of chemistry. This is particularly true in industry where the production of a particular product can require detailed knowledge of physical chemistry (equilibrium and rate considerations), organic chemistry (how the reaction occurs and how to optimise yield), analytical chemistry (to monitor quality of raw materials and the product), industrial chemistry or chemical engineering (to be able to ‘scale up’ a laboratory experiment to industrial production quantities with inherent problems of energy inputs or outputs, mass flow problems and the selection of suitable construction materials) and environmental chemistry (to appreciate the significance of possible wastes).

and how to manage them in an environmentally responsible way). Solving such broad-ranging and complex problems requires input from many chemists with different specialties, and they cannot solve their aspect of the problem in isolation: it may have implications for other aspects being handled by other chemists. Therefore it is essential that chemists work collaboratively, regularly talk to one another and exchange their different viewpoints about problems as they arrive.

This need to collaborate means that chemists must have good communication skills—that they are able to communicate essential aspects of their particular sub-disciplines to others not expert in the same fields without using too much specialised jargon.

While collaboration between chemists is important, of equal importance is collaboration between chemists and other scientists. For example environmental problems often require input from chemists (who do analysis), microbiologists (who monitor organisms), botanists and horticulturalists (who can identify problems for flora and crops), ecologists (who oversee the interrelationships between organisms, plants and animals), geologists (who can determine the effects of constructions and earth-moving), hydrologists (who study changing water-flow patterns) and engineers (who design and supervise the construction of major works). As the work of one scientist or engineer has consequences for other areas of science or the environment, it is essential that all professionals involved work in close collaboration and talk to each other on a frequent and regular basis. And again good communication skills with the avoidance of excessive technical jargon is essential.

## 6.5 NEED FOR MONITORING

In industry it is important to monitor the conditions (such as temperature, pressure, state of catalyst) under which a chemical reaction is being conducted and the amount of product being formed in order to ensure:

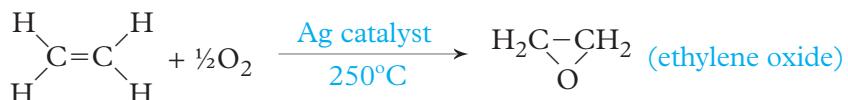
- that the maximum amount of desired product is being formed while production of unwanted by-products is minimised
- that no pollutants are being produced, either from the reaction itself or from impurities in the starting materials
- that the reaction is going to completion and not coming to an unfavourable equilibrium
- that, if the reaction is being used to generate energy, the maximum amount of energy is being produced.

We saw on pp. 286–8 *CCPC* that combustion reactions can produce solely carbon dioxide or a mixture of carbon dioxide with carbon monoxide and/or soot (carbon), depending upon the relative amount of oxygen provided. In such reactions it is important to monitor products of the reaction, so that if an undesirable product starts to form, conditions can be changed in order to stop its formation—in this case by increasing the proportion of oxygen (air) in the reaction mixture.

Another example is the reaction of ethylene with oxygen. In a plentiful supply of oxygen at a high temperature ethylene reacts to form carbon dioxide (normal combustion):



However at a lower temperature ( $250^{\circ}\text{C}$ ), with lesser amounts of oxygen and with a silver catalyst a quite different product is formed, namely ethylene oxide (Section 1.5):



Even with this catalyst and the lower temperature some ethylene reacts by Reaction 6.1. Therefore it is important to monitor reaction conditions and products to ensure that the yield of the desired product is maximised. In this reaction we would monitor the reaction temperature and pressure (to ensure that they were at the values that maximised production of ethylene oxide) and monitor the concentration of the unwanted product  $\text{CO}_2$  (to ensure its concentration was low and that the catalyst was in good condition and not becoming poisoned).

Another example of a reaction where careful monitoring of reaction conditions is needed to maximise yield is the very important industrial synthesis of ammonia. But first: why is synthesis of ammonia so important?

## 6.6 USES OF AMMONIA

Ammonia ranks second to sulfuric acid in terms of quantity produced worldwide per year. It is used to make:

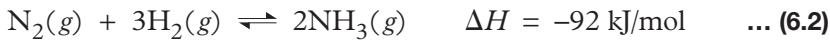
- fertilisers (sulfate of ammonia, ammonium nitrate, urea)
- fibres and plastics (rayon, acrylics, nylon)
- nitric acid, which in turn is used to make fertiliser (ammonium nitrate), dyes, fibres and plastics, and explosives such as ammonium nitrate, TNT (trinitrotoluene) and nitroglycerine (in dynamite)
- household cleaners
- detergents (non-ionic ones).

By the beginning of the twentieth century there was a growing need for an industrial method of synthesising ammonia. Increasing demands for nitrogenous fertiliser to grow food for increasing world populations were placing strains on the supply of naturally-occurring Chile saltpetre (sodium nitrate), the main ‘artificial’ fertiliser at that time. In addition the growing militancy of Germany was promoting calls for more explosives (generally made from nitric acid which in turn was mainly produced from saltpetre).

## 6.7 INDUSTRIAL SYNTHESIS OF AMMONIA

The German, Fritz Haber, in 1908 first developed a method of synthesising ammonia from its elements, though it was not until 1914 that Carl Bosch successfully converted it into an industrial process. This synthesis contributed significantly to the German war effort in World War I in that it insulated German agriculture from any harm caused by interrupted supplies of saltpetre from South America and it facilitated the production of nitric acid and hence of explosives.

The synthesis of ammonia uses the simple exothermic reaction:



This is an equilibrium reaction which at ordinary pressures and temperatures lies well to the left.

## Equilibrium considerations

Le Chatelier's principle (Section 4.7) shows us how to maximise the conversion of nitrogen and hydrogen to ammonia.

- 1 If the pressure on a reaction system is increased, the equilibrium moves in the direction which tends to reduce pressure; that is, the direction which corresponds to a decrease in the number of moles of gas, since a decrease in the number of moles of gas in a container of fixed volume leads to a decrease in pressure. This is because the pressure of a gas arises from gas particles hitting the walls of the container. The more particles in a given volume, the more collisions there are (per unit area per unit time) between gas particles and walls.

If the pressure on an equilibrium mixture of  $\text{N}_2$  and  $\text{H}_2$  is increased, the reaction moves to the right: some  $\text{N}_2$  and  $\text{H}_2$  react to form  $\text{NH}_3$ . This happens because that direction corresponds to a decrease in the number of moles of gas:



- 2 If the temperature is lowered, the equilibrium will move in the direction which tends to increase temperature (release heat). Reaction 6.2 is exothermic, so if temperature is lowered, it will move towards the right (form more ammonia).

Figure 6.1 shows how the percentage conversion of nitrogen to ammonia varies with pressure (at constant temperature) and temperature (at constant pressure). On equilibrium considerations alone the reaction should be conducted at high pressure and low temperature.

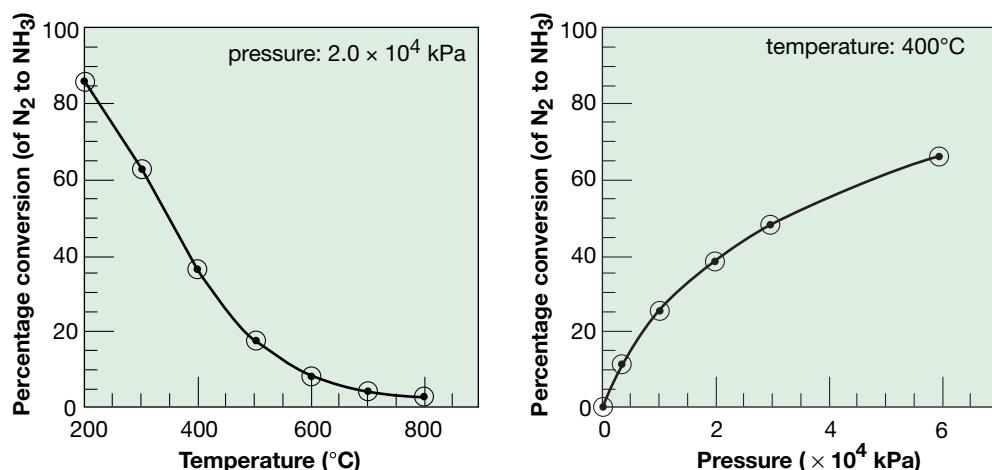


FIGURE 6.1  
The temperature and pressure dependence of the equilibrium percentage conversion of nitrogen to ammonia for a stoichiometric mixture of  $\text{H}_2$  and  $\text{N}_2$

## Rate considerations

However another consideration is *how long* it will take for the reaction to reach equilibrium: that is, we need to consider the *rate* of the reaction. As for most reactions, the rate of Reaction 6.2 decreases as temperature decreases. If we lower the temperature in order to move the equilibrium towards the right, we make the reaction very slow and so it takes a very long time to reach equilibrium. The reason for rate of reaction increasing as temperature increases (or decreasing as temperature decreases) was explained on p. 295 CCPC.

One way to increase the rate of a reaction is to find a suitable catalyst (pp. 291, 296 CCPC). Iron is a good catalyst for Reaction 6.2. While this catalyst does speed up the reaction, the rate is still too low at room temperature to be practical. Remember that while a catalyst speeds up a reaction, *it does not affect the position of equilibrium*. This is because it speeds up both the forward and reverse reactions.

Hence we have these situations: a low temperature produces a high yield (say 90% conversion of hydrogen to ammonia), but a very long time (weeks to months) is required to reach equilibrium, even with a catalyst. A high temperature causes equilibrium to be reached quickly (in a few minutes) but the equilibrium yield is extremely low (say 0.1%).

## Compromise

Compromise conditions are therefore used. A moderate temperature produces a moderate yield moderately quickly. Typical conditions for the industrial process, called the **Haber process** are:

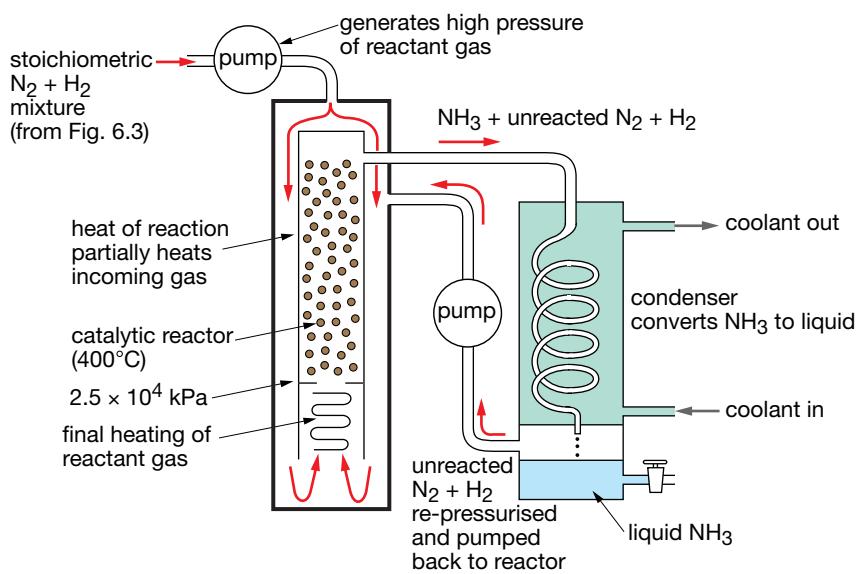
- a temperature of about 700 K (or about 400°C) and
- a total pressure of about  $2.5 \times 10^4$  kPa (250 times standard atmospheric pressure).

With a reactant mixture having H<sub>2</sub> and N<sub>2</sub> in the ratio of 3:1, these conditions give an equilibrium conversion to ammonia of about 45%. However industrial plants generally do not allow sufficient time for equilibrium to be reached and so yields of about 30% are more common. The catalyst is magnetite, Fe<sub>3</sub>O<sub>4</sub>, with its surface layer reduced to free iron.

The process is illustrated in Figure 6.2. Reactants pass through the catalytic reactor, then the mixture is cooled to condense out the ammonia formed; this can be drained off as required. Unreacted gases are fed back into the catalyst chamber along with incoming fresh reactants. None of the reactant mixture is wasted. We essentially drive the reaction to completion by condensing out the reaction product.

A stoichiometric mixture of hydrogen and nitrogen is used so that, as ammonia is formed and condensed out, left-over reactants can be recycled

**FIGURE 6.2**  
The Haber process  
for making ammonia  
(schematic)



through the process (with some fresh reactant mixture added) without any build-up of one reactant over the other.

An important factor in designing an industrial process is energy management. In the Haber process we would like to use the heat released by Reaction 6.2 to heat up, at least partially, the incoming reactants and so minimise our energy costs: this has the added advantage that it stops the catalyst overheating and so losing activity. This is the reason for the incoming reactants flowing over the outside of the catalyst chamber before entering it.

## The source of reactants

Nitrogen can be obtained from the atmosphere, so hydrogen is the ‘difficult’ or expensive reactant to obtain.



Huge quantities of ammonia are synthesised mainly for making fertiliser in production facilities such as this one operated by CSBP Limited in Kwinana, WA

In the laboratory we make hydrogen gas by reacting zinc or magnesium with hydrochloric acid. This process is too expensive for industrial use. Alternatively hydrogen can be made by the electrolysis of water (p. 71 *CCPC*), but except in special situations this also is very expensive. Industrially, hydrogen is generally produced by reacting methane (natural gas) or some other hydrocarbon with steam in the presence of a nickel catalyst at a temperature of about 750°C:



Carbon monoxide poisons the iron catalyst in the Haber process and so must be removed. This is done with another catalytic reaction:

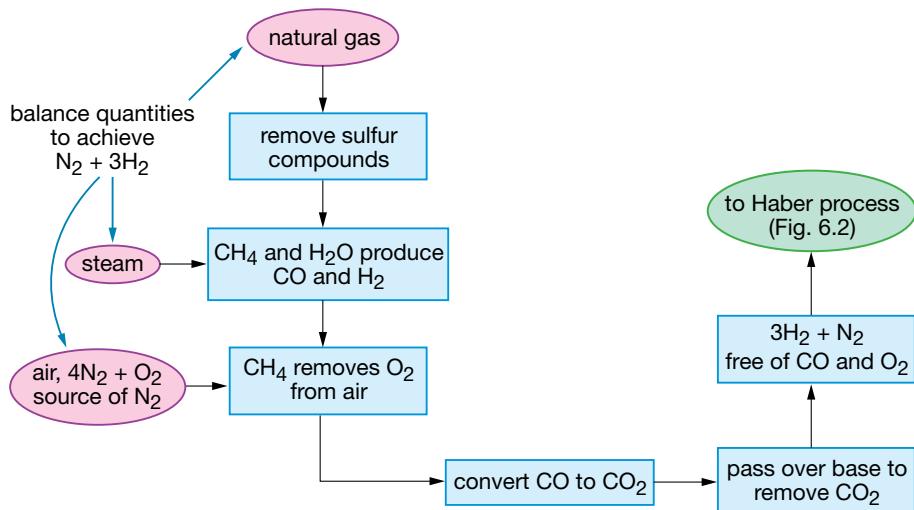


which has the added advantage of producing more hydrogen. The catalyst used is either  $\text{Fe}_3\text{O}_4$  at 500°C or Cu at 250°C.

A complication for the Haber process is that we want a mixture of hydrogen and nitrogen that does not contain any oxygen (which can react explosively with hydrogen under the conditions used). Methane is also used to remove oxygen from air (in effect just normal combustion to  $\text{CO}_2$  and steam). By adjusting the quantities of methane, steam and air used, this combination of reactions can be

made to produce a 3:1 mixture of hydrogen and nitrogen. The only unwanted gas in the mixture is carbon dioxide. This is removed by reaction with a base. If oxygen has to be excluded and if the reactant mixture has to be recycled through the reactor (Fig. 6.2), then use of a 3:1 mixture is the most efficient way of making ammonia. Figure 6.3 presents a flowchart for this preparation of the H<sub>2</sub>, N<sub>2</sub> mixture.

**FIGURE 6.3**  
A flowchart for the preparation of reactants for the Haber process



## Monitoring

Because many different conditions must be maintained for efficient and safe operation of the Haber process, monitoring is essential. The conditions that need to be monitored include:

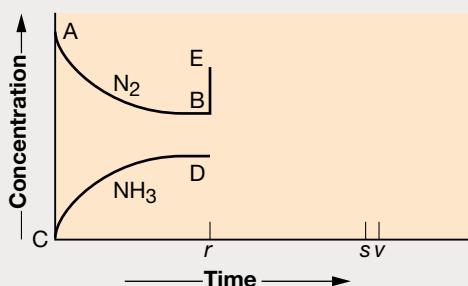
- *temperature and total pressure in the reaction vessel*, to keep them in the range for optimum conversion of reactants to products: in addition excessive temperature can damage the catalyst
- *ratio of H<sub>2</sub> to N<sub>2</sub> in the incoming gas stream*: we need to ensure that this ratio is kept at 3:1 to avoid a build-up of one reactant
- *concentrations of O<sub>2</sub>, CO, CO<sub>2</sub> and sulfur compounds in the incoming gas*: we must ensure that oxygen is absent to avoid risk of explosion, and that concentrations of CO, CO<sub>2</sub> and sulfur-containing species are sufficiently low to prevent poisoning of the catalyst; with a well-maintained plant the catalyst can last up to eight years
- *concentrations of argon and methane in the reaction vessel*, because any build-up of these gases will lower the efficiency of the conversion
- *purity of the product ammonia*, to ensure that no impurities contaminate the product of the process.

## Exercises

- 1 A mixture of 3 moles of hydrogen and 1 mole of nitrogen in a container of fixed volume was brought into contact with a suitable catalyst at 400°C. When equilibrium was reached 40% of the nitrogen had been converted to ammonia.
  - a Write an equation for this equilibrium reaction, then draw a graph showing the concentrations of the three substances as functions of time until well after equilibrium had been reached. Make the relative starting and equilibrium concentrations as quantitative as possible.



- b** After equilibrium was reached the mixture was rapidly cooled to remove (by liquefaction) 90% of the ammonia; the remaining gas mixture was brought back to 400°C (still in contact with the catalyst). Show on your graph how the concentrations would change from this point forward until equilibrium had been re-established. Explain why your curves have the shape and equilibrium values that you gave them.
- 2** A mixture of nitrogen and hydrogen gases was brought into contact with an iron catalyst at 700 K. The concentrations of nitrogen and ammonia followed curves AB and CD respectively on the graphs below. At time  $r$  extra nitrogen was added to the mixture: this immediately increased the concentration of nitrogen from B to E. By time  $s$  the system had returned to equilibrium. Copy both graphs into your workbook and sketch the curves that the concentrations of nitrogen and ammonia would follow between  $r$  and  $s$ .



At time  $v$  the volume available to the reaction mixture was suddenly doubled. Show on your graphs how the concentrations would change after time  $v$ . Explain why your graphs have their particular shapes.

- 3** For the gaseous reactions:

- a**  $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2$  (exothermic)
- b**  $\text{CH}_3\text{OH} \rightleftharpoons \text{CO} + 2\text{H}_2$  (endothermic)
- \*c**  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$  (exothermic)
- d**  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$  (endothermic)

predict the effect upon the position of equilibrium of:

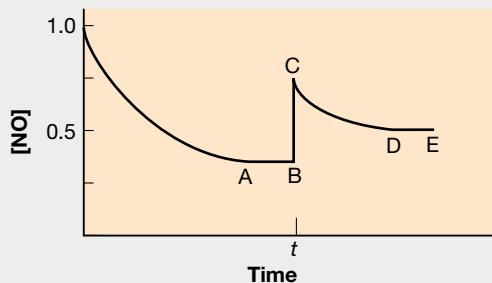
- i** increasing the pressure (i.e. compressing the reaction mixture into a smaller volume)
- ii** adding oxygen to (a) and (c)
- iii** adding hydrogen to (b) and (d)
- iv** increasing temperature
- v** increasing the volume available to the reaction mixture.

- 4** If each of the reactions in Exercise 3 were at equilibrium in a flask of fixed volume, and if helium were added so that the total pressure in the flask doubled, what change, if any, would there be in the equilibrium position?
- 5** Select conditions which would maximise the conversion of the underlined reactant to the underlined product in the following reactions at room temperature:
- a**  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
  - \*b**  $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$
  - c**  $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$
- 6** Nitric oxide reacts with chlorine to form nitrosyl chloride:



The graph below shows the concentration of NO as a function of time after mixing 1.0 mol NO with 0.5 mol  $\text{Cl}_2$  in a 1.0 L flask at a constant temperature. At time  $t$

the gaseous mixture is suddenly compressed into a volume which is half of the initial volume.



a Explain:

- i why  $[NO]^{\dagger}$  remains constant from A to B on the graph
  - ii why  $[NO]$  increased to C when the volume was decreased
  - iii why  $[NO]$  decreases from C to D
  - iv why  $[NO]$  between D and E is higher than between A and B.
- \*b Suppose that the volume available to the reaction mixture had been doubled at B. Copy the graph into your workbook and sketch on it the curve you would expect for  $[NO]$  versus time after B. Give your reasoning.
- \*c Sketch the curve you would expect if a catalyst had been used in the original experiment.

7 The reaction:



is the main way that polluting oxides of nitrogen are formed in petrol driven motor cars. This reaction proceeds to greater extents at higher temperatures. Is the reaction exothermic or endothermic? Explain.

## 6.8 MONITORING MANUFACTURED PRODUCTS

Not only is it essential to monitor production processes, but also the final products of chemical factories must be monitored, for example food, drugs and household chemicals. This is to ensure that the products match their stated specification (i.e. contain the stated percentage of active ingredients) and that they do not contain unacceptable amounts of impurities.

Some impurities or minor constituents that can be present in manufactured chemicals are ionic compounds. Therefore it is often necessary to determine, first qualitatively then quantitatively, which if any cations or anions are present in substances.

## 6.9 IDENTIFICATION OF CATIONS IN SOLUTION

There are two types of problems involving the identification of cations:

- 1 identification of the one and only cation present in a sample known to be a pure substance (such as a bottle in a chemical store which has lost its label)
- 2 identification of all the cations present in a sample known to be a mixture.

† Remember, square brackets around a formula mean ‘concentration of’.

The second is by far the more common situation: it occurs in the analysis of ore samples from mines and of effluents being discharged by factories, and in testing for impurities in manufactured chemicals. It is also the more difficult task, so let us start with the simpler one.

## Tests for identifying the one cation in a solution

In this discussion we will consider only the six cations  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . In the real world chemists have to consider many more cations than this, but this limited list will demonstrate the principles involved in identification without needing to get involved with large numbers of tests.

*Cations in solution are primarily identified by precipitation reactions.* By observing whether or not precipitates form when solutions of hydrochloric acid, sulfuric acid and sodium hydroxide are added to samples of the solution to be identified we can deduce which cation is present. Hence it is necessary to be familiar with the solubility table, Table 8.1 on p. 205 CCPC. This would be a good time to revise pp. 202–7 CCPC. That table is reproduced inside the back cover of this book. Table 6.1 shows selected information from that table which is relevant to the present discussion.

**TABLE 6.1 Cations (from our list of six) that form precipitates with chloride, sulfate and hydroxide. Precipitates are white unless a colour is given**

with $\text{Cl}^-$	$(\text{Pb}^{2+})^a$
with $\text{SO}_4^{2-}$	$\text{Pb}^{2+}$ , $\text{Ba}^{2+}$ , $(\text{Ca}^{2+})^a$
with $\text{OH}^-$	$\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ (blue), $\text{Fe}^{2+}$ (green), $\text{Fe}^{3+}$ (brown), $(\text{Ca}^{2+})^a$

a provided concentration is high enough, say  $> 0.05 \text{ mol/L}$ , and the mixture is well shaken

Table 6.2 gives the common tests we use to identify each of the cations in the above list. The cations are shown in an order in which we can conveniently test for them, by using solutions of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  in that sequence.

Before performing any test we would first note the colour of the solution: colour sometimes gives us a clue to the identity of the cation. Common colours (of our selected cations) are:

- copper: pale blue
- iron(II): pale green (may be colourless if dilute)
- iron(III): yellow (nearly colourless if dilute)

While evidence based on colour is useful, it cannot be taken as positive identification of the cation.

## 6.10 PROCEDURE WHEN ONLY ONE CATION IS PRESENT

If we know that our solution contains only one cation, then we would perform the  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  tests in that order on separate samples of the solution. In outline:

- 1 Add  $\text{HCl}$ : if a precipitate forms, then the cation is  $\text{Pb}^{2+}$
- 2 Add  $\text{H}_2\text{SO}_4$ : if a precipitate forms, the cation is either  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$
- 3 Add  $\text{NaOH}$ : if a precipitate forms, the cation is one of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ .

**TABLE 6.2 Tests used to identify cations (from our set of six)**

**Cation Tests**

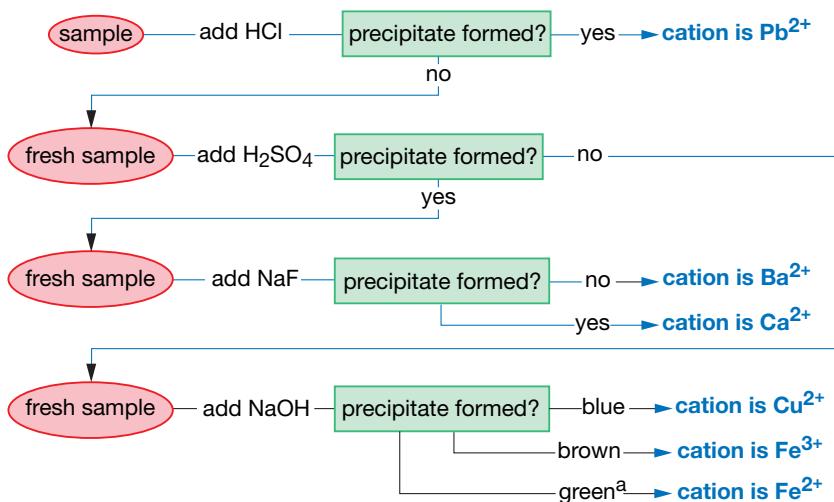
Pb <sup>2+</sup>	1 with Cl <sup>-</sup> forms a white precipitate (if solution not too dilute, say > 0.05 mol/L) 2 with I <sup>-</sup> forms a yellow precipitate
Ba <sup>2+</sup>	1 with SO <sub>4</sub> <sup>2-</sup> forms a white precipitate 2 gives a pale green flame colour <sup>a</sup> 3 no precipitate with OH <sup>-</sup> or F <sup>-</sup> (compare Ca <sup>2+</sup> )
Ca <sup>2+</sup>	1 with SO <sub>4</sub> <sup>2-</sup> forms a white precipitate (if solution not too dilute, say > 0.05 mol/L) 2 with F <sup>-</sup> forms a white precipitate 3 gives a brick-red flame colour <sup>a</sup>
Cu <sup>2+</sup>	1 with OH <sup>-</sup> forms a blue precipitate 2 this precipitate dissolves in NH <sub>3</sub> to form a deep blue solution 3 gives a blue-green flame colour <sup>a</sup>
Fe <sup>2+</sup>	1 with OH <sup>-</sup> forms a green or white precipitate which may turn brown <sup>b</sup> 2 decolorises acidified dilute potassium permanganate solution
Fe <sup>3+</sup>	1 with OH <sup>-</sup> forms a brown precipitate 2 with thiocyanate, SCN <sup>-</sup> forms a deep red solution

a See Section 6.14.

b *Fe(OH)<sub>2</sub> most commonly forms as a green crystalline precipitate, but under some conditions can be a white amorphous precipitate. Green Fe(OH)<sub>2</sub> is oxidised by dissolved oxygen to brown Fe(OH)<sub>3</sub>. Freshly prepared solutions of Fe<sup>2+</sup> will generally give a green precipitate that goes brown very slowly if at all; older solutions of Fe<sup>2+</sup> tend to form darker green precipitates that discolour to brown fairly rapidly.*

The detailed procedure is shown in Figure 6.4.

**FIGURE 6.4**  
Flowchart for identifying the one cation (of our set of six) present in a solution



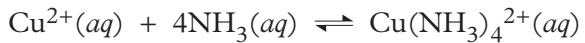
<sup>a</sup> though it may go brown on standing (oxidation to Fe(OH)<sub>3</sub>). See footnote to Table 6.2.

If a precipitate forms when HCl solution is added, the cation present is Pb<sup>2+</sup> and we need proceed no further (since the sample contained only one cation).

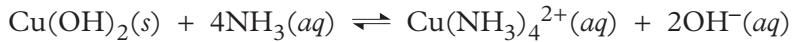
If H<sub>2</sub>SO<sub>4</sub> solution produces a precipitate, the cation is either Ba<sup>2+</sup> or Ca<sup>2+</sup>; to determine which, we use the fact that calcium fluoride is insoluble while barium fluoride is soluble. A fresh sample of the solution is used for this.

If HCl and H<sub>2</sub>SO<sub>4</sub> produce no precipitate, we test the solution with NaOH solution. A blue precipitate shows that the cation is Cu<sup>2+</sup>: in this case the original

solution probably had a pale blue colour. We can confirm that the cation is  $\text{Cu}^{2+}$  by adding ammonia to the blue precipitate: it dissolves to form a deep blue solution. Copper ion reacts with ammonia solution to form a *complex ion*:



or in this particular case:



A **complex ion** is an ion formed when one or more small molecules or ions attach themselves to a cation to form a combined ion that has properties that are quite distinct from those of the parent ions or molecules.

In the complex ion  $\text{Cu}(\text{NH}_3)_4^{2+}$  four  $\text{NH}_3$  molecules are attached to a  $\text{Cu}^{2+}$  ion; the complex ion has an intense blue colour while  $\text{Cu}^{2+}$  is pale blue and ammonia is colourless. The species  $\text{Fe}(\text{SCN})^{2+}$  mentioned below is also a complex ion, being made by a thiocyanate ion,  $\text{SCN}^-$ , attaching itself to a  $\text{Fe}^{3+}$ . This complex ion has a blood red colour whereas thiocyanate,  $\text{SCN}^-$  is colourless and  $\text{Fe}^{3+}$  is pale yellow.

If  $\text{NaOH}$  produces a green or white precipitate, then the cation present is  $\text{Fe}^{2+}$ ; if it produces a brown precipitate, the cation present is  $\text{Fe}^{3+}$ .

## Distinguishing between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$

Because of the ease of oxidation of  $\text{Fe}(\text{OH})_2$  to  $\text{Fe}(\text{OH})_3$ , the results of the hydroxide test may not clearly show which of these two cations is present. In that case there are two further tests we can perform to resolve the difficulty. An  $\text{Fe}^{3+}$  solution forms a blood red colour when drops of colourless potassium thiocyanate KSCN solution are added to it:



When drops of purple potassium permanganate solution are added to a colourless solution containing  $\text{Fe}^{2+}$  ions, the  $\text{Fe}^{2+}$  decolorises the permanganate:



One or both of these tests can be used to determine which iron cation is present.

## Solubility problems

We saw on p. 205 CCPC that lead chloride and calcium sulfate are only sparingly soluble. This means that if the concentration of  $\text{Pb}^{2+}$  or  $\text{Ca}^{2+}$  is low, then a precipitate of  $\text{PbCl}_2$  or  $\text{CaSO}_4$  will not form.

If no precipitate is formed with  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ , then the cation present (of the six possibilities under consideration) is either  $\text{Pb}^{2+}$  or  $\text{Ca}^{2+}$ . Therefore a fresh sample of the unknown solution is tested with potassium iodide solution: if a yellow precipitate is formed, then  $\text{Pb}^{2+}$  is present.<sup>†</sup> If no precipitate forms then the solution is tested with a dilute solution of sodium fluoride: a white precipitate shows that  $\text{Ca}^{2+}$  is present.

<sup>†</sup> We do not use iodide instead of chloride in the basic procedure because iodide reacts with  $\text{Cu}^{2+}$  to form a mixture of white  $\text{CuI}$  precipitate and brown iodine solution.

The procedure just described for identifying which one of the nominated six cations is present in a solution of a pure substance is not the only one that can be used. However it has the advantage of using simple chemicals and most of the reactions involved should already be familiar to you.

## 6.11 IDENTIFYING CATIONS IN MIXTURES

When we are trying to identify the one cation present in a solution of a pure substance, we can perform our HCl,  $\text{H}_2\text{SO}_4$ , NaOH tests on fresh samples of solution, because there is no fear of interference: one cation cannot foul up the test for another cation, because there is only one cation present.

However when we come to the more usual task of identifying the several cations present in a mixture, we have to modify our procedure to prevent one cation interfering with the test for another cation. For example, if both  $\text{Pb}^{2+}$  and  $\text{Ba}^{2+}$  are present in a solution, the  $\text{Ba}^{2+}$  does not upset the test for  $\text{Pb}^{2+}$  (formation of  $\text{PbCl}_2$ ), but  $\text{Pb}^{2+}$  gives a precipitate with  $\text{H}_2\text{SO}_4$  which complicates interpretation of the test for  $\text{Ba}^{2+}$  (precipitate with  $\text{H}_2\text{SO}_4$ ).

Hence when we analyse mixtures, we separate the precipitate from the filtrate in each major test and perform the next test on the filtrate from the preceding test. In this way we eliminate interference. However, before separating off the precipitate we must ensure that all of the relevant cation has been precipitated (removed from the solution); hence we add drops of the reagent (HCl or  $\text{H}_2\text{SO}_4$ ) until no further precipitate forms.

Although filtration can be used to separate the precipitate from the filtrate, it is slow. A quicker method is to use a centrifuge.

A **centrifuge** is a machine that spins test tubes at high speed and so flings the precipitate to the bottom of the tube very quickly.

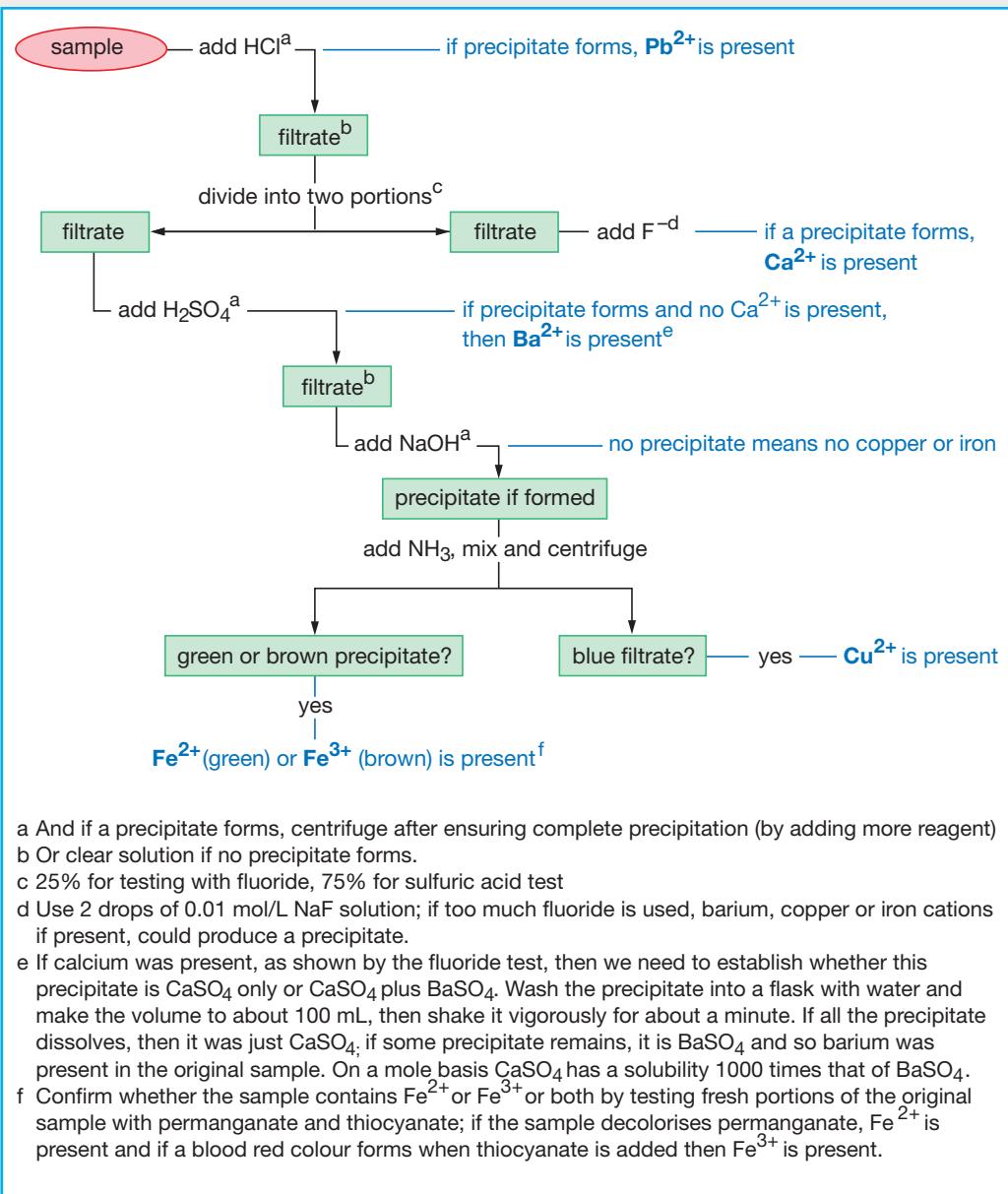
Figure 6.5 shows a typical laboratory centrifuge. After centrifuging, the filtrate is removed with an eye dropper (Pasteur pipette), and the next test performed on that solution.

Providing each of the  $\text{H}_2\text{SO}_4$  and NaOH tests is done on the filtrate from the previous test, the method of determining the cations present in a mixture is the same as for a pure substance. A flowchart is set out in Figure 6.6.

FIGURE 6.5  
(a) A typical laboratory centrifuge (b) samples of iron(III) hydroxide (left) and lead iodide (right) before and after centrifuging



FIGURE 6.6  
A scheme for identifying cations in mixtures



## Exercises

- 8 Write net ionic equations for all the reactions mentioned in Table 6.2.
- 9 Describe tests to determine whether a solution of a pure substance contained:
- a lead nitrate or barium nitrate
  - b copper sulfate or iron(II) sulfate
  - c calcium chloride or iron(III) chloride
  - \*d iron(II) sulfate or iron(III) sulfate
  - \*e barium nitrate or copper nitrate
- 10 A pair of students were given six solutions and told that each solution contained one (and only one) of the cations,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ . To determine the cation present in each solution they added solutions of hydrochloric acid, sulfuric acid and sodium hydroxide in turn to separate samples of each solution. Their results are tabulated below. Identify the cation present in each solution. If for a particular solution the tests do not identify just one cation, state the possibilities and suggest further tests to distinguish between the possibilities. If the tests performed do not allow the



identification of any cation in a particular solution, suggest further tests and explain why they are necessary.

Reagent	A	B	C	*D	*E	*F
HCl	NP <sup>a</sup>	NP	NP	ppt	NP	NP
H <sub>2</sub> SO <sub>4</sub>	ppt <sup>b</sup>	NP	NP	ppt	ppt <sup>b</sup>	NP
NaOH	NP	brown ppt	blue ppt	ppt	NP	NP

a NP = no precipitate; ppt = precipitate formed.

b When sodium fluoride solution was added to Solution A a precipitate formed; when added to Solution E, no precipitate formed.

- 11 Would sodium carbonate solution be a suitable reagent for deciding which cation (out of Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>) was present in a solution? Explain.
- 12 With the only possibilities being Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, what cations are present in a solution which:
  - a forms a white precipitate with sulfate and with fluoride, no precipitate with chloride, and a blue precipitate with hydroxide which dissolves in ammonia solution
  - b forms a white precipitate with chloride (with the filtrate from this giving no precipitate with sulfate), and a brown precipitate with hydroxide: when ammonia solution is added to this precipitate, none of the precipitate appears to dissolve and the filtrate remains colourless. The original solution does not decolorise permanganate solution.
  - c forms a brown precipitate with hydroxide but no precipitate with chloride or sulfate: separate samples of the original solution decolorise permanganate and form a red colour with thiocyanate.
- 13 A solution was thought to contain at least one of the cations, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup>, but it gave no precipitate with chloride, sulfate or hydroxide. Offer an explanation for this and suggest ways of proving the presence of one or more of these cations.
- 14 You may use Table 6.1 or the solubility table inside the back cover for this question. Some students were asked to identify the (one) cation present in a solution. They tested samples of the solution with sulfuric acid, sodium hydroxide and potassium carbonate solutions and obtained precipitates with sulfuric acid and with potassium carbonate but not with sodium hydroxide. Student A decided that the sample contained Pb<sup>2+</sup>, student B that it contained Ca<sup>2+</sup> and student C that it contained Ba<sup>2+</sup>. Which student or students gave an answer that is consistent with the results? Explain your reasoning.
- 15 To determine the cations present in five unknown samples labelled P, Q, R, S and T a group of students performed the following procedure on each sample:
  - i Add HCl solution; if precipitate forms, centrifuge it off.
  - ii To the solution or filtrate from (i) add H<sub>2</sub>SO<sub>4</sub> solution; if precipitate forms centrifuge it off.
  - iii If a precipitate forms in (ii), repeat (i) and test the solution or filtrate with NaF solution.
  - iv To solution or filtrate from (ii) add NaOH solution; if precipitate forms, centrifuge it off and note its colour.
  - v To precipitate from (iv), if any, add ammonia solution, centrifuge and note colour of solution and of precipitate, if any remains.
  - vi If a brown precipitate remains in (v) test a portion of the original sample with (a) permanganate solution and (b) thiocyanate solution.

Their results are summarised below. What cations are present in each solution?

Test	P	Q	R	*S	*T
i (HCl)	ppt <sup>a</sup>	NP	NP	ppt	ppt
ii (H <sub>2</sub> SO <sub>4</sub> )	NP <sup>a</sup>	ppt	NP	ppt	ppt
iii (NaF) <sup>b</sup>		NP		ppt	NP
iv (NaOH)	blue ppt	brown ppt	blackish ppt	NP	ppt
v (NH <sub>3</sub> ) <sup>c</sup>	blue soln, no ppt left	colourless soln, brown ppt <sup>d</sup>	blue soln, green- brown ppt <sup>e</sup>		blue soln, no ppt left

a NP = no precipitate; ppt = precipitate formed

b only performed if (ii) gave a precipitate

c only performed if a precipitate formed in (iv)

d Test (vi) (a) did not decolorise MnO<sub>4</sub><sup>-</sup> (b) deep red colour with SCN<sup>-</sup>.

e Test (vi) (a) decolorised MnO<sub>4</sub><sup>-</sup> (b) no colour with SCN<sup>-</sup>.

## 6.12 IDENTIFICATION OF ANIONS IN SOLUTIONS

Often we need to identify the anions present in a solution. As with cations we shall illustrate the general approach by using only four anions, namely carbonate, chloride, phosphate and sulfate.

As with cations there are two situations:

- 1 identifying the one anion present in a solution known to contain only one pure substance
- 2 identifying all the anions present in a mixture.

Again the first task is the simpler, so let us start with it.

The common tests for identifying the four chosen anions are set out in Table 6.3. The order of listing provides a convenient sequence to use for identifying an unknown anion.

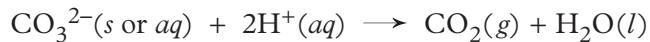
Because the metal ions used in these tests form precipitates with more than one of our anions, care is needed in interpreting results. Table 6.4 shows which combinations of four common cations and the four selected anions (plus hydroxide) produce precipitates.

Note that colour of the solution is of no help in identifying these anions, because they are all colourless: any colour in the solution is due to the cation(s) present.

Note also that a precipitate with silver nitrate does not prove the presence of chloride (footnote to Table 6.3).

### Carbonate

Because carbonates form precipitates with many cations, including those we want to use to test for sulfate, phosphate and chloride, we need to avoid using a precipitation reaction to test for carbonate. Hence we use a common acid–base reaction of carbonates. *All carbonates react with dilute acids to form carbon dioxide gas:*



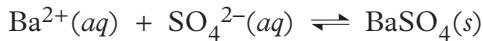
In analysing mixtures we use enough nitric acid to destroy all the carbonate so it will not interfere with tests for the other anions.

## Use of Ba<sup>2+</sup> for sulfate and phosphate

In dilute acid solution barium ions produce a precipitate with sulfate but not with phosphate. This is because HPO<sub>4</sub><sup>2-</sup> is a much weaker acid than HSO<sub>4</sub><sup>-</sup>. In dilute acid solution the reaction



proceeds to sufficient extent to produce enough SO<sub>4</sub><sup>2-</sup> to form a precipitate with Ba<sup>2+</sup>:

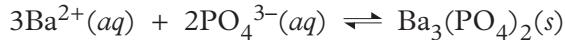


On the other hand HPO<sub>4</sub><sup>2-</sup> is so weak that in dilute acid solution the equilibrium



lies so far to the left that insufficient PO<sub>4</sub><sup>3-</sup> is formed to produce a precipitate of Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.

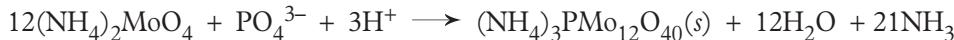
However in ammonia solution (pH about 10 or 11), [H<sub>3</sub>O<sup>+</sup>] is so low that Reaction 6.4 moves well to the right (Le Chatelier's principle) and so produces enough PO<sub>4</sub><sup>3-</sup> for barium phosphate to precipitate:



A similar situation occurs for phosphate with silver and lead ions.

## Other tests for phosphate

Two tests for phosphate not involving barium ion are listed in Table 6.3. Both of these have the advantage that they can be applied directly to the sample without interference from any of our anions. The equations for these tests are:



The polynuclear phosphomolybdate complex (NH<sub>4</sub>)<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> can be thought of as (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub>.

TABLE 6.3 Tests used to identify the four selected anions

Anion	Test
carbonate	1 solution has a pH between 8 and 11 (pH paper suffices) 2 addition of dilute HNO <sub>3</sub> produces bubbles of colourless gas (CO <sub>2</sub> ) <sup>a</sup>
sulfate	1 addition of Ba(NO <sub>3</sub> ) <sub>2</sub> to an acidified sample of the solution produces a thick white precipitate 2 acidification and addition of Pb(NO <sub>3</sub> ) <sub>2</sub> produces a white precipitate
phosphate	1 addition of ammonia followed by Ba(NO <sub>3</sub> ) <sub>2</sub> produces a white precipitate 2 addition of Mg <sup>2+</sup> in an ammonia, ammonium nitrate buffer produces a white precipitate of Mg(NH <sub>4</sub> )PO <sub>4</sub> 3 acidification with HNO <sub>3</sub> followed by addition of ammonium molybdate solution (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> produces a yellow precipitate; warming the mixture for a few minutes may be necessary
chloride	1 addition of AgNO <sub>3</sub> to an acidified sample produces a white precipitate <sup>b</sup> 2 this precipitate dissolves in ammonia solution and darkens in sunlight

<sup>a</sup> Any strong acid (i.e. H<sub>3</sub>O<sup>+</sup>) would do but for analysing mixtures (next section) we do not want to introduce any Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup>.

<sup>b</sup> In non-acidic solutions silver nitrate also produces precipitates with carbonate and phosphate (and with sulfate at all pHs if sulfate concentration is moderately high), so this test alone does not prove the presence of chloride: it is also necessary to prove the absence of sulfate.

**TABLE 6.4 Does each of the cations in the left-hand column form a precipitate with the anions in the top row?**

	$\text{OH}^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$ <sup>a</sup>	$\text{CO}_3^{2-}$ <sup>b</sup> in alkaline solution	$\text{PO}_4^{3-}$	
					solution pH < 2	solution pH > 6
$\text{Ba}^{2+}$	no	no	yes	yes	no	yes
$\text{Pb}^{2+}$	yes	yes <sup>c</sup>	yes	yes	no	yes
$\text{Ag}^+$	yes <sup>d</sup>	yes	yes <sup>c</sup>	yes	no	yes
$\text{Cu}^{2+}$	yes	no	no	yes	no	yes

a in acidic or alkaline solution

b cannot have carbonate in acid solution: it decomposes to  $\text{CO}_2(g)$

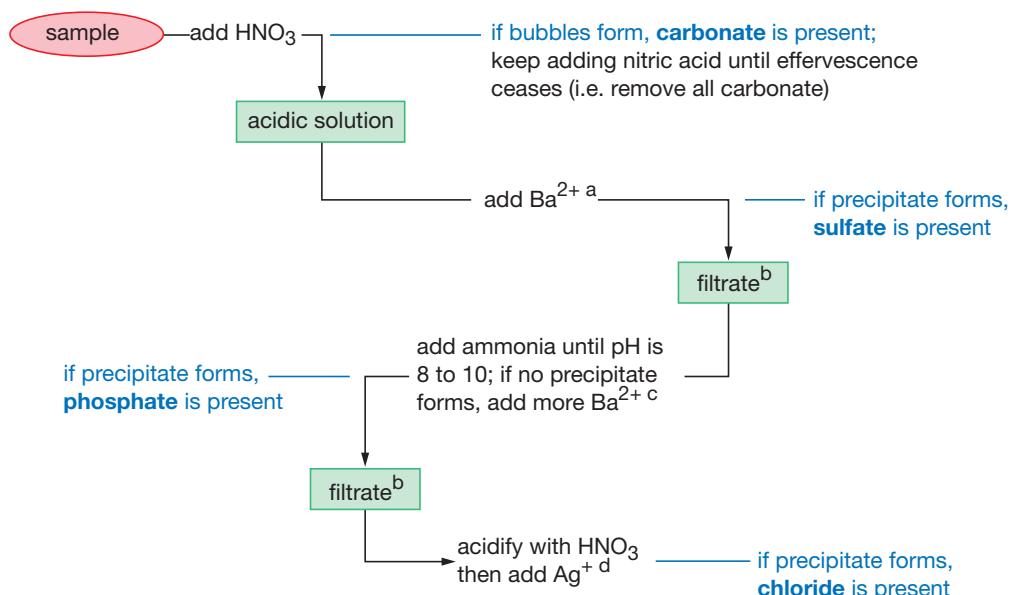
c provided concentration of  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  is not too low, say  $> 0.05 \text{ mol/L}$

d precipitate is brown  $\text{Ag}_2\text{O}$

## 6.13 IDENTIFYING ANIONS IN MIXTURES

As with identifying cations in mixtures (Section 6.11) we use the same tests as for identifying single anions, but again we need to follow a sequence that avoids one anion interfering with the test for another anion. This is done by performing tests for sulfate, phosphate and chloride on the solutions left over from the previous test.

Figure 6.7 presents a flow chart for identifying anions (from our list of four) in a solution. Other schemes are possible.



**FIGURE 6.7**  
A scheme for identifying anions in mixtures

a If a precipitate forms, add more  $\text{Ba}^{2+}$  until no further precipitation occurs, then centrifuge (or filter).

b or the solution if no precipitate formed.

c A precipitate may form when  $\text{NH}_3$  is added because there may be sufficient  $\text{Ba}^{2+}$  left from the sulfate test; if not, add more  $\text{Ba}^{2+}$  which may or may not produce a precipitate, depending on whether or not phosphate is present.

d Acidification is necessary because  $\text{Ag}^+$  will precipitate brown  $\text{Ag}_2\text{O}$  in alkaline solution.

## 6.14 FLAME TESTS

When compounds of some elements are volatilised in a flame, they give the flame a distinctive colour. Common ones are shown in Table 6.5. The flame decomposes the compound into elements and it is atoms of one of the elements that give the flame its colour. The flame colour can be used to confirm the presence of such elements in samples for analysis. The elements with distinctive flame colours (Table 6.5) are all metals, so a flame test confirms the presence of certain cations in the sample but gives no information about anions.

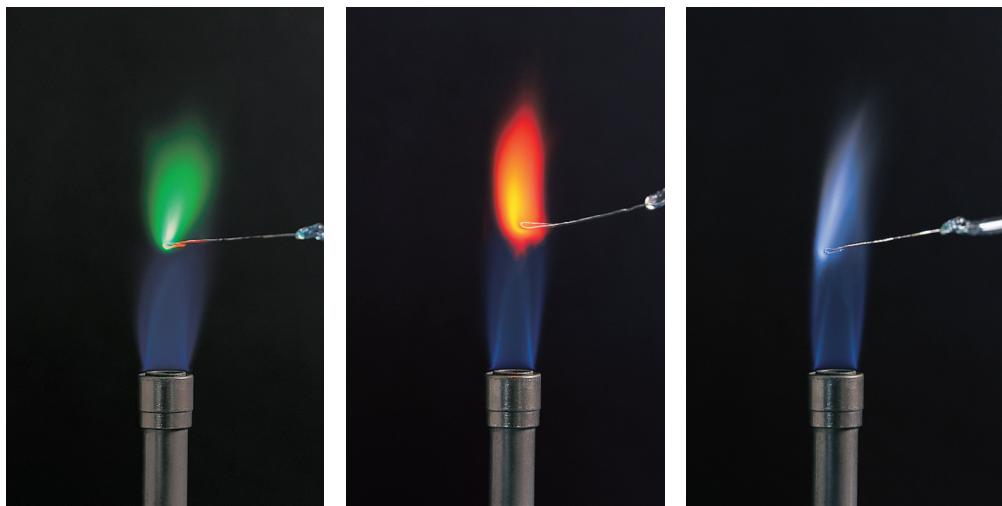
**TABLE 6.5 Flame colours for some elements**

Element <sup>a</sup>	Flame colour
lithium	carmine (dull red)
sodium	yellow
potassium	light purple (lilac)
calcium	brick-red (orange-red)
strontium	scarlet (deep red)
barium	pale green (apple-green)
copper	blue-green

a The element must be present as a compound which will vaporise at the temperature of the flame, typically 1000 to 1500°C.

To perform a **flame test**, a piece of platinum wire mounted in the end of a glass tube as holder is used. The wire is first carefully cleaned by repeatedly dipping it into concentrated hydrochloric acid and heating it to red heat in the flame. Care is taken not to heat the glass tube because it can give off sodium compounds. The reason for stringent cleaning is to eliminate sodium which has an intense flame colour that can mask other colours. Sodium is so common that it can easily contaminate samples. After cleaning, the wire is dipped into the sample to be tested and placed back into the flame. Figure 6.8 illustrates. *The flame colour is characteristic of the cation present and is independent of the anion present.*

**FIGURE 6.8**  
The flame colours produced by barium (left), strontium (centre), and potassium (right)



Flame tests are particularly useful in distinguishing between barium (pale green) and calcium (brick-red), and between sodium (yellow) and potassium (lilac). Sometimes two elements produce similar colours (for example different shades of green from copper and barium). Hence flame tests should not be used as the only method of identification.

## Exercises

- 16** **a** Write equations for all the reactions mentioned in Table 6.3.
- b** Why must sulfate be removed before testing for chloride and phosphate?
- 17** How would you distinguish between solutions of:
- sodium chloride and sodium sulfate
  - potassium chloride and potassium phosphate
  - sodium carbonate and sodium hydroxide
  - \*ammonium phosphate and ammonium sulfate
  - sodium carbonate, sodium sulfate and sodium phosphate.
- 18** What anion is present in a solution (known to contain only one anion):
- which produces a precipitate with barium chloride solution both when acidic and when alkaline?
  - which has a pH of about 11 and which produces precipitates with neutral solutions of both silver nitrate and barium nitrate?
  - which produces a precipitate with alkaline barium chloride solution but not with an acidic solution of that substance?
  - \*which produces a precipitate with silver nitrate but not with barium nitrate?
  - which has a pH of 13 but which does not produce any bubbles when hydrochloric acid is added to it?

- 19** A solution was known to contain one pure substance (apart from water). Describe tests you would perform to determine which of the ions  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  were in the solution.

- 20** Four solutions, A, B, C and D, are known to contain one pure substance each. Solutions of nitric acid, barium nitrate (both in acidic and alkaline solutions) and silver nitrate (in near neutral solution) were added to separate portions of each solution in turn. Results are given below. Which anion (out of the possibilities,  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ) is present in each solution?

Test	A	B	*C	*D
$\text{HNO}_3$	NR <sup>a</sup>	bubbles of gas	NR	NR
$\text{Ba}(\text{NO}_3)_2$ in acid soln	NR	TNP	white ppt	NR
$\text{Ba}(\text{NO}_3)_2$ in $\text{NH}_3$ soln	NR	white ppt	TNP	white ppt
$\text{AgNO}_3$	white ppt <sup>a</sup>	TNP <sup>a</sup>	white ppt	TNP

*a NR = no reaction; ppt = precipitate; TNP = test not performed.*

- 21** To determine the anions present in several solutions labelled P, Q, R, S and T a group of students performed the following tests:
- Add  $\text{HNO}_3$  until effervescence, if any, ceases.
  - Add  $\text{Ba}(\text{NO}_3)_2$  solution to the solution from (i); centrifuge off any precipitate.



- iii** Add ammonia solution to the solution or filtrate from (ii); if no precipitate forms, add more  $\text{Ba}(\text{NO}_3)_2$ ; if a precipitate forms at either stage, centrifuge it off.
- iv** Acidify the solution or filtrate from (iii) with nitric acid then add silver nitrate solution.

Use the results of these tests tabulated below to determine which anions are in each solution.

Test	P	Q	R	*S	*T
i $\text{HNO}_3$	NR <sup>a</sup>	gas forms	NR	gas forms	NR
ii $\text{Ba}(\text{NO}_3)_2$ in acid	ppt <sup>a</sup>	ppt	ppt	NR	NR
iii $\text{Ba}(\text{NO}_3)_2$ in $\text{NH}_3$	NR	NR	ppt	NR	ppt
iv $\text{AgNO}_3$	ppt	NR	NR	ppt	ppt

a NR = no reaction; ppt = precipitate.

- 22** Identify the one (and only) cation present in a solution that:

- a** formed a white precipitate with sodium sulfate solution but not with sodium chloride solution and which in a flame test coloured the flame green
- b** formed a precipitate with sodium carbonate solution but not with sodium chloride, sulfate or hydroxide and which in a flame test coloured the flame orange-red
- c** was pale blue and gave a precipitate with sodium hydroxide and which in a flame test gave the flame a green colour.

Explain all the observations in each test and write equations for all reactions.

- 23 a** Two solutions, each containing one unidentified cation, each gave no precipitate with sodium hydroxide, hydrochloric acid, sulfuric acid or sodium carbonate. When flame tests were performed, one solution coloured the flame lilac while the other coloured it red. Which cation is present in each solution? Justify your answer fully.
- b** A third solution, again containing just one cation, gave the same negative tests as in (a), but the flame test for this solution was also negative. Which cation is likely to be present in this solution? Explain. What further test could you perform to verify your conclusion?

- 24** How would you distinguish between solutions of:

- a** calcium chloride and barium chloride
- b** sodium nitrate, potassium nitrate and nitric acid
- \*c** copper sulfate and potassium sulfate?

Give more than one test if possible.

- 25** Describe tests that you could perform that would establish beyond doubt that a pure solid was:

- |                            |                               |
|----------------------------|-------------------------------|
| <b>a</b> copper sulfate    | <b>*e</b> lead carbonate      |
| <b>b</b> barium chloride   | <b>*f</b> iron(II) sulfate    |
| <b>c</b> iron(III) sulfate | <b>*g</b> potassium phosphate |
| <b>d</b> calcium carbonate | <b>*h</b> potassium chloride  |

- 26** Identify the one pure substance that is present in a solution which:

- a** after acidification, gives a precipitate with  $\text{Ag}^+$  but not with  $\text{Ba}^{2+}$ , gives no precipitate with  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , but gives a green precipitate with  $\text{OH}^-$ ; when colourless potassium thiocyanate solution was added to a fresh sample of the original solution, a blood red colour was formed
- b** gives no precipitate with  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$ , but with  $\text{OH}^-$  produces a pale blue precipitate that dissolves in ammonia solution to form a deep blue solution; fresh samples of the original solution, after acidification, gave precipitates with  $\text{Ag}^+$  and  $\text{Ba}^{2+}$

- c when acidified, forms a precipitate with  $\text{Ag}^+$  but not with  $\text{Ba}^{2+}$ ; no precipitate with chloride or hydroxide but forms a white precipitate with sulfate
- d when acidic, gives no precipitate with silver or barium ions, but when alkaline forms a precipitate with barium ions; no precipitate with chloride, sulfate, hydroxide or carbonate, but colours a flame light purple.

If the tests do not conclusively identify the substance, state the possibilities and describe tests that would distinguish between them. Write net ionic equations for all reactions involved in these tests.

## 6.15 WHY MONITOR CATIONS AND ANIONS?

Determining qualitatively which cations and anions are present in a sample is only part of the job of monitoring. Generally we need to know *how much* of each ion is present. This is because many ions are present in the natural environment and in manufactured products and are quite harmless at low concentrations, but can become harmful at higher concentrations. Some examples are:

- *Phosphate* often occurs in natural waterways at low concentration and is essential for normal aquatic plant growth. However if its concentration becomes too high, it can set off an algal bloom. This is a rapid growth of excessive amounts of algae that can completely cover the surface of a lake or river and kill fish: then when the algae finally uses up all the phosphate, it dies and this has further detrimental effects upon the water body. By monitoring the amounts of phosphate in waterways and in consumer goods that ultimately get into waterways, scientists can guard against algal blooms.
- *Zinc and copper* are both trace elements (meaning living organisms including humans need them in very small amounts), and so small concentrations in water bodies are not just acceptable but desirable; however at higher concentrations both ions are harmful to humans and so we need to monitor their concentrations in waterways and in consumer goods to guard against poisoning.
- *Lead* is a poison: it retards intellectual development in young children, causes brain damage and can lead to neurological disorders. Until recently it was widely used in petrol and so was released to the atmosphere in vehicle exhausts and deposited out on soil near busy highways. Until a few decades ago lead was a constituent of house paints and it is often released to air, water and soil when old houses are renovated. Monitoring lead concentrations in soil near highways, in waterways and in the atmosphere in urban areas is essential to ensure that people are not exposed to harmful concentrations.
- *Iron and copper* cations are sometimes present in municipal water supplies, iron from natural sources and from a common process used to clarify water (Section 8.13), and copper from corrosion of pipes or sloppy pipe repair work. Iron causes stains on household fittings such as sinks, bath tubs and toilet bowls while high concentrations of copper ions can give water an unpleasant taste and be detrimental to health. Monitoring water for these cations (and others) is therefore important.

These and many other similar examples demonstrate the need to monitor quantitatively the amounts or concentrations of potentially harmful substances in consumer goods and in the environment. In all of the above examples (and

in many others) the element of concern is present as a cation or anion. Let us therefore look at an example of the quantitative determination of an anion.

## 6.16 AN EXAMPLE OF GRAVIMETRIC ANALYSIS

Determining *amounts or concentrations* of specific substances is called **quantitative analysis**. Determining which species are present in samples (as was done in Sections 6.9 to 6.14) is called **qualitative analysis**.

Amounts or concentrations of ionic species in samples are measured by a wide variety of techniques, such as volumetric analysis (described in Sections 5.8 to 5.12), **gravimetric analysis** (precipitating out the ion as an insoluble compound and weighing it) and a wide range of instrumental methods, particularly atomic absorption spectroscopy which will be described in Section 6.18. The following example will illustrate gravimetric analysis.



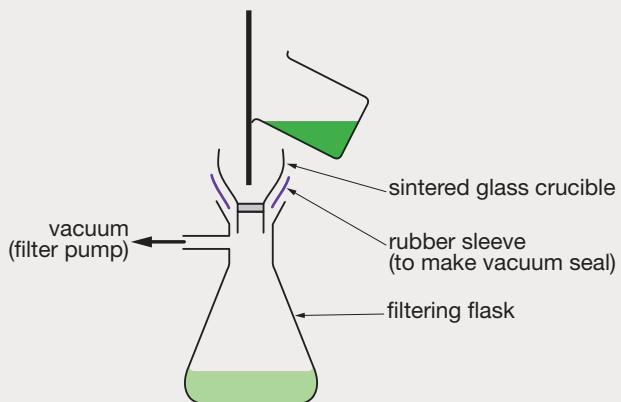
### Example 1

A chemist determined the percentage of sulfate in a lawn food (fertiliser) as follows:

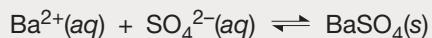
Some of the fertiliser was ground into a fine powder in a mortar and pestle then 1.03 g was placed in a beaker and dissolved in about 250 mL of 0.1 mol/L hydrochloric acid, and stirred to dissolve as much of the solid as possible. Insoluble material was filtered off. The solution was heated to near boiling, then barium chloride solution was slowly added from a burette with continuous stirring to precipitate barium sulfate until no more precipitate formed (that is, excess barium chloride was added). The mixture was digested (heated just below its boiling point) for about 30 minutes with intermittent stirring, then allowed to cool to room temperature, during which time the precipitate settled to the bottom of the beaker. The beaker and contents were then cooled in ice and filtered through a weighed sintered (porous) glass crucible as shown in Figure 6.9. After washing (first with water, then ethanol) and drying (in an oven) to constant mass, the precipitate had a mass of 1.22 g. Calculate the percentage sulfate in the fertiliser.

FIGURE 6.9

Arrangement for collecting a precipitate on a sintered glass crucible



The analysis is based on the fact that barium sulfate is very insoluble, so if we add an excess of  $\text{Ba}^{2+}$  ion to the sample it will precipitate virtually all of the sulfate as  $\text{BaSO}_4$ . The equation for the reaction is:



This equilibrium lies well to the right and by using excess  $\text{Ba}^{2+}$  we force it virtually to completion.

Mass of  $\text{BaSO}_4$  formed = 1.22 g

$$\begin{aligned}\text{mass of } \text{SO}_4^{2-} \text{ in this} &= \frac{\text{relative formula mass of } \text{SO}_4^{2-}}{\text{relative formula mass of } \text{BaSO}_4} \times 1.22 \\ &= \frac{32.1 + 4 \times 16.0}{137.3 + 32.1 + 4 \times 16.0} \times 1.22 \\ &= 0.502 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Percentage sulfate in the fertiliser} &= \frac{0.502}{1.03} \times 100 \\ &= 49\% \text{ (to an accuracy of } \pm 2\% \text{ which is all that is justified by the sensitivity of the mass measurements)}\end{aligned}$$

## Experimental difficulties

In principle, this is a simple experiment—weigh out some fertiliser, dissolve it in water, add barium chloride solution to precipitate barium sulfate, then collect, dry and weigh the precipitate. However considerable care is needed to avoid the many sources of error such as:

- 1 loss of barium sulfate due to its small but possibly significant solubility
- 2 passage of some barium sulfate through the sintered glass filter because the precipitate had formed as very small particles
- 3 leaving some of the precipitate adhering to the walls of the beaker while transferring the mixture to the sintered glass funnel
- 4 loss of some precipitate by spillage during the transfer from beaker to funnel
- 5 contamination of the precipitate with substances adsorbed from the solution during precipitation; this occurs more severely when the precipitate is formed as very small particles (greater surface area for impurities to stick to)
- 6 loss of some precipitate by dissolution while washing it if the volume of wash water is too great
- 7 incomplete drying of the precipitate so that it still contains water when it is weighed.

Errors 1, 2, 3, 4, and 6 would cause the precipitate to weigh less than it should and so would lead to a low percentage of sulfate in the fertiliser. Errors 5 and 7 would cause the precipitate to weigh more than it should and so would lead to a percentage sulfate that was too high.

The experimental procedure is devised to minimise all these errors. Minimising solubility losses (1) requires concentrated solutions but that maximises contamination by adsorption (5) so a compromise is needed. We need to use solutions that are sufficiently dilute so as to minimise contamination by adsorption but not so dilute that solubility of barium sulfate losses are significant. Using starting solutions in which the sulfate concentration is between 0.005 and 0.05 mol/L minimises both types of error.

Forming the precipitate *slowly* from *hot* solutions causes the particles to be large; this minimises contamination by adsorption (smaller surface area). Digesting the mixture causes the particles to grow larger, which makes the precipitate easier to filter and minimises losses from small particles passing through the filter;

The fertiliser being analysed in Example 1



it also reduces adsorption. Cooling the mixture in ice before filtering reduces solubility losses without changing particle size.

To minimise losses during washing, the precipitate is washed with three or four 5 mL portions of water and sucked dry between each, then finally washed with 5 mL ethanol (to aid drying). To minimise errors due to incomplete drying, the precipitate is dried, cooled, weighed, then dried again, cooled and weighed again, and this cycle is repeated until a constant mass is obtained (called *drying to constant mass*).

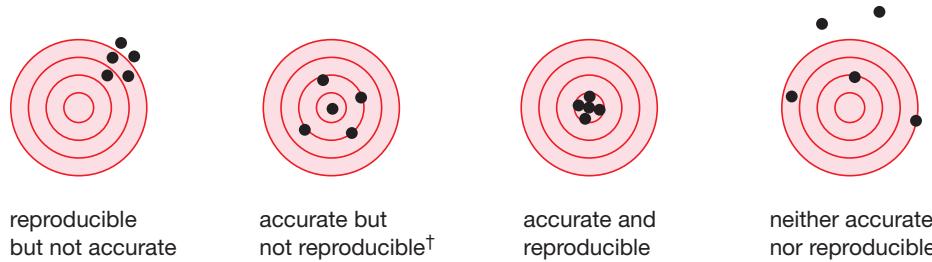
## Reproducibility and accuracy

For any experiment we perform there are two aspects we need to consider: *reproducibility* and *accuracy*.

The **reproducibility** of an experiment is the ability to get the same result when we repeat the experiment several times.

The **accuracy** of an experiment is the closeness of the result of the experiment to the true value of the quantity being measured.

An experiment may give *reproducible* results but that does not mean that they are necessarily *accurate*. However getting results that are reproducible is generally a first step to getting accurate results. The meanings of the two terms are illustrated in Figure 6.10 in which shooters fire five shots at a target, aiming to hit the bullseye (the centre circle).



<sup>†</sup>If the experiment is performed many times, the average answer is the correct value; this is not true of the far left-hand or far right-hand experiments.

*Reproducibility* depends both upon how carefully we can control all the variables that affect the results of an experiment, such as temperature, heat losses to surroundings, material losses in transfers, and upon how accurately we can make individual measurements.

*Accuracy* depends upon the design of the experiment as well as upon the sensitivity of the instruments used to make critical measurements.

We can use the sulfate analysis experiment just described to illustrate the two terms. If we had used a mass balance that could measure to only  $\pm 0.1$  g, then the mass of fertiliser taken would have been  $1.0 \pm 0.1$  g (that is,  $\pm 10\%$ ) and the mass of barium sulfate obtained have been  $1.2 \pm 0.1$  g (that is,  $\pm 8\%$ ). So in repeat experiments, even if great care was taken to use exactly the same procedure, our results would have varied by  $\pm 20\%$  or more; they would not have been very reproducible. By using a mass balance that could measure to  $\pm 0.01$  g we would have obtained results that varied by only 2 to 3%; they would have been quite reproducible. However if we did not take precautions to minimise contamination of the precipitate by adsorption or solubility or filtration losses,

FIGURE 6.10  
An illustration of reproducibility and accuracy, sometimes called *precision* and *accuracy* or in the NSW HSC syllabus *reliability* and *accuracy*

these reproducible results could still have been quite inaccurate (the left-hand diagram in Fig. 6.10).

Only by using instruments of sufficient sensitivity and adopting procedures that minimise all other sources of error can we obtain results that are both reproducible and accurate.

Many standard chemistry texts use the term **precision** for reproducibility. This is unfortunate because the meaning of the word *precision* is not as inherently obvious as that of *reproducibility*. The NSW HSC examiners in 2001, 2003 and 2004 used the term **reliability** for reproducibility, though the syllabus document itself is less clear-cut<sup>†</sup>.

<sup>†</sup> Reliability is used in several places in the NSW HSC syllabus document though its meaning is not defined, and in fact it seems to have more than one meaning there. From comments in Examiners' Reports for 2001 and 2003, the HSC examiners, at least in those years, have interpreted *reliability* to mean *reproducibility*. While it appears to have that meaning in HSC Course outcome H12 on page 17 in the phrase *accuracy and reliability*, on pages 20 and 45 in outcome 12.4(e) *reliability* would seem to have the meaning *correctness or accuracy*. It is a pity that syllabus writers and examiners, when they mean *reproducibility*, do not use that word, because its meaning is unequivocal.

## Exercises

- 27** The sulfate content of a fertiliser was measured by dissolving 1.63 g of the fertiliser in 300 mL water, then slowly adding a solution of barium chloride until no further precipitation occurred. After filtration and drying the mass of precipitate was 1.81 g. Calculate the percentage of sulfate in the fertiliser. In addition calculate the percentage sulfur in the fertiliser (assuming that sulfate is the only source of sulfur).
- 28** a A pair of students performed the experiment in Exercise 16 of Chapter 5 several times but obtained results that were not reproducible. Suggest reasons for this.  
b Another pair of students also performed the same experiment several times (though they made up the sodium carbonate solution only once) and they obtained results that were reproducible but were not accurate. Suggest reasons for this.
- 29** To determine the concentration of magnesium ion in sea water a chemist measured out 250 mL of sea water (by volumetric flask), put it in a beaker and gently heated it to evaporate off about half of the water. Excess sodium hydroxide solution was then slowly added with stirring to precipitate magnesium hydroxide. Then the mixture was allowed to settle and cool to room temperature. The precipitate was filtered off and dried: its mass was 0.703 g.  
a Calculate the percentage magnesium in the sea water.  
b Why did the chemist (i) reduce the volume before adding the sodium hydroxide solution, (ii) add the sodium hydroxide solution before cooling the sample?  
c Suggest additional things the chemist could have done to improve the accuracy of the experiment.
- 30** The phosphate content of a laundry washing powder (detergent) was determined as follows. 6.92 g of the powder was dissolved in approximately 500 mL water. A slight excess of a solution of magnesium chloride in an ammonia, ammonium chloride buffer was added to this with stirring until precipitation was complete. The precipitate



was filtered off and dried; its mass was found to be 1.83 g. The precipitate is pure magnesium ammonium phosphate hexahydrate of formula,  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . Calculate the number of moles of phosphorus in the precipitate and hence the percentage phosphorus in the original laundry powder.

The package this laundry powder came in carried a large letter P, meaning that its phosphorus content was less than 5%. Is this labelling justified?

- 31 To determine the sulfate concentration in a liquid fertiliser (aqueous solution), an analyst first diluted 50 mL of the fertiliser solution to 250 mL, pipetted out 25 mL of the dilute solution, added 200 mL water to it then precipitated the sulfate with barium nitrate solution. The precipitate was filtered, washed and dried to constant mass. In repeated experiments the mass of precipitate was 0.728 g, 0.773 g, 0.722 g and 0.732 g. As accurately as you can, calculate the percentage sulfate in the original fertiliser solution. Justify the procedure you followed.

## Sensitivity

Volumetric analysis as described in Sections 5.8 to 5.12 and the gravimetric analysis described in this section are adequate for analysing samples that contain more than about  $10^{-4}$  to  $10^{-5}$  mol (or 1 to 10 mg) of the element being detected or measured. They are not sensitive enough for much of the monitoring that is necessary today where concentrations below 1 ppm routinely need to be measured. One technique widely used for measuring concentrations of metal ions in the ppm range is *atomic absorption spectroscopy* or AAS.

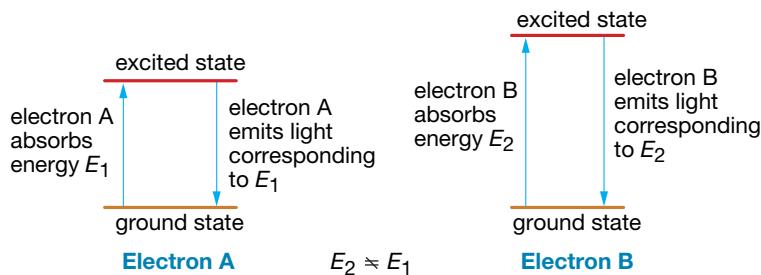
To understand how AAS works we first need to look at what is called atomic *emission spectroscopy*.

## 6.17 ATOMIC EMISSION SPECTROSCOPY<sup>†</sup>

On pp. 43–5 CCPC it was explained that electrons in atoms exist in discrete energy levels. If we heat atoms to a high temperature ( $>1500^\circ\text{C}$ ), some of the electrons get excited out of their normal energy levels into higher energy levels. However after a short time these electrons fall back from these higher energy levels to the normal levels. As they do this the excess energy is liberated as light (either visible or ultraviolet, u.v.). The energy emitted as an electron falls back to its normal state (called the **ground state**) is the same as that absorbed when it was raised to the **excited state** as shown in Figure 6.11.

If we break the emitted light into its various wavelength components (by passing it through a prism), we find that the emissions have occurred at just a few discrete wavelengths as shown in Figure 6.12. The pattern of lines

FIGURE 6.11  
How each bright line in an emission spectrum is generated; electrons A and B give rise to separate bright lines in the spectrum



The electrons absorb energy either from a high temperature flame or from an electric discharge.

<sup>†</sup> not actually required for the NSW HSC core, though it is part of the Forensic Chemistry option; it is included here to aid understanding of AAS in the next section

(wavelengths) is called an **emission spectrum** of the element (a set of bright or coloured lines on a black background). Each wavelength corresponds to the energy required to excite a particular electron in the atom from its ground state to an excited state and this is equal to the energy released when that electron falls from the excited state back to the ground state (Fig. 6.11).

Each element has its own unique emission spectrum. Several such spectra are shown in Figure 6.12. By measuring the emission spectrum of a sample and comparing it with the known spectra of elements we can identify the elements present in the sample. Measuring, studying and using such spectra is called **atomic emission spectroscopy**. It is extremely useful for qualitatively identifying elements present in samples.

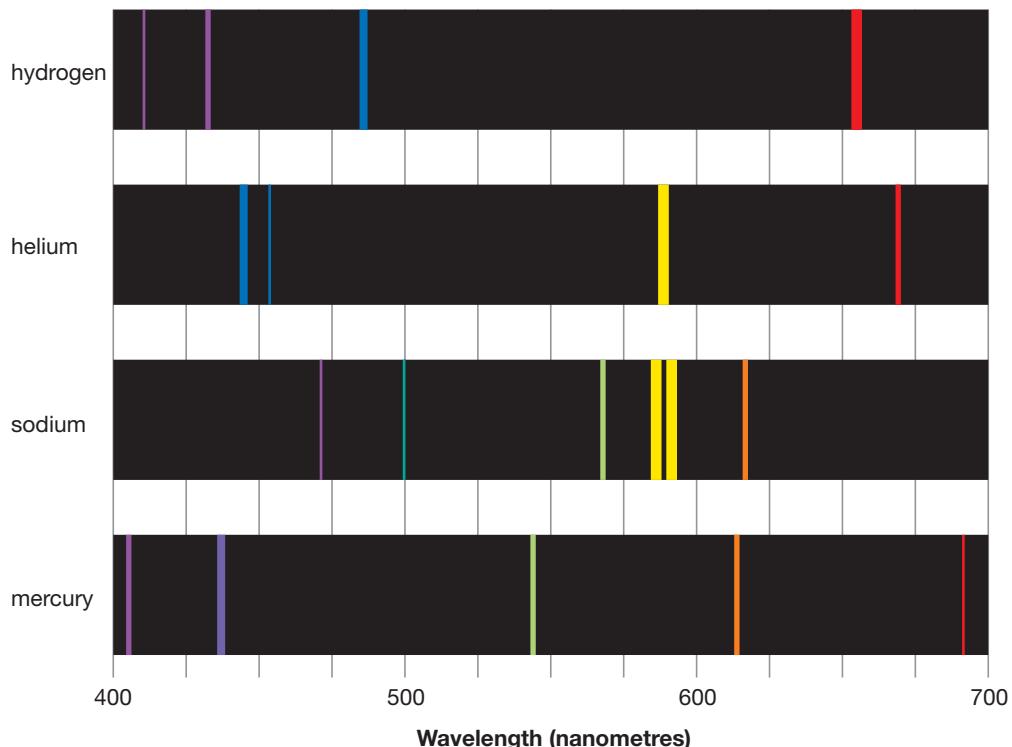


FIGURE 6.12  
Emission spectra of some common elements

By measuring the intensity of the emitted light at particular wavelengths we can also determine the amounts of particular elements present; that is, use it for quantitative analysis. However atomic *absorption* spectroscopy is often more convenient and sensitive for quantitative work.

The emission spectrum of an element tells us the wavelengths at which that element will absorb light, because an electron only absorbs light if the energy of the light corresponds to what is required to move the electron to a higher energy level (excited state). Such emission spectra are the light sources for AAS.

## 6.18 ATOMIC ABSORPTION SPECTROSCOPY

*Atomic absorption spectroscopy*, AAS, was originally developed by Alan Walsh and his team of co-workers in Australia's CSIRO in the early 1950s. Instruments were originally manufactured here, but the local manufacturer was soon bought out by an overseas company and production was later moved off-shore. Although many companies were licensed to make atomic absorption spectrometers, none have been manufactured in Australia for the past three decades. AAS is in general use throughout the world for the measurement of ppm concentrations of

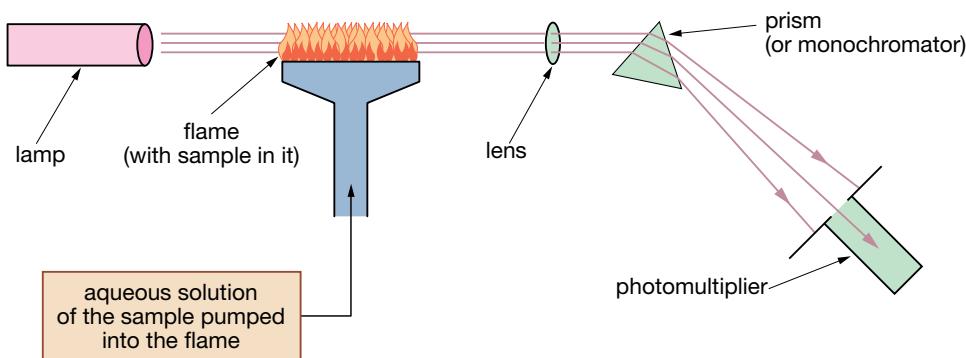
over sixty elements (mainly metals).

If ground state atoms of an element are irradiated with light of a wavelength known to be absorbed by them (i.e. of a wavelength in that element's emission spectrum), then those atoms will absorb some of that light. By measuring the fraction of the light at that wavelength that is absorbed, we can determine the concentration of the element. This is the basis of **atomic absorption spectroscopy**.

The experimental arrangement is shown in Figure 6.13. The sample to be analysed is fed into a flame which vaporises it and converts molecules and ions into atoms. The light source is a lamp that emits radiation of a wavelength which is absorbed by the element to be measured. A separate lamp is required for each element. The lamp actually produces the emission spectrum of the element to be analysed so there is an exact match of emitted and absorbed wavelengths. The light passes through the flame and into a prism or monochromator. The monochromator has a photomultiplier as detector. By rotating the prism (or grating) of the monochromator, light of different wavelengths can be focused on to the photomultiplier. By measuring the intensity of the light reaching the detector with and without the sample in the flame, the instrument calculates and displays a function called **absorbance**<sup>†</sup>.

*Absorbance is proportional to concentration*, so the measured absorbance can be used to calculate the concentration of the particular element being examined.

FIGURE 6.13  
Schematic layout of an atomic absorption spectrometer



## Why AAS is so sensitive

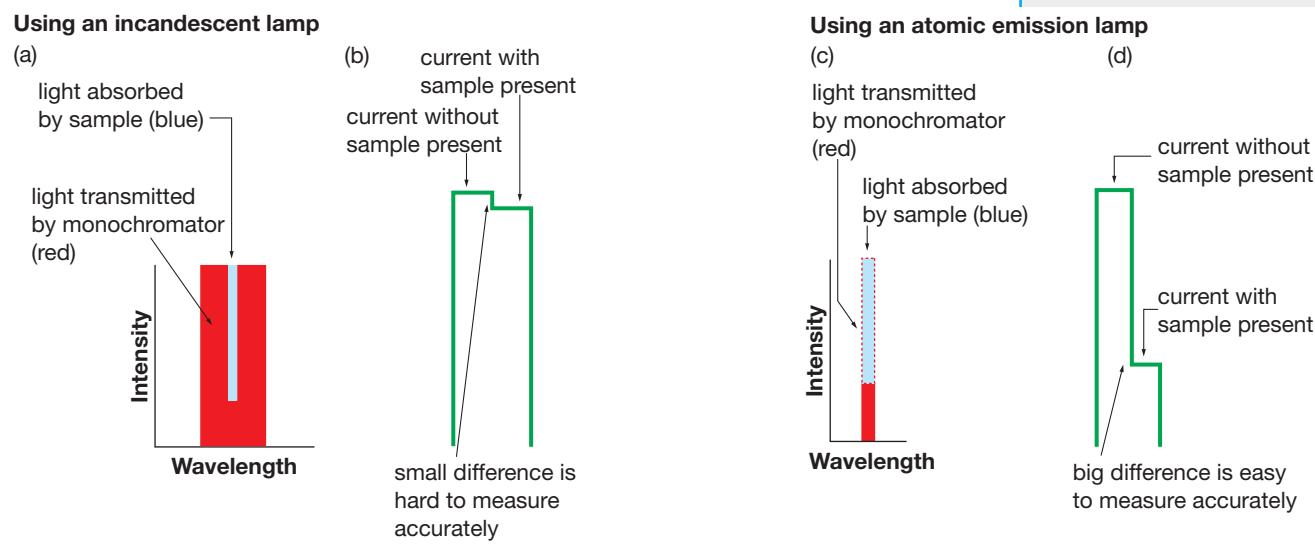
Atomic absorption spectroscopy is extremely sensitive. The reasons for this are:

- Measurements are made from absorption by the nearly 100% of the atoms that are in the ground state rather than from emission by only the 0.1% to  $10^{-5}\%$  of the atoms that are in the excited state as occurs in atomic emission spectroscopy.
- AAS uses one of the lines in the emission spectrum of the element concerned as the light source for the measurement. Figure 6.14 illustrates this.

If the light source had been an incandescent light bulb with a very high quality monochromator<sup>‡</sup> to select a very narrow band of light of the appropriate

<sup>†</sup> Absorbance is  $\log_{10} (I_0/I)$  where  $I$  and  $I_0$  are the intensities of the light reaching the detector with and without the sample being present in the flame.

<sup>‡</sup> A monochromator is an instrument that is able to select a narrow wavelength band of light (light of one colour) from a source that emits many wavelengths (colours).



wavelength range to pass through the sample, this ‘narrow’ band of light would still be very much broader than the emission (or absorption) line of the sample, so only a very small fraction of the incident light would be absorbed by the sample as in Figure 6.14(a). The intensity of light reaching the detector (and so the current produced by it) with the sample present would be only slightly less than that without the sample present (b), and because it is this difference that is related to the concentration, we would not be able to measure it very accurately.

When the light source is one line from the emission spectrum of the element to be measured, the sample absorbs a large proportion of the incident light because the emission and absorption lines are both extremely narrow and overlap exactly (c). This results in a big change in the current from the detector when the sample is present (d) and so we can measure low concentrations quite accurately.

As a result of both of these factors AAS can easily measure part per million concentrations on quite small samples. In fact detection levels of 0.01 ppm are quite common.

However because a different lamp is required for each element, the technique is not as convenient as emission spectroscopy for determining qualitatively which elements are present in a sample or for routinely measuring concentrations of several elements in the one sample.

## Uses

Atomic absorption spectroscopy is widely used to monitor:

- small concentrations of metals (and some other elements such as As and B) in the environment, particularly heavy metals such as Pb, Hg, Cd, Cr, Cu, Zn; some examples being the detection of copper and aluminium in waterways, zinc in oysters, lead fallout beside highways and mercury in fish.
- concentrations of micro-nutrients (ones needed in very small amounts) in soils
- small amounts of contaminants in foods (particularly processed foods) and medicines and other manufactured goods
- the presence of small concentrations of a variety of elements in living organisms.

**FIGURE 6.14**  
How using an atomic emission lamp increases the sensitivity of AAS

Because it is able to measure very low concentrations of a wide variety of elements, particularly metals, *atomic absorption spectroscopy is extremely effective in monitoring pollution*, particularly water and soil pollution.

A typical atomic absorption spectrometer. Notice the flame into which the sample is vaporised; the sample is being pumped into the flame from the conical flask



### Example 2

Atomic absorption spectroscopy was used to measure the concentration of iron in several natural water samples. The samples were filtered then sprayed into the flame of the instrument at a carefully regulated rate; absorbance by the iron atoms produced in the flame was measured using the appropriate lamp for iron. Results are tabulated below.

Sample	L	M	P	Q
Absorbance	0.74	0.05	0.53	0.28

To convert absorbances into concentrations a calibration curve was constructed as follows. 3.62 g hydrated iron(II) ammonium sulfate, a very pure compound of iron of formula  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , was dissolved in dilute acid solution and the volume made up to 0.500 L. Volumes of this solution were then accurately diluted to 1.000 L. These diluted solutions were analysed in the instrument in exactly the same way as was used for the samples for analysis. Results are recorded below.

Volume (in mL) of concentrated solution diluted to 1.000 L	1.00	2.00	5.00	10.00
Absorbance	0.07	0.13	0.34	0.69

Calculate the concentration (in ppm) of iron in each of the standard solutions and draw a graph of absorbance versus concentration. Use this to estimate the iron concentration in each of the unknown samples. Does this analysis measure iron(II) or iron(III) or both? Explain.

We first need to calculate the concentration of iron in the original standard solution, then the concentrations in the solutions used to calibrate the instrument, and then draw a calibration curve:

Molar mass of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  =

$$55.9 + 2 \times (14.0 + 4 \times 1.0) + 2 \times (32.1 + 4 \times 16.0) + 6 \times (16.0 + 2 \times 1.0) \\ = 392.1 \text{ g/mol}$$

$$\text{Fraction of the solid that is iron} = \frac{55.9}{392.1}$$

$$\therefore \text{mass of iron in the solution} = \frac{55.9}{392.1} \times 3.62 \\ = 0.516 \text{ g}$$

This is in 0.500 L,

$$\text{so concentration of iron in the solution} = 2 \times 0.516 \\ = 1.032 \text{ g/L}$$

If 1.00 mL of this solution is diluted to 1.00 L,

$$\text{concentration of dilute solution} = \frac{1.032}{1000} \\ = 1.032 \times 10^{-3} \text{ g/L} \\ = 1.032 \text{ ppm (taking 1.00 L as 1000 g)}$$

Concentrations corresponding to 2, 5 and 10 mL are 2.064, 5.16 and 10.32 ppm respectively.

Absorbance is plotted against concentration for these solutions in Figure 6.15. The origin is a point for the graph, because at zero concentration absorbance is zero. We note that the highest absorbance for our test solutions (0.74) is somewhat greater than for our calibration solutions (0.69) so we use a scale on the graph that extends a bit beyond the 10.32 ppm of that solution, say to 12 ppm.

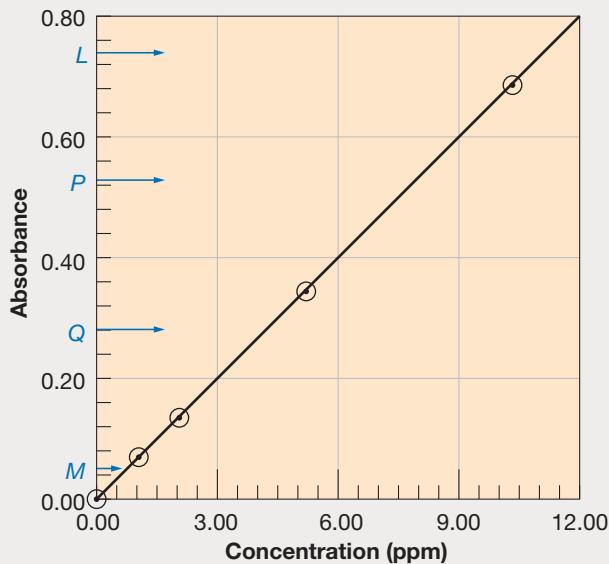


FIGURE 6.15  
Absorbance versus  
concentration for the  
calibration measurements

We can now use this graph to read off the concentrations of our natural water samples. Concentrations are: for **L**, 11.1 ppm, for **M** 0.8 ppm, for **P** 8.0 ppm and for **Q** 4.2 ppm with an accuracy (from reading the graph) of about  $\pm 0.2$  ppm.

Because the sample is decomposed into atoms in the flame, AAS measures the *total concentration of the element in the sample*; in this case it measures Fe(II) plus Fe(III).

#### Alternative calibration method

While the most accurate method of calibrating the instrument is to measure absorbances of several standard solutions and draw a calibration graph, sometimes analysts measure just one standard solution and use the fact that absorbance is proportional to

concentration. In this example, had the only calibration measurement been that a solution with 5.16 ppm iron had an absorbance of 0.34, we should have proceeded in one of two ways.

Because absorbance is proportional to concentration, we can write either

$$\frac{\text{concentration in solution L}}{\text{concentration in standard solution}} = \frac{\text{absorbance of solution L}}{\text{absorbance of standard solution}}$$

That is,

$$\frac{\text{concentration in solution L}}{5.16} = \frac{0.74}{0.34}$$

$$\text{concentration of solution L} = 11.2 \text{ ppm} \text{ (compare } 11.1 \pm 0.2 \text{ above)}$$

The other three concentrations are obtained similarly.

$$\text{or } c = kA \quad \dots (6.5)$$

where  $c$  is concentration,  $A$  is absorbance and  $k$  is the proportionality constant.

From the calibration measurement

$$k = \frac{5.16}{0.34} \\ = 15.2$$

Now applying Equation 6.5 and this value of  $k$  to the absorbance of solution L,

$$\begin{aligned} \text{concentration of solution L} &= 15.2 \times 0.74 \\ &= 11.2 \text{ ppm} \end{aligned}$$

and similarly for the other solutions.

## 6.19 AAS AND TRACE ELEMENTS

**Trace elements** are elements that are required by living organisms in very small amounts. Their concentrations in plants and/or animals are generally in the 1 to 100 ppm range. Common trace elements in humans are Zn, Co, Cu, Ni, Mo, I and Se. Small amounts of these elements are needed to help enzymes function. For plants important trace elements are Mn, Cu, B, Mo and Zn.

The need for most of these trace elements, particularly in soils, was first recognised when scientists started using AAS for measuring concentrations of species in soils and organisms. Before the introduction of AAS the commonly used analytical methods were not sensitive enough to detect the low concentrations of these elements and so their presence had gone unnoticed.

AAS not only showed that there were trace elements in living organisms and soils: it also helped demonstrate that these trace elements were essential for the well-being of the organisms and has been used to work out how these trace elements help the functioning of organisms. In these ways AAS has had a great impact upon scientific understanding of trace elements in organisms.

### Exercises

- 32 Samples were being analysed for lead by atomic absorption spectroscopy. The samples also contained significant concentrations of copper and barium. Would these ions interfere with the analysis for lead? Explain why or why not.



- 33** In order to measure the concentration of mercury in sea water near an industrial plant, a team of chemists used atomic absorption spectroscopy. They first calibrated their instrument by admitting some standard solutions to it and determining the absorbance (a measure of the fraction of incident light absorbed by the sample) for each. Then they measured the absorbance of several water samples collected from different locations near the industrial plant. For their standards they made a stock solution by dissolving 0.106 g mercury (as mercury(II) nitrate) in water and making the volume to 250 mL in a volumetric flask, then they quantitatively diluted (by pipette) 1 mL, 2 mL and 4 mL of this solution to 100 mL (volumetric flask). Absorbances for the standards and the samples are shown below.

Standards (mL)	1.00	2.00	4.00	Samples	A	B	C	D
Absorbance	0.083	0.164	0.331		0.32	0.46	0.21	0.055

Draw a calibration curve of absorbance versus concentration in parts per million (ppm) for the standards. Take 1.00 mL of aqueous solution as 1.00 g. Determine the concentration of mercury (in ppm) in each of the samples.

- 34** It was suspected that strawberry jam made from fruit grown near to a major highway was contaminated by lead (from fallout from motor car exhausts). A chemist analysed the jam for lead content as follows. Approximately 10 gram samples of jam from three separate jars were taken and mixed thoroughly with dilute nitric acid and the volume made to 50.0 mL. The mixture was then centrifuged to remove solid material. Portions of the clear solutions were then fed into an atomic absorption spectrometer. Absorbances (which are proportional to lead concentration) are shown below.

Sample	standard	A	B	C
Mass of jam taken (g)	—	10.14	9.97	10.08
Absorbance	0.28	0.30	0.19	0.24

A standard solution (for calibrating the instrument) was prepared by dissolving 0.0507 g lead nitrate in water and making the volume to 250 mL in a volumetric flask. 10 mL of this solution (by pipette) was diluted to 1 L (volumetric flask). This dilute solution was also fed into the AA spectrometer: its absorbance is shown in the table also.

Calculate the concentration of Pb in the diluted standard solution in ppm. Take 1.00 mL of solution as 1.00 g. Then use the absorbance values to calculate the concentration (in ppm) of Pb first in the sample solutions analysed then in the jam samples themselves.

AAS measurements on lead in this concentration range are generally accurate to better than 1%. Suggest reasons for the larger variation in results in this experiment.

- 35** Some householders complained to the water authority that at the beginning of each day their water had an unpleasant taste. The authorities suspected that the taste was due to copper being leached out of the water pipes overnight, so they performed the following tests. Early one morning before any water had been used by the household they collected a sample of water from an offending tap (call this sample A). Water was allowed to flow for a few minutes to partially flush out the pipes then a second sample was collected (sample B). Finally the tap was let run for a sufficiently long time to completely flush out the household pipes and sample C was collected. Water from a water main in the street about halfway between the reservoir and the house was also collected (sample D). These four samples were analysed for copper by atomic absorption spectroscopy along with a laboratory standard sample that was known to contain 2.16 ppm copper. The absorbance values were:

Sample	standard	A	B	C	D
Absorbance	0.310	0.91	0.44	0.063	0.057

Absorbance is proportional to concentration. Calculate the concentration of copper (in ppm) in each of the samples A to D. Offer an explanation for these results.

## Important new terms

You should know the meaning of the following terms:

absorbance (p. 226)  
accuracy (p. 222)  
atomic absorption spectroscopy (p. 226)  
atomic emission spectroscopy (p. 225)  
centrifuge (p. 210)  
complex ion (p. 209)  
emission spectrum (p. 225)  
excited state (p. 224)  
flame test (p. 216)

gas chromatography (p. 196)  
gravimetric analysis (p. 220)  
ground state (p. 224)  
Haber process (p. 202)  
precision (p. 223)  
qualitative analysis (p. 220)  
quantitative analysis (p. 220)  
reliability (p. 223)  
reproducibility (p. 222)  
trace elements (p. 230)

## CHAPTER 6

## Test yourself

- Explain the meaning of each of the items in the ‘Important new terms’ section above.
- Give a chemical reaction in which the products depend upon the conditions used and write equations for the formation of at least two different products from it.
- List the major uses of ammonia.
- Use Le Chatelier’s principle to explain the conditions that would be most favourable for the synthesis of ammonia (from nitrogen and hydrogen gases) on equilibrium grounds alone. Why are these conditions not used industrially? What are the conditions used and why?
- How are the reactants for the Haber process generally produced? Why must oxygen be excluded?
- Why is careful monitoring of reactant composition and reaction conditions so necessary in the Haber process?
- Describe how you would determine if the cation in a pure substance was  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . Write equations for all reactions involved.
- A solution of a pure substance produced a precipitate with sodium sulfate solution. What does this tell you about the identity of the cation in the solution?
- Why is the absence of a precipitate with chloride not conclusive proof of the absence of  $\text{Pb}^{2+}$  in a solution? How would you confirm the presence of  $\text{Pb}^{2+}$ ?
- How would you decide whether the iron ion in a solution was  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ?

- 11** Explain how you would determine which cations (of those listed in Question 7) were present in a mixture. Explain why you would use that particular sequence of tests.
- 12** Give two examples of complex ions.
- 13** Explain how a centrifuge separates precipitates from solutions and why it is preferable to ordinary filtration.
- 14** Describe tests you would perform to decide whether a solution of a pure substance contained  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$ .
- 15** Explain why the formation of a precipitate with  $\text{Ag}^+$  does not prove the presence of chloride in a solution.
- 16** Explain why phosphate ion produces a precipitate with barium ion in alkaline solution but not in acid solution whereas sulfate ion produces a precipitate in both acid and alkaline solution.
- 17** Explain how you would determine which anions (of those listed in Question 14) were present in a mixture. Explain why you would use that particular sequence of tests.
- 18** How would you perform a flame test? What precautions would you take to avoid false results?
- 19** List four elements that have characteristic flame colours and state what they are.
- 20** Give two situations in which a low concentration of a substance is desirable but a high concentration is harmful.
- 21** Describe one example of a gravimetric analysis.
- 22** What is an atomic emission spectrum? What feature of an atom gives rise to it?
- 23** Explain in words and with a diagram how atomic absorption spectroscopy works.
- 24** What is the relevance of atomic emission spectra to atomic absorption spectroscopy?
- 25** Why is atomic absorption spectroscopy, AAS, for any particular element generally free from interference from other elements?
- 26** Why is atomic absorption spectroscopy able to measure lower concentrations than most other analytical techniques?
- 27** What, if any, information does AAS provide about the compound in which an element being detected occurs? Why?
- 28** Give two everyday applications of AAS.
- 29** Explain the involvement of atomic absorption spectroscopy with trace elements.

# CHAPTER 7

# Chemistry and the atmosphere

## IN THIS CHAPTER

Composition of the atmosphere  
The layered structure of the atmosphere  
The main air pollutants and their sources  
Ozone in the atmosphere  
Photochemical smog and ozone  
Structure of ozone and coordinate covalent bonds  
Allotropes of oxygen  
Oxygen gas, ozone and oxygen atoms

Depletion of ozone in the stratosphere  
Haloalkanes, particularly CFCs  
Destruction of stratospheric ozone by CFCs  
Why over the Antarctic and why in spring?  
Combating the ozone-hole problem  
Monitoring stratospheric ozone

Human activity has released enormous amounts of material into the atmosphere and into water bodies and dumped large quantities of waste on to the land. A hundred years ago the quantities of wastes produced caused localised pollution: the air in industrial cities was unhealthy and rivers near industrial and mining sites were badly polluted, but the problems were essentially localised. Today the quantities of wastes are much larger and pollution is not just local, it has become global. Oceans remote from human activity now show signs of pollution and the whole atmosphere generally has been affected by human emissions.

Chemistry has contributed to this pollution through the manufacture of many of the products of modern society. But equally importantly chemistry has been responsible for devising ways of overcoming environmental damage. It does this in three ways:

- 1 by developing processes that create less waste and devising methods for cleaning up industrial effluents
- 2 by monitoring the environment to identify localised pollution and its sources and to detect gradual and small but significant global changes in the atmosphere and oceans, and
- 3 by working out how secondary pollutants (ones not directly released into the environment but which are made there by chemical reactions) are formed and how their formation can be minimised.

Chemists are also involved with publicising the problems and the need for remedial action.

In this chapter we shall look at the structure and chemistry of the atmosphere and at some forms of atmospheric pollution.

## 7.1 COMPOSITION OF THE ATMOSPHERE

The atmosphere is a layer of gas about 200 to 300 km thick that surrounds the Earth. Of its mass, 75% is in the lower 15 km with 99.997% being below 90 km. The composition of the atmosphere is shown in Table 7.1. We generally use percentages for the major constituents such as N<sub>2</sub> and O<sub>2</sub> and part per million for the minor ones such as CO<sub>2</sub>, He, N<sub>2</sub>O. The percentages of nitrogen, oxygen, carbon dioxide and the noble gases (in dry air) are remarkably constant at least up to an altitude of 90 km.

The percentage of water vapour, particularly in the troposphere, varies considerably, from about 0.5 to 5%. It is measured by relative humidity.<sup>†</sup> In the stratosphere its concentration is only about 5 ppm.<sup>‡</sup>

**TABLE 7.1 Composition of the dry atmosphere**

Major constituents	Percentage (v/v)		
nitrogen	78.08		
oxygen	20.95		
argon	0.93		
Minor constituents	ppm	Minor constituents	ppm
carbon dioxide	350	nitrous oxide	0.2
neon	18	carbon monoxide	0.1
helium	5	ozone	0.02
methane	1.5	NO + NO <sub>2</sub>	<0.01
krypton	1	ammonia	<0.01
hydrogen	0.5	SO <sub>2</sub> + H <sub>2</sub> S	<0.002

The ways that pollutants are dispersed through, or removed from, the atmosphere depend upon the physical structure of the atmosphere, so let us take a look at this.

## 7.2 THE LAYERED STRUCTURE OF THE ATMOSPHERE

There is an unusual vertical temperature profile through the atmosphere. It allows us to define several quite distinct zones that have been given special names.

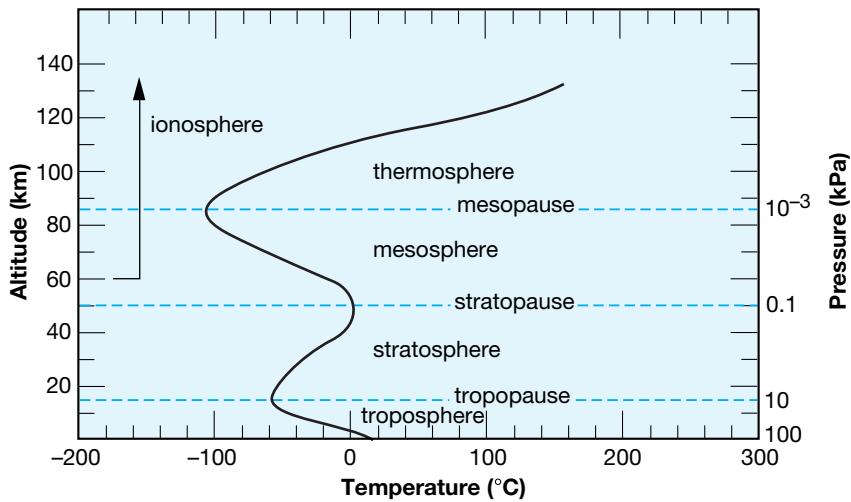
Starting from ground level, as we go up, temperature decreases—from about 15°C at the Earth's surface to a minimum of about –50°C at an altitude of around 15 km (50 000 feet). Then as altitude increases further the temperature starts to increase. Temperature increases with altitude until about 50 km when it is roughly 0°C; then it starts to decrease again. This region from 15 to 50 km

<sup>†</sup> Relative humidity is the actual pressure of water vapour expressed as a percentage of the saturated vapour pressure at the prevailing temperature.

<sup>‡</sup> ppm for gases was defined in Section 4.9.

is called the *stratosphere*. The lower portion of the atmosphere is called the *troposphere* and the region above the stratosphere is called the *mesosphere*. These regions are shown in Figure 7.1. The boundary between the troposphere and stratosphere is called the **tropopause**.

**FIGURE 7.1**  
The way temperature changes with altitude through the Earth's atmosphere



The **troposphere** is the region of the atmosphere closest to the Earth in which temperature generally decreases as altitude increases: it extends from sea level to an altitude of about 15 km.

The **stratosphere** is the region of the atmosphere in which temperature increases as altitude increases: it is from an altitude of about 15 km to 50 km.

When temperature decreases as altitude increases (as in the troposphere), we get good mixing of gases—patches of hot air near ground level rise (because hot air has a lower density) and cause cooler air at higher altitudes to fall to take place; this is convection. It is part of the weather we experience. This convective mixing of the air in the troposphere means that substances released into the air at ground level get mixed throughout the troposphere.

However when temperature rises as altitude increases (as in the stratosphere), there can be very little vertical mixing, because if we heat the air at the bottom of the stratosphere, it cannot rise as in the troposphere, because the air above it still has a lower density (it's warmer). Hence the stratosphere is a region of great stability. There is very little 'weather' in the stratosphere. Because of the temperature minimum at the tropopause, substances do not easily transfer from the troposphere to the stratosphere or *vice versa*. Hence very little of the ozone present in the stratosphere transfers to the troposphere and impurities (pollutants) in the troposphere only very slowly transfer into the stratosphere by slow diffusion not convection.

This slowness of transfer of gases across the tropopause is a key factor in the ozone hole problem (Section 7.9). First it means that the ozone that is present in the stratosphere (it is actually formed there from ordinary oxygen gas) stays there, and does not come down to ground level where it would poison us (and most other living matter). Secondly it means that pollutants released at ground level (which fairly quickly get mixed throughout the troposphere) diffuse into the stratosphere only extremely slowly. Hence it is only pollutants that survive a long time before being destroyed by sunlight which can get into the stratosphere.

Pressure steadily decreases as altitude increases: there are no minima or

maxima for pressure. At the tropopause pressure is about 10 kPa and at the stratopause 0.1 kPa (compare with 101 kPa at sea level).

The **stratopause** is the boundary between the stratosphere and the mesosphere.

### Exercises

- 1 Express the parts per million concentrations for CO<sub>2</sub>, Ne, H<sub>2</sub> and ozone in Table 7.1 as percentages.
- 2
  - a Use the molar volume of a gas (24.8 L) at 25°C and 100.0 kPa pressure to calculate the total concentration of gas in the atmosphere in moles per litre under these conditions.
  - b Calculate the number of moles of carbon dioxide per litre of dry atmosphere under these conditions of temperature and pressure.
- 3
  - a Use the data below to draw a graph of atmospheric pressure *versus* altitude. In graphs we generally make the independent variable (in this case altitude) the x axis and the dependent variable the y axis. However atmospheric profiles are generally drawn with altitude as the y axis (e.g. Fig 7.1) so in your graph make altitude the y axis. Draw a smooth curve through the points.
  - b Use your graph to explain qualitatively why 75% of the mass of the atmosphere lies below 15 km and 99.997% below 90 km.



Altitude (km)	0	2.0	5.0	10.0	15.0	20.0	30.0	40.0	50.0
Pressure (kPa)	101.3	79.7	52.5	23.7	10.8	4.6	1.3	0.6	0.2

## 7.3 THE MAIN AIR POLLUTANTS AND THEIR SOURCES

The major source of atmospheric pollution is combustion, from both stationary and moving sources (power stations and vehicles). On pp. 286–8 CCPC we saw that the main pollutants from combustion were carbon monoxide and soot, sulfur dioxide, oxides of nitrogen and particulates. Other important sources of air pollutants are factories, farms and homes.

Table 7.2 lists the major air pollutants and gives their sources.

The word **particulates** (in Table 7.2 and elsewhere) is used to describe a mixture of small solid particles and small droplets of liquid.

Two of the major sources of air pollution are electricity generation and motor cars, particularly on congested city highways



**TABLE 7.2 The major air pollutants and their sources**

Pollutant	Source
carbon monoxide, CO	motor cars, cigarettes, bush, forest and farm fires, slow combustion stoves
oxides of nitrogen ( $\text{NO} + \text{NO}_2$ )	combustion (vehicles and power stations)
hydrocarbons	vehicles and factories using solvents
other volatile organic compounds (VOCs)	industry, commerce (e.g. dry cleaners) and homes (from solvents and a variety of everyday processes)
particulates (including asbestos)	combustion (transport and industry), many industrial processes (including mining), bush fires, farm and forest burn-offs, backyard incineration; asbestos in dust from insulation and pre-1986 fibrous cement board in old buildings and from their demolition
airborne lead	lead smelters (Broken Hill and Port Pirie), paint dust from renovating old houses (Section 6.15), and until recently from leaded petrol (used in pre-1986 cars)
sulfur dioxide, $\text{SO}_2$	combustion (impurities in the fuel), metals extraction (from sulfide ores), some chemical manufacturing
radioactivity	combustion (coal contains some radioactive substances), uranium mining, nuclear weapons testing, nuclear power plants (not in Australia), medical and scientific use of radioisotopes
carcinogenic compounds	benzene and toluene from unleaded petrol, vinyl chloride from plastics manufacture, dioxin from using and incinerating chlorine-containing compounds, cigarette smoke
fluoride	aluminium smelters
chlorofluorocarbons (CFCs) and other halogenated organic compounds	before 1996 from refrigeration, air conditioning, foam plastics, electronics cleaning, halon fire extinguishers
ozone	no direct sources; formed in photochemical smog (Section 7.5)

## 7.4 OZONE IN THE ATMOSPHERE

Ozone,  $\text{O}_3$ , is an *allotrope* of the element oxygen, the main allotrope being ordinary oxygen gas,  $\text{O}_2$ . Ozone is naturally present in the atmosphere. Near ground level its concentration (in clean air) is only 0.02 ppm: in the stratosphere it ranges from 2 to 8 and back to 2 ppm as altitude changes from 15 to 30 to 50 km. Ozone is poisonous to humans and most other life forms, if they breathe it in or come into contact with it. For people ozone causes breathing difficulties, aggravates respiratory problems, and produces headaches and premature fatigue. However in the stratosphere ozone protects all life forms by filtering out short-wavelength ultraviolet (u.v.) light which damages living tissue: in other words it acts as a *radiation shield*.

It is ironic that human activity is both *producing* ozone at ground level where we do *not* want it and *destroying* it in the stratosphere where we *do* want it.

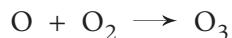
Table 7.2 lists ozone as a pollutant but there is no significant direct release of ozone to the atmosphere. It is formed in the atmosphere from other pollutants

## 7.5 PHOTOCHEMICAL SMOG AND OZONE<sup>†</sup>

**Photochemical smog** is a type of air pollution that is produced when sunlight acts upon motor car exhaust gases to form ozone and other harmful substances.

It occurs in cities which have plenty of sunlight and lots of motor cars, such as Los Angeles, Denver, Tokyo, Singapore, and to a lesser extent, Sydney and Brisbane. The most harmful component of photochemical smog is ozone, O<sub>3</sub>.

Ozone forms in the lower atmosphere when sunlight is very intense (summer) and when concentrations of nitrogen dioxide, NO<sub>2</sub>, are well above clean-air levels. This happens when there is no breeze to disperse pollutants. The sunlight splits off an oxygen atom from the NO<sub>2</sub> molecule, and this O atom combines with an oxygen molecule, O<sub>2</sub>, to form ozone:



However NO can destroy ozone:



We have already seen (pp. 290–2 CCPC) that the rate of a reaction depends upon concentration of reactants. Consequently if the concentration of NO<sub>2</sub> is low and the concentration of NO high, then the rate of the NO + O<sub>3</sub> reaction is much greater than the rate of the NO<sub>2</sub> + light reaction, and so ozone is destroyed nearly as quickly as it is formed, thus keeping its concentration below harmful levels. This is the situation when the ratio of NO<sub>2</sub> to NO in the atmosphere is less than about 0.3. However if the concentration of NO<sub>2</sub> is high and that of NO low, then ozone is formed at a much greater rate than that at which it is being destroyed, and so there is a build-up in ozone concentration, often to levels in the range of 0.1 to 0.3 ppm (0.1 ppm is harmful to health). This occurs when the ratio of NO<sub>2</sub> to NO in the air is greater than about 3:1.

As we saw in Section 4.9 motor cars are a major source of NO and NO<sub>2</sub>. The NO plus NO<sub>2</sub> mixture emerging from motor car exhausts is usually about 80% NO. If the ratio of NO<sub>2</sub> to NO stayed at about this value of 0.25, there would be no harmful build-up of ozone.

However other reactions in the air, involving other substances from the same motor car exhausts, convert

One of the NSW Department of Environment and Conservation's network of air monitoring stations around the Sydney and Wollongong metropolitan areas. This one is at Albion Park. The tall projection measures air pressure and wind speed: the smaller uprights near the roofline are intake tubes for various monitoring instruments



† not strictly required for the NSW HSC, but a discussion of ozone in the atmosphere would not be complete without it

‡ In the laboratory when a gas jar of NO is exposed to air, the reaction between NO and O<sub>2</sub> seems almost instantaneous. This is because the concentration of NO is very high. When NO concentration is less than a few ppm, however, this reaction is too slow to convert significant amounts of NO to NO<sub>2</sub> in the time available (a few hours).

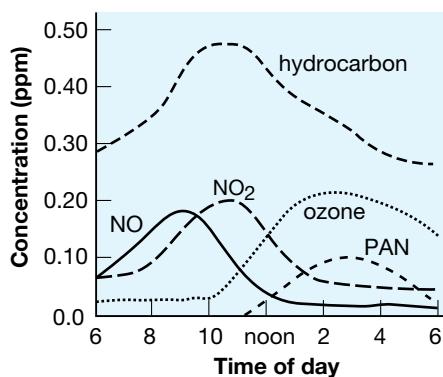
$\text{NO}$  to  $\text{NO}_2$ . This leads to a build-up of harmful concentrations of ozone. These ‘other substances’ are hydrocarbons (unburnt petrol) and their partial oxidation products.



Hundreds of such reactions involving a wide range of carbon compounds occur. These all increase the ratio of  $\text{NO}_2$  to  $\text{NO}$ .

On a smoggy day we first observe a build-up of  $\text{NO}$  and hydrocarbon (with the morning traffic peak), followed by a gradual conversion of  $\text{NO}$  to  $\text{NO}_2$  during the rest of the morning, and then a build-up of ozone in the early afternoon, particularly if there is no breeze to disperse the smog: Figure 7.2 shows this. Because reaction rate depends upon reactant concentration, high concentrations of hydrocarbons and  $\text{NO}_x$  lead to rapid rates of formation (and hence high final concentrations) of ozone.

FIGURE 7.2  
Variation in pollutant concentrations during a windless sunny day



In addition to the health problems mentioned in Section 7.4, photochemical smog can cause people’s eyes to water and to sting. The compounds responsible for this are PANs, *peroxyacetyl nitrates*. The simplest PAN is  $\text{CH}_3\text{CO}-\text{OO}-\text{NO}_2$ , *peroxyacetyl nitrate*. PANs like ozone are formed by the action of sunlight on car exhaust gases:



The chemical reactions occurring in photochemical smog also lead to the formation of relatively high concentrations of particulates, which gives rise to the haze normally associated with such smog; particulates, because of their ability to scatter light, are also the cause of the brown colour often associated with photochemical smog<sup>†</sup>.

## Minimising photochemical smog

To minimise photochemical smog formation, governments have laid down maximum permissible exhaust emissions for both hydrocarbons and oxides of nitrogen (and also for carbon monoxide which is poisonous without further reaction). Currently in Australia, the maximum allowable exhaust emissions for passenger cars (regardless of size) correspond to reductions of 90%, 90% and 70% for hydrocarbons, CO and  $\text{NO}_x$  respectively relative to uncontrolled (pre-1972) vehicles.

Since 1986, new cars in Australia have been fitted with catalytic exhausts (Fig. 10.7 on p. 297 CCPC). Current ones convert  $\text{NO}$  to  $\text{N}_2$  and hydrocarbons

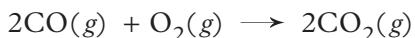
<sup>†</sup> Although  $\text{NO}_2$  is a brown gas, its concentration never gets high enough in photochemical smog for it to be the cause of the observed brown colour.

and CO to carbon dioxide. Rhodium and platinum are the catalysts. Rhodium catalyses the removal of nitric oxide before it is converted to nitrogen dioxide:



Part of the strategy to minimise pollution from motor cars is to measure exhaust emissions from selected vehicles on a dynamometer to simulate actual driving conditions to check that they are complying with statutory emission limits

Platinum metal catalyses the conversion of carbon monoxide and hydrocarbons to carbon dioxide and water. For this purpose extra air is added to the exhaust gas upstream of the catalytic converter. The reaction with carbon monoxide is:



A typical hydrocarbon reaction is



Conditions (and the relative amounts of platinum and rhodium used) need to be carefully chosen so that the  $\text{CO} + \text{NO}$  reaction proceeds more rapidly than the  $\text{CO} + \text{O}_2$  reaction. Otherwise all the CO will be converted to  $\text{CO}_2$  before it can remove all the NO. This is a situation where rates of reactions and factors affecting them are of critical importance.

## Exercises

- \*4 Prepare a table showing the main sources of air pollution (transport, electricity generation, metals processing, mining, heavy industry, homes and commercial activity, agricultural pursuits) and the main pollutants each produces.
- 5 Diesel engines use a much higher air to fuel ratio than do petrol engines. What effect do you expect this to have on the relative amounts of carbon monoxide and oxides of nitrogen produced by the two types of engine? Explain.



- \*6 It is often claimed that electrically powered vehicles that use batteries charged from the electricity mains are much less polluting than petrol engines. Explain how this claim is true in one respect but false in another.
- 7 a Why does afternoon peak hour traffic have much less effect on city ozone concentrations than the morning peak?
- b Which would be the more effective strategy for controlling photochemical smog: reducing hydrocarbon emissions or reducing emissions of  $\text{NO}_x$ ? Explain why.
- \*c What effect, if any, does daylight saving have on formation of photochemical smog? Explain carefully.
- 8 a When the ratio of  $\text{NO}_2$  to NO is so low that all the ozone formed from the  $\text{NO}_2 + \text{sunlight}$  and  $\text{O} + \text{O}_2$  reactions is destroyed by NO, what is the net result of the three reactions in this cycle? Consider energy as well as mass.
- b Do you expect the  $\text{O} + \text{O}_2$  reaction to be exo- or endothermic? Why? Can you make a prediction about the exo- or endothermicity of the  $\text{O}_3 + \text{NO}$  reaction? Explain.



#### WEBSITES

[www.epa.nsw.gov.au/envirom/princairpol.htm](http://www.epa.nsw.gov.au/envirom/princairpol.htm)

(a simple introduction to the major air pollutants; also move the cursor over *Resource Centre*, then click *For teachers and students*; under *State of Environment* click *atmosphere*) (watch the m in envirom!)

[www.deh.gov.au/soe/2001/atmosphere/introduction-9.html](http://www.deh.gov.au/soe/2001/atmosphere/introduction-9.html) and  
[... atmosphere/summary.html](http://www.deh.gov.au/soe/2001/atmosphere/summary.html)

(both addresses take you to various extracts from the 2001 State of the Environment Report and present useful information about air pollutants)

[www.epa.gov/air/urbanair/6poll.html](http://www.epa.gov/air/urbanair/6poll.html)

(a simple introduction to the six major air pollutants; also near the bottom of the page select *Ozone—good up high bad nearby* for a clear account of ozone in both the troposphere and the stratosphere)

## 7.6 STRUCTURE OF OZONE AND COORDINATE COVALENT BONDS

Molecular oxygen consists of a pair of O atoms joined by a double bond: its electron-dot structure is



Ozone consists of three O atoms joined together. We envisage this as occurring by one of the lone pairs of electrons on one of the O atoms of an  $\text{O}_2$  molecule forming a new covalent bond with the third O atom:



We call this a *coordinate covalent bond*.

A **coordinate covalent bond** is a covalent bond in which both of the shared electrons came from the one atom.

Although we envisage this bond as forming differently from an ordinary covalent bond, once formed it is identical to an ordinary covalent bond.

Figure 7.3 shows models of the oxygen and ozone molecules. Ozone has a bent shape.

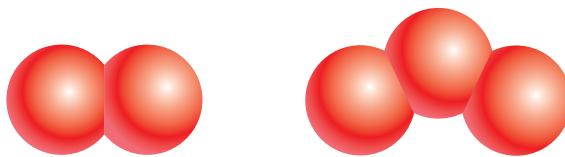


FIGURE 7.3  
Space-filling models of the O<sub>2</sub> and O<sub>3</sub> molecules

Other compounds with coordinate covalent bonds are:

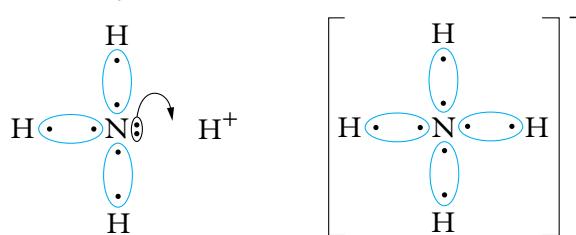
- *carbon monoxide*. Two covalent bonds are formed in the normal way:



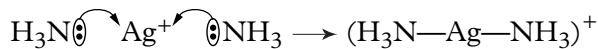
but this leaves carbon ‘unsatisfied’ in that it has only six valence electrons surrounding it instead of the desired eight. So oxygen uses one of its lone pairs to make a shared pair. Hence there is a triple bond between the O and C atoms:



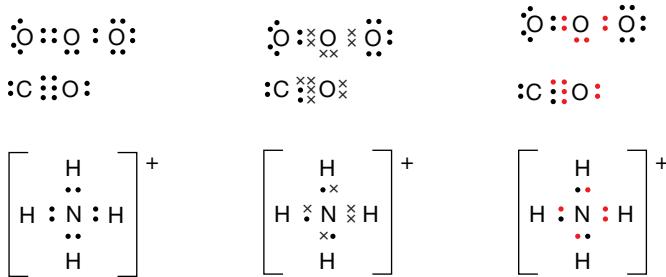
- *ammonium ion*. When ammonia combines with a hydrogen ion to form the ammonium ion, NH<sub>4</sub><sup>+</sup>, a coordinate covalent bond is formed:



- *complex ions such as Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>*. We saw in Section 6.10 that complex ions form by one or more small molecules or ions attaching themselves to a central metal ion. They do this by forming coordinate covalent bonds. For example two ammonia molecules each use their lone pair of electrons to form a coordinate covalent bond with a silver ion:



As was explained on p. 252 CCPC, there are different ways of drawing electron-dot structures. For ozone, carbon monoxide and the ammonium ion we could draw:



The right-hand ones in this set are the only ones that can be described as *Lewis* electron-dot structures (because that is the way that Lewis, who introduced this type of structure, drew them).



## Exercises

- 9 Nitrous oxide,  $\text{N}_2\text{O}$ , has the atoms arranged NNO. Draw an electron-dot structure for  $\text{N}_2\text{O}$  with a double bond between the O atom and the central N atom and a single bond between the N atoms. Why is this an unsatisfactory structure for this molecule? Show how a better structure can be obtained by introducing a coordinate covalent bond.
- 10 Nitrous acid,  $\text{HNO}_2$ , has the atoms arranged HONO. Draw an electron-dot structure for it. Nitric acid,  $\text{HNO}_3$ , has the extra O atom attached to the N atom. Draw an electron-dot structure for nitric acid.
- 11 Draw electron-dot structures for hydrogen chloride,  $\text{HCl}$ , and hydrocyanic acid,  $\text{HCN}$ . The chloride ion and cyanide ion form by loss of a proton from the respective acid. Draw electron-dot structures for these two ions. Both chloride and cyanide form a complex ion with the zinc ion,  $\text{ZnCl}_4^{2-}$  and  $\text{Zn}(\text{CN})_4^{2-}$ . Using the  $\text{Ag}(\text{NH}_3)_2^+$  ion discussed above as a guide, describe the chemical bonding in these two complex ions and draw structural formulae for them.

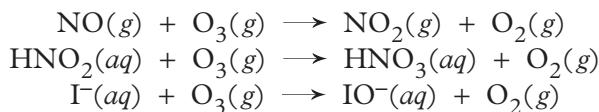
## 7.7 ALLOTROPES OF OXYGEN

Recall (from p. 249 CCPC) that *allotropes* are forms of the one element (in the same physical state) that have distinctly different physical properties (colour, density, hardness, electrical conductivity). There are two allotropes of oxygen,  $\text{O}_2$  and  $\text{O}_3$ : they have quite distinct properties as shown in Table 7.3.

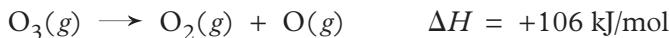
Many of the differences in properties between oxygen and ozone can be explained in terms of their different chemical structures. When molecular oxygen reacts, the double bond between O atoms in the molecule has to be broken, for example in  $\text{H}_2 + \text{O}_2$ ,  $\text{N}_2 + \text{O}_2$ ,  $\text{NO} + \text{O}_2$ ,  $\text{Mg} + \text{O}_2$ ; even in  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$  and  $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$  the  $\text{O}_2$  has to be split in order to put the C or S atom in the middle. This splitting of the O=O double bond requires considerable amounts of energy:



However when ozone reacts, it generally just splits off one O atom, leaving behind a stable  $\text{O}_2$  molecule, for example in



The energy required to do this is much less than that needed to break a double bond:



Ozone is dangerous to living organisms because it attaches an O atom to many of the complex carbon molecules making up living matter and this sets off a series of reactions that lead to the breakdown of key biological compounds and so interferes with the proper functioning of the organism.

## 7.8 OXYGEN GAS, OZONE AND OXYGEN ATOMS

In discussing chemical bonding in Chapter 2 of CCPC we saw that atoms with incomplete valence shells of electrons were not stable and tended to combine

**TABLE 7.3 Properties of oxygen and ozone**

Property	Oxygen, O <sub>2</sub>	Ozone, O <sub>3</sub>
	<ul style="list-style-type: none"> <li>■ colourless gas condensing to a pale blue liquid</li> <li>■ odourless</li> <li>■ essential for all living matter (though pure O<sub>2</sub> for extended periods will kill)</li> </ul>	<ul style="list-style-type: none"> <li>■ colourless gas condensing to a distinctly blue liquid</li> <li>■ strong and distinctive odour (0.01 ppm is detectable)</li> <li>■ poisonous (with detrimental effects observable at concentrations as low as 0.1 ppm)</li> </ul>
boiling point	-183°C	-111°C
density	about the same as air	about 1.5 times that of air
solubility in water	sparingly soluble (9 ppm from air at 20°C)	considerably more soluble than O <sub>2</sub>
stability	very stable	easily decomposed to O <sub>2</sub>
reactivity	<ul style="list-style-type: none"> <li>■ reacts with most other elements to form oxides</li> <li>■ moderately strong oxidising agent</li> </ul>	<ul style="list-style-type: none"> <li>■ much more reactive than oxygen</li> <li>■ very strong oxidising agent</li> </ul>
uses	<ul style="list-style-type: none"> <li>■ widely used medically to overcome breathing problems</li> <li>■ steel-making (to oxidise carbon from pig iron)</li> <li>■ oxy-acetylene torches</li> <li>■ liquid O<sub>2</sub> used in space shuttles and rockets as oxidiser for the fuel (often liquid H<sub>2</sub>)</li> </ul>	<ul style="list-style-type: none"> <li>■ in sterilisers in food shops and kitchens (prepared <i>in situ</i> by passing air through a silent electric discharge)</li> <li>■ purification of water and as a bleaching agent in paper and textile making (it is replacing chlorine for these uses)</li> </ul>

with each other to form molecules. For example H atoms combine to form H<sub>2</sub> molecules, Cl atoms to form Cl<sub>2</sub> molecules (pp. 52–4 CCPC). Similarly O atoms, with six valence electrons, tend to combine to form O<sub>2</sub> molecules:



This means that oxygen does not normally exist as free atoms, but as diatomic molecules.

However it is possible to produce small concentrations of O atoms for short periods of time by passing an electrical or microwave discharge through low pressure oxygen gas:



But if the concentration of O atoms gets too great, they recombine to form molecules again (remember rate increases as concentration of reactants increases):



We saw in Section 7.5 that oxygen atoms are formed in very small concentrations in the lower atmosphere by the action of sunlight on nitrogen dioxide:



Where there is a relatively high pressure (concentration) of O<sub>2</sub>, as in the lower atmosphere, O atoms quickly combine with it to form ozone:



In the stratosphere (as we will discuss more fully in the next section) oxygen atoms are formed by the action of short wavelength ultraviolet radiation on O<sub>2</sub> and on O<sub>3</sub>. There O atoms react with O<sub>2</sub> to form O<sub>3</sub> and they also react with O<sub>3</sub> to re-form O<sub>2</sub>:



(because the concentration of O<sub>2</sub> in the stratosphere is not high enough to make Reaction 7.1 so fast that Reaction 7.2 becomes negligible).

The high reactivity of O atoms means that their concentration is always very low. Whenever we try to get high concentrations of O atoms, they recombine to form O<sub>2</sub>. Consequently, we cannot measure properties such as boiling and melting points for O atoms.

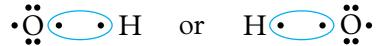
O<sub>2</sub> and O<sub>3</sub> are stable molecules, O<sub>2</sub> more so than O<sub>3</sub>. O<sub>2</sub> can be kept in a container at high pressure indefinitely without any decomposition or change; O<sub>3</sub> can be stored at moderate pressures for reasonable periods of time (days to weeks) with only small amounts of decomposition (to O<sub>2</sub>). The stability of O<sub>2</sub> and O<sub>3</sub> (relative to that of O atoms) arises because the atoms in these molecules all have completed valence shells (see the electron-dot diagrams in the previous section).

O<sub>2</sub> is moderately reactive: O<sub>3</sub> is much more reactive (Table 7.3), and O atoms are more reactive still: O atoms react with O<sub>2</sub>, O<sub>3</sub>, CO, NO, SO<sub>2</sub> (to form O<sub>3</sub>, 2O<sub>2</sub>, CO<sub>2</sub>, NO<sub>2</sub>, SO<sub>3</sub> respectively). O atoms readily react with most organic compounds at room temperature (abstracting an H atom from them). By contrast ozone reacts with organic compounds only if they contain a double or triple bond, and O<sub>2</sub> reacts with organic compounds only at elevated temperatures (combustion).

## Free radicals

A neutral species that has an unpaired electron and which can be formed by splitting a molecule into two neutral fragments is called a **free radical** (or sometimes just a **radical**).

Hydrogen peroxide, H—O—O—H can be split into two OH fragments; each OH fragment contains an unpaired electron and so is called a free radical, in this case the *hydroxyl free radical*. Its electron-dot structure is:



The molecule H—O—Cl can be split into an H atom and a ClO fragment which is called the *ClO free radical*. We shall meet it again in Section 7.11.

By the definition just given an atom that can be formed by splitting a molecule into two pieces is a free radical. We can talk about the H, O, N, Cl atoms or about the H, O, N, Cl free radicals (coming from molecules such as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>). Although the O atom has six valence electrons, two of these are unpaired (based on evidence we need not go into) and so the O atom is a free radical. On the other hand atoms of metals such as Na, Li, Al are not considered to be free radicals, despite having unpaired electrons, because they cannot be formed by splitting up a molecule.

Note that the free radicals discussed here are *neutral species*: they are not ions. The chlorine free radical (or atom), Cl, has the electron-dot structure : $\ddot{\text{Cl}}$ . Compare this with the chloride ion, Cl<sup>-</sup>: : $\ddot{\text{Cl}}$ : which is not a free radical (no unpaired electron). The Cl free radical has completely different properties from the chloride ion, Cl<sup>-</sup>.

Free radicals are sometimes written with the unpaired electron shown as in HO<sup>•</sup>, ClO<sup>•</sup>, and Cl<sup>•</sup>, and sometimes without, as HO or OH (same species), ClO and Cl. The unpaired electron is almost always shown on free radicals formed from carbon compounds (such as CH<sub>3</sub><sup>•</sup> and usually not shown on atoms (for example O).

*Because of the presence of an unpaired electron, and an incomplete valence shell, free radicals are much more reactive than stable molecules.*

## In summary

O<sub>2</sub> and O<sub>3</sub> are stable molecules in which all the atoms have completely filled valence shells; the free O atom is a free radical in that it has an incomplete valence shell (6 electrons with two unpaired instead of 8 all paired); it is not at all stable in that pairs of O atoms readily combine to form O<sub>2</sub> molecules. Free O atoms are much more reactive than either O<sub>2</sub> or O<sub>3</sub>.

## 7.9 DEPLETION OF OZONE IN THE STRATOSPHERE

One of the most worrying global environmental problems of the past twenty years has been depletion of ozone in the stratosphere—the so-called ozone hole problem. There has been a severe reduction in the amount of ozone in the stratosphere, particularly over the Antarctic in spring. This has been attributed to the presence of what are called chlorofluorocarbons (CFCs). However before we consider the chemistry of ozone destruction, let us look at what u.v. light is, the role of ozone in the stratosphere, why destruction of ozone is a problem and what CFCs really are.

### Ultraviolet radiation

**Ultraviolet radiation** (or **u.v. light**) is one of several types of radiation which go under the general name of **electromagnetic radiation**; the common types are shown in Table 7.4. All these types of radiation can transmit energy from one point to another (including across a vacuum) without any matter being transferred—that's what radiation means—and they all travel at the speed of light,  $3 \times 10^8$  metres per second. The different types of electromagnetic radiation are characterised by different *wavelengths* or *frequencies*.

The sun emits predominantly u.v. and visible radiation (with a small amount of infrared). Its wavelength range is from about 200 to 2000 nm (0.2 to 2  $\mu\text{m}$ ) with the greatest intensity being between 300 and 800 nm. Solar u.v. radiation is frequently divided into three classes:

- **u.v.-A**: 400 to 320 nm, generally considered beneficial in that it facilitates photosynthesis and helps form Vitamin D in humans; it also produces a good suntan.
- **u.v.-B**: 320 to 280 nm, considered harmful in that it causes skin cancer, eye cataracts, decreased immune response (and so more disease generally) and it damages plants; it also causes severe sunburn.

**TABLE 7.4 Types of electromagnetic radiation**

Type of radiation	Wavelength	Uses
radiowaves AM FM	200–600 m <sup>a</sup> 1–5 m <sup>a</sup>	radio broadcasts and long distance communications
microwaves	1–100 mm	telecommunications, radar, cooking
infrared	1–1000 μm <sup>b</sup>	radiant heat (lamps)
visible light	400–800 nm <sup>b</sup>	normal light
u.v. light	10–400 nm	suntan lamps, solar energy
X-rays	0.01–50 nm	medical diagnosis, structural analysis
γ-rays	10 <sup>-4</sup> –0.1 nm	cancer treatment

*a* correspond to frequencies of 1600–500 kHz (AM) and 300–60 MHz (FM)

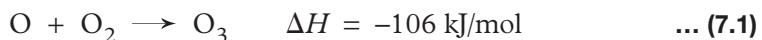
*b* μm = micrometre = 10<sup>-6</sup> m; nm = nanometre = 10<sup>-9</sup> m

- **u.v.-C:** wavelengths shorter than 280 nm, more harmful still, but there is virtually no u.v.-C in the solar radiation reaching Earth's surface.  
(u.v.-A is all right, u.v.-B is bad and u.v.-C is worse.)

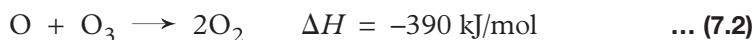
Oxygen in the stratosphere absorbs nearly all of the u.v.-C: ozone in the stratosphere absorbs most of the harmful u.v.-B and the rest of the u.v.-C, while letting through a large proportion of useful u.v.-A.

## Ozone in the stratosphere

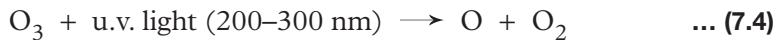
In the stratosphere short wavelength u.v. acts upon oxygen gas to form oxygen atoms which then combine with O<sub>2</sub> molecules to form ozone:



Oxygen atoms can also react with ozone:



The ozone in turn absorbs longer wavelength u.v. which decomposes the ozone back to ordinary oxygen:



There is a balance between the formation and destruction of ozone in these four reactions which leaves a ‘steady state’ concentration of ozone in the stratosphere.

These four reactions also explain why the temperature in the stratosphere is higher than at the tropopause. Reactions 7.3 and 7.4 absorb u.v. radiation and Reactions 7.1 and 7.2 release the energy as heat and so directly warm up the air.

An illustration of just how much (little) ozone there is in the stratosphere is this: if all the ozone in the stratosphere were separated out and spread as a uniform layer of pure ozone gas at standard atmospheric pressure over the whole of the Earth's surface it would be just 3 mm thick!

Decreasing the amount of ozone in the stratosphere means that more short wavelength u.v. radiation (u.v.-B) reaches the Earth's surface.

## Why ozone depletion is a problem

Depletion of ozone in the stratosphere is a problem because it results in more u.v. radiation reaching Earth's surface. This causes:

- increased incidence of sunburn and skin cancer, particularly in fair-skinned people and those who spend a lot of time in the sun
- increased risk of eye cataracts
- increased risk of disease and illness, generally because of a lowering of people's immune response
- reduced plant growth (for some species) due to u.v. interference with their mechanisms for photosynthesis, with rice being particularly vulnerable in this regard, while there is also concern that phytoplankton may suffer damage to its DNA
- increased damage (such as increased brittleness and surface powder formation) to many synthetic materials, particularly polymers (plastics) such as PVC.



The Cape Grim (Tasmania) Baseline Air Pollution Station is one of a series in remote locations worldwide that collects data on air quality away from localised pollution. The aim is to monitor long-term changes in concentrations of trace constituents of the atmosphere that are important in climate change and ozone depletion. The Cape Grim Baseline Air Pollution Station is operated by the Australian Bureau of Meteorology as part of a joint science program with CSIRO Atmospheric Research.

## 7.10 HALOALKANES, PARTICULARLY CFCs

There are many carbon compounds that contain halogen atoms (F, Cl, Br, I). The simplest are the *haloalkanes*.

**Haloalkanes** are compounds in which one or more H atom(s) of an alkane has been replaced by a halogen atom.

Figure 7.4 shows structures of some haloalkanes.

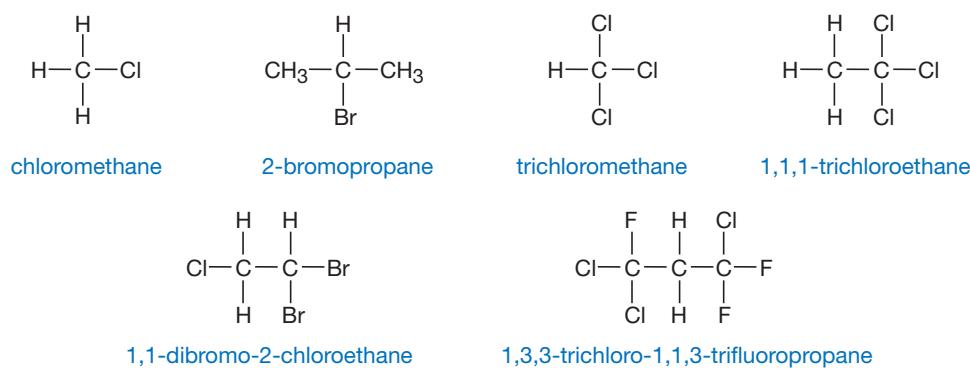


FIGURE 7.4  
Some simple haloalkanes

## Naming straight-chain haloalkanes

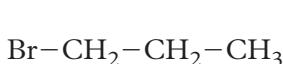
Straight-chain haloalkanes are named using the following rules (with examples in Figure 7.4):

- 1 Bromo-, chloro-, fluoro- and iodo- are used as prefixes to the alkane name; for example chloromethane.
- 2 The position of the halogen (halo) atom is denoted by a number (as was done for double bonds in alkenes (p. 265 CCPC) and for position of the alcohol group in alkanols (Section 5.16). If more than one of a particular type of halo atom is present, di-, tri-, tetra- are used and a location number is given for each such atom, for example 2-bromopropane, 1,1,1-trichloroethane, but just trichloromethane.
- 3 Number from the end of the molecule that leads to the smaller sum of all the substituent numbers; for example 1,1-dibromo-2-chloroethane, not 2,2-dibromo-1-chloroethane ( $1 + 1 = 4$ ;  $2 + 2 + 1 = 5$ ).
- 4 If more than one type of halo atom is present, they are listed alphabetically with any di-, tri-, tetra- being ignored in deciding this order; for example 1,1-dibromo-2-chloroethane, not 2-chloro-1,1-dibromoethane.
- 5 If Rules 1 to 4 lead to more than one possible name, then the correct name is the one that gives the lowest numbers to the most electronegative halogen, the order of electronegativity being F > Cl > Br > I: for example 1,3,3-trichloro-1,1,3-trifluoropropene not 1,1,3-trichloro-1,3,3-trifluoropropene.

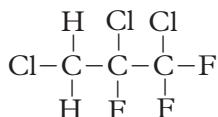
In the IUPAC system for naming compounds there must be only one correct name for a compound.

## Isomers

As explained on pp. 264–5 CCPC, *isomers* are compounds that have the same molecular formula but different structural formulae. On those pages we discussed isomers for alkenes and in Section 5.16 of this book we had isomers for alkanols. We can also have isomers for haloalkanes. The compounds below are isomers of 2-bromopropane ( $C_3H_7Br$ ) and of 1,3,3-trichloro-1,1,3-trifluoropropene.



1-bromopropane



1,2,3-trichloro-1,1,2-trifluoropropene

## Chlorofluorocarbons (CFCs)

**Chlorofluorocarbons** (CFCs) are compounds containing chlorine, fluorine and carbon only, that is, they contain no hydrogen.

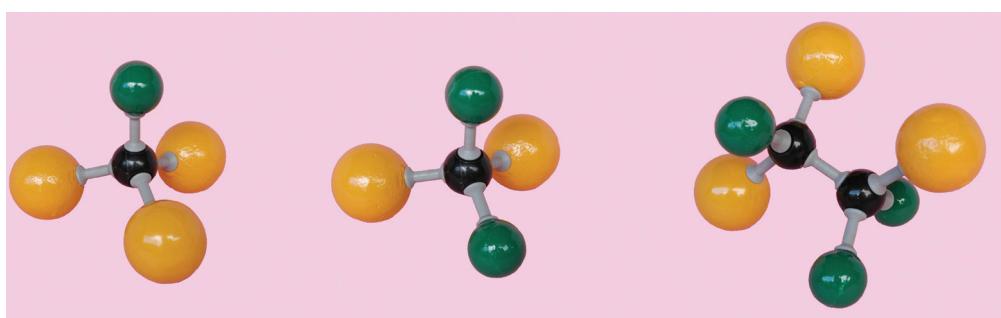
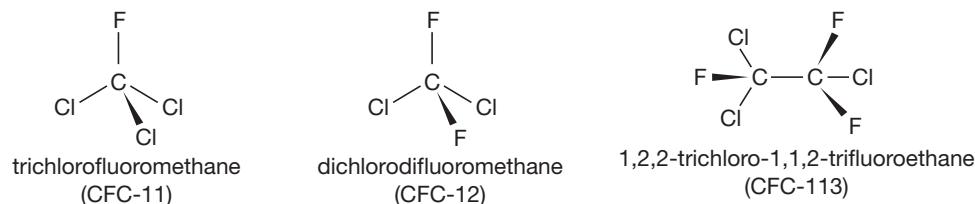
Common CFCs are shown in Table 7.5. CFCs were widely marketed under the trade name of freons—particularly freon-11 and freon-12. Figure 7.5 presents models of some CFCs.

**TABLE 7.5 Common chlorofluorocarbons (CFCs) currently in the troposphere<sup>a</sup>**

Structure	Systematic name	Common name	Major use (before 1996)
$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{F} \\   \\ \text{Cl} \end{array}$	trichlorofluoromethane	CFC-11	working fluid in refrigeration and air conditioning; making foam plastics (insulation); propellant in aerosol spray cans
$\begin{array}{c} \text{Cl} \\   \\ \text{Cl}-\text{C}-\text{F} \\   \\ \text{F} \end{array}$	dichlorodifluoromethane	CFC-12	
$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ \text{Cl}-\text{C}-\text{C}-\text{Cl} \\   \quad   \\ \text{Cl} \quad \text{F} \end{array}$	1,2,2-trichloro-1,1,2-trifluoroethane	CFC-113	

*a Production and use of these compounds is now banned by international agreement*

**FIGURE 7.5**  
Ball-and-stick and space-filling models of some chlorofluorocarbons, CFCs (yellow is S, green is F)



## Why are there CFCs in the atmosphere?

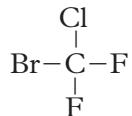
CFCs were introduced, under the trade name ‘freons’, in the 1930s as replacements for ammonia in *refrigeration*; the boiling points and their dependence on pressure made them ideal working fluids. In addition CFCs are odourless, non-flammable, non-toxic and very inert, which made them eminently more attractive than the ammonia they replaced. After World War II

they also became widely used in *aerosol spray cans* and later as *foaming agents* in the manufacture of foam plastics such as polystyrene. With the miniaturisation of electronics from the 1960s onwards they came into common use for *cleaning circuit boards*. In these latter three uses the CFCs were released directly into the atmosphere; even in refrigeration and later in air conditioners the CFCs were released into the atmosphere, but only after the ten to twenty year lifetimes of such appliances. This release into the atmosphere was considered of no concern because CFCs were inert and non-toxic.

However it was just this inertness combined with their insolubility in water (rain) that caused them to become a problem. Because they were not destroyed by sunlight or oxygen (as most organic compounds are), they spread out uniformly around the world, their concentrations in the troposphere gradually built up and slowly they diffused into the stratosphere where they began to cause a problem (see the next section).

## Halons

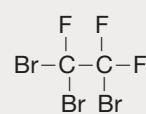
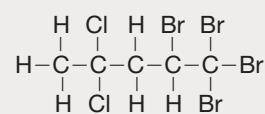
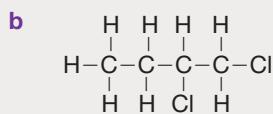
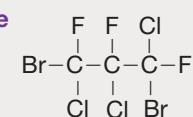
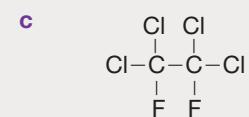
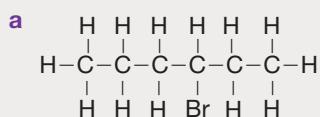
**Halons** are compounds of carbon, bromine and other halogens. They are dense, non-flammable liquids that are particularly good at extinguishing fires. The commonest one is bromochlorodifluoromethane,  $\text{CBrClF}_2$ :



This substance was used in so-called BCF fire extinguishers (BCF = bromine, chlorine, fluorine), the small yellow ones that were commonly used in cars and boats until they were banned in 1994. Another halon that had been in widespread use in automatic fire extinguishing systems is bromotrifluoromethane,  $\text{CBrF}_3$ .

## Exercises

**12** Name the following compounds:



**13** Draw structural formulae for:

- a** 1,1,1-tribromopropane
- b** 1,1,3,3-tetrabromobutane
- c** 1-chloro-3-fluoro-2-iodoheptane
- d** 1,1,2,2-tetrafluoro-1,1-dichloroethane
- \*e** 1,1,3,3-tetrabromo-1-chloro-1,2,3-trifluoropropane
- \*f** 1,1,1,4,4,4-hexachloro-2,2,3,3-tetrafluorobutane

**14** Give the molecular formulae of the compounds in Exercises 12 and 13.

**15** Give the structure and name of one isomer of each of the compounds in Exercise 13.

**16** Some haloalkanes in everyday use are:

- a chloroform,  $\text{CHCl}_3$  (solvent, anaesthetic)
- b methylene chloride,  $\text{CH}_2\text{Cl}_2$  (paint stripper)
- c halothane,  $\text{CF}_3\text{CHClBr}$  (anaesthetic).

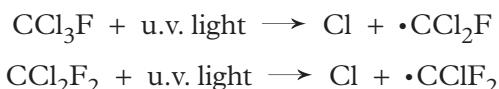
Give the systematic names of these compounds.

**17** How many isomers can there be of CFC-113 (Table 7.5)? Draw structures to justify your answer.

## 7.11 DESTRUCTION OF STRATOSPHERIC OZONE BY CFCs

CFCs are not destroyed at low altitudes by sunlight and oxygen as are most compounds released to the atmosphere. In addition they are insoluble in water so they do not get washed out of the atmosphere by rain (another major natural process for cleaning the atmosphere). Hence CFCs remain in the troposphere for very long periods of time—for several decades. This means that they are able to diffuse slowly into the stratosphere.

In the stratosphere they come into contact with short wavelength u.v. radiation (before the ozone has filtered it out) and this short wavelength u.v. breaks a chlorine atom off the CFC molecule:



### The basic destruction process

The chlorine atom formed then abstracts an oxygen atom from an ozone molecule, forming a ClO free radical (Section 7.8):



ClO, like all free radicals, is very reactive.

Because of the continual formation and destruction of ozone in the stratosphere, there are free oxygen atoms present as well as  $\text{O}_2$  and  $\text{O}_3$  molecules (Section 7.9). ClO reacts with a free oxygen atom to form a molecule of oxygen,  $\text{O}_2$  and this regenerates the chlorine atom:



The net result, the sum of Equations 7.5 and 7.6 is, that an ozone molecule and an oxygen atom have been converted into two oxygen molecules and our reactive chlorine atom has not been used up. This chlorine atom is able then to attack another ozone molecule and repeat the process all over again. And so it goes on: one chlorine atom can destroy thousands of ozone molecules. We call this a **chain reaction**, a reaction in which the reactive species—in this case the chlorine atom—is regenerated and so can go on repeating the reaction more or less indefinitely. Hence one CFC molecule can do a tremendous amount of damage. Only a very small amount of CFC needs to reach the stratosphere for a very significant amount of ozone destruction to occur.

If the above two chemical reactions were the only ones occurring then just one chlorine atom (or just one CFC molecule) could destroy all of the ozone in the stratosphere. Actually there is evidence to show that on average each chlorine

atom destroys a few thousand ozone molecules before the chain reaction is broken. There are other reactions going on in the stratosphere and some of these remove the *chain carriers* (as the reactive Cl atom and ClO radical are called).

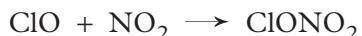
## Other reactions of Cl and ClO

One particularly important reaction is between a chlorine atom and a methane molecule. Small quantities of methane are present in the stratosphere as a result of slow diffusion up from the troposphere. This reaction forms hydrogen chloride:



This reaction effectively removes a chlorine atom and so brings the chain reaction to a halt. Another chlorine atom will need to be generated (from a CFC molecule) for destruction of ozone to continue. The hydrogen chloride formed in this reaction has no effect upon ozone and so reactive chlorine atoms are converted into unreactive HCl molecules. The  $\text{CH}_3\cdot$  radical undergoes further reactions but they have no effect upon ozone.

Another important reaction for stopping the ozone-destroying chain involves the ClO species:



Small amounts of nitrogen dioxide are present in the stratosphere.  $\text{ClONO}_2$  is chlorine nitrate (compare with nitric acid,  $\text{HONO}_2$ ); it is formed when a ClO radical hits an  $\text{NO}_2$  molecule. The occurrence of this reaction essentially removes ClO from the above chain reaction and so this is another way of bringing the destruction of ozone to an halt. Chlorine atoms cannot be regenerated from chlorine nitrate.

The importance of the chain-reaction nature of this process needs to be strongly emphasised. It is because one CFC molecule can destroy thousands, perhaps tens of thousands, of ozone molecules that the very small concentrations of CFCs that actually diffuse into the stratosphere can cause significant damage.

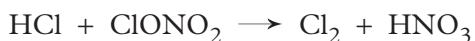
The process that has just been described for destruction of ozone could (and does) occur throughout the whole of the stratosphere and throughout all of the year. However dramatic depletion of stratospheric ozone has been observed only over the Antarctic and then only in spring.

## 7.12 WHY OVER THE ANTARCTIC AND WHY IN SPRING?

The story so far is that CFC molecules diffuse into the stratosphere where u.v. light splits off chlorine atoms. These chlorine atoms destroy ozone molecules but eventually get converted into hydrogen chloride and chlorine nitrate which are unreactive and quite harmless to ozone. And this happens globally.

Serious ozone depletion is localised and seasonal (over the Antarctic in spring) because winter in the Antarctic is a period of continuous darkness *and* the stratosphere there is extremely cold (due to certain wind patterns called a polar vortex which stop Antarctic air mixing with warmer lower-latitude air).

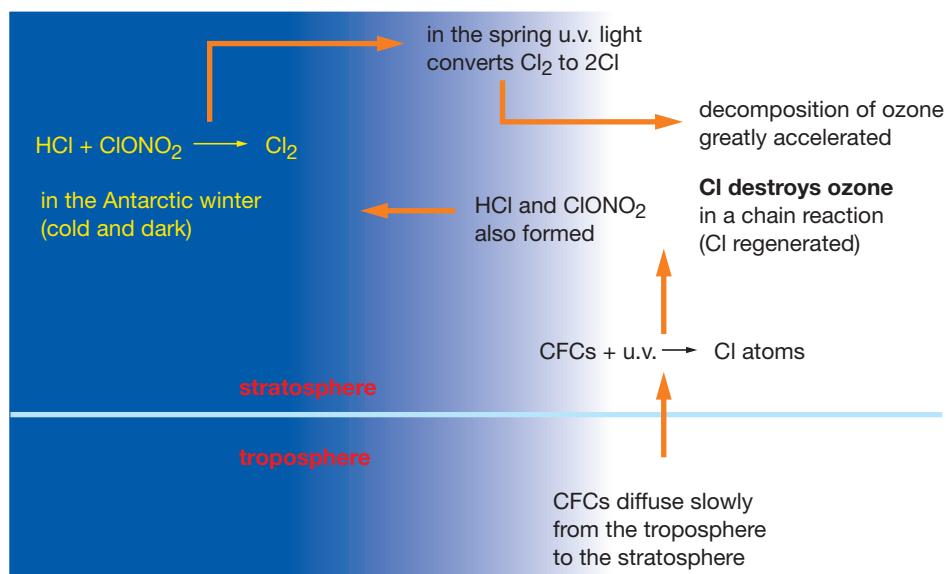
Under these extremely cold conditions certain solid particles form that are able to catalyse a reaction between hydrogen chloride and chlorine nitrate.



This conversion of hydrogen chloride and chlorine nitrate to molecular chlorine has no effect upon ozone concentrations during winter. However when the sun comes up in early spring, the situation changes dramatically. Sunlight is able to split a chlorine molecule into two separate chlorine atoms:

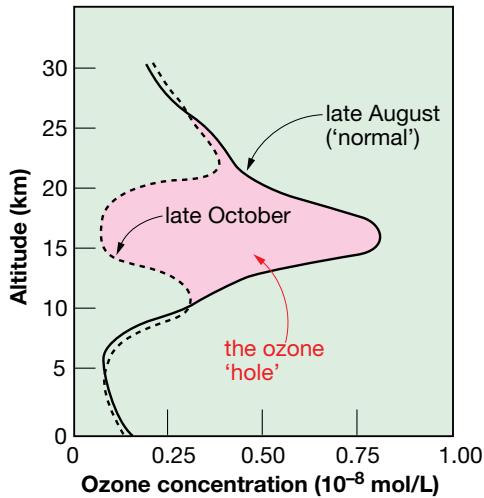


and each of these can destroy ozone in exactly the same way as chlorine atoms formed from CFCs. In spring, then, there is an extra source of chlorine atoms and so increased destruction of ozone. The concentration of ozone over the Antarctic is greatly reduced and so the ‘ozone hole’ is formed. The hole is at its deepest (ozone depletion at its greatest) in late October to early November. Figure 7.6 shows schematically this mechanism for ozone destruction.



**FIGURE 7.6**  
The mechanism for destruction of ozone, both globally all year and over the Antarctic

Figure 7.7 shows the variation of ozone concentration with altitude on two different days, one in late winter (a normal profile) and one in spring clearly showing the ozone hole; on the latter day about 80% of stratospheric ozone had been destroyed over that location which would have been fairly typical of the Antarctic generally.



**FIGURE 7.7**  
Changes in the ozone profile through the stratosphere between winter (normal) and spring (severely depleted). This graph is typical of those observed from 1985 onwards. The pink shading represents the amount of ozone depletion—about 80% in this case

Only a finite amount of molecular chlorine is formed during the polar winter. By early summer this has been virtually all used up, so the rate of destruction

of ozone returns to the ‘normal’ CFC level. In addition the polar vortex breaks up in early summer and so there is mixing of Antarctic air with lower-latitude air. This brings the ozone concentration back to its normal level. The break up of the polar vortex has occasionally brought ozone depleted stratospheric air over Tasmania and parts of Victoria in early summer. Generally the ozone hole disappears by about Christmas or mid-January.

## Other ozone destroying compounds

Some other halogen-containing compounds are also sources of ozone-destroying atoms in the stratosphere. In particular:

- *Halons* (p. 262); these compounds contain C–Br bonds which can be broken by u.v. light in the same way as C–Cl bonds are, and Br atoms can decompose ozone in the same way as Cl atoms do
- *Carbon tetrachloride* (tetrachloromethane) and *1,1,1-trichloroethane* (methyl chloroform), widely used as industrial solvents; as with CFCs the C–Cl bonds cause the problem
- *Methyl bromide* (bromomethane), widely used as a fumigant for seeds and soil; the C–Br bonds cause ozone destruction (as with halons).

## In summary

On a global year-round basis, CFCs have caused a 3 to 8% decrease in the amount of ozone in the stratosphere: however, (of much greater concern) in recent years they have caused a 50 to 90% decrease over the Antarctic during spring.

## Exercises

- 18 a** Draw an electron-dot diagram for the HOCl molecule and hence for the ClO free radical (formed from HOCl by removal of an H atom).
- b** Nitric oxide and nitrogen dioxide are sometimes considered to be radicals rather than molecules. Explain why this is so. Drawing electron-dot diagrams may help.
- c** Use the electron-dot diagrams you drew in (a) and (b) to explain why you would expect ClO to react with NO<sub>2</sub>.
- 19 a** Explain why Cl and ClO can be considered catalysts for the reaction between O and O<sub>3</sub>.
- b** In the late 1960s and early 1970s there was concern that NO and NO<sub>2</sub> from exhausts of supersonic aeroplanes (which fly in the lower stratosphere) would catalyse the decomposition of ozone (in the same way as Cl and ClO do). Write equations to show this.



## WEBSITES

For the ozone hole:

<http://www.atm.ch.cam.ac.uk/tour>

(a simple but thorough account of the history, chemistry and monitoring of the ozone hole; just click on the first tutorial and follow through to the others sequentially)

<http://jwocky.gsfc.nasa.gov>

(click on the globe under ozone to see the latest global map of ozone concentrations; or click on *Ozone hole monitoring page* to see how the current year’s data compares with previous years or click on *direct access* to get maps of particular days over many years)

## 7.13 COMBATING THE OZONE-HOLE PROBLEM

The only way to stop ozone destruction by CFCs is to stop releasing them to the atmosphere, because once they are released it is impossible to remove them, and they do not decompose or get washed out by rain.

### International agreements

Since 1987 there have been several international agreements in which nations have undertaken to phase out the use of CFCs and other ozone-destroying compounds. The original agreement was called the Montreal Protocol. The most recent agreement (1992) was to:

- stop using halons by the end of 1994
- cease the manufacture and use of CFCs and 1,1,1-trichloroethane by 1996
- phase out HCFCs (see below) by early in the 21st century
- allow less developed countries some period of grace and provide some financial assistance to help them phase out CFCs.

### Alternatives to CFCs

Most of the more developed countries have been able to meet these goals because alternative compounds have been made to replace CFCs.

The first replacements were **HCFCs, hydrochlorofluorocarbons**: these compounds contain C–H bonds which are susceptible to attack by reactive radicals and atoms in the troposphere and so are decomposed there to a significant extent: this means that only a small proportion of them reach the stratosphere. Consequently their ozone-destroying capacity is much less than that of the CFCs. Nevertheless it is still significant. HCFCs were seen as temporary substitutes for CFCs until better compounds could be made and tested.

HFCs are now widely used as replacements for CFCs. **HFCs** are **hydrofluorocarbons** (compounds containing hydrogen, fluorine and carbon, but no chlorine). They contain C–H bonds so undergo some decomposition in the troposphere, and contain no C–Cl bonds so do not form Cl atoms in the stratosphere: their ozone-destroying capacity is zero. The most widely used HFC is HFC-134a (generally marketed in Australia as R134a–R for refrigerant): its systematic name is 1,1,1,2-tetrafluoroethane. It is now widely used in refrigeration and air conditioning. It is more expensive than the CFCs it replaces and somewhat less efficient, but these are small prices to pay for protecting stratospheric ozone.

### How long until improvement is seen?

The good news is that if we remove CFCs from the atmosphere, stratospheric ozone will recover: the damage is reversible. The bad news is that even if all nations observe the current restrictions it will take from 50 to 100 years for complete recovery to occur. This is because there is now so much CFC in the troposphere that it will take a long time for it all to diffuse into the stratosphere and do its damage (and so be destroyed).

However as we reduce emissions to the troposphere, the concentrations of CFCs there will fall and so diffusion into the stratosphere and ozone destruction

will decrease. Computer models suggest that ozone destruction over the Antarctic should be peaking about now (2005–2010) and then the problem should start to become less severe.

## Progress to date

Progress in reducing emissions of CFCs worldwide appears to be quite significant, since the introduction of the Montreal protocol and its later revisions (at least in terms of published inventories of quantities released). Most countries are meeting (or attempting to meet) the required targets. This has been largely due to the availability of acceptable alternative compounds such as the HFCs. However there has not as yet been much reduction in measured atmospheric concentrations of CFCs and the ozone hole has not yet been getting any ‘shallower’, though perhaps it is progress to report that it has not been getting worse!

At least there has been significant progress in solving the ozone hole problem, which is more than can be said for that other serious global atmospheric problem, the enhanced greenhouse effect (global warming).



## Exercises

- 20** The 134 in the code name R134a means two C atoms, two H atoms and 4 F atoms: the a means one particular isomer (named above). Draw structures of all possible isomers that could be called R134.
- 21** The code for labelling CFCs and related compounds is a three-digit number: the units digit is the number of F atoms in the molecule, the tens digit is the number of H atoms plus 1 and the hundreds digit is the number of C atoms minus one (and is omitted if zero) with any extra atoms if needed being Cls. A letter a, b, c... is added to signify a particular isomer if relevant.

Some intermediate and long-term replacements for CFCs are:

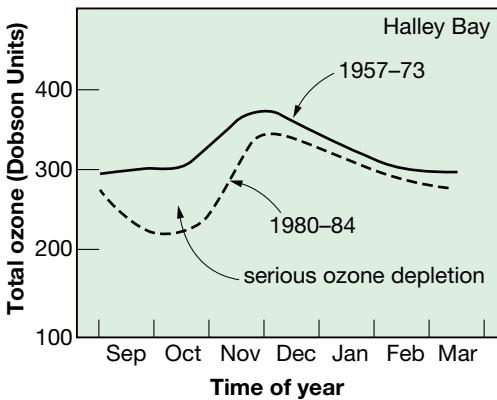
- a** HCFC-123      **\*b** HCFC-141      **c** HFC-32      **\*d** HFC-125

Draw structures and name all isomers that could be represented by these code names.

## 7.14 MONITORING STRATOSPHERIC OZONE

Stratospheric ozone is monitored from ground-based instruments, from instruments in satellites and from instruments in balloons.

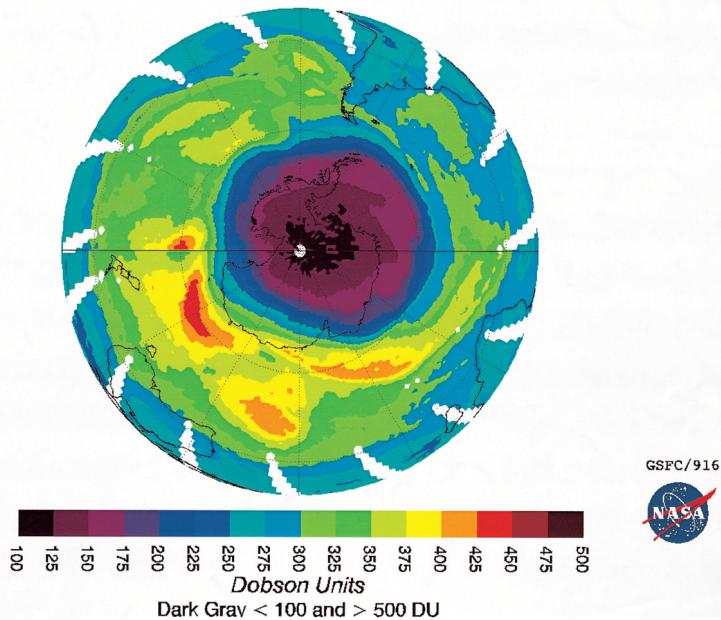
The ground based instruments are u.v. spectrophotometers pointing vertically upwards through the atmosphere. They measure the intensity of light received (from the sky, i.e. sun) at a wavelength at which ozone absorbs and then at wavelengths either side of this at which ozone does not absorb. A comparison of these intensities gives a measure of the total ozone in the atmosphere per unit area of Earth surface at that location (i.e. the average concentration multiplied by the thickness of the atmosphere). The ozone hole was first observed by such measurements (Fig. 7.8). Such spectrophotometers are located in many places around the world and provide valuable total ozone measurements as a function of geographic location.



Total ozone per unit area above a location is generally measured in **Dobson Units**, DU. 1 DU is the amount of ozone that corresponds to a 0.01 mm thickness of pure ozone at atmospheric pressure. The normal amount of ozone is 300 DU (= 3 mm; Section 7.9).

The total ozone mapping spectrophotometers (TOMS) that have been on board several US satellites over the past 20 years work similarly, but because the satellites have been in orbit, these instruments have been able to scan through the atmosphere and measure the ozone concentration as a function of altitude and of geographic position. Such measurements can produce profiles such as the one in Figure 7.7. They can also produce contour maps of total ozone over different areas of the Earth's surface as in Figure 7.9.

**EP/TOMS Version 8 Total Ozone for Oct 5, 2004**



Huge helium-filled balloons have been used to carry instruments including u.v. spectrophotometers up into the stratosphere to measure concentrations of various substances including ozone as a function of altitude. Some of the early profiles of the type in Figure 7.7 were obtained in this way (though they can also be obtained from the satellite measurements described above).

**FIGURE 7.8**  
Total ozone per unit area measurements at Halley Bay in Antarctica as a function of time of year: average values for the years 1957 to 1973 compared with 1980 to 1984 averages. This is a simplified drawing of the original data that first detected the ozone hole. It shows that in spring the total ozone has been depleted by about 30%. Worse depletions were observed in subsequent years

**FIGURE 7.9**  
A total ozone contour map from a NASA satellite

## Important new terms

You should know the meaning of the following terms:

chain reaction (p. 253)  
chlorofluorocarbons (CFCs) (p. 250)  
coordinate covalent bond (p. 242)  
Dobson Unit, DU (p. 259)  
electromagnetic radiation (p. 247)  
free radical (p. 246)  
haloalkanes (p. 249)  
halons (p. 252)  
HCFCs and HFCs (p. 257)

hydrochlorofluorocarbons, HCFCs (p. 257)  
hydrofluorocarbons, HFCs (p. 257)  
particulates (p. 237)  
photochemical smog (p. 239)  
radical (p. 246)  
stratopause (p. 237)  
stratosphere (p. 236)  
tropopause (p. 236)  
troposphere (p. 236)  
ultraviolet radiation (p. 247)  
u.v.-A, u.v.-B and u.v.-C (p. 247–8)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 List the five most abundant components of the atmosphere in their order of abundance. List another eight constituents of the atmosphere and give an order of magnitude for their concentrations (i.e. 10, 1, 0.1, 0.01 ppm).
- 3 Sketch a temperature profile through the atmosphere and identify the various regions.
- 4 Explain why pollutants from the lower atmosphere generally do not get into the stratosphere and why ozone in the stratosphere does not get down to sea level.
- 5 List the main atmospheric pollutants and give their major sources.
- 6 What is photochemical smog? How does it form? What conditions are needed for its formation?
- 7 How do most industrialised countries minimise the formation of photochemical smog?
- 8 Explain the operation of catalytic exhausts for motor cars: include at least two equations.
- 9 Draw electron-dot structures for the oxygen and ozone molecules.
- 10 Draw structures of two other species that involve coordinate covalent bonds.
- 11 Explain what is meant by saying that oxygen gas and ozone are allotropes of oxygen.
- 12 Give three properties of oxygen gas and ozone that are distinctly different for the two substances.
- 13 Why do we consider the oxygen atom a free radical? Why is it not possible to form high concentrations of O atoms?
- 14 List some contrasting properties of O atoms and O<sub>2</sub> and O<sub>3</sub> gases.
- 15 Draw structures and name three haloalkanes.
- 16 Draw structures and name a pair of isomeric haloalkanes.

- 17** What are CFCs? Give names and draw structures for three common ones. Until recently what were these compounds used for?
- 18** Explain, with equations, how ozone is formed in the stratosphere.
- 19** Explain, with equations, how CFCs destroy ozone in the stratosphere. Include explanation of how small amounts of CFC can destroy large amounts of ozone.
- 20** Explain why ozone destruction occurs most extensively over the Antarctic in spring. Include relevant equations.
- 21** How is the ozone-hole problem being overcome? When is some alleviation of the problem expected and when, if ever, will it be fully ‘cured’? Comment on the effectiveness of current strategies.
- 22** Where do HCFCs and HFCs fit into the ozone problem?
- 23** Describe ways in which stratospheric ozone is being monitored.

# CHAPTER 8

# Monitoring water quality

## IN THIS CHAPTER

Water quality	Water hardness
Temperature and pH	Tests for common anions
Turbidity	Cations in environmental water
Total dissolved solids (TDS)	Factors affecting concentrations of ions
Salinity	Algal blooms and eutrophication
Dissolved oxygen and biochemical oxygen demand (BOD)	Water treatment for domestic consumption
Micro-organisms	Membrane filters

Human activities often discharge wastes into water bodies such as oceans and rivers. To ensure that these wastes do not significantly lower the quality of the water that we use, we need to monitor effluents and the water bodies themselves. But first, what do we mean by ‘good quality’ water?

## 8.1 WATER QUALITY

The meaning of the phrase *good quality water* depends upon the purpose for which the water is being used. Humans have four major uses of water:

- 1 water for human consumption (drinking and preparing food)
- 2 water for other human domestic uses (washing, laundry, toilets, cleaning, gardens)
- 3 water for agriculture (irrigation and watering stock) and industry (often as a coolant)
- 4 water for recreation (swimming, fishing and boating) and for aesthetic appeal (attractive land- and seascapes).

Water that is considered of good quality for agriculture may not be considered good quality for drinking; water bodies that are aesthetically pleasing and suitable for boating and fishing may be considered of poor quality for agriculture. Different standards apply to the different uses.

In addition there is the question of what constitutes good quality water in a general environmental sense—the properties that water should have to maintain the health of rivers and streams, the aquatic life they support and the land they flow through.

## Good quality drinking water

- is completely colourless and clear
- is odourless
- has a pleasant taste
- has a relatively low salt content
- contains no pathogens (disease causing agents)
- contains no poisonous chemicals.

For other domestic uses such as bathing and laundering, water should be 'soft', not 'hard'.

**Hard water** is water that does not lather with soap and which leaves a grey scum around baths and basins; if water is not 'hard', we call it **soft water**.

Hardness will be discussed in Section 8.8.

## Good quality environmental water

For the wellbeing of the environment generally, water should:

- contain adequate concentrations of dissolved oxygen (needed by most aquatic organisms)
- not contain high levels of oxygen-consuming substances
- be relatively free of suspended solids (which by excluding light interfere with photosynthesis), and
- contain only low concentrations of phosphate and nitrate, because higher concentrations of these nutrients promote algal blooms.

**Algal blooms** are excessive growths of algae which cover streams and dams with a green sludge and make the water unusable for people, stock or irrigation.

Algal blooms will be discussed in Section 8.12.

A wide variety of scientific tests and measurements can be performed to assess water quality.

## Criteria for assessing water quality

In scientific terms the criteria used to assess water quality are:

- 1 turbidity (or lack of clarity, which is indicative of the amount of suspended solids present)
- 2 total dissolved solids (generally salts)
- 3 pH
- 4 temperature
- 5 dissolved oxygen
- 6 amount of biochemical oxygen demand
- 7 concentrations of nitrate and phosphate
- 8 hardness
- 9 presence of pathogens (bacteria, viruses and parasites)
- 10 concentrations of heavy metals such as iron, lead, mercury, chromium, copper, zinc
- 11 presence of toxic organic compounds such as pesticides and herbicides.

Values for some of these criteria for 'environmentally clean' and polluted fresh water are shown in Table 8.1. The meaning of some of the terms in this table will be explained as you progress through the chapter.

**TABLE 8.1 Some properties of 'environmentally clean' and polluted fresh water**

Property	Typical 'clean water' values	Polluted water <sup>a</sup>
Turbidity (NTU) <sup>b</sup>	<3	>20
TDS <sup>b</sup> (mg/L)	<100	>1000 (for fresh water)
pH	6.5–8.5	<6 or >9.0
DO <sup>b</sup> (mg/L)	7–9	<4
BOD <sup>b</sup> (mg/L)	<5	>10
total phosphate (mg/L)	<0.03	>0.05 for lakes and dams >0.1 for rivers and streams
nitrate (mg/L)	<0.1	>0.50
faecal coliforms (CFU/100 mL) <sup>b</sup>	<5	>200

<sup>a</sup> Any one of these values would make the water polluted.

<sup>b</sup> NTU = nephelometric turbidity units: less than 1 is very clear water, 30 is quite turbid; TDS = total dissolved solids; DO = dissolved oxygen; BOD = biochemical oxygen demand; CFU = colony forming units.

Sea water differs from fresh water in that total dissolved solids are much higher (35 000 ppm compared with fewer than 500 ppm for fresh water) and pH is a little higher—often slightly greater than 7 whereas fresh water is commonly just less than 7. The other properties are similar for both fresh and sea water.

## Tests used

A variety of methods can be used to test for each of the eleven criteria of water quality listed above. The emphasis in this chapter will be on tests that either:

- can be performed in a school laboratory, or
- are commonly used by local agencies to monitor the quality of drinking water or of environmental water (fresh and marine).

Several of the tests are those used by Streamwatch, an organisation set up by several water and conservation authorities in NSW to help students monitor their local waterways.



### WEBSITE

For an introduction to the Streamwatch program:

<http://streamwatch.org.au>

(the home page leads you to assorted information about the program. Select *Electronic library*, then *Streamwatch Manual* for details about various tests, often with more detail than in CCHSC)

## Sampling

Care needs to be taken when collecting water samples for testing to ensure:

- that the sample is truly representative of the water body to be tested, and

- that collecting the sample does not change the value of the parameter to be measured.

Taking a sample too close to the water's edge may give a non-representative reading; for example the temperature may be higher than the water body as a whole (because shallow water heats up more easily) or it may contain more suspended solids or micro-organisms than the bulk of the water. Not being gentle enough in collecting a sample may stir up sediments so that the sample contains more suspended matter (and hence has a greater turbidity) than the water body as a whole.

Water samples for analysis are generally collected by using a jar attached to the end of a long handle such as the telescopic handle of a swimming pool brush or leaf scoop. To ensure an accurate sample, the sampling bottle is generally filled once then emptied then filled again.

Students performing water-quality tests as part of the Streamwatch program

## 8.2 TEMPERATURE AND pH

Temperature is measured to ensure that it is not outside the acceptable range for the life forms that normally live in it in that locality. Basically this is checking that there are no significant discharges of hot or cold water into the stream (thermal pollution, p. 227 CCPC).

The pH of water samples is measured by indicator solutions, papers or a pH meter as explained in Section 4.19.



LEFT A portable pH meter for use in the field. Although the delicate sensing glass membrane (in the inset) is well protected, care is still needed not to break it



A pH outside the normal range of 6.5 to 8.5 indicates that some form of pollutant has been discharged into the water body. Possibilities are industrial waste, fertiliser run-off or, for low pH, acid drainage from a mine site: sulfide ores on exposure to moist air often form sulfuric acid.

## 8.3 TURBIDITY

**Turbidity** in water means cloudiness or lack of transparency.

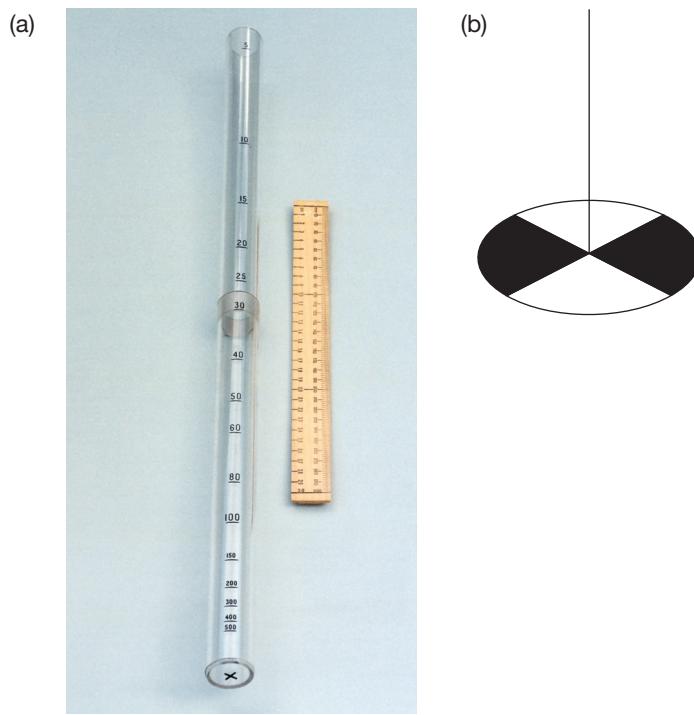
It is caused by suspended solids. Sometimes suspended particles are sufficiently large that they settle out on standing, but very small particles can remain suspended indefinitely. Such small particles cannot easily be filtered out either, because they are small enough to pass through the pores of most filter papers. It is these small particles that cause turbidity. Turbidity not only gives water an undesirable appearance but also can give it an undesirable taste.

Turbidity can be assessed by measuring the depth of water needed to render invisible a mark (such as a black cross) on the flat bottom of a specially made tube that looks like a very long measuring cylinder. The water to be assessed is slowly added to the cylinder until the mark just becomes invisible. If the tube or cylinder has been engraved with marks at different heights (depths) showing the turbidity values, turbidity can be read off directly. Alternatively the depth of water can be measured and a calibration graph used to obtain the turbidity. Figure 8.1(a) shows the turbidity tube supplied to schools by Streamwatch.

Another piece of equipment used to measure relative turbidity is a **secchi disc**. This is a circular disc divided into four quadrants with alternate ones painted black and silver as in Figure 8.1(b); a string is attached to the centre. The disc is lowered into the water until the quadrants just become invisible; the length of the string gives a relative measure of the turbidity of the water: the shorter the length of string, the higher is the turbidity. This device is a convenient method of making comparative estimates of turbidity from one location to another or at different times at the same location.

FIGURE 8.1

(a) A typical tube used to measure turbidity (from the Streamwatch test kit); for comparison the ruler is 30 cm long (b) a secchi disc for measuring relative turbidity



Turbidity is measured in *nephelometric turbidity units*, NTU. This is a fairly arbitrary scale. The absolute values have little meaning, but they are useful for comparative purposes.

Turbidity gives a measure of the amount of suspended solids present. While filtering off suspended solids and determining their mass may work on fairly dirty water in the environment (flooded rivers and polluted lagoons), it is not practical on drinking water because it contains too small a mass of particles that are usually too small to be filtered off.

## Causes of turbidity

High concentrations of suspended solids and hence high turbidities arise naturally from heavy rain and floods. Run-off across grasslands or through forests picks up suspended matter which is carried into waterways, while rapid flows in streams stir up sediments from the bottom or edges of the waterway and make all the water turbid. These natural processes are greatly accelerated by human activities. Land-clearing (cutting down forests) and farming (ploughing fields and often having bare loose earth exposed to heavy rain) both lead to increased amounts of suspended matter being carried into waterways. Cutting down trees and scrub along water courses and farming right to river banks are the most damaging practices in this regard.

## 8.4 TOTAL DISSOLVED SOLIDS (TDS)

As the name implies,

**Total dissolved solids (TDS)**, is the mass of solids dissolved in unit volume of water.

It is generally reported as mg/L or as ppm (both terms are virtually equivalent). Streams and rivers that flow through undisturbed bushland typically have TDS of less than 100 ppm. If they receive significant in-flows from underground aquifers or if they flow through farming and grazing areas, TDS often rises to 200 to 300 ppm. Drinking water for humans should have a TDS of less than 500 ppm. A TDS of greater than 1000 ppm signifies a seriously degraded waterway and such water has only limited value for irrigation, though it is still suitable for stock and poultry. Sea water has a TDS of about 35 000 ppm (3.5%).

### TDS by evaporation

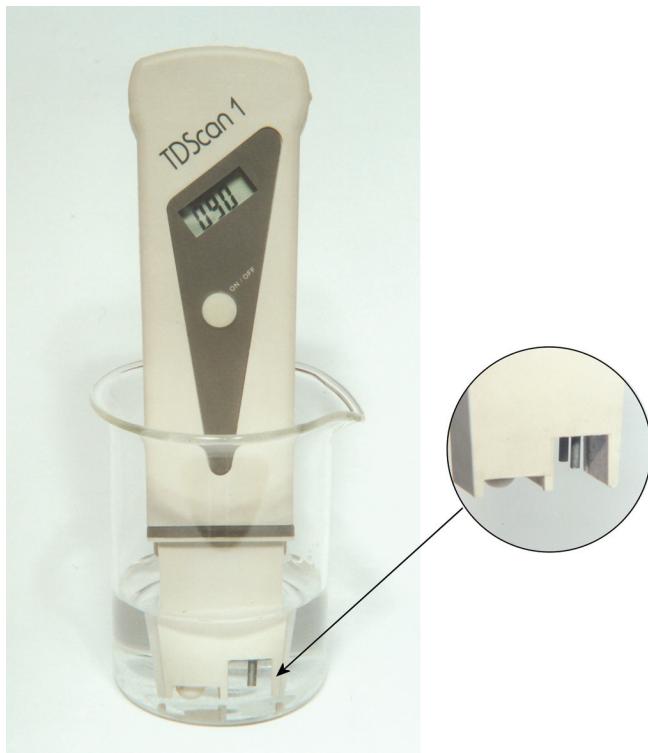
The amount of total dissolved solids can be measured first by filtering off suspended solids then by evaporating a sample of water to dryness and weighing the solids left. In practice this requires considerable care if it is to be done accurately, particularly for drinking water because of the small amount of solid present. Evaporating 1.00 L of water containing 100 ppm TDS produces only 0.1 g solid, and some of this could easily be lost by turbulent bubbling and spitting during evaporation.

### TDS by conductivity measurements

Nearly all of the solid dissolved in natural water is ionic, that is, made up of salts. Therefore environmentalists frequently use *electrical conductivity* of water to measure TDS. This is much quicker and can be done in the field.

Electrical conductivity is the current that flows when a voltage of 1.000 volt is applied across opposite faces of a unit cube. In water contexts the cube is generally taken as a 1.00 cm cube (compare the 1 m cube on p. 103 CCPC). Conductivity is measured in siemens  $\text{cm}^{-1}$ ,  $\text{S cm}^{-1}$  or in millisiemens  $\text{cm}^{-1}$ ,  $\text{mS cm}^{-1}$ . A portable conductivity meter is shown in Figure 8.2.

FIGURE 8.2  
Portable conductivity meter used to measure total dissolved solids (TDS). In this meter, from the Streamwatch kit, the electrodes are a pair of stainless steel rods (inset)



By comparing conductivities of water samples with the masses of solids obtained by evaporating them to dryness, scientists have established that the relation between total dissolved salts and conductivity is:

$$\text{TDS (in ppm)} = 0.65 \times (\text{conductivity in } \text{mS cm}^{-1}) \quad \dots (8.1)$$

Although conductivity gives a measure of total dissolved *salts*, this is generally a fair approximation to total dissolved *solids* and is widely used as a measure of TDS.

## 8.5 SALINITY

**Salinity** is a term that is often used instead of total dissolved solids, though salinity can have a broader meaning in that we can talk about the salinity of land as well as of water. We often read reports about the increasing salinity of farmland in the Murray River irrigation areas or in the wheat lands of south-west Western Australia. And there is often talk about the salinity of the Murray and Darling Rivers, particularly in times of drought.

When used in connection with rivers, salinity means total dissolved *salts*, which approximates closely to total dissolved solids. The word ‘salinity’ arises from the fact that the most abundant of the dissolved solids is sodium chloride, common salt, though there are significant amounts of other salts as well.

When talking about the salinity of soils or farm land, we mean specifically the concentration of common salt (because most other salts are harmless and in fact necessary).

## Causes of salinity

A small amount of salinity (TDS) in waterways is quite natural. Rain contains 10 to 50 ppm sodium chloride, because of sea spray being caught up into rain clouds, and water as it flows across undisturbed land dissolves small amounts of various salts. However human activities have greatly increased the salinity of many rivers.

*Land clearing and deforestation* have increased both the amount of water running off land into rivers (instead of being absorbed by the trees) and the amount of solids dissolved in the water. *Farming* increases TDS because rain run-off easily dissolves salts from ploughed soil. However the greatest cause of increased salinity in rivers is *irrigation*. Water is pumped out of rivers and onto farm land; the excess water percolates through the soil, dissolving significant amounts of salt from the soil, then returns to the river, and so the salinity of the river increases, and this happens to the water several times on its way from source to mouth. This problem becomes particularly severe when a large proportion of the water in the river, say 50 to 80%, is taken out for irrigation. And the problem is further aggravated if some farming areas draw irrigation water with relatively high TDS from underground aquifers and let the excess percolate into a river. All these problems are occurring along the Murray River with the result that salinity increases from about 100 ppm at Albury (well upstream) to 500 ppm near Morgan (from near where Adelaide draws its water) in good times and up to 1000 ppm during droughts.

Increasing salinity of farmland soils causes decreased crop yields and in fact can render farmland useless. Salinity results from rising water tables that bring salt from well underground into the root zone of crops. One cause of this is land clearing and deforestation, which replaces trees that absorb large amounts of rainwater with grasses and crops that use much less water, and so more seeps into the underground aquifers and causes the water table to rise. This is called *dry land salinity* and occurs in the Western Australian wheat belt and parts of the Murray–Darling basin, and is likely to occur in recently cleared pastures in the north of Queensland.

Irrigation is the other major cause of soil salinity, called *irrigation salinity*. Because plants take up water but not the salts the irrigation water contains, irrigators apply more water than the plants need so that the excess water can carry all the salt out of the topsoil. This excess either flows back into the river, increasing its salinity (a problem for the river), or seeps into underground aquifers and causes the watertable to rise. This brings extra salt into the root zone of plants. Irrigation salinity causes decreases in crop yields and is a growing problem in many of the irrigation areas in the Murray–Darling basin.

## Solutions

To limit dry land salinity we need to restrict land clearing and to replant trees, particularly salt-tolerant ones, in affected areas. To control irrigation salinity we need to reduce the volume of water taken from rivers for irrigation (so more is left to flush out the rivers), manage irrigation more carefully and divert salty run-offs into evaporation pans instead of letting them return to the river. Unfortunately these solutions are much more difficult to put into practice than they sound!

Because of the seriousness of salinity to Australia's agriculture, careful monitoring of total dissolved solids, particularly salts by conductivity, is essential.



#### WEBSITE

For further information on salinity:

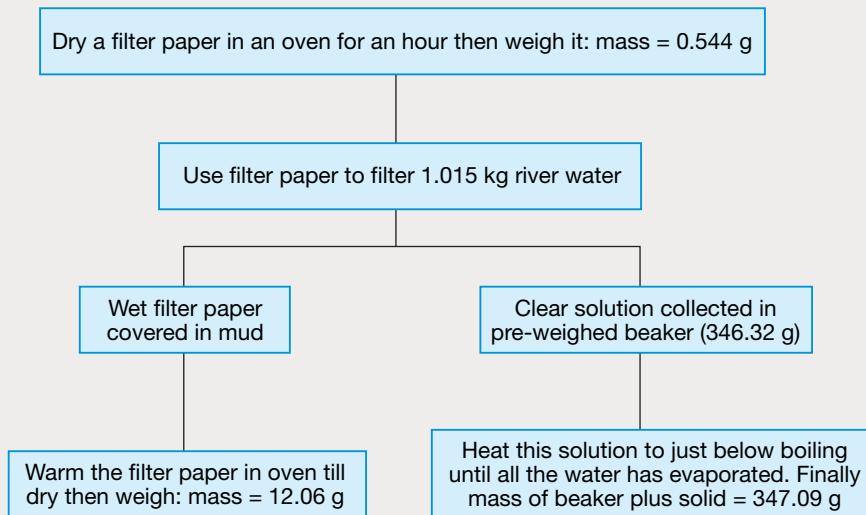
<http://www.acfonline.org.au>

(select *Salinity* in the Topics list on the left, select *Facts and figures* on the right, then click on the various fact sheets)



### Exercises

- 1 Concentrations in mg/L are approximately the same as ppm. Why are they not identical?
- 2
  - a A sample of water contained 5.0 ppm magnesium and 2.0 ppm lead ions. Express these concentrations in moles of ions per litre.
  - b Another sample of water contained  $1.05 \times 10^{-4}$  mol/L sulfate and  $3.1 \times 10^{-4}$  mol/L dissolved oxygen. Express these concentrations in ppm.
- 3 An environmental chemist did the analysis shown below on a sample of muddy river water.



Calculate the percentages of suspended solids and of dissolved solids in the sample of river water.

## 8.6 DISSOLVED OXYGEN AND BIOCHEMICAL OXYGEN DEMAND (BOD)

We saw previously (Table 7.3) that oxygen has a very low solubility in water (9 ppm at 20°C). However the small amount that does dissolve is of vital importance to fish and other aquatic life forms. Fish extract the oxygen they need by passing water through their gills. If the water is depleted in dissolved oxygen, fish die. Only a few marine species such as whales, dolphins and turtles obtain their oxygen by breathing air.

In an aquatic system, animal life (zooplankton, fish, crustaceans, worms) uses up dissolved oxygen while other life forms such as rooted plants (on shorelines or in shallows) and phytoplankton (microscopic floating plants) form it during photosynthesis. In addition surface water absorbs oxygen directly from the air. Hence there is a steady state concentration of oxygen of about 10 ppm.

One measure of the quality of water bodies is the concentration of dissolved oxygen. If this falls below about 5 ppm, many aquatic species will die or fail to reproduce with the result that the water body will develop unpleasant smells, experience increases in populations of undesirable species, develop an unsightly appearance and become unfit for human consumption.

## Causes of low levels of dissolved oxygen

The main cause of decreased concentrations of dissolved oxygen in natural water is the discharge into it of untreated or poorly treated sewage and other organic wastes. ‘Other organic wastes’ include wastes from food-processing plants such as meat works and fruit preserving factories, and from poultry farms and cattle feedlots (places where high numbers of cattle are hand fed on small areas of land; open grazing is not a problem).

These organic wastes are decomposed in the water by *aerobic bacteria*, which convert them into carbon dioxide, water, nitrate, sulfate and phosphate. Aerobic bacteria are ones that use oxygen to digest their food (that is, to decompose organic matter). *Anaerobic bacteria* live without needing oxygen: they convert organic matter into methane, ammonia and amines and hydrogen sulfide and make the water very unpleasant (from a human viewpoint).

We say that these organic wastes have a high oxygen demand or, more technically, a high *biochemical oxygen demand*.

The **biochemical oxygen demand** or **BOD** of a water body is a measure of the concentration of dissolved oxygen that is needed for the complete breakdown of the organic matter in the water by aerobic bacteria.

If a water sample has a BOD of 4 ppm, that means that the decomposition of the organic matter in the sample would reduce the dissolved oxygen



The sewage treatment works at Rouse Hill, north-west of Sydney. One of the main functions of sewage treatment is to reduce biochemical oxygen demand. This is being done in the three large cylindrical tanks

concentration from 10 to 6 ppm—not too serious a problem. However if a sample had a BOD of 100 ppm (quite typical of raw sewage), that would mean that 1 L of this water would use up all the oxygen from 10 L of clean water, which would leave the water seriously degraded. BOD is important in deciding how much dilution of effluent from sewage works is needed so as not to lower the dissolved oxygen level of the receiving water body to harmful levels.

Typical BOD levels are:

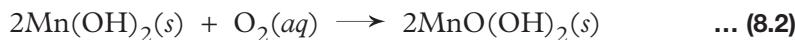
- unpolluted natural waterways, < 5 ppm
- reasonably well treated sewage, 20 to 30 ppm
- raw sewage, 150 to 300 ppm
- stormwater run-off from urban areas, 100 to 500 ppm.

## Measuring dissolved oxygen

Two methods are commonly used—one involves a chemical titration that can be done in a school laboratory while the other uses a special electrochemical sensor (using electrolysis).

### Titration method

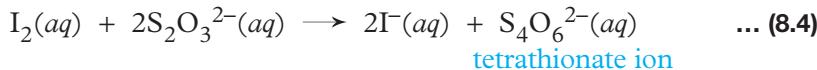
Dissolved oxygen oxidises  $Mn^{2+}$  to Mn(IV) in alkaline solution:



If this mixture is then acidified with iodide in the solution, the Mn(IV) oxidises iodide to iodine:



Iodine can then be titrated with sodium thiosulfate solution,  $Na_2S_2O_3$ , using starch as indicator (starch forms an intensely blue colour with iodine which disappears at the equivalence point):

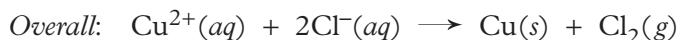
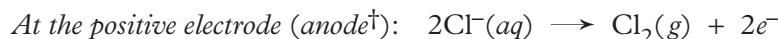
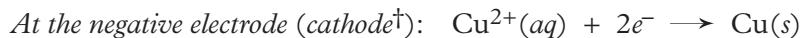


To perform the test, sample bottles of known volume, typically 250 mL, are completely filled (all air excluded) at the test site. Back at the laboratory sufficient water is removed to allow addition of small aliquots (2 to 5 mL) of a manganese sulfate solution and a solution containing both iodide and hydroxide. The bottle is firmly stoppered and agitated then allowed to stand for several minutes to let Reaction 8.2 go to completion. A few mL of concentrated sulfuric acid is then added: this redissolves the solids and causes the  $MnO(OH)_2$  to oxidise the iodide (Equation 8.3). The iodine is then titrated with a 0.01 to 0.03 mol/L standard solution of sodium thiosulfate (Reaction 8.4).

### Electrolysis method (oxygen sensor)

**Electrolysis** is a process in which a chemical reaction that does not occur naturally is brought about by passing an electric current through a molten mixture or through an aqueous solution.

We saw on p. 71 CCPC that electrolysis could be used to break molten lead bromide into liquid lead and gaseous bromine. Similarly an aqueous solution of copper chloride can be electrolysed to produce solid copper and gaseous chlorine:



If there is no cation that can easily be reduced (as in electrolysing a solution of potassium chloride), then the reaction that occurs at the cathode is often:



The *electrolytic oxygen sensor* uses the fact that, at constant voltage and with constant electrode surface area and constant separation between electrodes, the rate of electrolysis of a substance is proportional to its concentration. A diagram of the sensor is shown in Figure 8.3.

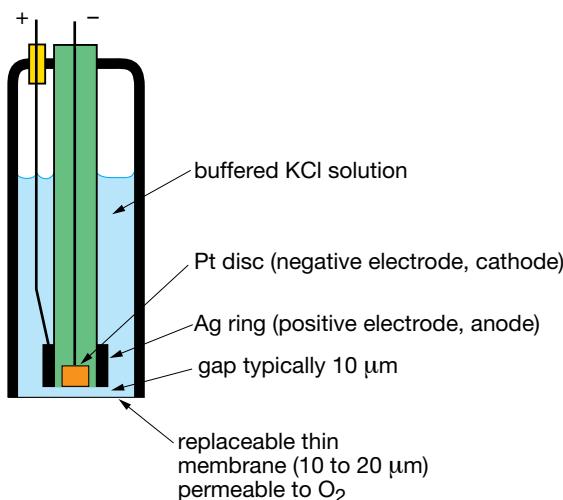


FIGURE 8.3  
An electrolytic sensor for measuring dissolved oxygen

A platinum disc cathode (negative electrode) is embedded in the end of an insulating rod. A silver ring as anode (positive electrode) is attached to the outside. A thin layer of a buffered KCl solution separates this from a polymer membrane that is permeable to oxygen gas. Oxygen diffuses from the test solution through the membrane, through the liquid film and to the cathode where it is electrolysed (reduced)—Equation 8.5 above.

The reaction at the anode (positive electrode) is:



This electrolysis causes a current to flow; this current is measured and converted to an oxygen concentration. The solution in the sensor in the absence of oxygen contains nothing that can be electrolysed at the voltage used and so current only flows when oxygen diffuses into it.

This device is simple and convenient to use and is battery operated. The membrane is easily replaceable if it becomes contaminated or clogged, so the device is widely used in environmental monitoring.

## Measuring biochemical oxygen demand (BOD)

The method used for measuring biochemical oxygen demand depends on the nature of the water to be tested. For municipal water supplies where BOD is

† Remember from Section 2.7 the definition of anode (where oxidation occurs) and cathode (where reduction occurs). This means that the anode, which was the negative electrode in a galvanic cell, becomes the positive one in electrolysis.

expected to be low (because of protection of the catchment from contaminated run-offs), it is measured by adding nutrient to the sample and incubating it at 20°C in a sealed air-free container in the dark for 5 days then measuring the residual dissolved oxygen. The difference between the dissolved oxygen readings before and after incubation is the BOD.

Samples with high BOD such as untreated or partially treated sewage would quickly use up all the dissolved oxygen, so they are analysed by adding oxygen to keep the sample saturated and measuring the amount of oxygen used. For these samples a suitable micro-organism as well as nutrient is added before incubation.

## **Exercises**

- 4 \*a** Use the data below to draw a graph of dissolved oxygen concentration versus temperature. Include zero on the temperature scale. Draw a smooth curve through your points.

Temperature (°C)	5.0	10.0	15.0	20.0	25.0	30.0
Dissolved oxygen concentration (mg/L)	12.6	11.1	9.9	9.0	8.2	7.5

- b** What is the dissolved oxygen concentration at **i** 22°C **ii** 7.0°C **iii** 1.0°C? Are any of your answers here less accurate than the others? Explain why or why not.

**c** At what temperature is the oxygen concentration **i** 13.5 mg/L **ii** 7.8 mg/L?

**d** Express your answer to (b)(i) in moles per litre.

**5** What is often more important than actual oxygen concentration in assessing water quality is percentage saturation. Percentage saturation is the actual concentration of dissolved oxygen expressed as a percentage of the solubility of oxygen at the prevailing temperature. Using your graph from Exercise 4, calculate the percentage saturation in water samples in which the concentrations of dissolved oxygen and temperatures are as follows:

**a** 7.2 ppm at 25.0°C                           **c** 5.4 ppm at 22.0°C  
**b** 7.2 ppm at 8.0°C                           **d** 8.8 ppm at 13.0°C

**6** **a** The treated waste from a food-processing plant had a BOD of 45 ppm. If this waste was added to a river (with a normal dissolved oxygen level of 9.0 ppm) in such a way that it was diluted by a factor of 20, what would be the concentration of dissolved oxygen a sufficient distance downstream of the discharge point for all the waste to have been decomposed (say about 3 km)? What would be the effect of this discharge on the river? What would you expect the state of the river to be a few kilometres further downstream?

**b** If the untreated waste (with a BOD of 220 ppm) had been discharged into this river with the same factor of 20 dilution, what would the dissolved oxygen level have been 3 km downstream from the discharge point? Explain. What effect would this have had on the river?

**c** Contrast the state of the river a few kilometres further downstream in the two scenarios in (a) and (b).

**7** **a** In planning its sewage treatment plant a town decided that it would be able to discharge its treated waste into a river with a 50 to 1 dilution ratio. If it did not wish to lower the dissolved oxygen concentration by more than 2.5 ppm, to what level must it reduce the BOD in its treated waste?

**b** Another town was able to discharge its treated sewage into the ocean and achieve a dilution of over 200 to 1. To what level does it need to reduce the BOD

of its sewage in order not to lower the dissolved oxygen concentration by more than 2.5 ppm?

- 8 A sample of water from a river was collected in a bottle known to contain 312 mL when completely filled and tightly stoppered. There were no air bubbles in the sample. Back in the laboratory 10.0 mL was removed by pipette, and 5 mL (by cylinder) of manganese(II) sulfate solution and enough of an alkaline potassium iodide solution to completely fill the bottle again were added. The bottle was tightly stoppered and inverted several times then left to stand for five minutes for reaction to go to completion and for the precipitate to settle to some extent. 5 mL of clear solution was removed and replaced by 5 mL concentrated sulfuric acid. After replacing the stopper the mixture was agitated until all the precipitate had dissolved and the solution had taken on a pale brown colour (of iodine). The mixture was transferred to a 500 mL conical flask and titrated with 0.0224 mol/L sodium thiosulfate solution using starch as indicator; 13.1 mL was required.

The reactions involved are Reactions 8.2, 8.3 and 8.4. Calculate the number of moles of iodine that were in the final solution, hence the number of moles of oxygen in the starting solution. Finally calculate the concentration of oxygen in the original sample in ppm.

- 9 A second sample of the same water as in Exercise 8 was collected in a 321 mL airtight bottle and stored in the dark at 20°C for 5 days. Then it was analysed for oxygen content as in Exercise 8. In the final titration 3.4 mL thiosulfate solution was needed. Calculate the BOD of the original water. Would you regard the original water as slightly, moderately or severely polluted or not polluted at all? Explain your answer and suggest possible sources of the pollution, if any.

## 8.7 MICROORGANISMS

Natural water can contain a wide range of microorganisms. Most are harmless but some can be extremely dangerous such as the pathogens that spread typhoid, cholera and dysentery. The elimination of such disease-causing agents from public water supplies has been the greatest contributor to public health in the last 200 years.

Because there are so many possible microorganisms that can be present in water, it is not possible to monitor all of them. Consequently scientists routinely monitor for an indicator organism that can signal the possible presence of pathogens. The chosen organism is *Escherichia coli*, commonly abbreviated to *E. coli*. This bacterium is generally quite harmless to humans and other animals, but is present in the intestinal tract (and so in faeces) of all animals. If it is found in water, it is a signal that the water is contaminated with sewage or animal wastes. People can be warned not to use the water while a search is made for the source of the contamination. Tests can also then be made for other organisms that are considered a particular threat to the locality.

To test for *E. coli* a sample is placed on a suitable nutrient bed and incubated for 12 to 24 hours, during which time the individual bacteria grow into colonies that are large enough to count by eye. Results are reported as *colony forming units* per 100 mL of water, CFU/100 mL. If there is more than 1 CFU/100 mL, the water is not suitable for drinking; if more than 200 CFU/100 mL, the water is unsafe for swimming.

An example will illustrate how the various tests described so far can be used to obtain information about the origin of water samples or about the pollution in them.



## Example

Some measurements on several water samples are shown in the following table.

Sample	L	M	N	P	Q	R	S
pH	6.5	6.9	7.8	6.6	9.2	3.4	7.6
DO <sup>a</sup> (ppm)	5.7	8.9	5.7	8.7	6.0	7.6	2.2
TDS <sup>a</sup> (ppm)	400	350	850	50	200	600	250
turbidity (NTU <sup>a</sup> )	90	50	15	4	30	60	65
<i>E. coli</i> (CFU <sup>a</sup> /100 mL)	35	0	0	0	15	0	150

*a DO = dissolved oxygen; TDS = total dissolved solids; NTU = nephelometric turbidity units; CFU = colony forming units*

Which of these samples would you consider to be from:

- a** a clean mountain stream
- b** a stream after it had flowed through an area that had recently been cleared of forest
- c** a stream that had flowed through a mixed farming area (cattle and grain crops)
- d** a stream polluted from run-off from a sulfide mine site
- e** an underground bore
- f** down stream from a raw sewage outlet?

To answer this question we need to be aware of the characteristics of each of the types of waterway listed.

- a** A clean mountain stream will be virtually unpolluted; its values for the various properties listed will be similar to those shown for clean water in Table 8.1. **Sample P** is the only one that meets these requirements.
- b** A stream running through a recently cleared forest area will have high turbidity (large amount of suspended solids) and high TDS, but its other properties will be close to those of clean water. **Sample M** is this stream, because its TDS and turbidity are high while pH, DO and *E. coli* are close to clean water values.
- c** A stream flowing through an area in which cattle graze will be contaminated with faecal coliforms (*E. coli*) and will probably have somewhat depleted DO, because of oxygen demanding wastes being washed into the stream. If crops are grown also, then we would expect high turbidity (erosion of suspended solids) and high TDS (again from run-off across ploughed ground). Samples L and S seem to meet these requirements (high *E. coli*, turbidity and TDS and low DO); however the DO in S is probably too low for just run-off from cattle droppings—it is more consistent with a genuine sewage discharge—so **Sample L** is the stream that flows through farm land. Q would be a candidate except that its pH is too high.
- d** Mine sites often suffer from acid drainage (conversion of sulfide on exposure to air and moisture to sulfuric acid) so we are looking for a stream with low pH. It may well have high TDS and turbidity (because of all the broken ground) but pH is the key. **Sample R** fits this profile.
- e** An underground bore will produce water with a high TDS and probably a somewhat low DO. pH may be a little higher than clean surface water, but other properties will be close to ‘clean’ values. **Sample N** meets these requirements; L, R and S also have high TDS but L and S have high *E. coli* which rules them out, and R has too low a pH.
- f** Discharge of raw sewage into a stream markedly lowers DO and increases *E. coli* counts; it also increases turbidity and TDS. These characteristics point us to S and L. However in L the DO is not excessively low and the *E. coli* not excessively high, so **Sample S** is the sewage-contaminated stream (particularly as we have the farmland option for L).

Sample Q does not fit any of the suggested categories. We can say that it is polluted, particularly with some alkaline waste and some microorganisms and has a low DO, suggestive of organic wastes also, but we cannot be more specific.

### Exercise

10 Some measurements on various water samples are shown in the following table.

Sample	A	B	C	D	E	F
TDS <sup>a</sup> mg/L	>10 <sup>4</sup>	900	80	150	>10 <sup>4</sup>	200
DO <sup>a</sup> (mg/L)	4.6	7.2	8.5	9.2	8.7	5.7
BOD <sup>a</sup> (mg/L)	60	1.6	4.2	2.5	1.8	75
coliforms (CFU <sup>a</sup> /100 mL)	500	0	30	3	0	250

a TDS = total dissolved solids; DO = dissolved oxygen; BOD = biochemical oxygen demand; CFU = colony forming units

Which of these samples would you consider to be

- a i sea water ii bore water iii fresh surface water
- b polluted with sewage
- c likely to be contaminated with parasites from animals
- d relatively unpoluted?

Give your reasons in each case.

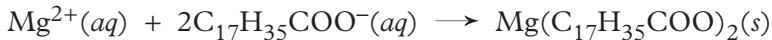
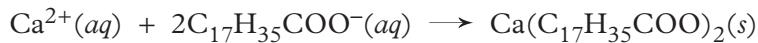


## 8.8 WATER HARDNESS

Hard water was defined in Section 8.1. Water is hard because of the presence of significant concentrations of calcium and magnesium ions. Water with very low concentrations of these ions is called *soft water*.

Soap is sodium stearate, C<sub>17</sub>H<sub>35</sub>COONa. It is a salt of the carboxylic acid, stearic acid (Section 5.16). We use soap because it makes water ‘wetter’. Technically it lowers the surface tension so that the water can stick to oily particles, and remove them from our skin or clothes.

The calcium and magnesium salts of stearic acid are insoluble in water. This means that if our tap water contains these cations, then a precipitate of calcium and magnesium stearates will form when soap is added to this water:



The formulae of the precipitates could equally well be written as (C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub>Ca or (C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub>Mg.

These precipitates appear as a grey scum on the surface of the water and often stick to the enamel of baths and handbasins. The formation of this scum removes soap from solution and hence spoils its cleaning power. The scum can often settle on fabrics being washed and discolour them, as it does not rinse away easily.

Sydney and Melbourne have relatively soft water. Brisbane water is moderately hard, while Adelaide’s water is very hard. Water from underground bores or from the downstream end of a very long river tends to be hard. This

is because it has been in contact with earthy materials for long periods and has been able to dissolve out calcium and magnesium salts. Rainwater is very soft.

An old solution to the problem of hard water was to fit a water softener to the household water supply. This is an ion exchanger which replaces calcium and magnesium ions with sodium ions. A disadvantage is that it needs to be regenerated regularly.

Another solution is to use synthetic detergents instead of soap. These do not form precipitates with calcium and magnesium ions. Hence synthetic detergents are more effective than soap in hard water. However, even detergents work better (clothes rinse more effectively) if the water is softened (e.g. by adding washing soda,  $\text{Na}_2\text{CO}_3$ , to precipitate the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions).

# Measuring the hardness of water

Water hardness is measured by determining the total concentration of calcium and magnesium ions in the water and expressing the result as milligrams of  $\text{CaCO}_3$  per litre.

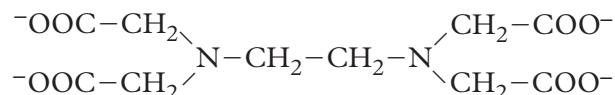
For example, for a sample of water containing  $1.0 \times 10^{-4}$  mol/L  $Mg^{2+}$  and  $2.5 \times 10^{-4}$  mol/L  $Ca^{2+}$ :

Total concentration of 'hardness' =  $(1.0 + 2.5) \times 10^{-4}$  mol/L  
 molar mass of  $\text{CaCO}_3$  = 100.1 g/mol

$$\text{So equivalent concentration of } \text{CaCO}_3 = 3.5 \times 10^{-4} \times 100.0 \text{ g/L} \\ = 3.5 \times 10^{-2} \text{ g/L} = 35 \text{ mg/L (or 35 ppm)}$$

Hardness of this water would be reported as 35 mg/L or 35 ppm.

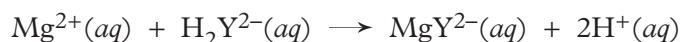
A volumetric titration is used for the analysis. It uses the fact that both calcium and magnesium ions in an ammonia, ammonium ion buffer (pH about 10) form a complex with the quadruply charged anion of ethylenediamine tetra-acetic acid, commonly called EDTA. The anion has the structure:



For simplicity in equations we often write EDTA as  $\text{H}_4\text{Y}$ . The titrant used is the disodium salt of EDTA,  $\text{Na}_2\text{H}_4\text{Y}$  (or  $(\text{Na}^+)_2(\text{H}_4\text{Y}^{2-})$ ). The reactions are:



and



The indicator used for this titration is another complexing agent Eriochrome Black T. In solution it has a blue colour but forms a reddish complex with  $Mg^{2+}$ . The equivalence point is when the solution changes from purple to blue (loses the last tinge of red). If a 0.0100 mol/L solution of  $Na_2H_2Y$  is used, then each mL of titrant corresponds to  $1.00 \times 10^{-5}$  mol of metal ion or to 1.00 mg of  $CaCO_3$  (molar mass 100 g/mol).

In the Sydney region, water from Warragamba Dam has a hardness of about 40 mg/L while that from dams closer to the source of the Nepean River (such as the Woronora and Cordeaux Dams) is only about 20 mg/L.

## Qualitative test for hardness

By trial and error it is determined how many drops of a soap solution need to be added to 5 mL distilled water in a test tube in order to produce a good lather (lots of bubbles or froth) when the mixture is shaken. This number of drops of soap solution is then added to 5 mL of the water to be tested and the mixture shaken. By comparing the amount of lather produced from the sample and the distilled water, it is decided whether the water is very hard (very little lather), moderately hard (significant amount of lather but well less than in the distilled water) or soft (similar amount of lather in the test sample as in the distilled water).

This test can be used to compare qualitatively the hardness of different samples of water but it cannot put a value to the hardness.

### Exercises

- 11 a When the quadruply charged anion of EDTA complexes with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , it forms six coordinate covalent bonds with the metal ion. Identify the six atoms which each contribute an electron pair for this.  
b EDTA titrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions are performed at a pH of about 10, because the complexing does not occur quantitatively at significantly lower pHs. Suggest a reason for this.
- 12 a Water from a particular source was quoted as having a hardness of 54 mg/L. Express this in total moles of calcium and magnesium ions per litre.  
b What is the hardness of water in which the calcium and magnesium ions have concentrations of  $3.7 \times 10^{-4}$  and  $0.9 \times 10^{-4}$  mol/L respectively?
- 13 When a 250 mL water sample was titrated with 0.0113 mol/L EDTA solution as described in Section 8.8, 18.4 mL was required. Calculate the hardness of the water (expressed in mg/L calcium carbonate). Why is it not necessary to determine  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  separately in order to calculate hardness?



## 8.9 TESTS FOR COMMON ANIONS

Anions that are generally present in fresh water are chloride and sulfate and to a lesser extent carbonate. Their presence can be detected by using the tests of Table 6.3. However because of the low concentrations likely to be present in unpolluted fresh water some modification may be needed.

### Carbonate

First check the pH of the water: carbonate is unlikely to be present in significant amounts if the pH is less than 6.5. Then heat the sample to about 80°C and carefully add drops of 0.1 mol/L hydrochloric acid: if colourless bubbles of gas form, carbonate is present. The high temperature is used to facilitate release of carbon dioxide which may remain in solution at low temperature. If there is evidence of significant amounts of carbonate, it may be estimated quantitatively by precipitating it as calcium carbonate from neutral or slightly alkaline solution (to ensure that hydrogen carbonate converts to carbonate and precipitates also).

## Chloride and sulfate

Chloride is detected qualitatively by adding a drop of silver nitrate solution. If chloride is present, the sample goes turbid (milky) because of the formation of insoluble silver chloride<sup>†</sup>.

Sulfate is detected by adding a drop of barium nitrate (or chloride) solution. If sulfate is present, the sample goes turbid because of the formation of insoluble barium sulfate. We can get a rough estimate of the concentration of chloride or sulfate in a sample by varying the amount of silver or barium ion added and seeing if turbidity is still produced as shown in Table 8.2

**TABLE 8.2 Semi-quantitative estimates of chloride and sulfate concentrations in water**

Amount of cation solution <sup>a</sup> added and volume of sample it is added to	If solution goes turbid, concentration (in mg/L) is	
	chloride	sulfate
1 drop $1.0 \times 10^{-2}$ mol/L to 10 mL	>0.2	>0.5
1 drop $1.0 \times 10^{-3}$ mol/L to 10 mL	>2	>5
1 drop $1.0 \times 10^{-3}$ mol/L to 100 mL	>20	>50
1 drop $1.0 \times 10^{-4}$ mol/L to 100 mL	>200	>500

a Ag<sup>+</sup> for chloride, Ba<sup>2+</sup> for sulfate.

## Phosphate

The best test for detecting the presence of phosphate at the low concentrations at which it is present in environmental water is the ammonium molybdate test, test 3 in Table 6.3. The water sample is acidified, then ammonium molybdate solution added and the mixture gently heated for a few minutes. The appearance of a yellow precipitate or just a yellow turbidity indicates the presence of phosphate.

Phosphate is generally the key nutrient involved in the formation of algal blooms (Section 8.12), so we often need to measure its concentration.

## Quantitative measurement of phosphate

Because of the low phosphate concentrations involved—often less than 1 ppm—a sensitive colorimetric method is used. A *colorimetric method* is one that relies on the quantitative measurement of the absorption of light by a coloured solution. Simple instruments for doing this are called *colorimeters*: they use filters to select the wavelength of light. More elaborate instruments are called *spectrophotometers*: they use monochromators to select the wavelength more precisely and so are generally more accurate.

To estimate phosphate quantitatively, a variation on the molybdate qualitative test is used. A measured quantity of a solution of ammonium molybdate with a catalyst is added to the sample followed by careful mixing. Then a measured quantity of solid ascorbic acid (Vitamin C) is added to this mixture. This

† Sulfate does not interfere with the chloride test here as it did in Sections 6.12 and 6.13, because in environmental water, sulfate concentrations never get high enough.

produces an intense blue colour (called molybdenum blue). By comparing the absorbance of this solution with that produced by a standard phosphate solution treated identically, we can calculate the concentration of phosphate. This method can be used for phosphate concentrations in the range 0.01 to 3 mg/L (ppm).

The yellow phosphomolybdate complex contains only Mo(VI). Ascorbic acid reduces some of this to Mo(V) and this causes the intense blue colour to develop.

## 8.10 CATIONS IN ENVIRONMENTAL WATER

In Sections 6.9 to 6.11 we looked at tests that could be used to identify six particular cations in solution:  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Table 8.3 lists some tests that can be used to identify some other cations that if present in water are of considerable concern to us.

**TABLE 8.3 Tests used to identify cations (additional to those in Table 6.1)<sup>a</sup>**

Cation	Tests
$\text{Hg}^{2+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a yellow or red precipitate of <math>\text{HgO}</math></li> <li>2 with KI forms a red precipitate, <math>\text{HgI}_2</math> which dissolves in excess KI</li> <li>3 acidify and add <math>\text{Na}_2\text{S}</math>: a black precipitate of <math>\text{HgS}</math> forms</li> </ol>
$\text{Cd}^{2+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a white precipitate of <math>\text{Cd}(\text{OH})_2</math> which does not dissolve in excess NaOH but it does dissolve in ammonia</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: a yellow precipitate of <math>\text{CdS}</math> forms</li> </ol>
$\text{Zn}^{2+}$	<ol style="list-style-type: none"> <li>1 with NaOH, forms a white precipitate of <math>\text{Zn}(\text{OH})_2</math> which dissolves in excess NaOH and also in ammonia (forming a colourless solution in both cases)</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: no precipitate forms. Make slightly alkaline and a white precipitate of <math>\text{ZnS}</math> forms</li> </ol>
$\text{Cr}^{3+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a grey-blue precipitate of <math>\text{Cr}(\text{OH})_3</math> which dissolves in excess NaOH (to form a green solution) but does not dissolve in ammonia</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: no precipitate forms. Make slightly alkaline and a grey-blue precipitate of <math>\text{Cr}(\text{OH})_3</math> forms<sup>b</sup></li> </ol>
$\text{Al}^{3+}$	<ol style="list-style-type: none"> <li>1 with NaOH forms a white precipitate of <math>\text{Al}(\text{OH})_3</math> which dissolves in excess NaOH (to form a colourless solution) but does not dissolve in ammonia</li> <li>2 acidify and add <math>\text{Na}_2\text{S}</math>: no precipitate forms. Make slightly alkaline and a white precipitate of <math>\text{Al}(\text{OH})_3</math> forms<sup>b</sup></li> </ol>

*a* None of these five cations forms a precipitate with chloride or sulfate.

*b* Chromium and aluminium sulfides in aqueous solution react with water (hydrolyse) to form hydroxides.

As was explained in Section 6.11, one cation can interfere with the test for another cation. In that section we overcame this problem by testing for the cations in a particular sequence and performing the tests on the filtrates left over from the previous tests (Figure 6.6). Similar schemes can be worked out for more comprehensive sets of cations but that is beyond the scope of this account. By carefully noting the results from several of the tests in Tables 6.2 and 8.3 you can probably work out just which cation(s) is(are) present in a given water sample.

## A simple test for heavy metals

In environmental contexts **heavy metals** are the transition metals plus lead, though in some contexts the semi-metal arsenic is also included.

The heavy metals that are of most concern, because of their detrimental health effects, are mercury, lead, cadmium, chromium, arsenic, and to a lesser extent, silver, zinc and copper.

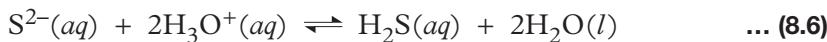
A solution of sodium sulfide can be used to get a quick indication of whether or not any heavy metals are present in a sample of water.

The water sample is acidified then drops of  $\text{Na}_2\text{S}$  solution are added: if a precipitate forms, then one or more of the following cations is present:  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^{3+}$ .

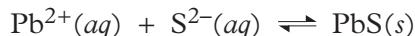
If no precipitate forms with acid present, the solution is made slightly alkaline. If this produces a precipitate, then one or more of the following cations is present:  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ . If a precipitate forms in acid solution, it should be centrifuged (or filtered) off and the remaining solution made alkaline to check whether any of this second group of cations is present.

### The chemistry involved

This heavy metal test is based on the facts that hydrogen sulfide is a very weak acid and that the two groups of cations have quite different solubilities in water (though all are insoluble). In acid solution the sulfide ion of sodium sulfide is almost completely converted to  $\text{H}_2\text{S}$ :



Only a minute concentration of  $\text{S}^{2-}$  is left in solution, but it is sufficient to precipitate extremely insoluble sulfides such as lead and copper; for example:



If a small amount of  $\text{PbS}$ , for example, can form, then that lowers the concentration of  $\text{S}^{2-}$  and this forces Reaction 8.6 to move to the left (Le Chatelier's principle) and so it keeps producing more  $\text{S}^{2-}$  until all the lead is precipitated.

The concentration of  $\text{S}^{2-}$  in acidified sulfide solution is too small to cause any precipitate with the cations that form *less insoluble* sulfides such as  $\text{Zn}^{2+}$  and  $\text{Fe}^{2+}$ , so reactions such as



do not get started so do not affect Equilibrium 8.6 and so no precipitate forms.

However in alkaline solution Reaction 8.6 does not move very far to the right at all, and so there is a high enough  $\text{S}^{2-}$  concentration for Reaction 8.7 to move to the right and go to virtual completion and so we get a precipitate of zinc sulfide (and similarly for the other cations of that group).

If an appreciable amount of precipitate forms in either the acidic or alkaline test, then the tests of Tables 6.2 and 8.3 can be used to identify which heavy metals are present.

## Measurement of concentrations of cations

While knowing qualitatively that particular cations are present in water may be of some value, generally we need to know the concentrations of these cations in order to decide whether they present a risk to human health or to the environment.

A wide variety of methods is used to measure such concentrations. Traditional methods such as gravimetric analysis and titrations have limited use because of the low concentrations involved in environmental water samples. Instrumental methods are more commonly used. In Sections 6.18 and 6.19 we saw that atomic absorption spectroscopy is widely used for environmental monitoring. Mention was also made of atomic emission spectroscopy (Section 6.17): this is also widely used for monitoring water quality. This has the advantage of being able to analyse for several metals in the one measurement. With atomic absorption, metals must be measured one at a time because each requires a separate lamp.

## 8.11 FACTORS AFFECTING CONCENTRATIONS OF IONS

The ions present in natural water bodies (such as rivers, dams and oceans) and their concentrations depend upon the following factors:

### ■ The pathway from rain to water body

*Rain* contains very few ions—just small concentrations of carbonate (from dissolved  $\text{CO}_2$ ) and some  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions from sea spray that winds carry into clouds. When rain runs off bushland into streams, it picks up small amounts of nitrates and phosphates from natural nutrients on the surface and perhaps small amounts of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from decomposing minerals. In such cases TDS is generally below 50 ppm.

If, however, rain water soaks into the ground and flows through *underground aquifers* and then into a stream, it will contain increased amounts of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  by dissolving them from the soils and rocks that it flows through. For such water TDS will commonly be in the range 100 to 300 ppm.

If water percolates down to *deep underground aquifers* as in artesian basins and then comes to the surface centuries later for storage and use, it contains much higher levels of the above-mentioned ions and may contain various other cations such as  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . TDS values of 1000 ppm and above are common, though the higher TDS becomes, the less suitable the water is for humans and cattle and sheep.

### ■ The pH of the rain

Water from acid rain ( $\text{pH} < 5$ ) is better able to leach certain cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  from the soil it passes over or through and so concentrations of these ions increase.

### ■ The nature and amount of human activity in the catchment

*Land clearing* generally leads to more water rapidly running across disturbed land and into streams. This increases sediment loads (and so increases turbidity) and facilitates the dissolution of a variety of ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ .

*Agricultural pursuits* (growing crops and improving pastures) often lead to fertiliser run-off. This increases the concentration of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  in the water.

#### ■ Effluents discharged into the water bodies

Discharges of *raw and/or treated sewage* into rivers or oceans increase the concentrations of many ions, particularly phosphate and nitrate, but also many common ions such as those in the previous paragraph. Even good sewage treatment that removes nearly all suspended matter, BOD and pathogens can increase the TDS of the water by 200 ppm or more, this being made up of a wide variety of common ions.

*Storm water run-off* in urban areas can similarly increase the concentration of a variety of ions in water bodies.

*Industrial effluents*, if not carefully monitored and controlled, can discharge heavy metal ions into water bodies, ions such as  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .

#### ■ Leaching from rubbish dumps

When rain and storm water flow over and seep through poorly designed rubbish tips, they dissolve many harmful substances and carry them into waterways: the term for this is **leaching**. Dangerous cations such as cadmium from nickel–cadmium rechargeable batteries, mercury and lead from other batteries, zinc from old galvanised iron and anions such as nitrate and phosphate from decaying organic wastes are carried into streams.

## Oceans as well as rivers and dams

Because of their smaller volumes, rivers and dams are more vulnerable than oceans to increases in ion concentrations. Nevertheless discharge of poorly treated sewage from big cities (such as Sydney) and large run-offs from flooded rivers that flow through agricultural land can affect the ion concentrations in coastal ocean water quite significantly. The Great Barrier Reef off the north Queensland coast is being detrimentally affected by sediments, nutrients and possibly heavy metals that are being carried into the surrounding waters by coastal rivers flowing through agricultural and urban areas.

## Exercises

- 14 A group of students used the method described in Section 8.9 to determine the phosphate concentration in some environmental samples. First they calibrated their colorimeter by making up solutions of sodium phosphate of known concentration and ‘analysing’ them according to the above procedure and measuring the absorbance with the colorimeter. Results are shown below. Construct a calibration curve for this instrument of absorbance *versus* concentration of phosphate.

Concentration of phosphate (ppm)	0.030	0.060	0.100	0.150
Absorbance	0.07	0.16	0.25	0.41

Four environmental water samples were then put through the same test procedure. They gave the following absorbances:

Sample	A	B	C	D
Absorbance	0.14	0.36	0.48	0.025

Calculate the concentration of phosphate in each of these samples. Does the fact that two of these absorbances are outside the range of the calibration values make the results less accurate? Explain.

- 15** When 1 drop of 0.0010 mol/L silver nitrate solution was added to 10 mL of a sample of water and the mixture shaken, it went turbid. When the test was repeated with 100 mL of the same water, the mixture remained clear. When 1 drop of 0.010 mol/L barium nitrate solution was added to 10 mL of this water and the mixture shaken, the mixture went turbid. When the test was repeated using 0.0010 mol/L barium nitrate solution the mixture remained clear. With the aid of Table 8.2, what can you deduce about the concentrations of chloride and sulfate in this water?
- 16** Describe the tests you would perform (along with the results you would expect) to decide whether:
- a** a sample of fresh water was contaminated with sewage that also contained heavy metals
  - b** a creek was contaminated by acid drainage from a nearby coal mine (sulfides exposed to the air under certain conditions produce sulfuric acid)
  - c** the water in a stream just downstream of a partially-treated sewage discharge was a threat to the aquatic life of the stream
  - \*d** the sea water near a coastal chlor-alkali plant (which uses a lot of mercury) was contaminated with mercury
  - \*e** a river was contaminated with copper ions escaping from a nearby copper mine.

Explain why you used the particular test or tests that you chose.

- 17** A bore on a coastal farm draws water from a fresh water underground aquifer. It was suspected that sea water was encroaching into the aquifer. What test(s) would you perform to decide whether this was so?
- 18** What tests would you perform to decide whether the water in a river several kilometres downstream from the point at which treated sewage was discharged into the river was safe for human use? Explain why you would use the chosen tests.
- 19** When 1 drop of  $1.0 \times 10^{-3}$  mol/L silver nitrate solution was added to a 100 mL sample of water, it produced turbidity. What does this tell you about the chloride ion concentration in that water? How could you modify the test so that you could use the information in Table 8.2 to obtain a better estimate of the chloride ion concentration in the water?
- 20** **a** A river was contaminated with a heavy metal. How would you determine whether the contamination was chromium from a leather factory on one bank of the river or lead from a car battery manufacturer on the other bank?  
**b** A cadmium electroplating factory was accused of polluting a nearby creek with cadmium ions. The factory claimed that the heavy metal detected was zinc (leached out of the galvanising on the roofs of houses in the surrounding areas). Describe tests you would perform to decide whether the contaminant was zinc or cadmium ions.  
**\*c** How would you decide whether the heavy metal contaminant in a water sample was lead, silver or barium ion? Explain carefully how your test results prove the presence of one ion and the absence of the other two.

- \*21** Five major sources of water pollution are (1) sewage (treated and untreated) (2) urban storm water run-off (3) industrial effluents (4) agricultural run-off (crop growing, including irrigation, and grazing) (5) erosion from clearing forests and bushland.

Draw up a table that shows which water quality criteria (of those in Section 8.1) are affected, and in what ways, by each of these forms of pollution.

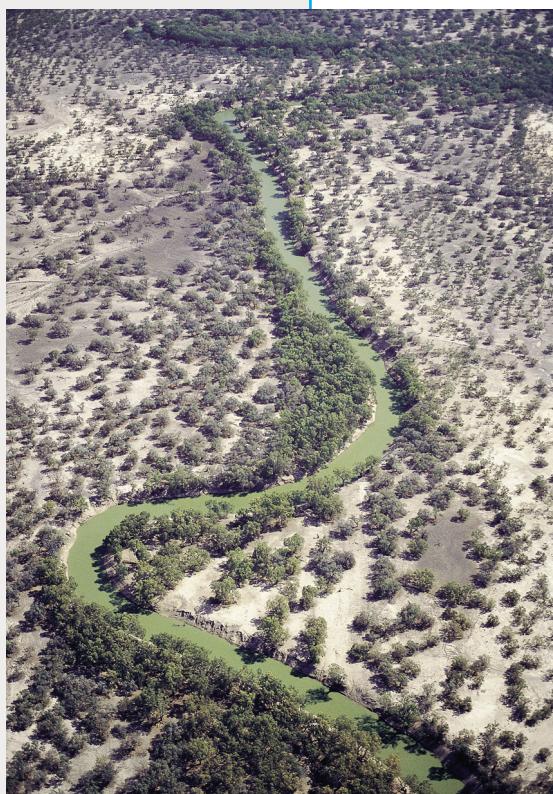
## 8.12 ALGAL BLOOMS AND EUTROPHICATION

So-called algal blooms, defined in Section 8.1, have presented a serious problem for many Australian rivers and dams in recent years. In the summer of 1991–2 an algal bloom made the water in a 1000 kilometre length of the Darling River unusable for people and livestock for many weeks.

Algal blooms lead to such deterioration of water quality that it becomes unsuitable for its normal uses. For rivers and lakes such blooms can also lead to permanent degradation.

Algal blooms occur when nutrients are readily available in the water and when environmental conditions are favourable (warm temperatures, plenty of sunlight and not much water movement). The two nutrients which are normally in shortest supply to plants and which generally limit plant growth are nitrate and phosphate. Of the two, it is generally phosphate which is present in least amount and which therefore has the greatest control on growth rate.

If there is an abundant supply of phosphate in the water, then algae grow and multiply rapidly. Generally it appears as a greenish scum floating on the water surface. A great variety of aquatic species can be involved. Many species of green algae are commonly present; these are the green scum. Green algae, while a nuisance, are not toxic. However other species that are frequently present in algal blooms in fresh water are so-called *blue-green algae*. Actually these are not algae at all! They are types of bacteria called *cyanobacteria*. The cyano part of the name comes from the name of a particular colour, cyan, which is blue-green.



The algal bloom that occurred along the Darling River in the summer of 1991–2 extended for over 1000 km

### Detrimental effects

The detrimental effects of algal blooms are these:

- Cyanobacteria, if present, produce certain poisons that can kill livestock and cause serious illness in humans.
- The water becomes unsuitable for its normal uses because the high concentrations of non-poisonous algae are difficult to filter out, give the water an unpleasant taste and clog pumps used for moving water to irrigation land and animal drinking troughs.
- During the night algae consume dissolved oxygen from the water. This causes fish to suffocate and die, and in so doing make the river or dam very unpleasant (though during daylight hours algae, being plants, generate oxygen through photosynthesis).
- They lead to a build-up of sediments in the river or dam.

Sediments build up because eventually the uncontrolled growth of algae uses up all of one nutrient, so that there is insufficient to support its continued life; hence the algae die and decompose and in so doing use up any remaining dissolved oxygen. They then decay anaerobically (without oxygen); this creates a putrid mess which results in the death of any remaining life forms in the water.

This decay of the organisms produces much sediment which builds up on the floor of the river or dam.

Occasional algal blooms in a river or dam are reversible; the next flood or heavy rain flushes out the river or dam and it recovers. If algal blooms occur too frequently, then the river or dam does not fully recover after the next flood; sediments build up (which facilitates future algal blooms and the growth of rooted aquatic plants) and so the process of degradation continues and becomes very difficult to reverse.

A term often used in this context is *eutrophication*.

## Eutrophication

**Eutrophication** is the process in which a water body becomes enriched with nutrients such as phosphate and nitrate to such an extent that algal blooms become highly likely.

This enrichment of water bodies with nutrients followed by algal blooms is part of the natural process by which a clear stream or lake containing minimal amounts of living matter is converted into a swamp or marsh containing abundant life forms and eventually to meadow (dry land). In nature this is a slow process, taking tens of thousands of years. However human activity frequently accelerates the transition from a clear water body to a weed- and sediment-infested one by discharging nutrient-rich effluents into rivers and dams: such enrichment of nutrients as a result of human activity is called *cultural eutrophication*.

## Sources of nutrients

There are two main sources of nutrients in our waterways, sewage and farm fertilisers.

### Sewage

The organic matter in raw sewage contains significant amounts of phosphorus and nitrogen. The decomposition of organic matter whether in ‘normal’ sewage treatment works or in a waterway converts phosphorus to phosphate and some of the nitrogen to nitrate. In this way sewage increases the nutrient load of the water body. Tertiary sewage treatment removes much of the phosphate, but such treatment is rare in Australia (except for Canberra and a few other inland places).

Laundry washing powders often contain phosphates: they stop dirt re-settling onto the clothes and help maintain an optimum pH (act as a buffer). Since wash water generally ends up in the sewers, such washing powders contribute significantly to the phosphate load of the effluent from sewage treatment plants.

### Fertiliser

Fertiliser run-off is the most direct way that farming contributes to algal blooms. The main components of fertilisers are phosphate and fixed nitrogen, meaning nitrate and ammonia (in a variety of forms).

If too much fertiliser is used, the excess is washed away either by irrigation water or by rain and eventually drains into the nearest waterway and so into the overall river system.

## Monitoring for eutrophication

Because of the detrimental effects of the algal blooms that generally follow eutrophication, we need to monitor vulnerable water bodies on a regular basis. This means monitoring concentrations of the key nutrients, nitrate and phosphate. A colorimetric method for estimating phosphate was described in Section 8.9. There is also a colorimetric method available for estimating nitrate. Because in most Australian waterways phosphate is the growth-limiting nutrient, it is the best one to monitor to check for eutrophication.

An algal bloom is likely:

- in a dam or lake, if phosphate concentration > 0.05 ppm
- in a river or stream, if phosphate concentration > 0.1 ppm (a higher value because the water is more likely to be flowing). In other words, we say that a water body has become *eutrophic* if phosphate concentration > 0.05 ppm (dam or lake) or > 0.1 ppm (river).

### Exercises

\*22 Some test results on water samples taken from seven different streams are listed below.

Sample	A	B	C	D	E	F	G
turbidity <sup>a</sup> (NTU)	60	30	0.2	14	7	1	10
TDS <sup>a</sup> (mg/L)	620	200	45	450	120	150	180
pH	6.8	8.4	6.5	7.2	6.0	7.2	4.7
DO <sup>a</sup> (mg/L)	8.1	9.1	8.7	7.8	3.1	9.0	8.3
phosphate (ppm)	0.06	0.25	0.02	0.5	0.07	0.01	0.04

a NTU = nephelometric turbidity units: less than 1 is very clear water, 30 is quite turbid; TDS = total dissolved solids; DO = dissolved oxygen.

- a Which stream(s) would you consider to be relatively free of pollution?
- b Which sample(s) was(were) taken well downstream from the point where treated sewage was discharged into the stream?
- c Which stream if any has serious soil erosion upstream of the sampling point?
- d Which stream if any has suffered damage from acid drainage from a mine site?
- e Which stream(s) is(are) susceptible to an algal bloom?
- f Which stream is likely to contain very little aquatic life at the sampling point?

Give your reasons for each of your choices.

- \*23 a How would you decide that (i) a sluggish stream (ii) a storage dam was on the verge of producing an algal bloom? Why are the criteria slightly different in the two cases?
- b At sewage treatment plants that discharge their effluents into inland streams, phosphate is much more commonly removed (by precipitation with  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  or  $\text{Ca}^{2+}$ ) than is nitrate. Give two reasons for this being so.
- 24 Use the results in the table below to determine what, if any, types of pollution are affecting the streams from which the samples were taken. Indicate which, if any, stream you would expect to be vulnerable to an algal bloom. Give reasons for your decisions.

Sample	A	B	C	D	*E	*F	*G
turbidity (NTU <sup>a</sup> )	35	80	12	8	4	25	45
pH	8.2	6.6	9.7	7.1	6.5	7.2	3.7
DO <sup>a</sup> (mg/L)	3.1	7.2	8.5	8.2	8.7	8.3	6.5
BOD <sup>a</sup> (mg/L)	86	1.6	2.2	3	1.2	5	3
Na <sub>2</sub> S/H <sup>+</sup> test <sup>a</sup>	NR <sup>b</sup>	NR <sup>b</sup>	NR <sup>b</sup>	black ppt	NR <sup>b</sup>	NR <sup>b</sup>	black ppt
phosphate (mg/L)	0.35	0.04	0.03	0.02	0.01	0.23	0.02

a NTU = nephelometric turbidity unit; DO = dissolved oxygen; BOD = biochemical oxygen demand, Na<sub>2</sub>S/H<sup>+</sup> test is to add Na<sub>2</sub>S solution to an acidified sample of the water.

b NR = no reaction

#### WEBSITE

For a detailed survey of water pollution in NSW and steps being taken to alleviate it:

<http://www.epa.nsw.gov.au/soe/soe2003/Chapter5>

(this is the *State of the Environment Report* prepared by the NSW Environment Protection Authority; it treats nutrients, algal blooms and salinity (TDS) quite extensively)



## 8.13 WATER TREATMENT FOR DOMESTIC CONSUMPTION

The qualities that we expect of our drinking water were listed at the start of this chapter. To achieve these we need to protect the water catchment, and then to give the raw water an adequate treatment before piping it to homes and industries.

### Catchment

The geographic area from which all the streams and rainfall drain into a city's water storage dam is called its **catchment**. The first step in supplying good quality water is to protect the catchment. This means preserving the natural environment of the area as much as possible (no logging, land-clearing and minimal roads) and keeping out all human activity such as farming, grazing and mining. In that way the water that flows into the dam is relatively free of sediments and animal wastes (which often carry parasites or pathogens).

### Water treatment

In Australia water treatment generally means clarifying the water and sanitising it. 'Clarifying' means removing any turbidity or colour so that the water is sparklingly clear and colourless. 'Sanitising' means removing anything, particularly organisms, that would cause the water to be harmful to people.

Clarification is done by causing a precipitate to form in the water. Initially the precipitate forms as very small particles but as the water is gently stirred, these small particles stick together to form bigger ones in a process called **coagulation**. Sometimes the word **flocculation** is used for this process. Many of the other small particles that were originally present in the raw water adsorb onto the surface of these small precipitate particles and so get incorporated into the larger particles

that coagulation produces<sup>†</sup>. In this way the coagulated precipitate takes most of the suspended matter out of the water and is then filtered off, generally by passing the mixture through a coarse sand filter or sometimes through a mixture of sand and granulated anthracite (high quality coal). Anthracite with its high carbon content is able to adsorb much of the organic matter present in solution and this can remove odour and taste from the water.

This water treatment plant removes suspended particles by co-precipitation with an insoluble hydroxide followed by sand filtration before piping the water to domestic users

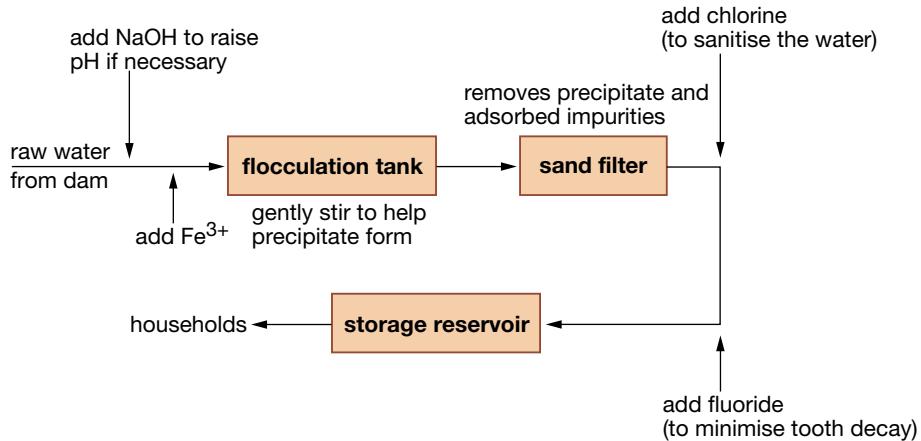


A precipitate that is widely used to clarify water is iron(III) hydroxide. This is formed first by adjusting (if necessary) the pH of the incoming water to above 7 (by adding lime or sodium hydroxide), then by adding a solution of an iron(III) compound such as iron(III) chloride. Iron(III) hydroxide is extremely insoluble and forms even at a pH as low as 7. Aluminium hydroxide is also widely used as the flocculating precipitate. Figure 8.4 is a flowchart for a typical water treatment plant.

After clarification the water is generally sanitised (sterilised) by having gaseous chlorine dissolved in it. Chlorine at a concentration of 1 or 2 ppm destroys bacteria and *some* viruses. Sufficient chlorine is added to the water (with careful monitoring) to ensure that the concentration stays slightly above 1 ppm until the water reaches the end user. If the starting water was reasonably clean and if the right amount of chlorine is used, there is no odour when it reaches the user.

Some water authorities add sodium fluoride (at a concentration of 1 ppm) to the water supply generally just downstream of the chlorination plant. Fluoride is added to strengthen tooth enamel in growing children: it is a form of enforced medication. It does not improve the safety of the water. The decision to add fluoride is made by each state or water authority.

<sup>†</sup> We previously met adsorption of impurities on to a precipitate in the sulfate analysis of Section 6.16. There it was a problem because it caused an error in our analysis; here the same adsorption is of great benefit to us.



**FIGURE 8.4**  
A flowchart for a water treatment plant

## How effective?

Like many other human enterprises, water treatment is a balance between cost and quality of the finished product. Sand filtration removes a high proportion of the particulate matter in the water after flocculation, but not the extremely small particles; and it is sufficiently fast to produce the volume of treated water that a big city needs. In addition chlorination is a cost-effective way of removing most disease-causing agents.

However as the *Giardia* and *Cryptosporidium* scare in the Sydney region in mid-1998 showed (when householders were advised to boil all water for human consumption because of fears that small amounts of these harmful parasites might have been present), there can be situations when sand filtration and chlorination are not adequate for removing such organisms. Use of membrane filters (Section 8.14) and/or ozone sterilisation would probably remove these parasites but at considerably increased costs. The present treatment methods coupled with better catchment management may be the more cost-effective approach.

## FOR INVESTIGATION

Prepare a report on your local city or town water supply. Include a map of the catchment and identify any likely sources of contamination in the catchment. Describe the purification processes used and list any additives that are put in the water and the reasons for adding them. Describe the testing that is done to monitor water quality, and assess the overall effectiveness of the purification and testing procedures. Include some comparisons of the quality of your town water with accepted national standards.



## Exercises

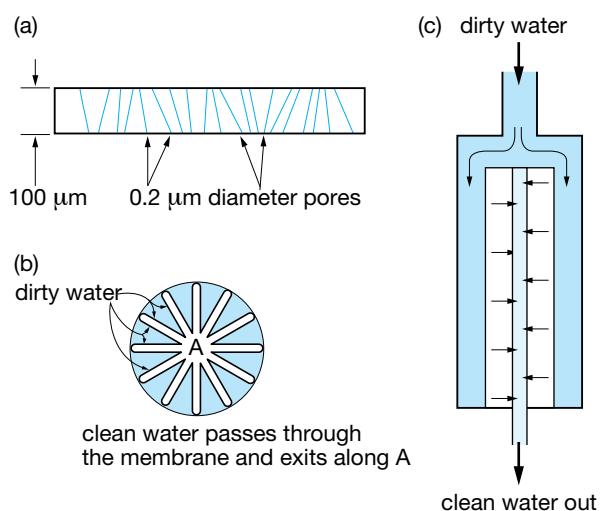
- 25 a** Write an equation for the formation of iron(III) hydroxide when iron(III) chloride is added to slightly alkaline water.
- b** Aluminium hydroxide is often used as a flocculating agent instead of iron(III) hydroxide. Write an equation for the formation of aluminium hydroxide.
- c** Why are aluminium and iron(III) hydroxides used in water clarification and not hydroxides of copper, zinc or magnesium?
- \*26** A first step in clarifying water by flocculation is to adjust the pH to above 7 before adding iron(III) chloride. Providing that the correct amount of iron(III) chloride is added, why is there no need to re-adjust the pH of the water after flocculation and filtration?



## 8.14 MEMBRANE FILTERS

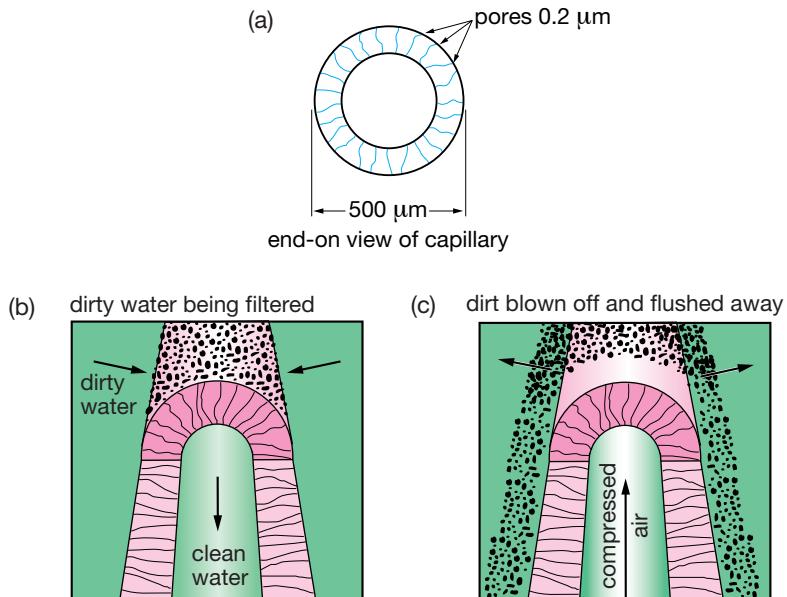
A **membrane filter** is essentially a thin film of a synthetic polymer through which there are pores (small holes) of fairly uniform size. This is shown schematically in Figure 8.5(a). Polymers that are commonly used are polypropylene, polytetrafluoroethylene and polysulphone. The simplest type of membrane filter is just a sheet of porous polymer that is pleated (folded) around a central rigid porous core and held in place with a surrounding mesh as in Figure 8.5(b). This filter cartridge is placed in a suitable housing (c) mounted in the water pipe and filters the water as it flows through it.

FIGURE 8.5  
A membrane filter: (a) the thin sheet of polymer with small pores through it; (b) the way a sheet is folded (pleated) to make a filter cartridge; (c) a cartridge in operation



Another type of membrane filter has the porous material made into hollow capillaries with an outside diameter of about 500 μm, inside diameter about 200 μm and a pore size of 0.2 to 0.5 μm, shown in cross-section in Figure 8.6(a); these are commonly called *hollow fibre* membrane filters. For each capillary dirty water flows from the outside through the wall of the capillary and clean water comes out of the inside as in Figure 8.6(b). Large numbers of such capillaries are bundled together to make a filtering unit with a very large surface area.

FIGURE 8.6  
(a) Cross-section of a hollow fibre (capillary) membrane filter; (b) how one capillary works; (c) backflushing (cleaning) a capillary



Many membrane filters, particularly hollow fibre ones, can be cleaned by blowing air from the clean side to dislodge trapped particles which are then washed away by the dirty water on the outside as shown in Figure 8.6(c). Figure 8.7 shows a bundle of such capillaries assembled into a filtering unit.



FIGURE 8.7  
Capillary membrane filters are bundled together parallel to one another as in the white cylinder in the middle of the photo; at the top left is a bundle that has been 'let loose' to show individual capillaries. The bundle is mounted in a housing that allows dirty water (under pressure) to pass over the outer surfaces of the capillaries; clean water flows through the walls of the capillaries as in Figure 8.6 and is collected from both ends

## Membrane filters compared with 'ordinary' filters

'Ordinary' filters such as (home or laboratory) filter papers or coarse sand filters (home swimming pools or water processing plants) consist of coarse material—fibres in filter papers, granules in sand filters—packed into a relatively thick bed. As the suspension seeps through this bed, big particles get trapped in it while small ones pass through. Such filters are called *depth filters*. A membrane filter consists of a solid film through which uniformly sized holes have been punched. Membrane filters are much thinner than depth filters and have a sharp cut-off in terms of diameter of particle they will let through—the diameter of the hole. While depth filters often have size ratings, stating the maximum size of particle they will let through, there is no sharp cut-off as is the case of membrane filters. Solutions pass through the thinner membrane filters much more quickly than through depth filters. Applying high pressure to depth filters is generally not effective, because it just pushes bigger particles through the matted filter material: high pressures can be used with membrane filters to speed up filtration, because the definite-sized holes do not let bigger particles through.

## Advantages

The advantages of membrane filters are:

- they can filter out much smaller particles than paper or sand filters can
- they filter out virtually all particles larger than their specified pore sizes

- they are quite thin and so liquids flow through them fairly rapidly
- they are reasonably strong and so can withstand pressure differences across them of typically 2 to 5 times atmospheric pressure
- they can be cleaned (back-flushed) and reused.

Membrane filters are widely used for filtering both drinking water and treated sewage (for reuse), though the latter not to any significant extent by public authorities in Australia. For drinking water, membrane filters can remove virtually all particles larger than  $0.2\text{ }\mu\text{m}$  including *Giardia* and *Cryptosporidium*.<sup>†</sup> Because of the relatively high quality of the raw water available for domestic use in the Sydney area, membrane filtration is currently considered too expensive for the relatively small improvement in water quality that it would provide.

It is impractical to use membrane filters to process untreated sewage, because it contains so much suspended matter that the filter pores would become clogged far too quickly. Before Sydney can consider using membrane filters to clean up sewage so the water can be re-used, good quality secondary treatment plants need to be added to the simple primary treatment plants that are currently used at the ocean outfalls (Manly, Bondi and Malabar). Membrane filtration is an effective form of tertiary treatment when it is desired to reuse the water for industry or for limited domestic purposes or before discharging the water into a river that is used by towns further downstream. Membrane filtration is widely used in industry, particularly for beverage preparation. Most bottled drinking water has been purified by passing it through a membrane filter. Membrane filters are used as a final stage in purifying recycled water at Olympic Park and the adjacent suburb of Newington in Sydney.

Although membrane filters can remove quite small suspended particles, typically ones larger than  $0.2\text{ }\mu\text{m}$  ( $= 200\text{ nm}$ ), they cannot remove substances that are actually dissolved in the water, because ions and other dissolved solids have diameters in the order of tens of nm, so they pass easily pass through membrane filters. This means that such filters cannot remove nitrate or phosphate or heavy metal ions from water.

An industrial scale capillary membrane filter plant similar to the one at Olympic Park in Sydney. The vertical grey cylinders in the middle left of the photo are the filter elements (shown in the foreground of Fig. 8.7)



<sup>†</sup> In Australia most water authorities ‘eliminate’ these parasites first by trying to keep them out of the storage dam, then if they are present, by drawing water from locations and depths in the dam where their concentrations are minimal. Sand filtration does remove some of these organisms.

## Important new terms

You should know the meaning of the following terms:

algal bloom (p. 263)  
biochemical oxygen demand (BOD) (p. 271)  
catchment (p. 289)  
coagulation (p. 290)  
electrolysis (p. 272)  
eutrophication (p. 287)  
flocculation (p. 290)

hard water (p. 263)  
heavy metals (p. 282)  
leaching (p. 284)  
membrane filter (p. 292)  
salinity (p. 268)  
secchi disc (p. 266)  
soft water (p. 263)  
total dissolved solids (TDS) (p. 267)  
turbidity (p. 266)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 List eight properties (criteria) that are used to assess water quality.
- 3 How would you measure the pH of water in a creek? If the water is environmentally clean, in what range should the pH lie?
- 4 How would you measure the turbidity of a sample of water? What does turbidity tell you about the water?
- 5 Describe two methods of determining **a** the total dissolved solids and **b** the concentration of dissolved oxygen in a sample of river water. For each property what are the advantages and disadvantages of each method? What range of values would you expect for each property for relatively clean environmental water?
- 6 Explain how you would measure the biochemical oxygen demand of a sample of river water. Why is such a measurement useful?
- 7 Why are we interested in the ‘hardness’ of water? How is hardness measured and in what form is it reported?
- 8 What are the two most abundant anions present in water in the environment? What three other anions are present in small but significant amounts? How would you test qualitatively for the two most abundant ones? How would you ensure that carbonate did not interfere with these tests?
- 9 Explain how you would test for the presence of **a**  $\text{Cu}^{2+}$  (as distinct from  $\text{Fe}^{3+}$ ) and **b**  $\text{Zn}^{2+}$  (as distinct from  $\text{Pb}^{2+}$ ) in separate samples of water.
- 10 Describe a test you could perform to determine whether there were any heavy metals in a water sample.
- 11 List five factors that affect the concentrations of ions in water bodies.
- 12 What four conditions are needed for an algal bloom to occur? What are the detrimental effects of algal blooms?
- 13 Explain how algal blooms form.
- 14 What procedures do most Australian cities follow in order to supply good quality tap water to their citizens? Explain how these procedures eliminate particular undesirable impurities.

- 15** Assess the effectiveness of the procedures in the previous question for supplying safe and high quality drinking water.
- 16** Describe the nature of membrane filters and list their advantages over paper or sand filters. Give several common uses of membrane filters.

# EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR MODULE 3

MODULE  
**3**

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination: for more information see p. 93.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

- |   | MARKS |
|---|-------|
| 1 Assess the importance of collaboration among chemists as they collect and analyse information in order to solve problems in the everyday world.   | 3     |
| 2 Explain why ozone in the stratosphere is beneficial to humans while ozone in the lower atmosphere is a problem for us.  | 3     |
| 3 Outline the process used for the industrial synthesis of ammonia. List three or four factors the designers and operators of the plant would need to consider to produce significant quantities of ammonia as cheaply as possible. | 8     |
| 4 Evaluate the usefulness of flame tests for identifying elements in samples.   | 4     |
| 5 Describe experiments (both qualitative and quantitative) that you have performed to assess the quality of different water samples.  | 7     |
| 6 Evaluate the work of Fritz Haber and Carl Bosch in developing an industrial process for the synthesis of ammonia, both at the time they did it and over the next 100 years.   | 4     |
| 7 Compare the physical properties and general chemical reactivity of ozone and molecular oxygen. Interpret the difference in terms of molecular structure.  | 5     |
| 8 Assess the impact of atomic absorption spectroscopy upon the study of trace elements in biological systems.   | 4     |
| 9 Describe a chemical process in which different products are formed when different experimental conditions are used. Outline how you would ensure that the process formed the maximum amount of desired product.                   | 5     |
| 10 Explain why the water supplies in different towns often contain different concentrations of ions such as $Mg^{2+}$ , $Ca^{2+}$ , $Na^+$ , $Cl^-$ , $SO_4^{2-}$ and $HCO_3^-$ .   | 4     |
| 11 Identify five major air pollutants and their main sources.   | 5     |
| 12 Compare the structures of membrane filters and ordinary filters (such as filter paper) and identify two advantages of membrane filters.  | 5     |
| 13 Assess the success of international agreements that aim at reducing concentrations of chlorofluorocarbons (CFCs) in the atmosphere.  | 4     |
| 14 Evaluate the effectiveness of monitoring phosphate concentration in a water body as a method of predicting the likelihood of an algal bloom.   | 3     |
| 15 Explain how chlorofluorocarbons (CFCs) have a detrimental effect upon ozone concentrations in the stratosphere, particularly over the Antarctic in spring.   | 7     |

- 16** Assess the effectiveness of procedures used to clarify and sanitise your local town water supply. **5**
- 17** Outline the benefits and shortcomings of Le Chatelier's principle in predicting yields of chemical reactions, using the reaction between hydrogen and nitrogen as an example. **4**
- 18** Evaluate the effectiveness of current methods of monitoring the so-called ozone hole. **4**
- 19** Explain why in atomic absorption spectroscopy **a** a different lamp is used for each element to be analysed, and **b** the technique only provides an estimate of the amount (concentration) of a particular element in the sample but no information about the compound the element is present in. **4**
- 20** In recent years chlorofluorocarbons (CFCs) have been replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). Evaluate the effectiveness of these substitutions for minimising damage to the ozone layer in the stratosphere. **5**

# REVISION TEST FOR MODULE 3

MODULE  
**3**

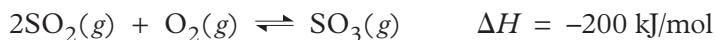
**Total marks: 50 Suggested time: 90 minutes**

The table of solubility data inside the back cover of this book may be used if needed.

## MULTIPLE CHOICE QUESTIONS (1 mark each)

Select the alternative **a**, **b**, **c**, or **d** which best answers the question.

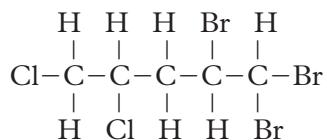
- 1** The equilibrium reaction:



is an important step in the industrial synthesis of sulfuric acid. One way of increasing the percentage conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is to:

- a** increase the temperature
- b** lower the total pressure
- c** increase the concentration of  $\text{O}_2$  in the reaction mixture
- d** add a high pressure of  $\text{N}_2$  to the reaction mixture

- 2** The correct name for the compound having the structure



is:

- a** 4,5-dichloro-1,1,2-tribromopentane
  - b** 4,4,5-tribromo-1,2-dichloropentane
  - c** 1,1,2-tribromo-4,5-dichloropentane
  - d** 1,2-dichloro-4,4,5-tribromopentane
- 3** The table below shows the results of some tests performed on environmentally clean water and on two samples of polluted water.

	Clean water	Sample P	Sample Q
dissolved oxygen (ppm)	9.0	2.8	8.5
total dissolved solids (ppm)	50	340	650
micro-organisms (CFU/100 mL <sup>a</sup> )	2	350	5
phosphate (ppm)	0.02	2.0	0.55

*a CFU = colony forming units*

The most likely sources of the pollution in the two samples are:

- a** land-clearing for P and a spill from a mine-site for Q
  - b** grazing land run-off for P and factory discharges for Q
  - c** treated sewage for P and cotton-field run-off for Q
  - d** raw sewage for P and farmland erosion for Q
- 4** When excess barium chloride solution was added to a solution made by dissolving 2.51 g of commercial lawn food in 250 mL water, 1.03 g barium sulfate was formed. The percentage sulfate in the lawn food is:

- a** 10.0%      **c** 24.1%  
**b** 16.9%      **d** 41.0%
- 5** Of the species,  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{O}_2$ ,  $\text{Ag}(\text{NH}_3)_2^+$ , the one that does *not* involve a coordinate covalent bond is:
- a**  $\text{O}_2$       **c**  $\text{Ag}(\text{NH}_3)_2^+$   
**b**  $\text{CO}$       **d**  $\text{N}_2\text{O}$
- 6** A sample of water known to contain only *one* of the cations  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  was divided into three portions for testing with solutions of hydrochloric acid, sulfuric acid and sodium hydroxide respectively. A precipitate was formed in each case. The cation present in the solution is:
- a**  $\text{Pb}^{2+}$       **c**  $\text{Cu}^{2+}$   
**b**  $\text{Ba}^{2+}$       **d**  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$
- 7** In the Haber process for synthesising ammonia an iron catalyst (reduced magnetite) is used because:
- a** it moves the equilibrium in the desired direction  
**b** it decreases the formation of unwanted by-products  
**c** it removes unwanted oxygen and so prevents a hydrogen–oxygen explosion  
**d** it allows a lower temperature to be used for the process
- 8** The table below compares some measurements on the air from three polluted areas with those of clean air.

	Clean air	Sample L	Sample M	Sample N
Hydrocarbons (ppm)	0.1	0.05	2.6	1.8
$\text{NO}_x$ (ppm)	0.01	0.3	0.4	0.12
CO (ppm)	0.5	1	3	10
$\text{SO}_2$ (ppm)	0.02	0.2	0.15	0.03
particles ( $\mu\text{g}/\text{m}^3$ )	20	200	350	80

- The most likely causes of the pollution are:
- a** L from motor cars, M from heavy industry and N from electricity generation  
**b** L from mining, M from dust storms and N from heavy industry  
**c** L from electricity generation, M from heavy industry and N from motor cars  
**d** L from motor cars, M from mining and N from electricity generation
- 9** Of the compounds,  $\text{CCl}_2\text{F}_2$ ,  $\text{CH}_3-\text{CCl}_3$ ,  $\text{CH}_2\text{F}-\text{CF}_3$ ,  $\text{CBrClF}_2$ ,  $\text{CF}_3-\text{CHCl}_2$ ,  $\text{CH}_2\text{F}_2$ ,  $\text{CCl}_4$ ,  $\text{CF}_3-\text{CF}_3$  the ones that have no detrimental effect upon the stratosphere are:
- a**  $\text{CH}_2\text{F}-\text{CF}_3$  and  $\text{CH}_2\text{F}_2$   
**b**  $\text{CH}_2\text{F}-\text{CF}_3$ ,  $\text{CH}_2\text{F}_2$  and  $\text{CF}_3-\text{CF}_3$   
**c**  $\text{CH}_3-\text{CCl}_3$ ,  $\text{CH}_2\text{F}-\text{CF}_3$ ,  $\text{CF}_3-\text{CHCl}_2$ ,  $\text{CH}_2\text{F}_2$   
**d**  $\text{CBrClF}_2$ ,  $\text{CCl}_4$
- 10** A simple way of detecting ozone in polluted air is to bubble the air through a potassium iodide solution. Ozone oxidises colourless iodide to yellow-brown iodine. The correct equation for this reaction is:

- a**  $2\text{O}_3(g) + 2\text{I}^-(aq) \rightarrow \text{I}_2(aq) + 3\text{O}_2(g)$
- b**  $\text{O}_3(g) + 2\text{I}^-(aq) + 3\text{H}^+(aq) \rightarrow \text{I}_2(aq) + 3\text{OH}^-(aq)$
- c**  $\text{O}_3(g) + 2\text{I}^-(aq) + 2\text{H}^+(aq) \rightarrow \text{I}_2(aq) + \text{H}_2\text{O}(l) + \text{O}_2(g)$
- d**  $\text{O}_3(g) + 2\text{I}^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{I}_2(aq) + 3\text{OH}^-(aq)$

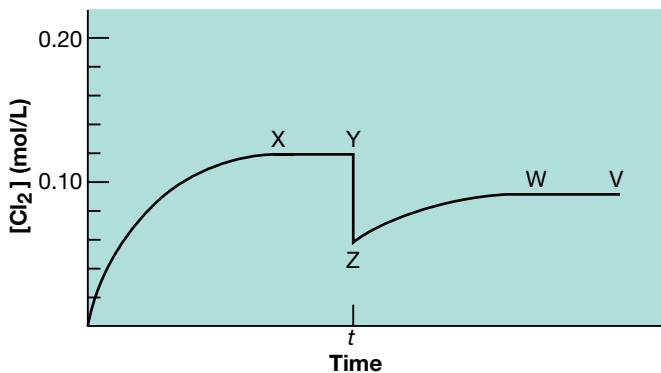
### SHORT ANSWER AND EXTENDED RESPONSE QUESTIONS

The number of marks for each part of each question is shown at the right-hand end of the question. Marks allocated are based on the HSC scale of 1 mark per 1.8 minutes.

- |  | MARKS    |
|--|----------|
| <b>11</b> Ammonia is synthesised industrially by passing a stoichiometric mixture of $\text{N}_2$ and $\text{H}_2$ over a catalyst at a pressure of about $2.5 \times 10^4 \text{ kPa}$ and a temperature of $400^\circ\text{C}$ .                                     |          |
| <b>a</b> Write a balanced equation for the reaction and name the catalyst used. <b>1</b>   |          |
| <b>b</b> Explain why:  |          |
| <b>i</b> a high pressure is used   |          |
| <b>ii</b> a significantly higher or lower temperature is <i>not</i> used   | <b>2</b> |
| <b>c</b> Explain how <i>all</i> of the reactant mixture is eventually converted to ammonia, even though at equilibrium there is only a 40% conversion of reactants to ammonia.   | <b>1</b> |
| <b>12</b> <b>a</b> Draw electron dot structures for an oxygen atom and for an ozone molecule. <b>1</b>   |          |
| <b>b</b> Explain how ozone is produced in photochemical smog. <b>2</b>   |          |
| <b>13</b> Describe, with at least one chemical equation, an experiment you have performed to measure the sulfate content in a lawn fertiliser. Identify several possible sources of error in your experiment and outline the steps you took to minimise them. <b>7</b> |          |
| <b>14</b> Gaseous phosphorous pentachloride decomposes at elevated temperatures to phosphorous trichloride and chlorine:   |          |



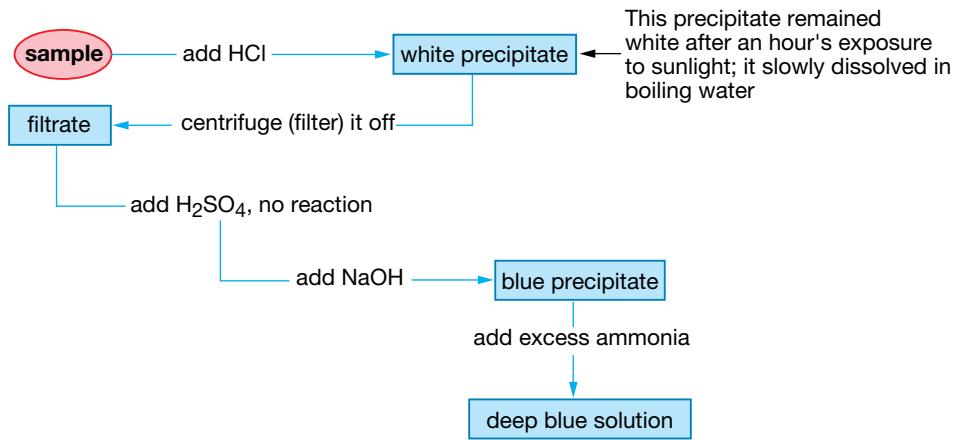
At a fixed temperature 0.020 mol  $\text{PCl}_5$  was placed in a large syringe with the volume adjusted to 0.100 L. The concentration of chlorine as a function of time is shown in the diagram. At time  $t$ , the volume available to the gas mixture was suddenly increased to 0.200 L. The diagram shows the variation in chlorine concentration at and also after that time.



- a** Explain why the chlorine concentration remained constant from X to Y and why it did not get to 0.20 mol/L.

- b Why did the concentration decrease suddenly to Z (at time  $t$ )?
  - c Why did the concentration of chlorine increase from Z to W and why did it remain constant from W to V?
  - d Suppose that the volume had been decreased to 0.050 L at time  $t$  (instead of being increased). Copy the diagram from time zero to  $t$  into your workbook then sketch the curve you would have expected for chlorine concentration after point Y.
  - e On the diagram you drew in (d), draw the curve for concentration of chlorine that you would have expected if a catalyst had been used.
- 4

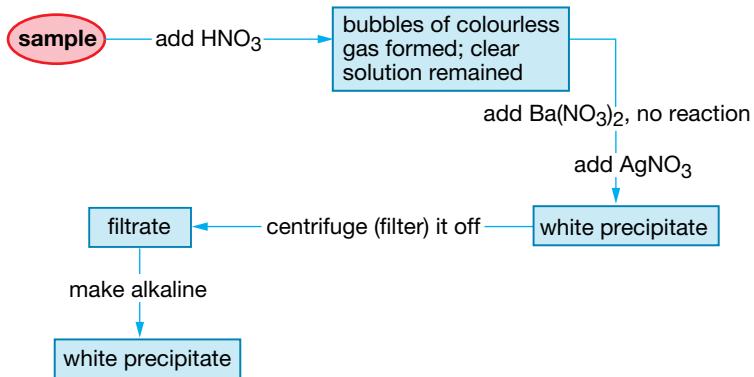
- 15 a** In order to determine the cation(s) present in a solution a chemist performed the tests in the following chart.



What cation(s) is(are) present in the solution? Write chemical equations for two of the reactions involved in this analysis.

3

- b Our chemist then determined the anion(s) present in a second sample by performing the tests in the next chart.



What anion(s) is(are) present in the solution? Explain your reasoning.

3

- 16 a** Describe the effect chlorofluorocarbons (CFCs) are having on stratospheric ozone. Write equations for all important chemical reactions that you mention, and include explanations for the facts that:
- i quite small amounts of CFCs can have very large effects
  - ii CFCs have this effect while many other halogenated compounds do not

- |     |   |   |
|-----|---|---|
| iii | the problem is most severe over the Antarctic and in spring   | 6 |
| b   | Assess the effectiveness of the way that the world is trying to solve this problem.   | 3 |
| 17  | List six properties (or criteria), excluding temperature and pH, that are used to assess the quality of water in the environment. For <i>four</i> of these outline how various forms of pollution cause values to be different from those of environmentally clean water. | 7 |

# MODULE 3 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for Module 3 of the New South Wales Higher School Certificate HSC Course.

## Syllabus content

The following table lists (for Module 3) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

Location of HSC Course material in *Conquering Chemistry* for Module 3

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.4.1 Much of the work of chemists involves monitoring the reactants and products of reactions and managing reaction conditions</b>	
■ outline the role of a chemist employed in a named industry or enterprise, identifying the branch of chemistry undertaken by the chemist and explaining a chemical principle that the chemist uses	6.1, 6.2
■ identify the need for collaboration between chemists as they collect and analyse data	6.4
■ describe an example of a chemical reaction such as combustion, where reactants form different products under different conditions and thus would need monitoring	6.5
<b>9.4.2 Chemical processes in industry require monitoring and management to maximise production</b>	
■ identify and describe the industrial uses of ammonia	6.6
■ identify that ammonia can be synthesised from its component gases, nitrogen and hydrogen	6.7
■ describe that synthesis of ammonia occurs as a reversible reaction that will reach equilibrium	6.7
■ identify the reaction of hydrogen with nitrogen as exothermic	6.7
■ explain why the rate of reaction is increased by higher temperatures	6.7
■ explain why the yield of product in the Haber process is reduced at higher temperatures using Le Chatelier's principle	6.7
■ explain why the Haber process is based on a delicate balancing act involving reaction energy, reaction rate and equilibrium	6.7
■ explain that the use of a catalyst will lower the reaction temperature required and identify the catalyst(s) used in the Haber process	6.7
■ analyse the impact of increased pressure on the system involved in the Haber process	6.7

Syllabus reference Students learn to	Sections where found in CCHSC
■ explain why monitoring of the reaction vessel used in the Haber process is crucial and discuss the monitoring required	6.7
<b>9.4.3 Manufactured products, including food, drugs and household chemicals, are analysed to determine or ensure their chemical composition</b>	
■ deduce the ions present in a sample from the results of tests	6.8 to 6.14
■ describe the use of atomic absorption spectroscopy (AAS) in detecting concentrations of metal ions in solutions and assess its impact on scientific understanding of the effects of trace elements	6.18, 6.19
<b>9.4.4 Human activity has caused changes in the composition and the structure of the atmosphere. Chemists monitor these changes so that further damage can be limited</b>	
■ describe the composition and layered structure of the atmosphere	7.1, 7.2
■ identify the main pollutants found in the lower atmosphere and their sources	7.3
■ describe ozone as a molecule able to act both as an upper atmosphere UV radiation shield and as a lower atmosphere pollutant	7.4, 7.5
■ describe the formation of a coordinate covalent bond	7.6
■ demonstrate the formation of coordinate covalent bonds using Lewis electron dot structures	7.6
■ compare the properties of the oxygen allotropes O <sub>2</sub> and O <sub>3</sub> and account for them on the basis of molecular structure and bonding	7.7
■ compare the properties of the gaseous forms of oxygen and the oxygen free radical	7.8
■ identify the origins of chlorofluorocarbons (CFCs) and halons in the atmosphere	7.10
■ identify and name examples of isomers (excluding geometrical and optical) of haloalkanes up to eight carbon atoms	7.10
■ discuss the problems associated with the use of CFCs and assess the effectiveness of steps taken to alleviate these problems	7.9, 7.11 to 7.13
■ analyse the information available that indicates changes in atmospheric ozone concentrations, describe the changes observed and explain how this information was obtained	7.14
<b>9.4.5 Human activity also impacts on waterways. Chemical monitoring and management assists in providing safe water for human use and to protect the habitats of other organisms</b>	
■ identify that water quality can be determined by considering:	8.1 to 8.10
<ul style="list-style-type: none"> <li>- concentrations of common ions</li> <li>- total dissolved solids</li> <li>- hardness</li> <li>- turbidity</li> <li>- acidity</li> <li>- dissolved oxygen and biochemical oxygen demand</li> </ul>	

■ identify factors that affect the concentrations of a range of ions in solution in natural bodies of water such as rivers and oceans	8.11
■ describe and assess the effectiveness of methods used to purify and sanitise mass water supplies	8.13
■ describe the design and composition of microscopic membrane filters and explain how they purify contaminated water	8.14

## Compulsory experiments

The table below lists the compulsory experiments (from the right-hand column of the syllabus), along with places where you can find procedures for these experiments (in *CCHSC BLM*) and the location of relevant information in *CCHSC*.

*CCHSC* is an abbreviation for this book *Conquering Chemistry HSC Course*.

*CCHSC BLM* is *Conquering Chemistry HSC Course Blackline Masters* by Debra Smith, Cengage Learning Australia.

### Information about compulsory experiments for Module 3

Experiment	Location in <i>CCHSC BLM</i>	Related material in <i>CCHSC</i> <sup>a</sup>
1 Perform tests, including flame tests, to identify a range of cations and anions.	Module 3 Worksheets 2 and 3 (pp. 120 and 125)	Sections 6.9 to 6.14 Chapter 6 Exercises 9 to 26 interpret results from these tests
2 Measure the sulfate content of a lawn fertiliser.	Module 3 Worksheet 5 (p. 135)	Section 6.16 Chapter 6 Exercises 27 and 31 Revision Test Question 13
3 Perform qualitative and quantitative tests to analyse and compare the quality of water samples.	Module 3 Worksheets 9 and 10 (pp. 144 and 150)	Sections 8.2 to 8.10 Chapter 8 Exercises 3 to 20 interpret or calculate results from these tests Exam-style Question 5

<sup>a</sup> Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.

### Other items in the student activity (right-hand) column

The table below lists (in abbreviated form) the non-experimental items in the student activity (right-hand) column of the syllabus and indicates where in *Conquering Chemistry* relevant information is located.

## Location of material for other Module 3 activities

Syllabus item	Relevant material in CCHSC
<b>9.4.1</b> ■ gather, process and present information ... about the work of practising scientists ...	Sections 6.2 and 6.3
<b>9.4.2</b> ■ gather ... information ... to describe the conditions under which Haber developed the industrial synthesis of ammonia and evaluate its significance ...	First paragraph in Section 6.7 gives a start for this
<b>9.4.3</b> ■ Experiment 1 (see previous table)	
■ gather ... information to describe and explain evidence for the need to monitor levels of one of the above ions ...	Section 6.15
■ Experiment 2 (see previous table)	
■ analyse information to evaluate the reliability of the results ... and to propose solutions to problems ...	Section 6.16 Revision Test Question 13
■ gather ... information to interpret ... AAS measurements and evaluate the effectiveness of this in pollution control	Uses and Example 2 in Section 6.18
<b>9.4.4</b> ■ present information ... to write the equations ... involving CFCs ... to demonstrate the removal of ozone from the atmosphere	Sections 7.11 and 7.12
■ gather ... information ... including simulations, molecular model kits or ... to model isomers of haloalkanes	Figure 7.5 shows photos of some molecular models
■ present information ... to identify alternative chemicals used to replace CFCs and evaluate the effectiveness of their use ...	Section 7.13
<b>9.4.5</b> ■ Experiment 3 (see previous table)	
■ gather ... information on the range and chemistry of the tests used to:	Sections 8.10 and 8.12
– identify heavy metal pollution ... – monitor possible eutrophication ...	
■ gather ... information on the features of the local town water supply in terms of ...	Section 8.13 and the For investigation box in that section

## Prescribed focus areas

The five prescribed focus areas of the syllabus are listed on p. 101.

As with most modules, the material of Module 3 (in this book and in the syllabus) relates strongly to focus areas 2 and 3, the nature and practice of chemistry, and applications and use. This module has a strong emphasis on applications and use, ranging from the application of chemical principles to the industrial synthesis of ammonia to the use of a wide range of chemical tests for assessing water quality.

However Module 3, with its emphasis on air and water pollution, also relates strongly to area 4, implications for society and the environment. Problems such as the ozone hole and pollution of urban atmospheres should grab students'

attention and interest, particularly as they have enough background knowledge to be able to understand the chemistry involved in these problems. General societal concerns about water quality should stimulate students to delve into the questions of water pollution and why our water bodies are under such threat. Salinity is such a topical and urgent issue nationally that a short section on it is included (though it is on the margins of the syllabus).

Much of the air and water pollution material that supports area 4 can also, with a slightly different emphasis, provide opportunities to develop area 5, current issues, research and development, particularly the current issues aspect.

There is not much scope for involving area 1, the history of chemistry, in this module, apart from the historical consequences of the development of the Haber process in Germany just before World War I and possibly the story of Alan Walsh's development of atomic absorption spectroscopy.

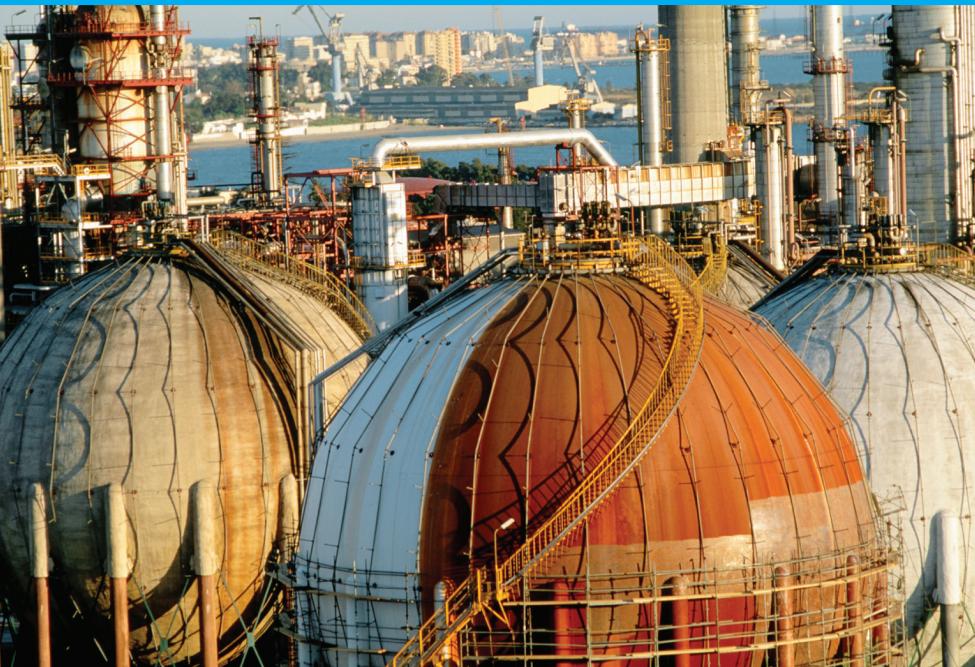
OPTION 1

# Industrial chemistry

The chemical manufacturing industry is an important part of any industrialised society, although consumers have direct contact with very few of its products.

The chemical industry produces many substances that are used primarily by other industries to make the products that we consumers buy and use. For example the chemical industry makes huge quantities of sulfuric acid and sodium hydroxide but, apart from car batteries and some domestic cleaners, consumers do not come into contact with these substances. However we do use large quantities of synthetic fibres, detergents, fertilisers, drugs, pigments, dyes, pesticides, steel, other metals, and products from crude oil: all of these require sulfuric acid for their manufacture or processing. Similarly soap, paper, synthetic fibres and aluminium all require sodium hydroxide for their manufacture or extraction. The chemical industry produces huge quantities of plastics as granules or powders. We consumers only see plastics after other manufacturers have converted them into fibres, film, sheets or various objects such as bottles and kitchen containers, garden hoses, car bumper bars, furniture and video or audio tapes.

An important role of the chemical industry is to make substitutes for natural products that are not available in the quantities required by modern society or which through scarcity have become too expensive for everyday use. Synthetic rubber, detergents, synthetic fibres and margarine were all developed in response to (long-term or temporary) shortages of supply of such natural products as rubber, soap, wool, linen and butter.



Although the industrial manufacture of many substances uses the same reactions as are used in the laboratory, the equipment and operating conditions are often very different, because of the scale of the production.

In this module we shall explore some aspects of industrial chemistry, starting with a look at some natural products that have been (or are being) replaced by synthetic ones. Industry is always concerned with getting the maximum yield of product from its starting materials and with getting it quickly. This requires further development of our understanding of chemical equilibrium. It also requires that we consider the compromises that sometimes have to be made between rate and equilibrium (as was needed for ammonia synthesis in Chapter 6).

We shall then look at the manufacture of a few selected chemicals such as sulfuric acid, sodium hydroxide, soap and sodium carbonate. These specific examples will illustrate the range of reactions that are used industrially and will show how equilibrium, rate and stoichiometric factors need to be considered in designing industrial processes and plants.

Today energy efficiency and environmental responsibility are major considerations for all industry, so discussion of these aspects will be included. We shall see that utilising wastes from other processes (such as minerals refining) and minimising discharges to the atmosphere and waterways are major factors in locating and designing chemical plants. Other factors will also be identified.



## INDUSTRIAL CHEMISTRY, MORE THAN JUST LABORATORY WORK ON A LARGE SCALE

Industrial chemical plants do not look at all like chemical laboratories; nor do the containers used for their products resemble the small bottles and cans that are used for laboratory chemicals.

A major use of sodium hydroxide is the extraction of white alumina ( $\text{Al}_2\text{O}_3$ ) from bauxite; the alumina dissolves in hot sodium hydroxide solution and the mud, mainly iron(III) oxide,  $\text{Fe}_2\text{O}_3$ , is filtered off



# Chemical equilibrium and sulfuric acid

## IN THIS CHAPTER

Replacing natural products

Chemical equilibrium: qualitative features

Quantitative aspects of chemical equilibrium

Rules for writing equilibrium expressions

Measurement of equilibrium constants

Use of equilibrium constants

Equilibrium expressions and Le Chatelier's principle

Temperature dependence of equilibrium constants

Uses of sulfuric acid

Extraction of sulfur

Industrial synthesis of sulfuric acid

Production of sulfur dioxide

Conversion of  $\text{SO}_2$  to  $\text{SO}_3$

Conversion of sulfur trioxide to sulfuric acid

Properties of sulfuric acid

Ionisation of sulfuric acid

Reactions of sulfuric acid

Safety precautions when using sulfuric acid

Industrial chemistry not only produces materials that do not occur naturally, such as plastics and paints, pesticides and pharmaceuticals, and chemicals for photography, printing and batteries, it also produces materials to replace natural substances that have been largely used up or which because of short supply have become very expensive.

## 9.1 REPLACING NATURAL PRODUCTS

In Sections 6.6 and 6.7 we saw how the synthesis of ammonia was developed in response to growing demand for fertiliser and nitric acid and the inadequacy of supplies of Chile saltpetre (sodium nitrate) to meet these demands. Some other examples of the development of synthetic chemicals to replace or supplement the supply of natural products follow.

### Rubber

Until the 1940s rubber had been obtained from plantations of rubber trees in tropical areas such as Malaya and Burma. Demand for rubber increased greatly during World War II (needed for tyres of military vehicles) while supplies were interrupted by the conflict. Consequently scientists in Germany and the US developed synthetic polymers that could replace rubber. Even after the war ended the traditional sources of natural rubber could not meet the greatly increased demand, so synthetic rubbers virtually 'took over' the market:

today about 80% of the world's rubber production is synthetic polymers. The commonest synthetic rubber is called SBR (styrene–butadiene rubber).

## Soap

Before the 1950s soap, made from left-over animal fats (Section 10.11), was virtually the only available cleaning agent. However, with increasing world population increasing the demand for these fats for food, the manufacture of natural soap could not keep up with its growing demand. Consequently synthetic detergents were developed and eventually became the dominant cleaning agents: soap is now mainly used just for personal hygiene. Another factor in the rise in importance of synthetic detergents was the ready availability (as by-products from petrol refining) of starting materials.

## Wool

Until the 1950s wool was one of the two major fibres used for clothing and textiles (cotton was the other). When demand increased after World War II as a result of increased population, growing affluence and increasing defence forces worldwide, supply was unable to keep up. Wool prices escalated dramatically and so synthetic substitutes became more competitive, especially as increasing oil refining was producing increasing amounts of starting materials for synthetics at decreasing prices. Eventually the synthetic fibres, polyester, acrylics and nylon, came to dominate the market. Today wool has become a 'specialty' rather than a common fibre.

## The key issues

The key issues that lead to a natural product being replaced by a synthetic one are:

- increasing demand for the product, even if only temporarily
- inability of the natural sources to keep up with demand, even if only temporarily
- depletion of the natural resources (such as Chile saltpetre)
- competition for the natural resource from another use (fats for food, not soap)
- escalating prices for the natural product, often a result of resource depletion
- increasing availability and/or decreasing cost of starting materials for the synthetic product
- decreasing price for the synthetic product as quantities produced increase
- greater reliability of supply and stability of price for the synthetic product (without the vagaries of weather).

The need to replace products or materials originally obtained from natural resources with ones made synthetically (from more readily available resources) will continue, because the human population is increasing, its level of consumption per person is increasing and natural resources currently in use are being depleted at significant rates.



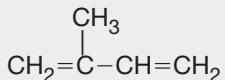
## FOR INVESTIGATION

Search out information about one non-fuel natural substance or material that is in common use today and for which demand is increasing so rapidly that in the near future demand is likely to outstrip supply. Find out what has been or is being done to develop a synthetic replacement. Evaluate the consequences and likely success of using the synthetic in place of the original natural substance or material.

## Exercise

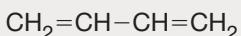


- 1 a Natural rubber is a polymer of isoprene which has the structure:



When isoprene polymerises the end double bonds 'open out' to form bonds to neighbouring molecules while a new double bond forms between the two non-terminal C atoms. Draw a segment of polyisoprene, showing at least four isoprene molecules.

- b The first synthetic rubber was neoprene or poly(chloroprene): it has a Cl atom replacing the  $\text{CH}_3$  group of isoprene. Draw the structure of chloroprene and hence of neoprene: include four monomer units.  
c The commonest synthetic rubber, SBR, is made from two monomers, butadiene, B (structure below), and styrene, S (Table 1.2).



Butadiene polymerises like isoprene in (a) with styrene undergoing 'normal' addition polymerisation (Sections 1.6 and 1.7). SBR has the monomers arranged

... BBBB BBBB BBBB BBBB ...

Draw the structure of a segment of SBR showing at least one styrene unit and three butadiene units.

Before looking at particular industrial processes, let us revise and extend our understanding of an important chemical principle that is often involved in manufacturing chemicals.

## 9.2 CHEMICAL EQUILIBRIUM: QUALITATIVE FEATURES

We first considered the nature of reversible reactions and chemical equilibrium on pp. 208–10 CCP when we were looking at dissolution and precipitation. Then other aspects of equilibrium were introduced in this book in Sections 4.6 to 4.8 in connection with the solubility of carbon dioxide in water and again when we considered weak and strong acids (Section 4.20), buffers (Sections 5.13 and 5.14) and the synthesis of ammonia (Section 6.7). Let us summarise the qualitative features of chemical equilibrium.

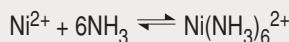
### Qualitative features of chemical equilibrium

- 1 Some chemical reactions are reversible and therefore come to equilibrium.
- 2 It is a dynamic equilibrium that is set up, in which the rate of the forward reaction equals the rate of the reverse reaction.
- 3 Provided we start with appropriate amounts of materials, the final equilibrium state is the same, regardless of the direction from which it is approached.
- 4 *Le Chatelier's principle* summarises the way in which an equilibrium adjusts when experimental conditions are changed: when an equilibrium is disturbed it moves in the direction that tends to minimise the disturbance. The common 'disturbances' are changes in concentration, pressure, volume and temperature. Exercises 2 to 7 of Chapter 6 illustrated the use of this principle.

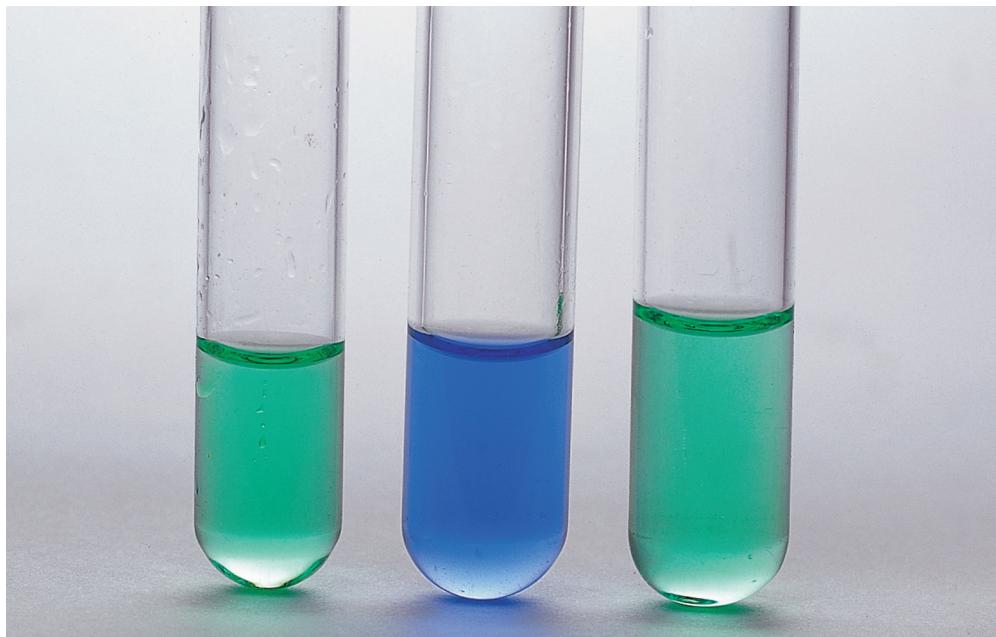
- 5** Reversible reactions can often be driven to virtual completion by use of this principle.

Before turning to quantitative aspects of chemical equilibrium, some revision exercises on qualitative aspects may be appropriate.

Green  $\text{Ni}^{2+}$  (left test tube) reacts with ammonia to form blue  $\text{Ni}(\text{NH}_3)_6^{2+}$  (centre) in the equilibrium reaction

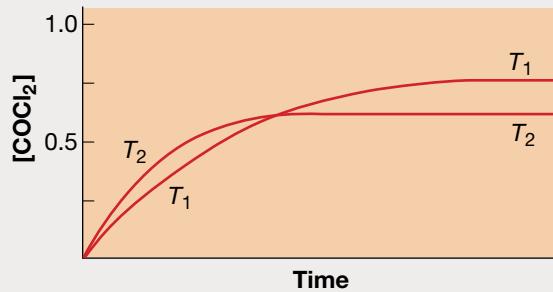


If the ammonia is removed (by adding HCl to form  $\text{NH}_4^+$ ), the equilibrium moves back to the left (right test tube)



## Exercises

- 2** Carbon monoxide reacts with chlorine to form phosgene,  $\text{COCl}_2$ . At each of two temperatures 1.0 mol  $\text{Cl}_2$  was mixed with 1.0 mol of CO in a 1.0 L container. The concentration of  $\text{COCl}_2$  was measured as a function of time in each experiment; the results are shown in the graph below.

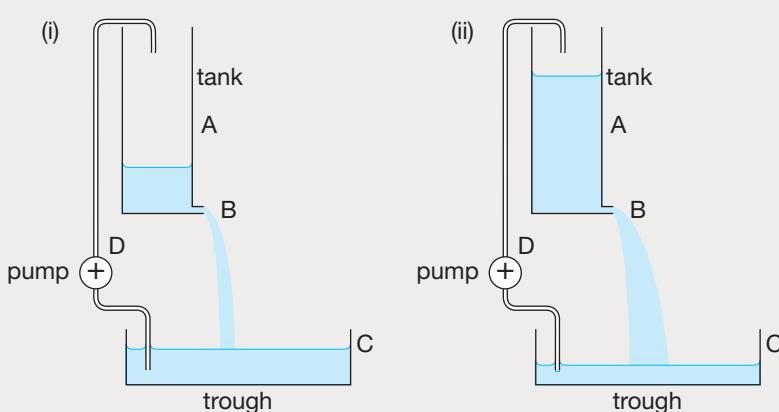


- a** Write a balanced equation for the reaction.
- b** At which of the temperatures,  $T_1$  or  $T_2$ , does the reaction have the higher initial rate? Hence which of the temperatures is the higher? Why?
- c** Explain why the concentration of  $\text{COCl}_2$  reached after long reaction times is different in the two experiments, and why both values are different from 1.0 mol/L.
- d** Deduce whether the reaction is exo- or endothermic, giving your reason.
- e** Copy the graph for temperature  $T_1$  into your workbook. Suppose that 1.0 mol phosgene was placed in a 1.0 L container at  $T_1$ . Sketch on the graph the curve you would expect for the concentration of  $\text{COCl}_2$  as a function of time. Explain why this curve would end where it does.
- 3** For the gaseous reactions (a) to (d) below, predict the effect of each of the following changes upon the position of equilibrium of:

- i** increasing the pressure (by pumping more equilibrium mixture into a fixed volume)
  - ii** adding  $\text{H}_2$  to (b) and (c)
  - iii** adding  $\text{Cl}_2$  to (a) and CO to (c)
  - iv** increasing the volume being occupied by the equilibrium mixture
  - v** increasing the temperature
- a**  $\text{SO}_2(g) + \text{Cl}_2(g) \rightleftharpoons \text{SO}_2\text{Cl}_2(g)$  (exothermic)
- \***b**  $\text{CO}(g) + \text{H}_2(g) \rightleftharpoons \text{HCHO}(g)$  (exothermic)
- c**  $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$  (endothermic)
- \***d**  $3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)$  (endothermic)

- 4** Sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , decomposes to form sulfur dioxide and chlorine gas. A sample of sulfuryl chloride was placed in a container under such conditions that at equilibrium 33% of the starting compound had decomposed.

- a** Draw a graph showing the concentrations of  $\text{SO}_2\text{Cl}_2$  and  $\text{SO}_2$  as functions of time until well after equilibrium had been reached.
  - b** At time  $x$ , well after equilibrium had been established, the volume of the reaction vessel was suddenly increased from 100 mL to 150 mL. Show on your graph how concentrations would change at time  $x$ . Be quantitative about this. Show how concentrations would change with time after  $x$  as the system moved to re-establish equilibrium. Explain why your curves have the shape and final equilibrium values that you have given them.
  - c** Re-draw the graph from part (a). Show as a dashed line the concentration of chlorine as a function of time; you may have to displace this curve slightly up or down to make it show up. Now suppose that at time  $x$  additional chlorine had been added to the reaction vessel, sufficient to increase its concentration by 50%. Show how the concentrations of the three species would change at and after time  $x$  as the system re-established equilibrium. Explain the shapes and final concentrations of your curves.
- 5 a** Two students set up the experiment shown in (i) below. A tall tank A with an outlet B near the bottom was mounted above a long trough C; both tank and trough contained water. A small pump D was used to lift water from the trough into the tank. Water flowed back to the trough through outlet B. After a short time the water levels in the tank and trough became constant.



Explain how this experiment models the essential features of a dynamic equilibrium reaction.

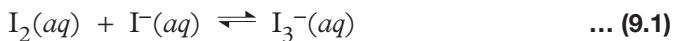
- b** The students then increased the speed of the pump. After a short time the system again settled down with constant water levels in tank and trough and with a greater flow rate of water from tank to trough as shown in (ii).

Explain how this second experiment simulates the effect of temperature upon a chemical equilibrium.

## 9.3 QUANTITATIVE ASPECTS OF CHEMICAL EQUILIBRIUM

When a reaction is at equilibrium, there is a quantitative relationship involving concentrations of reactants and products. We shall explore it using some examples.

Iodine, in aqueous solution, reacts with iodide to form what is called the triiodide ion,  $\text{I}_3^-$ :



The triiodide ion absorbs light at a different wavelength from iodine itself. If this light absorption is used to measure the concentrations of the species in solutions at equilibrium, the results shown in Table 9.1 are obtained. As the right-hand column shows, when Reaction 9.1 is at equilibrium at a constant temperature, the expression  $[\text{I}_3^-]/[\text{I}_2][\text{I}^-]$  has a constant value; that is:

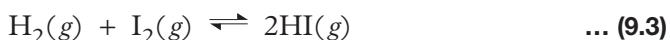
$$\frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]} = K_1 \quad \dots (9.2)$$

where the constant  $K_1$  has the value 723 at  $25^\circ\text{C}$ <sup>†</sup>.

**TABLE 9.1 Equilibrium concentrations at  $25^\circ\text{C}$  for the reaction**  
 $\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$

$[\text{I}_2]$ ( $\times 10^{-5}$ mol/L)	$[\text{I}^-]$ ( $\times 10^{-3}$ mol/L)	$[\text{I}_3^-]$ ( $\times 10^{-5}$ mol/L)	$\frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]}$
4.31	0.218	0.680	724
2.75	1.130	2.244	722
2.30	0.720	1.198	723
0.61	6.48	2.857	723
1.12	1.085	0.877	722
			average: 723

Similarly we can measure the equilibrium concentrations for all the species involved in the reaction:



Results from several different starting mixtures are shown in Table 9.2. These show that when Reaction 9.3 is at equilibrium at constant temperature:

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = K_2 \quad \dots (9.4)$$

The constant  $K_2$  has the value 45.5 at  $491^\circ\text{C}$ .

Many equilibrium reactions have been investigated in this way, and it has been found that for each, there is a function of the concentrations of the species involved that has a constant value at equilibrium.

<sup>†</sup> Strictly speaking  $K_1 = 723 \text{ (mol/L)}^{-1}$ ; look at the units of the left-hand expression in Equation 9.2. For the NSW HSC units are not required for equilibrium constants, so sometimes they will be omitted in this book. An explanation for ‘units’ or ‘no units’ is on p. 321–2.

**TABLE 9.2 Equilibrium concentrations at 491°C for the reaction**  
 $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$

[I <sub>2</sub> ] (× 10 <sup>-3</sup> mol/L)	[H <sub>2</sub> ] (× 10 <sup>-3</sup> mol/L)	[HI] (× 10 <sup>-3</sup> mol/L)	[HI] <sup>2</sup> [H <sub>2</sub> ][I <sub>2</sub> ]
2.840	2.276	17.15	45.50
1.634	0.967	8.49	45.61
4.058	1.720	17.79	45.34
2.597	2.597	17.62	46.03
1.896	1.896	12.84	45.88
1.011	1.011	6.83	45.64
average: 45.5			

Let us represent any chemical reaction by:



where A and B are reactants, L and M are products (molecules, ions or atoms);  $a$ ,  $b$ ,  $l$  and  $m$  are the number of each species involved. When this reaction is at equilibrium, the expression:

$$\frac{[\text{L}]^l[\text{M}]^m}{[\text{A}]^a[\text{B}]^b}$$

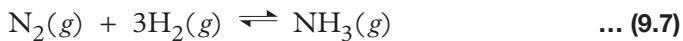
has a constant value, regardless of the starting concentrations of the substances involved. The constant is called the **equilibrium constant**,  $K$ . In other words, when Reaction 9.5 is at equilibrium:

$$\frac{[\text{L}]^l[\text{M}]^m}{[\text{A}]^a[\text{B}]^b} = K \quad \dots (9.6)$$

Equations 9.2 and 9.4 are simply this general relation applied to Reactions 9.1 and 9.3 respectively.

### To illustrate further

The reaction between hydrogen and nitrogen to form ammonia (considered in Section 6.7):



will be at equilibrium, according to Equation 9.6, when:

$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = K_3 \quad \dots (9.8)$$

Equation 9.6 is called the **equilibrium expression** (at constant temperature) for Reaction 9.5. Alternatively, it is called the **condition for equilibrium** for Reaction 9.5. Sometimes it is referred to as the *expression for the equilibrium constant*.†

† The phrase ‘expression for the equilibrium constant’, though widely used, can be misleading. It implies that the left-hand expression of Equation 9.6 (called the reaction quotient,  $Q$ ) is the equilibrium constant. This is not true. The equilibrium constant is a physical constant, that is, a number; the reaction quotient,  $Q$ , is a reaction variable, that is, it can have all sorts of values. Only at equilibrium is the reaction quotient equal to the equilibrium constant. Hence the phrases ‘equilibrium expression for the reaction’ and ‘condition for equilibrium’ are preferable.

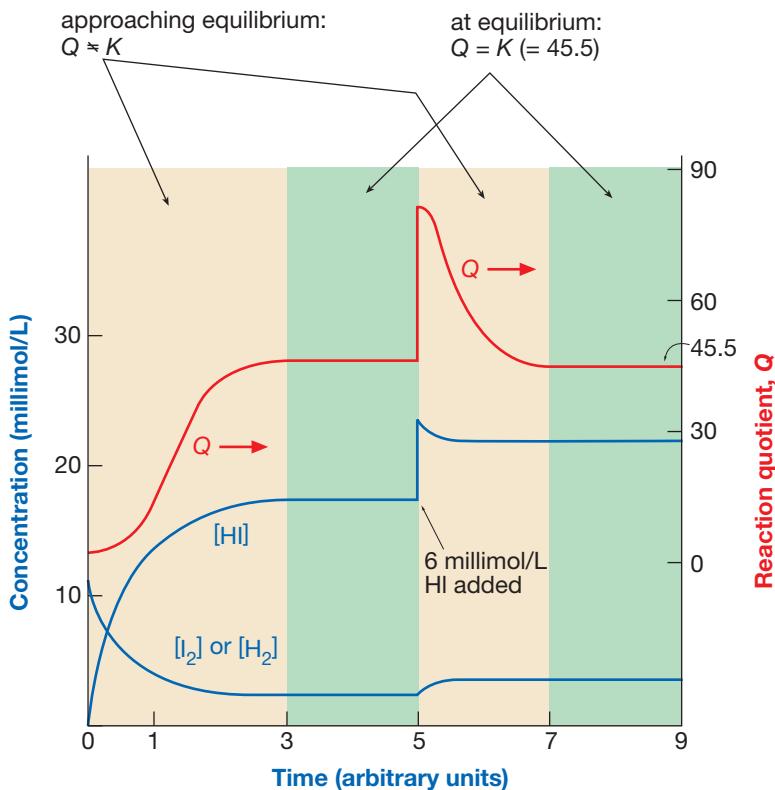
The left-hand expression of Equation 9.6 is called the **reaction quotient**: the symbol  $Q$  is often used for it. By definition:

$$Q = \frac{[L]^l[M]^m}{[A]^a[B]^b} \quad \dots (9.9)$$

A reaction is at equilibrium if its reaction quotient,  $Q$ , is equal to the equilibrium constant,  $K$ . If the reaction is not at equilibrium,  $Q$  has a value different from  $K$ , and chemical reaction occurs until  $Q$  equals  $K$ , that is, until equilibrium is reached.

If we mix hydrogen and iodine (Reaction 9.3) at 491°C in the absence of hydrogen iodide, then initially the reaction quotient,  $[HI]^2/[H_2][I_2]$ , is virtually zero, that is,  $Q$  is very much less than  $K_2$  which has the value 45.5. Hence hydrogen and iodine react to form hydrogen iodide so that  $[H_2]$  and  $[I_2]$  decrease and  $[HI]$  increases. This causes  $Q$  to increase. Reaction continues in this direction until  $Q$  equals  $K_2$ , when the reaction will be at equilibrium. This is illustrated in the left part of Figure 9.1 (up to Time = 5). Alternatively, if we suddenly heat a sample of pure hydrogen iodide to 491°C,  $Q$  will be extremely large (because  $[H_2]$  and  $[I_2]$  in the denominator are both extremely small). Hence HI will decompose to H<sub>2</sub> and I<sub>2</sub>, causing  $[H_2][I_2]$  to increase and  $[HI]$  to decrease, and therefore  $Q$  to decrease. Reaction will continue in this direction until  $Q$  equals  $K_2$ , when again the system will be at equilibrium.

**FIGURE 9.1**  
Changes in concentrations of reactants and products and in the reaction quotient  $Q$  as the reaction  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  approaches equilibrium, starting with an equimolar mixture of H<sub>2</sub> and I<sub>2</sub>. Note that at Time = 7 to 9 the equilibrium concentrations of H<sub>2</sub>, I<sub>2</sub> and HI are different from those in the earlier equilibrium at Time = 3 to 5, though the value of  $Q$  is the same for both equilibrium mixtures—equal to the value of the equilibrium constant  $K$ , 45.5



If in Figure 9.1 at Time = 5 some hydrogen iodide is added to the equilibrium mixture, the concentrations and the value of  $Q$  will follow the curves shown there. Equilibrium will be re-established when  $Q$  again becomes equal to  $K$ ; that is, after Time = 7. Although  $Q$  has returned to the original value, the actual concentrations are all different from the values at Time = 5.

In general:

If  $Q < K$ , reaction goes from left to right until  $Q = K$ .

If  $Q > K$ , reaction goes from right to left until  $Q = K$ .

If  $Q = K$ , reaction is at equilibrium.

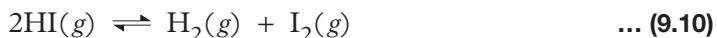
## 9.4 RULES FOR WRITING EQUILIBRIUM EXPRESSIONS

The equilibrium constant,  $K$ , for a reaction is the constant to which the reaction quotient,  $Q$ , is equal when the reaction is at *equilibrium* at the specified temperature. Two rules must be noted:

- 1 *The reaction quotient (and hence the equilibrium expression) is always written with products (right-hand side) in the numerator (top line) and reactants (left-hand side) in the denominator (bottom line).*

$$\begin{aligned} Q \text{ or } K &= \frac{[\text{products}]}{[\text{reactants}]} \\ &= \frac{\text{concentration of right-hand substances}}{\text{concentration of left-hand substances}} \end{aligned}$$

It follows then that  $K_4$ , the equilibrium constant for:



is the reciprocal of  $K_2$ , because by the rule just given:

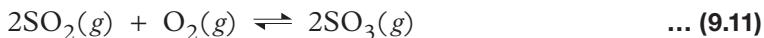
$$\text{at equilibrium, } K_4 = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

whereas for Reaction 9.3:

$$\text{at equilibrium, } K_2 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

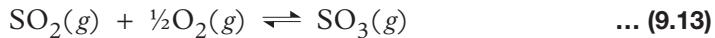
- 2 *The equilibrium expression always uses the coefficients of the reaction as written.*

For the reaction:



$$\text{at equilibrium, } K_5 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \quad \dots (9.12)$$

whereas for the reaction:



$$\text{at equilibrium, } K_6 = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{\frac{1}{2}}} \quad \dots (9.14)$$

It follows then that:

$$K_5 = K_6^2$$

## Units for equilibrium constants

Reaction quotients generally have units, and hence equilibrium constants, as here defined, generally have units. For Reaction 9.11 the reaction quotient and hence

the equilibrium constant,  $K_5$ , have the units  $(\text{mol/L})^{-1}$  (from Equation 9.12). On the other hand for Reaction 9.13,  $K_6$  has the units  $(\text{mol/L})^{-\frac{1}{2}}$ . The equilibrium constant,  $K_3$ , for Reaction 9.7, has the units  $(\text{mol/L})^{-2}$ . For some reactions the equilibrium constant is dimensionless, that is, a pure number. For Reaction 9.3 it follows from the equilibrium expression 9.4 that  $K_2$  has no units.

More advanced chemistry texts often define equilibrium constants in a slightly different way to make them dimensionless for all reactions (though they have the same numerical values as those defined here). While this book will usually give units for equilibrium constants, it has to be recognised that equilibrium constants will often be given just as pure numbers. You may please yourself whether you give units or not.<sup>†</sup>

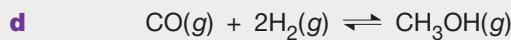
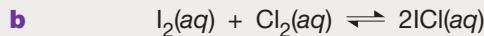
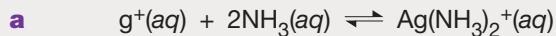
*If units are not given, concentrations must always be in mol/L.*

† This is the reason for the NSW HSC Syllabus saying that units are not required for equilibrium constants.

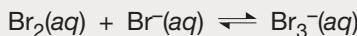


## Exercises

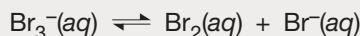
6 What is the equilibrium expression for each of the following reactions?



7 a The equilibrium constant for:



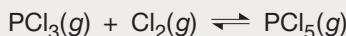
at 25°C is 18 (mol/L)<sup>-1</sup>. Calculate the equilibrium constant for:



b For the reaction:



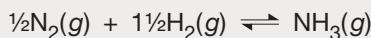
the equilibrium constant is 0.040 mol/L at 252°C. Calculate the equilibrium constant for:



8 For the reaction:



the equilibrium constant at 400°C is 39 (mol/L)<sup>-2</sup>. Calculate the equilibrium constant for:



9 At 300 K the equilibrium constant for:



is  $5.0 \times 10^{-3}$  (mol/L)<sup>-1/2</sup>. Calculate the equilibrium constant for:



## 9.5 MEASUREMENT OF EQUILIBRIUM CONSTANTS

Since the equilibrium constant for a reaction is equal to the equilibrium value of the reaction quotient,  $Q$ , equilibrium constants are frequently obtained by measuring equilibrium values of  $Q$ . The problem is to measure the concentration of the substances present at equilibrium without disturbing the equilibrium in the process. A simple titration of one species is often not possible. For example, if we attempt to estimate the concentration of iodine in the equilibrium:



by titrating an equilibrium mixture with sodium thiosulfate, we find that as we remove  $\text{I}_2$  during the titration, the equilibrium adjusts so quickly that  $\text{ICN}$  converts back to iodine, and therefore our titration actually gives us the sum of the  $\text{I}_2$  and  $\text{ICN}$  equilibrium concentrations.

The equilibrium constant for this reaction can be measured by using the fact that iodine is coloured whereas iodine cyanide is colourless; equilibrium concentrations of iodine can be obtained from measurements of the intensity of light absorption at suitable wavelengths without disturbing the equilibrium. Absorption of light is often used to measure concentrations of species involved in equilibria.

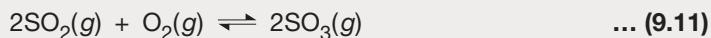
A pH meter measures the hydrogen ion concentration in a solution without altering its value and is therefore extremely useful for measuring equilibrium constants.

If we know the initial concentrations of all substances put into the equilibrium mixture, we only need to determine the equilibrium concentration of *one* species, because the reaction stoichiometry allows us to calculate all the other concentrations.

Some examples will illustrate how we calculate equilibrium constants from experimental measurements.

### Example 1

For the gaseous reaction:



it was found that at equilibrium at 900 K, the concentration of  $\text{SO}_3$  was nine times that of  $\text{SO}_2$  when the equilibrium concentration of oxygen was 0.068 mol/L. Calculate the equilibrium constant.

The equilibrium expression is:

$$K_5 = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

We are told that at equilibrium  $[\text{O}_2] = 0.068 \text{ mol/L}$  and  $[\text{SO}_3]/[\text{SO}_2] = 9$ . Hence:

$$K_5 = \frac{9^2}{0.068}$$

so that

$$K_5 = 1.2 \times 10^3 \text{ (mol/L)}^{-1}$$





## Example 2

0.0100 mole phosphorus pentachloride was placed in a 1.00 L flask at 523 K. It partially dissociated according to the equation:



At equilibrium, the concentration of chlorine was 0.0083 mol/L. Calculate the equilibrium constant for the reaction.

At equilibrium:

$$\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = K_7$$

The chemical equation tells us that one mole  $\text{PCl}_5$  produces one mole  $\text{Cl}_2$  and one mole  $\text{PCl}_3$ . If in our litre flask 0.0083 mole  $\text{Cl}_2$  was formed, then 0.0083 mole  $\text{PCl}_3$  was also formed; that is, at equilibrium:

$$\begin{aligned} [\text{PCl}_3] &= [\text{Cl}_2] \\ &= 0.0083 \text{ mol/L} \end{aligned}$$

Now this  $\text{PCl}_3$  and  $\text{Cl}_2$  came from  $\text{PCl}_5$ ; hence in our 1 L flask, 0.0083 mole  $\text{PCl}_5$  must have decomposed. Initially we had 0.0100 mole  $\text{PCl}_5$ , so at equilibrium we have only  $0.0100 - 0.0083 = 0.0017$  mole.

A simple but clear way of setting out such calculations is first to write the chemical equation, then to tabulate initial and equilibrium concentrations under the various species:

$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$			
Initially:	0.0100 mol/L	0	0
At equilibrium:	0.0100 – 0.0083	0.0083	0.0083
	0.0017	0.0083	0.0083
$K_7 = \frac{(0.0083)^2}{0.0017} \frac{(\text{mol/L})^2}{(\text{mol/L})}$			= 0.041 mol/L

Example 2 highlights the fact that if we know what we started with (in this case 0.0100 mol/L  $\text{PCl}_5$ ), then we only need to measure the equilibrium concentration of one substance, because we can use it along with the reaction stoichiometry to calculate the equilibrium concentrations of all other species involved in the equilibrium expression.

## 9.6 USE OF EQUILIBRIUM CONSTANTS

The value of  $K$  gives us both qualitative information about the position of equilibrium for the reaction and quantitative information about the equilibrium concentrations of species.

### Magnitude of $K$ and position of equilibrium

Recall from Section 4.6 that *position of equilibrium* means the extent to which the reaction has gone in the forward or reverse direction.

If  $K$  is large—say greater than  $10^3$ —then the equilibrium lies well to the right; it favours products. If  $K$  is small—say less than  $10^{-3}$ —then the equilibrium lies well to the left; it favours reactants. In other words, if  $K$  is large, the reaction goes almost to completion, but if  $K$  is small the reaction hardly goes at all. If  $K$

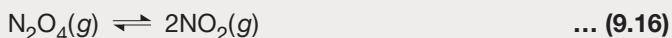
has a ‘middling’ value—say about 10 to 0.1—then at equilibrium there will be appreciable concentrations of reactants and products present.

## Using $K$ to decide if a reaction is at equilibrium

The value of  $K$  can be used to decide whether a particular reaction mixture is at equilibrium or not (by comparing the value of the reaction quotient,  $Q$ , with the value of  $K$ ). The following example illustrates.

### Example 3

For the equilibrium reaction:



the equilibrium constant is 0.48 at 100°C. 0.1 mol  $\text{N}_2\text{O}_4$  and 0.25 mol  $\text{NO}_2$  were placed in a 1.00 L flask at 100°C. Is the mixture at equilibrium? If not, in which direction will the reaction proceed?

The reaction is at equilibrium if the reaction quotient,  $Q$ , is equal to the equilibrium constant,  $K$ . Hence we need to calculate  $Q$ . For this reaction:

$$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad \dots (9.17)$$

$[\text{NO}_2] = 0.25/1 = 0.25 \text{ mol/L}$  and  $[\text{N}_2\text{O}_4] = 0.10/1 = 0.10 \text{ mol/L}$ .

Hence

$$Q = \frac{(0.25)^2}{0.10} \\ = 0.63$$

$K = 0.48$  so  $Q > K$ . Hence the reaction is not at equilibrium. It will proceed in the direction which decreases  $Q$  to make it equal to  $K$ . To decrease  $Q$  we need to decrease  $[\text{NO}_2]$  and increase  $[\text{N}_2\text{O}_4]$ . Hence reaction proceeds from right to left.



## Using $K$ to calculate an equilibrium concentration

If we know  $K$  for a reaction and equilibrium concentrations of some of the species involved, then we can use the equilibrium expression for the reaction to calculate equilibrium concentrations of other species.

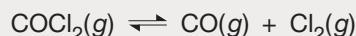
### Example 4

At 1000 K the equilibrium constant for the decomposition of phosgene into carbon monoxide and chlorine is 0.40.

- A sample of phosgene was placed in an evacuated container and heated to 1000 K. When equilibrium was reached, the concentration of carbon monoxide was 0.24 mol/L. Calculate the equilibrium concentration of phosgene.
- In a second experiment in which a different sample of phosgene was brought to equilibrium at 1000 K, the equilibrium concentration of phosgene was 0.18 mol/L. Calculate the equilibrium concentration of chlorine.



The chemical equation for the reaction is



for which the equilibrium expression is

$$\frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = K \quad \dots (9.18)$$

- a We want to calculate  $[\text{COCl}_2]$ , so rearranging:

$$[\text{COCl}_2] = \frac{[\text{CO}][\text{Cl}_2]}{K} \quad \dots (9.19)$$

We started with pure  $\text{COCl}_2$ , so from the chemical equation we know that at all stages,

$$[\text{CO}] = [\text{Cl}_2]$$

Hence if  $[\text{CO}] = 0.24 \text{ mol/L}$ , then  $[\text{Cl}_2] = 0.24 \text{ mol/L}$  and so substituting in Equation 9.19

$$\begin{aligned} [\text{COCl}_2] &= \frac{0.24 \times 0.24}{0.40} \\ &= 0.14 \text{ mol/L} \end{aligned}$$

- b Again we started with pure  $\text{COCl}_2$  so again we know that throughout the reaction and at equilibrium

$$[\text{CO}] = [\text{Cl}_2]$$

so we can rewrite Equation 9.18 as

$$\frac{[\text{Cl}_2]^2}{[\text{COCl}_2]} = K$$

and rearrange it to

$$[\text{Cl}_2] = \sqrt{K[\text{COCl}_2]}$$

Substituting the given values into this

$$\begin{aligned} [\text{Cl}_2] &= \sqrt{0.40 \times 0.18} \\ &= 0.27 \text{ mol/L} \end{aligned}$$

## Constancy of $K$ at constant temperature

Depending on conditions, the position of equilibrium may change, individual concentrations may change, the reaction quotient may change, but the value of the equilibrium constant does not change: it remains constant, provided temperature remains constant.

*The only factor that changes  $K$  is temperature;* we shall look at that in Section 9.8.

## Exercises

- 10 Dinitrogen tetroxide, in chloroform solution, dissociates into nitrogen dioxide:



The concentrations of the two species at equilibrium at 298 K can be determined from absorption of light (spectrophotometry). Values for three equilibrium mixtures are given below. Calculate the equilibrium constant for the reaction.

$[N_2O_4]$ (mol/L)	0.129	0.324	0.778
$[NO_2]$ (mol/L)	0.00117	0.00185	0.00284

- 11 To measure the equilibrium constant for the reaction:



1.00 mole of pure acetic acid and 0.18 mole of pure ethanol were mixed. At equilibrium, there was 0.171 mole of ethyl acetate. Calculate the equilibrium constant. (Hint: Let the volume of the equilibrium mixture be  $V$ ; you do not need to know its value!)

- 12 Methanol can be made by the reaction:



At 100°C, an equilibrium mixture was found to have the following concentrations:

$$[CO] = 3.76 \times 10^{-3} \text{ mol/L}; [H_2] = 4.30 \times 10^{-3} \text{ mol/L}; [CH_3OH] = 4.17 \times 10^{-8} \text{ mol/L}$$

Calculate the equilibrium constant for the reaction. What would be the effect on the value for  $K$  of using a catalyst for this reaction?

- 13 One mole of each of hydrogen and carbon dioxide was placed in a closed container of 1.00 L volume and brought to equilibrium at 1260 K, the reaction being:



The equilibrium mixture was rapidly cooled—so rapidly that the equilibrium was unable to adjust itself as the temperature changed (because the rates of both the forward and reverse reactions became very small). The system was therefore ‘frozen’ into the state corresponding to equilibrium at 1260 K. The amount of  $CO_2$  present was measured; it corresponded to a concentration of 0.44 mol/L at 1260 K. Calculate the equilibrium constant for this reaction at 1260 K.

- 14 For the reactions listed below, the values of the equilibrium constants at specified temperatures are given in brackets after the equations. For each reaction at the specified temperature, does the equilibrium lie:

- i well to the left
- ii well to the right or
- iii about in the middle (comparable concentrations of reactants and products)?

- a  $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$  ( $K = 1.6 \times 10^7$  at 298 K)
- b  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  ( $K = 1.6 \times 10^{-3}$  at 1000 K)
- c  $Br_2(aq) + Br^-(aq) \rightleftharpoons Br_3^-(aq)$  ( $K = 18$  at 298 K)
- d  $I_2(g) \rightleftharpoons 2I(g)$  ( $K = 4 \times 10^{-5}$  at 1000 K)
- e  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  ( $K = 0.48$  at 373 K)
- \*f  $Zn^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Zn(CN)_4^{2-}(aq)$  ( $K = 10^{19}$  at 298 K)
- \*g  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$  ( $K = 10^{-3}$  at 2000 K)
- \*h  $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$  ( $K = 4 \times 10^5$  at 400 K)

- 15 For the reaction:



the equilibrium constant is 159 at 500 K. Two mixtures are prepared with the concentrations given below. For each mixture, is the reaction at equilibrium? If not, in which direction will reaction proceed?

- a  $[H_2] = 0.14, [I_2] = 0.078, [HI] = 1.74 \text{ mol/L}$
- b  $[H_2] = 0.32, [I_2] = 0.24, [HI] = 0.83 \text{ mol/L}$

**16** For the reaction:



the equilibrium constant at 1500 K is  $1.0 \times 10^{-5}$ .

- a** A particular mixture at 1500 K was 0.050 mol/L in  $\text{N}_2$ , 0.025 mol/L in  $\text{O}_2$  and 0.0030 mol/L in NO. Is this mixture at equilibrium? If not, in which direction will the reaction go? Give your reasoning.
- b** Another mixture at the same temperature was 0.35 mol/L in  $\text{N}_2$ , 0.60 mol/L in  $\text{O}_2$  and 0.0010 mol/L in NO. Is this mixture at equilibrium? If not, in which direction will the reaction go?

**17** At 100°C the equilibrium constant for the reaction:



is 0.48.

- a** A mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  is brought to equilibrium. The equilibrium concentration of  $\text{N}_2\text{O}_4$  is 0.15 mol/L. Calculate the concentration of  $\text{NO}_2$ .
  - b** Another equilibrium mixture at the same temperature has  $\text{NO}_2$  at a concentration of 0.25 mol/L. Calculate the equilibrium concentration of  $\text{N}_2\text{O}_4$ .
- 18** **a** Calculate the ratio  $[\text{I}_3^-]/[\text{I}_2]$  in a solution at 298 K in which the equilibrium concentration of iodide is  $7.00 \times 10^{-3}$  mol/L, using the equilibrium constant from Table 9.1.
- b** What equilibrium concentration of iodide is needed to convert 99% of the iodine initially added to a solution to triiodide?

**19** For the reaction



the equilibrium constant at 250°C is 0.042.

- a** A sample of  $\text{PCl}_5$  was placed in a vessel and heated to 250°C. At equilibrium the concentration of chlorine was 0.084 mol/L. Calculate the equilibrium concentrations of  $\text{PCl}_3$  and  $\text{PCl}_5$ .
- b** Another sample of  $\text{PCl}_5$  was similarly heated to 250°C. At equilibrium the concentration of  $\text{PCl}_5$  was 0.095 mol/L. Calculate the equilibrium concentration of  $\text{PCl}_3$ .

## 9.7 EQUILIBRIUM EXPRESSIONS AND LE CHATELIER'S PRINCIPLE

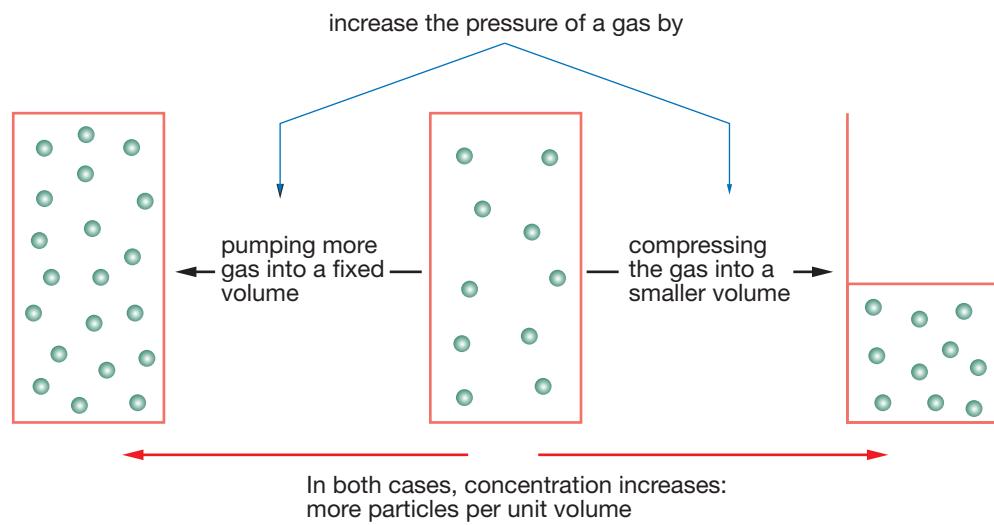
In Sections 4.6 to 4.8, we saw that Le Chatelier's principle could be used to predict the way an equilibrium reaction adjusts itself in response to a change in conditions, for example addition of a reactant or change in pressure. The equilibrium expression in Equation 9.6 allows similar predictions to be made, with the added advantage that it allows them to be made quantitatively as Example 4 and Exercises 17 to 19 show.

For gaseous reactions we often consider pressure changes and use Le Chatelier's principle to deduce their effects. The equilibrium expression leads to the same conclusions once we recognise that in a gas at constant temperature:

*pressure is proportional to concentration*

If we compress a gas mixture into half its original volume, then we double the pressure and we double the concentration of each of the species present (same number of moles in half the volume). This is because pressure of a gas results

from gas particles hitting the walls of the container. The more particles in a given volume, the more collisions there are (per unit area per unit time) between gas particles and the walls of the container and so the greater is the pressure. Figure 9.2 illustrates the relation between pressure and concentration.



**FIGURE 9.2**  
In a gas concentration is proportional to pressure

Because pressure is proportional to concentration,

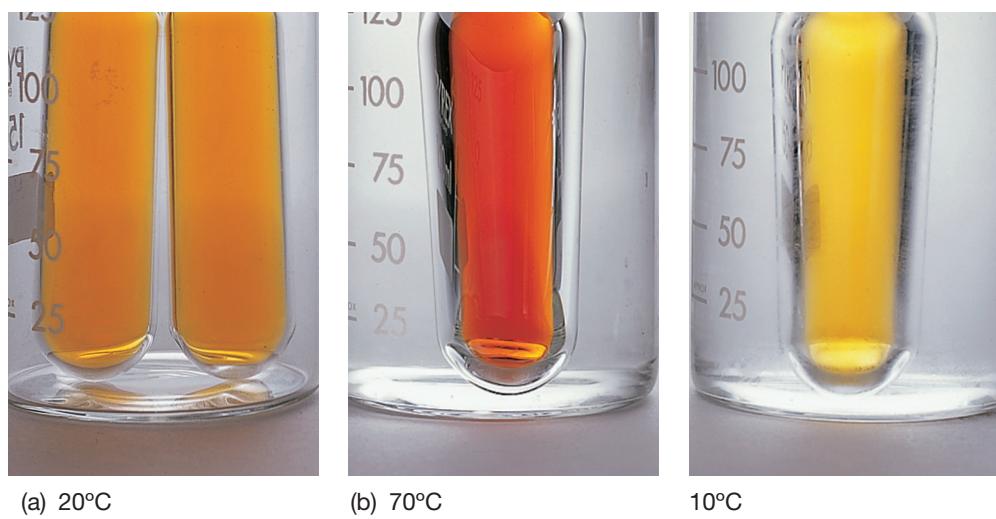
predictions from the equilibrium expression and from Le Chatelier's principle are the same (provided temperature remains constant).

Because the equilibrium expression, Equation 9.6, applies only to constant temperature, it tells us nothing about how temperature changes the position of equilibrium. Le Chatelier's principle is particularly useful in this regard.

## 9.8 TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANTS

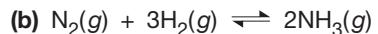
The values of equilibrium constants change quite significantly with temperature. When temperature is increased, some equilibrium constants increase while others decrease. Values for some reactions are shown in Table 9.3.

Le Chatelier's principle can be used to predict the effect of temperature upon an equilibrium constant as Exercise 20 will illustrate.



Effect of temperature upon the equilibrium  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ .  $\text{N}_2\text{O}_4$  is colourless while  $\text{NO}_2$  is brown. Both sealed containers in (a) (at 20°C) have the same colour which shows that they contain the same amount of reaction mixture. One sealed container is then placed in a beaker of water at 70°C while the other is placed into water at 10°C. This is shown in (b). The changes in colour show that as temperature decreases the equilibrium moves to the left

**TABLE 9.3 Temperature dependence of some equilibrium constants<sup>a</sup>**



Temperature (K)	K	Temperature (K)	K
273	$5.7 \times 10^{-4}$	298	$4.0 \times 10^8$
298	$4.7 \times 10^{-3}$	500	60
373	0.48	700	0.26
500	41.4	900	$5.4 \times 10^{-3}$
(c) $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$		(d) $\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$	
Temperature (K)	K	Temperature (K)	K
600	450	273	1360
700	30	298	723
850	1.6	330	372
1000	0.21	370	190

a Equilibrium constants are as defined in Equation 9.6.

## Exercises

- 20 a** By Le Chatelier's principle, in which direction does an exothermic reaction move when the temperature is increased? What is the effect of this on the equilibrium value of the reaction quotient? Hence how does the value of the equilibrium constant change as temperature increases?
- b** Repeat (a) for an endothermic reaction.
- c** Hence write a general statement summarising the way that equilibrium constants change as temperature increases.

- 21** Predict whether the equilibrium constant for each of the following reactions increases or decreases as temperature rises:

- a**  $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$   $\Delta H$  is negative
- b**  $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$   $\Delta H$  is positive
- c**  $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$  exothermic
- d**  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$  endothermic

- 22** At 1000 K the equilibrium constant for



is  $174 \text{ (mol/L)}^{-1}$ .

- a** Calculate the concentration of oxygen needed to obtain:
- i** a 50% conversion of  $\text{SO}_2$  to  $\text{SO}_3$  (that is to make  $[\text{SO}_3]/[\text{SO}_2] = 1.0$ ) and
  - ii** a 90% conversion (that is to make  $[\text{SO}_3]/[\text{SO}_2] = 9.0$ ).
- b** Are your answers for (a) (i) and (ii) consistent with Le Chatelier's principle? Explain.

Having considered a major chemical concept that is often involved in industrial chemistry, let us now turn to the manufacture of a very important industrial chemical, sulfuric acid.

## 9.9 USES OF SULFURIC ACID

Worldwide more sulfuric acid is produced than any other chemical. Some of the major uses of sulfuric acid are for the manufacture of:

- **fertiliser.** Most of the sulfuric acid produced is used to make superphosphate fertiliser. Rock phosphate contains  $\text{Ca}_3(\text{PO}_4)_2$  which is insoluble and so of no use to plants. Reaction with sulfuric acid forms a mixture of calcium dihydrogen phosphate, which is soluble, along with calcium sulfate; this mixture is sold as superphosphate.
- Sulfate of ammonia, another common fertiliser, is made from ammonia and sulfuric acid.
- **ethanol** from ethylene (Section 1.16).
- **detergents** (discussed in Sections 10.12 and 10.14).
- **lead-acid batteries for motor cars.** The electrolyte in car batteries is approximately 4 mol/L sulfuric acid.
- **viscose rayon and other synthetic fibres.** Rayon or viscose is reconstituted cellulose: degraded or short-fibre cellulose is dissolved in sodium hydroxide solution, treated chemically to facilitate chain growth then spun through small holes into dilute sulfuric acid solution to form new fibres.

The starting compounds for some nylons use sulfuric acid in their manufacture.

- **pigments** for paints, plastics and paper, particularly titanium dioxide from ilmenite.
- **explosives, drugs, dyes and pesticides** (generally with nitric acid).

In addition sulfuric acid is widely used in:

- **steel processing (pickling).** Sulfuric acid is used to remove surface rust (iron(III) oxide) from steel before galvanising, coating it with tin or applying powder coatings.
- **oil refining.** Many unwanted impurities are removed from petroleum products by reaction with sulfuric acid.
- **extraction of metals from their ores.** Zinc is often extracted from sulfide ores by first roasting the ore to form oxide, dissolving the oxide in sulfuric acid then obtaining the metal by electrolysis. Uranium compounds are commonly obtained from their ores by leaching with sulfuric acid.

The starting point for manufacture of sulfuric acid is either pure sulfur obtained from deposits of the element at several locations around the Earth or sulfur compounds that are by-products from other manufacturing or extraction processes. Let us start with elemental sulfur.

## 9.10 EXTRACTION OF SULFUR

Although most sulfur in the Earth exists as sulfides or sulfates, there are a few deposits of elemental sulfur, notably in Louisiana and Texas in the USA, Mexico and Poland. Sulfur is extracted from these deposits by what is called the **Frasch process**.

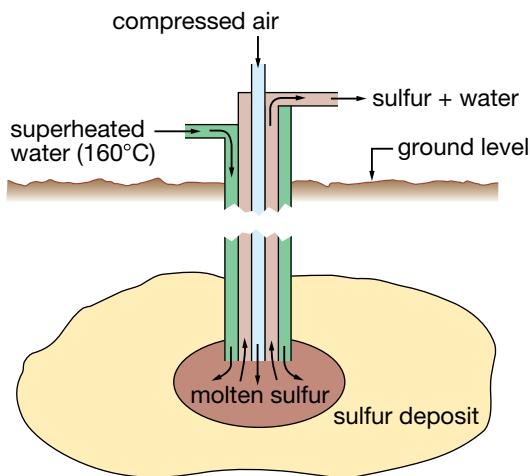
### Frasch process

Superheated water at 160°C (meaning water heated under pressure so that it does not boil) is forced down the outer of three concentric pipes into the sulfur

deposit (Figure 9.3). This melts the sulfur (melting point 113°C) and forms an emulsion (small droplets of one liquid dispersed through another liquid). Compressed air is blown down the inner pipe and this forces the water–sulfur emulsion up the middle pipe. When the mixture cools, solid sulfur separates from liquid water and so 99.5% sulfur is obtained.

FIGURE 9.3

The Frasch process for extracting sulfur from underground deposits



Worldwide about half of the sulfur used to make sulfuric acid is obtained by this process.

This process works because of the low melting point and low density of sulfur. The superheated water easily melts the sulfur and the water–sulfur emulsion has a sufficiently low density for the compressed air to be able to lift it to the surface. The insolubility of sulfur in water is also a factor; it means that after cooling the sulfur easily separates from the water.

## Environmental issues

While sulfur itself is non-volatile and odourless and so does not escape into the environment, sulfur is easily oxidised to sulfur dioxide or reduced to hydrogen sulfide, both of which are serious air pollutants at quite low concentrations. Consequently care is needed to ensure that there is no inadvertent oxidation or reduction of the sulfur. Because the water used may have dissolved impurities that were present in the deposit, it is necessary to re-use the water and not discharge it into the environment. Unlike many other underground mining ventures where it is possible to back-fill the mine with processed tailings from the extraction process, it is very difficult to back-fill the underground caverns left by extraction of sulfur. Earth subsidences over the mining area are therefore possible.

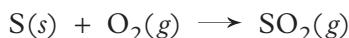
## Sulfur from natural gas and oil

Natural gas and crude oil often contain significant amounts of hydrogen sulfide—up to 25% in the natural gas from France and Canada. The usual method of removing hydrogen sulfide from gas and oil produces elemental sulfur. Natural gas and crude oil are therefore major sources of sulfur for the manufacture of sulfur dioxide (and sulfuric acid).

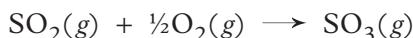
## 9.11 INDUSTRIAL SYNTHESIS OF SULFURIC ACID

The industrial synthesis of sulfuric acid involves three steps:

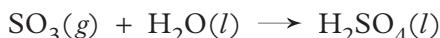
- 1 conversion of sulfur to sulfur dioxide:



- 2 conversion of sulfur dioxide to sulfur trioxide:



- 3 absorption of sulfur trioxide in water to form sulfuric acid:



This process is called the **contact process** (because the  $SO_2$  and  $O_2$  gases must come into contact with a catalyst). Let us look at the three steps in turn.

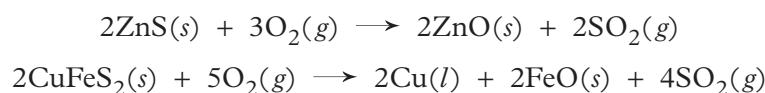
## 9.12 PRODUCTION OF SULFUR DIOXIDE

When the process starts with pure sulfur, liquid sulfur is sprayed into an excess of dry air at atmospheric pressure. The amount of dry air used is such that it contains about 33% more oxygen than is needed for conversion of  $S$  to  $SO_2$  and to  $SO_3$ . The air is dried by passage through sulfuric acid.

The combustion of sulfur generates a lot of heat. It is therefore necessary to cool the reacted gas stream, often at  $1000^{\circ}\text{C}$  to about  $400^{\circ}\text{C}$ , the optimum temperature for admission to the  $SO_2$  to  $SO_3$  converter (see below).

### Alternative sources of sulfur dioxide

Some sulfuric acid plants have been deliberately built near copper or zinc smelters so that they can use the unwanted  $SO_2$  from roasting sulfide ores as their starting material:



This has the advantages of disposing of the potentially polluting  $SO_2$  from the smelters and providing a relatively cheap starting material for the sulfuric acid plant. In Australia most sulfuric acid plants obtain their  $SO_2$  in this way.

## 9.13 CONVERSION OF $SO_2$ TO $SO_3$

The oxidation of  $SO_2$  to  $SO_3$  is the most difficult part of the process. The reaction is an equilibrium one:



### Equilibrium considerations

From Le Chatelier's principle the way to force this equilibrium to the right—that is to increase the percentage conversion of  $SO_2$  to  $SO_3$ —is to use:



Part of the sulfuric acid plant operated by WMC Resources Limited at Mt Isa, Queensland. The plant is located near a large copper smelter so that it can use the sulfur dioxide formed there as the starting material for making sulfuric acid

- excess of oxygen
- high pressure (because  $1\frac{1}{2}$  moles  $\rightarrow$  1 mole) and
- a low temperature (for an exothermic reaction lowering the temperature pushes the reaction in the heat-releasing direction, that is to the right).

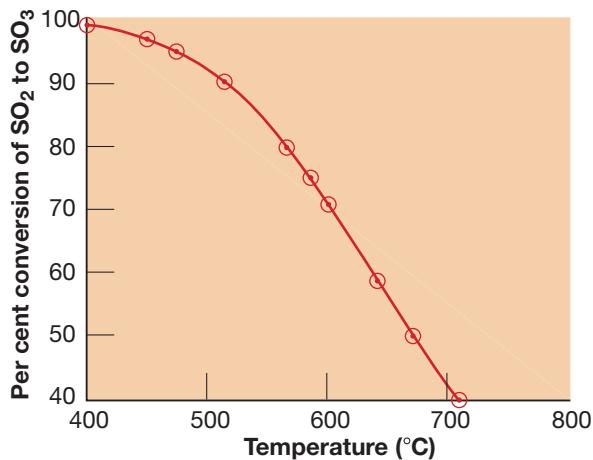
In terms of the equilibrium expression, we can rearrange Equation 9.14 on p. 321 to:

$$\frac{[\text{SO}_3]}{[\text{SO}_2]} = K_6[\text{O}_2]^{\frac{1}{2}}$$

This shows that percentage conversion is increased by increasing the oxygen pressure (equivalent to concentration, Section 9.7). A typical input mixture for the  $\text{SO}_2$  to  $\text{SO}_3$  converter is 10 kPa  $\text{SO}_2$ , 10 kPa  $\text{O}_2$  and 80 kPa  $\text{N}_2$ , assuming an initial mixture into the sulfur burner of 1 mol S, 2 mol  $\text{O}_2$  and thus 8 mol  $\text{N}_2$  (as air) at a total pressure of about 100 kPa. The pressure (concentration) of oxygen can be increased either by operating at a higher total pressure or by using pure oxygen as reactant instead of air. It turns out that neither alternative is cost effective for the small increase in yield that it would produce. Most sulfuric acid plants operate at slightly above atmospheric pressure using just a small excess of oxygen in the mixture.

The main determinant of yield is temperature (since  $K_6$  decreases rapidly with temperature, Table 9.3(c)). Figure 9.4 shows how the percentage conversion varies with temperature. From an equilibrium viewpoint an operating temperature of about 400°C would produce yields of around 99%.

**FIGURE 9.4**  
Percentage conversion of  $\text{SO}_2$  to  $\text{SO}_3$  as a function of temperature for an initial mixture of 10 kPa  $\text{SO}_2$  and 10 kPa  $\text{O}_2$  (with 80 kPa  $\text{N}_2$ )



## Rate considerations

As we saw with the synthesis of ammonia (Section 6.7), for an industrial process there are rate considerations as well as equilibrium ones, and rate generally increases as temperature increases. A low temperature such as 400°C may mean that the equilibrium lies further to the right, but it also means that the rate becomes very low. Reaction 9.13 is quite slow even at high temperatures. Therefore *a catalyst is needed*.

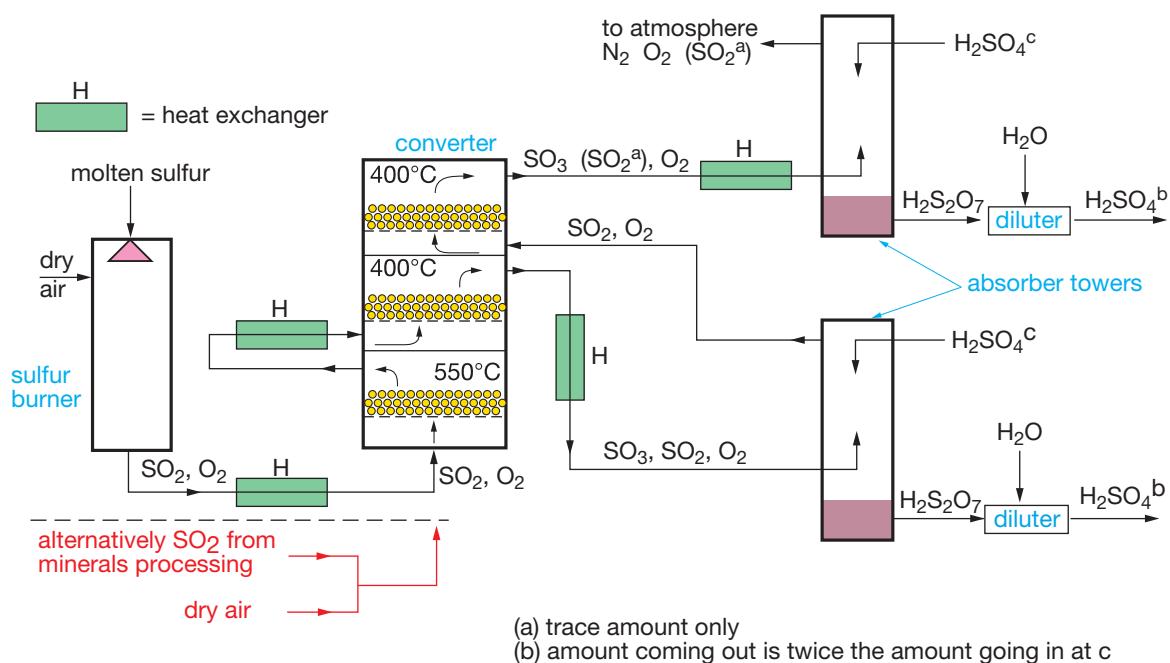
The catalyst used in the contact process is vanadium(V) oxide,  $\text{V}_2\text{O}_5$ , supported on porous silica pellets (made by heating silica gel). It produces a high reaction rate at above 500°C, while the reaction is not too slow at 400°C.

## Compromise conditions

As with ammonia synthesis a compromise between high yield and high rate is used. For sulfur dioxide oxidation the compromise takes the following form.

The reaction mixture is passed over a catalyst bed at an operating temperature of about 550°C. Approximately 70% of the SO<sub>2</sub> is oxidised very quickly. The reaction mixture is then cooled to about 400°C before being passed over a second catalyst bed. At this temperature reaction proceeds more slowly but the yield increases to about 97%. In the past this was considered satisfactory, the SO<sub>3</sub> was removed and the remaining gas exhausted to the atmosphere.

However today discharge of that amount of SO<sub>2</sub> to the atmosphere is not acceptable and so steps have to be taken to increase the yield further. This is done by removing the SO<sub>3</sub> from the gas stream (next sub-section) then passing the remaining gas mixture over another bed of catalyst to convert most of the remaining SO<sub>2</sub> to SO<sub>3</sub>, which is again dissolved out. In total this produces about a 99.7% conversion of SO<sub>2</sub> to SO<sub>3</sub> and emission of the remaining 0.3% of the original SO<sub>2</sub> to the atmosphere is acceptable (and allowed by government regulations in most countries). A flowchart of the whole process is shown in Figure 9.5.



## In summary

The conditions used for conversion of SO<sub>2</sub> to SO<sub>3</sub> are:

- a pressure of a little above normal atmospheric pressure (100 kPa)
- a small excess of oxygen
- a catalyst of vanadium(V) oxide supported on silica
- temperatures of catalyst beds of 550°C (for high rate) and 400°C (for high conversion).

## Energy considerations

Both the burning of sulfur and the conversion of SO<sub>2</sub> to SO<sub>3</sub> are exothermic reactions. Modern plants arrange to use some of the heat released during

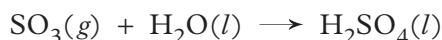
FIGURE 9.5  
Production of sulfuric acid by the contact process

the process to melt the sulfur and use the rest to form steam for electricity generation. In this way the process can produce a large proportion of the energy needed to operate the plant. Designing energy efficiency into such plants is not only cost effective, but it also minimises environmental damage.

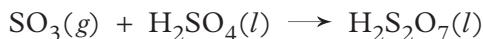
The temperature of the gas stream entering the converter is reduced to 400°C so that the heat of reaction will produce the desired 500 to 600°C in the first catalyst bed. Each catalyst bed is a shallow tray of porous pellets with large surface areas and with the vanadium(V) oxide catalyst deposited thinly but uniformly over the whole surface area.

## 9.14 CONVERSION OF SULFUR TRIOXIDE TO SULFURIC ACID

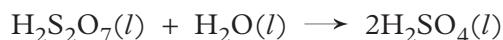
The final step in the synthesis of sulfuric acid is effectively reaction of SO<sub>3</sub> with water:



Because this reaction is so exothermic, spraying water into the SO<sub>3</sub>-containing gas stream produces a fine mist of sulfuric acid droplets in the residual gas (N<sub>2</sub> with some O<sub>2</sub>). It is difficult to separate this sulfuric acid mist from the gas. To overcome this problem the SO<sub>3</sub> gas stream is passed into concentrated sulfuric acid: SO<sub>3</sub> readily dissolves in sulfuric acid to form *oleum*:



Oleum reacts with water to form sulfuric acid:



In the absorber towers of Figure 9.5 SO<sub>3</sub> is dissolved in sulfuric acid and water is added at a controlled rate to convert the oleum to sulfuric acid.

Modern sulfuric acid plants use two absorber towers, one which absorbs the bulk of the sulfur trioxide formed and which passes the residual gas back to the final catalyst tray of the converter and a second which absorbs the final amounts of SO<sub>3</sub> formed then vents its residual gas (N<sub>2</sub> with a small amount of O<sub>2</sub> and just a trace of SO<sub>2</sub>) to the atmosphere.

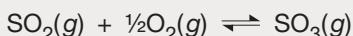
98% sulfuric acid (with the remaining 2% being water) is drawn off periodically from both absorbers. This constant boiling point mixture is the final product of the plant. It is common ‘concentrated’ sulfuric acid.

### Exercises

- 23** In the industrial synthesis of ammonia (Section 6.7) the problem of incomplete conversion of reactants to NH<sub>3</sub> was overcome by condensing out the ammonia then recycling the unreacted gas back through the catalytic reactor. Why would recycling not work in the synthesis of sulfuric acid? Alternatively what conditions would need to be in place to make reactant recycling work?
- \*24** Explain how a mixture of 1 mol S, 2 mol O<sub>2</sub> and thus 8 mol N<sub>2</sub> going into the sulfur burner in the contact process gives rise to pressures of 10 kPa SO<sub>2</sub>, 10 kPa O<sub>2</sub> and 80 kPa N<sub>2</sub> (if the total pressure is 100 kPa) going into the converter. Also explain why we can say that this mixture provides a 100% excess of oxygen for the SO<sub>2</sub> to SO<sub>3</sub> conversion.

**25** Suppose that passage of the reactant mixture through the first two stages of the converter in Figure 9.5 had converted 97% of the  $\text{SO}_2$  to  $\text{SO}_3$ . This  $\text{SO}_3$  was then removed by passage through the absorber. The gas stream was then returned to the converter where it passed through the third catalyst bed. This converted 90% of the remaining  $\text{SO}_2$  to  $\text{SO}_3$  which was removed by the second absorber before the gases were vented to the atmosphere. What percentage of the original  $\text{SO}_2$  is released to the atmosphere?

**26** For the reaction:



at  $600^\circ\text{C}$  an equilibrium concentration of oxygen of  $9.0 \times 10^{-4}$  mol/L ( $= 6.5 \text{ kPa}$ ) produces a 70% conversion of  $\text{SO}_2$  to  $\text{SO}_3$  (meaning that  $[\text{SO}_3]/[\text{SO}_2] = 70/30$ ).

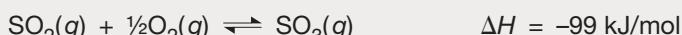
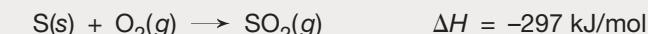
- Calculate the equilibrium constant at this temperature.
- Calculate the equilibrium concentration of oxygen that would be needed to produce an 80% conversion. At this temperature

$$\text{pressure in kPa} = 7.25 \times 10^3 \times \text{concentration in mol/L}$$

Hence calculate the pressure of oxygen required. A 70% conversion is obtained at  $600^\circ\text{C}$  using a total pressure in the reactor of 100 kPa. Show that the pressure in the reactor would need to be increased to about 160 kPa in order to obtain an 80% conversion by using air to provide the extra oxygen pressure needed.

- 27 a** A particular sulfuric acid plant produced 1000 tonnes of sulfuric acid per day while operating at a 99.7% conversion of  $\text{SO}_2$  to  $\text{SO}_3$ . What mass of  $\text{SO}_2$  does this plant discharge to the atmosphere per day?
- b** Compare this with the  $\text{SO}_2$  emissions from a coal-burning power station. A 600-megawatt power station burns 150 tonnes of coal per hour 24 hours per day. If this coal contains 0.3% sulfur, what mass of  $\text{SO}_2$  is discharged per day?

**28** The heats of reaction for the contact process are:



Calculate the amount of heat released by these chemical reactions per tonne of sulfuric acid formed. What mass of water could this amount of energy heat from  $20^\circ\text{C}$  to  $100^\circ\text{C}$ ? The specific heat capacity of water is  $4.18 \text{ J K}^{-1} \text{ g}^{-1}$ .

#### WEBSITE

For a survey of where and by whom sulfuric acid is manufactured in Australia and what it is used for:

<http://www.chemlink.com.au/sulfuric.htm>

(no chemistry involved!)



## 9.15 PROPERTIES OF SULFURIC ACID

Sulfuric acid is a colourless, viscous, dense, non-volatile liquid. The 98% product has a constant boiling point of  $338^\circ\text{C}$  and a density of 1.84 g/mL. It is a strong acid, meaning that it readily gives up hydrogen ions to water or to a base.

Most of the uses of sulfuric acid are based on its acid properties rather than on the fact that it contains sulfur or sulfate.

Sulfuric acid is the cheapest of the common acids to produce.

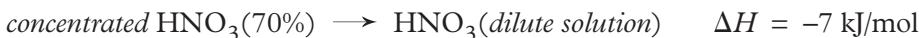
## 9.16 IONISATION OF SULFURIC ACID

Sulfuric acid as produced by the contact process is 98%  $\text{H}_2\text{SO}_4$ . When this is diluted with water, a large amount of heat is released:



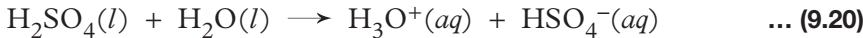
This dilution is very exothermic. So much so that there is serious risk of boiling the water and splashing acid. The risk is minimised by adding acid *slowly* to water: *never add water to concentrated sulfuric acid!*<sup>†</sup>

When concentrated hydrochloric or nitric acid is added to water, heat is released, but the amount is much less than for sulfuric acid:



Although you must always take great care when using concentrated acids, the danger in diluting hydrochloric and nitric acids is far less than for sulfuric. Why, then, is diluting sulfuric acid so much more exothermic?

The main reason is that diluting concentrated sulfuric acid involves the ionisation of molecular  $\text{H}_2\text{SO}_4$  into hydrated hydrogen and  $\text{HSO}_4^-$  ions:



Every 100 g of 98% sulfuric acid contains 0.1 mol  $\text{H}_2\text{O}$  and 1.0 mol  $\text{H}_2\text{SO}_4$ . Therefore no more than 10% of the  $\text{H}_2\text{SO}_4$  molecules can be ionised. In fact most of the water is tied up as hydrates such as  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  so that there are very few ions in 98% sulfuric acid.

When this acid is added to water, the  $\text{H}_2\text{SO}_4$  molecules can ionise. This ionisation is strongly exothermic and so a large amount of heat is liberated.

In concentrated hydrochloric and nitric acids there is sufficient water for all the acid molecules to be already ionised. So adding water to these acids just dilutes the ionic solutions and this releases much less heat (as the  $\Delta H$  values above show).

<sup>†</sup> Follow the old saying: *always do what ya oughter, add the acid to the water.*

### Exercises

- 29** Concentrated hydrochloric acid is 35% HCl and concentrated nitric acid is 70%  $\text{HNO}_3$ , the balance being water in each case. What is the ratio of moles of water to moles of acid in each of these solutions? (Hint: calculate the number of moles of each of  $\text{H}_2\text{O}$  and HCl or  $\text{HNO}_3$  in 100 g of each solution.) Do these results confirm the claim made above that in these concentrated acids HCl and  $\text{HNO}_3$  are already fully ionised? Explain.
- 30** Use the  $\Delta H$  values in Section 9.16 to calculate the change in temperature when:
- 5.0 g 98% sulfuric acid (0.051 mol)
  - 5.0 g 35% hydrochloric acid (0.050 mol)
- is carefully dissolved in 100 mL water. Take the specific heat capacity of the final solution as  $4.2 \text{ J K}^{-1} \text{ mL}^{-1}$ .
- 31** Write the ionisation reaction(s) that occur in dilute solutions of sulfuric acid, say at about 0.01 mol/L. Explain the difference between what you have written here and Equation 9.20.

## 9.17 REACTIONS OF SULFURIC ACID

Two important reactions of sulfuric acid involve it acting as:

- an oxidising agent and
- a dehydrating agent.

### As an oxidising agent

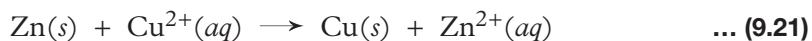
Sulfuric acid is a moderately strong oxidising agent. So what is an oxidising agent?

#### Oxidising and reducing agents

Oxidation and reduction were defined in Section 2.1.

An **oxidising agent** is a substance that brings about oxidation.

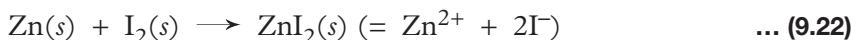
In the reaction (also from Section 2.1):



copper ions oxidise zinc metal to zinc ions (i.e.  $\text{Cu}^{2+}$  takes electrons from Zn).  $\text{Cu}^{2+}$  is therefore an *oxidising agent*. Note that the oxidising agent gets reduced ( $\text{Cu}^{2+}$  to Cu).

A **reducing agent** is a substance that brings about reduction.

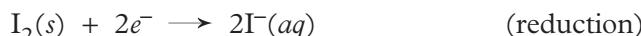
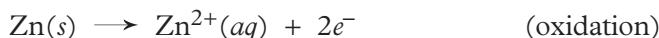
In the reaction:



zinc metal reduces iodine to iodide ions (i.e. Zn gives electrons to  $\text{I}_2$ ). Zn is therefore a *reducing agent*. Note that the reducing agent gets oxidised (Zn to  $\text{Zn}^{2+}$ ).

An oxidising agent is sometimes called an **oxidant** or an **oxidiser**. A reducing agent is sometimes called a **reductant** or a **reducer**.

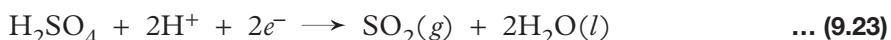
We commonly write half equations for redox reactions. Those for Reaction 9.21 were given in Section 2.1. The half equations for Reaction 9.22 are:



Half equations make it easier to identify the oxidant and reductant in a reaction.

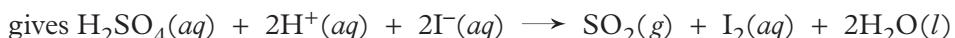
### Sulfuric acid as an oxidising agent

The half reaction for sulfuric acid acting as an oxidising agent is:

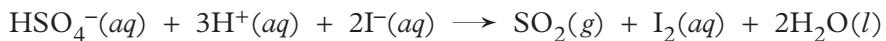


Common redox reactions involving sulfuric acid are:

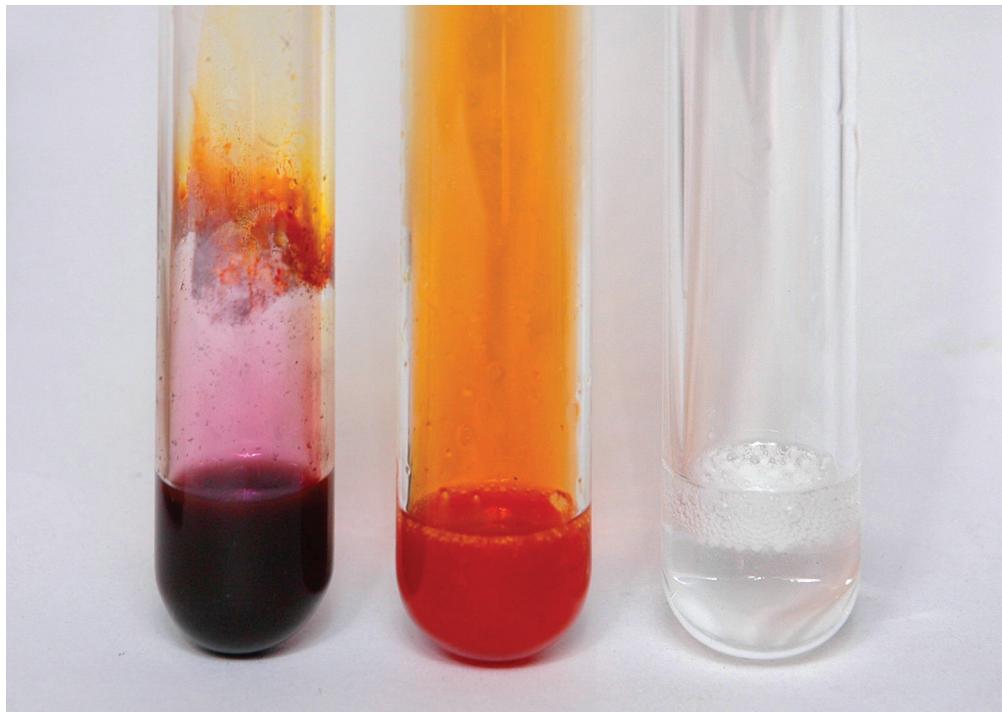
- *oxidation of iodide and bromide*. Being just a moderately strong oxidising agent, moderately concentrated sulfuric acid is able to oxidise iodide solution to iodine and bromide solution to bromine, but cannot oxidise chloride. For example, combining Equation 9.23 with



or considering that the reaction occurs in moderately concentrated aqueous solution in which sulfuric acid exists as  $\text{H}^+ + \text{HSO}_4^-$ , we can write it as:



Sulfuric acid oxidises colourless iodide and bromide to purple iodine and brown bromine, but does not oxidise chloride (right-hand test tube); however it does convert chloride to colourless hydrogen chloride gas



- *oxidation of copper.* Hot concentrated sulfuric acid oxidises copper to copper ions.

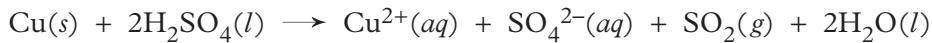
Combining Equation 9.23 with



gives

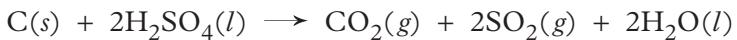


or recognising that the reaction occurs in concentrated sulfuric acid,



Other metals such as silver, mercury and lead react similarly, though the more reactive metals such as Zn, Mg, Fe and Al are preferentially oxidised by hydrogen ions to form hydrogen gas (p. 116 CCPC).

- *oxidation of non-metals such as carbon, sulfur and phosphorus.* Hot concentrated sulfuric acid oxidises C, S and P to carbon dioxide, sulfur dioxide and phosphorus pentoxide respectively. For example:



The reactions of sulfuric acid with reactive metals (p. 116 CCPC) are redox reactions but the oxidant is the hydrogen ion rather than sulfuric acid itself. For example with magnesium, the neutral species equation is



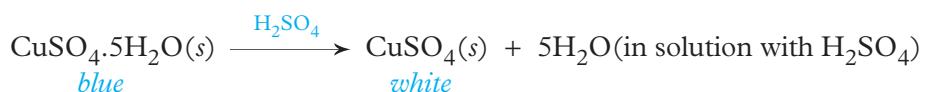
while the net ionic equation is



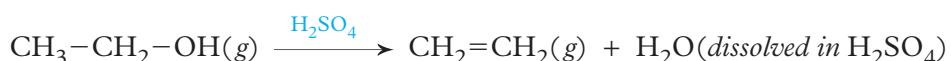
Hydrogen ions have oxidised magnesium metal to magnesium ions; the sulfate ion is just a spectator ion.

## As a dehydrating agent

Concentrated sulfuric acid has a very strong affinity for water; it absorbs water from mixtures such as moist air and other wet gases and from many hydrated salts. Sulfuric acid can be used to dry gases which do not react with it (such as air, helium, natural gas or LPG) by bubbling the gas through it; an aqueous solution of sulfuric acid forms. Blue copper sulfate pentahydrate can be converted to white anhydrous copper sulfate by storing it in a dessicator using concentrated sulfuric acid as the absorbent:



In addition *concentrated sulfuric acid can remove hydrogen and oxygen from compounds as water*. For example, as we saw in Section 1.16, sulfuric acid can dehydrate ethanol to ethylene:



The most dramatic demonstration of the dehydrating power of concentrated sulfuric acid is its reaction with sucrose (ordinary sugar),  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (or  $\text{C}_{12}(\text{H}_2\text{O})_{11}$ ) as shown in Figure 9.6:

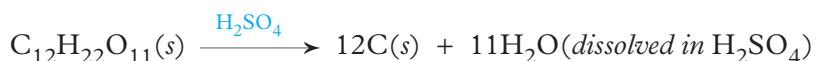
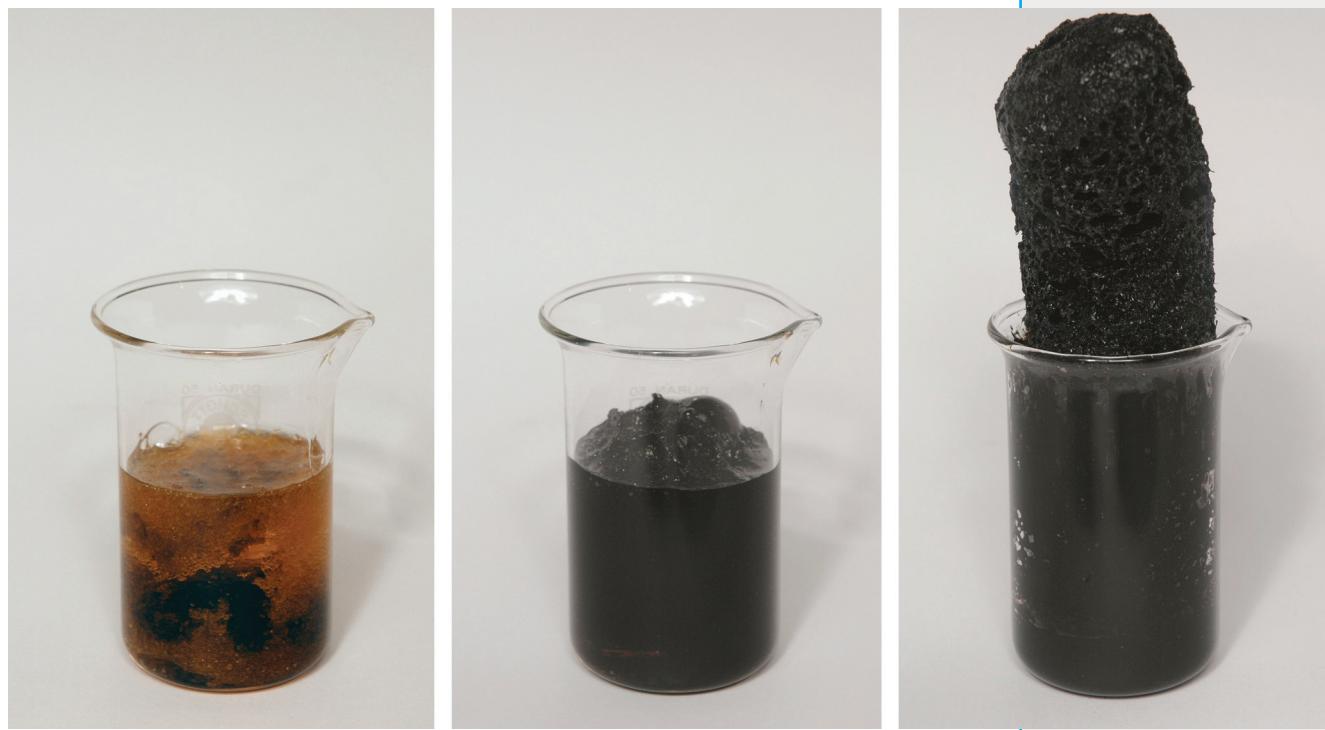


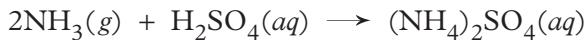
FIGURE 9.6  
Concentrated sulfuric acid dehydrates ordinary sugar (sucrose) to spongy carbon; the three photos show the progress of the reaction from soon after mixing the substances to the end of the reaction



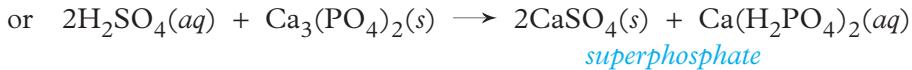
## Other reactions of sulfuric acid

Other important reactions of sulfuric acid are:

- *acid–base reactions* such as its reaction with ammonia to form sulfate of ammonia fertiliser (ammonium sulfate):



and with rock phosphate to form superphosphate fertiliser (mixture of soluble calcium dihydrogen phosphate and sparingly soluble calcium sulfate):



- *precipitation reactions* such as its reaction with barium ions as used in the analysis in Section 6.16.

## 9.18 SAFETY PRECAUTIONS WHEN USING SULFURIC ACID

Before using concentrated sulfuric acid you should carry out a thorough risk assessment in order to identify and address all potential hazards. This will lead you to observe the following safety precautions:

- Always wear safety goggles (splashes into an eye can cause serious permanent damage).
- Wear protective gloves and a laboratory coat or apron (because sulfuric acid, like all concentrated strong acids, is very corrosive to skin and clothing).
- Work near a ready supply of running water (to wash off or dilute any splashes to body or clothing).
- Have a supply of sodium carbonate or hydrogen carbonate at hand to neutralise any spills.
- For regular use store the acid in glass bottles no larger than one litre (the 2.5 L bottles the acid is purchased in are too heavy and awkward for safe handling during experiments).
- Try to avoid dribbling acid down the outside of the bottle and if you do, wipe it off carefully with wet tissue.
- Always place the storage bottle in a drip tray (such as a glass Petri dish) to ensure that any drips do not contact the bench or shelf.
- When diluting concentrated acid, *always* add the acid to the water, and do it slowly.

The properties of sulfuric acid that give rise to these safety precautions are:

- Sulfuric acid is a strong acid that can corrode metals and other materials and damage both the structure and functioning of living organisms.
- Sulfuric acid is an oxidising agent, which means that it can attack materials that are normally resistant to attack from just the hydrogen ions of simpler acids.
- Sulfuric acid is a dehydrating agent, which means that it can easily destroy a wide range of organic materials (including living tissue).

## Transport and storage

98% sulfuric acid is virtually all molecular (very few ions); see Section 9.16. Therefore it does not attack iron and steel, so can safely be stored in steel containers or transported in steel tankers. Steel has the advantage of greater strength when compared with glass and plastic containers (sulfuric acid does not react with these either).

However, sulfuric acid that has been diluted contains hydrogen ions and vigorously attacks metals such as iron and steel. Hence dilute acid must be stored in glass or plastic containers. This makes it more difficult to transport.

When storing or transporting this acid in steel containers, care must be taken to avoid contamination with water, because that could set off a vigorous reaction between the acid and the container.

## Exercises

- 32** When sodium chloride is heated with concentrated sulfuric acid, a colourless gas forms which readily dissolves in water to give an acidic solution. By contrast, when sodium bromide is similarly heated with concentrated sulfuric acid, a brown vapour forms which can be condensed to a brown liquid which is only slightly soluble in water. What are the substances formed in these reactions? Write equations for their formation. Which, if either, of these reactions is a redox reaction? Explain why.
- 33 a** Write an equation for the reaction of silver with hot concentrated sulfuric acid.  
**b** Write an equation for the reaction of sulfur with hot concentrated sulfuric acid. Identify the atom(s) in the equation that has (have) been  
(i) oxidised  
(ii) reduced.
- 34** Write equations for the reactions of sulfuric acid with Mg and \*Al. Are these redox reactions? Explain why or why not.
- 35** Some chemical reactions occur because a volatile product can be driven off. When concentrated sulfuric acid is heated with solid sodium nitrate, nitric acid vapour forms and readily condenses to pure liquid. This is the common way of making 100% nitric acid (as opposed to the 70% commercial product that is made from ammonia). Write an equation for this reaction. Is this a redox reaction? Explain.
- 36 a** Sulfuric acid can dehydrate formic acid (methanoic acid, HCOOH) to carbon monoxide. Write an equation for the reaction. Why is this reaction too dangerous to perform in a school laboratory?  
**b** Would you expect concentrated sulfuric acid to react with (i) methanol



## Important new terms

You should know the meaning of the following terms.

condition for equilibrium (p. 319)  
contact process (p. 333)  
equilibrium constant (p. 319)

equilibrium expression for a reaction  
(p. 319)

Frasch process (p. 331)  
oxidising agent (oxidant, oxidiser) (p. 339)  
reaction quotient (p. 320)  
reducing agent (reductant, reducer)  
(p. 339)

## Test yourself

1 Explain the meaning of each of the items in the ‘Important new terms’ section above.

2 Name three natural products that have been replaced to significant extents by synthetics and describe the nature of the synthetics currently being used.

3 What factors lead to a natural product being replaced by a synthetic?

4 List four qualitative characteristics of chemical equilibria.

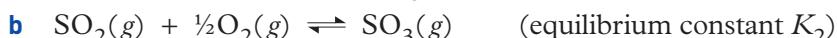
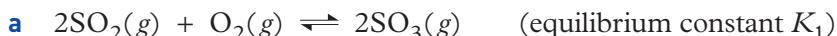
5 For the generalised chemical reaction:



what is the condition for the reaction to be at equilibrium at constant temperature? That is, what is the *equilibrium expression* for the reaction?

6 What happens if the reaction quotient is greater than the equilibrium constant? What happens if the reaction quotient is less than the equilibrium constant?

7 What relation exists between the equilibrium constants  $K_1$  and  $K_2$ , for the following reactions:



8 In order to measure the equilibrium value of the reaction quotient (and hence to measure  $K$ ), why is it necessary to be able to measure the concentration of a species without changing its value? Name two methods that are often used (for different reactions).

9 For the reaction  $2\text{A} \rightleftharpoons \text{B} + \text{C}$  what do you conclude about the position of equilibrium if  $K$  is:

a  $10^3$

b 1

c  $10^{-3}$

10 Use Le Chatelier’s principle to decide how the value of  $K$  changes as temperature increases for:

a an exothermic reaction

b an endothermic reaction

11 Describe three commercial or industrial uses for sulfuric acid.

12 Explain how sulfur is extracted from underground deposits. What is the process called?

13 Describe the basic steps for the industrial production of sulfuric acid.

14 What are the conditions used for the conversion of  $\text{SO}_2$  to  $\text{SO}_3$ ? Why is the reaction mixture passed over at least two trays of catalyst at different temperatures? What is the catalyst?

15 Why is  $\text{SO}_3$  dissolved in sulfuric acid rather than in water? What is formed by this dissolution and how is sulfuric acid obtained?

16 Is the overall synthesis of sulfuric acid exo- or endothermic? How do such plants keep their energy costs to a minimum?

17 List five properties of sulfuric acid.

- 18** Why is greater care needed when diluting concentrated sulfuric acid than when diluting nitric or hydrochloric acids? What is the explanation for this?
- 19** Give an example (with equation) of sulfuric acid acting as:
  - a** an oxidising agent
  - b** a dehydrating agent
- 20** Write equations for the formation of two common fertilisers made from sulfuric acid.
- 21** Write equations for two redox reactions involving sulfuric acid excluding the one you wrote in Question 19. In the first identify the oxidising agent and in the second the reducing agent.
- 22** List safety precautions that you would take in using concentrated sulfuric acid, giving a reason for each.

# CHAPTER 10

# Alkalies and detergents

## IN THIS CHAPTER

Properties and uses of sodium hydroxide	Making soap
Electrolysis	Soap, detergent and surfactant
Electrolysis of sodium chloride	Emulsions
Industrial preparation of sodium hydroxide	Synthetic surfactants (detergents)
Diaphragm cell	Surfactants and hard water
Mercury cell	Environmental effects
Membrane cell	Manufacture of sodium carbonate: the Solvay process
Saponification	Location of industrial plants
Fats and oils	Uses of sodium carbonate

Having examined the industrial synthesis of the most widely used acid, sulfuric, we shall now look at the synthesis of two of the most commonly used alkalies, sodium hydroxide and sodium carbonate. In addition we shall explore one major use of both alkalies, the production of soap and detergents.

## 10.1 PROPERTIES AND USES OF SODIUM HYDROXIDE<sup>†</sup>

The key properties of sodium hydroxide are:

- it is very soluble in water (42 g/100 mL at 0°C and 347 g/100 mL at 100°C)
- it is a strong base, completely dissociating into  $\text{Na}^+$  and  $\text{OH}^-$  ions in aqueous solution.

It is the combination of these two properties that makes it particularly useful because there are many chemical reactions that require a high concentration of hydroxide ion.

Sodium hydroxide is used in the manufacture of:

- soap and other detergents (Section 10.11)
- rayon (viscose) and other fibres and plastics
- paper
- domestic cleaning agents such as oven and drain cleaners.

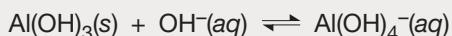
<sup>†</sup> Not required for the NSW HSC, but included here because before studying the industrial synthesis of sodium hydroxide we really should have some idea of *why* we want to make it.

It is also used for:

- extraction of alumina from bauxite (for preparation of Al) (right-hand photo on p. 311)
- removal of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in the processing of natural gas and oil.

## Exercises

- 1 **a** Calculate the molarity of saturated solutions of sodium hydroxide at  $0^\circ\text{C}$  and  $100^\circ\text{C}$  (concentrations are given above).  
**b** A 50% (by mass) solution of sodium hydroxide in water has a density of 1.525 g/mL. Calculate its concentration in **(i)** g/100 mL **(ii)** mol/L.
- 2 **a** As mentioned above sodium hydroxide is used to absorb  $\text{H}_2\text{S}$  and  $\text{SO}_2$  from natural gas. Write equations for the reactions involved. Describe the experimental arrangement you would use to do this.  
**\*b** Sodium hydroxide also absorbs carbon dioxide. Write an equation.  
**c** In submarines, lithium hydroxide is used to absorb carbon dioxide from stale air. Why is lithium hydroxide preferable to sodium hydroxide? (They are both equally corrosive.)
- 3 The key equilibrium reaction involved in the extraction of aluminium oxide from bauxite can be written as:



- a** Aluminium hydroxide precipitates out when the solution of  $\text{Al(OH)}_4^-$  is cooled. Is the reaction just written exo- or endothermic? Explain why.
- b** Precipitation of aluminium hydroxide could be brought about by lowering the concentration of hydroxide (by adding some acid). Explain why this would happen. Why would this be a less efficient way of precipitating the aluminium hydroxide?
- c** The final step in preparing aluminium oxide is to filter off the hydroxide and heat it. Write an equation for the reaction.



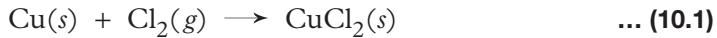
Sodium hydroxide is made by electrolysis, so before discussing the actual process let us explore what is meant by electrolysis.

## 10.2 ELECTROLYSIS

**Electrolysis** is the process in which an electric current is used to bring about a chemical reaction which does not occur spontaneously.

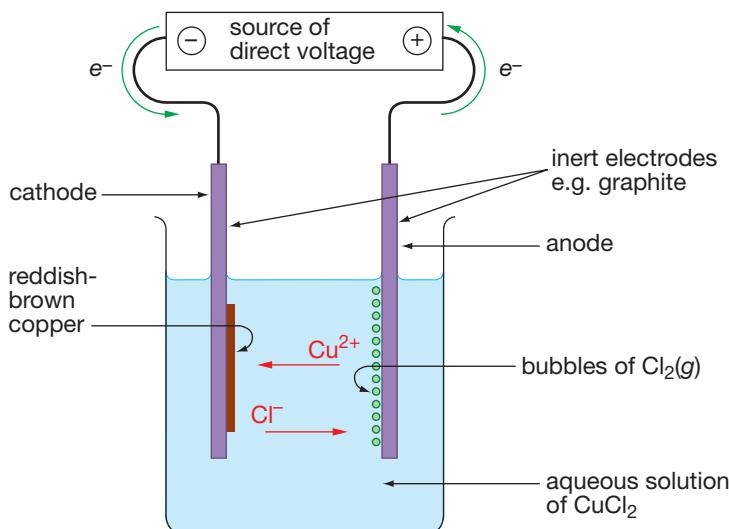
Electrolysis was used on p. 71–2 CCPC as a method of decomposing compounds (lead bromide and water).

Let us consider another example. Copper reacts with chlorine to form copper chloride:

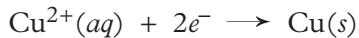


Copper chloride does not of its own accord fall apart into copper and chlorine. However, if we pass an electric current through an aqueous solution of copper chloride using inert electrodes (graphite or platinum) as in Figure 10.1, copper deposits at the negative electrode and chlorine gas evolves at the positive electrode. Copper chloride is decomposed by electrolysis.

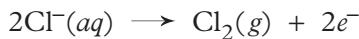
**FIGURE 10.1**  
A simple example of electrolysis



What happens during electrolysis is this. The voltage source (commonly a battery) is an electron pump. It pushes electrons out of its negative terminal into the electrode attached to it (the left-hand one in Figure 10.1). The positive copper ions are attracted to this negative electrode and they take electrons from it and deposit on the surface as neutral copper atoms:



The voltage source ‘pulls’ electrons out of the right-hand electrode, making it positive. Negative chloride ions are attracted to it and give up electrons to it; this forms neutral Cl atoms which quickly combine to form  $\text{Cl}_2$  molecules which come out of solution as gas:

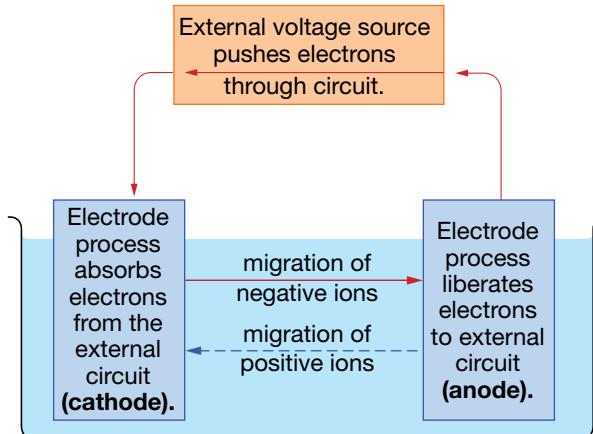


The overall process is the sum of these two electrode processes (half reactions):



Electrolysis has reversed the normal spontaneous reaction, Equation 10.1.

The essential features of electrolysis are shown in generalised form in Figure 10.2.



A cell in which electrolysis occurs is called an **electrolytic cell**, in contrast to a **galvanic cell** which produces electricity. Sometimes we use the term, **electrochemical cell**, to cover both types of cell, galvanic and electrolytic.

**FIGURE 10.2**  
Essential features of electrolysis

## In energy terms

A *galvanic cell* is a device that uses a spontaneous chemical reaction to generate electricity; that is, it converts chemical energy into electrical energy.

An *electrolytic cell* is a device that uses an electric current to bring about a chemical reaction that does not occur spontaneously; that is, it converts electrical energy into chemical energy.

## Anode and cathode again

In Section 2.7 the *anode* was defined as the electrode where oxidation occurred and the cathode as where reduction occurred. This means that in Figure 10.1 the positive electrode is the anode (as  $\text{Cl}^-$  gets oxidised to  $\text{Cl}_2$  there). The negative electrode is the cathode (because  $\text{Cu}^{2+}$  is reduced to Cu there).

In electrolysis the anode is the positive electrode and the cathode is the negative electrode.

This is the reverse of the situation in galvanic cells (Section 2.7).

Because the polarity of the anode and cathode depends upon whether the cell involved is galvanic or electrolytic, we should be careful in using these words. Think of them primarily in terms of oxidation and reduction, rather than in terms of sign.

The terms anion and cation are actually derived from anode and cathode. *Anions* are ions which migrate towards the *anode*, *cations* are ions which migrate towards the *cathode*.

We can extend Box 2.1 from Section 2.7 to include electrolytic cells

### BOX 10.1 IN ELECTROCHEMICAL CELLS

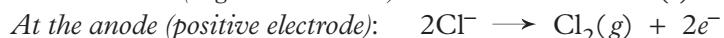
Electrode reaction	Name of the electrode	Sign of the electrode	
		Galvanic cell	Electrolytic cell
oxidation	anode	negative	positive
reduction	cathode	positive	negative

## 10.3 ELECTROLYSIS OF SODIUM CHLORIDE

The products obtained from the electrolysis of sodium chloride depend upon the conditions used. Solid sodium chloride, like all solid salts, does not conduct electricity so to electrolyse pure sodium chloride, we have to use it molten.

### Electrolysis of molten sodium chloride

During the electrolysis of molten sodium chloride, sodium ions migrate to the cathode (negative electrode) and are reduced to sodium metal, while chloride ions migrate to the anode (positive electrode) and are oxidised to chlorine gas:



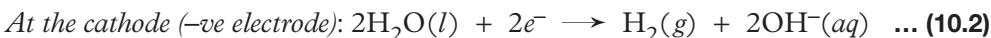
Doubling the first half equation and adding it to the second gives the overall reaction:



This electrolysis of molten sodium chloride is used to prepare metallic sodium. The design of the cell must be such as to keep the chlorine and sodium separated from each other (otherwise they would react violently to re-form sodium chloride). In addition air must be excluded from around the cathode, because sodium reacts with both oxygen and nitrogen.

## Electrolysis of concentrated aqueous solutions of sodium chloride

When concentrated aqueous solutions of sodium chloride (greater than about 2 mol/L) are electrolysed, sodium ions migrate to the cathode, but they are too stable to be reduced; instead water (or hydrogen ion) is reduced to hydrogen gas:

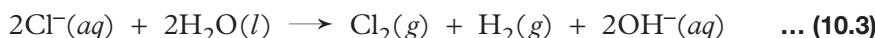


Chloride ions migrate to the anode where they are oxidised to chlorine gas:

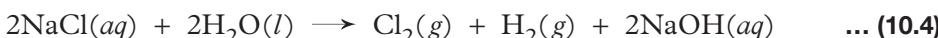


Addition of these two half reactions gives the overall reaction:

*Overall reaction:*

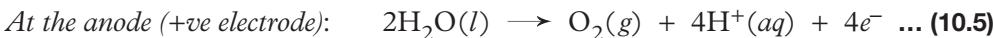


If we add the spectator ions,  $2\text{Na}^+$ , to this equation we get:

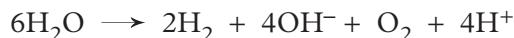


## Electrolysis of dilute aqueous solutions of sodium chloride

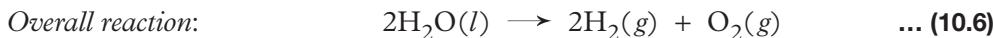
When dilute aqueous solutions of sodium hydroxide (less than about 0.1 mol/L) are electrolysed, hydrogen forms at the cathode as above, but at the anode water is oxidised instead of chloride:



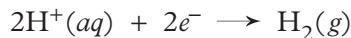
To get the overall reaction we double Equation 10.2 (to balance electrons so they cancel out) and add the result to Equation 10.5:



Recognising that  $4\text{OH}^- + 4\text{H}^+ = 4\text{H}_2\text{O}$  and cancelling this on both sides of the equation leads to



In other words, the electrolysis of dilute sodium chloride solution is effectively the hydrolysis of water. We would have obtained this result more directly had we written the cathode reaction in an equivalent form:



Doubling this and adding it to 10.5 would have produced 10.6 directly.

These three different sets of products from electrolysing sodium chloride are illustrated in Figure 10.3.

## Explanations

When molten sodium chloride is electrolysed, no species other than  $\text{Na}^+$  and  $\text{Cl}^-$  are present, so reduction of  $\text{Na}^+$  and oxidation of  $\text{Cl}^-$  are the only possible electrode reactions. This is also true of the electrolysis of molten magnesium chloride or aluminium oxide (used to extract these metals from their ores).

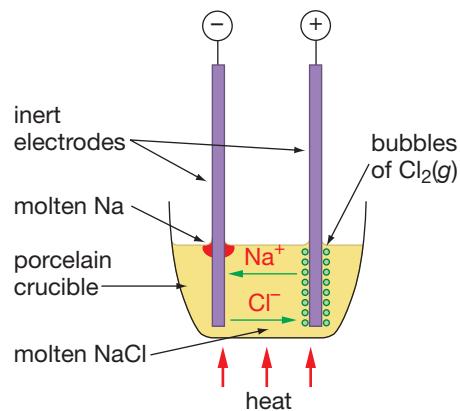
In aqueous solutions where water is present as well as the ions from the electrolyte, there is often more than one possible reaction at each electrode. *The reaction that occurs at the cathode is the reduction of the more easily reduced species.* Sodium ions are very difficult to reduce, so water gets reduced instead. On the other hand copper ions are relatively easy to reduce, so in the electrolysis of aqueous copper chloride,  $\text{Cu}^{2+}$  is reduced instead of water (Section 10.2 and Figure 10.1).

*At the anode the reaction that occurs is oxidation of the more easily oxidised species.* Chloride ion and water have comparable ease of oxidation and so the one that gets oxidised depends upon concentration: if chloride is present in moderately high concentration it gets oxidised, while if it is present at low concentrations water is oxidised instead. On the other hand iodide is much more easily oxidised than water, so electrolysis of iodide solutions always produces iodine, regardless of concentration.

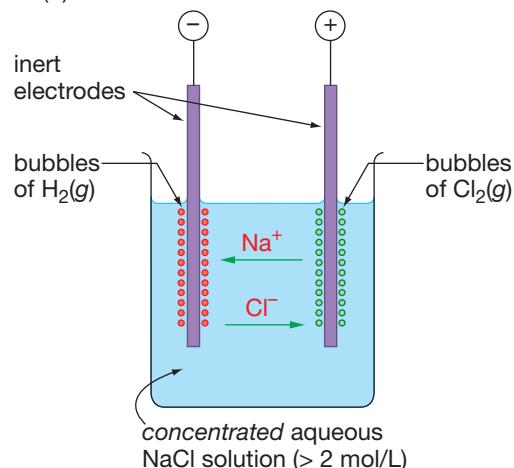
## Exercises

- 4 a Write the electrode reactions you would expect for the electrolysis of a dilute solution of sodium hydroxide. Explain why this can be regarded as the electrolysis of water.  
b Why is it not possible to electrolyse pure water itself?
- 5 Compared with water (or more strictly with hydrogen ions), magnesium and barium ions are more difficult to reduce while silver ions are easier to reduce. Also compared to water (or more strictly to hydroxide ions), sulfate and nitrate ions are much more difficult to oxidise. Hence what electrode reactions and overall reactions would you expect for the electrolysis of aqueous solutions of:  
a magnesium sulfate      c sulfuric acid  
b silver nitrate      d barium hydroxide?

(a)



(b)



(c)

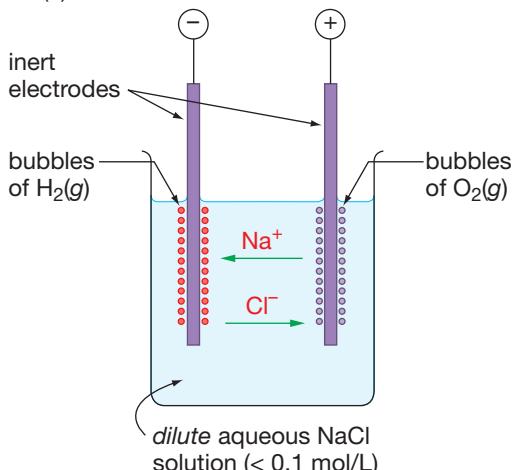
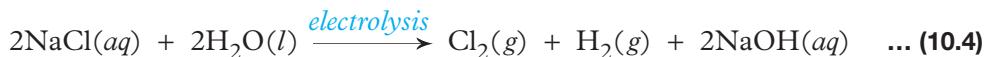


FIGURE 10.3  
Electrolysis of sodium chloride under different conditions: (a) molten (b) as concentrated aqueous solution (c) as dilute aqueous solution

## 10.4 INDUSTRIAL PREPARATION OF SODIUM HYDROXIDE

Industrially sodium hydroxide is made by electrolysing a concentrated sodium chloride solution. Sodium chloride is obtained from sea water or from underground salt mines. A concentrated solution of sodium chloride is called **brine**.

As discussed in the previous section the neutral species equation for the process is:



while the net ionic equation is



Chlorine is just as important a product as is the sodium hydroxide. Over the past 100 years three different electrolysis cells have been used: the diaphragm cell, the mercury cell and the membrane cell.

## 10.5 DIAPHRAGM CELL

The **diaphragm cell**, the first to be used commercially, uses inert electrodes—a titanium anode (to withstand attack from the chlorine formed) and an iron mesh cathode (which is not affected by hydroxide solution).

### The basic chemistry

The basic chemistry of this cell is as described in *Electrolysis of concentrated aqueous solutions of sodium chloride* in the previous section. The electrolysis produces chlorine and hydrogen gases and leaves behind a solution of sodium hydroxide.

The process is as much for producing chlorine as for making sodium hydroxide. Large quantities of chlorine are needed for making polymers such as PVC (Section 1.7), for bleaching paper and textiles, and for sterilising water. This electrolysis is often referred to as the **chlor-alkali industry**: both products are equally important. Although there are cheaper ways of making hydrogen, the hydrogen made here is nevertheless sold to other industries that need it (such as hydrogenation of oils for margarine, synthesis of ammonia, catalytic reforming of petroleum).

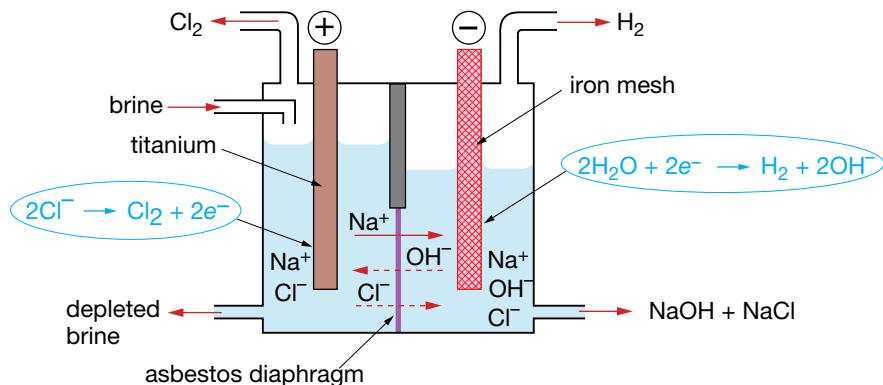
Practical problems that have to be addressed in the design of the electrolysis cell include:

- keeping the gases  $\text{H}_2$  and  $\text{Cl}_2$  separated (they react quite vigorously if they come in contact)
- minimising contact between hydroxide ion and chlorine in solution (because  $\text{OH}^- + \text{Cl}_2$  forms unwanted chlorite,  $\text{ClO}^-$ )
- minimising the amount of chloride that is present in the final hydroxide solution.

### General description

A schematic drawing of a diaphragm cell is shown in Figure 10.4. The diaphragm of the name is a porous barrier between the anode and cathode

compartments intended to allow sodium ions to flow through (to complete the flow of electricity in the circuit and to allow a build-up of sodium hydroxide in the cathode compartment). The diaphragm is made of asbestos, which is not damaged by hydroxide solution.



**FIGURE 10.4**  
A diaphragm cell for production of sodium hydroxide and chlorine (schematic only)

Formation of gaseous chlorine in the anode compartment depletes the brine solution of chloride and so there is a slow flow of fresh brine into this compartment and removal of an equivalent volume of spent solution.

A barrier separates the hydrogen and chlorine gases which are taken off and compressed into cylinders or piped to neighbouring industries that need them.

Sodium ions migrate from the anode compartment through the diaphragm and into the cathode compartment to balance the charge of the hydroxide ion formed there. Small amounts of hydroxide migrate in the reverse direction also. There is also some diffusion of chloride into the cathode compartment, so even if the solution in the cathode compartment were initially just dilute sodium hydroxide, after some time there would be some sodium chloride in it. Preventing the migration of hydroxide into the anode compartment is more important than stopping chloride migration, so a slight positive pressure is maintained on the anode side of the diaphragm.

The voltage across the electrodes is between 3.5 and 5 V. Each cell is quite small, in order to keep the gaps between electrodes and diaphragm small and so maximise the current flow. Large numbers of cells are assembled together in such a way that they feed products into common collection areas so that there needs to be only one take-off point for each product (NaOH, Cl<sub>2</sub>, H<sub>2</sub>) and only one input point for brine. Chlor-alkali plants draw total currents (at these low voltages) of tens of thousands of amperes. Electricity costs are a large proportion of the total cost of the products.

The solution taken from the cathode compartment contains sodium chloride as well as sodium hydroxide. Water is evaporated from this solution until it is about 50% by mass of sodium hydroxide. At that stage most of the sodium chloride has crystallised out, so it can be filtered off and the solution of nearly pure sodium hydroxide can be sold as such or evaporated to dryness to produce solid hydroxide. The product from the diaphragm cell generally contains about 1% sodium chloride.

## Advantages and disadvantages

Advantages of the diaphragm cell are that it produces large quantities of sodium hydroxide and chlorine, two high-demand industrial chemicals, at quite reasonable costs and at quite acceptable levels of purity for most purposes.

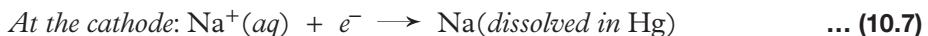
The disadvantages are:

- there is always a small amount of chloride in the NaOH produced
- there are health and environmental problems with small losses of asbestos in making and using the diaphragms
- there may be hypochlorite,  $\text{ClO}^-$ , a strong oxidant, in the waste brine solution and this needs to be removed before brine is discharged to the environment.

Diaphragm cells are now ‘old technology’. No new ones have been built for many decades and worldwide not many are still in operation. The mercury cell was developed to overcome some of these problems, particularly contamination of product with chloride.

## 10.6 MERCURY CELL

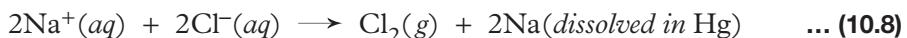
The mercury cell uses liquid mercury as the cathode. This results in a different reaction at the cathode. Sodium, not water, is reduced and it is simultaneously incorporated into the mercury to form an amalgam (a solution):



The anode reaction is the same as in the diaphragm cell:



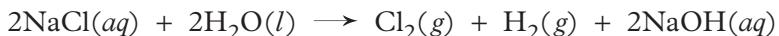
The overall reaction in this cell is therefore:



The mercury then flows from the electrolysis cell into another chamber containing pure water. Without any electrical potential between the water and amalgam, sodium reacts with water to form sodium hydroxide (just as pure sodium itself reacts, p. 115–16 CCPC):



The overall reaction is the sum of Equations 10.8 and 10.9:



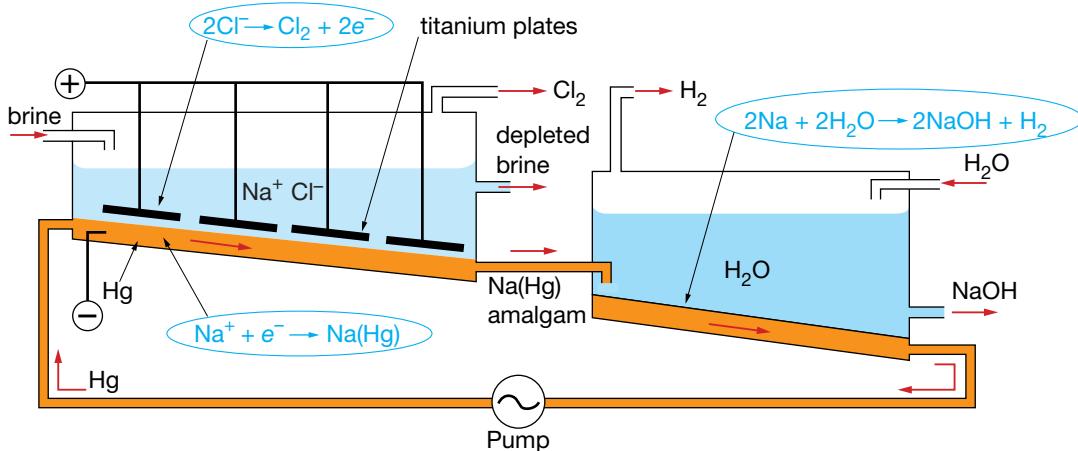
(writing  $2\text{NaCl}(aq)$  for  $2\text{Na}^+ + 2\text{Cl}^-$ ). This is the same as for the diaphragm cell, Equation 10.4.

## General description of the mercury cell

A typical arrangement for a **mercury cell** is shown in Figure 10.5.

Mercury flows across the sloping floor of a large tank: it has the negative terminal of the voltage source immersed in it. The anodes are plates of titanium suspended quite close to the mercury (to produce large current flows). Brine flows slowly through the tank and chlorine is collected from the top of the tank.

The mercury (with sodium dissolved in it) then flows into another tank which originally contained only water. Reaction 10.9 occurs here and so a solution of sodium hydroxide is formed. The hydrogen that forms is collected and compressed into cylinders or piped to another factory that needs it. Periodically the sodium hydroxide solution is drained off and replaced by water. The flow rate of mercury through this tank is such that all the sodium has reacted by the time the mercury exits the tank and so it can be pumped back to the electrolysis cell for re-use.



**FIGURE 10.5**  
A mercury cell for the production of sodium hydroxide and chlorine

Rather than a battery of many small cells (as with the diaphragm cell), plants using mercury cells generally have just one large cell, typically 15 m long and 1 m wide. Mercury cells operate at between 3 and 4 V and a typical plant would draw current of the order of thousands of amperes.

As with the diaphragm cell, the solution of sodium hydroxide is concentrated to about 50% and sold as such or evaporated to dryness to form a solid product. Because the sodium hydroxide solution was produced from pure water reacting with the mercury amalgam, there is no contamination of the product with chloride (as there was in the diaphragm cell).

## Advantages and disadvantages

The advantages of the mercury cell are:

- it produces very pure sodium hydroxide
- it avoids using asbestos.

The main disadvantage is that mercury cells lose mercury to the environment, sometimes as much as 100 to 200 g per tonne of NaOH produced. Theoretically the process should not lose any mercury: as described above all the mercury is recycled indefinitely. However it appears that there is some almost unavoidable mechanical transfer of mercury to the brine solution which is discharged to the environment (generally back to the ocean).

## Mercury pollution

Metallic mercury is extremely insoluble and if it stayed as such at the bottom of the ocean it would be of little concern. Unfortunately there are some bacteria that convert mercury into compounds such as dimethyl mercury,  $\text{Hg}(\text{CH}_3)_2$ . Compounds of mercury in ocean water can be taken up by organisms and passed along the food chain with biological concentration (amplification) at each stage. The result is that end consumers, such as humans eating fish (particularly tuna and shark), can receive quite significant doses of mercury. Mercury affects the nervous system and can cause brain damage; in addition it tends to stay within the human body for long times. Mercury is regarded as a particularly dangerous poison.

Consequently environmental protection agencies in many countries have set limits on the amount of mercury that chlor-alkali plants can discharge. Typical

figures of less than 1 g per tonne of NaOH produced are very difficult to meet and so few new mercury cells are being built. Fortunately a better diaphragm has been developed for the diaphragm cell: the new versions are called *membrane cells*.

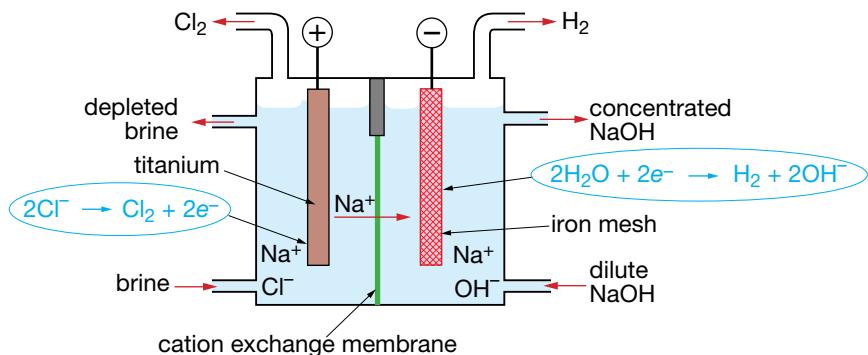
## Starting materials

The starting material for both the mercury cell and the membrane cell (next section) is generally commercially pure crystalline sodium chloride. This is dissolved in water to produce a nearly saturated solution (about 30%). Some purification, particularly removal of calcium and magnesium ions, is generally necessary.

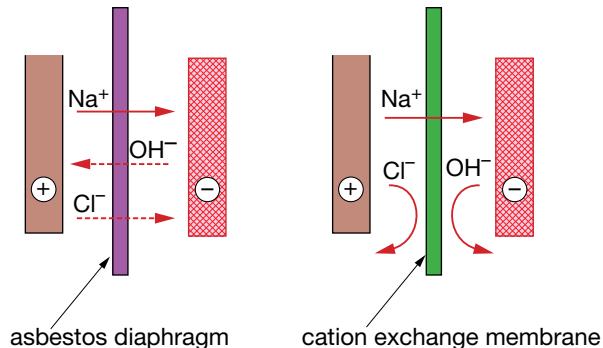
## 10.7 MEMBRANE CELL

A **membrane cell** is a diaphragm cell with an improved diaphragm called a ‘membrane’. The new membrane is made from polytetrafluoroethylene (PTFE) which has been modified to incorporate anionic groups so that it acts as an ion exchange membrane. In this way sodium ions are able to pass through it but not chloride or hydroxide ions. Figure 10.6 is a schematic drawing of a membrane cell while Figure 10.7 contrasts the key differences between the old diaphragm cell and the new PTFE membrane cell. PTFE is a very inert substance and so can stand immersion in hydroxide solutions for long periods of time.

**FIGURE 10.6**  
A schematic drawing  
of a membrane cell for  
production of sodium  
hydroxide and chlorine



**FIGURE 10.7**  
The old ‘diaphragm’ and  
the new ‘membrane’ for  
chlor–alkali cells



Use of this synthetic membrane results in virtually pure sodium hydroxide being produced (no contamination by chloride) and there is virtually no oxidant in the spent brine. In addition the hazards of working with asbestos or mercury are avoided. The chemistry of the membrane cell is the same as that of the diaphragm cell.

In recent years all new chloro-alkali plants have been of the membrane cell type.

This is an example of how advances in chemistry lead to changes in technology; the availability of new materials led to the development of a superior diaphragm, the ion exchanging PTFE membrane that overcame the disadvantages of the old asbestos diaphragm cell without introducing any new problems. Earlier the mercury cell had been introduced to avoid the disadvantages of the diaphragm cell but it introduced another problem, namely the loss of mercury from the cell into the environment. The development of the membrane cell has meant that in recent years all new chlor-alkali plants have been of the membrane-cell type. Orica, the large Australian chemicals manufacturer, recently replaced its mercury-based chlor-alkali plant on Botany Bay with a plant using membrane cells.

## 10.8 SUMMARY

The different products formed during electrolysis of sodium chloride are summarised in Table 10.1.

**TABLE 10.1 Products of electrolysis of sodium chloride under different conditions**

Conditions used	Product formed	
	at the anode (+ve)	at the cathode (-ve)
molten	Cl <sub>2</sub>	Na
concentrated aqueous solution, inert electrodes	Cl <sub>2</sub>	H <sub>2</sub>
dilute aqueous solution, inert electrodes	O <sub>2</sub>	H <sub>2</sub>
concentrated aqueous solution, Hg cathode	Cl <sub>2</sub>	Na

### WEBSITE

For an overview of the manufacture and uses of sodium hydroxide and chlorine in Australia:

<http://www.chemlink.com.au/caustic.htm>

(click on Chlorine also)

(no chemistry included!)



### Exercises

- 6 a Calculate the ratio by mass in which the three products of chlor-alkali plants are produced. Does this vary with the different types of cell used? Explain.
- b Rarely would the demand for sodium hydroxide and chlorine be in this ratio. Suggest ways for adjusting the demand for these two products so that the demands are in the same proportion as the production. Why is there less need to balance the demand for hydrogen with the demands of the other products?
- c Is it possible to vary the ratio in which chlorine and sodium hydroxide are produced in order to balance production to demand? Explain why.



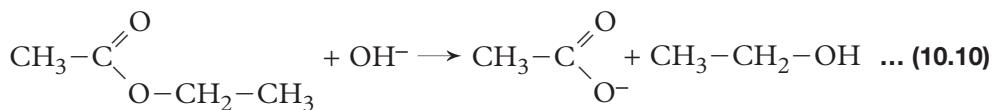
- 7** What volume of **(a)** chlorine **(b)** hydrogen (measured at 298 K and 100 kPa pressure) is produced in the chlor–alkali process per kilogram of sodium hydroxide formed?
- B a** For the operation of a particular diaphragm cell, electrical measurements showed that 0.20 mol of hydroxide ion had been produced. Chemical analysis showed that the cathode compartment contained 0.18 mol of hydroxide and 0.22 mol of sodium ions. How do you explain these observations, given that a solution must be electrically neutral?
- b** If a membrane cell had been used instead and if electrical measurements had shown that 0.20 mol of hydroxide had been formed, what quantities of hydroxide and sodium ions would you expect in the cathode compartment of this cell? Explain.
- 9** Sodium hydroxide solution from the diaphragm cell is usually concentrated to about 50 g/100 g water before filtering off deposited sodium chloride. Generally the amount of sodium chloride remaining in this solution is about 1 g/100 g. The solubility of sodium chloride in pure water is 34 g/100 g at 0°C and 35 g/100 g at 25°C. Offer an explanation for the discrepancy.

Having considered how to make sodium hydroxide, let us now turn to one of the major uses of sodium hydroxide, the production of soap from fats and oils. The reaction involved is called *saponification*.

## 10.9 SAPONIFICATION

In Section 5.18 we saw that an ester was a compound formed when a carboxylic acid was combined with an alcohol.

Esters can be converted back to the original alcohol and the sodium salt of the carboxylic acid by heating them with sodium hydroxide solution. For example ethyl acetate (ethanoate) can be converted into ethanol and the acetate anion:



An alkyl alkanoate is converted into an alkanol and an alkanoate anion. We can write the reaction in a general form as



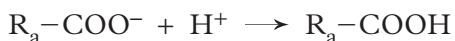
where  $\text{R}_a$  is one alkyl group and  $\text{R}_b$  is another alkyl group ( $\text{R}_b$  may be the same as  $\text{R}_a$ ). Remember, as stated in Section 5.21, for convenience of printing, esters are sometimes written as  $\text{R}_a-\text{COO}-\text{R}_b$  but the actual structure of the  $-\text{COO}-$  part is as in Equation 10.10.

The reaction between an ester and hydroxide ion to form an alcohol and a carboxylate anion is called **saponification**.

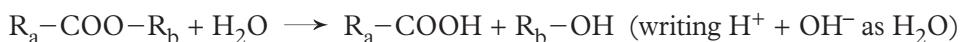
Originally the term *saponification* was used for the process of making soap. Fats and oils (next section) are esters and soap is made by heating them with aqueous sodium hydroxide solution. Since this reaction was the splitting of an

ester into an alcohol and a carboxylate anion, *saponification* came to have the more general meaning given in the above definition, and not just the splitting of fats and oils into soap and glycerol.

The carboxylate anion from saponification is often separated from the reaction mixture by acidifying the mixture. This brings about the reaction



The sum of this reaction and Reaction 10.11 gives:



Essentially then the overall process is reaction with water. *A reaction between a compound and water is called hydrolysis*, as was explained in Section 5.5.

Saponification can be described as the hydrolysis of an ester under alkaline conditions.

## Saponification of esters in the laboratory

Most esters are liquids and are insoluble in water. Therefore to saponify them, we need to boil the ester with a solution of sodium hydroxide. In addition most esters (and many of the alcohols they form) are fairly volatile, so saponification is usually performed with a reflux condenser attached (as in Section 5.18). After the reaction is complete the reaction mixture is generally a homogeneous solution: the carboxylate anion is soluble in water and many alcohols are water soluble, at least at high temperatures.

The procedure used to separate the reaction products depends on the *solubilities* and *boiling points* of the products (Table 10.2). If the carboxylate anion contains more than four carbon atoms, the carboxylic acid has a low solubility in water. In such cases the reaction mixture is acidified to convert the carboxylate anion to the carboxylic acid which precipitates out of solution and so can be filtered off.

If the alcohol has a sufficiently different boiling point from water, simple distillation may separate them, otherwise fractional distillation may be needed. If the alcohol has a long hydrocarbon chain, its solubility in water may be sufficiently low for it to separate out as a separate liquid layer when the reaction mixture is cooled in ice.

**TABLE 10.2 Boiling points and solubilities of some alcohols and acids**

Compound	Boiling point (°C)	Solubility in water <sup>a</sup>
methanol	65	m <sup>b</sup>
1-butanol	117	8
1-hexanol	157	0.6
acetic (ethanoic) acid	118	m
butanoic acid	164	m
pentanoic acid	186	3.4
hexanoic acid	205	1.0

*a* in g/100 g water at 25°C; solubilities are considerably lower at 0°C.

*b* m = miscible in all proportions.

## Exercises

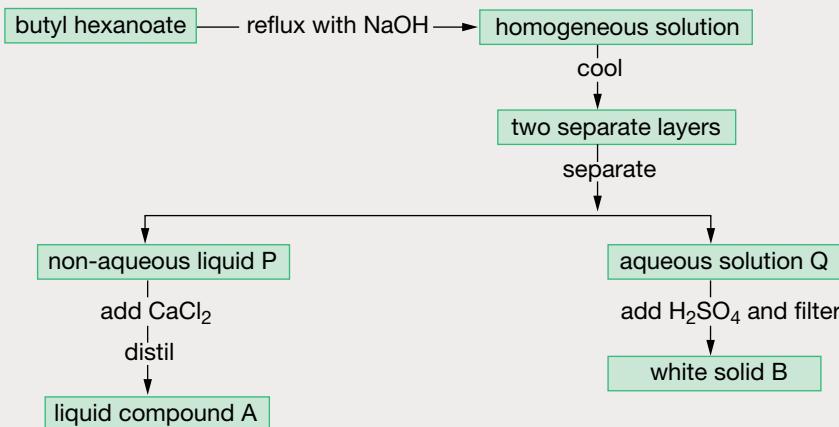
10 Write equations for the saponification of:

- a ethyl formate (methanoate)
- \*c 1-propyl acetate
- b methyl propanoate
- \*d ethyl heptanoate

11 a Esters that are insoluble in water often produce alcohols that are soluble in water. Why are the alcohols more soluble than the esters?

- b When acid is added to an aqueous solution of a carboxylate anion, the carboxylic acid generally precipitates from solution. Why is the acid insoluble in water whereas the anion is soluble?

12 1-butyl hexanoate was refluxed with sodium hydroxide solution until a homogeneous solution was formed. The reaction mixture was processed as shown in the following flowchart.



Anhydrous calcium chloride is often used to dry liquids that contain small amounts of water: this ensures that no water carries across when the liquid is subsequently distilled. You may consult Table 10.2 to answer the following questions.

- a Write an equation for the reaction that occurred during the refluxing.
- b Identify compounds A and B, explaining how you made your decision.
- c How would the experimenter have decided that liquid P was non-aqueous?
- d Why was sulfuric acid added to aqueous solution Q?

## 10.10 FATS AND OILS

**Fats and oils** are esters of glycerol (1,2,3-propanetriol). **Glycerol** is a derivative of propane containing an alcohol group on each carbon atom:

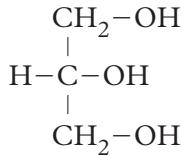
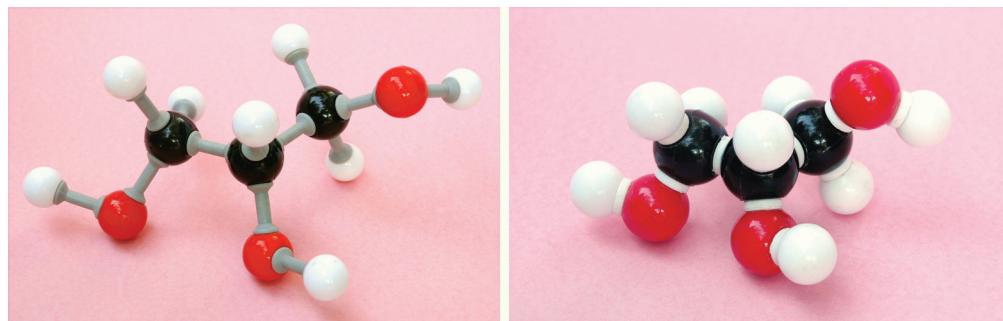


Figure 10.8 shows molecular models of glycerol.

Fats are solids at room temperature while oils are liquids. In Figure 10.9 copha, lard and dripping are fats while the other four products are oils.

The only difference between fats and oils and ordinary esters is that in fats and oils the *one* alcohol molecule is combined with *three* acid molecules. The acids involved are usually long-chain ones such as *saturated* palmitic and stearic



**FIGURE 10.8**  
Ball-and-stick and  
space-filling models of  
glycerol

acids and *unsaturated* ones such as oleic, linoleic and linolenic acids. These are shown in Table 10.3. Carboxylic acids obtained from fats and oils are called **fatty acids**.

**TABLE 10.3 Common carboxylic acids occurring in fats and oils (called fatty acids)**

Name (no. of C atoms)	Structure	Melting point (°C)
<i>Saturated</i>		
lauric (12)	$\text{CH}_3-(\text{CH}_2)_{10}-\text{COOH}$	44
myristic (14)	$\text{CH}_3-(\text{CH}_2)_{12}-\text{COOH}$	58
palmitic (16)	$\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$	63
stearic (18)	$\text{CH}_3-(\text{CH}_2)_{16}-\text{COOH}$	70
<i>Unsaturated</i>		
oleic (18)	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	16
ricinoleic (18)	$\text{CH}_3-(\text{CH}_2)_5-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	8
linoleic (18)	$\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	-5
linolenic (18)	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	-11



**FIGURE 10.9**  
Some common fats  
and oils. The four  
vegetable oils on the right  
contain more than 80%  
unsaturated triglycerides.  
Lard and dripping are  
animal fats; they contain  
higher percentages of  
saturated triglycerides.  
Coconut oil is an  
exceptional vegetable  
oil in that it is about 80%  
saturated; it is converted  
to solid copha by  
hydrogenating (saturating)  
the unsaturated  
components

## Saturated and unsaturated

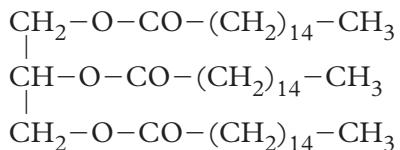
When all the carbon–carbon bonds in a molecule are single bonds, we say that the molecule is **saturated**. When the molecule contains one or more double or triple carbon–carbon bonds, ( $\text{C}=\text{C}$  or  $\text{C}\equiv\text{C}$ ), we say that the molecule is **unsaturated**.

The terms refer to the molecule being saturated or unsaturated with hydrogen atoms. If a double or triple bond is present, then more hydrogen could be added to the molecule by opening up a double or triple bond to form two or four more  $\text{C}-\text{H}$  bonds so the molecule could contain more hydrogen atoms. Since the molecule contains less than the maximum number of hydrogen atoms it is described as *unsaturated*. If all the carbon–carbon bonds are single ones, then no more hydrogen atoms could be added to the molecule and so it is described as *saturated*. Note that the terms refer to carbon–carbon bonds only and not to functional groups that contain double or triple bonds to other atoms such as  $\text{C}=\text{O}$ ,  $\text{C}=\text{N}$  or  $\text{C}\equiv\text{N}$ .

*Saturated* and *unsaturated* are widely used in the everyday world in connection with fats and oils; healthwise unsaturated fats and oils are generally considered to be preferable to unsaturated ones.

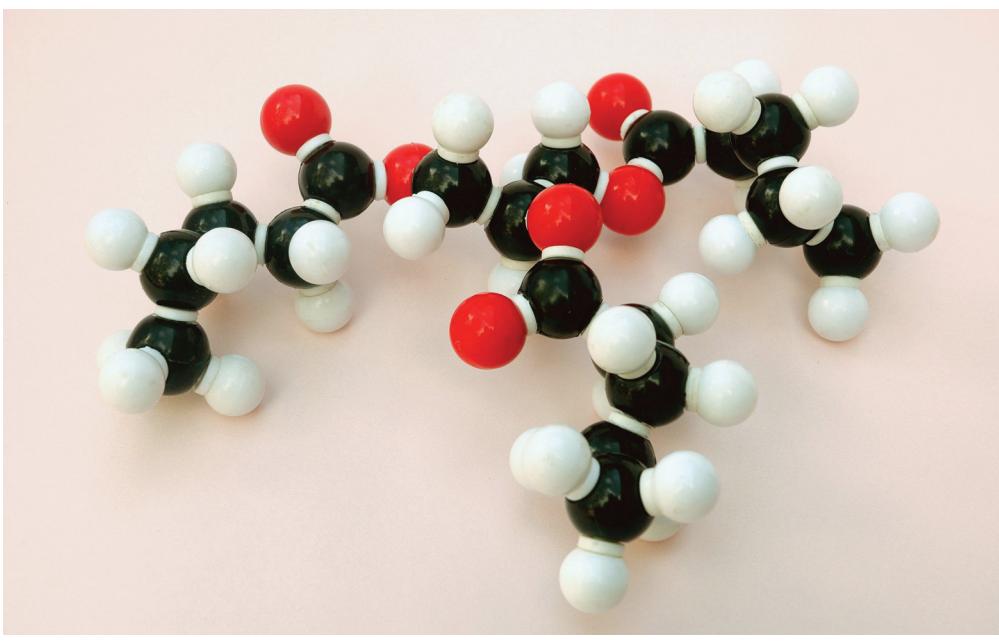
Saturated fatty acids lead to *solid fats* while unsaturated ones form *liquid oils*. The more double bonds in an acid, the lower its melting point and the lower the melting point of the oil formed.

These fats and oils (esters formed between glycerol and the acids in Table 10.3) are called **triglycerides**. A common triglyceride is glyceryl tripalmitate, a fat extracted from palm oil:

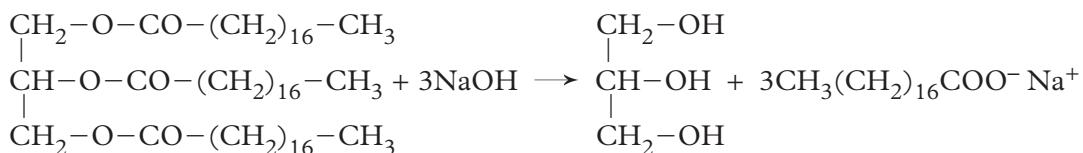


Glyceryl tristearate is found in animal fat. Figure 10.10 shows a molecular model of an ester of glycerol.

FIGURE 10.10  
A molecular model of a simple triglyceride (ester of glycerol), glyceryl tripentanoate



When such fats and oils are heated with sodium hydroxide solution, they saponify (just like any other esters) to form glycerol and the sodium salts of the carboxylic acid; for glyceryl tristearate:



In general



The main use of saponification of fats and oils is to make soap.

**Soap** is a soluble salt of a fatty acid, most commonly sodium stearate,  $\text{CH}_3-(\text{CH}_2)_{16}-\text{COO}^-\text{Na}^+$ , or sodium palmitate,  $\text{CH}_3-(\text{CH}_2)_{14}-\text{COO}^-\text{Na}^+$ .

## 10.11 MAKING SOAP

Although soap is made by the same saponification reaction as is used in the laboratory for ordinary esters, the conditions used are somewhat different. This is because the fat or oil being used and the glycerol formed are non-volatile, so refluxing is not necessary. The method of separating the soap and glycerol from water is also different.

To make soap commercially, various vegetable oils or chopped up fats (residues from butcher shops, abattoirs and other food processing factories) are heated with about 30% sodium hydroxide solution until all the oil or fat has dissolved. If necessary any solid residues are skimmed off then the solution is cooled and mixed with nearly saturated brine (NaCl solution). Upon standing this mixture settles into two layers—curds of soap on top of a solution of glycerol in brine. This process is called **salting out** the soap—causing a precipitate to form by greatly increasing the concentration of ions in the solution.

The curds of soap are removed and washed, various additives such as perfumes and colouring agents are introduced then the mixture is pressed and cut or moulded into bars for packaging and use.

Glycerol is obtained from the brine solution first by neutralising excess NaOH and distilling off the water (much lower boiling point than glycerol) then distilling the glycerol (from NaCl and other residues) under reduced pressure. The glycerol is used for making confectionery, cosmetics, pharmaceuticals and explosives (nitroglycerine in dynamite).

Bar soaps are sodium salts of stearic, palmitic and lauric acids, while shampoos and shaving soaps are generally potassium salts (they produce more foam with less water).

The saponification of a fat or oil to make a soap can be done in the laboratory by essentially the same process as described above. However, great care must be taken in handling concentrated sodium hydroxide solution, particularly when it is being heated to near its boiling point: it is extremely corrosive, particularly to hair, skin, flesh and eyes. Before performing this experiment you must carry out a thorough risk assessment in order to identify and manage all potential hazards. Goggles, protective clothing and gloves must be worn.

## School laboratory versus factory

In the school laboratory soap is made by mixing a relatively pure fat or oil such as dripping, lard or peanut or olive oil with excess sodium hydroxide solution. After salting out the soap, it is washed with water and partially dried by patting with filter paper. No attempt is made to recover the glycerol from the aqueous solution.

In industry the starting fats and oils are generally far from pure: they are commonly wastes from abattoirs and butcher shops. Industry is careful not to waste expensive reagents such as sodium hydroxide, so regularly monitors the amount of hydroxide required for its feedstock so only a very small excess of hydroxide is used. Industrially the glycerol is recovered from the aqueous residue (by distillation), because that is a readily saleable product. The remaining salt from the brine is reused. The raw soap has to be very carefully washed, then dried (to meet national standards) and blended with various perfumes, colouring agents and other additives and finally cut or pressed into blocks and packaged. While the actual saponification is generally done in a batch-wise process, the subsequent steps are usually performed as a continuous operation.

### Exercises

- 13 a** Draw the structures of (i) glyceryl tripropanoate \***(ii)** glyceryl trilauroate (use Table 10.3).
- b** Write equations for the saponification of the above esters.
- \*14** Comment on the logic of calling fats and oils triglycerides.
- 15 a** Draw the structures of (i) glyceryl trioleate \***(ii)** glyceryl trilinoleate.
- b** How many double bonds per molecule are there in (i) and (ii) above?
- c** In dietary contexts glyceryl trioleate is described as *monounsaturated* while glyceryl trilinoleate is described as *polyunsaturated*. How do you think these two terms are defined? Glyceryl tristearate is described as *saturated*. How, in terms of these three adjectives (if possible), would you describe a triglyceride made from one stearic acid molecule and two oleic acid molecules?
- 16 a** What acid is formed when (i) oleic (ii) linoleic acid is completely hydrogenated? How would this be done experimentally?
- b** How many moles of hydrogen are needed per mole of each acid?

## 10.12 SOAP, DETERGENT AND SURFACTANT

Three terms that are used in cleaning contexts are soap, detergent and surfactant. Soap was defined at the end of Section 10.10: it is a cleaning agent made from naturally occurring fats and oils. Originally a **detergent** was a *cleaning agent* (i.e. soap or a synthetic substitute). As synthetics came into prominence (after the 1950s) the word ‘detergent’ came to mean a *synthetic* cleaning agent as opposed to soap. Today the word detergent is also used for a cleaning *mixture* such as a laundry powder or liquid, dishwashing liquid, automatic dishwasher powder or floor cleaner.

A surfactant (short for surface active substance) is the key ingredient in detergent mixtures for doing the actual cleaning.

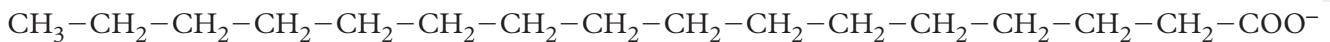
A **surfactant** is a substance that decreases the surface tension of water or, alternatively, that disperses dirt and grease as small particles throughout the water.

Soap is a surfactant. There are also many synthetic surfactants, which will be discussed in the next section.

Today the word ‘detergent’ tends to be used both for the actual surfactant and for the complete cleaning mixture. If you want to make it clear that you are talking about the active cleaning compound, use *surfactant*; there is no ambiguity about the meaning of that word.

## Soap as a surfactant

Soap works as a surfactant because it has a long hydrocarbon tail that readily dissolves in oily or waxy substances and an ionic head that easily dissolves in water:



Schematically:



This is sometimes described as a ‘tadpole’ structure.

The water soluble anionic head is said to be **hydrophilic** (water loving) while the water-repelling tail is described as **hydrophobic** (water hating).

By having the hydrophobic tail attach to oily particles while the hydrophilic head is dissolved in water, the surfactant anion acts as a ‘bridge’ between oily particles and water. The surfactant thus floats such particles off fabrics, fibres or skin as shown in Figure 10.11.

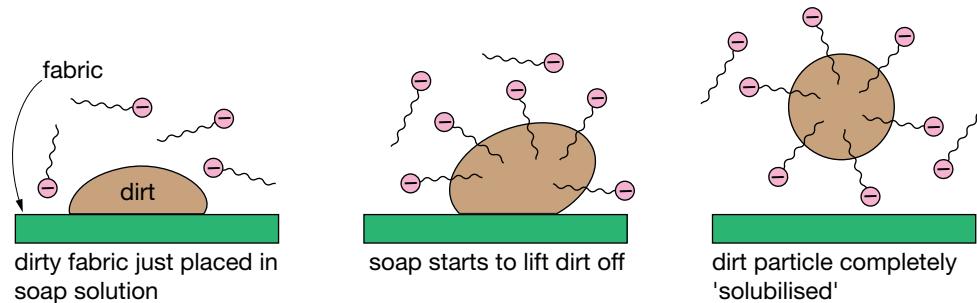


FIGURE 10.11  
How soap (or any surfactant) floats oily or waxy dirt off a surface

Once the oily particles are dispersed in the solution they tend not to combine together or resettle on surfaces because they are negatively charged and so repel one another. They remain dispersed throughout the water solution.

Soap and other surfactants remove non-oily dirt because they lower the surface tension of the water and so the water is more easily able to wet dirt particles and so move them off the skin or fabric. Surfactants lower the surface tension because they accumulate in the surface of the liquid where their hydrophobic tails can stick into the air and so be out of the water while their hydrophilic heads remain in the water and tend to repel one another.

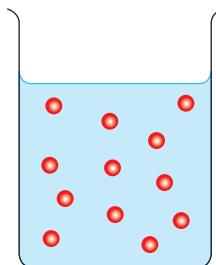
## 10.13 EMULSIONS

A dispersion of small droplets of one liquid throughout another liquid is called an **emulsion**.

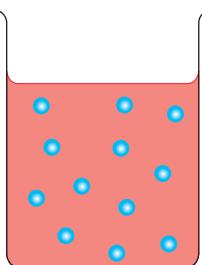
Soap, water and oil form an emulsion. In such mixtures soap acts as the **emulsifier**, the substance which causes large drops of oil to break up into very small droplets that can remain dispersed through the water almost indefinitely.

Common emulsions are milk, cream and mayonnaise; all of these are dispersions of oil particles through aqueous solutions. Butter and margarine are also emulsions; they are dispersions of aqueous solutions throughout an oil. The difference between oil-in-water emulsions and water-in-oil ones is illustrated in Figure 10.12. Many cosmetics are emulsions; moisturisers are usually oil-in-water emulsions while lipsticks are water-in-oil ones. Cleansing creams can be of either type. Water-based paints are often described as emulsions, but strictly they are not because the particles dispersed through the watery medium are solid, not liquid.

FIGURE 10.12  
The two types of emulsion, oil dispersed through water and water dispersed through oil



Small droplets of oil dispersed through water (or an aqueous solution). Examples are milk, cream, mayonnaise, moisturising cream, barrier cream.



Small droplets of water (or an aqueous solution) dispersed through oil. Examples are butter, margarine, lipsticks, sunscreen lotions.

All emulsions need a surfactant to stabilise them. This can be a naturally occurring compound (such as casein in milk or lecithin from egg yolk in mayonnaise), or can be a synthetic surfactant (next section) in cosmetics and pesticides.

Common emulsions.  
Contrast butter and margarine with lard and copha (Fig. 10.9): the latter are almost pure fat

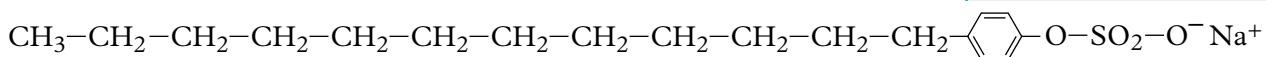


## 10.14 SYNTHETIC SURFACTANTS (DETERGENTS)

There are three types of synthetic surfactants (detergents): anionic (negatively charged), non-ionic and cationic (positively charged) ones.

### Anionic surfactants

**Anionic surfactants** are the oldest and still the most widely used synthetic detergents. Their structure is similar to that of soap as shown in Table 10.4. They have a long hydrocarbon tail and an anionic head, which is a sulfonate,  $\text{R}-\text{O}-\text{SO}_2-\text{O}^-$  instead of a carboxylate  $\text{R}-\text{COO}^-$ . The commonest anionic surfactant is sodium laurylbenzene sulfonate:



Its action is exactly the same as that of soap, except that it is a more effective surfactant. Consequently it is not used for personal hygiene (it removes too much oil from skin and hair). It is the major surfactant in laundry detergents and dishwashing liquids.

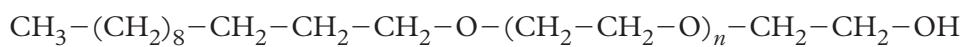
TABLE 10.4 Structure and common uses of different classes of surfactant

Type of surfactant	Structure (schematic)	Common uses
soap		personal hygiene
anionic		general cleaning, particularly in laundry and dishwashing detergents
non-ionic		low foam applications: dishwasher powders, paints, pesticides, cosmetics
cationic		hair conditioner, fabric softener, disinfectants and antiseptics

Soaps and synthetic anionic detergents generate a lot of foam. Contrary to popular belief, foam is not an essential part of cleaning (except in low water applications such as carpet cleaning and hair shampooing) and in fact can be a problem in some applications such as automatic dishwashers and front-loading washing machines.

### Non-ionic surfactants

**Non-ionic surfactants** also have a long hydrocarbon tail, but their ‘head’ is a long polar segment (containing many O atoms) ending in an alcohol group as shown schematically in Table 10.4. As the name implies they are molecules not ions. The polar end is made by joining several ethoxy groups ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) together with an H on the end one. These compounds are called *ethoxylates* or *polyoxyethylene ethers*. A typical non-ionic surfactant is dodecyl alcohol ethoxylate:



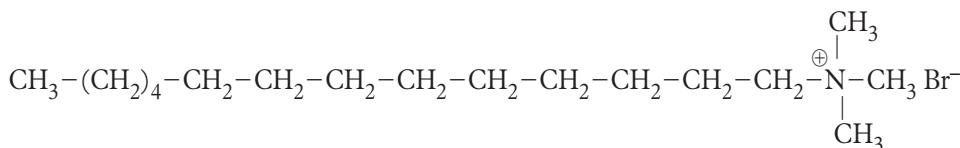
where  $n$  is typically between 5 and 50. The string of ethoxy groups is formed from ethylene oxide (Section 1.5).

Non-ionic surfactants form much less foam than do the anionics. Hence they are used where foam can be a problem. Significant amounts of non-ionic surfactants are used in dishwasher powders: there is also a small amount in laundry detergents. However, the main uses of non-ionic surfactants are in paints, adhesives, pesticides and cosmetics.

Foam is made up of large numbers of bubbles which are thin spherical films of water with air trapped inside. Bubbles form when surfactant molecules concentrate in the surface layer of water and make a very stable film. Anionic and cationic surfactants can accumulate in surface layers because their charge is concentrated at one end of the molecule and they have an oppositely charged ion with them. Non-ionic surfactants cannot accumulate in surface layers nearly so easily, because they have smaller charges spread out over a greater proportion of the molecule. Hence non-ionic surfactants do not form bubbles (foam) nearly so readily.

## Cationic surfactants

**Cationic surfactants** are derivatives of the ammonium ion in which the H atoms are replaced by alkyl groups (shown schematically in Table 10.4). Generally there are one or two long chain alkyl groups (10 to 20 C atoms) and two or three methyl groups. The long chain group(s) is(are) the oil soluble tail(s), while the charged N atom is the water soluble part. The simplest cationic surfactant is cetyl trimethyl ammonium bromide:



Cationic detergents clean plastics much better than anionics do. Cationics also tend to adsorb onto hair and fibres in textiles: they reduce friction and stop static electrical charges developing. Consequently cationic surfactants are widely used in hair conditioners and fabric softeners.

Many cationic surfactants are effective biocides (i.e. they kill many organisms), so most domestic and industrial disinfectants and sanitisers contain cationic detergents.

The common uses of the different classes of surfactants are summarised in Table 10.4.

## 10.15 SURFACTANTS AND HARD WATER

We saw in Section 8.8 that soap forms a scum (precipitate) with the magnesium and calcium ions in hard water and so it is much less effective than in soft water.

*Synthetic surfactants do not form precipitates with magnesium and calcium ions.* The efficiency of non-ionic and cationic surfactants is not affected by hard water. However the efficiency of anionic surfactants is decreased to some extent by hard water (but not nearly as greatly as for soap). This is because the anions are able to form soluble complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . This ‘ties up’ some of the surfactant and so to some extent prevents the surfactant from doing its intended job.



Some cleaning products used in homes. The synthetic surfactants they contain are: 'Finish', 'Fab', dishwashing liquid, shampoo, anionic and non-ionic surfactants; disinfectant and fabric softener, cationic ones; 'Soft as Soap', anionic; conditioner, cationic and non-ionic ones

One way of overcoming the problem of hard water interfering with the functioning of soap and anionic detergents is to add washing soda (sodium carbonate) to the water. This removes the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as insoluble carbonates. However, a better approach is to 'tie up' the calcium and magnesium ions with other complexing agents and so stop these ions interfering with the action of the surfactant.

Substances added to laundry detergents to remove or 'tie up'  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are called **builders**. Builders improve the 'cleaning power' of laundry detergents.

One widely used builder is sodium tripolyphosphate,  $\text{Na}_5\text{P}_3\text{O}_{10}$ . It works in three ways: it buffers the solution to a slightly alkaline pH (at which the surfactants work most efficiently), it complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and so stops them 'tying up' surfactant anions, and it stops removed dirt from flocculating and re-settling on the clothes.

However, there are environmental problems with using phosphates in detergents.

## 10.16 ENVIRONMENTAL EFFECTS

Soap has very little environmental impact because it is readily broken down to carbon dioxide and water by organisms such as bacteria in sewage works and in natural waterways. Substances that are easily broken down in this way are said to be *biodegradable*.

### Biodegradability

The earliest synthetic surfactants were *branched-chain*<sup>†</sup> alkylbenzene sulfonates (anionic). These were not easily biodegradable and led to considerable environmental damage: rivers and dams became covered in foam from a build-up of detergent, which was a problem in the 1960s. Subsequently the linear chain alkylbenzene sulfonates described above were developed. The

<sup>†</sup> See pp. 259–60 of CCPC for the meaning of this term.

biodegradability of these compounds is similar to that of soap, so the ‘rivers of foam’ problem disappeared in the 1970s.

Caution is needed with cationic surfactants. Their biocidal properties mean that if their concentration gets too great in sewage treatment works, they can kill the bacteria that normally decompose the sewage. However, at lower concentrations they are broken down by the bacteria normally in sewage treatment works. Their more specialised uses mean that smaller amounts of cationics are discharged so that they rarely create a problem.

The most serious environmental problem comes not from the actual surfactants themselves but from the phosphate builders normally present in laundry detergents.

## Phosphates in washing powders and liquids

As was explained in Section 8.12, phosphate is a nutrient for many organisms and increased concentrations of it in natural waterways can lead to harmful algal blooms. Washing powders and liquids are a major source of phosphate in domestic sewage and so in effluents discharged to natural waterways.

*It is the phosphate content of washing powders and liquids that is the major environmental concern with detergents today.*

Builders are not added to soap because soap is used almost exclusively for personal hygiene and builders have no effect on body cleaning. Therefore phosphate is not a problem with soap.

In many countries there are restrictions on the amount of phosphate that can be included in washing powders and liquids. In Australia there is a voluntary code in operation.

## Exercises

- 17** Why do paints and liquid insecticides for spraying on plants need to contain a surfactant?
- 18 a** The water soluble end of a simple non-ionic surfactant molecule is
- $$-(\text{CH}_2-\text{CH}_2-\text{O})_7-\text{CH}_2-\text{CH}_2-\text{OH}$$
- Explain why this structure would be hydrophilic (have a great affinity for water).
- b** Why is this surfactant unaffected by water hardness?
- 19** A common cationic surfactant is distearyl dimethyl ammonium chloride. Stearyl is the alkyl group,  $\text{C}_{17}\text{H}_{35}$ . Draw the structure of this surfactant.
- \*20** Unlike mixtures of anionic and non-ionic surfactants which are very effective detergents, cationic and anionic surfactants cannot be used together: the mixture loses its surfactant properties. Suggest a reason for this.
- 21 a** Glass tends to develop negative surface charges (because of the large number of O atoms there: glass contains  $\text{SiO}_4$  units). Anionic surfactants are more effective in removing neutral oily particles of dirt from glass surfaces than are cationic ones. Explain, with the help of a diagram, why this is so.
- \*b** Certain plastics such as polyethylene and polypropylene tend to develop positive surface charges (because of the large number of C–H units in the surface). Cationic surfactants are more effective in removing neutral oily particles of dirt from such plastics than are anionic ones. Explain, with the help of a diagram, why this is so.

- c** If cationic surfactants are used to clean glass, it is very difficult to remove all traces of the surfactant even after rinsing several times with clean water. Explain why. If objects made of polyethylene or polypropylene are washed with an anionic surfactant, it is difficult to remove all traces of the surfactant by rinsing. Explain why.
- 22** Both oil-in-water and water-in-oil emulsions need a surfactant to stabilise them. Draw diagrams to show how the surfactant molecules stabilise each type of emulsion.
- 23** Write an equation for the reaction between:
- sodium palmitate and calcium ion
  - sodium carbonate solution and magnesium ions.
- 24** Suggest one reason why complexing calcium and magnesium ions with tripolyphosphate would be preferable to precipitating them with washing soda.
- 25** The label on a certain laundry powder stated that it contained 4.0% phosphorus. What is the percentage of sodium tripolyphosphate  $\text{Na}_5\text{P}_3\text{O}_{10}$  in this laundry powder?

Another alkali in widespread use industrially is *sodium carbonate*. Its main uses are in the manufacture of glass, paper and detergents. Let us therefore look at how it is made (and return to the question of its uses in more detail after that).

## FOR INVESTIGATION<sup>†</sup>

Search out the meaning of the P and NP symbols that are displayed on laundry detergents in supermarkets. Find out whether this factor is of importance in selecting a detergent in your locality.

Also seek out information on what builders, other than phosphate, are commonly used in laundry detergents and how they work.



## 10.17 MANUFACTURE OF SODIUM CARBONATE: THE SOLVAY PROCESS

Although more sodium hydroxide is used than any other alkali, it is not the cheapest alkali available; sodium carbonate is cheaper, though the price gap has been closing in recent decades. Sodium carbonate is cheaper because it is made from relatively cheap materials, brine (sodium chloride solution) and limestone (calcium carbonate), and does not require the large amounts of electricity that sodium hydroxide does. The other product is calcium chloride. Relatively expensive ammonia is used in the process but it is recycled, so its cost does not affect the overall price too greatly. The industrial process for making sodium carbonate is called the Solvay process.

### The basic outline

The key steps in the **Solvay process** are:

- Saturate a concentrated brine solution with ammonia.
- Bubble carbon dioxide (from decomposing limestone) through this to form a precipitate of sodium hydrogen carbonate.

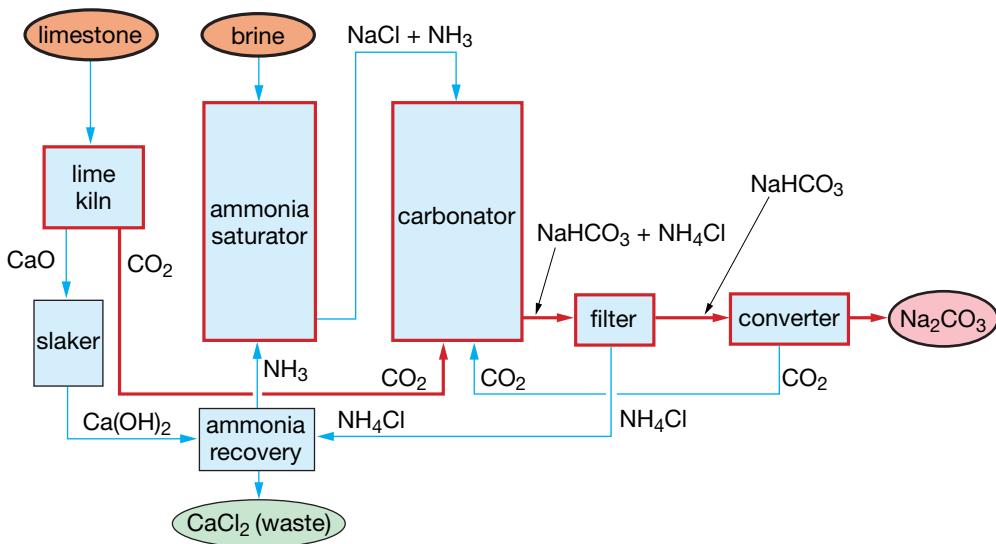
<sup>†</sup> Not required for NSW HSC.

- 3 Filter off the sodium hydrogen carbonate and heat it to form sodium carbonate.
- 4 Regenerate the ammonia from the filtrate from Step 3.

Carbon dioxide is obtained from heating limestone ( $\text{CaCO}_3$ ). The calcium oxide so formed is ‘slaked’ (reacted with water to form hydroxide) then used to recover the ammonia ( $\text{Ca}(\text{OH})_2 + \text{NH}_4^+ + \text{heat}$ ).

A flowchart of the process is shown in Figure 10.13.

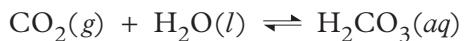
FIGURE 10.13  
A flowchart for the Solvay process



## The chemistry

### Steps 1 and 2

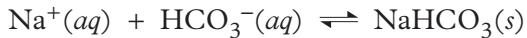
When carbon dioxide is bubbled through the brine saturated with ammonia, CO<sub>2</sub> first dissolves:



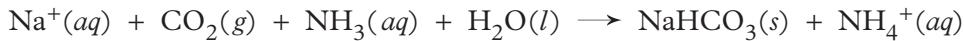
Then the weak acid H<sub>2</sub>CO<sub>3</sub> reacts with the weak base NH<sub>3</sub>:



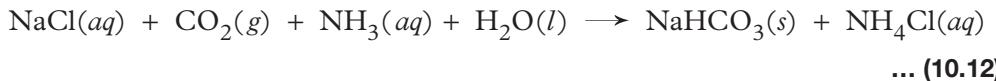
and finally sodium ions form a precipitate with the hydrogen carbonate ion:



The overall reaction that occurs in the carbonator tower is the sum of these three reactions:

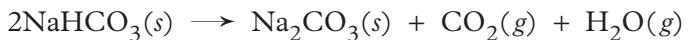


If we add Cl<sup>-</sup> to this equation (the spectator ion from NaCl) and write it in neutral species form we get:



### Step 3

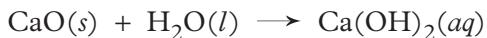
Sodium hydrogen carbonate is filtered off and converted to sodium carbonate by heating:



The carbon dioxide formed here is recycled to the carbonator tower, but it is only half what was originally absorbed. Therefore fresh  $\text{CO}_2$ , from heating limestone in the lime kiln, has to be supplied continuously. The reaction is:



The calcium oxide is converted to a calcium hydroxide solution in the slaker:

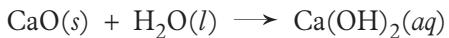


#### Step 4

This calcium hydroxide solution is mixed with the filtrate from Step 3 (containing  $\text{NH}_4\text{Cl}$ ) and the mixture heated to regenerate ammonia which is re-used in Step 1:



There are five chemical reactions involved. To see what the overall change is we add these five equations up, but to do this we must first double Equation 10.12. The five equations to add are then:



These add up to give:



This shows that sodium chloride and calcium carbonate are the raw materials for making sodium carbonate and that calcium chloride is the other (unwanted) product.

Note that this reaction does not occur directly: if we mix sodium chloride solution with calcium carbonate, no reaction occurs. In fact it is the reverse reaction that occurs in the laboratory: sodium carbonate and calcium chloride react to form a precipitate of calcium carbonate.

The Solvay process makes Reaction 10.13 occur first by reacting the weak acid  $\text{H}_2\text{CO}_3$  with the weak base  $\text{NH}_3$ , then by using the fact that sodium hydrogen carbonate has quite a low solubility and so can be made precipitate out of fairly concentrated solutions. There is a considerable energy input to make the whole process work.

Potassium carbonate cannot be made in this way because potassium hydrogen carbonate is too soluble.

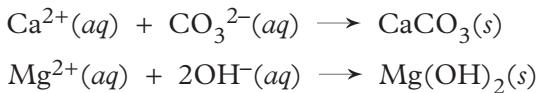
### Brine purification

Brine for the process is obtained either from salt water stored deep underground in some parts of the world (so-called brine wells), from underground rock salt deposits (by pumping water into the deposit to dissolve it) or from sea water (by solar evaporation). A solution of about 30%  $\text{NaCl}$  in water is required for the Solvay process.

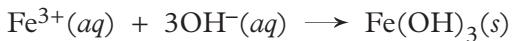
The Solvay plant at Osborne near Adelaide, operated by Penrice Soda Products Pty Ltd



Impurities that could lead to solids precipitating out with the sodium hydrogen carbonate need to be removed. The impurities actually present depend upon the source of the brine, but generally some calcium and magnesium ions will be present, possibly with iron ions as well. Sodium carbonate is added to precipitate calcium, then hydroxide is added to precipitate magnesium (its carbonate is slightly soluble so does not precipitate with carbonate at the low concentrations involved):



Hydroxide also precipitates iron and other heavy metals, if they are present:



After flocculation all solids are filtered off, including any suspended matter that may have been in the original brine.

## Environmental issues

The major environmental issue associated with the Solvay process is the disposal of the calcium chloride solution left over from recovery of ammonia. The best way to handle a waste problem is to find a use for the waste. A certain amount of calcium chloride is used as a drying agent by industry and in cold countries in parts of Europe and North America for de-icing roads (like NaCl it lowers the melting point of ice): it is more effective than sodium chloride which is more commonly used. However, far more calcium chloride is produced than is required for these purposes. In Australia there is little demand for calcium chloride.

### Disposal of calcium chloride solution

Solvay plants close to the sea discharge their wastes (with suitable dilution) into the ocean. Any residual alkali in the waste is neutralised by the buffering action of bicarbonate present in sea water and the wastes do not significantly

increase the existing concentrations of calcium ions in sea water. If calcium ion concentrations were to rise too much, harmless calcium carbonate would precipitate out.

The Solvay plant at Osborne near Adelaide uses brine from sea water and discharges its wastes into the ocean.

Solvay plants remote from oceans are not allowed to discharge their wastes into rivers because they would significantly increase the chloride concentration in the water and this is unacceptable. Evaporation to dryness and disposal in specially designed burial sites is an acceptable (though much more expensive) method of disposal in such cases. However because of the high solubility of calcium chloride, it will leach out to some extent over time. Small additions of calcium and chloride ions to natural waterways over long time periods are not too great a concern.

## Ammonia losses

There is often some loss of ammonia to the atmosphere from Solvay plants, partly as leakage from the ammonia saturator, carbonator and ammonia recovery unit, and partly from evaporation of ammonia adsorbed on the solid sodium hydrogen carbonate when it is heated in the converter. With good design and careful monitoring, however, this can be kept down to an acceptable level. Ammonia is a significant air pollutant, particularly if discharged near cities.

## Waste heat

The overall reaction for the Solvay process, Equation 10.13, is close to thermally neutral ( $\Delta H \approx 0$ ). Some of the reactions making up this overall reaction are exothermic, while others are endothermic. However, it is not possible to capture all of the heat released in the exothermic ones and use it for the endothermic ones. Consequently there are considerable energy inputs into the Solvay process as well as significant amounts of waste heat at the end of the reaction. Plants near the sea can discharge this as hot water with sufficient dilution not to cause any significant thermal pollution (p. 227 CCPC). Inland plants need more careful waste heat management, perhaps by using cooling ponds.

## Mining

Other environmental issues relate to the common concerns about mining generally. The Solvay process needs limestone and brine. Mining or extraction of these can cause environmental damage particularly if the ores are in sensitive areas.

## Quantity calculations

In any industrial plant for making chemicals it is important that raw materials are purchased and used in the correct proportions so as to minimise waste. Industry tries to use reagents in stoichiometric amounts (unless the chemical reaction requires an excess of one reagent to make it go to completion or unless one reagent is very cheap, such as air). In addition industry needs to be able to calculate the quantities of wastes (or unwanted products) that it will produce and have to dispose of.

In the Solvay process both starting materials involve significant costs and there is an unwanted product to dispose of at the end. Example 1 illustrates the type of calculation that is frequently needed in an industrial plant.



### Example 1

What masses of limestone (88% calcium carbonate) and brine (31% sodium chloride) are needed per tonne of sodium carbonate produced by the Solvay process?

The overall equation for the process is Equation 10.13:



$$\text{Molar mass of Na}_2\text{CO}_3 = 2 \times 23.0 + 12.0 + 3 \times 16.0$$

$$= 106.0 \text{ g/mol}$$

$$\text{Number of moles in 1.00 tonne Na}_2\text{CO}_3 = \frac{1.00 \times 10^6 \text{ g}}{106.0 \text{ g/mol}}$$
$$= 9.43 \times 10^3 \text{ mol}$$

From the chemical equation,

$$\text{Number of moles of CaCO}_3 \text{ needed} = \text{number of moles of Na}_2\text{CO}_3 \text{ produced}$$
$$= 9.43 \times 10^3 \text{ mol}$$

$$\text{Molar mass of CaCO}_3 = 40.1 + 12.0 + 3 \times 16.0$$
$$= 100.1 \text{ g/mol}$$

$$\text{Mass of CaCO}_3 \text{ needed} = 9.43 \times 10^3 \times 100.1$$
$$= 9.44 \times 10^5 \text{ g}$$

But CaCO<sub>3</sub> is only 88% of the limestone.

$$\therefore \text{mass of limestone required} = 9.44 \times 10^5 \times \frac{100}{88}$$
$$= 1.07 \times 10^6 \text{ g} = \mathbf{1.1 \text{ tonne}}$$

Also from the chemical equation,

$$\text{Number of moles of NaCl required} = 2 \times \text{number of moles of Na}_2\text{CO}_3 \text{ produced}$$
$$= 2 \times 9.43 \times 10^3 \text{ mol}$$

$$\text{Molar mass of NaCl} = 23.0 + 35.5$$
$$= 58.5 \text{ g/mol}$$

$$\text{Mass of NaCl required} = 2 \times 9.43 \times 10^3 \times 58.5$$
$$= 1.10 \times 10^6 \text{ g}$$

But NaCl is only 31% of the brine.

$$\therefore \text{mass of brine required} = 1.10 \times 10^6 \times \frac{100}{31}$$
$$= 3.56 \times 10^6 \text{ g} = \mathbf{3.6 \text{ tonne}}$$

Per tonne of sodium carbonate produced, the Solvay process requires 1.1 tonne of limestone and 3.6 tonne of brine.

## 10.18 LOCATION OF INDUSTRIAL PLANTS

The main factors in selecting the location for an industrial plant are:

- availability of raw materials
- availability of sufficient energy at competitive prices
- location of markets for the product
- availability of a workforce at reasonable cost
- suitability of nearby sites for disposal of wastes
- environmental controls on discharges to air and water.

When there is more than one significant raw material, the relative costs of transporting the quantities of the materials required must be taken into account.

The Solvay process requires limestone and brine as raw materials: limestone, being a solid, is probably easier to transport than brine (which is usually at least 70% water). Although ammonia is used, it is recycled so the high costs of bringing in the initial amounts required probably do not greatly affect the overall costs in the long run. The end product is also an easily transported solid, so closeness to the markets may not be a high priority consideration. Disposal of the waste calcium chloride however would be a major consideration.

### FOR INVESTIGATION

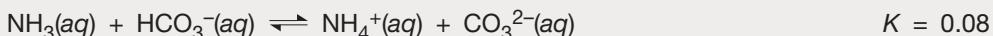
Search out information about the geographic surroundings of the Solvay plant at Osborne in South Australia and work out the advantages and disadvantages of locating this plant there.

Similarly, find information about the sodium hydroxide plants at Yarwun, near Gladstone in Queensland, and at Botany (Sydney) to work out the advantages and disadvantages of locating those plants at those locations.



### Exercises

26 For the following reactions the equilibrium constants are:



Use these equilibrium constants to explain qualitatively why it is just the first reaction (and not the second also) that occurs in the Solvay process.



27 Would you regard ammonia as a catalyst in the Solvay process? Explain why or why not.

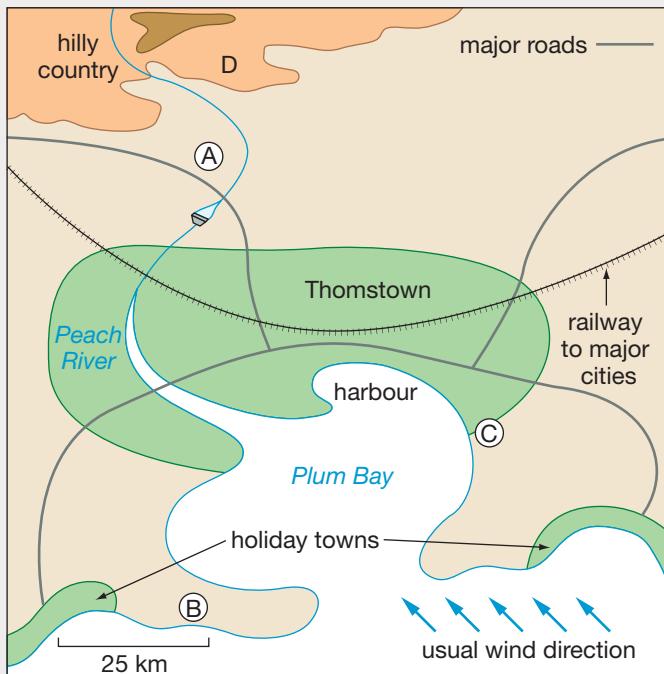
28 What mass of calcium chloride is produced per tonne of sodium carbonate in the Solvay process? If this is formed as a 30% (w/w) aqueous solution, what mass of calcium chloride solution has to be disposed of per tonne of sodium carbonate produced?

29 For every tonne of dry sodium hydrogen carbonate produced by the Solvay carbonator, what mass of ammonia needs to be fed back into the ammonia saturator?

30 What mass of calcium carbonate needs to be decomposed to produce sufficient calcium oxide and calcium hydroxide to regenerate 1.00 tonne ammonia in the Solvay process?

31 What mass of anhydrous sodium carbonate is obtained per kilogram of dry sodium hydrogen carbonate produced by the carbonator in the Solvay process?

- 32** What volume of carbon dioxide (measured at 25°C and 100.0 kPa) is required per tonne of (a) sodium hydrogen carbonate and (b) sodium carbonate produced by the Solvay process? Why are these amounts different?
- 33** The Solvay process produces anhydrous sodium carbonate. Much of this is dissolved in water and crystallised from solution as the decahydrate for sale as washing soda. What mass of washing soda is produced from 1.00 tonne of anhydrous sodium carbonate?
- 34** What mass of brine (30% NaCl in water) is required per tonne of limestone (85% CaCO<sub>3</sub>) in the Solvay process? What factors other than quantity would influence the costs of transporting these raw materials? Comment on the desirability of locating a Solvay plant near the brine or limestone source, based on transport alone.
- 35** Below is a map of the region surrounding Thomstown, a city of about one million people. The city has a very good harbour for local and international shipping and is connected by rail and freeways to other major cities. It draws its water from a dam on the Peach River. One of its major industries is a glass-making factory which is growing rapidly. There are good limestone deposits in the hills at D, about 50 km from the city. Company X wants to construct a Solvay plant for the manufacture of sodium carbonate. It has available to it three possible sites for the plant, A, B and C. Evaluate the advantages and disadvantages of each site.



## 10.19 USES OF SODIUM CARBONATE

The Solvay process produces anhydrous sodium carbonate. Much of this is converted into sodium carbonate decahydrate, Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O, which is commonly called **washing soda**. The anhydrous substance is also known as **soda ash**, a name that comes from the historical method of obtaining the substance—from extracting the ash from wood fires with water.

The main uses for sodium carbonate are:

- *glass-making*. More than half the sodium carbonate produced is used to make glass. Soda glass or common bottle and window glass is made by melting a mixture of sodium carbonate, calcium carbonate and sand (silicon dioxide).
- *water treatment*. Sodium carbonate is used to soften water (by precipitating magnesium and calcium carbonates) both industrially and domestically: it is present for this purpose in some washing powders (as washing soda). It is also used to make zeolite builders which are increasingly being used to replace phosphate builders in washing powders and liquids (Section 10.16).
- *making soaps and detergents*. Often used as a cheaper alternative to sodium hydroxide.
- *paper making*. Sodium carbonate is used to make sodium hydrogen sulfite which is used in one method of paper making.
- *as a common base* in many chemical factories, because it is generally cheaper than sodium hydroxide.
- *making sodium hydrogen carbonate*, which is used as **baking soda** and in fire extinguishers (the sodium hydrogen carbonate from the Solvay process is contaminated with ammonia; heating this product to remove ammonia usually decomposes some  $\text{NaHCO}_3$  so  $\text{Na}_2\text{CO}_3 + \text{CO}_2$  is a more efficient way of getting  $\text{NaHCO}_3$ ). Sodium hydrogen carbonate is also known as sodium bicarbonate and bicarbonate of soda.
- *removing sulfur dioxide from flue gases* in power stations. This process is becoming increasingly common, particularly overseas where power stations have to meet more stringent emission controls.

## Exercises

- 36** Sodium carbonate is used as a base in many chemistry laboratories. Write equations for the reactions of sodium carbonate with **(a)** nitric acid **\*(b)** sulfuric acid **\*(c)** acetic acid.
- 37** **a** Sodium hydrogen carbonate is made by bubbling carbon dioxide into a solution of sodium carbonate. Write an equation for the reaction.  
**b** What volume of  $\text{CO}_2$ , measured at 298 K and 100 kPa, is needed to convert 1.55 kg sodium carbonate to hydrogen carbonate? What mass of sodium hydrogen carbonate is produced?
- 38** **a** Sodium hydrogen carbonate is used in dry-powder fire extinguishers. When the powder is sprayed over the fire, the heat of the fire decomposes it. Write an equation for the decomposition and explain how this extinguishes the fire.  
**b** Sodium hydrogen carbonate is also used in soda-acid fire extinguishers. These contain separate containers of  $\text{NaHCO}_3$  and HCl solution. To use the extinguisher, it is tipped upside down to mix the reagents and a stream of carbon dioxide foam comes out. Write an equation for the reaction that occurs.  
**c** On the basis of volume of  $\text{CO}_2$  produced per total mass of chemicals used, explain why  $\text{NaHCO}_3 + \text{HCl}$  is more efficient than  $\text{Na}_2\text{CO}_3 + \text{HCl}$  would be.
- 39** **a** Baking soda, sodium hydrogen carbonate, mixed with cream of tartar, potassium hydrogen tartrate,  $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$ , a weak monoprotic acid, is used as a baking powder (releases  $\text{CO}_2$  which causes the cake mixture to rise). Write an equation for the reaction forming  $\text{CO}_2$ .  
**b** Sometimes calcium dihydrogen phosphate is used with baking soda in baking powders. Write an equation for this reaction. (Remember that  $\text{HPO}_4^{2-}$  is a very weak acid.)



**40** Granulated sodium carbonate is used to remove sulfur dioxide from flue gases of power stations.

- Write an equation for the reaction.
- What mass of anhydrous sodium carbonate is needed to remove all the SO<sub>2</sub> from 1.00 × 10<sup>6</sup> L of flue gas (at 298 K and 100 kPa) if it contains 1.00% by volume of SO<sub>2</sub>?

## Important new terms

You should know the meaning of the following terms.

anionic surfactant (p. 367)  
baking soda (p. 379)  
brine (p. 352)  
builders (p. 369)  
cationic surfactant (p. 368)  
chlor–alkali industry (p. 352)  
detergent (p. 364)  
diaphragm cell (p. 352)  
electrochemical cell (p. 348)  
electrolysis (p. 347)  
electrolytic cell (p. 348)  
emulsifier (p. 366)  
emulsion (p. 365)  
fats and oils (p. 360)

fatty acid (p. 361)  
glycerol (p. 360)  
hydrophilic (p. 365)  
hydrophobic (p. 365)  
membrane cell (p. 356)  
mercury cell (p. 354)  
non-ionic surfactant (p. 367)  
salting out (p. 363)  
saponification (p. 358)  
saturated (p. 362)  
soap (p. 363)  
soda ash (p. 378)  
Solvay process (p. 371)  
surfactant (p. 365)  
triglyceride (p. 362)  
unsaturated (p. 362)  
washing soda (p. 378)

## Test yourself

- Explain the meaning of each of the items in the ‘Important new terms’ section above.
- Give the two key properties of sodium hydroxide that determine its uses.
- Describe three important uses of sodium hydroxide.
- Sketch the apparatus you would use to electrolyse an aqueous solution of copper chloride. Explain what would happen at each electrode. Identify the anode and cathode.
- Explain the difference between galvanic and electrolytic cells: which type produces electrical energy and which uses it?
- Describe (with equations for electrode reactions) what happens when a concentrated aqueous solution of sodium chloride is electrolysed using inert electrodes. What happens if **a** a mercury cathode is used **b** a very dilute solution is used **c** molten sodium chloride is used?
- Describe the essential features of **a** the diaphragm cell **b** the mercury cell and **c** the membrane cell for the production of sodium hydroxide. What are the advantages and disadvantages of each type of cell?
- Write an equation for the saponification of a simple ester.
- Draw the structure of one fat or oil. Draw the structure and name the products of the saponification of the fat or oil you drew.

- 10** What is a triglyceride? Draw a structure to illustrate.
- 11** Explain how soap is made. What other important product is obtained from this process?
- 12** What is the difference between a detergent and a surfactant?
- 13** Explain how soap removes dirt from soiled objects.
- 14** Name the three classes of synthetic surfactant and explain their essential structures in terms of simple diagrams.
- 15** List common uses for each of these classes of surfactant and explain why each is so used.
- 16** What is the effect of hard water on **a** soap **b** synthetic surfactants?
- 17** Describe the effects that **a** soap **b** synthetic detergents have upon the environment. How are these minimised?
- 18** Outline the basic chemistry of the Solvay process for making sodium carbonate. Include equations for all reactions involved. What are the raw materials and what is the other product (apart from sodium carbonate)?
- 19** Draw a flowchart of the Solvay process, showing clearly which substances are recycled.
- 20** What are the environmental impacts of a Solvay plant? How are these minimised?
- 21** List the main factors that influence the decision to build a chemical manufacturing plant at a particular location. Illustrate by referring to the Solvay process.
- 22** Describe four major uses of sodium carbonate.
- 23** How is sodium hydrogen carbonate made? By what other names is it known? What are some of its uses?

# EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR OPTION 1

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination: for more information see p. 93.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

- |  | MARKS |
|--|-------|
| 1 Use one specific example that is not a fossil fuel to demonstrate the factors involved in the replacement of natural products with chemically manufactured ones.                           | 4     |
| 2 Describe, with chemical equations where appropriate, three major uses of sulfuric acid.  | 5     |
| 3 Outline the chemistry of the industrial production of sodium hydroxide and identify potential hazards with the procedure.  | 6     |
| 4 Distinguish between galvanic and electrolytic cells, including mention of energy differences.  | 4     |
| 5 Compare the usefulness of Le Chatelier's principle and the equilibrium expression for a reaction in predicting the effects of various changes upon the equilibrium position of a reaction. | 4     |
| 6 Describe an experiment you performed to demonstrate the effect of soap as an emulsifier.   | 3     |
| 7 Discuss the ways that operators of Solvay process plants minimise environmental impacts of the process.  | 4     |
| 8 Explain why sulfuric acid plants are often located near metal-extraction plants and identify the advantage of this to both. Include at least one chemical equation.                        | 4     |
| 9 Describe an experiment you have performed to analyse qualitatively an equilibrium reaction.  | 5     |
| 10 Discuss the environmental impacts of using current-day detergents rather than soap.   | 4     |
| 11 Use the industrial manufacture of sodium hydroxide to demonstrate the way in which advances in science can lead to improvements in technology.  | 5     |
| 12 Demonstrate the relationship between soap and fats and oils and mention some specific raw materials for soap manufacture.   | 4     |
| 13 Describe an experiment you have performed to identify the products of the electrolysis of aqueous sodium chloride solutions.  | 6     |
| 14 Outline the method used to extract sulfur from naturally occurring deposits of the element and explain how the properties of sulfur allow this procedure to work.                         | 5     |
| 15 Compare the environmental impacts of the current membrane cell for producing sodium hydroxide with those of the methods used previously.  | 4     |

- 16** Describe an experiment you have performed to carry out one of the chemical steps involved in the Solvay process. Identify any hazards associated with the experiment and explain how you minimised them. **5**
- 17** Explain (on the molecular level) how a small amount of soap in water allows an emulsion to be formed between water and oil. List four everyday situations where this is used. **4**
- 18** Assess the procedures commonly used for the safe handling of concentrated sulfuric acid in school laboratories. **4**
- 19** Use the Solvay process to demonstrate the main criteria that are used to decide where to locate a chemical manufacturing plant. **6**
- 20** Describe an experiment you have performed to determine the properties of one particular emulsion and to relate its properties to its uses. **5**

# REVISION TESTS FOR OPTION 1: INDUSTRIAL CHEMISTRY

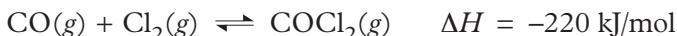
## TEST A

**Total marks: 25**

**Suggested time: 45 minutes**

**MARKS**

- a Phosgene is prepared by the reversible reaction:



What is the effect upon the equilibrium percentage conversion of CO to  $\text{COCl}_2$  of

- i increasing the pressure (by pumping more equilibrium mixture into a fixed volume)
- ii adding extra  $\text{Cl}_2$  to an equilibrium mixture
- iii increasing the volume being occupied by the equilibrium mixture
- iv increasing the temperature?

Explain how you determined each of your answers.

3

- b i Explain how environmental issues affect the design of the  $\text{SO}_2$  to  $\text{SO}_3$  converter in the industrial manufacture of sulfuric acid.

2

- ii Describe experiments you have performed (or seen performed) to demonstrate the effectiveness of sulfuric acid as an oxidising agent and as a dehydrating agent.

5

- c i Describe, using chemical equations, the membrane cell method for making sodium hydroxide.

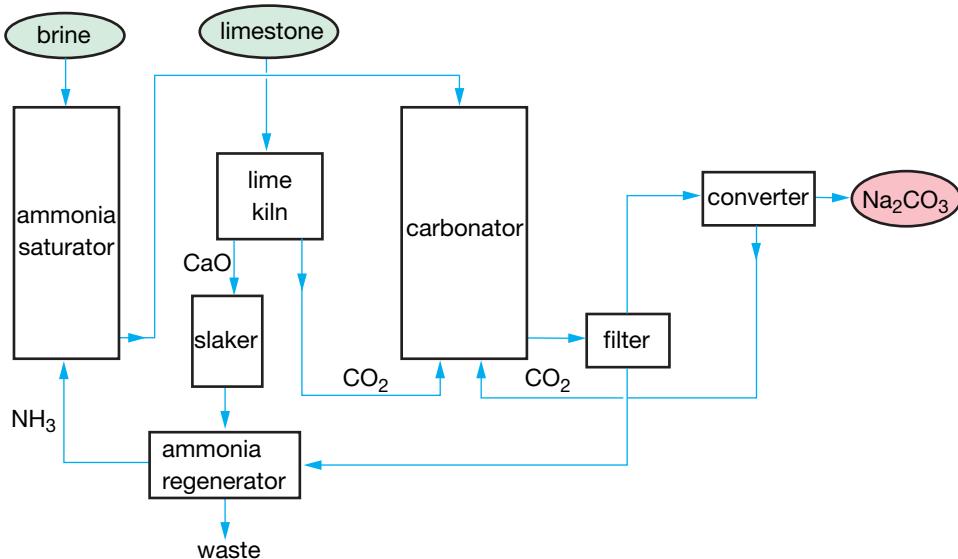
3

- ii What are the advantages of the membrane cell over the older diaphragm cell and the mercury cell?

2

- d The diagram below is a flow chart for the Solvay process. Use this to summarise the chemistry of the process.

4

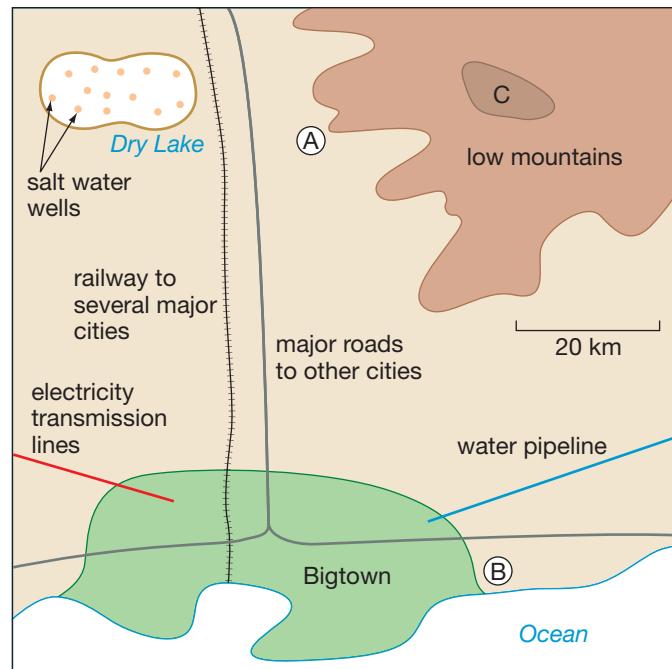


- e Outline the chemical structure and different uses of three types of surfactant (detergent).

6

**TEST B****Total marks: 25****Suggested time: 45 minutes**

- |  | MARKS |
|--|-------|
| a Identify the main chemical reactions in the industrial manufacture of sulfuric acid.   | 3     |
| b i Write equations for the electrode reactions and the overall reaction in the electrolysis of a concentrated aqueous solution of sodium chloride using inert electrodes.   | 3     |
| ii Assess the benefits of replacing the diaphragm cell with the mercury cell for the production of sodium hydroxide.   | 4     |
| c i Describe a saponification reaction you have performed in the laboratory.   | 3     |
| ii Compare and contrast your experiment with the industrial manufacture of soap.   | 3     |
| d Nitrosyl bromide, NOBr, decomposes in a reversible reaction to form nitric oxide and bromine. $3.8 \times 10^{-3}$ mol NOBr was placed in a 250 mL vessel at 300 K and allowed come to equilibrium. At equilibrium the concentration of bromine was $2.3 \times 10^{-3}$ mol/L.<br>i Write the equilibrium expression (condition for equilibrium) for this reaction.   | 1     |
| ii Calculate the equilibrium constant at 300 K for the reaction.   | 2     |
| iii This reaction is endothermic. How (if at all) does the value of the equilibrium constant change as temperature is increased?   | 1     |
| e The map below shows Bigtown, a large city located in an isolated and relatively arid region. It is connected to other major cities by road and rail. Its water and electricity supplies come from quite distant locations. Dry Lake is a large salt pan that has water in it only after twenty- to fifty-year floods. There are plentiful supplies of brine under Dry Lake and the nearby hills contain rich deposits of limestone at C. A chemical company wants to set up a Solvay process for manufacturing sodium carbonate. There are two possible sites for the plant, A and B.<br>Assess the relative merits of sites A and B for such a plant. | 5     |



# OPTION 1 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for the Industrial Chemistry option of the New South Wales Higher School Certificate HSC Course.

## Syllabus content

The following table lists (for Option 1) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

Location of HSC Course material in *Conquering Chemistry* for Option 1 Industrial Chemistry

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.5.1 <i>Industrial chemistry processes have enabled scientists to develop replacements for natural products</i></b>	
■ discuss the issues associated with shrinking world resources with regard to one identified natural product that is not a fossil fuel, identifying the replacement materials used and/or current research in place to find a replacement for the named material	9.1
<b>9.5.2 <i>Many industrial processes involve manipulation of equilibrium reactions</i></b>	
■ explain the effect of changing the following factors on identified equilibrium reactions <ul style="list-style-type: none"><li>– pressure</li><li>– volume</li><li>– concentration</li><li>– temperature</li></ul>	9.2
■ interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions	9.3, 9.4
■ identify that temperature is the only factor that changes the value of the equilibrium constant ( $K$ ) for a given equation	9.7, 9.8
<b>9.5.3 <i>Sulfuric acid is one of the most important industrial chemicals</i></b>	
■ outline three uses of sulfuric acid in industry	9.9
■ describe the processes used to extract sulfur from mineral deposits, identifying the properties of sulfur which allow its extraction and analysing potential environmental issues that may be associated with its extraction	9.10
■ outline the steps and conditions necessary for the industrial production of $\text{H}_2\text{SO}_4$ from its raw materials	9.11 to 9.14
■ describe the reaction conditions necessary for the production of $\text{SO}_2$ and $\text{SO}_3$	9.13
■ apply the relationship between rates of reaction and equilibrium conditions to the production of $\text{SO}_2$ and $\text{SO}_3$	9.13

Syllabus reference	Sections where found in CCHSC
Students learn to	
<ul style="list-style-type: none"> <li>■ describe, using examples, the reactions of sulfuric acid acting as:           <ul style="list-style-type: none"> <li>– an oxidising agent</li> <li>– a dehydrating agent</li> </ul> </li> </ul>	9.17
<ul style="list-style-type: none"> <li>■ describe and explain the exothermic nature of sulfuric acid ionisation</li> </ul>	9.16
<ul style="list-style-type: none"> <li>■ identify and describe safety precautions that must be taken when using and diluting concentrated sulfuric acid</li> </ul>	9.18
<b>9.5.4 The industrial production of sodium hydroxide requires the use of electrolysis</b>	
<ul style="list-style-type: none"> <li>■ explain the difference between galvanic and electrolytic cells in terms of energy requirements</li> </ul>	10.2
<ul style="list-style-type: none"> <li>■ outline the steps in the industrial production of sodium hydroxide from sodium chloride solution and describe the reaction in terms of net ionic and full formulae equations</li> </ul>	10.4
<ul style="list-style-type: none"> <li>■ distinguish between the three electrolysis methods used to extract sodium hydroxide:           <ul style="list-style-type: none"> <li>– mercury process</li> <li>– diaphragm process</li> <li>– membrane process</li> </ul> <p>by describing each process and analysing the technical and environmental difficulties involved in each process</p> </li> </ul>	10.5 to 10.7
<b>9.5.5 Saponification is an important organic industrial process</b>	
<ul style="list-style-type: none"> <li>■ describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids</li> </ul>	10.9
<ul style="list-style-type: none"> <li>■ describe the conditions under which saponification can be performed in the school laboratory and compare these with industrial preparation of soap</li> </ul>	10.9, 10.11
<ul style="list-style-type: none"> <li>■ account for the cleaning action of soap by describing its structure</li> </ul>	10.12
<ul style="list-style-type: none"> <li>■ explain that soap, water and oil together form an emulsion with the soap acting as an emulsifier</li> </ul>	10.12, 10.13
<ul style="list-style-type: none"> <li>■ distinguish between soaps and synthetic detergents in terms of:           <ul style="list-style-type: none"> <li>– the structure of the molecule</li> <li>– chemical composition</li> <li>– effect in hard water</li> </ul> </li> </ul>	10.14, 10.15
<ul style="list-style-type: none"> <li>■ distinguish between anionic, cationic and non-ionic synthetic detergents in terms of:           <ul style="list-style-type: none"> <li>– chemical composition</li> <li>– uses</li> </ul> </li> </ul>	10.14
<b>9.5.6 The Solvay process has been in use since the 1860s</b>	
<ul style="list-style-type: none"> <li>■ identify the raw materials used in the Solvay process and name the products</li> </ul>	10.17
<ul style="list-style-type: none"> <li>■ describe the uses of sodium carbonate</li> </ul>	10.19

Syllabus reference	Sections where found in CCHSC
Students learn to	
<ul style="list-style-type: none"> <li>■ identify, given a flow chart, the sequence of steps used in the Solvay process and describe the chemistry involved in:           <ul style="list-style-type: none"> <li>– brine purification</li> <li>– hydrogen carbonate formation</li> <li>– formation of sodium carbonate</li> <li>– ammonia recovery</li> </ul> </li>   <li>■ discuss environmental issues associated with the Solvay process and explain how these issues are addressed</li> </ul>	10.17

## Compulsory experiments

The table below lists the compulsory experiments for this option (from the right-hand column of the syllabus), along with the location of relevant information in this book.

### Compulsory experiments for Option 1 Industrial Chemistry

Experiment	Related material in CCHSC <sup>a</sup>
1 Model an equilibrium reaction	Chapter 9 Exercise 4
2 Qualitatively analyse an equilibrium reaction	Section 9.2 Exam-style Question 9
3 Carry out reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent	Section 9.17 Revision Test B, Question b (ii)
4 Identify the products of the electrolysis of sodium chloride	Sections 10.3, 10.8 Exam-style Question 13
5 Carry out a saponification and test the product	Sections 10.9, 10.11 Revision Test B, Question c (i)
6 Determine the properties of a named emulsion and relate them to its uses	Section 10.13 Exam-style Question 20
7 Demonstrate the effect of soap as an emulsifier	Section 10.13 Exam-style Question 6
8 Carry out a step involved in the Solvay process, identifying any difficulties associated with the laboratory modelling of the step	Section 10.17 Exam-style Question 16

<sup>a</sup> Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.

## Location of material for other Option 1 (Industrial Chemistry) activities

Syllabus item	Relevant material in CCHSC
9.5.1	<ul style="list-style-type: none"> <li>■ identify data ... discuss the issues associated with the increased need for a natural resource ... and evaluate the progress ...</li> </ul>
9.5.2	<ul style="list-style-type: none"> <li>■ Experiment 1 (see previous table)</li> <li>■ Experiment 2 (see previous table)</li> <li>■ process ... information ...to calculate <math>K</math> from equilibrium conditions</li> </ul>
9.5.3	<ul style="list-style-type: none"> <li>■ gather ... information ... to describe the steps and chemistry involved in the industrial production of <math>\text{H}_2\text{SO}_4</math> and ... predict ways in which the output of sulfuric acid can be maximised</li> <li>■ Experiment 3 (see previous table)</li> <li>■ use available evidence to relate properties ... to safety precautions ...</li> </ul>
9.5.4	<ul style="list-style-type: none"> <li>■ Experiment 4 (see previous table)</li> <li>■ analyse information ... to predict and explain the different products of the electrolysis of aqueous and molten sodium chloride</li> </ul>
9.5.5	<ul style="list-style-type: none"> <li>■ Experiment 5 (see previous table)</li> <li>■ gather ... information ... to identify a range of fats and oils used for soap making</li> <li>■ Experiment 6 (see previous table)</li> <li>■ Experiment 7 (see previous table)</li> <li>■ solve problems ... to discuss ... the environmental impacts of the use of soaps and detergents</li> </ul>
9.5.6	<ul style="list-style-type: none"> <li>■ Experiment 8 (see previous table)</li> <li>■ process information to ... analyse the relative quantities of reactants and products ...</li> <li>■ use available evidence to determine the criteria used to locate a chemical industry ...</li> </ul>

## Prescribed focus areas

The nature of this option results in it being heavily slanted towards focus areas 3 and 4, applications and uses of chemistry and implications for society and the environment. The manufacture of sulfuric acid, sodium hydroxide, soap and sodium carbonate all illustrate the way that chemical principles are applied to the production of substances our current-day society needs. The discussion of synthetic detergents shows how the application of chemical principles to real-world problems can lead to good solutions, and reinforces the opening theme of the option of chemistry providing substitute materials when natural products become scarce.

There is heavy emphasis upon environmental consequences in all the manufacturing processes discussed, and so this option provides ample opportunities to develop the theme of the strong interrelation between chemistry and the environment and of the need for chemists to be environmentally responsible. The fact that environmental protection was a major consideration in the design of sulfuric acid and (newer) sodium hydroxide plants needs emphasising.

Focus area 2, the nature and practice of chemistry, should not be neglected, even though, apart from electrolysis which is systematically introduced here for the first time, the other chemical principles used in this option are not new—acid–base reactions, precipitation reactions, polarity and solubility, chemical equilibrium. This option provides the opportunity to reinforce and extend understanding of these basic principles by showing slightly different slants of them.

This option offers very little scope for the history of chemistry or current issues, research and development, except for the development of the membrane cell to overcome the environmental concerns of earlier cells.

OPTION 2

# Shipwrecks, corrosion and conservation

Shipwrecks and salvaging materials and objects from them have fascinated people for centuries. Many adventurers, historians, archaeologists and scientists have been stimulated by such challenges as:

- recovering and preserving the remains of sunken wooden ships such as Henry VIII's *Mary Rose* (it sank off the south of England in 1545) and the Swedish vessel the *Vasa* (it sank in the Baltic Sea in 1628)
- recovering treasure from sunken European ships that plundered Central and South America in the seventeenth century
- finding and restoring historic relics from Dutch ships that came to grief off Western Australia in the same century
- salvaging objects from the *Pandora*, which sank off Cape York in 1791 while trying to take the captured *Bounty* mutineers back to England
- locating the wreck of the *Titanic*, which sank in very deep water in the North Atlantic in 1912, and
- documenting and preserving sunken warships from World War II.

One of the major problems facing such people is corrosion, both of the sunken ships themselves and of the artefacts they contained. However, corrosion is not confined to sunken ships. Ever since the introduction of steel as a material for making ships in the middle of the nineteenth century, corrosion of this steel has been a major concern in the design, construction and maintenance of ships. Nor is



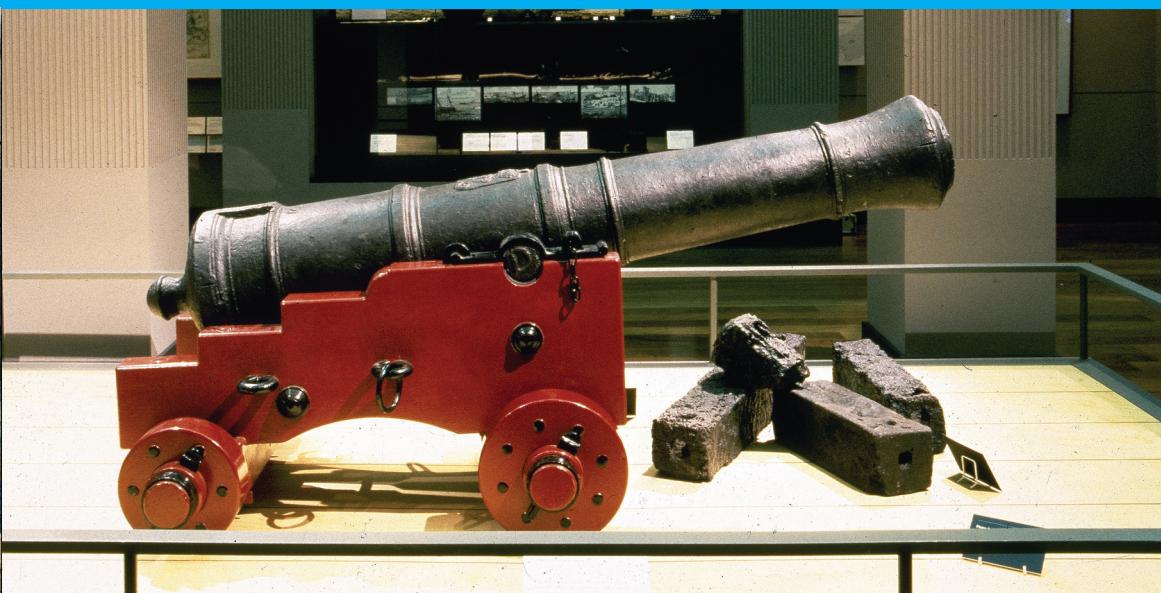
corrosion confined to ships. All steel structures on dry land as well as on water are subject to it—motor cars, bridges, buildings, machinery and household appliances.

Ships, however, are more susceptible to corrosion than land-based structures because of the nature of the ocean.

In this option we shall look at the nature of corrosion (particularly of steel) and its prevention, and at the ways of restoring corroded objects recovered from shipwrecks.

We shall begin this study of shipwrecks, corrosion and conservation by looking at some of the chemical ideas involved—the composition of ocean water, the properties of steels and other alloys used in shipbuilding, the involvement of redox reactions in studying corrosion and the basic principles of electrolysis, a technique that is widely used in restoring salvaged artefacts. This will constitute Chapter 11.

The corrosion of steel and its prevention will be considered in detail in Chapter 12. This will include discussion of galvanising and cathodic protection of steel structures such as ships, pipelines and underground storage tanks. The chapter will also include a discussion of the restoration of recovered objects from shipwrecks. Restoration without causing damage additional to that which has already been done by the ocean requires careful planning and good understanding of a wide range of chemical principles. Several specific examples of restoration will be described to illustrate the chemistry involved.



## OCEANS CORRODE AND SCIENTISTS RESTORE

Ships that sink at sea corrode quite rapidly in wet salty environments as do objects on the ships. Technicians with good chemical skills are often able to restore badly corroded artefacts that have been recovered from shipwrecks. The restored cannon (right) from Cook's *Endeavour*, jettisoned off what is now known as Cooktown in 1770, looked similar to the one being recovered from the *Pandora* (middle photo) which sank off Cape York in 1791.



# Oceans, steel and electrolysis

## IN THIS CHAPTER

Oceans as electrolyte solutions  
 Oceans and redox reactions  
 Galvani, Volta, Davy and Faraday  
 Iron and steel for shipbuilding  
 Corrosion

Predicting the tendency of metals  
 to corrode  
 Passivating metals  
 Electrolysis in aqueous solutions  
 Summary of electrolytic reactions  
 Rate of electrolysis

Shipwrecks corrode relatively quickly. Contributing factors are the ocean environment and the nature of the iron and steel used to make ships. The process is basically an electrochemical one. Therefore before considering the corrosion of shipwrecks we shall look at:

- the nature of ocean water
- the types of steels (alloys) used to make ships and
- extending our knowledge of electrochemical processes.

## 11.1 OCEANS AS ELECTROLYTE SOLUTIONS

The main characteristic of ocean water is its salt (sodium chloride) content: it is a 0.47 mol/L sodium chloride solution with small but significant concentrations of other ions also, as shown in Table 11.1. This makes sea water a strong electrolyte solution, meaning that it is highly conducting of electricity. This strongly influences the chemical reactions that can occur in it.

**TABLE 11.1 Concentration of ions in ocean water**

CATIONS		ANIONS	
Concentration (mol/L)		Concentration (mol/L)	
Na <sup>+</sup>	0.47	Cl <sup>-</sup>	0.55
K <sup>+</sup>	0.010	SO <sub>4</sub> <sup>2-</sup>	0.028
Mg <sup>2+</sup>	0.053		
Ca <sup>2+</sup>	0.010		

## Origins of the salts in sea water

There are two major sources of the salts in sea water:

- 1 *leaching* from rocks and soils on land by rain and ground water that eventually runs off into oceans
- 2 *dissolution* of salts under the sea by water passing through what are called *hydrothermal vents*.

### Leaching by rain and ground water

The main ions that are dissolved as rain water percolates through the soil and makes its way into creeks and rivers are sodium, calcium, magnesium, chloride and sulfate. Water that seeps down into underground aquifers dissolves greater quantities of these ions and under certain conditions (slightly lower pH than normal) picks up significant amounts of hydrogen carbonate (by dissolving carbonate). Small amounts of nitrate and phosphate are also dissolved; these result from decay of plant and animal matter.

Although leaching of salts from the ground is a natural process, it has been significantly increased by human activities such as clear felling of forests, land clearing for pastoral pursuits and cultivation for crop growing.

Some underground aquifers pick up quite high concentrations of sodium chloride (from the many salt deposits that exist there), and these carry large amounts of salt to the oceans.

### Hydrothermal vents

Mid-ocean ridges (totally submerged mountain ranges on ocean floors) exist near the boundaries of some of the tectonic plates that make up the Earth's crust. These often have fissures or cracks in the rock. Sea water is able to percolate down these fissures and come close to the up-welling magma (semi-molten material of the Earth's mantle (p. 9 CCPC)) and so the water is heated to high temperatures (typically 350°C) at high pressures. This hot water is forced back into the ocean through other fissures in the form of hot springs. As this hot water passes through these cracks it dissolves ionic substances from the rocks. These releases of hot water back to the ocean are called **hydrothermal vents**. Their operation is shown in Figure 11.1.

When the hot water from hydrothermal vents meets cold ocean water, many of the salts crystallise out of solution and settle as mineral deposits on the ocean floor. This happens particularly for sulfides of iron, copper, zinc, manganese and to a lesser extent silver. Chlorides and sulfates of magnesium, calcium, sodium and potassium remain in solution and contribute significantly to the total salt burden of ocean water.

## 11.2 OCEANS AND REDOX REACTIONS

Recall that *redox reactions* are reactions that involve the transfer of electrons from one species to another (the species being oxidised loses electrons while the species being reduced gains electrons). Such reactions are sometimes called *electron-transfer reactions*.

Redox reactions were introduced on pp. 115–18 CCPC when we were discussing reactions of metals with oxygen and dilute acids. Displacement reactions, another type of redox reaction, were discussed in this book in

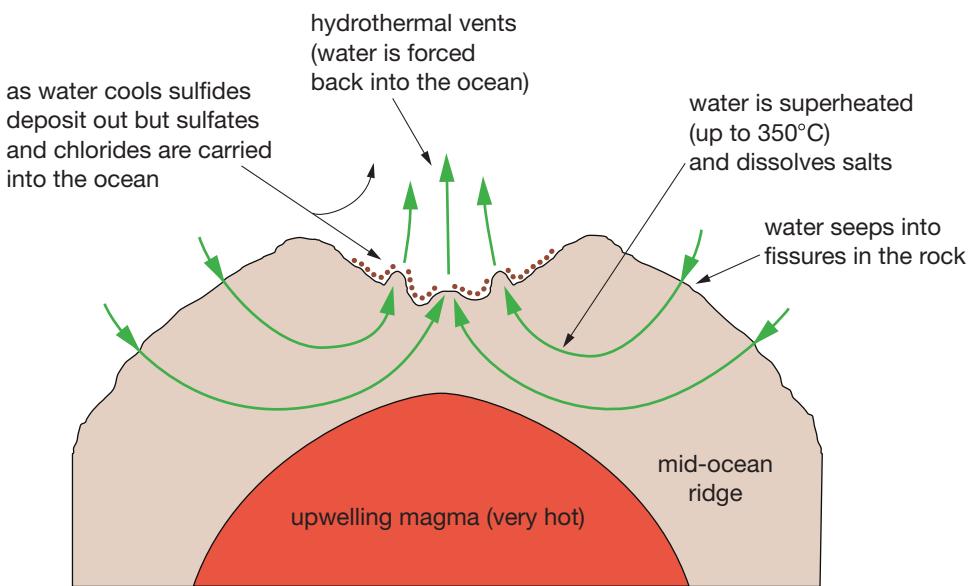


FIGURE 11.1  
Hydrothermal vents in ocean ridges

Section 2.1. The use of redox reactions to generate electricity was explained in Sections 2.4 to 2.6.

In some redox reactions the oxidation half reaction occurs at a different location from where the reduction half reaction occurs. In such cases there is a flow of electrons through the metal joining the locations and a flow of ions through the solution connecting the two locations. This occurs in galvanic cells (Section 2.6). We shall see in Section 12.3 that corrosion of iron also involves oxidation and reduction occurring at different sites and requires a flow of ions through moisture or solution from one site to the other. Such two-site redox reactions occur much more rapidly in ocean water than in land-based moist environments, because oceans contain a relatively high concentration of ions which can easily migrate from one site to the other.

#### WEBSITE

For more information about hydrothermal vents and mid-ocean ridges:

<http://www.ocean.udel.edu/deepsea>

(click on *Click here*, then on *Seafloor Geology*, then on *Hydrothermal Vents* and/or *Mid-Ocean Ridge*)



#### Exercises

- 1 Show that the data in Table 11.1 is consistent with the basic principle that in an ionic solution the total concentrations of positive and negative charges are equal.
- 2
  - a Calculate the concentration of the ions in sea water in % (w/v) and in parts per million.
  - b Show that your results in (a) are consistent with the common claim that the total concentration of salts in the ocean is approximately 3.5%.
- 3 One method of preparing magnesium metal is to precipitate magnesium hydroxide from sea water, convert it to magnesium chloride with hydrochloric acid, then electrolyse the molten dry salt. What is the maximum mass of magnesium that could be obtained from 1000 L of sea water?
- 4 Which of the following metals could possibly be mined from mid-ocean ridges near hydrothermal vents: calcium, magnesium, manganese, zinc. Explain why or why not.



**5 a** Write complete equations for:

- i** a metal reacting with oxygen
- ii** a metal reacting with a dilute acid
- iii** a metal reacting with water
- iv** a displacement reaction

**b** Write half equations for each of these reactions and indicate which is oxidation and which reduction.

**6** Would you expect:

- a** sodium to react more rapidly with sea water than with tap water
- b** zinc to react more rapidly with a copper sulfate solution made up in sea water than with one of the same concentration made up in distilled water?

Explain.

Four scientists who did much of the ground work that eventually led to our understanding of electron-transfer reactions were Galvani, Volta, Davy and Faraday. Let us review their work.

## 11.3 GALVANI, VOLTA, DAVY AND FARADAY

Until the end of the eighteenth century the only known form of electricity was static electricity.

### Luigi Galvani (1737–98)

Galvani is credited with the first generation of an electric current. In 1780 he joined together two wires of different metals and placed the unjoined ends into a freshly extracted muscle from a frog; the muscle contracted due to the passage of an electric current. Galvani (wrongly) thought that the muscle had generated the electricity. However, his work did inspire others to experiment further with the idea of generating electric currents. The name *galvanic cell* is used in his honour for chemical devices that generate electric current.

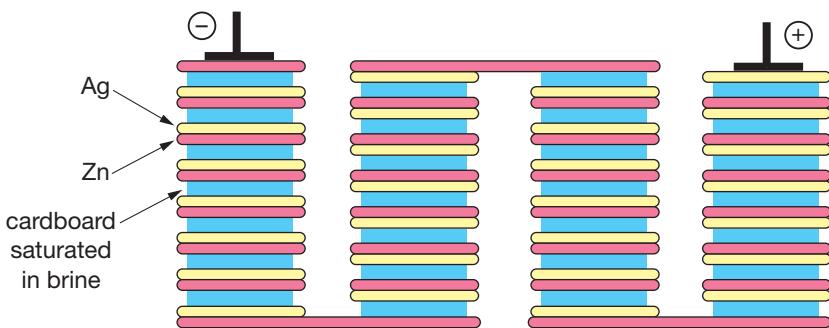
### Alessandro Volta (1745–1827)

Volta demonstrated that it was the wires of different metals in a solution, not the muscle, that generated the electric current. He made the first galvanic cell by sandwiching a piece of brine-soaked<sup>†</sup> cardboard between two different metallic plates (Cu and Sn). In 1800 he obtained much larger currents by setting up a stack of such cells as shown in Figure 11.2. This device became known as **Volta's pile**. It and variants of it were soon widely used in Europe to produce electricity. Volta (incorrectly) thought that it was the contacts between the pairs of metals that were generating the current. Galvanic cells are sometimes called *voltaic cells* in his honour. Volta's main contribution to science was the construction of a useable galvanic cell—the first source of direct electric current.

### Humphry Davy (1778–1829)

Davy quickly seized upon Volta's invention to perform chemical experiments. He used it to electrolyse water in 1800. Davy correctly recognised that chemical reaction was the source of the electric current from the pile and not the contact between two different metals. He also recognised that the reactions he was

<sup>†</sup> Brine is a concentrated solution of sodium chloride in water.



**FIGURE 11.2**  
A later version of Volta's pile: originally he used copper and tin, later changing to silver and zinc

bringing about were decomposition reactions. He had used electrolysis to decompose water into hydrogen and oxygen (thereby establishing that water was a compound and not an element). Electrolysis as a method of decomposing substances was introduced on p. 71 CCPC; details about how electrolysis works will be treated in Section 11.6.

Davy developed improved versions of Volta's pile and used them to decompose many substances. He was the first person to prepare samples of potassium and sodium metals; he did this by electrolysing molten potassium and sodium hydroxides respectively. He also prepared samples of magnesium, calcium, strontium and barium by electrolysing suitable molten compounds, and he recognised them as newly discovered elements.

*Davy's major contributions to chemistry* were to use electrolysis to decompose many compounds, to isolate many new elements, and to show that for many chemical reactions there was a definite (qualitative) connection between the reaction and electricity. At the time of Davy's experiments Dalton's ideas of atoms and molecules (his atomic theory) were just becoming widely accepted. There was no idea that many compounds were made up of charged species (ions). It remained for other scientists decades later to deduce from Davy's experiments that the compounds he was using must contain charged particles (ions) and that his electrolysis experiments were discharging these charges by removing or providing electrons; that is, bringing about redox or electron-transfer reactions.

Davy also recognised the correct nature of acids when he claimed that they were substances that contained replaceable hydrogen (Section 5.1).

## Michael Faraday (1791–1867)

Faraday got his 'big break' in science when Davy appointed him as his assistant in 1813. Faraday continued and extended Davy's electrolysis experiments. He devoted considerable effort to relating the amount of substance produced to the quantity of electricity that passed through the cell. This was no easy task in those days before ammeters and voltmeters had been invented. Faraday developed an electrolytic device for measuring electric charge; this consisted of a cell in which sulfuric acid was electrolysed and the oxygen gas collected and its volume measured. This cell was connected in series with the cell he was experimenting on. Faraday argued that the quantity of electric charge that flowed through the circuit was proportional to the volume of gas formed in his sulfuric acid *coulometer*, as this charge-measuring device was later called. Using this coulometer Faraday collected the experimental data that he used to develop his laws of electrolysis.



The young Michael Faraday at the time of his work on electrolysis; he later became one of the most distinguished scientists of his era and a brilliant scientific lecturer

Faraday proposed his first law of electrolysis in 1834 before the nature of electrolyte solutions or the exact nature of electrolysis were fully understood. It was a summary of many experimental observations.

*Faraday's first law of electrolysis* states that the mass of a substance formed at an electrode during electrolysis is proportional to the quantity of electricity that passes through the electrolytic cell.

The *quantity of electricity* or electrical charge,  $Q$ , is the product of the current flowing,  $i$ , and the time,  $t$ , it flows for; it is measured in *coulombs*, C.

*Faraday's second law of electrolysis* states that for sets of elements with the same valency (such as Cl, Br, I or Cu, Ni, Cd) the masses produced per unit quantity of electricity are in the same ratio as are their atomic weights. That is, the masses of chlorine, bromine and iodine are in the ratio 35.5 : 79.7 : 126.9 or the masses of copper, nickel and cadmium are in the ratio of 63.6 : 58.7 : 112.4.

By the time of Faraday's laws, the 1830s and '40s, the atomic theory was widely accepted, many elements had been identified, formulae had been determined for many compounds, the concept

of valency had been introduced and atomic weights had been determined for many elements.

*Faraday's major contribution to electrochemistry* was the recognition that there was a quantitative relationship between the mass of substance formed during electrolysis and the quantity of electricity involved, and further that the relationship was with the number of moles rather than with simple mass (using today's 'mole' rather than the older, more awkward terms used in Faraday's day). In other words he showed that there was a very definite link between quantity of electricity and moles of substances.

Faraday's greatest contribution to science was his work on electromagnetism. He discovered that an electric current could be generated by spinning a coil of wire between the poles of a magnet. This is the basis of the current method of generating the vast quantities of electricity that are produced today.

## Significance for electron-transfer reactions

Davy's and Faraday's work on electrolysis helped Arrhenius (in 1887) develop a theory of ionic solutions which is still accepted today. Following the recognition by George Stoney in 1874 that an electric current was a flow of small negative particles which he called *electrons*, Arrhenius proposed that electrolyte solutions consist of positively and negatively charged ions moving freely about in solution; these ions could carry one, two or three (positive or negative) charges with one such charge being equal in magnitude to the charge of an electron. Electrolysis is the discharge of these ions. Positive ions gain electrons (from the electric current) to form neutral metal atoms (or H<sub>2</sub> molecules in the case of H<sup>+</sup>), while negative ions give up electrons to form neutral atoms, which generally combine

to form molecules (such as  $\text{Cl}_2$ ). Subsequently it was recognised that many solids (such as  $\text{NaCl}$ ,  $\text{MgO}$ ,  $\text{KOH}$ ) consisted of positive and negative ions also.

After the recognition of the ionic nature of many solids and of electrolyte solutions, the idea of oxidation and reduction being electron-transfer processes soon developed, and this led to our current-day definitions.

Although the concept of electron-transfer reactions did not develop until long after the electrolysis experiments of Davy and Faraday, those experiments provided valuable information that led later scientists to develop that concept. In addition their pioneering work on electrolysis laid the foundations for many important industrial and laboratory processes.

#### WEBSITES

For more biographical information about Galvani, Volta, Davy and Faraday (though they do not contain much chemical information):

[http://www.acmi.net.au/AIC/GALVANI\\_BIO.html](http://www.acmi.net.au/AIC/GALVANI_BIO.html)

<http://www.italian-american.com/volta.htm>

<http://www.Woodrow.org/teachers/ci/1992>

(a page called *The History of Chemistry comes up; In 8 Electrochemistry* click on *Davy* and/or *Faraday*; a good biography of Davy but for Faraday it is a collection of interviews with him, which do not contain much chemical information but give good insights into his personality and character)

[http://www.acmi.net.au/AIC/FARADAY\\_BIO.html](http://www.acmi.net.au/AIC/FARADAY_BIO.html)

(a better biography, but still not much chemistry)

<http://www.bioanalytical.com/info/calendar/97/index.htm>

(biographies of all four chemists)



## 11.4 IRON AND STEEL FOR SHIPBUILDING

Since the 1860s ocean-going ships have been made of iron or steel. Steel has the advantages that it is relatively hard, has good mechanical strength, and can be rolled into sheets that can be pressed into desired shapes and extruded into various beam shapes. It can also be welded. **Welding** is a method of joining pieces of metal together in which the two edges are melted, either by an oxy-acetylene torch or an electric current, so that they fuse into the one solid piece.

**Steel** is an alloy of iron with no more than 2% carbon and often with varying amounts of other metals or silicon.

The composition, properties and uses of various forms of iron and steel, particularly those relevant to shipbuilding, are presented in Table 11.2. Table 4.2 on p. 102 CCPC presented similar information for a wider range of steels.

The properties of carbon steels depend not only upon the percentage of carbon in the steel but also upon the heat or mechanical treatment the steels receive. This arises because the properties of steel depend upon whether the carbon is present as a solution of carbon (graphite) in the iron or as a solution of *cementite*, an iron carbide, in the iron. Cementite,  $\text{Fe}_3\text{C}$ , is formed in the reversible reaction:



**TABLE 11.2 Composition, properties and uses of some types of steel and forms of iron**

Substance	Composition <sup>a</sup>	Properties	Uses
pure iron	100% Fe	soft and malleable, corrodes very slowly	not widely used commercially
pig iron (cast iron)	3 to 4% C, 1% Mn, 1% Si	hard and brittle, corrodes fairly rapidly	casting engine blocks, fire hydrants, decorative iron 'lace' for buildings
mild steel	<0.2% C	soft and malleable, corrodes fairly rapidly	car bodies, pipes, nuts and bolts, roofing, shipbuilding
structural steel	0.3 to 0.6% C	hard and malleable, high tensile strength, corrodes fairly rapidly	beams and girders, railways, reinforcing for buildings, shipbuilding
stainless steel	10 to 20% Cr, 5 to 20% Ni	hard, takes a high polish, very resistant to corrosion	food processing machinery, kitchen sinks and appliances, cutlery, surgical and dental instruments, some razor blades

a If not stated, the balance is Fe.

If molten iron containing less than 2% carbon is cooled, a homogeneous solid is formed. This is steel. If the cooling is rapid, called **quenching**, then the carbon is present as cementite dissolved in iron: this gives a hard but brittle steel. If the steel is cooled slowly, called **annealing**, the carbon is present as graphite dissolved in iron: this produces a very ductile product, but it is not as hard or as tough as quenched steel.

The properties of steel can be further modified by:

- **tempering** (holding it at a high temperature below the melting point for some time then cooling); this makes quenched steel tougher and less brittle while retaining its hardness, and
- **working** (rolling or hammering at different temperatures); this improves the mechanical properties of the steel such as tensile strength.

The properties of steel can be varied quite significantly by these various treatments.

## Progress in metallurgy and in shipbuilding

**Metallurgy** is the branch of science and engineering that is concerned with the extraction and processing of metals and the preparation of alloys, with the main emphasis being on providing materials to meet the needs of manufacturers of metals-based products.

Developments in the materials and procedures used for shipbuilding have often followed progress in metallurgy; that is, progress in our understanding of metals and alloys.

### Early developments

Steel ships were first built in the latter part of the nineteenth century after steel had become readily available at competitive prices. From that time until about the middle of the twentieth century the steels available for hulls of ships generally contained about 0.2% carbon and small but significant amounts of sulfur (0.1 to 0.2%) and phosphorus (up to 0.1%), because steel works at the time could not get these concentrations lower. Sulfur and phosphorus made the steel somewhat

brittle and subject to stress cracking, which were undesirable properties for ships as the following two examples show.

In 1912 a huge state-of-the-art luxury ocean liner, *Titanic*, was launched, amid claims that it was unsinkable. It sank on its maiden voyage after hitting an iceberg. It sank because the steel panels of its hull split instead of just bending or denting—they were too brittle.

The hulls of many of the ‘liberty ships’ mass-produced by the US in the latter stages of World War II (mid 1940s) developed stress cracks and had to be scrapped after quite short periods of service. Again the problem was high sulfur (and possibly high carbon) contents in the steel.

## After World War II

After steel manufacturers were able to control steel compositions more accurately and remove sulfur almost completely, mild steel that was less brittle and tougher became available for hulls of ships and so the durability of ships improved. Production of tougher alloy steels with small but accurately controlled amounts of other metals such as manganese saw further improvements in the hulls of ships.

While mild steel is generally used for hulls of ships, structural steel (0.3 to 0.6% carbon) is widely used inside ships for girders and columns and general structural features. As improved steels were produced by alloying and using various heat treatments, they were readily adopted by shipbuilders and so the rigidity, strength and general performance of ships increased.

Development of bronzes (alloys of copper and tin and in recent decades small amounts of other metals also) that were very resistant to corrosion in salt water led to the use of bronze propellers for ships. Steel propellers used to corrode much more quickly than the hulls, probably because of the rapidly moving, highly aerated water that passes over them.

The ready availability of metals such as aluminium and a range of non-ferrous alloys after the 1950s saw these being used in shipbuilding, but more in superstructures and fittings rather than in the basic structures and hulls.



Superliners are large and complex structures using a great variety of materials, particularly metals, but the hulls are still predominantly steel

Stainless steel, originally developed in the 1920s, came into common use after the 1950s. It has excellent resistance to corrosion. However, while stainless steel has been used in a wide range of equipment and fittings in ships, it has not been used for the basic structure or the hull of ships, primarily because of its high cost.

### More recently

Despite the introduction of many new alloys and the commercialisation of formerly exotic metals such as titanium in recent decades, there have not been any dramatic changes in materials used for the hulls of large ships in recent years; they are still basically made of steel. However, in recent years there have been some moves to use aluminium and non-ferrous alloys more extensively, particularly in smaller vessels such as commercial catamarans and hydrofoils.

While properties such as tensile strength, hardness, brittleness and malleability are important in choosing steel for making particular products such as cars, bridges and ships, the tendency of steel to corrode and the need to protect against this are always major considerations in using steel.



### Exercises

- 7 Molten steel is a solution of cementite,  $\text{Fe}_3\text{C}$ , in iron. If this steel is cooled slowly to room temperature the final product is a solid solution of graphite in iron. If molten steel is cooled rapidly to room temperature (by plunging it into a large volume of water), the final product is a solid solution of cementite in iron. Use Equation 11.1 to explain why different products result from these two procedures.
- 8 When iron is extracted from iron(III) oxide in a blast furnace the product, called pig iron or cast iron, contains 3 to 4% carbon. Steel (with a carbon content of less than 2%) is made by melting this pig iron and bubbling oxygen through it. Explain, with an equation, how this process reduces the carbon content of the liquid.
- 9 The melting points of pure iron, steel containing 1% C and cast iron containing 3% C are 1250°C, 1535°C and 1450°C but not necessarily in that order. Assign these melting points to the three substances and explain your reasoning.
- 10 What element would you mix with mild steel (0.2% C, 99.8% Fe) to make an alloy that was
  - a hard at high temperatures and good for making cutting and grinding tools
  - b very resistant to corrosion and capable of taking a high polish
  - c easily magnetised and good for making cores of electrical transformers
  - d hard and shock resistant and good for making safes and ball bearings?

If you choose to use the same element for two of these purposes, give an approximate percentage to use for each purpose.

## 11.5 CORROSION

**Corrosion** is the degradation (or eating away) of metal so that it loses strength and becomes unable to fulfil its intended purpose.

*Rusting of iron* is the commonest form of corrosion. It is the process that gradually destroys motor car bodies, steel bridges and other structures, railway lines and iron roofing and guttering. Rusting is also the process that destroys

shipwrecks, whether they be on the shoreline or totally submerged on the ocean floor. Salt water accelerates rusting. Both rusting itself (particularly of ships and motor car bodies) and processes aimed at preventing it (painting bridges and iron roofs, galvanising and so on) cost our society vast sums of money every year, and they are major concerns of any industry that makes or uses iron and steel products.

**Rust** is the reddish-coloured, flaky or porous deposit that forms on exposed iron and steel. Rust is hydrated iron oxide,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , where  $x$  can vary from about 0.5 to 2. This means that the composition of rust varies somewhat, depending upon the conditions under which it is formed. Rusting can be represented by the equation:



We shall look at how rusting occurs and how it can be prevented or minimised in the next chapter. For the moment let us consider the question of determining the ease with which metals corrode.

Corrosion of metals involves *oxidation* of the metal. For iron:



(followed by  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$  because  $\text{Fe}^{3+}$  is the ion in  $\text{Fe}_2\text{O}_3$ ).

This suggests that the more easily a metal is oxidised, then the more easily will it corrode. Magnesium is oxidised more easily than iron, so we expect magnesium to corrode more easily than iron. That is what we observe: a piece of cleaned shiny magnesium ribbon tarnishes more rapidly than a clean shiny iron nail. Gold is very difficult to oxidise, so we expect gold not to corrode. Again that is our observation: a gold ring or bracelet does not tarnish (corrode).

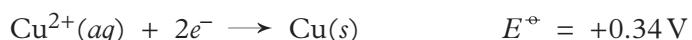
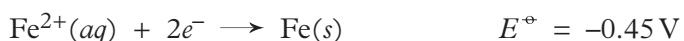
## 11.6 PREDICTING THE TENDENCY OF METALS TO CORRODE

At the end of Section 2.14 we saw that the table of standard electrode potentials is also a listing of substances (including metals) in order of oxidising or reducing strengths. *The greater the standard electrode potential, the greater is the tendency of the reduction half reaction to occur*; that is, the greater the oxidising strength of the oxidised form (left-hand side) of the redox half reaction. Conversely *the algebraically smaller the standard electrode potential, the greater is the tendency of the half reaction to go in the reverse direction*; that is, in the oxidation direction, which means the greater the reducing strength of the reduced form (right-hand side) of the redox couple. This last statement means:

For a metal M, the lower (algebraically smaller) its standard electrode potential, the greater is the tendency for  $M \rightarrow M^{z+} + ze^-$  to occur, which means the more readily does M get oxidised or the more readily does M corrode; -0.30 is a lower (algebraically smaller) number, for example, than +0.20. ( $z$  is the number of positive charges on the metal ion, 1, 2 or 3).

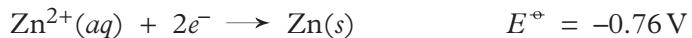
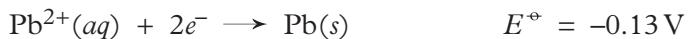
To illustrate:

From Table 2.1 on p. 67:



This tells us that Fe (with the lower  $E^\circ$ ) is more easily oxidised than Cu; that is, iron corrodes more readily than does copper.

Similarly for:

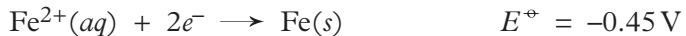
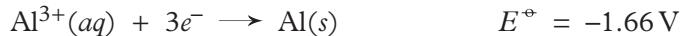


Zn (with the lower  $E^\circ$ ) is more easily oxidised than Pb, so zinc corrodes more easily than does lead.

In summary:

For metals, the algebraically smaller the standard electrode potential, the more easily the metal corrodes.

However let us consider another example. Again from Table 2.1 on p. 67:



From these values we would expect aluminium to oxidise and hence corrode more easily than iron. However, that is contrary to our everyday observation that aluminium is much more corrosion resistant than iron. Actually, on closer examination we find that aluminium does corrode by forming an oxide but this oxide forms as an impervious layer that covers up the metal and so prevents further corrosion. This leads to the idea of *passivating metals*.

## 11.7 PASSIVATING METALS

A **passivating metal** is a reactive metal that readily forms an unreactive surface coating with substances such as oxygen or water; this protects the metal from further reaction (that is, it protects it from corrosion).

Aluminium is the classic example of a passivating metal; bright shiny clean aluminium rapidly goes dull from the formation of an oxide coating, but that impervious oxide layer prevents more oxygen attacking the aluminium, so there is no further corrosion.

The term *active metal* is commonly used for reactive metals that do not passivate; iron is the classic example. The oxide that iron forms is porous and flaky and so oxygen is able to diffuse through it and ‘get at’ bare metal, and so corrosion keeps on going until a considerable amount, if not all, of the iron is converted to oxide.

Other passivating metals are zinc, chromium and stainless steel. In stainless steel it is the chromium that forms the protective layer (of chromium(III) oxide).

Chromium is widely used for protection and decoration. The impervious oxide it forms is chromium(III) oxide,  $\text{Cr}_2\text{O}_3$ . There is the added advantage that this oxide layer does not dull the shiny appearance of the chromium. Consequently chrome plating (using electrolysis to deposit a thin film of chromium on the surface of another metal) is widely used to protect active metals while providing an attractive finish for motor car parts and household appliances.

Copper also forms a protective layer of oxide or carbonate but we do not consider copper as a passivating metal, because it is not a reactive metal.

## Exercises



Use the table of standard electrode potentials on p. 67 for Exercises 11 and 12.

- 11 a** A strip of zinc foil was joined to a strip of tin foil and the combined strip was bent so that both the unjoined ends dipped into a well-aerated sample of seawater. Predict which metal, if either, would corrode. Explain your reasoning, and also explain what is meant by corrosion in this situation.
- b** Repeat (a) for strips of aluminium and cadmium.
- 12 a** The individual cells in Volta's first pile (Section 11.3) consisted of tin and copper plates in contact with a sodium chloride solution. Which metal has the greater tendency to oxidise? Hence which metal is the positive electrode of the cell? Explain.
- b** A later pile used by Volta (the one in Figure 11.2) consisted of individual cells with plates of silver and zinc. Explain why the zinc plate is the negative terminal of the cell.
- c** Why was the second cell a better source of electric current than the first?
- 13** A team of metallurgists developed two new alloys, A and B. To test the tendency of these alloys to corrode, relative to mild steel, they set up a galvanic cell for each alloy, consisting of a strip of the alloy and a clean 'ordinary' nail (mild steel), both dipping into a solution of sodium chloride, and measured the EMFs of the cells. They found that the EMFs of the alloys relative to the nail were  $-0.34\text{ V}$  for A and  $+0.22\text{ V}$  for B. Which alloy, if either, will corrode more readily than mild steel and which, if either, less readily? Explain.
- 14 a** Zinc and lead passivate by forming films of mixed hydroxide and carbonate on their surfaces. The reactions are between metal and oxygen in the first instance, followed by reaction with water and carbon dioxide from the air. Write equations for these reactions.
- b** Lithium reacts similarly but does not passivate. Explain why.
- 15** Articles made of titanium do not corrode to any noticeable extent. The standard electrode potential for  $\text{Ti}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ti}(\text{s})$  is  $-1.6\text{ V}$ . Would you consider titanium to be an inert metal or a passivating one? Justify your answer.

When we come to consider restoration of metal objects recovered from shipwrecks in the next chapter, we will find that electrolysis is often used. Before delving into the technology of restoring salvaged artefacts, let us explore some of the basic science of electrolysis.

## 11.8 ELECTROLYSIS IN AQUEOUS SOLUTIONS

The basic ideas about electrolysis are set out in Section 10.2. Read that section now before proceeding; it is an essential part of this option (as well as being part of the Industrial Chemistry option).

The electrode reactions that occur, and so the products formed during electrolysis, depend upon:

- the nature of the electrolyte
- the concentration of ions present
- the nature of the electrodes.

Examples will illustrate the effects of these factors.

## Nature of the electrolyte

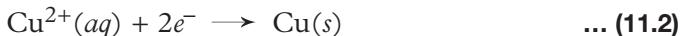
The following examples all use *inert electrodes* (graphite or platinum).

### Copper chloride solution

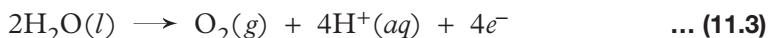
As seen in Section 10.2 the electrolysis of copper chloride solution leads to the deposition of metallic copper at the cathode and the formation of chlorine gas at the anode.

### Copper sulfate solution

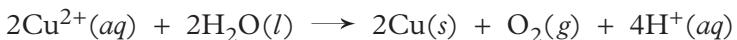
Electrolysis of copper sulfate solution again produces copper at the cathode:



but oxygen gas forms at the anode. In this electrolysis sulfate ions migrate to the anode but they are too stable to be oxidised, so water is oxidised instead:



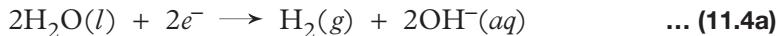
Doubling Equation 11.2 and adding it to Equation 11.3 leads to the overall reaction



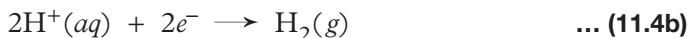
### Sodium sulfate solution

Electrolysis of sodium sulfate solution produces oxygen gas at the anode and hydrogen gas at the cathode. As with copper sulfate, sulfate ions migrate to the anode but because they are too stable to be oxidised, it is again Reaction 11.3 that occurs.

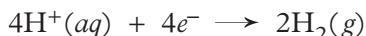
Sodium ions migrate to the cathode but they are too stable to be reduced to sodium metal, so instead water is reduced to hydrogen gas:



or more simply:



Because hydrogen and oxygen gases have been produced, electrolysis of aqueous solutions of sodium sulfate is simply the *electrolysis of water*. To show this with equations, we multiply Equation 11.4(b) by 2:



then add it to Equation 11.3 to get



As these three examples demonstrate, when we electrolyse a solution of a salt, both, one or neither of the ions of the salt may be discharged, depending upon the ease of oxidation or reduction of the particular ions relative to water.

## Concentration of ions present

The effect of concentration upon the products formed in electrolysis is best illustrated by sodium chloride solutions.

Read Section 10.3. Again, apart from *Electrolysis of molten sodium chloride*, that section is an essential part of this HSC option.

These two examples show that the product of an electrolysis can vary with the concentration of the ion or ions present. This happens when there are two species present that have similar tendencies to be oxidised or reduced; that is, their standard electrode potentials are similar.

## Nature of the electrodes

When we electrolysed copper sulfate solution with inert electrodes, oxygen formed at the anode (Equation 11.3). However if we use a copper anode, then copper is oxidised instead:



That is, the anode is eaten away and goes into solution as copper ions. This happens because copper is more easily oxidised than water. When we used an inert anode (graphite, platinum, stainless steel), water was more easily oxidised than the electrode material. Copper is still deposited on the cathode as before.

This electrolysis is used industrially to purify copper. Blister copper (about 98% pure) from copper smelters is made the anode in an electrolytic cell. As electrolysis proceeds copper goes into solution and deposits onto the cathode. Some impurities go into solution and stay there (do not deposit out) while more inert impurities just fall to the bottom of the cell as the copper is eaten away from around them. In this way 99.9% copper is obtained.

## Silver nitrate solution

With inert electrodes, electrolysis of silver nitrate solution is similar to that of copper sulfate solution: silver deposits on the cathode and oxygen is formed at the anode. However if a silver anode is used, it, silver, not water, is oxidised:



Again this is similar to the copper sulfate situation.

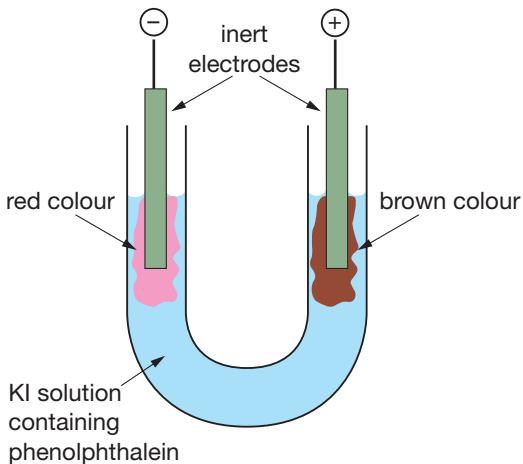
These two examples are the basis of **electroplating**, the process of using electrolysis to coat one metal with a thin layer of another metal. To silver-plate a metallic object we make it the cathode of an electrolysis cell, use a solution of silver nitrate and a silver anode. At the anode silver goes into solution and at the cathode silver ions from the solution ‘plate out’ (deposit as a coating on the cathode).

These two examples demonstrate that the product of an electrolysis can vary with the nature of the electrodes.

## Electrolysis of potassium iodide solution

This provides a good experimental demonstration, as shown in Figure 11.3. If this electrolysis is performed in a U-tube with a drop of phenolphthalein indicator (red in alkaline solution, colourless in neutral and acid solution: Table 4.1) in the solution (initially colourless), a red colour develops around the cathode and a brown colour around the anode. The reasons are that colourless iodide is oxidised to brown iodine at the anode, while water is reduced to hydrogen and hydroxide ion (which turns the indicator red) at the cathode, Equation 11.4(a). Potassium ions, like sodium ions, are too stable to be reduced.

FIGURE 11.3  
Electrolysis of potassium iodide solution containing some phenolphthalein indicator



## 11.9 SUMMARY OF ELECTROLYTIC REACTIONS

Table 11.3 shows the electrode reactions in the electrolyses discussed in the previous section.

**TABLE 11.3 Summary of electrode reactions in some electrolyses of aqueous solutions**

Electrolyte (inert electrodes unless otherwise stated)	Cathode reaction	Anode reaction
$\text{CuCl}_2$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
$\text{CuSO}_4$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
$\text{CuSO}_4$ (copper anode)	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
$\text{Na}_2\text{SO}_4^{\text{a}}$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
$\text{AgNO}_3$	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
$\text{AgNO}_3$ (silver anode)	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$
$\text{NaCl} (>2 \text{ mol/L})$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
$\text{NaCl} (<0.1 \text{ mol/L})^{\text{a}}$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
KI	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	$2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$

a These are both just electrolysis of water.

The reactions that occur at the electrodes during electrolysis can be summarised as follows:

- At the anode (positive electrode), in aqueous solution bromide and iodide are always oxidised (to  $\text{Br}_2$  and  $\text{I}_2$ ). Nitrate, sulfate and fluoride are never oxidised; instead water is oxidised to oxygen. Chloride is oxidised if it is relatively concentrated, but if it is dilute water is oxidised instead.

As a rough guide, the higher the standard electrode potential of the relevant reduction half reaction, the harder it is to oxidise the anion.

- At the cathode (negative electrode), in aqueous solution the cations of metals with positive standard electrode potentials are always reduced ( $\text{Ag}^+$  and  $\text{Cu}^{2+}$ ),

cations of metals with electrode potentials more negative than 1 V (such as  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Na^+$  and  $K^+$ ) are never reduced (water is reduced to hydrogen gas instead), while metals with less negative  $E^\circ$ 's ( $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Cr^{3+}$ ) are generally not reduced but can be reduced under special conditions (such as using high concentrations, a suitable electrode material or a high pH).

As a rough guide, the (algebraically) lower the standard electrode potential, the harder it is to reduce the metal ion.

- For electrolysis of molten electrolytes, the metal ion must be reduced and the anion oxidised because there are no other species present. (Electrolysis of molten sodium chloride is described in Section 10.3.)

## 11.10 RATE OF ELECTROLYSIS

The rate at which a substance is formed during electrolysis depends upon the current that passes through the electrolysis cell:

the higher the current, the greater the rate of formation of the product.

Factors that affect the current are:

- the voltage used—the higher the voltage the higher the current (in a cell of fixed electrical resistance)
- the electrical conductance of the electrolysis cell—the higher the conductance (meaning the lower the electrical resistance, because **conductance is the reciprocal of resistance**) the greater is the current (for a fixed voltage).

Conductance depends upon:

- the concentration of ions in the solution—increasing the concentration of ions increases the conductance
- the surface area of the electrodes used—the greater the surface area the greater the electrical conductance
- the distance between electrodes—the smaller the distance the greater is the conductance.

These three factors are illustrated in Figure 11.4.

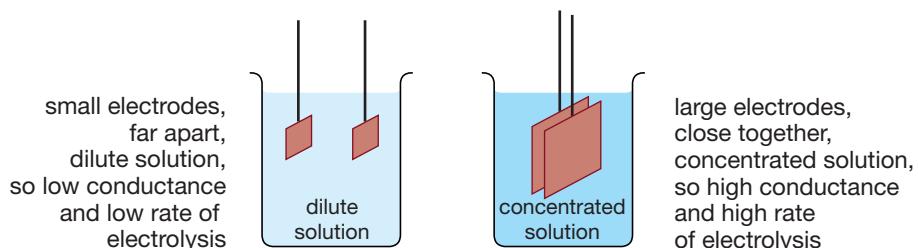
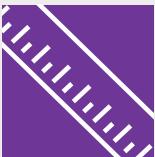


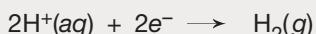
FIGURE 11.4  
Some factors affecting the rate of electrolysis

We need to be careful about increasing the voltage in order to increase the rate of electrolysis, because it may cause a different or extra electrolysis process to occur. This is because each electrolysis requires a certain minimum voltage to make it occur; if two electrolytic processes are possible (with different minimum voltages), then a low voltage may bring about the one with the lower minimum voltage but not the other, whereas a higher voltage could cause both processes to occur. Electrolysing a solution containing both copper and silver ions is an example: a low voltage deposits silver only while a high voltage deposits both metals.



## Exercises

- 16** What substance will form at each electrode when an aqueous solution of each of the following substances is electrolysed using inert electrodes (graphite, stainless steel or platinum)? Write equations for the electrode reactions and for the overall reaction.
- a** copper bromide                           **e** zinc nitrate  
**b** calcium chloride                           **\*f** magnesium sulfate  
**c** nitric acid                                   **\*g** very dilute hydrochloric acid  
**d** sodium hydroxide                           **\*h** potassium fluoride
- 17** Humphry Davy in the early 1800s produced potassium metal by electrolysing molten potassium hydroxide. At which electrode (cathode or anode) did the potassium form? What formed at the other electrode? Write equations for the electrode reactions and for the overall reaction.
- 18** Michael Faraday's coulometer (Section 11.3) for measuring quantity of electricity consisted of a solution of sulfuric acid which he electrolysed: the oxygen gas that formed at one electrode was collected and its volume measured. At which electrode (positive or negative) did this oxygen form? What formed at the other electrode? Write equations for the electrode reactions.
- \*19** When an aqueous solution of sodium nitrate containing some phenolphthalein indicator was electrolysed, bubbles of gas formed at the negative electrode and the solution near that electrode turned pink; after the experiment there had been no change in the mass of the negative electrode. When a solution of silver nitrate was similarly electrolysed, no bubbles of gas formed at the negative electrode and no pink colour developed; after the experiment the negative electrode had a greater mass than before.
- a** Explain these different observations in terms of what happened at the negative electrode during electrolysis. (Phenolphthalein is colourless in acid or neutral solution and pink in alkaline solution.)  
**b** What would you have observed at the positive electrode in each of these electrolyses? If you had used methyl red indicator (pink in acid solution, yellow in alkaline) instead of phenolphthalein, what would you have observed at this electrode?
- 20** In discussing the electrolysis of copper sulfate solution using a copper anode, it was stated that the copper electrode was oxidised 'because copper is more easily oxidised than water'. Use standard electrode potentials to justify this claim. If a gold anode had been used predict, again using standard electrode potentials, which of water or gold would have been oxidised.
- 21** A solution containing both copper and silver nitrates in about equimolar amounts was electrolysed using a relatively low voltage—one just high enough to cause a current to flow.
- a** What electrode reaction would you expect to occur at the anode? Explain.  
**b** If a much higher voltage was then used, what, if any, changes would you expect in the electrolysis? Explain.
- 22** If an aqueous solution containing equal concentrations of potassium iodide and bromide was electrolysed using a voltage just greater than the minimum needed to get a current to flow, what would form at the anode? Explain.
- 23** The electrode potential for the half reaction



is 0.0 V at pH = 0 and -0.41 at pH = 7.0.

If an aqueous solution of nickel sulfate with a pH of about 0 was electrolysed, what would you expect to form at the cathode? If a near neutral solution of nickel sulfate was electrolysed, would you expect the same or a different result? Explain.

- 24** Would you expect the product formed at the anode in the electrolysis of a sodium iodide solution to change if the concentration of the solution changed (as happens with sodium chloride)? Use standard electrode potentials to explain why or why not.
- 25** In an experiment to determine the effect of size and spacing of electrodes upon the rate of electrolysis, a group of students decided that it was good experimental practice to keep constant all possible variables other than the one they were investigating. Hence when they changed the size and spacing of the electrodes (in separate experiments), they maintained a constant current through their cell (by varying the applied voltage). To their surprise they found that the amount of electrolysis remained constant in all their experiments. Explain what their mistake was. What results should they have obtained from their experiments?

## Important new terms

You should know the meaning of the following terms:

annealing (p. 402)  
conductance (p. 411)  
corrosion (p. 404)  
electroplating (p. 409)  
hydrothermal vents (p. 396)  
metallurgy (p. 402)

passivating metal (p. 406)  
quenching (p. 402)  
rust (p. 405)  
steel (p. 401)  
tempering (p. 402)  
Volta's pile (p. 398)  
welding (p. 401)  
working (of steel) (p. 402)

## Test yourself

- 1** Explain the meaning of each of the items in the 'Important new terms' section above.
- 2** What are the major ions in sea water?
- 3** Describe the two main ways that various salts get into oceans.
- 4** Describe one major achievement in the field of electrochemistry made by Luigi Galvani, Alessandro Volta, Humphry Davy and Michael Faraday.
- 5** How does the presence of different amounts of carbon in iron affect the properties of the material? Illustrate by reference to cast iron, mild steel and structural steel.
- 6** What is the composition of stainless steel? Why is it so resistant to corrosion? Why is it not used for shipbuilding or pipeline construction?
- 7** Write an equation for the formation of cementite from iron and carbon. Why is cementite of relevance to the properties of steel?
- 8** In what ways do quenching, annealing, tempering and working steel change the properties of the steel?
- 9** Describe three developments in the preparation of metals and alloys that led to significant improvements in shipbuilding.
- 10** Write an equation to represent the formation of rust.
- 11** In terms of standard electrode potentials, which metals corrode more rapidly?
- 12** Why do we consider aluminium a passivating metal and how does this passivation arise?

- 13** Name two other passivating metals.
- 14** List three factors that determine the products that are formed in an electrolysis experiment.
- 15** Illustrate each of the factors in Question 14 by naming the different products formed in two different electrolyses. In each case *explain* why different products formed.
- 16** Describe an electrolysis that could be called the electrolysis of water.
- 17** State general rules (in terms of standard electrode potentials) for what products form at the positive and negative electrodes during electrolysis of aqueous solutions. Give examples to illustrate these rules.
- 18** What is meant by the electrical conductance of a solution? What factors affect electrical conductance?
- 19** What factors affect the rate of electrolysis?

# Corrosion and restoration

## IN THIS CHAPTER

Experimental facts about rusting

How rusting occurs

Explaining the experimental observations

Aluminium

Metals in contact

Preventing rust

Galvanising and cathodic protection

Cathodic protection in wet environments

Corrosion of shipwrecks, particularly  
the *Titanic*

Solubility of gases and salts

Consequences for corrosion of  
shipwrecks

Bacterial corrosion of shipwrecks

The state of long-submerged objects

Drying out recovered artefacts

Chloride removal by electrolysis

Removing crusty deposits

Restoring corroded metal objects

Examples of restoring metal artefacts

Restoration of wooden ships  
and artefacts

Now that we have considered some of the basic chemistry that underlies corrosion of shipwrecks and the restoration of artefacts recovered from them, we can turn to the details of these specific processes. However, corrosion is not confined to ships: it is a very widespread problem and so most of what we have to say about corrosion in this chapter is equally applicable to other corrodible metallic objects—motor cars, steel bridges, pipelines, tanks, machinery and domestic appliances.

In Section 11.5 we saw what rust was and what a serious problem it is. Now let us consider how it forms and how we can prevent it.

## 12.1 EXPERIMENTAL FACTS ABOUT RUSTING

Some of the experimental facts about rusting are:

- 1 Both oxygen and water are necessary for rust to form.
- 2 Salt water accelerates rusting.
- 3 Impure iron rusts more rapidly than pure iron.
- 4 Iron rusts more rapidly when attached to a less reactive metal such as copper or tin than when it is on its own.
- 5 Rust occurs most readily where iron is under mechanical stress—at bends in sheets, points of nails, sharp edges of knives and razor blades, and around bolts and rivets under tension.

Rust is slowly destroying this abandoned whale blubber boiler on Norfolk Island



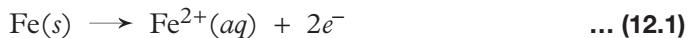
The essential conditions required for rusting to occur are the presence of both oxygen and water. Salt in the water and impurities in the iron accelerate rusting.

Because of these facts, it has been deduced that the formation of rust is an electrochemical process.

## 12.2 HOW RUSTING OCCURS

Figure 12.1(a) shows how rusting occurs. Essentially a galvanic cell is set up as shown in Figure 12.1(b).

At some spot on the iron surface (often a spot under stress), iron atoms lose electrons to form  $\text{Fe}^{2+}$  ions:



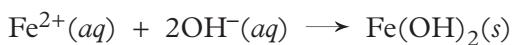
Sites where this oxidation occurs are called **anodic sites**.

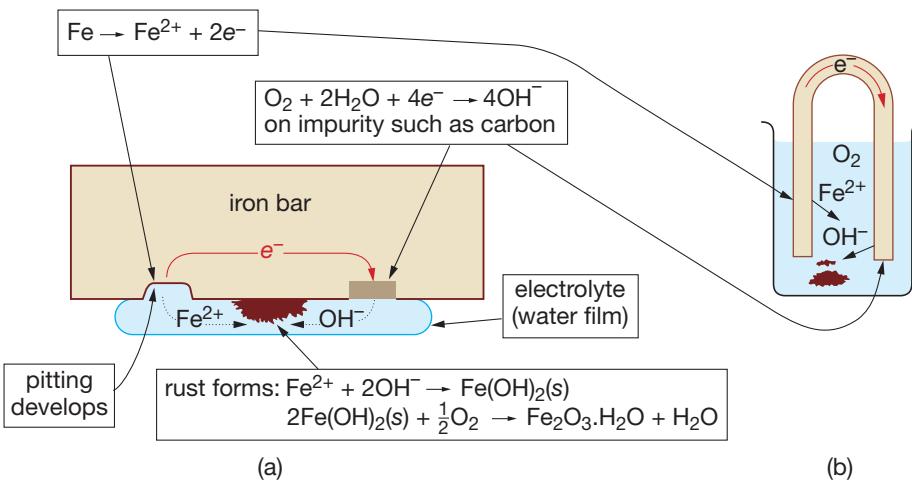
The electrons then flow through the iron to some other spot in the surface—usually where an impurity such as carbon (which can act as a cathode) is present—and there, the electrons reduce oxygen dissolved in the thin film of moisture on the iron surface or in the water touching the iron if the iron object is completely submerged:



Sites where this reduction of oxygen occurs are called **cathodic sites**.

In order for this galvanic cell to continue to operate, there has to be a migration of ions through the moisture layer from one location to the other (compare Figure 2.3). Because salt water is a better conductor than fresh water (which nevertheless is slightly conducting because of dissolved  $\text{CO}_2$  and so on) rusting proceeds more quickly in salt water. This migration of ions to preserve electrical neutrality in the galvanic cell moves  $\text{Fe}^{2+}$  and  $\text{OH}^-$  towards each other to form insoluble iron(II) hydroxide:





**FIGURE 12.1**  
Rusting (corrosion) of iron:  
(a) the actual process,  
(b) representing it as a  
galvanic cell

Iron(II) hydroxide is easily oxidised to iron(III) by oxygen to form rust:

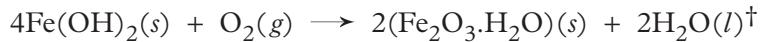


Figure 12.1(b) shows the process looking more like a galvanic cell. The piece of iron that is rusting acts both as the anode and the cathode and as the conducting wire connecting the two electrodes. The cathode is actually the impurities in the iron. Compare this with the galvanic cell in Figure 2.2.

## 12.3 EXPLAINING THE EXPERIMENTAL OBSERVATIONS

This mechanism for rusting explains all the observations listed in the previous section:

- 1 Both oxygen and water are necessary: O<sub>2</sub> needs to be reduced and a conducting film or liquid is needed to complete the circuit.
- 2 Salt water accelerates rusting because it is more conducting than fresh water and so ions migrate towards each other more quickly.
- 3 Impurity sites are needed to act as cathodes on which the reduction of O<sub>2</sub> can occur. Very pure iron is not a good surface for this reduction half reaction, so pure iron rusts very slowly.
- 4 The reduction process, Equation 12.2, occurs much more rapidly on large areas of less reactive metals such as copper and tin than on small areas of carbon impurities in iron. Hence rusting of iron in contact with tin (as in scratched tin cans) or with copper (as in iron–copper joins in water pipes) is much faster than for iron alone. When copper and iron water pipes are joined, the corrosion of iron is greater near the join because that minimises the distance ions have to migrate (through the water) in order to balance the current flow in the galvanic cell set up.
- 5 When iron is under stress as at bends, sharpened points or edges or at riveted joints (high pressure is used to form rivets), the orderly crystal structure of the iron is distorted and this makes it easier for individual Fe atoms to break away from the crystal as Fe<sup>2+</sup> ions.

† This is a ‘simplified’ equation, using  $x = 1$ . More generally:  
 $4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2(\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}) + (4 - 2x)\text{H}_2\text{O}$

One problem with rust is that it is porous and so offers no protection to the underlying metal, so steel sheets (for example, on cars and ships) keep rusting away until holes appear in them. Another problem is that rust has no structural strength; as iron beams rust away, for example in electricity transmission towers or bridges, they lose strength and eventually collapse. Preventing rust is therefore a major concern of any organisation that uses steel.

## 12.4 ALUMINIUM

In recent decades aluminium has replaced steel for many uses, such as door and window frames in buildings, guttering on houses and many factory and office fittings. A major reason for this is that aluminium does not corrode. As we saw in Section 11.7, aluminium *passivates*; that is, it becomes coated with an impervious layer of oxide. And this layer is self-healing: if it gets scratched and so exposes bare metal, it quickly forms more oxide which covers the scratch.

### Aluminium in marine environments

Although aluminium normally resists corrosion, when it is located in areas subject to sea spray, it corrodes quite significantly. This is because sodium chloride (from sea spray) prevents aluminium oxide forming as a non-permeable layer. Instead a porous mixture of sodium chloride and aluminium oxide builds up on the surface. Being porous, it does not prevent further corrosion. This is why aluminium window frames and fixtures corrode quite badly near the ocean.

Aluminium is widely used in the superstructures of ships; that is, in the parts that are not the hull or its basic support structures. It is used because it has a lower density and a lower corrosion rate than steel.

On dry land we often use aluminium without any form of protection. However because of its tendency to corrode in marine environments, aluminium in ships needs to be protected. While painting is often adequate, a better form of protection is *anodising*; this is a process in which a layer of aluminium oxide is formed on the surface of aluminium by electrolysis. Anodising can form a thicker layer of impervious oxide than forms naturally and, if done in a factory away from the sea, there is no interference from salt and so this oxide layer is effective in preventing corrosion even when the aluminium is used on ships.

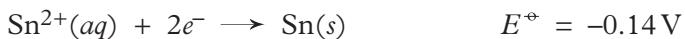
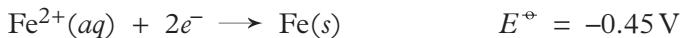
## 12.5 METALS IN CONTACT

Rusting or corrosion is often more serious when steel is in contact with another metal. As already mentioned, steel water pipes corrode more rapidly when they are attached to copper ones (this often happens when the copper water-pipe system of a house is connected to the steel water main in the street). And tin cans (steel coated with tin) rust more rapidly when scratched than bare steel does. Another example is the use of aluminium cylinder heads attached to cast iron blocks in car engines; in this case it is the aluminium that corrodes more rapidly.

In Section 11.6 we saw that standard electrode potentials can be used to predict which of two metals will corrode:

When comparing two metals, the one with the algebraically smaller (lower) standard electrode potential will corrode (oxidise to the cation) more easily than the other.

For iron and tin



Metallic iron, with the lower  $E^\ominus$ , has the greater tendency to go into solution as the positive ion (that is, to corrode). We can envisage the corrosion of a tin can as a galvanic cell as in Figure 12.2. The presence of a less reactive metal surface makes it easier for electrons to be absorbed by oxygen and so the reactive metal corrodes more rapidly (gives up electrons more rapidly) than if the active metal alone were in contact with the solution (or moisture layer).

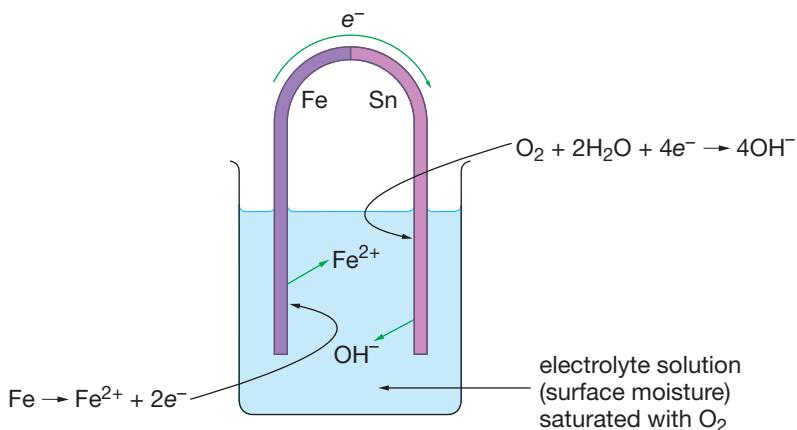


FIGURE 12.2  
Corrosion of tin-plated steel shown as a galvanic cell

## Exercises

- 1 **a** A certain object was made out of copper and nickel with the two metals tightly joined together. Use standard electrode potentials from p. 67 to decide which metal would corrode more extensively.
- b** Would the corrosion of the object in (a) be greater than, or less than or the same as that for a similar object made **(i)** entirely of copper **(ii)** entirely of nickel? Explain.
- 2 **a** A large drop of water is placed on a clean sheet of steel. Where would you expect to observe rust formation (i.e. a brownish red deposit)—inside the drop, around the edge of the drop, or well away from the drop? Explain.
- \*b** A steel pipe standing vertically in salt water rusts quite rapidly. The rust appears just above the waterline while the pitting of the steel surface occurs below the waterline. Explain why this is so.
- 3 Garden tools left with dirt stuck on parts of them rust more rapidly than do clean tools. Explain why. Where would you find deposits of rust and where pitting of the metal?
- 4 Ships for carrying goods around the world are generally made of steel. Small boats for personal use are often made of aluminium, never steel.
  - a** Why is steel and not aluminium used for large ships?
  - b** Why is aluminium and not steel used for small boats?
- 5 Calculate the standard EMF of the galvanic cell shown in Figure 12.2. If you measured the voltage between the iron and tin metals as they are in Figure 12.2, what voltage would you observe? What would you have to do to get a voltage that approximated the value you calculated?
- 6 Sometimes in telephone cabling and in the electrical wiring of caravans and car trailers, copper wires are joined to nickel-plated steel terminals using nickel-plated screws. Under what conditions, if any, would you expect corrosion to occur at such joins? Which metal would corrode?



## 12.6 PREVENTING RUST

There is a great variety of ways of avoiding the problems of rust. An obvious one is to use *substitute materials* (instead of iron and steel) that do not rust. This is widely done in buildings where aluminium has almost completely replaced steel for window and door frames, and often for guttering and downpipes, and sometimes for exterior walls. Stainless steel has often replaced carbon steel in machinery, particularly in food processing and sometimes in domestic appliances, though for the latter plastics are often used instead. Plastics have now largely replaced enamel-coated steel for bath tubs and handbasins.

A problem with using substitute materials, particularly aluminium and stainless steel, is that they are generally more expensive than ordinary steel. It is often more cost effective to use steel and protect it from rusting.

### Common methods of protecting steel from rusting

Three approaches to protecting steel objects against rust: (1) convert powdery rust and exposed surface iron to tightly bound and insoluble iron(III) phosphate (left), (2) clean the object back to bare metal and coat it with zinc from an aerosol spray pack—cold galvanising (middle), and (3) paint the object with an anti-corrosive paint after cleaning it



- 1 *Paint the object.* This stops oxygen and water coming into contact with the iron and so rust cannot form. This is how Sydney Harbour Bridge and most motor car bodies are protected. Painting has the disadvantage that if the paint gets scratched or chipped, some iron becomes exposed to the air and rust can start. The rust can creep along underneath the rest of the paint. This is a common problem with motor car bodies.
- 2 *Cover the iron with a thin coating of tin.* This is commonly done to make ‘tin cans’ for food packaging. Tinplating is similar to painting in that it prevents water and oxygen coming into contact with the iron. It has the advantage that it adheres more tightly to the steel than paint does but has the similar disadvantage that when the coating of tin gets scratched, rust can start.
- 3 *Cover the iron or steel with a vitreous enamel.* This is widely used for storage tanks in hot water services. A coating is placed on the steel and the whole object is heated to a sufficiently high temperature for the coating to melt. Upon cooling the coating solidifies into a glass-like material that is very tough, tightly bound to the underlying metal and quite impervious to oxygen and water: it is much superior to paint.
- 4 *Coat the steel with plastic.* This can be done in a variety of ways to make such household items as the dish-supporting racks in automatic dishwashers, dish drainers for kitchen sinks and soap holders for bathroom and laundry use. It is most effectively done by a process called *powder coating*, which is widely used for tubular steel fencing. Fine polymer particles are attached to the steel object by electrostatic attraction, then the object is heated to melt the particles which coalesce and form a tightly bonded tough film.
- 5 *Passivate the iron.* Although iron does not self-passivate as aluminium or chromium does, it is possible to form chemically a relatively inert surface

layer. Special rust-preventing paints often contain potassium chromate which oxidises surface iron atoms into a relatively impervious layer. Phosphoric acid, present in many rust converters or inhibitors, forms iron(III) phosphate which is very insoluble and bonds tightly to the surface. Such passivation is often done before painting steel objects, because it improves the protection offered by the paint.

- 6 *Galvanise the iron.* This means covering the iron surface with a thin layer of a more reactive metal such as zinc. The advantage of galvanising is that even if the zinc coating is scratched, it still offers protection. We will explore this further in the next section.

## Rust prevention in ships

Rust prevention in ships is a more serious problem than for motor cars, machinery, buildings and domestic appliances on dry land because ships are continuously immersed in sea water, which greatly facilitates rusting. While painting is still the most widely-used form of protection, two newer developments are particularly suitable for protecting the hulls of ships:

- 1 *Surface alloys.* Stainless steel effectively resists rusting and so would be a good metal for the hulls of ships except that it would be prohibitively expensive. It is possible however to form a stainless steel-like surface on ordinary steel by bombarding it with ions of chromium and nickel. The metal ions are formed in a high temperature gaseous discharge (called a plasma) and are directed onto the surface of ordinary steel where they become embedded as atoms and so form a surface alloy. The bulk of the steel below this surface remains unaltered. This stainless steel surface resists corrosion almost as well as solid stainless steel.
- 2 *New paints.*<sup>†</sup> In recent years new polymer-based paints have been developed that are particularly effective in protecting against rust. One such paint is called *Rustmaster Pro*. The polymer cures in air to form a film that is quite impervious to oxygen and water. In addition, additives in the paint react with surface atoms in the steel to form a layer of a very insoluble ionic substance called *pyroaurite*. This contains cations that are mixed hydroxides such as  $M_2Z(OH)_6^+$ ,  $M_3Z(OH)_8^+$  and  $M_4Z(OH)_{10}^+$  where M is a 2+ ion such as Mg, Zn, Fe, Co or Ni and Z is a 3+ cation such as Al, Fe or Mn, with the Fe ions coming from the steel itself. The anions accompanying these cations are generally chloride, sulfate or carbonate. This ionic layer is tightly bonded to the steel surface and extends well into the polymer layer. It effectively prevents any migration of ions from one place on the steel surface to another and so prevents rusting.

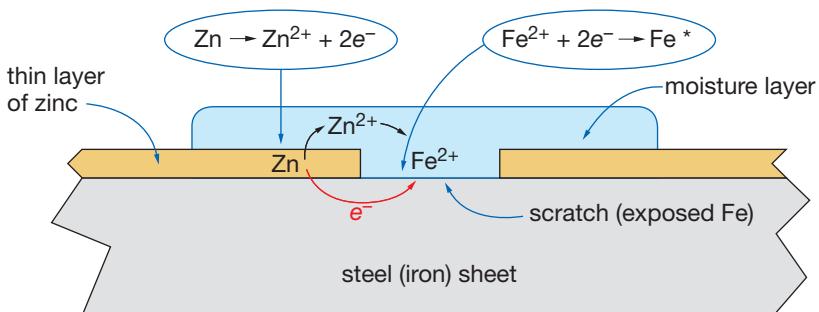
## 12.7 GALVANISING AND CATHODIC PROTECTION

**Galvanised steel** is steel coated with zinc. The particular advantage of galvanising is that if the layer of zinc is scratched, it is able to repair itself and continue protecting the steel. None of the other coatings described above can do this. The explanation is as follows.

<sup>†</sup> This information comes from Zumdahl, S. 1993, *Chemistry*, 3rd Edn, Heath, Lexington, p. 837.

Zinc is a reactive metal but it is moderately passivating. It develops a coating of hydroxide and carbonate (from  $\text{CO}_2$  in the air), which protects the underlying zinc, and this in turn protects the steel. This is the reason why shiny new galvanised steel develops a dull grey look as it ages. So galvanised steel normally does not corrode. If the zinc is scratched and iron becomes exposed to the air, iron tends to oxidise to  $\text{Fe}^{2+}$  as we saw in Section 12.2. However the nearby zinc sets up a galvanic cell as shown in Figure 12.3.

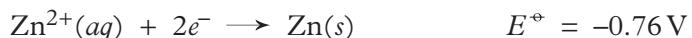
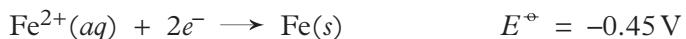
**FIGURE 12.3**  
How zinc protects steel (iron) even when it is scratched. Zinc hydroxide forms as an insoluble coating over the exposed iron and so prevents further corrosion



\* also occurring here:  
 $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$   
 with  $\text{Zn}^{2+}$  and  $\text{OH}^-$  migrating towards each other and forming insoluble  $\text{Zn}(\text{OH})_2$ , which covers up the exposed iron and prevents further corrosion

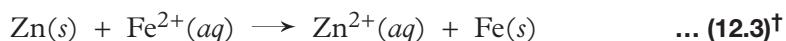
The film of conducting moisture on the surface of the metal acts as the salt bridge, and the bulk of the iron object forms the ‘external circuit’ for electron flow.

The standard electrode potentials,



combined with either of our two rules from Sections 2.14 or 11.6:

- 1 the reduction half reaction with the algebraically greater  $E^\ominus$  goes as written (and drives the other in the reverse direction), or
  - 2 the metal with the algebraically lower  $E^\ominus$  corrodes (oxidises) more easily,
- tell us that Zn reacts with any  $\text{Fe}^{2+}$  formed and converts it back to Fe:



The word ‘galvanise’ comes from this galvanic action.

Instead of  $\text{Fe}^{2+}$  combining with  $\text{OH}^-$  to form rust (Section 12.2),  $\text{Zn}^{2+}$  reacts with hydroxide to form  $\text{Zn}(\text{OH})_2$ , some of which is converted to  $\text{ZnCO}_3$  by atmospheric  $\text{CO}_2$ . This mixture of hydroxide and carbonate forms as an impervious layer over the scratched area and so restores the protection.

For iron exposed to the atmosphere, galvanising can give protection for scratches up to a few millimetres wide.

Even better protection is provided by coating the iron with a mixture of zinc and aluminium, called *zincaleume*. This mixture works in the same way as zinc

<sup>†</sup> It must be emphasised that this equation alone does not explain why a coating of zinc protects iron. If Equation 12.3 were all that happened, then we would be saving cheap iron by throwing away expensive zinc! The formation of an impervious layer of zinc hydroxide and carbonate over exposed iron is an essential part of the protection process.

alone, with the active metals oxidising preferentially to the iron, and forming a protective oxide, hydroxide or carbonate coating which prevents further corrosion. Zincalume is better than zinc alone, because aluminium is more passivating than zinc.

Tinplating is less effective than galvanising because tin is a less active metal than iron: it has an algebraically larger (higher)  $E^\circ$ . This means that tin will not reduce any  $\text{Fe}^{2+}$  ions back to metal, but rather any  $\text{Sn}^{2+}$  formed will oxidise Fe to  $\text{Fe}^{2+}$ . As explained above, scratched tin cans rust more rapidly than iron alone.

Galvanising is one form of *cathodic protection*.

**Cathodic protection** is a method of protecting a metal from corrosion by making it the cathode of a galvanic cell.

## 12.8 CATHODIC PROTECTION IN WET ENVIRONMENTS

Galvanising is relatively expensive. For steel tanks or pipelines buried in moist ground and for hulls of ships there are two other forms of cathodic protection that are considerably cheaper.

### Sacrificial electrodes

A **sacrificial electrode** is a block of zinc or magnesium which is attached to the hull of the ship or to a buried tank or pipeline and which corrodes preferentially. The action is again galvanic: the more reactive metal (Mg or Zn) oxidises preferentially to the iron, giving up electrons to the iron and so preventing iron oxidising to  $\text{Fe}^{2+}$  as shown in Figure 12.4. If any  $\text{Fe}^{2+}$  ions did form, they would be converted back to Fe by these electrons given up by the Zn or Mg.

For this method to work the zinc or magnesium block and the potential sites for iron oxidation (ship or pipe) need to be connected by a moderately conducting medium (sea water or moist earth). Otherwise it is like taking the salt bridge out of an ordinary galvanic cell: the cell does not work so there is no galvanic protection. Sacrificial electrodes do not work for objects in the atmosphere such as motor cars.

A sacrificial electrode is only able to protect the steel surface within a particular distance from it (of the order of many metres): hence the larger the ship, the more sacrificial electrodes that must be fitted.

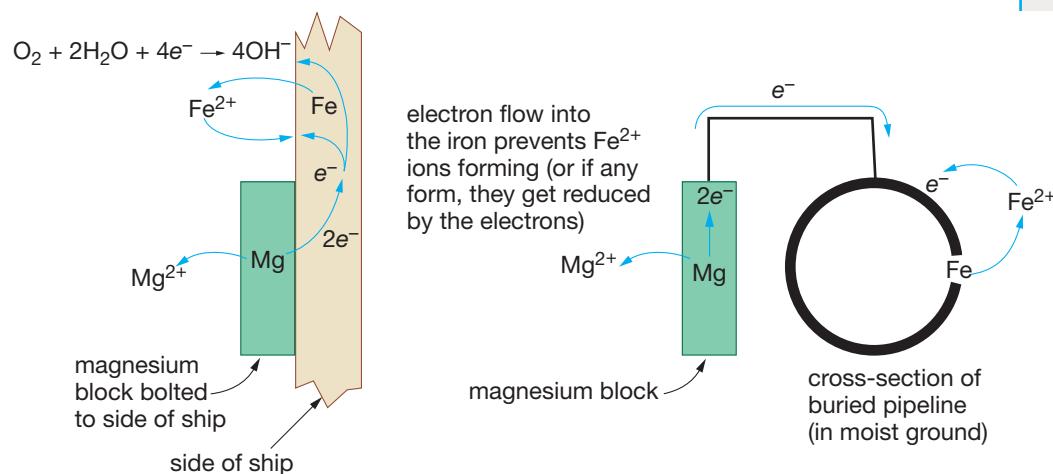


FIGURE 12.4  
Operation of a sacrificial electrode; zinc is often used instead of magnesium

The rate at which zinc or magnesium corrodes in sea water is moderately slow—slow enough for such blocks on hulls of ships to last several years yet fast enough to give the steel hull sufficient electrical charge to prevent its corrosion. Blocks of barium, calcium or sodium would react too quickly to be practical sacrificial electrodes.

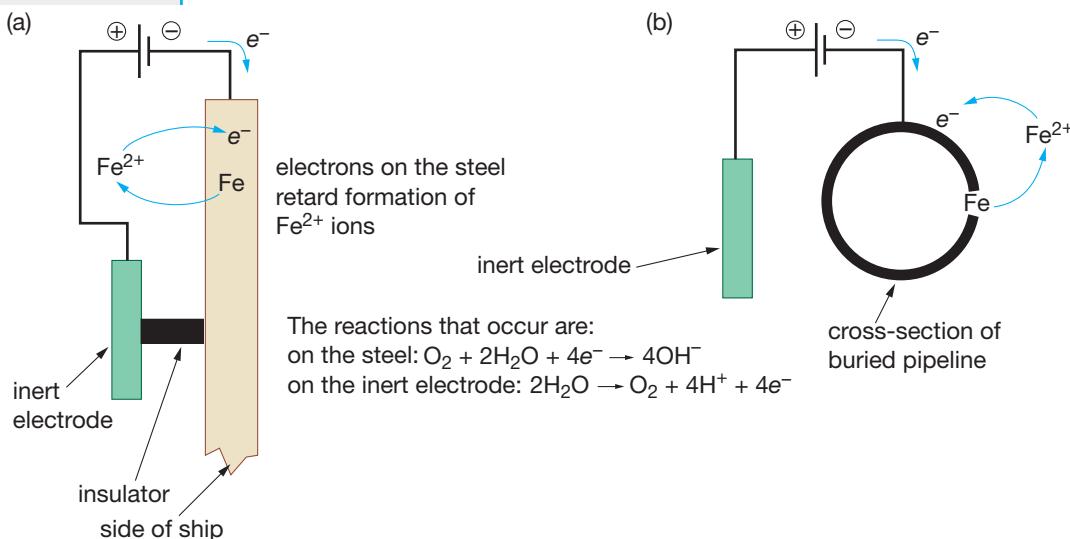
This method of protecting iron and steel is another form of *cathodic protection*; it protects steel by making it a cathode and by using a sacrificial *anode*.

## Applied voltages

**FIGURE 12.5**  
An applied voltage between the object to be protected and an inert anode prevents rusting:  
(a) on the side of a ship,  
(b) on an underground pipeline

Another form of cathodic protection is to use an inert (i.e. non-sacrificial) anode and apply a suitable voltage between it and the hull of the ship. Inert anodes are mounted below the waterline on the outside of the ship but insulated from it as in Figure 12.5(a). A suitable voltage is applied between the anode and the ship's hull (with the hull being negative). This voltage forces electrons into potentially active sites on the steel hull and so prevents oxidation in the same way as the sacrificial anode did.

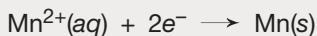
Such applied voltages are also used to protect underground storage tanks and pipelines as in Figure 12.5(b).



## Exercises

- 7 a** A builder used iron nails to attach some aluminium guttering to a house. What (if any) deterioration would you expect to occur over a period of several years?
- b** The same builder used iron nails to attach copper guttering to another house. What would you expect to happen over a period of years?
- 8** Calculate the standard EMF of the galvanic cell shown in Figure 12.3. What would its value be if aluminium were used instead of zinc?
- 9** Draw a diagram of a typical laboratory galvanic cell that would correspond to the sacrificial electrode setup shown in Figure 12.4. Write the electrode reactions that would occur and show the direction of electron flow and ion migration. Calculate the standard EMF of your cell.

- 10** The standard electrode potential for



is  $-1.18\text{ V}$ . Which would provide better protection for an object made of manganese, a coating of zinc or one of aluminium? Explain.

- 11** Motor cars generally have what is called a ‘negative earth’, meaning that the negative terminal of the car’s battery is connected to the steel body of the car. This is claimed to offer some protection against rusting whereas a positive earth is claimed to increase corrosion. Offer an explanation for this. (*Hint:* consider the situation where the car is stationary—that is, not being used.)
- 12** Cooling systems in motor cars are sealed: this means that the liquid (mainly water) is recirculated and is only occasionally replaced. A typical cooling system contains 10 L. If all the liquid was water containing 9 ppm dissolved oxygen, how much iron of the engine block would one filling of the system oxidise?
- 13** Some hardware items such as hinges, screws, and nuts and bolts are nickel plated while others are cadmium plated. Which plating offers the better protection? Why? Would zinc plating be better than either, both or neither of these? Explain. Suggest why zinc plating of such items is far less common than nickel or cadmium plating.

#### WEBSITE

For further information about corrosion:

<http://www.corrosion-doctors.org>

(click on *Major Index*, then on *Corrosion in Action* (takes you to an interesting experiment exploring the effects of copper and zinc on corrosion of iron), *Natural corrosion cells* (metals in contact), *Galvanic corrosion* and/or *Galvanic corrosion experiments* (two interesting experiments, one on metals in contact (click on *using rivets of dissimilar metals*), the other evaluating various rust inhibitors (click on *steel-copper couple ...*)))



## 12.9 CORROSION OF SHIPWRECKS, PARTICULARLY THE TITANIC

Shipwrecks, being mainly steel, normally corrode by the process described in Section 12.2. The rate of corrosion therefore depends upon the oxygen concentration and upon temperature. Wrecks on shorelines where they are periodically exposed to the atmosphere (and a plentiful supply of oxygen) and regularly covered by well-aerated sea water (so that they rarely dry out) corrode quite rapidly.

When a shipwreck is totally submerged all the time, the amount of oxygen available for corrosion is limited by the relatively low solubility of oxygen gas in the water. Temperatures under water are often much lower than on the seashore. Consequently totally submerged wrecks often corrode more slowly than ones that are only partly submerged.

The *Titanic* was a large passenger vessel that sank in very cold and deep (about 4 km) water about 500 km south of Newfoundland (Canada) on its maiden voyage in 1912. When the wreck was located and viewed for the first time in 1985, scientists were quite surprised at the large amount of corrosion it

The *Titanic* hit an iceberg and sank on its maiden voyage in 1912. The discovery of its wreck in 1985 led to greater understanding of deep-sea corrosion



had experienced. They had thought that, because very deep ocean water contains quite low concentrations of dissolved oxygen and because the temperature was low ( $4^{\circ}\text{C}$ ), there would have been only a limited amount of corrosion. They had to re-think their theories about deep-ocean corrosion. Before looking at the causes of *Titanic*'s extensive corrosion, let us examine the ways solubility of gases and salts depends upon temperature and pressure.

## 12.10 SOLUBILITY OF GASES AND SALTS

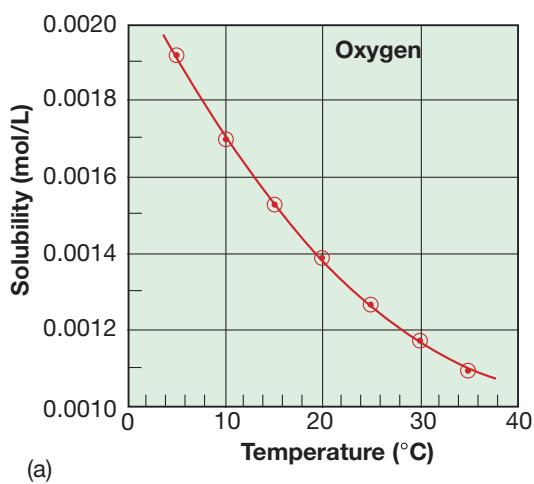
In Section 4.6 we saw that the solubility of carbon dioxide increases as the pressure of  $\text{CO}_2$  above the solution increases and it decreases as temperature increases. This is generally true for all gases.

### For all gases:

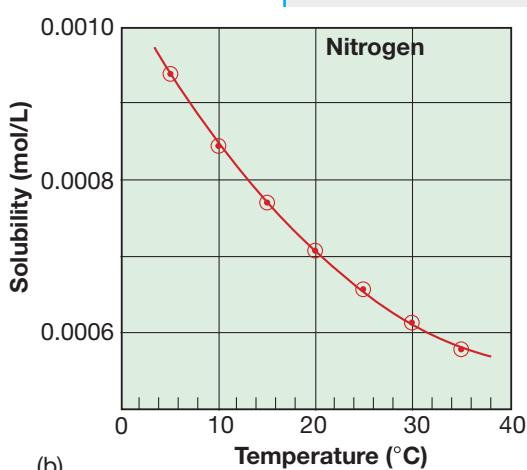
- solubility increases as gas pressure increases
- solubility decreases as temperature increases.

Solubility of a gas is simply proportional to the pressure of that gas above the solution (i.e. *not* the total pressure): double the pressure of gas and its solubility doubles. The variation of solubility with temperature for oxygen and nitrogen is shown in Figure 12.6. Figure 4.3 is a similar graph for carbon dioxide.

As we go down to greater depths from the ocean surface, temperature falls and pressure increases. Pressure increases by approximately 100 kPa for every 9 m of depth. So both pressure and temperature cause the solubility (as distinct from actual concentrations) of gases to increase as depth increases. The main gases present in ocean water are oxygen, nitrogen and carbon dioxide. Table 12.1 shows the solubility of these gases at the ocean surface at  $20^{\circ}\text{C}$ , and at a depth of



(a)



(b)

100 m (1200 kPa pressure) at 4°C (the minimum deep-ocean temperature); for comparison, the concentration of these gases in the atmosphere is also shown.

**TABLE 12.1 Concentrations (in mol/L) of three gases in the ocean and atmosphere**

Gas	Concentration in the atmosphere at 20°C	Concentration in ocean surface water at 20°C <sup>a</sup>	Solubility <sup>b</sup> at 100 m (1200 kPa) and 4°C
O <sub>2</sub>	$8.3 \times 10^{-3}$	$2.8 \times 10^{-4}$ <sup>c</sup>	0.024
N <sub>2</sub>	$3.3 \times 10^{-2}$	$5.6 \times 10^{-4}$	0.012
CO <sub>2</sub>	$1.5 \times 10^{-5}$	$1.4 \times 10^{-5}$	0.73

a with the gases present above the water at their normal atmospheric pressures: 20 kPa for O<sub>2</sub>, 80 kPa for N<sub>2</sub> and 35 Pa for CO<sub>2</sub>.

b this is the concentration that could be reached at 100 m, if the gas was present there at a pressure of 1200 kPa; the actual concentrations are much less than these solubilities.

c equivalent to 8.9 ppm.

The solubility at 100 m depth (1200 kPa) in Table 12.1 is the concentration of oxygen in water that we would get if we put some water in a steel cylinder, then added oxygen gas till its pressure reached 1200 kPa. Alternatively it is the localised concentration we would obtain if we took a cylinder of compressed oxygen to a depth of 100 m, then opened the valve to let oxygen gas out (at a pressure of just over 1200 kPa: it would not come out at a lower pressure). Neither of these situations resembles real oceans.

In fact the pressure dependence of solubility of gases is largely irrelevant for determining the actual concentrations of gases at great ocean depths as the following explanation shows.

Ocean water near the surface is generally saturated with the three gases we have been considering, O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub>, because there is good stirring of both the water and the atmosphere near the surface; this facilitates dissolution of the gases. Hence the concentration of oxygen in surface water is approximately 11 ppm at 10°C and 9 ppm at 20°C. There is not much mixing of surface water with deep water, so diffusion is the main way that these gases get to deeper water.

For oxygen there are four factors determining its concentration in deep ocean water:

- 1 diffusion of dissolved oxygen down from surface layers
- 2 production of oxygen by photosynthetic organisms such as phytoplankton (occurs in the top 100 m only; light can rarely penetrate further)

**FIGURE 12.6**  
The temperature dependence of the solubility of the two gases: (a) oxygen and (b) nitrogen (for a pressure of 100 kPa of the respective gases above the solutions)

- 3 consumption of oxygen by other organisms such as fish and aerobic bacteria. The result of these three factors is that oxygen concentration generally decreases with increasing depth, at least down to about 500 to 1000 m where oxygen concentrations are typically 0.5 ppm.
- 4 As depth increases further, a fourth factor comes into play, namely deep ocean currents that bring cold oxygen-rich surface water from polar regions into the bottom layers of ocean water. This injection of extra oxygen at great depths results in oxygen concentrations being of the order of 2 ppm at depths greater than 1000 m.

The concentration of carbon dioxide also does not depend solely on diffusion from the surface. Organisms generate it through their normal respiration, though unlike oxygen there are no organisms that remove it. However,  $\text{CO}_2$  concentration does not reach the solubility limit of Table 12.1, because calcium ions in seawater precipitate much of it as carbonate.

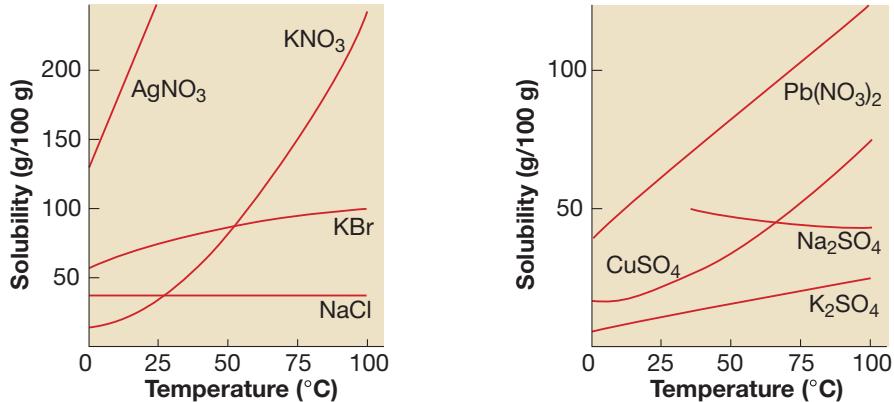
For nitrogen in the ocean, there are no significant production or removal processes, so as depth increases its concentration does not change much from its surface value of 15 to 20 ppm.

#### For salts:

- solubility generally but not always increases as temperature increases
- solubility is virtually unaffected by increasing the pressure applied to the mixture of solid and solution.

Figure 12.7 shows the temperature dependence of the solubility of some common salts. Note that the solubility of sodium chloride changes only slightly as temperature changes. This means that the salt in sea water stays in solution at all ocean temperatures.

**FIGURE 12.7**  
Temperature dependence  
of solubility of some salts



### Exercises

- 14 From Figures 12.6 and 4.3 the solubilities of oxygen, nitrogen and carbon dioxide at 20°C are  $1.4 \times 10^{-3}$ ,  $7.1 \times 10^{-4}$  and  $3.4 \times 10^{-2}$  mol/L respectively. Reconcile these values with the ones given in Table 12.1.
- 15 Express the concentrations of oxygen, nitrogen and carbon dioxide in surface water at 20°C in Table 12.1 in:
  - a per cent (w/v), that is grams per 100 mL
  - b parts per million w/w (taking the density of each solution as 1.00 g/mL)

- 16** The table below gives the solubility of hydrogen sulfide in water at different temperatures when the pressure of the gas above the solution is 100 kPa.

Temperature (°C)	5	10	15	20	25	30	35
Solubility (mol/L)	0.168	0.147	0.130	0.115	0.103	0.092	0.084

- \*a Draw a graph of solubility versus temperature.
  - b What is the solubility of hydrogen sulfide at (i) 12°C (ii) 23°C (iii) 32°C? Include estimates of the error in your values and explain how you decided upon these estimates.
  - c At what temperature is the solubility (i) 0.140 mol/L (ii) 0.096 mol/L? Again give estimates of error in your values.
  - d If the pressure of hydrogen sulfide gas above the solution falls to 30 kPa at 20°C, what is the solubility? If the pressure increases to 350 kPa, what is the solubility (again at 20°C)?
  - e If the pH of the solution is increased to 8 or 9 (at 20°C and 100 kPa pressure of H<sub>2</sub>S), what happens to the solubility? Explain why.
- 17** The following table gives the solubility of potassium chloride in water as a function of temperature.
- | Temperature (°C)            | 0  | 20 | 40 | 60 | 80 | 100 |
|-----------------------------|----|----|----|----|----|-----|
| Solubility of KCl (g/100 g) | 26 | 31 | 37 | 43 | 50 | 58  |
- \*a Plot solubility of potassium chloride against temperature.
  - b What is the solubility of potassium chloride at: (i) 15°C (ii) 73°C?
  - c At what temperature is the solubility of KCl: (i) 45 g per 100 g water (ii) 33 g per 100 g water?
  - d 35 g KCl was dissolved in 75 mL ( $\approx$  75 g) water at 90°C. The solution was slowly cooled to 0°C. At what temperature does potassium chloride start to crystallise out of this solution? At 0°C what mass will have crystallised out?
  - e If the original potassium chloride had contained some soluble impurities, would they still be in the crystallised material? Explain why (or why not).
- 18** Ocean water, like pure water, shows a maximum density at 4.0°C. Explain why shipwrecks on deep ocean floors never experience temperatures below 4°C.

## 12.11 CONSEQUENCES FOR CORROSION OF SHIPWRECKS

From the above discussion of oxygen solubility we conclude that shipwrecks in very deep ocean water, say deeper than 100 m, should corrode fairly slowly, because:

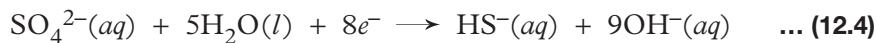
- there is only a small concentration of oxygen present at such depths (oxygen is essential for rusting: Section 12.1)
- the low temperature slows down the rates of the chemical reactions involved.

However when the wreck of the *Titanic* was discovered in 1985, the hull was much more extensively corroded than had been expected.

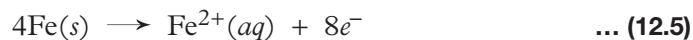
From analyses of samples of corroded materials and the silts and deposits attached to them, it was determined that much of the corrosion was caused by certain bacteria.

## 12.12 BACTERIAL CORROSION OF SHIPWRECKS

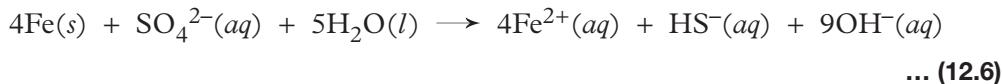
For shipwrecks in deep ocean water, some of the corrosion is caused by the electrochemical process described in Section 12.2. However, much of the corrosion is **bacterial corrosion**, that is corrosion caused by certain anaerobic bacteria<sup>†</sup> that obtain their energy by reducing sulfate to sulfide. The reduction half reaction is:



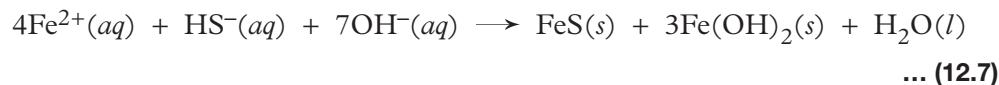
Chemically this reaction is very slow but can be brought about quite rapidly by bacteria of the *Desulfovibrio* family. The oxidation half reaction is the normal oxidation of iron:



(it has been multiplied by 4 so we can balance electrons). Addition of Equations 12.4 and 12.5 gives:



The  $\text{Fe}^{2+}$  formed reacts with  $\text{HS}^-$  and  $\text{OH}^-$  to form insoluble  $\text{FeS}$  and  $\text{Fe(OH)}_2$ :



Addition of Equations 12.6 and 12.7 and cancellation of one  $\text{H}_2\text{O}$  on each side gives the overall reaction for the process:



Black iron(II) sulfide forms on the steel along with iron(II) hydroxide which in the absence of oxygen is not converted to iron(III) as in normal corrosion.

This corrosion by bacterial reduction of sulfate accounts for much of the corrosion on deeply submerged shipwrecks. It forms as fingers of reddish-brown growth called **rusticles** that hang from the steel structure like small stalactites; in addition to mixed oxides and hydroxides of iron, rusticles usually contain other substances produced by bacteria such as calcium carbonate.

Bacterial corrosion of iron is not confined to shipwrecks; it occurs on tanks and pipelines buried in moist clays, particularly if oxygen is absent. If the black film is wiped away, pitting of the steel surface can be seen, often with shiny spots of bare iron showing.

## 12.13 CORROSION IN ACIDIC SEA WATER

Normal galvanic corrosion (Section 12.2) involves the half reaction:



This half reaction occurs more readily in acid solutions than in alkaline ones as is shown by the way the electrode potential changes with pH. The standard electrode potential for Reaction 12.9 is 0.40 V; this is the value at  $[\text{OH}^-] = 1.00 \text{ mol/L}$  (remember the meaning of ‘standard’). In neutral solution

<sup>†</sup> Anaerobic bacteria are ones that live without needing oxygen.

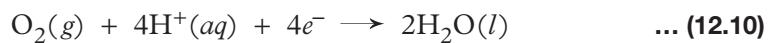


Rusticles hang from the wreck of the *Titanic* like stalactites

( $\text{pH} = 7.00$  or  $[\text{OH}^-] = 1.0 \times 10^{-7}$  mol/L) the (non-standard) electrode potential is 0.81 V and at  $\text{pH} = 4.00$ , it is 0.99 V. The fact that the electrode potential increases as acidity increases means that the half reaction has a greater tendency to occur as acidity increases.

*This shows that normal galvanic corrosion occurs more rapidly in acidic solutions than in alkaline ones.*

When we are working with acidic solutions, we usually write the half reaction in terms of  $\text{H}^+$  rather than using  $\text{OH}^-$ . To do this we add  $4\text{H}^+$  to each side of Equation 12.9, ‘convert’  $4\text{OH}^- + 4\text{H}^+$  to  $4\text{H}_2\text{O}$  and cancel  $2\text{H}_2\text{O}$  on each side to get:



Although Equation 12.10 looks different from Equation 12.9, they both represent the same thing, namely reduction of oxygen to water; all that changes between the two equations is the acidity of the solution in which it is occurring.

Ocean water is just slightly alkaline— $\text{pH}$  between 7 and 8. However there are bacteria in the ocean that produce hydrogen ions in their normal metabolism. Under normal conditions their populations are such that they do not significantly affect the  $\text{pH}$  of ocean water. However around shipwrecks generally (not specifically the *Titanic*) where there is an abundance of organic material such as wood and fabric for them to feed on, their numbers multiply, and so they can produce a slightly acidic environment. This accelerates the corrosion of shipwrecks (providing dissolved oxygen is available).

In effect these bacteria accelerate corrosion by producing slightly acidic conditions.

This corrosion where oxygen is bringing about the oxidation is quite distinct from the direct reaction of iron with dilute acid solutions ( $\text{pH} < 3$ ) where the oxidation is brought about by hydrogen ions (which are reduced to hydrogen gas).



## WEBSITES

About the *Titanic*:

<http://www.corrosion-doctors.org/Landmarks/Titanic.htm>

(read this page, then click on *What's happening to her now?* and *Did corrosion sink the Titanic?* at the bottom of the page)

<http://www.deepimage.co.uk/wrecks/titanic/titanic%20pages/titanic-science-mainpage.htm>  
(a good account of the so-called rusticles that have formed on the *Titanic*)

<http://www.archaeology.org/0101/abstracts/titanic1.html>

(another interesting account of the *Titanic* but not much chemistry in it)



## Exercises

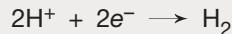
**18** In neutral or alkaline solution the reduction half reaction for corrosion of iron is usually written as:



At pHs between 4 and 6 it is generally written as:



At pHs below 3 oxidation is by hydrogen ions, not by oxygen gas:



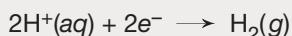
Write the equation for the overall corrosion of iron under each of these conditions.

**\*19** Under which conditions would a wet steel wool pot scourer rust most rapidly and least rapidly:

- a** left lying in a wet kitchen sink
- b** immersed in a jar of tap water
- c** stored in a jar of detergent solution (slightly alkaline)?

Explain your reasoning.

**20** It was stated above that the electrode potential for reduction of oxygen at pH = 4.00 was 0.99 V. For the reduction of hydrogen ions to hydrogen gas



the electrode potential at pH = 4.00 is -0.24 V. Use this information to explain why at pH = 4.00 iron is oxidised preferentially by oxygen, not by hydrogen ions.

**21** The Statue of Liberty in New York, USA, is a steel skeleton structure with a copper cladding. Originally the copper skin was separated from the steel structure by a layer of asbestos. This wore away with time and the steel structure corroded quite badly. In the statue's nearly 100 year lifetime (up to 1986) almost half of the steel had disappeared. However in the same time less than 5% of the copper skin had been lost.

- a** Explain why the steel was seriously corroded while the copper was not. What was the purpose of the asbestos?
- \*b** The statue was restored in 1986. The copper skin with its beautiful green patina (colour) was preserved while the internal structure was completely rebuilt. If you had been in charge of the restoration, what material would you have used to rebuild the structure? Explain your choice.

**22** Underground pipes used by water authorities for circulating water to businesses and houses in towns and cities are generally made of cast iron. However many building codes require that water pipes within buildings must be made of copper. What is the problem with joining a copper pipe to an iron pipe? Suggest a way or ways of overcoming this difficulty and explain why your suggestion(s) would work.

Having considered the corrosion of shipwrecks in considerable detail, let us now turn to the question of salvaging artefacts from such wrecks.

## 12.14 THE STATE OF LONG-SUBMERGED OBJECTS

There has been considerable interest over the years in recovering objects such as coins, ornaments, china, glassware, ship's furniture and fittings, and cannons from shipwrecks. Such artefacts often have considerable historical value and can sometimes give insight into the technology and artistic methods of past cultures. Unfortunately when they are recovered these artefacts are generally in very poor condition because:

- metals have been seriously corroded
- the objects themselves have often been severely encrusted with deposits of calcium carbonate (limestone) or coral
- porous objects, particularly of leather and wood, have been impregnated with sea water which contains salts such as chlorides and sulfates; metal objects will also have sea water trapped in them—in the microscopic pores of what appear to be smooth surfaces.

Restoring such artefacts to conditions as close to their original state as possible requires great skill and a good understanding of several aspects of chemistry. It also requires careful planning of the whole procedure to be followed, and the safe storage of recovered objects to prevent further corrosion or damage while procedures are being worked out and equipment assembled.

## 12.15 DRYING OUT RECOVERED ARTEFACTS

When a solution of a solid such as sodium chloride is evaporated, the solution becomes more concentrated (because only water, not the solid, evaporates). Eventually it becomes saturated. As further water is removed, solid starts to crystallise out until finally all the water has gone and only the solid remains.

If objects recovered from shipwrecks are dried simply by evaporating off the water, either by leaving the objects exposed to the air or by gently warming them in an oven, then the water evaporates but leaves the salt as solid particles throughout the object. The formation of salt crystals throughout porous objects can cause considerable damage by distorting the shape, cracking the object or reacting chemically with it. Hence the salt must be removed before the artefact is dried. When objects are recovered from the ocean they are usually stored in sea water (or suitable other solution, such as dilute sodium hydroxide for iron objects) until a suitable cleaning and drying procedure has been developed.

### Leaching salts from objects

One approach for removing impregnated salts is to leach them out of the object. This is done by immersing the

A brass bell from the *Titanic*, one of hundreds of artefacts that have been recovered and restored from that wreck



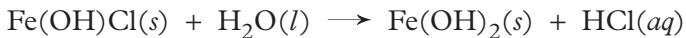
object in clean water for periods ranging from hours to weeks, and occasionally replacing the water as salt concentration builds up in it. Salts diffuse out of the object into the water so that after a suitable time the object is saturated only with pure water.

For iron objects dilute sodium hydroxide solution is generally used instead of pure water: it speeds up the removal of chloride (because the hydroxide ion can replace chloride in iron compounds), and it retards further corrosion of the object.

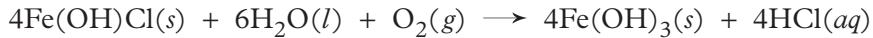
Chloride is often difficult to remove from metal objects just by leaching. This seems surprising, because our first thoughts are that chloride is present as iron(II) or iron(III) chloride or copper chloride, all of which are quite soluble in water, so they should readily leach out. It appears that much of the chloride is present as insoluble hydroxy chlorides such as  $\text{Fe(OH)Cl}$  or  $\text{Cu(OH)Cl}^\dagger$ . Being insoluble, they are very difficult to leach out.

## 12.16 CHLORIDE REMOVAL BY ELECTROLYSIS

Any chloride left in fine pores and cracks in recovered iron, copper, brass or bronze objects is a serious problem, because it can accelerate further corrosion after the object has been cleaned and restored. This is because these hydroxy chlorides react slowly with water to form hydrochloric acid:



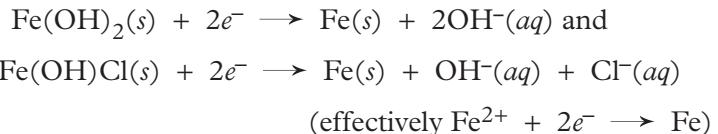
The latter reaction is usually accompanied by oxidation of the iron to the +3 state, leading to the overall reaction:



If chloride is not completely removed, hydrochloric acid forms after the object has been restored and it can cause further corrosion.

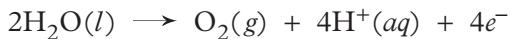
A more efficient way of removing chloride from such objects is by *electrolysis*. The metal object to be restored is made the cathode and a stainless steel anode is used as shown in Figure 12.8: the electrolyte is 0.5 mol/L sodium hydroxide solution.

*At the cathode:*

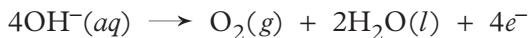


These electrode reactions free  $\text{Cl}^-$  and  $\text{OH}^-$  from the solids and they migrate towards the anode. While they do not react there, the migration at least moves them out of the iron and into the solution. For cleaning the recovered cannons from Captain Cook's *Endeavour* (Section 12.19) 6 to 8 weeks were required.

The reaction at the anode is the normal oxidation of water to oxygen:



or writing it in a form more appropriate to the alkaline solution:



† Hydroxy chlorides are sometimes called basic chlorides; these formulae are oversimplified but serve the current purpose of showing how HCl is generated.

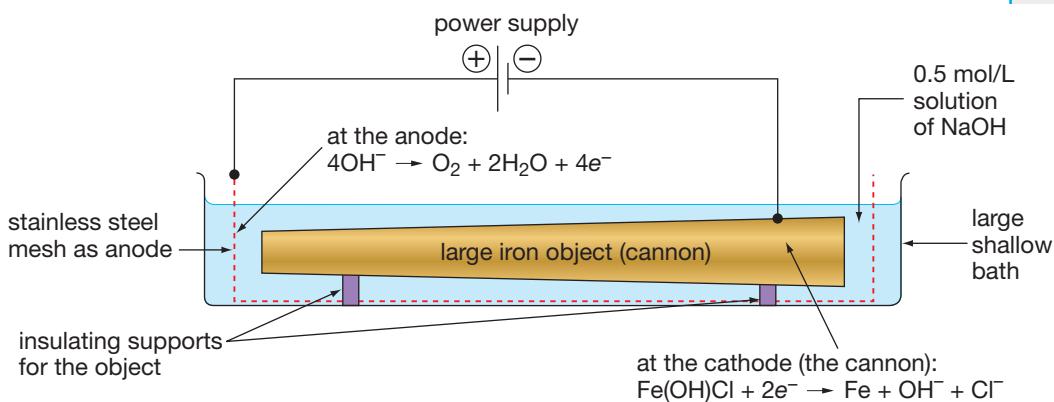


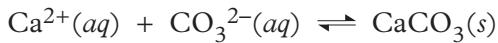
FIGURE 12.8  
Using electrolysis to remove chloride from an iron object such as a cannon

## 12.17 REMOVING CRUSTY DEPOSITS

Larger than normal concentrations of carbon dioxide (from the normal metabolism of many marine organisms) are often produced around wrecks, because the ready food supply provided by the materials of the wreck leads to increased populations of bacteria and other organisms. This extra carbon dioxide leads to the precipitation of calcium carbonate:



(both of these equilibria are pushed to the right by increasing  $\text{CO}_2$  concentrations)



Consequently many artefacts salvaged from wrecks are covered with crusty deposits of calcium carbonate, often with rust or other corrosion products mixed in with it. Such deposits on salvaged objects are called **concretions**.

There are two ways of removing such concretions. The first is to treat the artefact with dilute acid:



Typically 1 mol/L hydrochloric acid has been used, though some workers have preferred to use an acetic acid–sodium acetate buffer (pH 3 to 5, Table 4.7) in order to stop the evolution of carbon dioxide becoming too vigorous and possibly damaging the artefact.

The second method, widely used on large iron objects, is to hit the concretion with a hammer; often a sudden sharp hit is enough to cause a large slab of concretion to break away from the underlying metal.

In tropical waters coral often grows on submerged objects. Because of its high calcium carbonate content it can be removed in the same way. Hammer hits are particularly effective for coral deposits. This method was used as the first step in restoring the cannons salvaged from Captain Cook's *Endeavour* (Section 12.19).

## 12.18 RESTORING CORRODED METAL OBJECTS

Metal objects recovered from shipwrecks are often badly corroded. The actual form of the corrosion depends upon the nature of the metal.

## Restoration of silver artefacts

Silver ornaments and coins often become covered with silver sulfide. As explained in Section 12.12 *Desulfovibrio* bacteria reduce sulfate to sulfide (Equation 12.4). As well as reacting with  $\text{Fe}^{2+}$  as in that section, the hydrogen sulfide ion is in equilibrium with  $\text{H}_2\text{S}$  which reacts with silver:



A batch of silver coins recovered from the wreck of the Dutch ship the *Batavia* that sank off the West Australian coast in the seventeenth century. The coins as originally recovered (left photo) were heavily encrusted with calcium carbonate deposits formed by marine organisms. Treatment with dilute acid followed by electrolysis as described in the text was used to recover the coins with minimal damage (right photo)



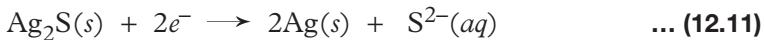
Silver sulfide forms as a relatively firm layer on the silver object and so prevents the whole object corroding away. The sulfide-coated objects gradually become covered with calcium carbonate deposits (concretions), which because of the smallness and/or fragility of the object are best removed by dissolving them in acid (see the previous section).

After removal of any concretions, an obvious way of cleaning off this deposit of silver sulfide would be to use an abrasive to clean it mechanically. However this would damage the engravings or embossings on the object and would lose some of the silver. A better approach is to reverse the corrosion process by electrolysis.

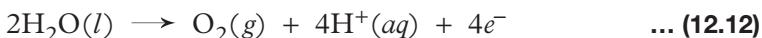
## Restoration by electrolysis

The formation of silver sulfide can be reversed by making the corroded object the cathode in an electrolysis cell as in Figure 12.9.

The reduction process is:



An inert anode is used (such as platinum or stainless steel) and the electrolyte is a solution of sodium hydroxide, chosen because it facilitates the above electrode reaction. At the anode the reaction is oxidation of water:

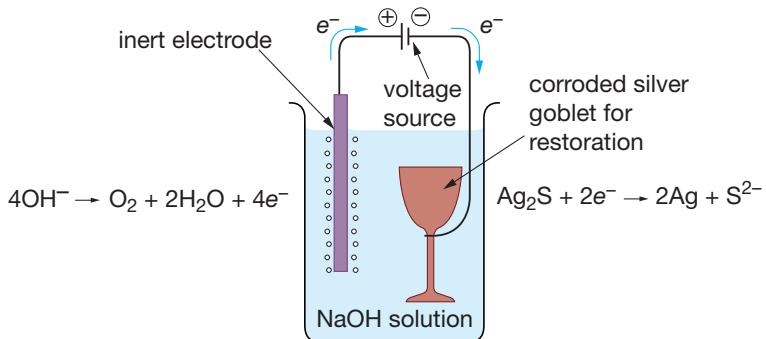


or writing it in a form more appropriate to alkaline solution:



Equation 12.13 is derived from 12.12 by adding  $4\text{OH}^-$  to each side of 12.12, ‘converting’  $4\text{H}^+ + 4\text{OH}^-$  to  $4\text{H}_2\text{O}$  and cancelling  $2\text{H}_2\text{O}$  from each side.

In this way silver sulfide is converted back to silver with little damage to the markings on the object. For long-term stabilisation such restored silver objects can be coated with a clear lacquer, though this is not always necessary.



**FIGURE 12.9**  
Restoring a corroded silver object by making it the cathode of an electrolytic cell

## Restoration of iron objects

A variety of methods have been used to restore iron objects. Carbonate or coral deposits are generally removed mechanically; sharp taps on the encrustations usually cause them to break off, leaving a layer of corroded iron exposed. After that there are two aims: first to remove chloride and second to convert various oxide deposits (rust) back to iron and so preserve the engravings on the object.

The electrolysis method described in Section 12.15 for removing chloride also converts much of the iron hydroxides or oxides back to iron and is an effective way of restoring the object: Cook's cannons were restored in this way. After electrolysis the object is thoroughly washed in pure water, completely dried by blowing hot air over it and finally coated with a special wax that gives the iron an attractive lustre while protecting it from further corrosion.

In more recent times iron objects have usually been restored by a combination of *reductive heating and electrolytic removal of traces of chloride*. The object is heated to  $120^\circ\text{C}$  to remove water, then to  $400^\circ\text{C}$  in a stream of hydrogen (to reduce iron oxides) for about two days, then slowly cooled. When the temperature falls to  $100^\circ\text{C}$ , the hydrogen is replaced by nitrogen until room temperature is reached. The object is then placed in sodium hydroxide solution (to prevent re-oxidation) and residual chloride removed by electrolysis (previous section). The object is then washed, dried and coated with wax as above.

## Restoration of copper and copper-alloy objects

Objects made of copper and copper alloys (such as brass and bronze) do not corrode as badly as silver and iron. Marine organisms do not readily grow on copper-based metals because copper ions are poisonous to them. Such objects are generally not heavily encrusted. They do, however, form surface layers of insoluble copper(I) chloride and copper(II) hydroxychloride,  $\text{Cu}(\text{OH})\text{Cl}$ .

Copper and copper alloys are usually cleaned by *chemical stripping*—dissolving the surface deposits with a chemical solution. A 5 to 10% solution of citric acid containing 1 or 2% thiourea as a corrosion inhibitor is often used. If the object is totally submerged in such a solution for several days, surface deposits are dissolved and the bare metal exposed. Such stripped objects still need to have residual chloride removed and this is generally done by prolonged soaking in sodium hydrogen carbonate solution or just pure water. Electrolysis as for iron can also be used to remove chloride. However, modification is needed with brass ( $\text{Cu} + \text{Zn}$ ) and bronze ( $\text{Cu} + \text{Sn}$ ), because both zinc and tin slowly dissolve in sodium hydroxide solution. A solution of sodium carbonate is used instead.

To prevent further corrosion such objects are usually coated with a clear acrylic lacquer.

## Lead

Lead artefacts can be restored in a similar way to those of brass and bronze.

Lead is poisonous to marine organisms and so very little concretion grows on lead objects in shipwrecks. As with other metals corrosion produces surface coatings of oxides, sulfides, and basic chlorides (hydroxy chlorides), though with lead some insoluble sulfate also forms. Some chloride penetrates into micro-pores in the lead.

Lead is restored first by using dilute hydrochloric acid to remove any carbonate concretions that have formed, then by soaking the object in an EDTA solution buffered at about pH 10 to 11. EDTA was discussed in Section 8.8; it dissolves the insoluble lead compounds because it forms a strong complex with  $Pb^{2+}$  ions. Leaching with water or electrolysis is used to remove residual chloride. If electrolysis is used to remove chloride, sodium carbonate solution is used because lead, like tin and zinc, slowly dissolves in hydroxide solution. As with other metals, the restored object must be coated with a suitable lacquer or wax to prevent further corrosion.

## 12.19 EXAMPLES OF RESTORING METAL ARTEFACTS

Two specific examples of restoring and conserving metal artefacts are as follow.

### Iron cannons from Captain Cook's Endeavour

When in 1770 the *Endeavour* hit a reef off what later became Cooktown, Cook jettisoned six of the ten cannons on board and a large number of iron ingots present as ballast in order to lighten the damaged vessel so it could reach the shore. These cannons and ingots were discovered in 1969.

They were:

- cleaned by chipping off the coral (calcium carbonate concretions)
- restored by electrolysis (both to remove chloride and to reduce oxides)
- preserved by coating with wax.

A restored cannon is shown on p. 393. Before restoration it looked very similar to the one from *Pandora*, also shown on p. 393.

### Silver coins from Dutch shipwrecks

During the seventeenth to nineteenth centuries several of the sailing ships involved in the vigorous trade between Holland (now the Netherlands) and its colony, the Dutch East Indies (now Indonesia), were wrecked along the West Australian coast. In recent times, heavily encrusted bundles of silver coins have been salvaged from these wrecks. The recovered coins were fused together by deposits of calcium carbonate and looked more like lumps of coral than silver coins (see the photo on p. 436). They were:

- cleaned by soaking in dilute acid solution for several hours to remove the calcium carbonate deposits which also separated the individual coins and bars from one another (giving black objects);

- restored by electrolytically converting this black silver sulfide to silver as described above. (This restored the coins fairly closely to their original state with their embossing clearly visible.)

Being silver (which in clean air does not corrode) special steps for preservation are not necessary, apart from ensuring the air they are in is free of even the smallest traces of hydrogen sulfide.

Similar methods have been used to restore silver coins from sunken or wrecked Spanish galleons engaged in the seventeenth and eighteenth century European plunder of Central and South America.

## 12.20 RESTORATION OF WOODEN SHIPS AND ARTEFACTS

In recent decades two sunken wooden ships have been recovered and restored. One is a Swedish ship the *Vasa* that sank in the Baltic Sea in 1628 and was recovered in 1956 and has been gradually restored over a forty-year period. The other is the *Mary Rose*, a naval ship from Henry VIII's time, which sank off the south coast of England in 1545 and was raised in 1982 and is currently being restored. In Australia a portion of the Dutch ship *Batavia* that was wrecked off the West Australian coast has been salvaged and restored. The techniques developed for restoring these ships have been widely applied to the restoration of wooden artefacts generally.



The stern timbers of the 1629 VOC Retour ship *Batavia*, preserved and displayed at the Shipwreck Galleries of the West Australian Maritime Museum

### Wood in sea water

When wood is immersed in sea water, there is fairly rapid decay; wood worms and various bacteria and fungi attack the wood, quickly eating much of it and causing the rest to fragment. Unless special circumstances exist, wood decays away completely within a century.

Special circumstances that can prolong the life of wood in oceans include:

- if the wreck or object is quickly buried in silt or mud; this excludes worms and aerobic bacteria and so the rate of decay is greatly reduced
- if the water is very cold (near the minimum ocean-floor value of 4°C)
- if the salt content of the water is low (as in the Baltic Sea, 0.4% instead of the normal 3.5%)
- if there is little water movement over the wreck (so restricting the inflow of oxygen for bacteria and limiting mechanical damage).

The *Vasa* was almost completely covered with silt; this along with the low salt content of the Baltic Sea and the low water temperature preserved the timbers of the ship surprisingly well. One half of the *Mary Rose* had become buried in silt and was well preserved; water temperatures were also quite low. The exposed half of the ship had decayed very extensively.

When bacteria and fungi attack wood, they first eat away the cellulose and leave behind the lignin which is able to maintain the shape and general structure of the wooden object (though it becomes very fragile). Sea water fills the gaps in the wood while the remaining wood becomes saturated (or heavily impregnated) with sodium chloride and various sulfates.

## Restoring wooden objects

When long-submerged wooden objects (including ships) are recovered, they are very fragile (because of the missing cellulose). If they are simply left to dry out, the wood shrinks, warps and splits. As water evaporates crystalline salts are left behind inside the wood and this causes swelling and further splitting. To preserve such wooden objects they must be kept wet and away from light while a plan is developed for their restoration.

The restoration and preservation (conservation) of wooden objects involves the following steps:

- The object is first cleaned of silt and mud and other debris by gentle washing with cold water for a long time. The *Vasa* and *Mary Rose* were cleaned by spraying them with chilled water (with intermittent gentle brushing) over many months.
- The salt water impregnating the object is replaced by an inert wax or oil; *Polyethylene glycol* is widely used. Polyethylene glycol is a polymer with the general structure



There are several polyethylene glycols available, each having a different range of values for  $n$  and so having somewhat different properties such as viscosity and melting point: some are waxes while others are oils. They are all soluble in water and in ethanol. The wooden objects are soaked in solutions of polyethylene glycol of gradually increasing concentrations over periods of several months until the polyethylene glycol almost completely replaces the sea water in the wood. The two salvaged ships were intermittently sprayed with polyethylene glycol solutions for several years. The polyethylene glycol fills all the cavities in the wood and so stabilises it by restoring some of its strength and stopping any further degradation.

- Finally the object is air-dried to remove residual water and if necessary coated with a higher melting point polyethylene glycol wax.

## WEBSITES

For conservation of artefacts recovered from shipwrecks:

[http://www.conservationsolution.com/port\\_industrial\\_titanic2.html](http://www.conservationsolution.com/port_industrial_titanic2.html)

(an account of cleaning and conserving a 17 tonne piece of the *Titanic*)



The following two sites give an idea of what conservation is being done at two Australian maritime museums but they contain virtually no chemistry:

<http://www.mm.wa.gov.au>

(click *Maritime Archaeology* on left-hand menu, then *Materials Conservation*; a very general survey)

<http://www.mtq.qld.gov.au>

(click *Research*, then *Pandora* under *Maritime Heritage*; again a general survey of salvage from a wreck)

## Exercises



**23** Silver plated cutlery in the home tarnishes by the formation of silver sulfide. One method of cleaning such tarnished cutlery is to place it on a sheet of aluminium foil in a large plastic dish and fill the dish with a solution of sodium hydrogen carbonate or sodium carbonate so that it covers the cutlery and let it sit for several hours.

- a** Explain how this procedure restores the silver to its original shiny state.
- b** It is essential that the cutlery be completely submerged. Why?
- c** Does all of each item being cleaned have to be in contact with the aluminium foil? Explain.
- d** Why is this a better method of cleaning silver cutlery than rubbing it with an abrasive cream?

**24** In restoring iron artefacts recovered from shipwrecks, chloride is commonly removed by electrolysis with regular replacement of the electrolyte solution until no further chloride is detected in it. What test would you use to determine whether chloride was present in the electrolyte? Remember that this electrolysis is carried out in alkaline solution.

**25** Bronze is an alloy consisting of 80 to 90% copper with the balance being tin. When submerged in the ocean it corrodes slowly to form a mixed hydroxide and chloride layer: if suitable bacteria are present the surface coating can also contain sulfide. How would you restore such a corroded bronze artefact recovered from a sunken ship while doing the least possible amount of damage to it? Carefully explain the chemistry involved using equations where appropriate. Draw a diagram to illustrate the method you would use.

- 26 a** If iron(III) chloride is left in the pores of a cleaned iron object, the object can corrode again quite rapidly because iron(III) chloride hydrolyses to form iron(II) hydroxide. Write an equation for this reaction and explain how it can lead to renewed corrosion. How does keeping the object in sodium hydroxide solution prevent this renewed corrosion?
- b** When Cook's cannons were first placed in sodium hydroxide solution, considerable quantities of hydrogen gas were formed. It was thought that iron(II) hydroxychloride present in the corroded metal was converted to iron(II) hydroxide which then reduced water to hydrogen using the graphite present from the original cast iron as catalyst. Write an equation for the conversion of iron(II) hydroxychloride to hydroxide, and half equations for the oxidation of iron(II) hydroxide to iron(III) hydroxide and for reduction of water to H<sub>2</sub> and hence an overall equation for the reaction.

- 27** Silver coins recovered from long-sunken shipwrecks need to be treated electrolytically (as described in Section 12.18) in order to restore them to as close to their original condition as possible. However, gold coins recovered from such wrecks can be restored either by chemically dissolving away any deposits or by mechanically removing them (by chipping or by using a gentle abrasive). Why is electrolysis not necessary and not effective for restoring gold coins?
- \*28** If chloride is not completely removed from bronze objects recovered from shipwrecks, the objects develop what is called ‘bronze disease’. This is the formation of powdery deposits and surface pitting on the object. Suggest a mechanism for the occurrence of bronze disease including mention of which metal (copper or tin) is actually corroding.
- 29** Polyethylene glycol can be considered as an addition polymer of ethylene oxide or a condensation polymer of ethylene glycol. Write equations (with partial structures of the polymer) to show that this is so. (Structures of the monomers are on p. 17.)

## Important new terms

You should know the meaning of the following terms.

anodic sites (p. 416)  
bacterial corrosion (p. 430)  
cathodic protection (p. 423)

cathodic sites (p. 416)  
concretions (p. 435)  
galvanised steel (p. 421)  
rusticles (p. 430)  
sacrificial electrode (p. 423)

# CHAPTER 12

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 List five experimental facts about rust formation.
- 3 Describe the accepted mechanism for formation of rust. Identify anodic and cathodic sites.
- 4 Why do we consider this a galvanic process and not just a simple redox reaction?
- 5 Use the mechanism you described in Question 3 to explain the experimental observations in Question 2.
- 6 Why is aluminium less resistant to corrosion in marine environments than on dry land?
- 7 How do you decide which of two metals in contact will corrode preferentially?
- 8 What is galvanising and how does it work?
- 9 Describe four other methods that are commonly used to protect steel against rusting.
- 10 Describe two newer methods that are being used to protect the hulls of ships against corrosion.
- 11 Explain how cathodic protection works to minimise rusting in wet environments.
- 12 Why did the discovery of the wreck of the *Titanic* in 1985 cause a re-think about corrosion in deep ocean waters?

- 13** Describe the temperature and pressure dependence of the solubility of  
**(a)** gases   **(b)** most salts.
- 14** Explain why **(a)** shipwrecks on the shore line rust much more rapidly than those that are completely submerged; **(b)** shipwrecks in very deep water were expected to rust much more slowly than those in shallow water; and **(c)** this prediction turned out to be incorrect.
- 15** Write a half equation for the reduction of sulfate to sulfide. What speeds this up in deep ocean water?
- 16** How does the rate of corrosion of iron change as pH decreases? What causes the pH of ocean water around some shipwrecks to be less than the normal value of 7 to 8?
- 17** List three problems that face technicians trying to restore artefacts recovered from the ocean after long periods of submersion.
- 18** Explain **(a)** how deposits of calcium and other carbonates can be removed from porous objects recovered after long submersion in the ocean  
**(b)** how dissolved salts can be removed from such objects.
- 19** Silver objects recovered from the ocean after long periods of submersion are generally covered with a layer of silver sulfide. Explain how this deposit was formed and describe a method of removing (or reversing) it that produces minimal damage to the object.
- 20** What alloys or other metals could be restored by the method described in Question 19? What modification to the method (if any) would be needed and why? Which common metals and alloys would be difficult to restore in this way? Why?
- 21** Describe two specific Australian examples of the restoration of artefacts recovered from old shipwrecks.
- 22** What factors determine how well wooden objects (including shipwrecks) survive in ocean water?
- 23** Outline the steps used to restore and conserve wooden artefacts recovered after long periods in the ocean. Start right from the initial recovery.

## EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR OPTION 2

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination: for more information see p. 93.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

- |   | MARKS |
|---|-------|
| 1 List the main ions present in sea water, and outline the processes by which these and other minerals are introduced into the oceans.  | 4     |
| 2 Discuss the dependence of the properties of various steels upon their composition and upon different heat treatments that they are commonly subjected to.   | 6     |
| 3 Evaluate the contributions made by Alessandro Volta, Humphry Davy and Michael Faraday towards our understanding of electron-transfer reactions.   | 5     |
| 4 Identify the conditions needed for iron and steel to rust and explain the chemistry involved in the formation of rust.  | 6     |
| 5 Demonstrate that the product of an electrolysis reaction can depend upon:<br>a the concentration of the electrolyte used<br>b the chemical nature of the electrode being used.  | 5     |
| 6 Describe an experiment you have performed to compare the corrosion rate in a suitable electrolyte solution of a variety of metals and named modern alloys. Assess the suitability of three of the metals or alloys you used for the hulls of ships. | 7     |
| 7 List the major problems to be overcome in order to restore and preserve wooden objects recovered from long-submerged shipwrecks. Outline the procedures commonly used to restore and preserve such objects.   | 6     |
| 8 Discuss the effect the discovery of the wreck of the <i>Titanic</i> had upon scientists' understanding of corrosion of metals at great ocean depths.  | 5     |
| 9 Assess, with examples, the importance of developments in making steel and other alloys to shipbuilding.   | 6     |
| 10 Describe, using half-equations, what happens in the electrolysis of aqueous solutions of sodium sulfate and magnesium nitrate, and explain why both these electrolyses can be considered the electrolysis of water.                                | 4     |
| 11 Outline the factors that affect the concentration of dissolved oxygen in ocean waters at different depths and compare the concentrations at the surface and at depths greater than two kilometres.   | 5     |
| 12 Explain how certain anaerobic bacteria contribute to the corrosion of shipwrecks in deep ocean water; include at least one chemical equation.  | 4     |
| 13 Describe an experiment you have performed to compare the rates of corrosion of materials in solutions having different <b>(a)</b> concentrations of dissolved oxygen <b>(b)</b> temperatures and <b>(c)</b> concentrations of salt.                | 4     |

- Outline the results you obtained and suggest how the accuracy of the experiment could be improved. **6**
- 14** Explain with examples and at least one chemical equation how passivating metals resist corrosion. **4**
- 15** Evaluate the effectiveness of two methods commonly used to protect the hulls of ocean-going ships against corrosion. **6**
- 16** Describe an experiment you have performed to compare and describe the rate of corrosion of metals in different acidic and neutral solutions. Suggest one way in which the reliability of the experiment could be improved. **4**
- 17** Describe two newer methods for protecting the hulls of ships and compare their effectiveness with that of more traditional methods. **4**
- 18** For objects made of one particular metal or alloy that have been recovered from shipwrecks, describe and evaluate the steps that are commonly used to restore and conserve them. **6**
- 19** Explain the chemistry involved in galvanising and in one other form of cathodic protection and evaluate their usefulness in protecting hulls of ships. **7**
- 20** For silver coins in shipwrecks, discuss the formation, protective value and removal of silver sulfide. **6**

# REVISION TESTS FOR OPTION 2: SHIPWRECKS, CORROSION AND CONSERVATION

## TEST A

**Total marks: 25**

**Suggested time: 45 minutes**

**MARKS**

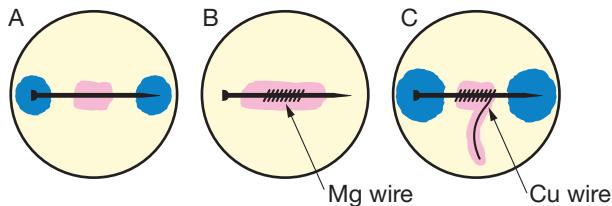
Table 2.1 on p. 67 may be used if needed.

- a i The *magnitude* of the standard electrode potentials for two metal, metal ion couples are:



When a galvanic cell is made using these couples as the electrodes, metal X is positive with respect to metal Y. What is the sign (positive or negative) for each of the electrode potentials? Explain your reasoning. **2**

- ii If metal Y were used as a protective coating on metal X, would it continue to protect metal X if the coating were scratched so as to expose bare metal X? Explain. **1**
- b i Describe an experiment that you have performed to identify the factors that influence the rate of an electrolysis reaction. **3**
- ii State the results you obtained. **1**
- iii Suggest ways of improving the reliability (reproducibility) of your experiment. **2**
- c Assess the importance of the work of Alessandro Volta, Humphry Davy and Michael Faraday to our understanding of electrolysis. **6**
- d A steel nail is placed in a shallow dish (Petri dish) and covered with a warm solution of agar in water that contains phenolphthalein indicator (pink in alkaline solution, colourless in neutral or acid solution) and potassium ferricyanide,  $\text{K}_3\text{Fe}(\text{CN})_6$  (pale yellow, but forms a deep blue precipitate with  $\text{Fe}^{2+}$  ions). When the solution cools, it sets to a jelly-like substance (because of the agar). After several hours colours develop in the agar gel as shown in A in the diagram below.



Two other similar experiments were also performed. In one of these a piece of cleaned magnesium wire was tightly wrapped around the middle of the nail, while in the other a piece of copper wire was tied around the nail with quite a long tail running into the gel. The results of these two experiments are shown in B and C respectively.

i	Explain, with equations, why the blue and pink colours developed in A and why they developed where they did.	3
ii	Explain why there is a pink colour in B but no blue colour.	1
iii	Explain why in C there is pink colour all along the copper wire and more blue colour at the ends of the nail than in A.	1
iv	Why was an agar gel used for these experiments and not just aqueous solutions?	1
e	Evaluate leaching and electrolysis as methods of removing chloride from artefacts recovered from long-submerged shipwrecks.	4

### TEST B

**Total marks: 25**

**Suggested time: 45 minutes**

### Marks

Table 2.1 on p. 67 may be used if needed

- |  |  |   |
|--|--|---|
| a  | Use electrode potentials to explain why:   |   |
| i  | when a neutral solution of copper sulfate is electrolysed, copper is formed at the cathode, whereas when a similar solution of magnesium sulfate is electrolysed hydrogen gas is formed.                 | 2 |
| ii   | when a neutral aqueous solution of potassium iodide is electrolysed, iodine forms at the anode whereas when a similar solution of potassium fluoride is electrolysed, oxygen is formed.                  | 2 |
| For $2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$ at pH = 7.0, $E = -0.41\text{ V}$ |  |   |
| For $\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq)$ at pH = 7.0, $E = +0.80\text{ V}$ |  |   |
| b  | i Describe an experiment that you have performed to compare the effectiveness of different protections used to coat a metal such as iron in order to prevent corrosion.                                  | 3 |
|  | ii Suggest ways of improving the accuracy of the experiment.   | 1 |
| c  | Demonstrate the effect that composition of a steel has upon its properties.  | 4 |
| d  | i Explain how rusting occurs.  | 3 |
|  | ii According to this mechanism, what would be the effect of ocean depth upon the rate of rusting of a sunken ship? Why?  | 2 |
|  | iii When the wreck of the <i>Titanic</i> was discovered in 1985, it showed much more corrosion than had been expected from (i) and (ii). What is the explanation for this increased amount of corrosion? | 2 |
| e  | Compare and contrast the conservation and restoration techniques that have been used in two Australian maritime archaeological projects.   | 6 |

# OPTION 2 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for the Shipwrecks, Corrosion and Conservation option of the New South Wales Higher School Certificate HSC Course.

## Syllabus content

The following table lists (for Option 2) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

Location of HSC Course material in Conquering Chemistry for Option 2  
Shipwrecks, Corrosion and Conservation

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.6.1 The chemical composition of the ocean implies its potential role as an electrolyte</b>	
■ identify the origins of the minerals in oceans as: – leaching by rainwater from terrestrial environments – hydrothermal vents in mid-ocean ridges	11.1
■ outline the role of electron transfer in oxidation-reduction reactions	11.2
■ identify that oxidation-reduction reactions can occur when ions are free to move in liquid electrolytes	11.2
■ describe the work of Galvani, Volta, Davy and Faraday in increasing understanding of electron transfer reactions	11.3
<b>9.6.2 Ships have been made of metals or alloys of metals</b>	
■ account for the differences in corrosion of active and passivating metals	11.5, 11.7, 12.4
■ identify iron and steel as the main metals used in ships	11.4
■ identify the composition of steel and explain how the percentage composition of steel can determine its properties	11.4
■ describe the conditions under which rusting of iron occurs and explain the process of rusting	12.1 to 12.3
<b>9.6.3 Electrolytic cells involve oxidation-reduction reactions</b>	
■ describe, using half-equations, what happens at the anode and cathode during electrolysis of selected aqueous solutions	11.8
■ describe factors that affect an electrolysis reaction – effect of concentration – nature of electrolyte – nature of electrodes	11.8, 11.9

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.6.4 Iron and steel corrode quickly in a marine environment and must be protected</b>	
■ identify the way that a metal may be protected including <ul style="list-style-type: none"><li>– corrosion resistant metals</li><li>– development of surface alloys</li><li>– new paints</li></ul>	12.6
■ predict the metal which corrodes when two metals form a galvanic cell using a list of standard potentials	11.6, 12.5
■ outline the process of cathodic protection, describing examples of its use in both marine and wet terrestrial environments	12.7, 12.8
■ describe the process of cathodic protection in selected examples in terms of the oxidation/reduction chemistry involved	12.7, 12.8
<b>9.6.5 When a ship sinks, the rate of decay and corrosion may be dependent upon the final depth of the wreck</b>	
■ outline the effect of: <ul style="list-style-type: none"><li>– temperature</li><li>– pressure</li></ul> on the solubility of gases and salts	12.10
■ identify that gases are normally dissolved in the oceans and compare their concentrations in the oceans to their concentrations in the atmosphere	12.10
■ compare and explain the solubility of selected gases at increasing depths in the oceans	12.10
■ predict the effect of low temperature at great depths on the rate of corrosion of a metal	12.9, 12.11
<b>9.6.6 Predictions of slow corrosion at great depths were apparently incorrect</b>	
■ explain that ship wrecks at great depths are corroded by electrochemical reactions and by anaerobic bacteria	12.12
■ describe the action of sulfate-reducing bacteria around deep wrecks	12.12
■ explain that acidic environments accelerate corrosion in non-passivating metals	12.13
<b>9.6.7 Salvage, conservation and restoration of objects from wrecks requires careful planning and understanding of the behaviour of chemicals</b>	
■ explain that artefacts from long-submerged wrecks will be saturated with dissolved chlorides and sulfates	12.14
■ describe the processes that occur when a saturated solution evaporates and relate this to the potential damage to drying artefacts	12.15, 12.20
■ identify the use of electrolysis as a means of removing salt	12.16
■ identify the use of electrolysis as a means of cleaning and stabilising iron, copper and lead artefacts	12.16, 12.18

Syllabus reference	Sections where found in CCHSC
Students learn to <ul style="list-style-type: none"> <li>■ discuss the range of chemical procedures which can be used to clean, preserve and stabilise artefacts from wrecks and, where possible, provide an example of the use of each procedure</li> </ul>	12.16 to 12.19

## Compulsory experiments

The table below lists the compulsory experiments for this option (from the right-hand column of the syllabus), along with the location of relevant information in this book.

CCHSC is an abbreviation for this book *Conquering Chemistry HSC Course*.

CCHSC BLM is *Conquering Chemistry HSC Course Blackline Masters* by Debra Smith, Cengage Learning Australia.

### Compulsory experiments for Option 2 Industrial Chemistry

Experiment	Location in CCHSC BLM	Related material in CCHSC <sup>a</sup>
1 Compare the rate of corrosion of iron and an identified form of steel	Module 4 Worksheet 3 (page 169)	
2 Identify the factors that affect the rate of an electrolysis reaction	Module 4 Worksheet 5 (pages 173–6)	Section 11.10 Revision Test A Question b
3 Compare the corrosion rate, in a suitable electrolyte, of a variety of metals, including named modern alloys to identify those best suited for use in marine vessels	Module 4 Worksheet 7 (pages 182–4)	Exam-style Question 6
4 Compare the effectiveness of different protections used to coat a metal such as iron and prevent corrosion	Module 4 Worksheet 8 (pages 185–6)	Section 12.6 Revision Test B Question b
5 Compare and describe the rate of corrosion of materials in different oxygen concentrations, temperatures and salt concentrations	Module 4 Worksheet 10, Parts A, B and C (pages 191–7)	Exam-style Question 13
6 Compare and describe the rate of corrosion of metals in different acidic and neutral solutions	Module 4 Worksheet 10, Part D (pages 191–7)	Exam-style Question 16
a Exercises, Exam-style and Revision test questions are listed here, because their answers at the back of the book often contain helpful information.		

Location of material for other Option 2 (Shipwrecks, Corrosion and Conservation) activities

Syllabus item	Relevant material in CCHSC
<b>9.6.1</b> <input type="checkbox"/> process information ... to outline and analyse ... Galvani, Volta, Davy and Faraday ...	Section 11.3
<b>9.6.2</b> <input type="checkbox"/> Experiment 1 (see previous table)	
<input type="checkbox"/> use available evidence to analyse and explain the conditions under which rusting occurs	Sections 12.1 to 12.3
<input type="checkbox"/> gather and process ...to compare composition, properties and uses of a range of steels	Section 11.4
<b>9.6.3</b> <input type="checkbox"/> Experiment 2 (see previous table)	
<b>9.6.4</b> <input type="checkbox"/> identify data ... to trace historical developments in ... materials used in ... ocean-going vessels	Section 11.4, last sub-section
<input type="checkbox"/> Experiment 3 (see previous table)	
<input type="checkbox"/> Experiment 4 (see previous table)	
<input type="checkbox"/> gather ... information ... applications of cathodic protection, and ... identify the reasons for their use and the chemistry involved	Sections 12.7, 12.8
<b>9.6.5</b> <input type="checkbox"/> Experiment 5 (see previous table)	
<input type="checkbox"/> use available evidence to predict the rate of corrosion of a metal wreck at great depths ... and give reasons for the prediction made	Sections 12.9 to 12.11
<b>9.6.6</b> <input type="checkbox"/> Experiment 6 (see previous table)	
<b>9.6.7</b> <input type="checkbox"/> perform investigations ...to compare conservation and restoration techniques applied in two Australian ... projects	Section 12.18

## Prescribed focus areas

This option with its emphasis on shipbuilding, corrosion and protection against it, and restoration of corroded objects is heavily slanted towards focus area 3, applications and uses of chemistry. However, it does allow significant attention to be given to focus area 2, the nature and practice of chemistry, by providing opportunities to revise and reinforce understanding of basic concepts such as redox reactions, galvanic cells and standard electrode potentials, and the nature of metals and alloys (from the Preliminary Course). Electrolysis is the one new concept that is introduced here and it is applied extensively; solubility of gases is extended considerably over what was included in Module 2.

There is considerable scope for focus area 1, the history of chemistry, in this option, ranging from the early work of Galvani, Volta, Davy and Faraday to the developments in the last hundred years in metals and alloys, particularly as they apply to shipbuilding.

For focus area 5 current issues, research and development there are the developments of surface alloys for steel and new corrosion-resistant paints that actually react with the iron surface (both discussed in Section 12.6) but there is not a strong emphasis on this focus area in this option.

Although building better and more durable ships and improved corrosion protection generally are of considerable significance to society, and while chemists must always be aware of environmental considerations (such as unsightly shipwrecks on coastlines and junked car yards), focus area 4 implications for society and the environment does not figure strongly in this option.

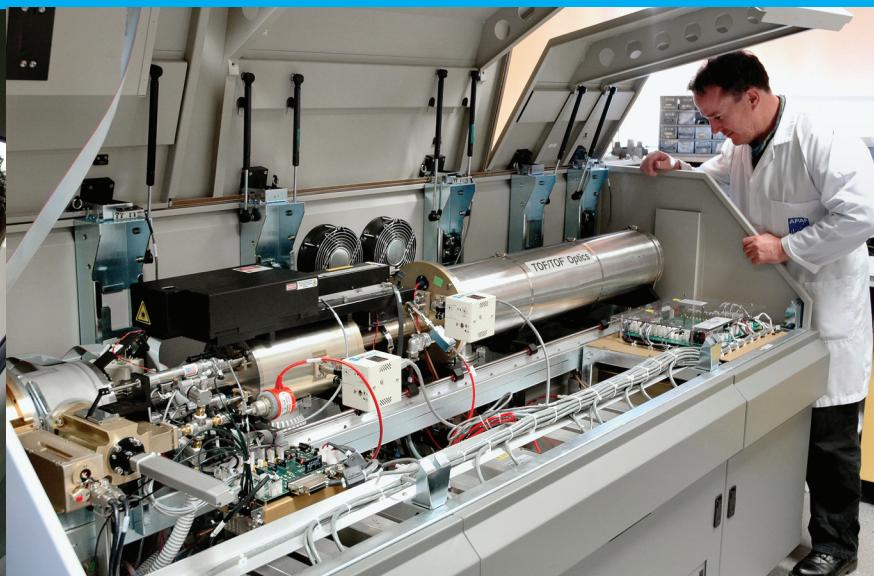
OPTION 3

# Forensic chemistry

Forensic chemistry is the branch of chemistry that provides information for use in courts of law or in public discussion and debate. For example forensic chemistry can provide information showing that:

- a sample of wine contained a substance known not to occur in the natural product (and so prove that the wine had been adulterated)
- the paint mark on one car came from another car (and so help establish that the first car was involved in a collision with the second one)
- that some hairs found at a crime scene came from a particular person (and so help identify the guilty party)
- that a sample of an athlete's urine contains prohibited substances (and so provide evidence of illegal use of performance-enhancing drugs)
- that certain compounds found in a waterway came from a particular factory (and so provide information about the polluting activities of that factory).

Forensic chemistry is a special branch of analytical chemistry—the branch of chemistry concerned with identifying the substances present in samples and how much of each there is. The first step in identifying a substance often involves



working out the broad class of compound the substance belongs to. That is where we shall start—first deciding whether a sample is organic or inorganic, and if organic performing tests to determine which class the substance belongs to. This will be done in the first part of Chapter 13.

Many forensic samples are biological in origin, so we will survey some major classes of biological (or biochemical) compounds such as carbohydrates (or sugars) and proteins. Chapter 13 will concentrate on carbohydrates while proteins will be treated in Chapter 14. Today there is considerable emphasis on using DNA to identify the person responsible for a biological sample found at a crime scene—samples such as blood, semen, saliva or hair follicle. Therefore in Chapter 14 we shall also discuss the structure of DNA and how it can be analysed for forensic purposes.

Samples for forensic analysis are often very small and frequently need to be analysed without being destroyed. A range of instrumental methods capable of handling very small samples without destroying much of them will be described in Chapter 15—mass spectrometry, atomic emission spectroscopy, gas–liquid chromatography and high performance liquid chromatography.



## FORENSIC CHEMISTRY—METICULOUS HAND COLLECTION OF SAMPLES AND SOPHISTICATED INSTRUMENTAL ANALYSIS

A first step in a forensic investigation is to collect evidence (samples) for analysis from the crime scene in a thorough and systematic way without contamination (far left and above left). Then very sophisticated

instruments such as the mass spectrometer in the photo (second left) are used to identify and trace the origins of such samples. Today DNA analysis is widely used not only to identify culprits but also to identify victims of disasters such as the December 2004 tsunami in S. E. Asia (above right): a simple swab of saliva from inside the cheek is all that is needed to collect enough DNA for accurate analysis



# Classifying and identifying substances (including sugars)

## IN THIS CHAPTER

Avoiding contamination of samples

The need for accuracy

Organic or inorganic?

Identifying some classes of inorganic compounds

Analysis of soils

Identifying classes of organic compounds

Simple carbohydrates

Disaccharides

Polysaccharides

Ring and open-chain forms

Reducing and non-reducing sugars

Test for starch

The job of a forensic chemist is to identify materials and to trace their origins. Often samples for identification are quite small—only a few milligrams. With all samples for analysis, but particularly with very small ones, an important consideration is avoiding contamination.

## 13.1 AVOIDING CONTAMINATION OF SAMPLES

There are three main sources of contamination of samples for analysis:

- *inadvertent addition of extraneous material* in the collection, handling and transporting of the sample before it reaches the laboratory; this is a reason for careful sealing of athletes' urine or blood samples immediately after collection, of the meticulous packaging of samples (in suitable bags, tins or specimen jars) from a crime scene, and the use of scrupulously clean bottles for storage of environmental water samples.
- *an unclean laboratory*: an old laboratory with flaking paint, corroding fittings and instruments, and dust-releasing floor or walls, free flows of dirty air through the laboratory and small amounts of stray chemicals from dirty benches or poorly maintained instruments can all lead to contamination of samples and so invalidate the analyses done.
- *a careless analyst*: not wearing suitable protective clothing such as laboratory coat, gloves, face mask and hair cover can result in the analyst 'shedding' contaminants such as dust, dandruff, sweat and associated dirt, and breath-born impurities into samples so producing erroneous results.

Careful handling of samples and meticulous attention to detail in performing analyses are essential for avoiding all of these three modes of contamination. This is true for all forms of analytical work, not just forensic work, especially when very small samples are involved.

However for forensic work there is an additional requirement and that is the validation of the *chain of custody* of the sample.

## Chain of custody

For forensic purposes there must be witnesses to the collection of the sample and the sealing of the container into which it was placed (for example in collecting urine samples from athletes for testing for performance-enhancing drugs), and detailed documentation of the passage of the sample from the collection point to the laboratory where the analysis was to be performed, and then witnesses to the breaking of the seal of the sample and the actual performance of the analysis. This is to ensure that there was no tampering with the sample between collection and analysis or substitution of a different sample for the original one.

The importance of this aspect of sample handling was demonstrated in a highly publicised trial in California, USA, of a nationally famous sports star, O.J. Simpson, in 1997 for the murder of his estranged wife. The DNA evidence against him was very convincing, but his lawyers argued that there was sufficient laxness in the chain of custody of the sample for there to be some doubt about whether the sample analysed had not been contaminated or substituted for; they raised sufficient doubt in the minds of jury members that Simpson was acquitted.

One safeguard for ensuring the legitimacy of the sample being analysed is to provide, at the time of collection of the sample, an identical sealed sample to the person being investigated and so allow that person to arrange their own analysis of the sample. This happens in the routine testing of athletes for prohibited substances and in the blood testing of persons suspected of driving a car under the influence of alcohol or drugs.

## 13.2 THE NEED FOR ACCURACY

Accuracy in forensic chemistry is particularly important because faulty forensic evidence could:

- *convict an innocent person* and force them to spend many years in jail
- *result in a person or company having to pay massive fines* for offences such as polluting the environment (by apparently exceeding allowed emissions) or selling allegedly contaminated products, all on the basis of inaccurate analyses.

In addition, even if the overall conclusions of the forensic investigations are correct, sloppy or inconsistent work can allow a defence counsel to cast doubt over the validity of the whole forensic evidence because of one small fault in part of it.

The classic example of faulty forensic work in Australia in recent decades was the Azaria Chamberlain case of the 1980s. Baby Azaria's mother was convicted of murdering her daughter, partly on the forensic evidence that there was foetal blood in the family motor car. After the mother had spent several years in jail, the baby's jacket was found in circumstances that supported the mother's claim that a dingo had taken her baby. In the enquiry that followed new forensic examination

showed that the so-called foetal blood was actually adult blood contaminated with rust (consistent with the parents' original story of giving a ride to an injured adult). Lindy Chamberlain was eventually declared innocent and released.

Another aspect of accuracy is *completeness or thoroughness*. Sometimes there is nothing wrong with the forensic results as such, except that not all desirable forensic examinations have been done: early evidence points towards one person, a few forensic tests support those suspicions so the investigation is ended, whereas further forensic tests might have revealed evidence that would clear the original suspect or implicate another person. Forensic chemists need to be aware of the dangers of stopping an investigation before it is complete.

While accuracy is important in forensic chemistry, it is just as important in all branches of chemistry. Careless results by a research worker can send colleagues on wild goose chases following up the work or disproving it. Inaccurate analyses by quality control chemists can cause a chemical factory to discard batches of product or modify production procedures unnecessarily and at great cost. Poor experimental technique in synthesis can result in synthesised chemicals being contaminated or yields being very low. Faulty monitoring of discharges to air and water can lead to a factory inadvertently exceeding allowable limits and harming people in surrounding areas.

All chemists need to ensure that their work is accurate, thorough and reliable.

## Ethical issues in a forensic investigation

Apart from avoiding contamination of samples and doing accurate analyses, forensic chemists must be aware of several ethical issues associated with their work. They must:

- *ensure that the analyses they do are accurate, complete and objective*, and that they do not just find a piece of information that will help build a case against a prime suspect and go no further
- *ensure that samples from all suspects are analysed* and not stop work when one sample appears to incriminate one particular suspect
- *report their scientific findings objectively* without exaggerating their accuracy or reliability and not obscure uncertainties in the results with large amounts of interpretation and opinion
- *not cover up findings* that cast doubt upon the guilt of the accused (such as by not reporting that certain analyses with unfavourable results were performed)
- *present their findings in clear and simple language* that non-chemists can understand and in such a way that juries can assess them fairly.

Overall, forensic chemists must act as unbiased scientists reporting their objective findings and not appear to be part of the prosecution team building a case against a particular suspect. This will sometimes involve resisting pressure from law enforcement officers to produce a particular result (when the analysis is inconclusive) or to confine their analyses to selected samples only.

## 13.3 ORGANIC OR INORGANIC?

One of the first tasks of an analyst is to determine whether a sample is an organic or inorganic substance, because the methods of analysis differ quite significantly for these two classes.

Originally the term organic compound was used for substances that were present in living matter. It had been thought that some 'life force' was required to

make them. However early in the nineteenth century it was shown that organic compounds could be made in a chemical laboratory. Today

**Organic compounds** are compounds of carbon (with the exception of CO, CO<sub>2</sub>, and carbonates, hydrogen carbonates and cyanides of metals).

Some organic compounds that we have already considered are the alkanes and alkenes of Sections 9.9 and 9.10 of CCPC, ethanol of Section 1.16, other alkanols, alkanoic acids and esters of Sections 5.16 to 5.19, and the haloalkanes of Section 7.10. Most of the other compounds dealt with in this book so far have been inorganic ones.

Organic compounds almost always contain hydrogen as well as carbon (exceptions being the CFCs of Section 7.10). Other elements commonly present in organic compounds are oxygen, nitrogen, halogens (F, Cl, Br, I) and sulfur.

## Distinguishing between organic and inorganic compounds

The simplest method of distinguishing between organic and inorganic compounds is to *heat a sample of the compound in air*. If the compound burns or reacts with air or decomposes to leave no residue, the compound is almost certainly organic. A quantitative analysis for carbon and hydrogen would confirm it.

## 13.4 IDENTIFYING SOME CLASSES OF INORGANIC COMPOUNDS

If the substance to be identified turns out to be inorganic (by the test from Section 13.3), a useful starting point for identifying the substance is to determine whether it is acidic, basic or neutral.

### Determining acidity or basicity of a sample

If the sample exists as a solution, this can be done by using a suitable pH paper or a pH meter (Sections 4.2, 4.18 and 4.19). If using pH paper, the forensic chemist would put a drop of the solution onto the paper rather than dipping a piece of paper into the sample (so as not to contaminate the sample). Similarly drops of indicator would not be added to the sample. Dipping the glass electrode of a pH meter into the solution would not contaminate it. The pH tells whether the substance is acidic ( $\text{pH} < 7$ ), neutral ( $\text{pH} = 7$ ) or basic ( $\text{pH} > 7$ ).

If the sample was a solid, the chemist would try to dissolve a small portion of it in water: this in itself provides useful information (is the compound soluble or insoluble?). If the substance is soluble, the pH of the solution would be determined as just described.

If the sample is insoluble, its acidity or basicity would be determined first by adding a drop of sodium carbonate solution to a small portion of the solid and heating it and observing whether any bubbles of gas form. If so, the substance is acidic (reacts with carbonate to form carbon dioxide).

If there was no reaction with sodium carbonate, drops of dilute nitric acid would be added to a fresh portion of the sample and the mixture warmed. If the sample dissolved, then it must have reacted with nitric acid (since it had already been established that it was insoluble in water) and so it must be a base (such as an insoluble oxide, hydroxide or carbonate).

One source of inorganic compounds that often has to be examined by forensic chemists is soil.

## 13.5 ANALYSIS OF SOILS

**Soil** is a complex mixture of inorganic materials (such as clay, silt, sand and gravel), decaying organic matter (called *humus*), water, air and living organisms.

Soil is formed by the combination of weathering of rocks, sedimentation, and decay of living matter. The solids in soils are typically 5% organic matter and 95% inorganic material. The amount of water present in soils depends upon their porosity and texture.

The order of size of particles in soils is clay < silt < sand < gravel.

Soils differ from one another in the proportions of these inorganic materials present. In addition the chemical composition of these materials in soils varies from place to place. Consequently an analysis of soil found at a crime scene can provide forensic chemists with useful evidence, such as the source of the sample.

Forensic chemists often need to identify the source of a sample of soil found at a crime scene. If the sample is greater than a couple of grams, the following tests can be performed:

- colour (soils differ in colour from red to brown to black)
- texture (depends upon the relative amounts of sand, clay, humus, etc and varies from place to place)
- appearance when shaken with water (the different components of soil settle out at different rates depending on their density—in the order, gravel, sand, silt—with clays usually staying in suspension and organic matter often floating on top)
- pH (universal indicator or an indicator paper is dipped into the solution of the previous test—after it has settled).

If these tests do not identify the source of the soil, or if the sample available is well less than a gram, then forensic analysis of soils is generally done by detecting the presence of (and determining the amounts of) the *less common* elements in soil. This is usually done by either atomic emission spectroscopy (Sections 6.17 and 15.12) or atomic absorption spectroscopy (Section 6.18). If a data base of soil compositions is available the source of a particular sample can be identified.

Analysis of soil from a muddy footprint left in the room in which a crime was committed may show that the perpetrator had recently been in (or came from) a particular locality; this may help narrow down the list of suspects. Alternatively analysis of the soil in the grooves of a suspect's shoes may show that she or he was recently at the crime scene.

### Other inorganic material

Other inorganic materials that can be analysed to provide forensic evidence include metal and alloy fragments, residues from certain building materials such as plasterboard and concrete, pigments from paints and various types of glass. Determination of concentrations of metal ions, particularly unusual ones, can provide information about the origin of such samples. Forensic chemists would generally use atomic emission spectroscopy (Sections 6.17 and 15.12) to perform such analyses.

Inorganic analysis, particularly for uncommon metal ions, often provides useful information in forensic investigations.

## 13.6 IDENTIFYING CLASSES OF ORGANIC COMPOUNDS

Having determined that a compound is organic (i.e. a carbon compound) from the test in Section 13.3, the analyst's next job is to work out which class of carbon compound the unidentified substance belongs to.

So far in this course we have met several different classes of carbon compound as summarised at the start of Section 13.3. There are tests that we can perform to determine the class of compound an unidentified sample belongs to. Tests relevant to the main classes we have examined so far are given in Table 13.1. The classes of compound are listed in a convenient sequence for testing.

**TABLE 13.1 Tests for distinguishing between some classes of carbon compounds**

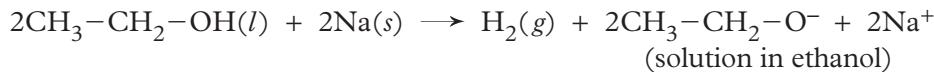
Class of compound <sup>a</sup>	Test and the result if the compound belongs to the class
alkanoic acid (or any carboxylic acid)	Add drops of sodium carbonate solution to a sample; bubbles of colourless gas form ( $\text{CO}_2$ ). This is a normal reaction of an acid with a carbonate (Section 6.12).
alkanol (or any alcohol)	Dry a sample carefully with granules of calcium chloride, then add a small piece of sodium; bubbles of colourless gas form ( $\text{H}_2$ ). (Alkanoic acids react in the same way but would have been identified by the previous test.)
alkene	In the absence of strong u.v. light, add drops of bromine in an organic solvent such as chloroform or hexachloroethane; the bromine solution loses its colour. Aqueous bromine can also be used: it is decolorised by alkenes (Section 1.4). (Many alkanols also react with aqueous bromine so if using this reagent it is necessary to perform the sodium test first to eliminate the possibility of the compound being an alkanol.)
alkane or ester	If all the above tests are negative, the compound is an alkane or ester. Add drops of a solution of bromine in hexachloroethane and expose the mixture to u.v. light; the colour slowly fades (Section 1.3)
ester	If the compound has a pleasant smell, it is probably an ester. We really need to measure its infrared spectrum (see below) to confirm that it is an ester

<sup>a</sup> The only classes of compounds considered here are those that are part of the NSW HSC core syllabus.

### Alkanol plus sodium reaction

Sodium metal reacts with an alkanol to form hydrogen gas and what is called an **alkoxide ion**:

for example for ethanol:



This particular alkoxide is called *ethoxide*; it forms by removal of an H<sup>+</sup> from ethanol.

An example will illustrate the use of these tests.

### Example 1

Describe how you would distinguish between members of the following groups of substances. All the compounds listed are colourless liquids. Write equations for all reactions which occur.

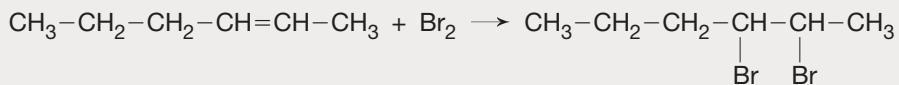


a hexane and 2-hexene

b ethanol, propanoic acid and ethyl ethanoate (acetate)

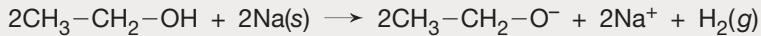
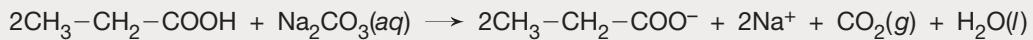
a Add drops of reddish-brown bromine solution to samples of each of the liquids.

With one liquid the whole mixture takes on a pale brown colour (that is, no reaction), whereas with the other liquid the colour disappears. The latter liquid is 2-hexene, because alkenes decolorise bromine solutions whereas alkanes do not.



b We have here an alkanol, an alkanoic acid and an ester. Hence add drops of sodium carbonate solution to samples of each liquid. With two of the liquids there is no reaction, while with the third liquid bubbles of colourless gas form. This third liquid is propanoic acid. To samples of the other two liquids add granules of calcium chloride to dry them then add a small piece of sodium to each dried sample. Bubbles of colourless gas (H<sub>2</sub>) form with one liquid but not with the other. The one that formed bubbles is ethanol, so the other must be ethyl ethanoate.

Equations for the reactions involved are:



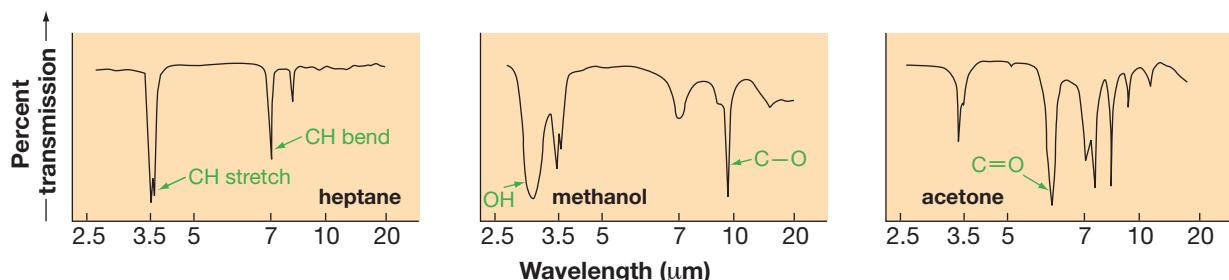
### School laboratory versus forensic chemist's laboratory

The tests described in Table 13.1 can be used in a school laboratory to identify the class a particular compound belongs to (providing a sample of at least several milligrams is available). However they are not sensitive enough for forensic chemists who would normally use **infrared (i.r.) spectroscopy** for this purpose.

#### Infrared (i.r.) spectroscopy

This is a technique in which a sample to be analysed is irradiated with i.r. radiation of changing wavelength, with the amount of radiation passing through the sample being measured. The percentage of the incident radiation that is absorbed by the sample is recorded as a function of wavelength of the incident radiation (either on a pen recorder in older-style instruments or on a computer screen in newer types). Such a graph is called an *infrared spectrum*. Several such i.r. spectra are shown in Figure 13.1.

*Different functional groups absorb i.r. radiation at different wavelengths*, and so an i.r. spectrum tells the analyst which functional groups are in the sample. In



**FIGURE 13.1**  
Infrared spectra of heptane, methanol and acetone. The functional groups or structural features that lead to major absorption peaks are shown beside the peaks

many cases, comparison of the measured spectrum of an unidentified compound with standard spectra of known compounds provides clear identification of the compound. Infrared spectroscopy is a quick and sensitive method of analysis and is widely used by forensic chemists.

### Identifying metal ions in samples

A similar situation exists for metal ions. In Chapters 6 and 8 we explored a range of test tube reactions that could be used in a school laboratory to identify the cation or cations present in a sample. In Chapters 5 and 6 we looked at some methods of quantitative analysis (volumetric and gravimetric) that can be performed in school laboratories. These qualitative and quantitative methods require samples of at least 1 to 10 mg. Forensic chemists often have samples that contain only microgram amounts of key cations. Hence for analysis of cations forensic chemists generally use instrumental techniques such as atomic emission spectroscopy (Sections 6.17 and 15.12) and atomic absorption spectroscopy (Section 6.18). These techniques are much more sensitive than school laboratory methods and provide more accurate results more rapidly (though at much greater cost).



### Exercises

- Three colourless liquids (at room temperature), A, B, and C, were tested to determine whether they were organic or inorganic. When gently heated in a stainless steel spoon-type spatula over a small Bunsen burner flame, C burnt with a clearly visible flame while A and B just vaporised. When analysed quantitatively for C, H and Cl, they gave the following results:  
 A: 13% C; 0% H, 57% Cl  
 B: 0% C; 0% H; 83% Cl  
 C: 68% C, 14% H; 0% Cl  
 Which of these compounds is(are) organic and which inorganic? Justify your choices.
- Write chemical equations for the reactions involved in the tests described in Table 13.1. Use the following compounds: acetic acid, methanol, 2-hexene, pentane and ethyl acetate.
- In the laboratory, how would you distinguish between the members of the following pairs of substances? Describe fully what you would do, and what you would observe with each substance. Write equations for all reactions that occur.
 

<b>a</b> hexane and 1-hexene	<b>d</b> glucose and sodium sulfate
<b>b</b> pentane and 2-butanol	<b>*e</b> 1-pentene and methanoic acid
<b>c</b> 2-propanol and propanoic acid	<b>*f</b> 1-pentanol and 2-hexene

- 4** Describe tests you would use to identify the members of the following sets of compounds. Write equations for all reactions involved.
- 2-pentene, 1-hexanol, propanoic acid
  - heptane, 3-heptene, ethyl propanoate
  - \*c 1-heptene, 2-propanol, hexane
- 5** Two compounds, P and Q, had molecular weights between 65 and 75. After careful drying, P reacted with sodium to form bubbles of colourless gas while Q did not. Q rapidly decolorised drops of a solution of bromine in hexachloroethane while P decolorised this solution only very slowly. Identify the two compounds and explain your reasoning.

Often the sample a forensic chemist is required to identify will not be a simple organic compound such as one of those in Table 13.1, but rather will be one of the many complex compounds that occur in living matter. Let us consider three major classes of such compounds, namely

- carbohydrates
- proteins
- DNA (deoxyribonucleic acids).

We shall look at the structures of these compounds and see what information a forensic chemist can get from them.

## 13.7 SIMPLE CARBOHYDRATES

**Carbohydrates** are compounds of C, H and O, having the general formula  $C_x(H_2O)_y$  where  $x$  and  $y$  may be the same or different.<sup>†</sup>

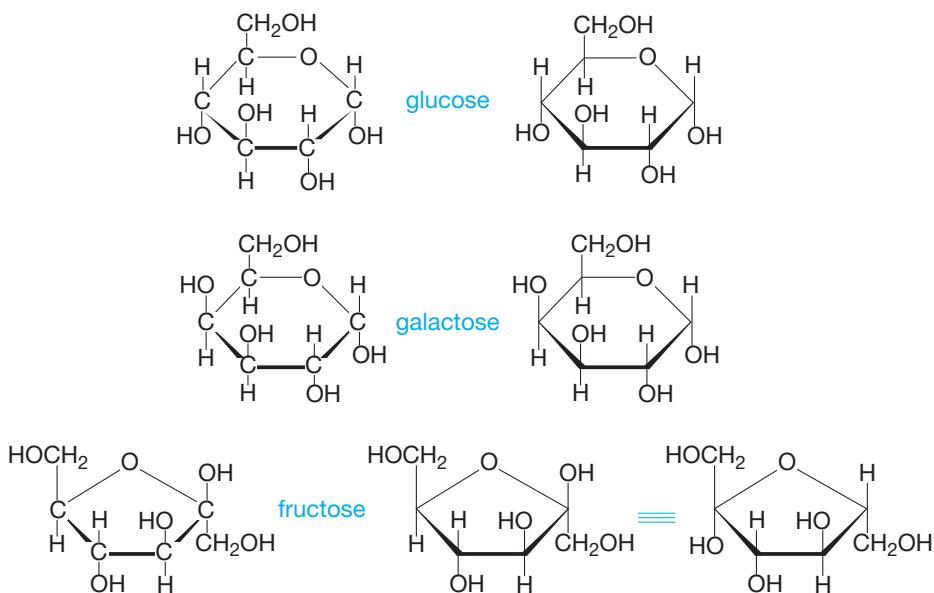
These compounds are also called **sugars**. In everyday language the word ‘sugar’ is used for one particular compound, sucrose; however in science ‘sugar’ is a general name used for many carbohydrates—for the so-called mono- and disaccharides (explained below). Glucose and sucrose are carbohydrates: glucose has the formula  $C_6H_{12}O_6 = C_6(H_2O)_6$ , while sucrose is  $C_{12}H_{22}O_{11} = C_{12}(H_2O)_{11}$ .

The simplest carbohydrates have three to six carbon atoms per molecule. The most common ones are those with five or six carbon atoms; they are called *pentoses* and *hexoses* respectively. Three important hexoses are glucose, fructose and galactose; all are isomers of  $C_6H_{12}O_6$ . The structural formulae of these three sugars are shown in Figure 13.1 in two different forms. In the left-hand structures all the atoms are shown. This gives rise to a rather cluttered structure. Hence we often omit the C atoms as in the right-hand structures (and as was done in Section 1.13 and Figure 1.7 for glucose). In such diagrams *there is a C atom at every junction of bonds* (or in different words, at every apex of the structure). These ‘unlabelled carbon’ structures are widely used in chemistry, particularly when cyclic (ring) compounds are involved.

The five- and six-membered rings are not strictly planar—they are buckled as was shown in Section 1.13 and Figure 1.7—but for simplicity we often draw

<sup>†</sup> This is the definition given in the NSW Board of Studies Chemistry Stage 6 Syllabus 2002. It is not strictly correct because there are many substances considered to be carbohydrates which do not conform to this formula, notable examples being deoxyribose (involved in DNA) and Vitamin C (ascorbic acid). A more accurate definition is that carbohydrates are polyhydroxylated aldehydes and ketones or compounds that hydrolyse to these. However aldehydes and ketones are not part of this syllabus, so we probably need to stick with the less accurate definition.

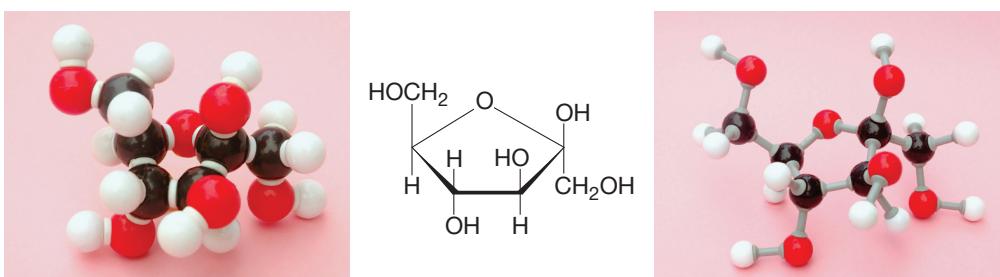
**FIGURE 13.2**  
Structures of three common monosaccharides. The left-hand structures show all the atoms in the molecules; in the right-hand ones the carbon atoms are not labelled. The right-hand structure for fructose is just the middle structure flipped through 180°



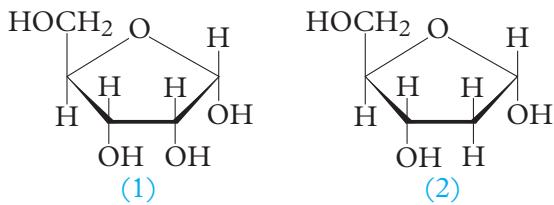
them planar as in Figure 13.2. We use thick and wedge-shaped bonds in these rings to indicate that the plane of the ring is perpendicular to the paper. The H atoms and OH and CH<sub>2</sub>OH groups attached to the ring are above and below that plane (though not actually perpendicular to the plane). The positioning of these groups above or below the plane is important, because it determines which compound the structure represents. Glucose and galactose differ only in the location of one OH group (Fig. 13.2). Despite this they are distinctly different compounds with noticeably different properties.

It is important that you carefully study a molecular model of glucose (or at least look closely at the photographs in Figure 1.7) to ensure that you fully understand the general structure of the six-membered ring hexoses. Similar models of fructose are shown in Figure 13.3. Fructose is a hexose that contains a five-membered ring.

**FIGURE 13.3**  
Space-filling (left) and ball-and-stick (right) molecular models of fructose along with the structure drawn in a similar orientation. Black is C, white is H and red, O



An important pentose is ribose, Structure (1). It is a basic unit in ribonucleic acid, RNA. Deoxyribose, Structure (2), is a reduced form of ribose. ‘Deoxy’ means without oxygen; the molecule has one less oxygen than ribose. Deoxyribose is one of the structural units in deoxyribonucleic acid, DNA, which will be discussed starting at Section 14.12.



The simple C<sub>3</sub> to C<sub>6</sub> sugars are called *monosaccharides*. The word means ‘one sugar’. We shall see in Section 13.9 that two simple carbohydrate molecules can join together to form what is called a *disaccharide* (two sugars). Many sugar molecules can join together to form what is called a *polysaccharide* (many sugars). These di- and polysaccharides react with water, with a suitable catalyst, to form single sugars or monosaccharides.

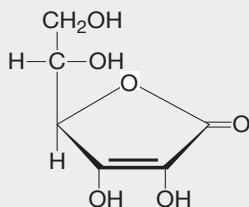
Recall from Section 5.5 that reaction with water is called *hydrolysis*.

Hence we have the definition:

**Monosaccharides** are carbohydrates that cannot be hydrolysed into two or more simpler sugars.

## Exercises

- 6 Upon analysis it was found that a particular compound contained 39.8% carbon and 6.7% hydrogen with the balance being oxygen. Calculate its empirical formula. Could this compound be a carbohydrate? Give your reason.
- 7 What is the (a) molecular formula and (b) empirical formula of:  
i ribose (Structure 1 in Section 13.7) and ii deoxyribose (Structure 2)?
- 8 Ascorbic acid (vitamin C) has the structure:



- a What is its (i) molecular formula (ii) empirical formula?  
b What functional groups are present?  
c By the definition in Section 13.7 is ascorbic acid a carbohydrate? Explain.
- 9 Covalent molecular compounds, and hence most organic compounds, are generally either liquids or soft solids with low melting points and are usually insoluble in water. On the other hand, carbohydrates are hard solids that can be heated to quite high temperatures and then they decompose rather than melt, and they are readily soluble in water. Account for these differences in properties.



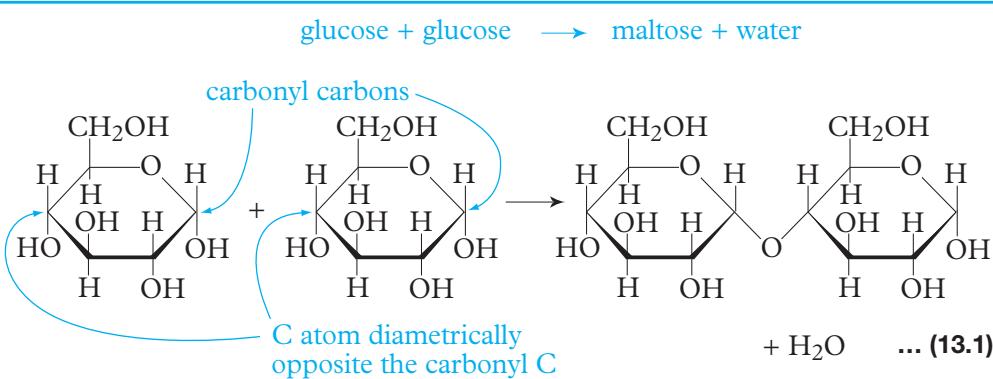
## 13.8 DISACCHARIDES

**Disaccharides** are carbohydrates that can be hydrolysed into two simple sugars.

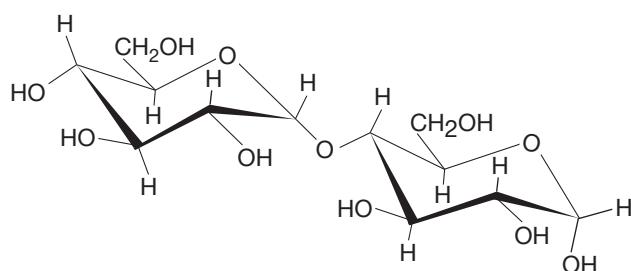
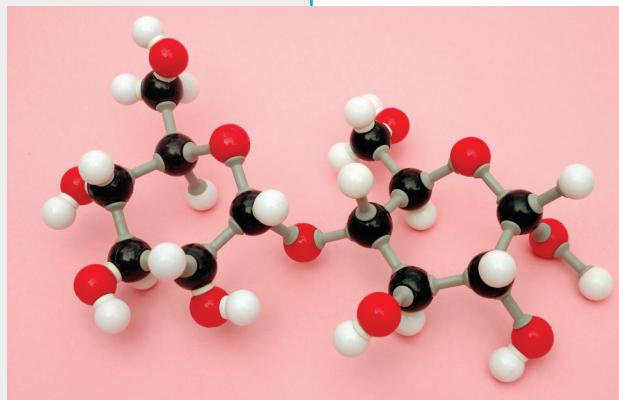
Common disaccharides are *sucrose* from cane sugar, *maltose* from malt and *lactose* from milk.

Maltose forms when two glucose molecules join together. The union is between the OH on what is called the *carbonyl carbon* of one molecule (the C that has an O and an OH attached to it<sup>†</sup>) and the OH of the diametrically opposite C of the other molecule as in Equation 13.1. A molecule of water is eliminated.

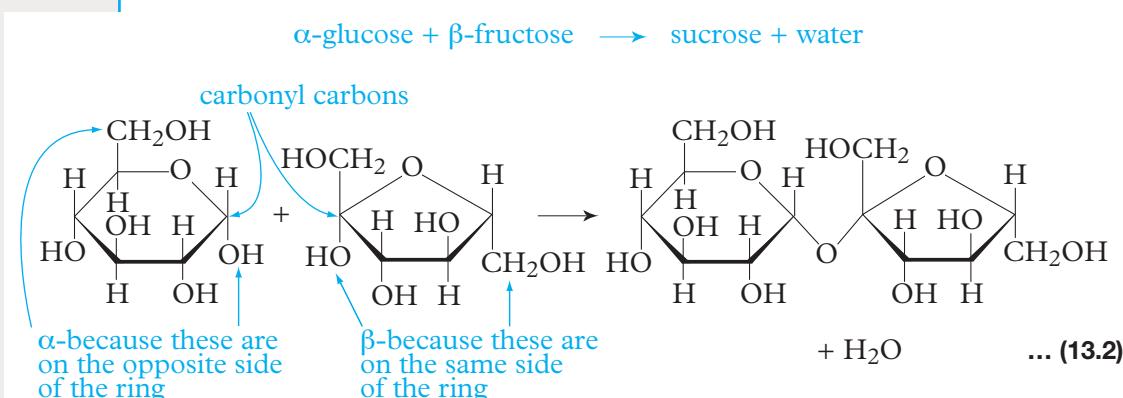
<sup>†</sup> more about this in Section 13.10



**FIGURE 13.4**  
A ball-and-stick model of maltose, showing the  $\alpha$ -linkage and the way the actual structure relates to the structural formula we draw

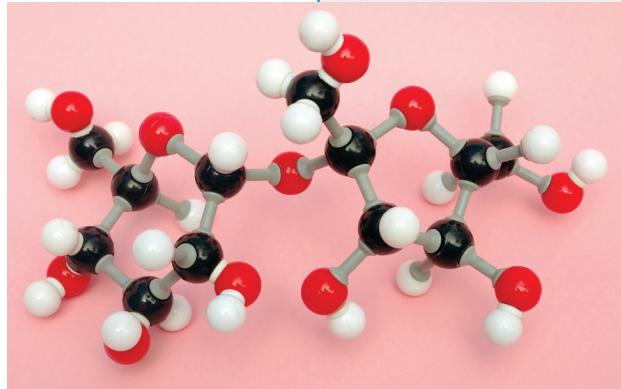
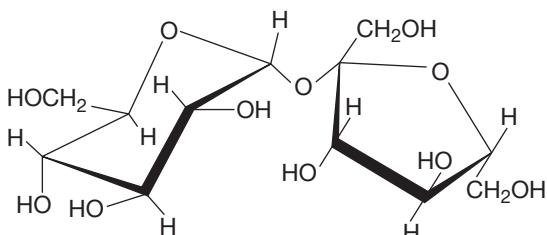


Sucrose is a disaccharide formed by linking the carbonyl carbons of  $\alpha$ -glucose and  $\beta$ -fructose:



The fructose structure used here is the right-hand structure from Figure 13.1—the one with the carbonyl carbon on the left.

Figure 13.5 shows a ball-and-stick model of sucrose along with its molecular structure oriented in approximately the same way as in the model.



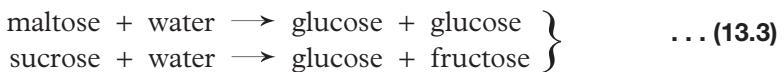
## Condensation reactions

A reaction in which two molecules join together with the elimination of a small molecule, such as water, is called a **condensation reaction**.

Formation of a disaccharide from two monosaccharides is a condensation reaction. Similarly a reaction in which many molecules join together end-to-end with the elimination of a small molecule between each pair of joining molecules is also called condensation. This happens when polysaccharides are formed (next section). It is also the way that condensation polymers such as nylon and polyester were formed in Section 1.12.

Disaccharides can be *hydrolysed* into two monosaccharides. In the laboratory we hydrolyse disaccharides by gently heating them in aqueous acid solution.

With aqueous  $\text{H}^+$ :



In living matter this is brought about by enzymes (biological catalysts, p. 298 CCPC).

FIGURE 13.5  
A ball-and-stick model of sucrose with its structure for comparison

## Exercises

- 10 Write an equation using molecular formulae for a condensation reaction that can occur between glucose and fructose.
- 11 Lactose is a disaccharide formed by making a link from the carbonyl OH of the  $\beta$  isomer of galactose to the same OH on glucose as is used for maltose. Draw the structure of lactose.  $\alpha$ -galactose is shown in Figure 13.2.
- 12 a Draw structures of two disaccharides that could be formed between ribose (Structure (1) in Section 13.7) and glucose.  
b Write an equation (using molecular formulae) for the reactions forming these disaccharides. Why does one such equation describe both reactions?
- 13 Write equations using molecular formulae for the two reactions given in Equation 13.3.



## 13.9 POLYSACCHARIDES

**Polysaccharides** are carbohydrates that consist of a large number of monosaccharide molecules joined to one another in a long string.

The linkage is the same as in disaccharides. The main polysaccharides are:

- starch and cellulose from plants and
- glycogen from animals.

All three are made from glucose units, but these units are joined together in slightly different ways.

Polymerisation of glucose to cellulose was briefly mentioned in Section 1.10. The terms polymerisation, polymer and monomer were defined in Sections 1.12 and 1.13. Starch, cellulose and glycogen are polymers. The monomer from which all three are made is glucose.

Many of our staple foods have a high starch content

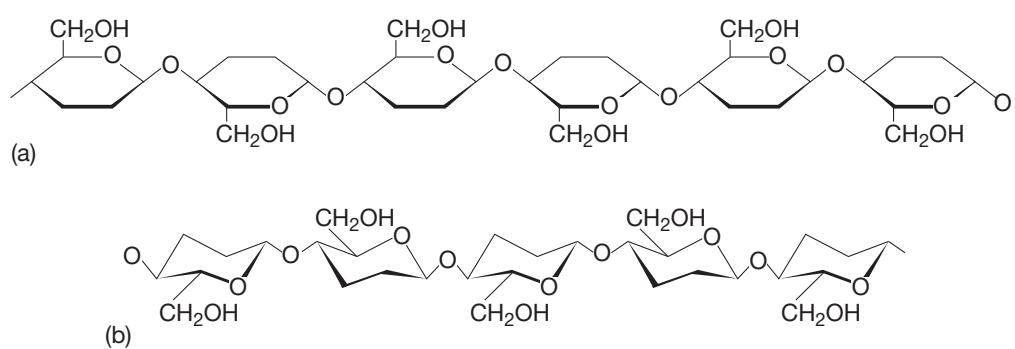


The difference between cellulose on the one hand, and starch and glycogen on the other, is that they use different isomers of glucose.

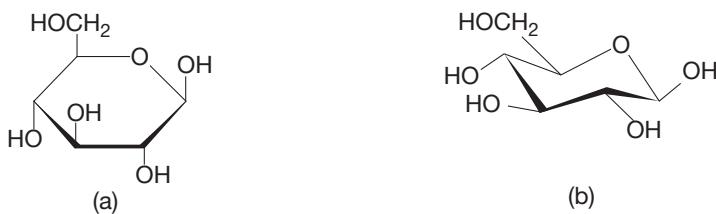
*Cellulose consists of long chains of  $\beta$ -glucose units joined together.* This is shown in Figure 13.6. In (a) the glucose units have been drawn using the planar rings we have mainly been drawing. However, as already mentioned, six-membered rings are not strictly planar. (b) shows cellulose using the accurate geometry of these rings. For simplicity the H and OH groups have been omitted. The  $\text{CH}_2\text{OH}$  group is shown; remember that in  $\beta$ -glucose this  $\text{CH}_2\text{OH}$  is on the same side of the ring as the OH on the carbonyl carbon. Because of this  $\beta$ -arrangement, it is necessary to invert every second glucose unit in the cellulose structure.

The structures in Figure 13.7 may help you convert from planar rings to ‘bent’ rings. (a) is the planar structure we have been using, except that the H atoms directly attached to C atoms are omitted. This is another convention that chemists often use (in addition to not labelling C atoms).

*At every apex of a structure there is a C atom and attached to that C atom is the number of H atoms needed to bring the number of bonds up to the normal four for C atoms.*



This convention is used in both structures in Figure 13.7.



Structure (b) shows the accurate geometry of the  $\beta$ -glucose molecule: note that two OHs are ‘below’ the ring and two OHs and the  $\text{CH}_2\text{OH}$  are ‘above’ the ring. This is best seen by handling models: the photographs of molecules in Figure 1.7 (p. 25) may help.

As Figure 13.6 shows, the use of  $\beta$ -glucose results in a fairly linear molecule. Typically there are 2000 to 4000 glucose units per cellulose molecule. Because of all the OH groups and the hydrogen bonding they can produce, these linear chains intertwine with one another and stick together to form fibres. Cellulose is an insoluble fibrous substance. It forms the structural material of cells and plants (including trees).

*Starch* and *glycogen* consist of  $\alpha$ -glucose molecules joined together as shown in Figure 13.8. When we draw planar rings for glucose as in (a), the starch

**FIGURE 13.6**  
The structure of cellulose:  
(a) showing glucose rings  
as planar, (b) showing the  
geometry of the glucose  
rings more accurately. For  
clarity OH groups on the  
rings have been omitted

**FIGURE 13.7**  
Different ways of drawing  
 $\beta$ -glucose: (a) using a  
planar ring, (b) using more  
accurate ring geometry

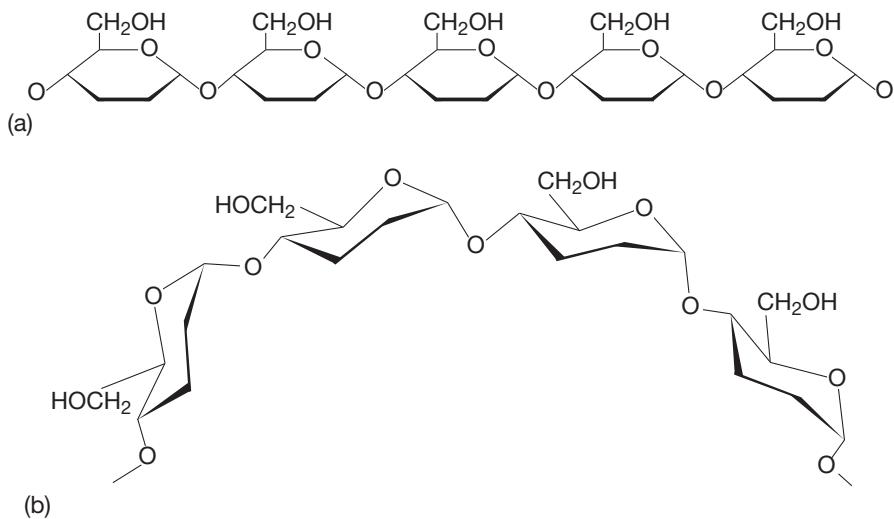


Rayon (or viscose or viscose rayon) is a common semi-synthetic fibre for fabrics; it is reconstructed cellulose. Wood pulp or low grade cotton is processed chemically then spun into fibres suitable for making textiles

molecule looks linear. This is because we have distorted the geometry around the linkage between pairs of rings. When we draw the proper shape for the glucose rings and use the proper angle for the C–O–C bond (about 109°), we find that our structure curls around as shown in Figure 13.8(b). This is the true situation in starch and glycogen. The molecules are curled up into globular shapes; they are quite different from the linear and fibrous appearance of cellulose. The  $\alpha$  linkage in starch and glycogen is the same as that in the maltose model in Figure 13.4.

FIGURE 13.8

The structure of starch:  
(a) using planar rings for glucose, (b) using more accurate geometry. For clarity ring OH groups have been omitted. In this unbranched structure each glucose unit is joined to two other glucose units. Glycogen has these same  $\alpha$ -glucose linkages.



There are actually two forms of starch. When starch from plants is warmed in water, about 20% of it dissolves. This soluble starch has a somewhat different structure from the other 80% of insoluble starch. *Soluble starch is called amylose; insoluble starch is called amylopectin.*

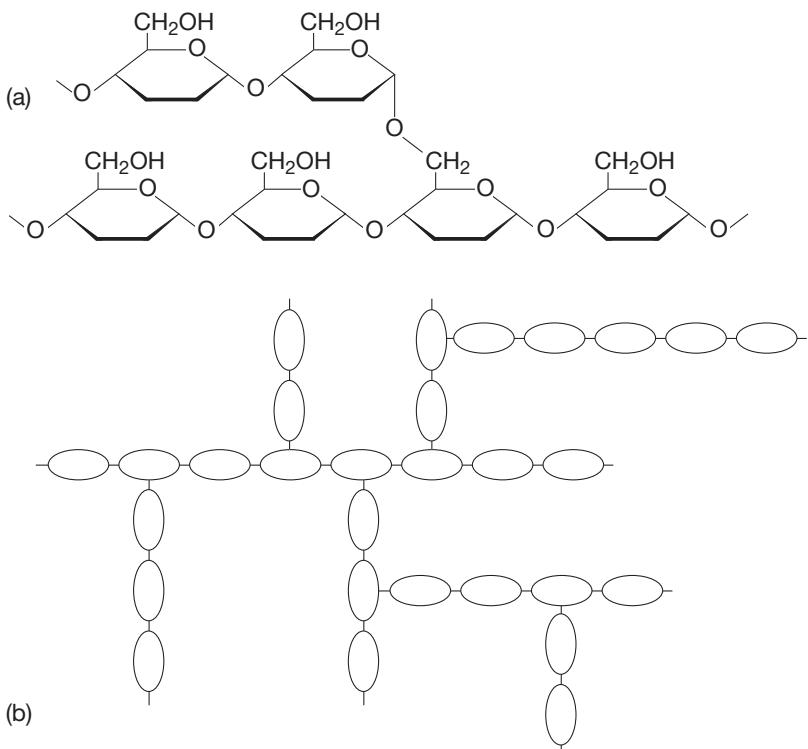
Amylose is an unbranched-chain molecule (see Fig. 13.8) with 60 to 300 glucose units per molecule. Amylopectin is a branched-chain molecule with about 300 to 6000 glucose units per molecule. Chain branching occurs when one glucose molecule condenses with three other glucose molecules instead of with the normal two as in Figure 13.8. Condensation with three other glucose units occurs through the ‘normal’ alcoholic OH to one molecule, through the carbonyl OH to a second molecule and through the terminal OH (that is, the CH<sub>2</sub>OH) to a third molecule (Fig. 13.9(a)). Chain branching is shown schematically in Figure 13.9(b).

Glycogen or animal starch is also highly branched. *Glycogen has a lower molecular weight than amylopectin but is more highly branched.*

#### In summary:

- Cellulose is made of  $\beta$ -glucose units (Fig. 13.6(b)), while starch and glycogen use  $\alpha$ -glucose (Fig. 13.8(b)).
- Cellulose and amylose have unbranched molecules while amylopectin and glycogen have branched-chain structures.
- Glycogen and amylose are soluble in water, while cellulose and amylopectin are not.

In order to use polysaccharides as energy sources, animals must first hydrolyse them to glucose. Enzymes are used for doing this. However enzymes are very specific in the bonds that they can break. The human body contains enzymes that can break  $\alpha$ -glucose linkages but not  $\beta$  ones. Hence humans can



**FIGURE 13.9**  
Chain branching in amylopectin (starch) and in glycogen. (a) shows the actual carbonyl OH-terminal OH union while (b) shows schematically how branching extends through the molecule: the ovals represent glucose units

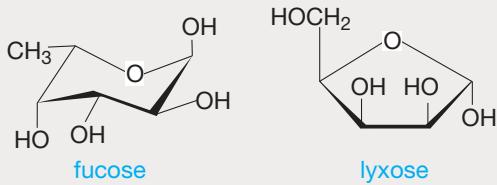
hydrolyse starch and glycogen to glucose but not cellulose. Herbivores (cattle, horses, sheep) have bacteria in one of their stomach chambers that contain enzymes that can break  $\beta$ -linkages; hence these animals are able to use cellulose from grass and leaves as an energy source.

## Laboratory hydrolysis of polysaccharides

In the laboratory, polysaccharides can be hydrolysed in the same way as disaccharides; an aqueous suspension or solution of the polysaccharide is refluxed with a strong acid such as hydrochloric or sulfuric until a clear solution (of glucose) results.

### Exercises

- 14** Structures of two less common sugars, fucose and lyxose, are given below in conventional abbreviated form. What is the molecular formula for each of these?



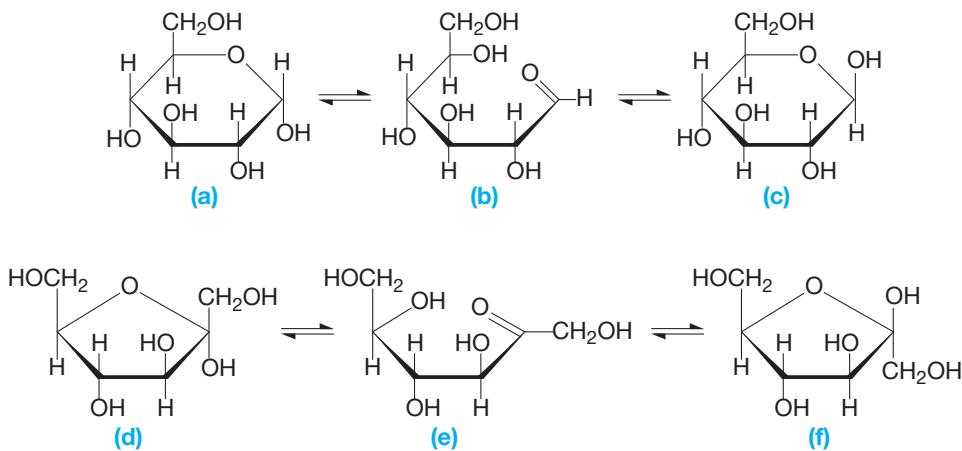
- 15 a** Deduce the empirical formula for amylopectin, based upon the molecule of amylopectin being formed from 1000 glucose molecules with the elimination of 999 water molecules.
- b** Would there be any significant difference if the number of glucose units was 500 or 5000 instead of 1000? Explain.
- c** Explain why the number of water molecules eliminated in **(a)** is 999.
- d** Based on **(a)**, **(b)** and **(c)**, what do you expect to be the empirical formula for amylose, glycogen and cellulose?

- 16** The empirical formula of starch is usually given as  $C_6H_{10}O_5$ . What would be the molecular weight of a type of starch that contained 300 glucose units?
- 17** Calculate the percentage oxygen in starch, using the empirical formula given in Exercise 16.
- 18** Starch can be considered as a polymer of maltose. Explain why. Could a polymer of sucrose be formed by a normal sugar reaction? Explain why or why not.
- 19** Two molecules of  $\beta$ -glucose condense to form the disaccharide cellobiose using the same C atoms as in maltose. Draw a structure for cellobiose. What relationship exists between cellobiose and cellulose?
- 20** Using the empirical formula for starch,  $C_6H_{10}O_5$ , write an equation for its hydrolysis. If the starch contained 100 glucose units, what would this equation become in terms of molecular formulae? Is your equation strictly accurate? Explain.

## 13.10 RING AND OPEN-CHAIN FORMS: $\alpha$ - $\beta$ ISOMERISM

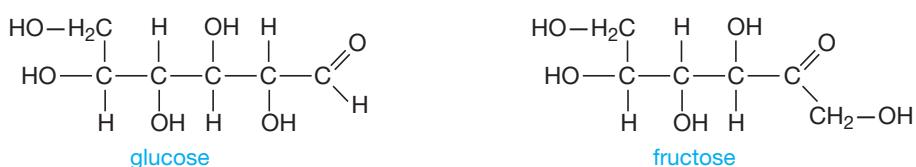
The ring structure of monosaccharides (Fig. 13.1) is able to open out into a chain structure as shown in (a) and (b) for glucose and (d) and (e) for fructose in Figure 13.10. Reaction occurs at the carbon atom with two O atoms attached to it. A C=O bond forms on that C atom and an O–H bond on the other C. This C=O group is called a **carbonyl group** and the C atom of it is called the **carbonyl carbon atom** of the molecule (even when the molecule exists as a ring).

FIGURE 13.10  
Ring and open-chain forms of glucose and fructose and how they lead to  $\alpha$  and  $\beta$  isomers



That (b) and (e) in Figure 13.10 are really open-chain structures may be better appreciated by drawing them as in Figure 13.11.

FIGURE 13.11  
More conventional drawings of the open-chain structures for glucose and fructose (b) and (e) in Fig. 13.10 respectively)



There is a dynamic equilibrium between the ring structure and the open-chain structure. When the ring closes again, the starting substance may be re-formed, but ring closure may also lead to a slightly different molecule, (c) from glucose and (f) from fructose in Figure 13.10. (a) and (c) are isomers of glucose (called  $\alpha$ - and  $\beta$ -glucose respectively) while (d) and (f) are isomers

of fructose (again called  $\alpha$  and  $\beta$  respectively). Each individual isomer can be crystallised from solution in pure form under different conditions. However when any one isomer is dissolved in solution, the equilibria in Figure 13.10 lead to a mixture with the other cyclic isomer *and* with a very small amount of the open chain form which is also an isomer.

Although the equilibrium mixture contains predominantly the ring form, the very small proportion present in the open-chain form is sufficient to bring about this isomerisation between  $\alpha$  and  $\beta$  forms.

This changing of the arrangement of H and OH about the carbonyl C in carbohydrates is called  **$\alpha$ - $\beta$  isomerism**.

When we draw structures of glucose and fructose, we need not worry too much about the arrangement of H and OH around the carbonyl carbon (that is, whether OH is above or below the ring), because in solution we get a mixture of both forms. However the geometry around the other carbon atoms is fixed, and we must be very careful to get the right groups above and below the ring; otherwise we will have drawn a different compound (for example galactose instead of glucose).

In maltose, in Equation 13.2 and Figure 13.4, the right-hand glucose unit still has an OH on a carbonyl carbon. This means that this ring can still open out into an open-chain form, and hence isomerise into  $\alpha$  and  $\beta$  forms. In solution, maltose is an equilibrium mixture of these two isomers.

Sucrose, on the other hand, has no OH on a carbonyl carbon, because the glucose and fructose joined through their carbonyl carbons. Hence sucrose has no  $\alpha$  and  $\beta$  forms and so is the one pure compound both as crystals and in solution.

This  $\alpha$ - $\beta$  isomerism is important in forming polysaccharides. As we saw in the previous section it is  $\alpha$ -glucose that is involved in forming cellulose and  $\beta$ -glucose for making starch and glycogen.

The presence of the carbonyl carbon in many carbohydrates and the ability of such compounds to isomerise to open-chain forms mean that these compounds are easily oxidised by quite mild oxidising agents. This leads to the classification of carbohydrates into *reducing* and *non-reducing sugars*.

## 13.11 REDUCING AND NON-REDUCING SUGARS

We have just seen that many carbohydrates exist as an equilibrium between a ring isomer (the predominant form) and an open-chain form. The open-chain forms of glucose and fructose (from Figures 13.10 and 13.11) can be written as:



For simplicity we can write these as



Both the  $-\text{CHO}$  and  $-\text{CO}-\text{CH}_2\text{OH}$  groups are easily oxidised to carboxylic acids,  $\text{R}-\text{COOH}$  and  $\text{R}-\text{CHOH}-\text{COOH}$  respectively.

We call sugars (carbohydrates) that in the open-chain form contain these  $-\text{CHO}$  and  $-\text{CO}-\text{CH}_2\text{OH}$  groups *reducing sugars*, because they are easily oxidised and when that happens they *reduce* the other reagent.

Glucose and fructose are reducing sugars. In fact most monosaccharides are reducing sugars.

Disaccharides may be reducing or non-reducing sugars. Maltose is a reducing sugar because it still has one ring that can isomerise into an open-chain structure (the right-hand ring in the maltose structure in Equation 13.1 on p. 468). On the other hand, sucrose (the right-hand structure in Equation 13.2 on p. 468) is a non-reducing sugar because neither of its rings can convert to an open-chain structure: it is not possible to form a C=O group because the linkage between the glucose and fructose units is through both carbonyl carbons. In summary:

Sugars that have both an OH group and a ring O atom attached to the one C atom are **reducing sugars**. If there is no C atom that has both an O atom and an OH group attached to it, the sugar is a **non-reducing sugar**.

Note that a C atom with two O atoms attached to it as in sucrose in Equation 13.2 and Figure 13.5 is non-reducing; to be reducing one of the Os must be an OH.

## A test for reducing sugars

To determine whether a sugar is reducing or non-reducing, we use a reagent that can oxidise a  $\text{--CHO}$  or  $\text{--CO--CH}_2\text{OH}$  group but which will not oxidise the many ordinary alcohol groups present in all sugars. Three reagents are available:

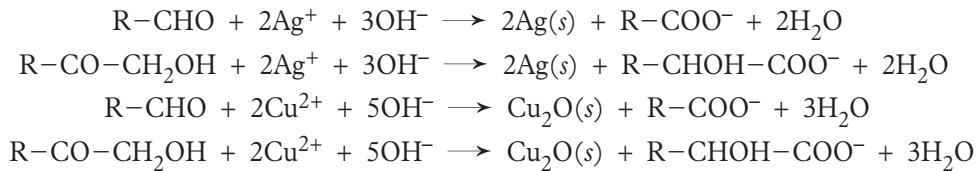
- 1 *Tollens' reagent*, a colourless solution of silver nitrate in aqueous ammonia
- 2 *Benedict's solution*, a deep blue solution of copper sulfate in alkaline citrate
- 3 *Fehling's solution*, a deep blue solution of copper sulfate in alkaline tartrate.

In all three solutions the cation is present as a complex ion, silver for example as  $\text{Ag}(\text{NH}_3)_2^+$  (Sections 6.10 and 7.6). The reason for this is that alkaline conditions are needed for oxidation of the  $\text{--CHO}$  and  $\text{--CO--CH}_2\text{OH}$  groups. However  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  normally precipitate out of alkaline solutions as  $\text{Ag}_2\text{O}$  and  $\text{Cu}(\text{OH})_2$ . By forming complex ions of silver with ammonia, and copper with citrate or tartrate, we can keep them in solution even in these alkaline conditions.

When a colourless solution of a reducing sugar is warmed with colourless Tollens' reagent, metallic silver is formed. Depending on conditions, it may appear as a black precipitate of finely divided metal or as a shiny mirror on the walls of a very clean test tube.

When a solution of a reducing sugar is warmed with deep blue Benedict's or Fehling's solution, a reddish-brown precipitate of copper(I) oxide is formed.  $\text{Cu}^{2+}$  is reduced to  $\text{Cu}^+$ .

If we write the two types of reducing sugars as  $\text{R--CHO}$  and  $\text{R--CO--CH}_2\text{OH}$ , then equations for these reactions are:



Glucose, galactose, fructose and maltose all give positive tests with these reagents. Sucrose gives a negative test. It is a non-reducing sugar (as explained above).

## 13.12 TEST FOR STARCH

Starch (both amylose and amylopectin) forms a deep blue complex with iodine. If drops of brown iodine solution are added to an aqueous solution or suspension of the substance to be tested, a deep blue colour will form if the substance is starch. At low concentrations this complex is more bluish-purple than pure blue.

### Test for glycogen<sup>†</sup>

Glycogen forms a *reddish-brown* colour when iodine solution is added to it. This colour is quite distinct from the blue to purple colour of the starch–iodine reaction.

### Plant or animal sugar?

The glycogen test can establish whether a polysaccharide came from an animal or from a plant, because glycogen is found only in animals, while starch and cellulose are found only in plants.

### School laboratory versus forensic laboratory

We have just looked at some simple tests that can be performed in a school laboratory to obtain information about carbohydrates; there are several others that can provide further information but we shall not delve into them. Simple laboratory tests can provide considerable information about the nature and origin of carbohydrates that could be useful to forensic chemists. However they require sample sizes of the order of milligrams, often take considerable time to perform, and the information they provide is not always very specific.

Forensic chemists determine the nature and origin of carbohydrate samples using sophisticated instrumental techniques such as high performance liquid chromatography, HPLC (to be discussed in Section 15.3). Compared with test tube tests performed in a school laboratory, instrumental analysis in a forensic laboratory provides more specific information much more quickly from much smaller samples; however it is much more costly.

<sup>†</sup> Not required for the NSW HSC; included here because it is a simple test that can give information about the origin of a polysaccharide sample.

### Exercises

**21** Classify:

- a ribose (Structure 1 in Section 13.7) and b deoxyribose (Structure 2) as reducing or non-reducing sugars.

**22** Is it possible to form a disaccharide between glucose and fructose which is a reducing sugar? If so, draw a structural formula.

**23** Which, if any, of the disaccharides you drew in Exercise 12(a) would be reducing sugars?

- \*24 a** Describe a chemical test for distinguishing between glucose and sucrose.  
**b** How could you determine whether or not a solution of sucrose had partially hydrolysed to glucose and fructose?



**25** Write half equations for the oxidation and reduction processes that are involved in tests for reducing sugars, namely:

- oxidation of R-CHO and R-CO-CH<sub>2</sub>OH
- reduction of Ag<sup>+</sup> to Ag and Cu<sup>2+</sup> to Cu<sub>2</sub>O

**26** Would it be possible to have a disaccharide that gave a negative test with Tollens' reagent, but which hydrolysed to form only glucose (which gives a positive test)? Explain.

**27** A group of students had four aqueous solutions of carbohydrates to identify. They performed the following tests on each solution:

- add Tollens' reagent
- add a solution of iodine.

Results are tabulated below.

Sample R was heated with hydrochloric acid for several minutes before being tested.

Sample	Tollens' reagent	Iodine solution
P	no reaction	blue colour
Q	silvery deposit	no reaction
R	silvery deposit	blue colour
S	no reaction	no reaction

- Which is the only sample that could be (i) galactose (ii) sucrose (iii) starch? Explain why.
- What test could you perform to provide further evidence that the sample you identified as sucrose really is sucrose? Explain.
- Which sample could be partially hydrolysed starch? Explain why.

**28** Trehalose is a sugar of molecular formula C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>. With Tollens' reagent and Benedict's solution it gives negative results. When warmed with aqueous hydrochloric acid one mole of trehalose yields two moles of glucose. Deduce the structure of trehalose.

## Important new terms

You should know the meaning of the following terms.

α-β isomerism (in sugars) (p. 475)  
alkoxide ion (p. 462)  
carbohydrate (p. 465)  
carbonyl carbon atom (p. 474)  
carbonyl group (p. 474)  
condensation reaction (p. 469)

disaccharide (p. 467)  
infrared (i.r.) spectroscopy (p. 463)  
monosaccharide (p. 467)  
non-reducing sugar (p. 476)  
organic compound (p. 460)  
polysaccharide (p. 470)  
reducing sugar (p. 476)  
soil (p. 461)  
sugars (p. 465)

## Test yourself

- 1 Explain the meaning of each of the items in the 'Important new terms' section above.
- 2 List three possible sources of contamination of small samples for analysis.
- 3 Give two reasons why accuracy is important in forensic analyses; give an example to illustrate.
- 4 How would you decide whether a substance was organic or inorganic?
- 5 How would you determine the source of some soil found at a crime scene?
- 6 Describe tests to distinguish between an alkanoic acid, an alkanol, an alkene and an alkane.
- 7 Draw structures for glucose, fructose, maltose and sucrose.
- 8 What is meant by ring and open-chain forms of common monosaccharides? Give an example.
- 9 Write an equation for a condensation reaction involving sugars.
- 10 Write equations for the hydrolysis of maltose and sucrose. What conditions are needed to bring these reactions about?
- 11 What is meant by  $\alpha$  and  $\beta$  linkages in di- and polysaccharides?
- 12 What are the structural differences between cellulose, amylose, amylopectin and glycogen?
- 13 Write an equation, using molecular formulae, for the hydrolysis of starch.
- 14 What structural features cause a sugar to be reducing?
- 15 Describe two tests for determining whether a sugar is reducing or non-reducing.
- 16 How would you determine whether a white powder was starch?

# CHAPTER 14

# Proteins and DNA

## IN THIS CHAPTER

Proteins	Electrophoresis and amino acids
Amino acids	Chromatography and electrophoresis compared
Zwitterions	DNA
Peptides	Structure of DNA
Hydrolysis of peptides and proteins	The role of DNA in organisms
Structure of proteins	Uniqueness of a person's DNA
Simple tests for proteins and/or amino acids	DNA analysis for forensic purposes
Chromatography	Use of DNA analysis
Separation of amino acids by paper chromatography	Data banks

In Chapter 13 we saw how forensic chemists first determine the class of compound that a particular sample belongs to and then identify the actual compound. We looked particularly at sugars in that chapter. Let us now turn to other important biological compounds, proteins and DNA.

## 14.1 PROTEINS

Proteins are an essential part of all living organisms. There are two general classes of protein—*fibrous proteins* and *globular proteins*.

**Fibrous proteins** are structural material, such as *keratin* of skin, fingernails, horns, wool and feathers, *collagen* of tendons, cartilage and hides, and *fibroin* of silk. These proteins are tough and insoluble in water and most other solvents. They are stringy in appearance and have a characteristic smell when burnt.

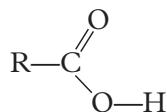
**Globular proteins** are roughly spherical in shape and are soluble in water. They are involved in the actual functioning of living organisms. Common globular proteins are *insulin* which controls glucose metabolism, *haemoglobin* (in blood) and *myoglobin* (in muscles) which transport and store oxygen and *antibodies* which fight diseases. **Enzymes**, the biological catalysts, are also globular proteins (pp. 298–9 CCPC).

**Proteins** are naturally occurring polymers of amino acids.

Hence to understand the structure of proteins we need to start with the basic monomer units, the amino acids.

## 14.2 AMINO ACIDS

We saw in Section 5.16 that *alkanoic acids* had the general structure:

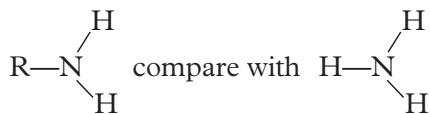


In those chapters R was any alkyl group. More generally R can be any carbon-containing group (not just alkyl) in which case the compound is called a *carboxylic acid*.

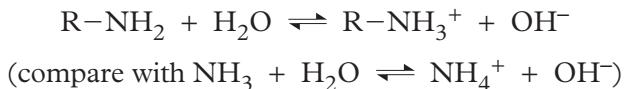
Another class of simple carbon compounds is called *amines*. These are derivatives of ammonia.

**Amines** are compounds in which one or more carbon-containing groups (such as alkyl groups) replace one or more H atoms in an ammonia molecule.

If one H of ammonia is replaced by a carbon-containing group, we get the structure:



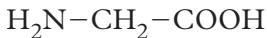
Like ammonia, amines are weak bases. They undergo the following equilibrium reaction:



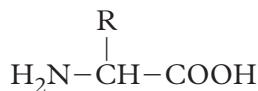
We call  $-\text{NH}_2$  the **amine functional group**.

**Amino acids** are compounds that contain both an amine and a carboxylic acid functional group.

The simplest amino acid is glycine:



There is a whole family of amino acids with the general structure:



where R is a carbon-containing side chain.

Proteins are long-chain molecules with thousands of amino acid molecules of this general structure joined together. (This is discussed below.)

There are 20 amino acids commonly found in proteins. Some of these are shown in Table 14.1. They fall into three broad groups; amino acids with:

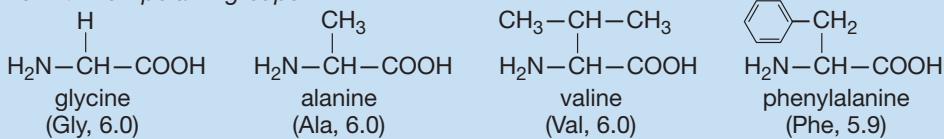
- non-polar R groups (alkyl or similar)
- polar R groups that are capable of forming ions; these have a  $-\text{COOH}$  or  $-\text{NH}_2$  group *additional* to the normal ones in the amino acid
- polar R groups that do not generally form ions; the simplest of these contain polar  $-\text{OH}$  or  $-\text{SH}$  groups as part of R.

Molecular models of three simple amino acids are shown in Figure 14.1.

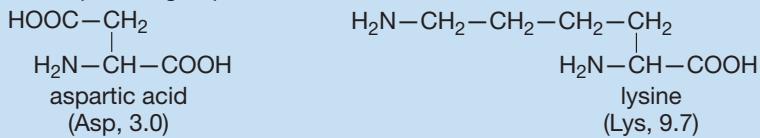
**TABLE 14.1 Common amino acids found in proteins**

(usual abbreviations and isoelectric points (Section 14.10) are given in brackets under the name)

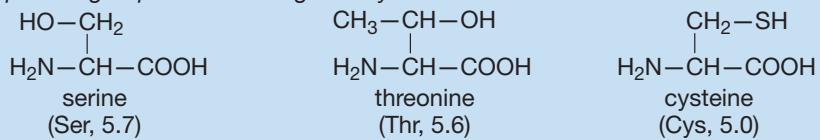
**a with non-polar R groups**



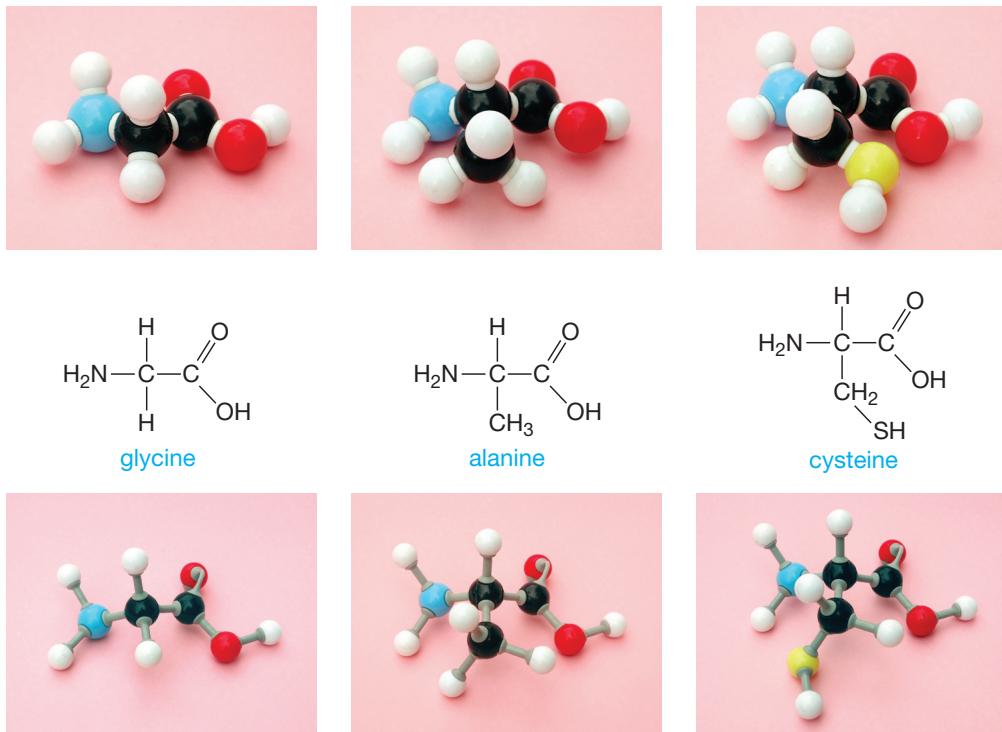
**b with polar R groups that form ions**



**c polar R groups that do not generally form ions**



**FIGURE 14.1**  
Space-filling and ball-and-stick models of glycine, alanine and cysteine along with structural formulae drawn with approximately similar orientations. Black is C, white, H, red, O, blue, N and yellow, S

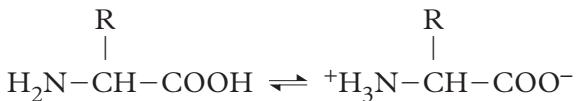


The occurrence of an acidic and a basic group on the one molecule leads to the possibility of an ionic structure for amino acids.

### 14.3 ZWITTERIONS

So far we have written amino acids as neutral molecules as in Table 14.1. However the  $-\text{COOH}$  group, being acidic, tends to lose a proton, while the amine group,  $-\text{NH}_2$ , being basic, tends to gain a proton. Hence in solution,

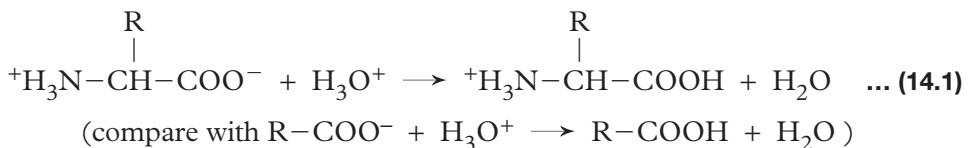
amino acids exist as an equilibrium mixture of neutral molecules with a dipolar ion:



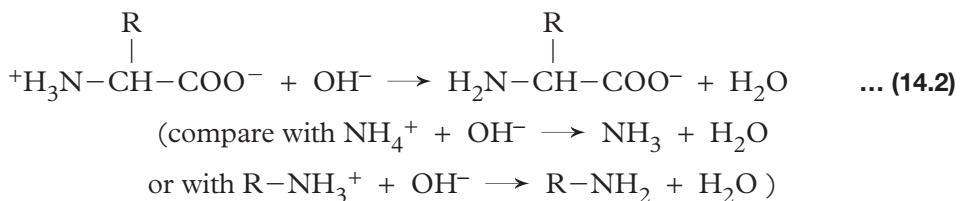
This dipolar ion is called a **zwitterion**. Most amino acids exist primarily as zwitterions.

Because of this dipolar structure of amino acids, they are crystalline solids with relatively high melting points, and they are soluble in water.

Because the  $-\text{COOH}$  group is a weak acid and the  $-\text{NH}_2$  group is a weak base, amino acids take on different forms in solutions of different pH. In acid solution, say pH 2 to 3, the zwitterion changes to a cation:



In alkaline solution it changes to an anion:



## Exercises

- 1 A certain amino acid contained 40.4% carbon, 7.9% hydrogen and 15.7% nitrogen. The balance was oxygen.
  - a Calculate the empirical formula.
  - b Draw the structural formula of the simplest amino acid that could have this empirical formula.
- 2 Glycine and alanine are the first two members of a homologous series of 'straight-chain' amino acids. Draw structures for the next two members of the series.
- 3 MSG (monosodium glutamate) is widely used as a flavour-enhancing agent (often in Chinese food). It is the sodium salt of glutamic acid. Glutamic acid is an amino acid with a propanoic acid side chain. Draw the structure of glutamic acid and hence of MSG. Why is it called 'monosodium'?
- 4 For each of the amino acids:
  - a glycine
  - b alanine
  - \*c cysteine
  - \*d lysine
 from Table 14.1, draw the structural formula of the zwitterion form of the molecule.
- 5 Draw the structures you would expect for (a) valine (b) aspartic acid (Table 14.1) in solutions of pH (i) 2 and (ii) 11.
- 6 a Draw the structural formula of the main species present in a solution of serine (Table 14.1) in water.  
 b Draw the structural formula of the main species present when:
  - i 1.00 mol of each of serine and sodium hydroxide is dissolved in 2.00 L water
  - ii 1.00 mol hydrochloric acid is added to the solution in (i)
  - iii another 1.00 mol HCl is added to the solution in (ii).



**7** Glycine can be used as a buffer at pHs around 6. Explain why (with equations).

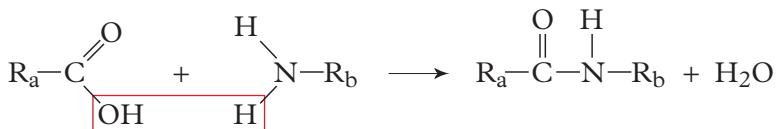
**\*8** Alanine is amphoteric. Write equations which show this.

## 14.4 PEPTIDES

As expected from our knowledge of acids and bases, an amine reacts with a carboxylic acid to form a salt:

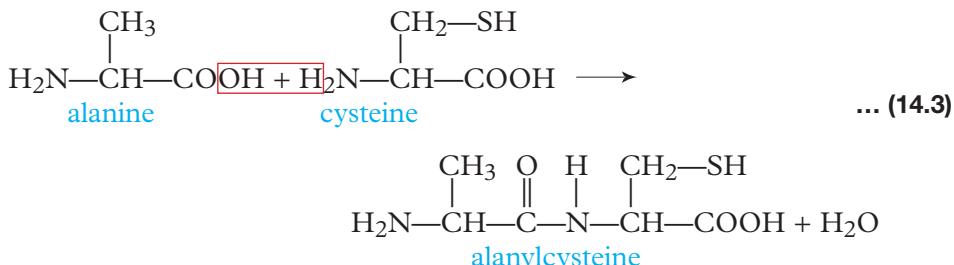


However *under certain conditions an amine reacts with a carboxylic acid by eliminating water to form what we call an amide*:



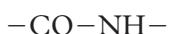
This amide product is a stable covalent compound with no acid or base properties at all.

Pairs of amino acid molecules undergo this same reaction. For example, alanine reacts with cysteine:

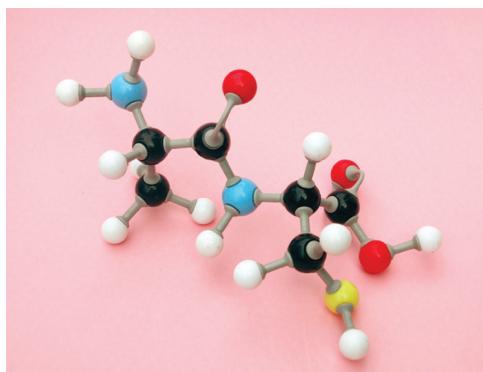
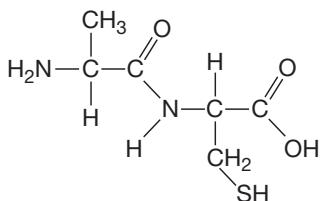
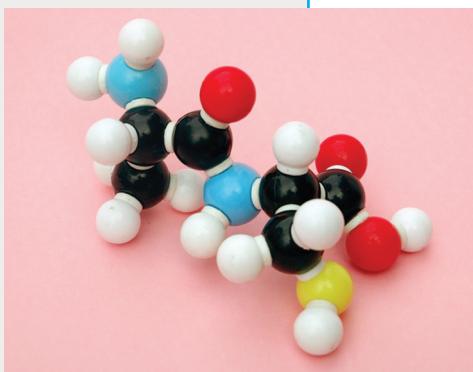


The compound formed when two amino acids react together is called a **dipeptide**. This amide linkage between two amino acids is called a **peptide bond**.

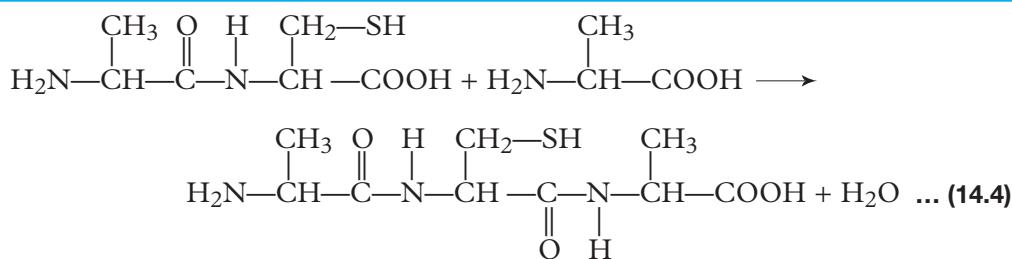
The peptide link which we have drawn out in full in Equation 14.3 is often written more concisely as:



Molecular models of alanyl cysteine are shown in Figure 14.2.



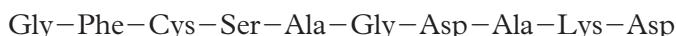
Our dipeptide in Equation 14.3 still has terminal COOH and amine groups, so it can join to other amino acids. For example, with another molecule of alanine we get:



The product is called a **tripeptide**, because it is made from three amino acid units.

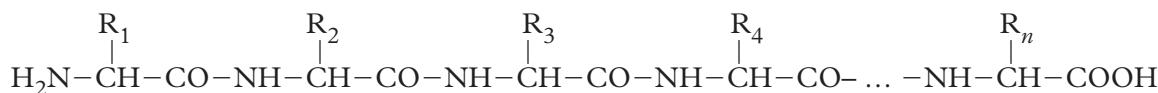
Peptide bonding can extend to form very long chains of amino acid units. We call such long molecules **polypeptides**, many peptide linkages or many amino acids joined together. Polypeptides are polymers. The monomers making up the polymer are amino acids. Formation of a peptide from amino acids is a *condensation reaction* (Section 13.8). Note that the peptide bond or amide linkage formed here is the same as the bond between monomer units in nylon (Section 1.12).

Because formulae of peptides are tedious to draw, biochemists frequently use a shorthand way of drawing them. Each of the twenty common amino acids has a three-letter abbreviation. Some are given in Table 14.1. These are often used instead of complete structural formulae. The dipeptide in Equation 14.3 is written as Ala—Cys. The tripeptide in Equation 14.4 is Ala—Cys—Ala. A possible peptide with ten amino acids is:



## Proteins as polypeptides

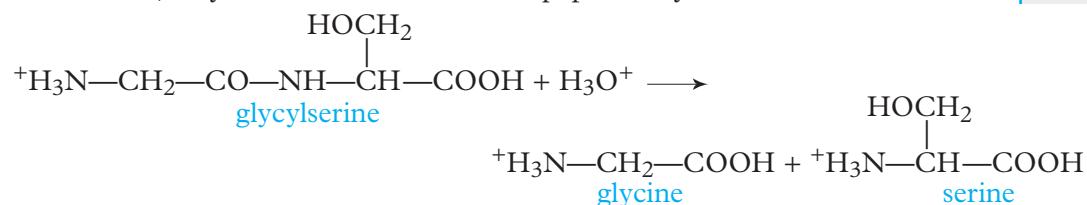
*Proteins* are polypeptides containing from hundreds to thousands of amino acid units per molecule. The generalised structure of a protein can be represented as:



where  $\text{R}_1, \text{R}_2, \text{R}_3, \dots \text{R}_n$  are the side groups of the various amino acids (hundreds to thousands in actual proteins). Some of these will be the same while others will be different. Nine of the twenty R groups (in amino acids) commonly found in proteins are shown in Table 14.1. Notice that one end of the protein molecule has an amino group,  $\text{NH}_2$ , while the other has a carboxylic acid group,  $-\text{COOH}$ .

## 14.5 HYDROLYSIS OF PEPTIDES AND PROTEINS

Peptides and proteins can be hydrolysed to amino acids by warming them with about 6 mol/L hydrochloric acid. For the dipeptide Gly—Ser the reaction is:



If the tripeptide of Equation 14.4 is treated in this way, alanine and cysteine are formed in the molar ratio of 2:1.



The reaction occurs with polypeptides and hence with proteins as well.

In humans and other animals, this hydrolysis of polypeptides (proteins) is brought about by certain enzymes. This occurs in digestion, both in the stomach and in the intestine. Some enzymes are very specific as to which peptide bonds they will break. For example trypsin will break a  $-\text{CO}-\text{NH}-$  peptide bond only if lysine or arginine is on the CO side of the bond: chymotrypsin will break the peptide bond only if the amino acid on the CO side is phenylalanine, tyrosine or tryptophan.

*Hence by using particular enzymes it is possible to break a protein into several smaller pieces (polypeptides) without completely breaking it into separate amino acids.*

In the laboratory it is also possible to break a protein into smaller pieces (rather than completely into individual amino acids) but the breakages occur randomly and not at particular sites as with enzymes.

## Exercises

Refer to Table 14.1 for the structures of the amino acids used in the following exercises.

- 9 Draw the structural formula of a dipeptide formed between:  
**a** glycine and valine      **\*c** cysteine and aspartic acid  
**b** threonine and alanine      **\*d** lysine and phenylalanine
- 10 Can more than one dipeptide be formed between each of the pairs of amino acids in Exercise 9? If so, draw the structures of the ones you did not draw in that exercise.
- 11 Draw structural formulae for the dipeptides which can be represented by:  
**a** Val-Ser      **\*b** Ala-Asp      **\*c** Thr-Lys
- 12 Write balanced equations (using structural formulae for all carbon-containing compounds) for the reactions that occur when the following compounds are heated with 6 mol/L hydrochloric acid. Make sure that you write each compound in the correctly protonated or deprotonated form:
  - a**  $\text{H}_2\text{N}-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-\text{COOH}$
  - \*b** 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_2\text{N}-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}-\text{COOH} \end{array}$$
  - c** 
$$\begin{array}{ccccc} \text{HOCH}_2 & & \text{CH}_3 & & \\ | & & | & & \\ \text{HOOC}-\text{CH}-\text{NH}-\text{CO}-\text{CH}-\text{NH}_2 & & & & \end{array}$$
  - \*d** 
$$\begin{array}{ccccc} \text{H}_2\text{N}-\text{CH} & -\text{CO}-\text{NH}-\text{CH} & -\text{COOH} & & \\ | & & | & & \\ \text{CH}_3-\text{CH}-\text{CH}_3 & & \text{CH}_2-\text{SH} & & \end{array}$$
  - \*e** 
$$\begin{array}{ccccc} \text{HOOC}-\text{CH} & -\text{NH}-\text{CO}-\text{CH} & -\text{NH}_2 & & \\ | & & | & & \\ \text{CH}_3 & & \text{CH}_2-\text{COOH} & & \end{array}$$

Identify the amino acids formed in each case.

- 13 Write a molecular equation for the reactions in (a) and (c) of Exercise 12.
- 14 **a** Aspartame is an artificial sweetening agent sold under the trade name, NutraSweet®. It is a derivative of a dipeptide formed from aspartic acid and

phenylalanine. The peptide linkage involves the carboxylic acid group of aspartic acid. Draw the structure of this compound.

- b Aspartame is the methyl ester of this dipeptide. The COOH group which has been esterified is the one 'belonging to' phenylalanine. Draw the structure of the ester.
- c What is the molecular formula of aspartame?
- d NutraSweet® is not recommended for use where cooking is involved. Suggest a reason for this.

## 14.6 STRUCTURE OF PROTEINS

The chemical composition (number of each type of atom present) and structure (how the atoms are arranged) of proteins determine their biological function; that is, whether they are structural material such as skin, hair, tendon, cartilage, or whether they are involved in the biochemical reactions that constitute life, such as enzymes, haemoglobin, insulin.

There are three aspects to the structure of a protein:

- the nature and sequence of the amino acids that make up the protein, called the *primary structure*
- the way that the amino acid chain is arranged within segments of the molecule (curled into a spiral or folded into pleated sheets and the dimensions of these arrangements), called the *secondary structure*
- the way that these segments are arranged to make up the whole molecule, called the *tertiary structure*.

Covalent bonds (peptide links) are responsible for the primary structure—how the amino acids are joined to one another. The secondary and tertiary structures arise from:

- *hydrogen bonding*, mainly between NH and CO groups on adjacent (but not neighbouring) amino acid units
- *ionic attractions*, between  $\text{COO}^-$  and  $\text{NH}_3^+$  groups on adjacent (but again not neighbouring) amino acid units
- *sulfur-sulfur links* (covalent bonds) between two nearby cysteine units ( $-\text{SH HS-}$  converted into  $-\text{S-S-}$ )
- dispersion forces and dipole-dipole forces.

The sequence of amino acids along the chain determines where these interactions can occur and hence decides the shape that the molecule can have.

If the final structure of the protein is fibrous (many polypeptide chains intertwined) or sheet-like, then its function will be structural—skin, cartilage, hair. If the final structure is globular with many  $\text{COO}^-$  and  $\text{NH}_3^+$  and  $-\text{OH}$  groups pointing outside the globule, the protein will be soluble in water and will be involved in the functioning of the organism.

### Determination of primary structure

To determine the primary structure of a protein a chemist needs to determine:

- the *identity* of all the amino acids present
- the *relative molar amounts* in which these amino acids are present
- the *sequence* in which the amino acids are linked together in the molecule.

To determine the identity and relative amounts of the amino acids present, the protein is hydrolysed completely (as explained above) into the amino acids

then the mixture is analysed by chromatography (Sections 14.8 and 14.9): this shows which amino acids are present and in what relative amounts.

The sequence of amino acids has to be determined by breaking off amino acids from the protein chain one at a time starting from one end (usually the NH<sub>2</sub> end) and identifying that amino acid by chromatography or electrophoresis (Section 14.10). Then the whole procedure is repeated to split off the next amino acid from the shortened chain. Because of the build-up of by-products, it is generally not possible to cut off more than about twenty amino acids in this way. Typically a protein contains 200 to 400 amino acid units. For full sequencing the protein is cut into smaller pieces by selected enzymes, the pieces separated, then the sequence in each piece determined. By using different enzymes, overlapping pieces can be formed, then after sequencing all the pieces, the chemist can work out the order in which the pieces were joined in the original protein by recognising the overlapping bits, rather like solving a jigsaw puzzle. In this way we get the complete sequence of amino acids in the protein.

## Secondary and tertiary structures

The secondary and tertiary structures of proteins are generally worked out by using X-ray studies of crystalline samples of the various proteins.

## Forensic identification of proteins

Forensic chemists do not need to work out the structure of proteins from scratch as just described. Rather they have to *identify* protein samples. And generally it is fibrous (structural) proteins that they need to identify, such as hair, skin, cartilage. This is usually done by microscopic examination, because fibrous proteins have quite distinct appearances. If it is necessary to identify a globular (functional) protein, this can generally be done by determining the amino acid composition of the protein (complete hydrolysis followed by electrophoretic or chromatographic analyses, to be described in Sections 14.8 to 14.11).

## 14.7 SIMPLE TESTS FOR PROTEINS AND/OR AMINO ACIDS

There are two tests that we can easily perform to determine whether or not a sample contains protein or amino acid.

### Ninhydrin test

Ninhydrin is a cyclic carbon compound that is able to convert an amino acid (or terminal amino acid group on a protein) into an aldehyde (compound containing a –CHO group). In so doing, ninhydrin is converted to a purple coloured compound.

The **ninhydrin test** is to add colourless ninhydrin solution to the solution suspected of containing protein or amino acid and to heat the mixture for a few minutes. If a purple colour develops, *protein or an amino acid* is present.

### Biuret test

The **biuret test** gives a positive result for proteins and peptides (including dipeptides) but not for amino acids.

The solution to be tested is made alkaline with NaOH solution, then a few drops of copper sulfate solution are added to it. A purple colour forms if the sample contains a protein or peptide. This test can be spoilt if too much copper sulfate solution is added, because then a precipitate of copper hydroxide can be formed. The purple colour is due to a complex which forms between Cu<sup>2+</sup> and two adjacent amide (peptide) linkages. This complex is similar to the copper complexes that were present in Benedict's and Fehling's solutions in Section 13.11.

The name of this test comes from one of the simplest compounds that give a positive result, biuret, H<sub>2</sub>N—CO—NH—CO—NH<sub>2</sub>.

These two tests just tell us that protein or amino acid is present. Two techniques that are widely used to determine which amino acids are present and how much of each there is in a sample of protein are chromatography and electrophoresis.

## Exercises

15 A chemist had three solutions, A, B and C. A gave a positive test with ninhydrin and with alkaline copper solution (Biuret test), and B gave negative results with these two tests but formed a deep blue colour when drops of iodine were added to it. C tested positively to ninhydrin and negatively to the Biuret test and to iodine. What do you conclude about the substances present in the three solutions?

16 How would you distinguish between four solutions that contained:

- a a protein
- b starch
- c glucose
- d none of these?

Describe carefully what you would observe for a positive result in each of the tests you use.

17 What would you observe if you tested solutions of:

- a myoglobin (a protein)
- b sucrose
- c amylose
- d jelly crystals (contain protein and sucrose)
- \*e honey
- \*f milk
- \*g 'diet' lemonade (containing NutraSweet®, see Exercise 14)
- \*h flour
- \*i apple juice
- \*j table salt
- \*k egg white

with

- i ninhydrin
- ii iodine
- iii Tollens' reagent?

18 How would you establish that:

- a Sample (g) in Exercise 17 did not contain sucrose or glucose
- b Sample (j) contained chloride but not carbonate or sulfate?



## 14.8 CHROMATOGRAPHY

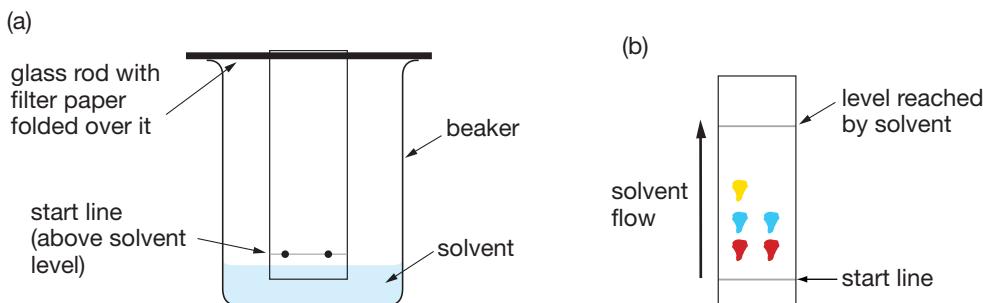
Before discussing the separation of amino acids by chromatography, let us take a general look at what is meant by chromatography.

**Chromatography** is the name given to a group of techniques used to separate substances based upon their differential distribution between two phases, one moving and the other stationary.

The name, chromatography (literally colour writing), arises because the technique was first used to separate coloured substances.

The simplest type of chromatography to demonstrate is *paper chromatography*. It can be used to separate the components of coloured inks. Spots of ink are placed near one end of a strip of filter paper which is then suspended in a suitable liquid as shown in Figure 14.3(a). As the liquid creeps up the paper (by capillary attraction), it ‘washes’ the components of the ink upwards at different rates. After a few minutes different-coloured, separated spots can be seen as shown in Figure 14.3(b).

FIGURE 14.3  
Separation of inks (from  
felt-point colouring pens)  
by paper chromatography



The separation occurs because the substances to be separated have different strengths of attachment to the filter paper (called the **stationary phase**) and different solubilities in the solvent being used (called the **mobile phase**). In paper chromatography the attachment of the substances to the stationary phase is a combination of *adsorption* onto the cellulose fibres of the filter paper and *solubility* in the water trapped in the pores of the paper. Substances that attach only weakly to the stationary phase but dissolve readily in the mobile phase move up the paper more quickly than ones that attach more strongly to the stationary phase and dissolve less readily in the mobile one, and so a separation occurs.

**Paper chromatography** is a technique for separating substances by using a solvent (mobile phase) to wash the substances in the mixture at different rates up (or down) a piece of absorbent paper such as filter paper (stationary phase).

A mixture of colouring matter extracted from leaves of plants using petroleum ether (a mixture of hydrocarbons) can also be separated by paper chromatography as can the colouring matter from ‘Smarties’ or similar confectioneries.

Apart from paper chromatography, there are broadly four types of chromatography, depending upon whether the mobile phase is a liquid or a gas, and upon whether the stationary phase is a solid or a liquid (adsorbed on a solid). If the stationary phase is a solid, then separation is based upon the differing strengths of *adsorption* (on the stationary phase) of the substances to be separated. If the stationary phase is a liquid, separation is based upon differing *solubilities* of the substances to be separated in that liquid.

The original form of chromatography was *liquid–solid chromatography*. It was introduced by the Russian botanist Mikhail Tswett in 1902 to separate a mixture of coloured material extracted from plants. A solution of the mixture

to be separated was added to the top of a column of finely divided solid. The solutes adsorbed onto this solid and were then washed down the column by a suitable solvent. Because of different strengths of adsorption of the substances onto the column, they moved down at different rates and so showed up as different coloured bands as in Figure 14.4. With continued addition of solvent to the top of the column these bands were eventually eluted from (washed off) the column and collected in separate beakers and so a separation was effected.

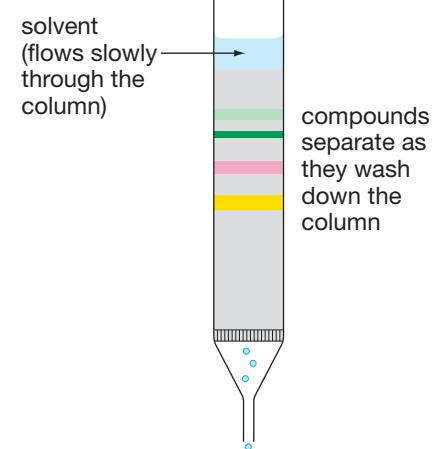
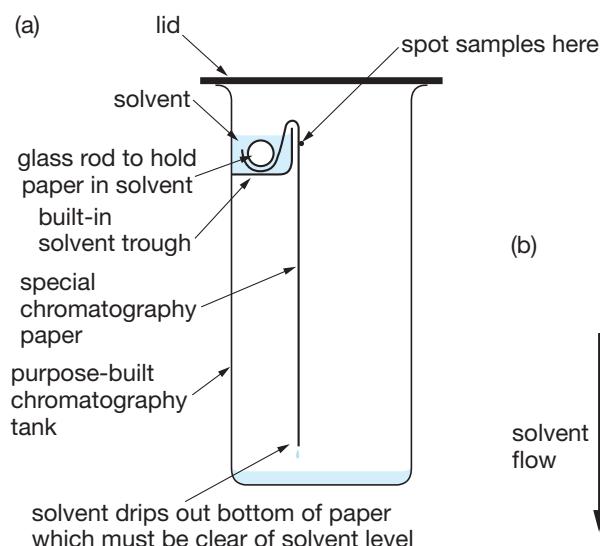
In *gas-solid chromatography* the mixture to be analysed (or separated) is vaporised into a flowing gas (mobile phase) and again separated by differential adsorption on a solid (Section 6.2).

For forensic purposes the most useful types of chromatography are liquid–liquid chromatography (sometimes called partition chromatography) and gas–liquid chromatography. These will be considered in Sections 15.2 and 15.3.

## 14.9 SEPARATION OF AMINO ACIDS BY PAPER CHROMATOGRAPHY

Amino acids can be separated by paper chromatography. The stationary phase is the very polar water–paper combination while the mobile phase is a less polar solvent such as a butanol–acetic acid mixture or a phenol in water solution.

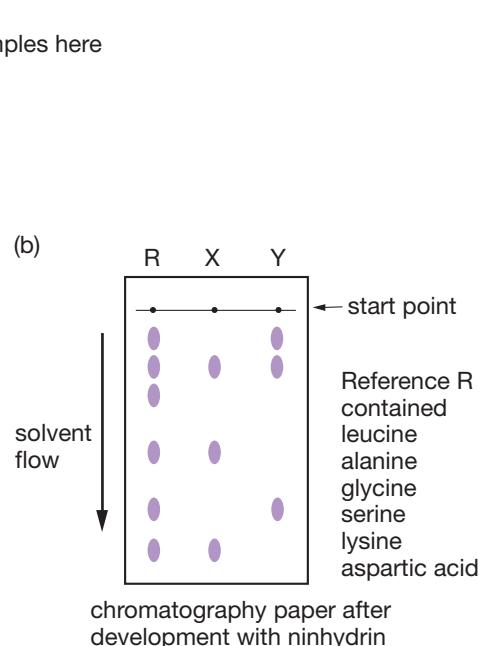
The arrangement of Figure 14.3 with the solvent creeping up the paper can be used, but a more efficient separation is effected if the solvent is allowed to run *down* the paper. The arrangement for this is shown in Figure 14.5. In either case the separation is better if the beaker or tank is kept covered so that the paper becomes saturated with solvent vapour.



**FIGURE 14.4**  
Separation of a mixture of coloured material from a plant using liquid–solid chromatography. With continued addition of solvent the individual substances can be washed off the column one after the other and collected in separate beakers

Amino acids can be separated by paper chromatography. The stationary phase is the very polar water–paper combination while the mobile phase is a less polar solvent such as a butanol–acetic acid mixture or a phenol in water solution.

The arrangement of Figure 14.3 with the solvent creeping up the paper can be used, but a more efficient separation is effected if the solvent is allowed to run *down* the paper. The arrangement for this is shown in Figure 14.5. In either case the separation is better if the beaker or tank is kept covered so that the paper becomes saturated with solvent vapour.



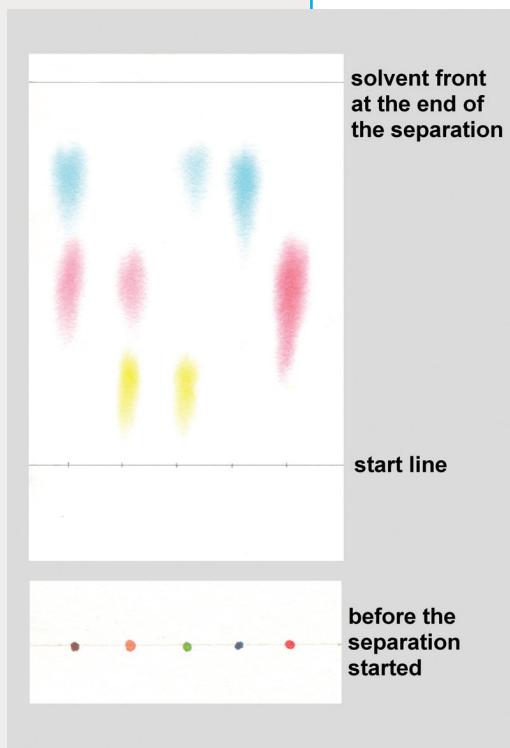
**FIGURE 14.5**  
(a) Paper chromatography for separating amino acids by allowing the mobile phase to flow down the paper which results in a more uniform flow rate and so a better separation.  
(b) A developed chromatogram: R is a reference sample containing known amino acids while X and Y are samples being analysed

## Basis of separation

Amino acids move through the chromatography paper at different rates because of different polarity and therefore different solubilities in the two phases. More polar amino acids attach to the more polar stationary phase (paper) more readily and so move through the paper at a lower speed. Less polar amino acids dissolve more readily in the less polar mobile phase and so move through the paper more rapidly. These differing solubilities are based on the general rule on p. 199 *CCPC*:

Like dissolves like

## Making the spots visible



A paper chromatogram showing the separation of the pigments in some common food dyes; the mobile phase is a 1:1:1 mixture of 1-butanol, ethanol and 2 mol/L aqueous ammonia

Amino acids are colourless, so we need some way of making the spots visible. The ninhydrin reaction (Section 14.7) is used. After the mobile phase has flowed through the paper for a suitable time, the paper is dried out (by exposing it to a flow of air in a fume cupboard). The dry paper is then sprayed with a ninhydrin solution and warmed in an oven for a few minutes. Ninhydrin reacts with the amino acids and so purple spots develop on the paper corresponding to positions of the amino acids. It is advisable to trace the outline of the spots with a pencil, because the spots can fade with time.

## Identifying the amino acids in the mixture

There are two methods for identifying the spots in the sample to be analysed. In the first method spots of known amino acids are placed beside the sample. The distance from the starting position of each spot in the sample is compared with the distances travelled by the known standards. The unknown spot is identified as being the amino acid that travelled the same distance.

In the second method a standard mixture of several amino acids is used: the order in which these will separate under the conditions of the experiment is known, so just one standard is run beside the sample to be analysed—it produces several spots but these can be identified because of the known order. Again comparison of distances travelled by spots in the sample to be analysed with these standard spots allows identification of the unknown spots as in Figure 14.5(b).

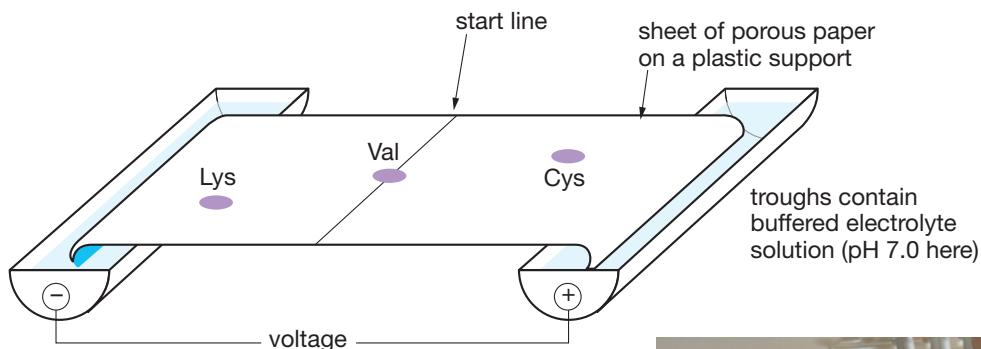
Amino acids can also be separated by ion exchange chromatography but we will not go into that.

## 14.10 ELECTROPHORESIS AND AMINO ACIDS

**Electrophoresis** is a method of separating charged substances based upon the different signs of their charges and upon their different mobilities.

Paper electrophoresis uses a strip of filter paper soaked in an electrolyte solution containing a suitable buffer. A voltage is applied across the strip of paper as shown in Figure 14.6 and the sample to be separated is placed on a line

across the middle of the strip. Positively charged particles migrate towards the negative electrode while negative particles move towards the positive electrode. Neutral particles do not migrate at all.



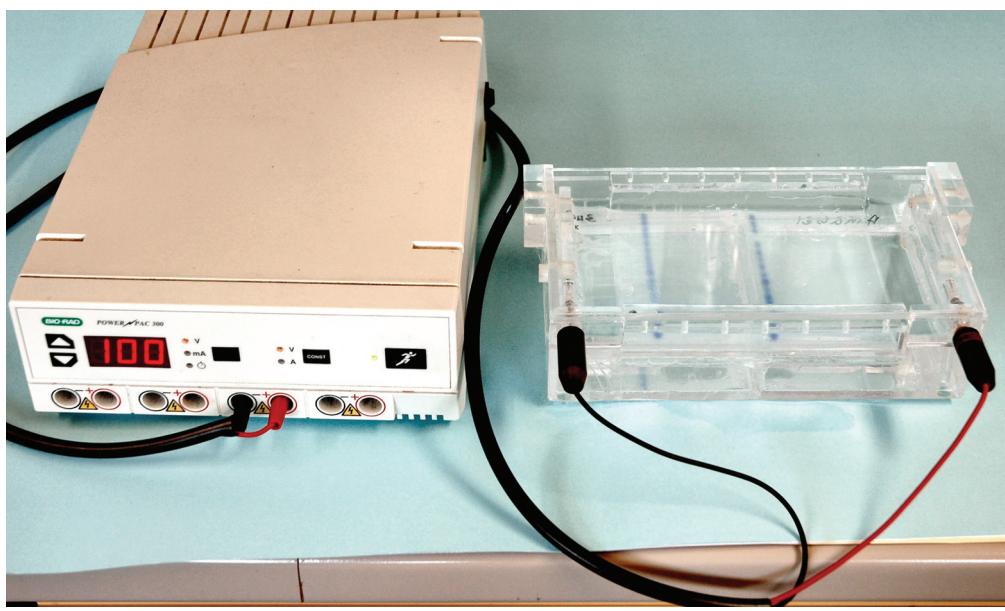
*The speed at which particles move depends upon their size and charge.* If two particles (ions) are singly charged, then the smaller ion will move more rapidly. If two ions are of similar size but one is doubly charged while the other is singly charged, then the doubly charged one will migrate more rapidly.

Electrophoresis is commonly used to identify amino acids or to analyse mixtures of amino acids. Amino acids are colourless, but their positions on an electrophoresis strip can be made visible by spraying the strip with a solution of ninhydrin (as for paper chromatography). This colourless compound turns purple in the presence of an amino acid (Section 14.7), so the sprayed strip shows a series of purple spots that indicate the location of the amino acids.

Instead of a strip of filter paper, electrophoresis can be performed using an agar gel spread on a sheet of glass. This can separate larger quantities of substances than paper.



FIGURE 14.6  
Electrophoresis: migration of charged particles through a buffered electrolyte when a voltage is applied



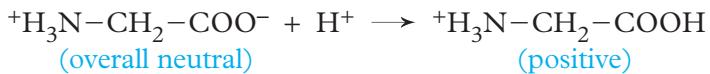
ABOVE A scientist loads samples into a gel for analysis in the electrophoresis apparatus in the photograph below

LEFT Electrophoresis apparatus using an agarose gel to separate fragments of DNA. The samples, about ten across each blue strip, are placed in holes (wells) in the gel along with blue dye to show where they are; the gel is saturated with and covered with buffer solution. Two sets of samples are being analysed here—the two blue strips. The separation will be stopped (after one to two hours) before the fragments in the left-hand strip reach the right-hand one (the starting line for the second set of samples)

## Charges on amino acid molecules or ions

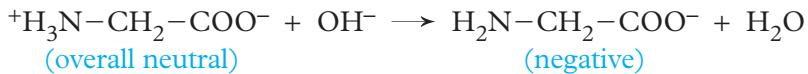
In Section 14.3 we saw that amino acids exist as zwitterions—molecules with both a positive and a negative charge. The overall molecule in this form is neutral and so does not migrate during electrophoresis.

However one end of the molecule is a weak acid while the other end is a weak base and so there can be proton transfer as pH changes as was shown in Equations 14.1 and 14.2. To illustrate further, glycine in near neutral solution exists as the neutral zwitterion, but in acid solution (say pH = 2) the carboxylate ion accepts a proton:



This forms a positive ion that will migrate towards the negative electrode in electrophoresis.

If the zwitterion is placed in alkaline solution (say pH = 11), then it gives up a proton and becomes negatively charged:



Consequently at pH 11 glycine migrates towards the *positive* electrode, while at pH 2 it migrates towards the *negative* electrode and at pH 6 to 8 it does not migrate at all.

This is true for all amino acids—at low pH they are positively charged, at high pH they are negatively charged and at an intermediate pH they are overall neutral. The actual pHs at which these charges form depend upon the structure of the amino acid in question.

For any given amino acid there is a pH at which it exists as the overall-neutral zwitterion. This is called the **isoelectric point**. At lower pH the amino acid exists as the positively charged species, while at higher pH it exists as the negatively charged species. The isoelectric point of an amino acid can be determined approximately by finding the pH at which it does not migrate during electrophoresis. Isoelectric points for the common amino acids are shown in Table 14.1.

The isoelectric point depends upon the structure of the amino acid. Amino acids with non-polar R groups have isoelectric points close to 6.0. For amino acids such as aspartic acid with an acidic R group (Table 14.1), a lower pH is needed to suppress the ionisation of the acid group in R; hence the isoelectric point is much lower than 6. If R contains a basic group (as in lysine, Table 14.1), a higher pH is needed to suppress the ionisation of this basic group in R; such amino acids have an isoelectric point much greater than 6. Figure 14.7 shows the forms of aspartic acid at different pHs.

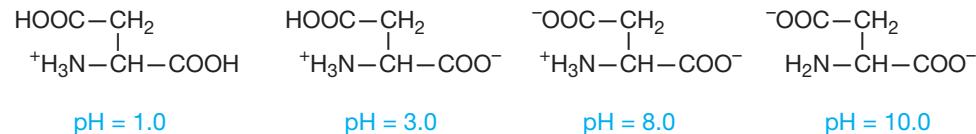


FIGURE 14.7  
Forms of aspartic acid at different pHs (isoelectric point 3.0)

## Use of electrophoresis for identifying proteins

As mentioned in Section 14.6 forensic scientists do not need to determine the structure of proteins, but rather just establish the identity and/or origin of

particular samples. Electrophoresis can be quite helpful in this regard. Simple acid hydrolysis of the protein sample converts it to a mixture of amino acids and then performing a few electrophoresis experiments in different buffers under standardised conditions allows the amino acids making up the protein to be identified (often by comparison with known samples).

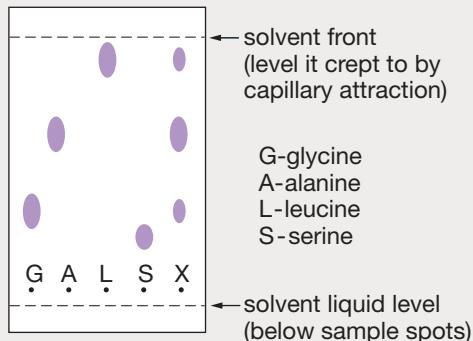
## 14.11 CHROMATOGRAPHY AND ELECTROPHORESIS COMPARED

The important similarities and differences between the two techniques just described are:

- Both chromatography and electrophoresis separate mixtures of amino acids.
- Chromatography separates them on the basis of their *different solubilities* in polar and non-polar solvents. Electrophoresis separates them on the basis of their *charges and sizes*.
- In electrophoresis we can vary the charge on a particular amino acid by changing the pH of the solution: this gives considerable flexibility in choosing conditions to get a good separation of particular amino acids. In chromatography, while changing the solvent gives some control over the degree of separation we can get, it is less effective than varying pH in electrophoresis.
- Electrophoresis requires more expensive equipment than does paper chromatography.
- Both methods are powerful tools for forensic chemists in that they allow the easy identification of the amino acids present in a protein and so can identify the protein and possibly its source.

### Exercises

- 19 Paper chromatography was used to identify the amino acids present in a sample, X. The unknown sample and samples of four known amino acids were run under identical conditions, with the spots of sample being placed near the bottom of a sheet of filter paper which was then dipped into a suitable solvent: the solvent crept up the paper by capillary attraction. After development (to make the spots visible) the chromatogram was as shown below. Which amino acids are present in the unknown sample?



- 20 In Figure 14.5(b) the standard sample contained leucine, alanine, glycine, serine, lysine and aspartic acid. The order of their rates of travel up a paper under the conditions used is the order of listing: leucine is the fastest, aspartic acid the slowest. By comparing the location of spots on the chromatogram, identify the amino acids present in Samples X and Y.



**\*21** In a paper chromatography experiment using a stationary phase that is more polar than the mobile phase, which of the three amino acids, alanine, serine, aspartic acid, moves the greatest distance and which the least (in a given time)? Explain why.

**22** The isoelectric points for some amino acids are given in Table 14.1. For each of the amino acids:

**a** glycine      **\*b** alanine      **c** cysteine      **\*d** lysine

draw the structure of the predominant species present in a solution of pH:

**i** 2.0      **ii** 6.0      **iii** 11.0

**23** You may use Table 14.1 for this question.

**a** In an electrophoresis experiment in a solution buffered at pH 4.0:

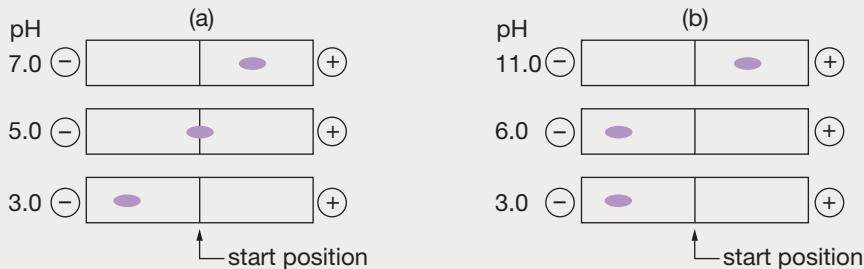
- i** Towards which electrode will each of the amino acids, glycine, valine and phenylalanine, migrate? Why?
- ii** Of these three amino acids which will migrate the greatest distance in a given time and which the least? Explain.

**b** Using Figure 14.7 if necessary, towards which electrode in an electrophoresis experiment will aspartic acid migrate in a solution buffered at pH of:

**i** 1.0      **ii** 3.0      **iii** 8.0      **iv** 11.0

**c** How would the distance moved (in a given time) by aspartic acid in a buffer at pH 11.0 compare with the distance travelled in a buffer at pH 8.0? Explain.

**24 a** In order to identify an amino acid Q, a chemist ran electrophoresis experiments on it using buffers at pHs 7.0, 5.0 and 3.0. The developed electrophoresis strips are shown at (a) below. Which of the amino acids in Table 14.1 is Q most likely to be? Explain.



**\*b** Electrophoresis experiments were run on another amino acid T, using buffers at pH 11.0, 6.0 and 3.0. Results are shown at (b) above. Identify T from the amino acids in Table 14.1. Explain your reasoning.

**\*25 a** To identify the amino acids present in a mixture, a chemist ran an electrophoresis experiment using a buffer of pH 6.0. The result was as in (a) below. If the only possibilities are the amino acids in Table 14.1, identify as many spots (labelled P, Q, R, S) as you can. (You will not be able to identify all of them from this one experiment.)



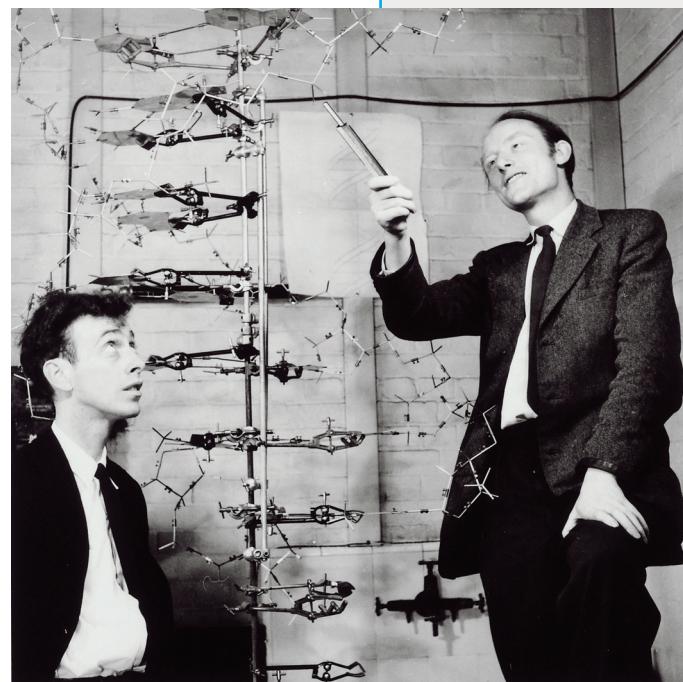
**b** The chemist repeated the experiment at pH 5.0 and obtained the result in (b) above. If possible identify additional spots and suggest possibilities for spot(s) you are unable to identify. Explain the basis of your identifications.

## 14.12 DNA

Let us now turn to the substance that in recent years has emerged as the most powerful tool for identifying the person responsible for a disputed activity, namely DNA. DNA was first used in a criminal trial (in Britain in 1987) to convict a rapist, and has been regularly used in court cases ever since. DNA can establish that two biological samples (such as blood, semen, saliva, skin, hair follicle) came from the same person with an error of less than one in ten billion. DNA analysis is also widely used in cases of disputed paternity and to establish other familial relationships between people.

DNA is present in the nucleus of all cells: it carries the genetic information that determines the nature of the cell, regulates its growth and division, and controls the biosynthesis of enzymes and other proteins required for the proper functioning of the cell.

DNA molecules are huge: molecular weights are of the order of  $10^{10}$ . The molecules exist as a double stranded helix coiled around a rod of protein material like cotton around a reel to form what are called chromosomes: the length of a DNA strand (molecule) is over 10 cm though the diameter is only about 2 nm.



The discoverers of the double helix structure of DNA, James Watson (b. 1916) at left and Francis Crick (b. 1916) seen with their model of part of a DNA molecule in 1953

## 14.13 STRUCTURE OF DNA

**DNA** is an abbreviation for **deoxyribonucleic acid**—*acid* because the molecule contains many phosphoric acid groups, *nucleic* because the molecule occurs in the nuclei of cells, *deoxyribo* because it also contains the sugar deoxyribose (Structure 2 on page 466).

DNA is a polymeric molecule for which the monomer units are called *nucleotides*.

A **nucleotide** consists of a sugar molecule (deoxyribose in DNA) attached to a phosphate unit and to a base as shown schematically in Figure 14.8(a).

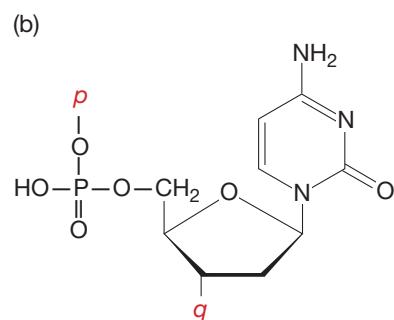
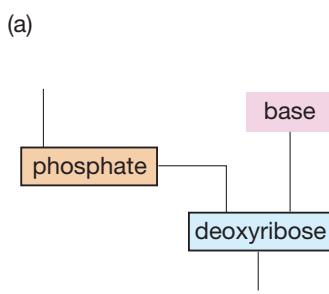
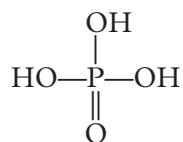


FIGURE 14.8  
The structure of a nucleotide, the monomer for DNA: (a) a schematic drawing, (b) a specific example. *p* and *q* are the points where the nucleotide joins on to its neighbouring nucleotides to make the polymer chain

One specific nucleotide is shown in (b). A molecular model of a nucleotide is shown in Figure 14.9.

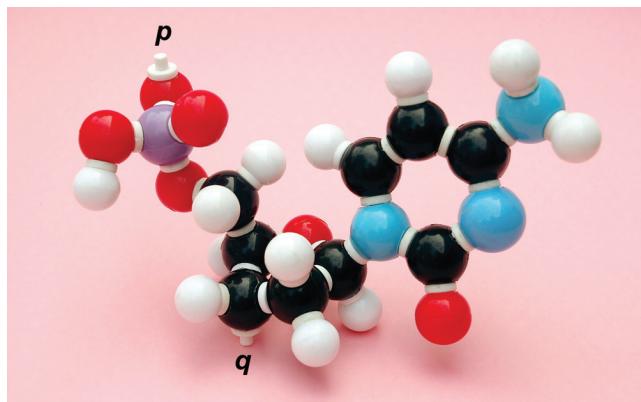
Phosphoric acid,  $H_3PO_4$ , has the structure:



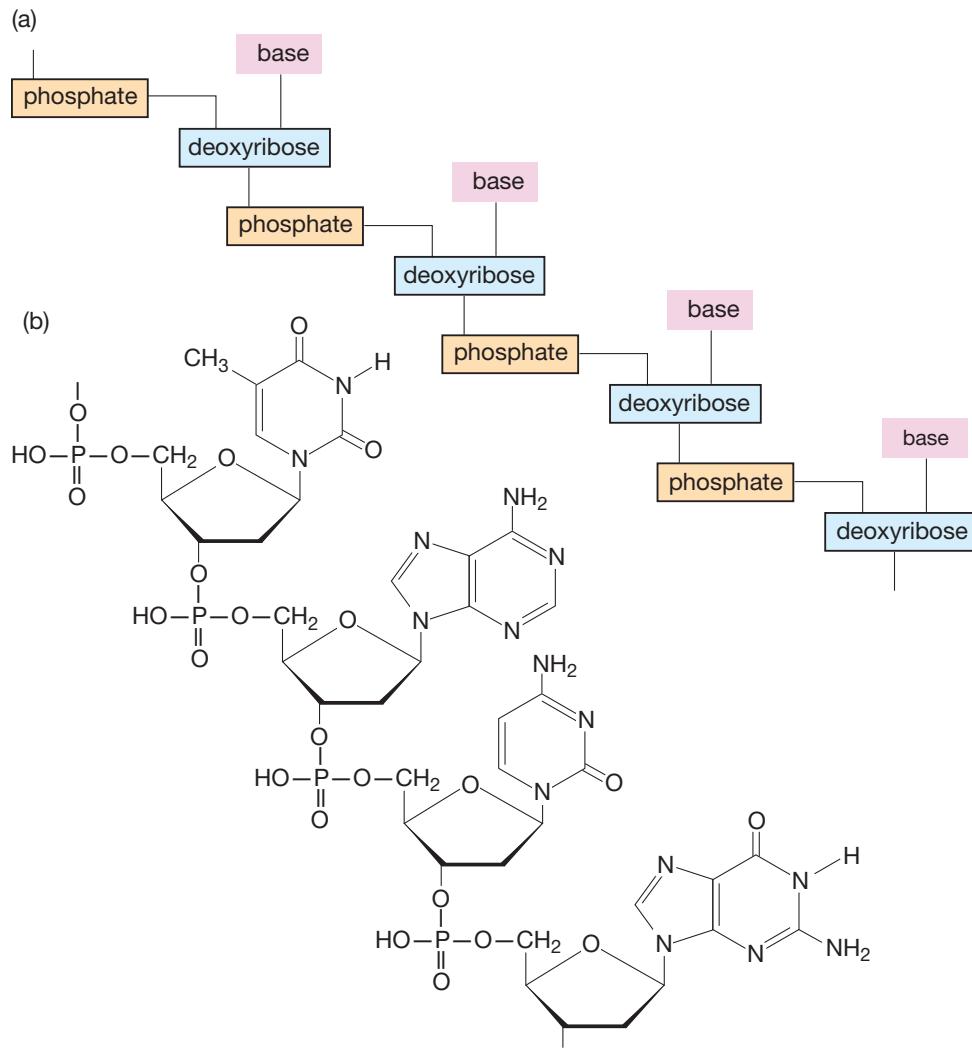
The four bonds around the P atom are arranged tetrahedrally.

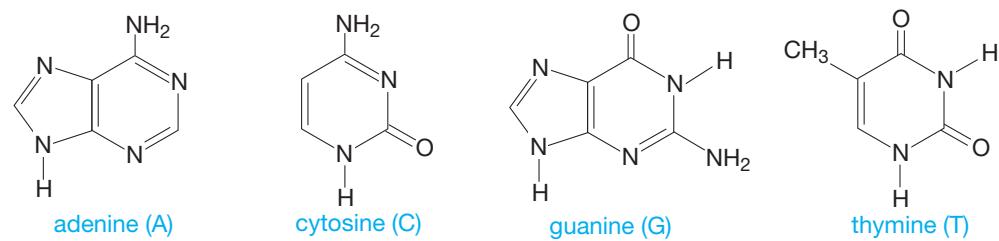
The nucleotides of DNA are joined together into long chains as shown in Figure 14.10: (a) is a schematic drawing while (b) is an example of a specific piece of a DNA molecule. There are only four bases used in DNA—adenine, guanine, cytosine and thymine: these are shown in Figure 14.11.

**FIGURE 14.9**  
A space-filling model of the nucleotide shown in Figure 14.8(b). Purple is P, while the other colours are as in Figure 14.1



**FIGURE 14.10**  
The structure of DNA: (a) schematic, (b) a section of the actual molecule





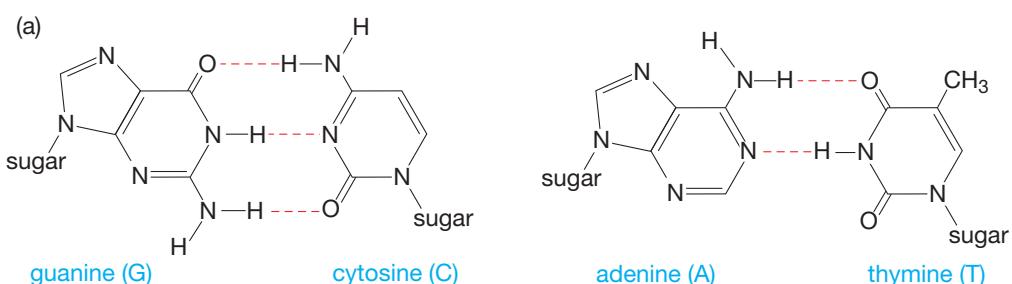
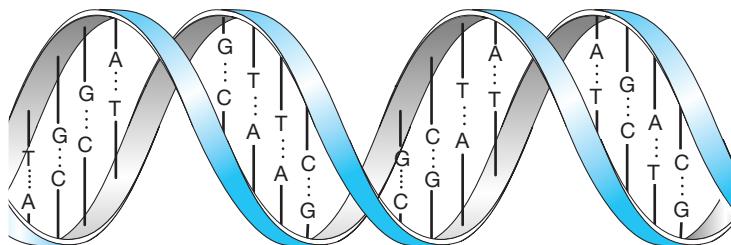
**FIGURE 14.11**  
The four bases that occur in DNA; the letters A, C, G, T are commonly used as abbreviations for these bases

DNA occurs as a double helix as shown in Figure 14.12. Imagine this as two older style telephone hand-set leads intertwined. The sugar-phosphate chains are on the outside of the helices with the bases pointing inwards. The two helices are held together by hydrogen bonding between pairs of bases.

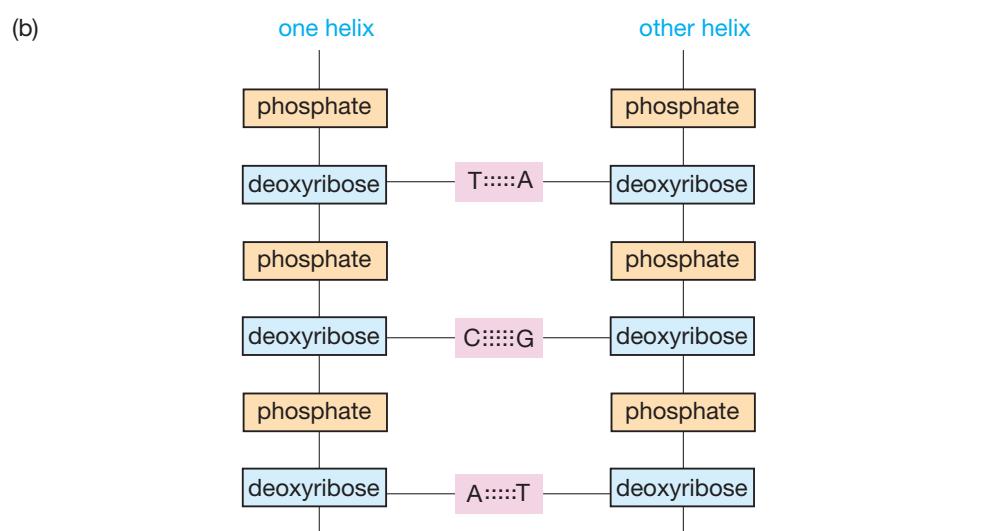
This hydrogen bonding occurs only between adenine and thymine and between guanine and cytosine: it is shown schematically in Figure 14.12.

Figure 14.13(a) shows the details of this hydrogen bonding while (b) shows schematically how hydrogen bonding holds the two strands together.

A strand of double-helix DNA contains about 10 to 100 million nucleotides and has a molecular weight of the order of  $10^9$  to  $10^{10}$ .



**FIGURE 14.12**  
The double helix structure of DNA: hydrogen bonding is shown schematically



**FIGURE 14.13**  
Hydrogen bonding between the pairs of bases in DNA: (a) its actual chemical nature, (b) schematically how it holds the two strands together



## Exercises

- 26 a** Why are the four compounds in Figure 14.11 called bases?  
**b** Draw the conjugate acid of cytosine.
- 27 a** What is the molecular formula of each of the four bases in Figure 14.11?  
**b** Determine the molecular formulae of the four nucleotide units that occur in DNA. Hence deduce an approximate empirical formula for DNA
- 28** Draw the structure of the dinucleotide that contains:  
**a** adenine and cytosine    **\*b** thymine and guanine
- \*29** The backbone of DNA molecules is always the same—alternate phosphate and deoxyribose units. Scientists often represent the structure of segments of DNA as the sequence of the bases on deoxyribose units, such as ACT or CGTA (letters from Figure 14.11). Draw the full chemical structure of these segments of DNA.
- 30** If a sample of DNA was completely hydrolysed (into bases, sugar and phosphoric acid), how many different compounds would be formed? Name them.
- 31** The diagram below represents a segment of one strand (helix) of a DNA molecule: P is a phosphate unit and D a deoxyribose unit, while A, C, G, T represent the attached bases. Using the same abbreviations, draw the complementary strand (helix) for this: that is, the strand that is hydrogen bonded to it.



- 32** (*For the mathematically inclined*) If a gene consisted of thirty nucleotides (generally it's far more than this), how many possible genes could be formed from just the four bases in Figure 14.11 (with no restrictions on how many times any one base can be used)?

## 14.14 THE ROLE OF DNA IN ORGANISMS

DNA carries the genetic code that allows living cells to function and reproduce themselves. Genes are actually sections of DNA molecules. The sequence of bases along the section determines the sequence of amino acids (primary structure) in the protein that the gene controls the synthesis of. By controlling the primary structure of the proteins that are made, genes determine the characteristics of the organism (person). Each DNA molecule contains thousands of genes.

A person has 46 chromosomes, 23 coming from each parent. Each of these chromosomes consists of a long DNA molecule wrapped around (and bonded to) a rod of protein material, so each person has 46 different types of DNA molecules<sup>†</sup>. It is possible to separate this DNA from the protein material of the chromosomes. *This mixture is called a person's DNA.*

Because all humans are very similar organisms—same number of fingers and teeth, same shaped limbs, same metabolism, same breathing mechanism etc—most of our genetic material is identical (except for that which controls colour of eyes and hair, height and weight, skin toning and so on). This means that there is great similarity between the DNA of one person and another. In fact over 99.9% of genetic material is the same from one person to another. When

<sup>†</sup> considering each complementary pair of hydrogen-bonded helices as one molecule, though strictly speaking it is two molecules.

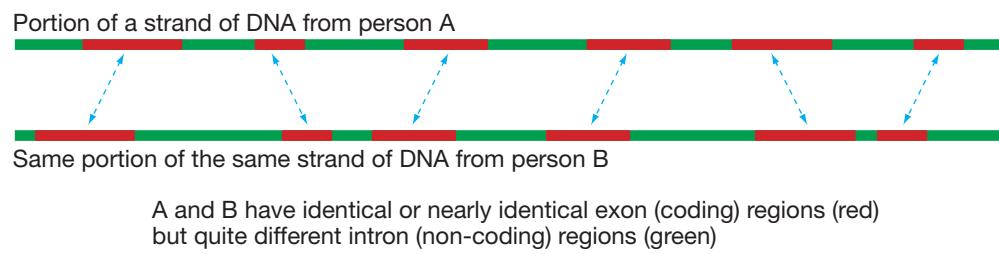
talking about genetics we tend to focus on the 0.1% of genes that are different and often overlook the similarities.

Despite this each person's DNA is unique.

## 14.15 UNIQUENESS OF A PERSON'S DNA

The uniqueness of a person's DNA arises mainly from the non-coding bits of DNA that separate the genes. As already stated, genes are segments of the DNA chain (containing from 200 to 100 000 nucleotides). They are separated by other segments that are not involved in the reproduction process and have no known function. The coding sequences along the DNA strand (the genes) are called **exons** while the non-coding sequences are called **introns**, sometimes called 'junk DNA'. Introns vary significantly from one person to another and it is these regions of the DNA molecules that are used for DNA analysis for forensic purposes. The relation between exons and introns is shown schematically in Figure 14.14.

If people are related, then their introns show some similarity. Fifty per cent of a person's DNA comes from each parent. If an analysis is based upon a certain set of introns, then for a particular person half of those introns will be identical with the corresponding ones of the mother and half with those of the father. Brothers and sisters have 50% of their DNA introns in common, cousins 25%. People who are not related at all have very little of their DNA introns in common. The only people who have the same DNA are identical twins.



## 14.16 DNA ANALYSIS FOR FORENSIC PURPOSES

DNA analysis allows forensic scientists to compare the DNA from different samples and to decide whether the samples came from the same person, related persons or completely different persons. This is a powerful tool for solving crime. It has been used to convict murderers and rapists, but it can also unequivocally clear a suspect in such a crime by showing that a sample could *not* have come from that suspect.

The steps in DNA analysis for forensic purposes are:

- separate the DNA from other material in the sample
- make multiple copies of selected segments of the DNA in intron regions (10 segments are currently being used in Australia)



ABOVE Preparing a sample for forensic analysis; care is needed to avoid contamination of the sample and to protect the operator from possible infection or poisoning

FIGURE 14.14 Equivalent portions of DNA molecules from two different people showing similarities and differences between exon and intron regions; intron regions are used for forensic DNA analysis

- determine the length (i.e. number of nucleotides or bases) of these copied segments by electrophoresis
- compare samples from different sources or persons to see if they match.

## Making multiple copies of selected segments

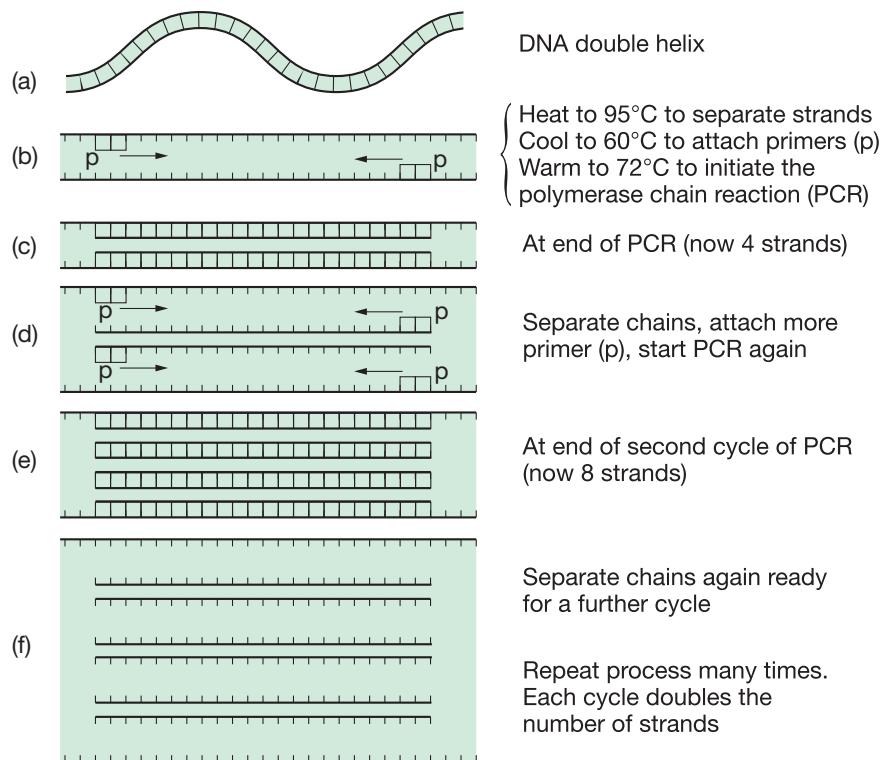
Portions of a DNA molecule can be copied by using what is called the **polymerase chain reaction**, often abbreviated to PCR. This works in a similar fashion to normal duplication of DNA in living cells.

Part of the process of cell division in living organisms is the duplication of the DNA in the cell. This occurs by the double helix unwinding and by each helix making its partner helix (its complementary helix): the end result is two DNA molecules, each with one strand from the original molecule and one newly synthesised strand.

If a pair of markers, called **primers**, is placed at the beginning and end of the segment of DNA we want to duplicate, the enzyme DNA polymerase can synthesise the complementary chains for both strands of that segment of DNA starting at a primer. The process can be repeated many times and so produce numerous copies of the required segment. This procedure for **PCR amplification** of segments of DNA, as it is called, is shown in Figure 14.15.

If several different primer pairs are used, we can duplicate fragments from several positions along the DNA molecules. Currently in Australia a mixture of ten primer pairs is used to grow fragments simultaneously at ten sites.

**FIGURE 14.15**  
Making multiple copies of a segment of DNA by using the polymerase chain reaction (PCR). The cycle is commonly repeated 28 times



Because a person has two types of DNA—one from each parent—each primer pair will have grown two DNA fragments—one from each original type of DNA. These fragments may be the same or different.

## Determining the length of the synthesised fragments

The synthesised DNA fragments are then separated by electrophoresis using a polyacrylamide gel. The longer the fragment, the more slowly it moves through the gel. A standard sample containing a mixture of polynucleotides of known chain lengths (number of base pairs) is run simultaneously and so the number of base pairs in the synthesised fragments is obtained by comparing the positions of the DNA fragments in the sample with those in the standard.

To detect the bands after electrophoresis and to sort out which bands come from which primer pairs, one member of each primer pair has a fluorescent 'tag' attached to it. This is a portion of a molecule that when hit by u.v. light emits visible light. Different tags emit light of different colours (usually yellow, blue and green). A laser shines u.v. light on the gel and a detector is able to detect the emitted fluorescent light and identify its colour. The detector determines the presence of a band and from the colour identifies the primer pair it came from and by comparison with the standard the operator determines how many base pairs the DNA fragment contains.

The non-genetic (or intron) material that is being amplified (or 'grown') for this analysis generally consists of multiple repeats of certain four-base units, for example –CGGT–CGGT–CGGT– or –ATTC–ATTC–ATTC–ATTC– repeated from 10 to 80 times, where C, G, A, T are the bases in Figure 14.11. Rather than record the number of base pairs in each fragment, the common practice is to record the number of repeat units, called **short tandem repeats (STRs)**. In the two examples just given there are three and four repeat units respectively.

## A DNA profile

Each pair of primers attaches to a DNA molecule at a certain known position: the above analysis tells us how many base pairs or how many repeat units there are in the synthesised fragments that start from those positions. Remember that there were two synthesised fragments per pair of primers because there were two types of DNA—one from each parent. This information can be compiled into a **DNA profile** which gives the number of repeats in each of the two fragments that formed from each of the locations used. For example, a possible profile might be:

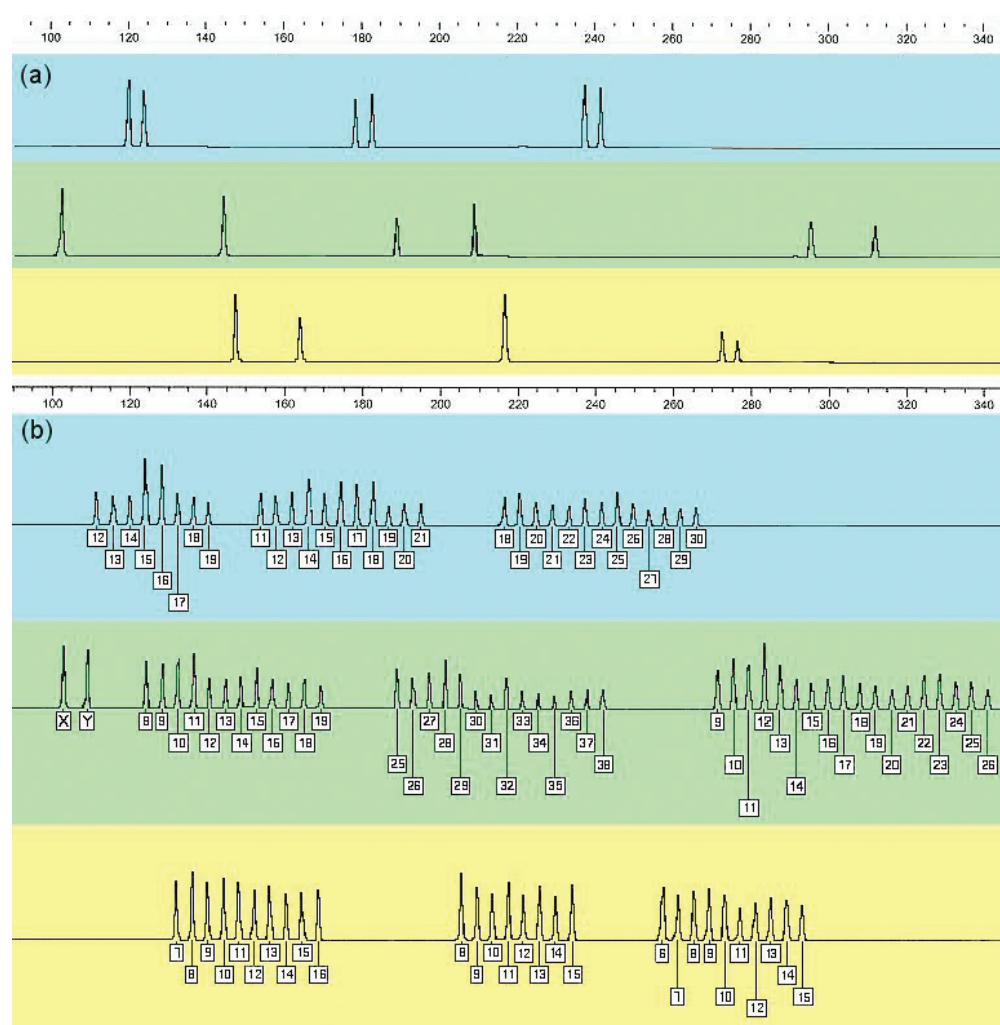
Location <sup>a</sup>	L	M	N	O	P	Q	R	S	T	U
Number of repeats	<sup>b</sup>	33, 34	23, 25	18, 18	22, 26	18, 23	37, 37	12, 16	32, 32	39, 46

<sup>a</sup> Scientists use particular names or 'addresses' for these locations (called loci) that include the identity of the chromosome and the position on it.

<sup>b</sup> one location gives the sex only: xx for female, xy for male.

At any particular locus (position) the number of repeats that can occur is limited: for example at position M the only numbers of repeats that can be found may be 32, 33, 34, 35 and 36: that is, there are only five possible repeat numbers. For position N, 10 different repeat numbers may be possible. If there were only five repeat numbers possible for each of the 9 positions in the above table (the tenth only tells the sex), then at each position there would be 15 possible combinations (remember 12, 13 is equivalent to 13, 12—order is not significant so by convention the smaller number is always given first) so with nine loci the

**FIGURE 14.16**  
 Electrophoresis results for a forensic DNA analysis; the peaks correspond to bands on the electrophoresis gel. **a** is the sample being analysed while **b** is a standard that contains all possible fragment lengths that can occur at each position used for the analysis. Each peak in the standard is labelled with the number of short tandem repeats that it contains. The blue, green, yellow shading on the chart represents the fluorescent colours emitted by the bands; the different colours allow the peaks (bands) to be assigned to the correct positions (loci) on the DNA. The chart has been simplified to some extent for teaching purposes



number of possible combinations would be  $15^9 = 4 \times 10^{10}$  (compare with the world population of  $6 \times 10^9$ ). In other words the chance of two people having the same profile would be less than 1 in  $4 \times 10^{10}$ . On average there are more than five repeat numbers possible per position, so this is an overestimate of the likely chance of a coincidental match.

The following example is too simple to be realistic but it illustrates the method used to identify the source of a DNA sample.



### Example 1

Suppose that we had a sample from a crime scene and samples from three suspects. Suppose we analysed all four samples using five primer pairs, which set off synthesis at five positions (or loci). Let us call the positions H, I, J, K, L (see the note under the table on p. 503 about labelling). The electrophoresis analysis gives us the number of repeats in the two chains formed from each of the five positions in each of the samples. These results are shown in Table 14.2. To identify the suspect whose DNA matches the sample from the crime scene, we look to see which suspect's sample has produced identical numbers of repeats for each position.

**TABLE 14.2 DNA profiles for a crime scene sample and three suspects (greatly simplified)**

Position on DNA	Number of repeat units at the position			
	Crime scene sample	Suspect A	Suspect B	Suspect C
H	23, 26	21, 22	23, 26	23, 25
I	32, 34	32, 32	32, 34	31, 36
J	19, 23	19, 24	19, 23	22, 22
K	15, 18	17, 20	15, 18	19, 22
L	12, 15	10, 13	12, 15	10, 18

We see that suspect B's repeat numbers exactly match those of the crime-scene sample. This shows that the sample came from suspect B; it could not have come from suspect A or C.

This illustration used only five loci. Forensic scientists more commonly use ten loci (sex plus nine other). The more loci that are used, the smaller the chance of a coincidental match. The chance of different persons producing eighteen identical repeat numbers (from nine loci) is negligible.

## Forensic versus medical/scientific DNA analysis

What has just been described is the method currently being used in Australia for DNA analysis for forensic purposes; that is, for the purpose of identifying the person from whom a biological sample came. It is virtually of no use medically or scientifically. For the medical and scientific study of DNA quite different methods of DNA analysis are used: they concentrate on the exon (genetic coding) regions of DNA, not the intron regions.

There has been intense medical and scientific study of DNA in recent decades, aimed, among other things, at:

- identifying and characterising genes in the DNA molecule
- identifying the variations in genes that lead to genetic abnormalities (such as cystic fibrosis and phenylketonuria) and to susceptibilities to certain diseases (such as breast cancer)
- determining the complete sequence of nucleotides (and the genes) along all the strands of the human DNA molecules, the so-called *human genome project* that was completed in 2000, after an unprecedented cooperative effort by thousands of scientists around the world.

For such studies, DNA molecules are generally isolated from individual chromosomes, then cut into smaller pieces (100 to 200 nucleotides) by what are called *restriction enzymes*. These smaller pieces are cut up further by chemical reactions, then the sequence of nucleotides determined by using electrophoresis and fluorescent or radioactive tags. Because these small pieces overlap, the sequence of nucleotide in the longer fragments can be worked out and ultimately the sequence along the whole DNA molecule. The procedure is similar to that used for sequencing proteins (Section 14.6).

The techniques currently used for forensic DNA analysis are 'spin-offs' from the methods originally developed for scientific research into DNA.

## 14.17 USES OF DNA ANALYSIS

Forensic scientists use DNA analysis for:

- identifying the person who produced a biological sample found at a crime scene: typical samples are blood, sperm, saliva, skin and hair follicles<sup>†</sup> with blood or saliva being preferred
- identifying the father of a child in disputed paternity cases
- establishing other familial links when there is a need to verify the claim of one person to be a relative of another person.
- identifying bodies from disasters such as the South-East Asia tsunami of December 2004, aeroplane crashes and terrorist bombings such as the ones in New York in 2001, Bali in 2002 and Madrid in 2004.

In DNA analysis the certainty of the identification of the person from whom the sample came is such that about the only way an accused person can dispute the analysis is to try to establish that the sample did not necessarily identify the actual culprit of the crime or that the crime scene sample had been contaminated, tampered with or substituted for; this is one reason for using great care with the chain of custody as discussed in Section 13.1.

The advantages of DNA analysis are:

- it is *extremely accurate* in identifying the source of the sample (though that may not necessarily be the culprit of the crime)
- it is *extremely sensitive*—only a minute sample is required (because of the PCR amplification).

The disadvantages are that

- it is quite time-consuming to perform
- it requires a specialised laboratory containing expensive equipment with well-trained technical staff and
- it can only be applied to certain biological samples such as blood, semen, saliva or hair follicles.

Some other techniques such as mass spectrometry (Sections 15.4 to 15.7) and infrared spectroscopy (Section 13.6) can be applied to a wider range of forensic samples (that is, not restricted to biological samples), but where DNA analysis is applicable it is much more sensitive than those other techniques.

## 14.18 DATA BANKS

Because of the great power of DNA analysis to identify persons guilty of criminal offences, moves are afoot in many parts of the world to establish data banks of DNA.

**DNA data banks** are collections of DNA profiles with which law enforcement authorities can compare samples collected from crime scenes, and where a match is found, from which they can obtain the identity of the person from whom the database sample came.

In Australia in the past decade various states have set up DNA data banks and now these have been combined into a national data bank. What this data bank records is just the DNA profile which consists of the sex and nine pairs of numbers, the number of tandem repeat units at each of the nine selected

<sup>†</sup> It is the hair follicle (root) that contains DNA, not the hair fibre itself.

intron regions that are used in the analysis; similar data from crime scenes from unidentified people are also stored.

The data bank is used in a similar way to a bank of fingerprints. A newly collected sample can be compared with the stored profiles, and if a match is found then the person from whom the sample came can be conclusively identified; with an extensive database it could be a very powerful tool for solving crimes. To date the only people required to provide DNA samples are convicted criminals in jails.

There is considerable opposition to such DNA data banks from civil liberties groups who claim that the widespread collection of DNA samples is an invasion of an individual's privacy. The argument is similar to the one used against the widespread collection of fingerprints. Often innocent suspects volunteer their DNA in order to clear themselves, but civil libertarians argue that people should not have to prove their innocence. While there is pressure from law enforcement authorities to make it compulsory for suspects to provide DNA samples, at the moment it is voluntary (unless a court orders otherwise) and there is considerable support for the existing situation.

It should be emphasised that the collection of the type of DNA profile currently being used is no more or less invasive of privacy than the collection of fingerprints. Fears that such DNA information could be used by insurance companies to weed out high risk cases or by potential employers to eliminate applicants who may have a tendency to certain diseases are completely unfounded, because the forensic DNA profile is quite useless for any genetic diagnosis purposes; it relates to the intron regions, not the exon regions of DNA. However there is considerable concern within the medical profession that the availability of a wide range of genetic diagnostic tests could lead to pressure from insurance companies and employers for applicants to provide such genetic information, but that is a completely separate issue from the matter of forensic DNA data banks.

#### WEBSITES

<http://www.crimtrac.gov.au/dna.htm>

(click on DNA; a simple account of DNA profiling, how it is done, history and data bases)

<http://www.industry.gov.au/biotechnologyOnline/human/dnaprofile.cfm>

(an introduction to DNA profiling; click on *DNA profiles for forensic use* and *DNA can reveal family relationships* in the left-hand column. You might enjoy solving the two problems in *DNA profiling interactives*.)

[http://www.ornl.gov/TechResources/Human\\_Genome/home.html](http://www.ornl.gov/TechResources/Human_Genome/home.html)

(information about the human genome project and DNA generally though not strictly relevant to NSW HSC; click on *Education* for general information. There are some good graphics in the *Picture gallery*, though slow to download by dial-up connection.)



#### Exercises

- \*33 To establish which of two males was the father of a baby, DNA analyses were done on samples from the baby, the mother and the two males. The method used was as described in Section 14.16 using six primer pairs for PCR amplification (i.e. 'growing' six fragments from the DNA). The numbers of repeat units in each of these fragments (as determined by electrophoresis) are tabulated below. Which male is the father of the baby? (Use the mother's DNA profile to identify the baby's fragments that came from her, then determine the male from which the baby's other fragments came.)



Position on DNA	Number of repeat units at the position			
	Mother	Baby	Male A	Male B
P	21, 22	19, 22	20, 22	19, 25
Q	37, 40	37, 42	32, 35	40, 42
R	17, 24	17, 24	19, 19	24, 26
S	14, 17	13, 17	14, 18	12, 13
T	25, 29	23, 25	28, 30	23, 28
U	13, 16	10, 13	13, 17	10, 12

**34** What is the most likely source of error in using DNA to identify the culprit of a crime?

**35** Three men were suspected of raping a woman who suffered abrasions and loss of blood in her struggles during the incident. Two of the suspects had blood on their clothes which they claimed came from scratches they had received in other activities. DNA analyses (using just five loci instead of the usual nine) were performed on saliva swabs taken from the three suspects and from the victim, on the blood on the suspects' clothes and on a vaginal swab from the victim. The results are tabulated below. What can you deduce from the DNA analyses?

Position on DNA	A	B	C	D	E
Victim's vaginal swab	20, 21, 26, 27, 29	32, 34, 35, 37, 38	13, 14, 16, 17, 18, 19	12, 13, 14, 15, 17, 18	21, 23, 25, 28
Victim <sup>a</sup>	20, 26	37, 38	13, 18	14, 15	23, 28
Suspect 1 <sup>a</sup>	22, 28	33, 39	15, 17	11, 16	24, 25
Suspect 2 <sup>a</sup>	21, 27	34, 35	16, 19	13, 17	21, 28
Suspect 3 <sup>a</sup>	26, 29	32, 37	14, 17	12, 18	23, 25
Blood on suspect 1	22, 28	33, 39	15, 17	11, 16	24, 25
Blood on suspect 3	20, 26	37, 38	13, 18	14, 15	23, 28

*a from saliva swab*

- \*36 a** Currently on the Internet there are laboratories offering paternity testing by mail. People can mail in DNA samples (saliva swabs, blood spots, hair follicles) of mother, child and suspected father to these laboratories which then send back the results; this can be done without the consent or knowledge of the mother or child. Suppose that a man used such a service to establish that he was not the father of the 'son' for whom he was paying considerable child support. Discuss the ethics of this procedure and the usefulness of this evidence in a possible court case to have his child-support payments discontinued.
- b** Also currently a mother can refuse to provide DNA samples from herself and her child to allow her divorced husband and alleged father of the child to have paternity testing done (again possibly to have child-support payments cancelled if he is not the father). Discuss the ethics of this situation.
- 37** Determine the sex and DNA profile of the sample being analysed in Figure 14.16.

## Important new terms

You should know the meaning of the following terms.

a person's DNA (p. 500)  
amide (p. 484)  
amine (p. 481)  
amine functional group (p. 481)  
amino acid (p. 481)  
biuret test (p. 488)  
chromatography (p. 490)  
dipeptide (p. 484)  
DNA data bank (p. 506)  
DNA (deoxyribonucleic acid) (p. 497)  
DNA profile (p. 503)  
electrophoresis (p. 492)  
enzymes (p. 480)  
exons (p. 501)  
fibrous proteins (p. 480)

globular proteins (p. 480)  
introns (p. 501)  
isoelectric point (p. 494)  
mobile phase (p. 490)  
ninhydrin test (p. 488)  
nucleotide (p. 497)  
paper chromatography (p. 490)  
PCR amplification (p. 502)  
peptide bond (p. 484)  
polymerase chain reaction (PCR) (p. 502)  
polypeptide (p. 485)  
primers (p. 502)  
protein (p. 480)  
short tandem repeats (STRs) (p. 503)  
stationary phase (p. 490)  
tripeptide (p. 485)  
zwitterion (p. 483)

## Test yourself

- 1 Explain the meaning of each of the items in the 'Important new terms' section above.
- 2 Describe the difference in structure and function of fibrous and globular proteins. Name examples of each.
- 3 Draw the neutral molecule and zwitterion structures of two amino acids. Explain why the zwitterion form is the dominant one.
- 4 Draw structures of and name five amino acids.
- 5 Draw the structure of a dipeptide and write an equation showing its formation.
- 6 Draw a general structure for a protein.
- 7 How would you hydrolyse a dipeptide? Write an equation for the reaction. How would you completely hydrolyse a protein?
- 8 What are the three steps involved in determining the primary structure of a protein?
- 9 Describe the ninhydrin and biuret tests, including the results they give. What compounds do they identify?
- 10 What can you deduce about a compound that gives a positive ninhydrin test but a negative biuret test?
- 11 Explain how you would use paper chromatography to separate a mixture of amino acids. How would you identify the separated amino acids?
- 12 What is the basis for a separation of amino acids in paper chromatography? If two amino acids do not separate completely, how would you try to improve the separation?
- 13 Explain how you would separate a mixture of amino acids by electrophoresis. What is the basis for this separation?

- 14** Why does changing the pH of the electrolyte being used often improve the separation in electrophoresis?
- 15** What are the advantages and disadvantages of electrophoresis compared with paper chromatography for separating amino acids?
- 16** Give the full name for DNA and describe its structure: include a schematic drawing of it.
- 17** What elements are present in DNA?
- 18** Draw a structural formula for one nucleotide.
- 19** If a sample of DNA were completely hydrolysed, how many compounds would be formed? Name them.
- 20** What is the function of DNA in organisms?
- 21** Outline the method used for analysing DNA for forensic purposes.
- 22** Why is forensic analysis of DNA based upon the non-genetic parts of DNA molecules (that is, upon ‘junk’ DNA)?
- 23** What is meant by PCR amplification and why is it so important in analysing DNA?
- 24** For forensic purposes what is meant by a person’s DNA profile?
- 25** Outline the advantages and disadvantages of setting up a national DNA data bank.

# Instrumental analysis

## IN THIS CHAPTER

Destructive and non-destructive testing  
Gas–liquid chromatography  
High performance liquid chromatography  
Mass spectrometry  
Cracking patterns  
Forensic use of mass spectrometry  
Other designs of mass spectrometers  
Electromagnetic radiation

Separating light into its components  
Emission of light from atoms  
Explaining emission spectra  
Atomic emission spectroscopy  
Use of emission spectra by forensic chemists  
Chemical progress and forensic outcomes

Many of the analyses described so far in this book require samples of at least a few milligrams or more. Often the samples available to forensic chemists are much smaller than this, so forensic chemists often need very sensitive analytical techniques.

In addition there is often the problem that the chemist is not allowed to damage the object to be analysed.

## 15.1 DESTRUCTIVE AND NON-DESTRUCTIVE TESTING

Most of the analyses discussed so far have essentially destroyed the sample by subjecting it to chemical reaction.

If the original sample is not recoverable, the analysis is called a **destructive analysis**; sometimes the term **destructive testing** of a material is used.

Often the forensic chemist is not allowed to carry out a destructive analysis, for example in the verification that a newly discovered artwork is genuine, establishing the authenticity of historical artefacts or ancient manuscripts, or investigations to prove that the metal in jewellery is a precious one (gold or platinum) and not a cheap alloy. **Non-destructive testing** is required in such cases.

There are some analytical techniques available for non-destructive testing of materials or objects; examples are X-ray analysis, neutron activation and reflectance spectroscopy. However such techniques are beyond the scope of this book.

As an alternative to non-destructive testing, the analyst may be allowed to take a very small sample from the object, such as a fragment of paint from an unobtrusive part of a painting or a scraping of metal from a concealed part of a piece of jewellery. Because such samples are generally very small, the analyst needs to have very sensitive techniques available. In this chapter then we shall consider four such sensitive analytical techniques:

- 1 gas–liquid chromatography
- 2 high performance liquid chromatography
- 3 mass spectrometry and
- 4 atomic emission spectroscopy.

## 15.2 GAS-LIQUID CHROMATOGRAPHY

Gas chromatography was briefly described in Section 6.2. Chromatography generally was introduced in Section 14.8. You should re-read those sections before proceeding.

There are two types of gas chromatography:

- *gas–solid chromatography*, which separates substances on the basis of their different strengths of adsorption on the solid and which is widely used for analysis of gases and volatile liquids, and
- *gas–liquid chromatography*, which separates substances on the basis of different solubilities in the stationary phase.

Gas–liquid chromatography, GLC, is the more versatile of the two in that it can separate a broader range of compounds, the main restriction being that the compounds must readily vaporise at temperatures below about 250°C. GLC is widely used for forensic analyses.

### Basic arrangement

In a typical gas chromatograph the sample to be analysed (either a mixture of liquids or a solution) is introduced by a syringe into the hot flowing carrier gas (generally helium or argon) as shown in the diagram at the top of p. 197. The sample vaporises immediately and the analysis proceeds by the components repeatedly dissolving into the liquid stationary phase and vaporising back into the gas again. The most frequently used columns today are *capillary columns*; these are long hollow silica tubes typically 0.1 to 0.5 mm internal diameter and from 10 to 100 m in length. The internal walls of the capillary tube are coated with a non-volatile liquid, the stationary phase. Figure 15.1 shows a typical capillary column. The more soluble a substance is in the liquid film, the more slowly it moves through the column.

FIGURE 15.1  
A typical capillary column for a gas–liquid chromatograph. This silica column is 30 m long with an internal diameter of 0.15 mm; the internal surface of the column is coated with the non-volatile liquid polydimethylsiloxane. This ‘column’ has been wound into a coil of about 20 cm diameter

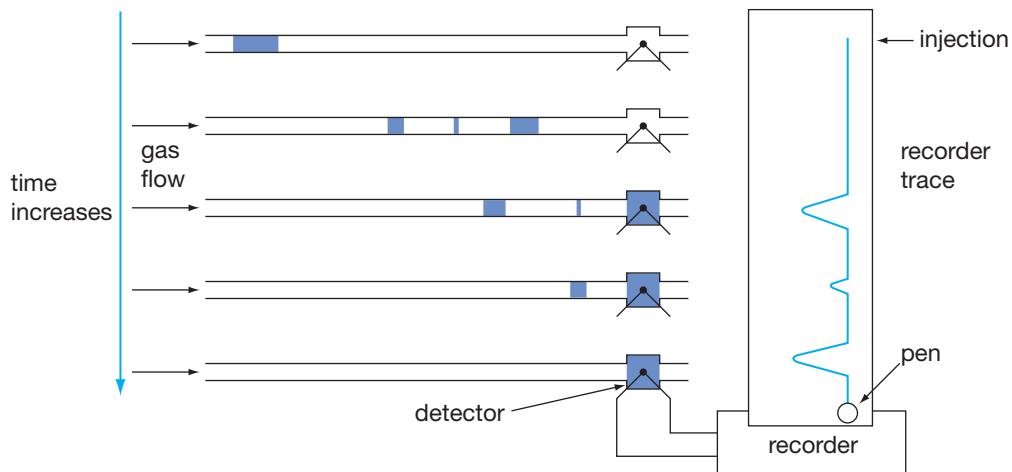


### Detecting the separated substances

At the end of the column is a detector which signals when a component is leaving the column (that is, passing through the detector). This is illustrated in Figure 15.2; the recorder trace is called a *chromatogram*. In the last decade or so computer screens have replaced pen recorders. The area under each peak in the trace is a measure of the amount of that substance present.

A *flame ionisation detector* is commonly used to signal when each substance emerges from the column. This consists of a small

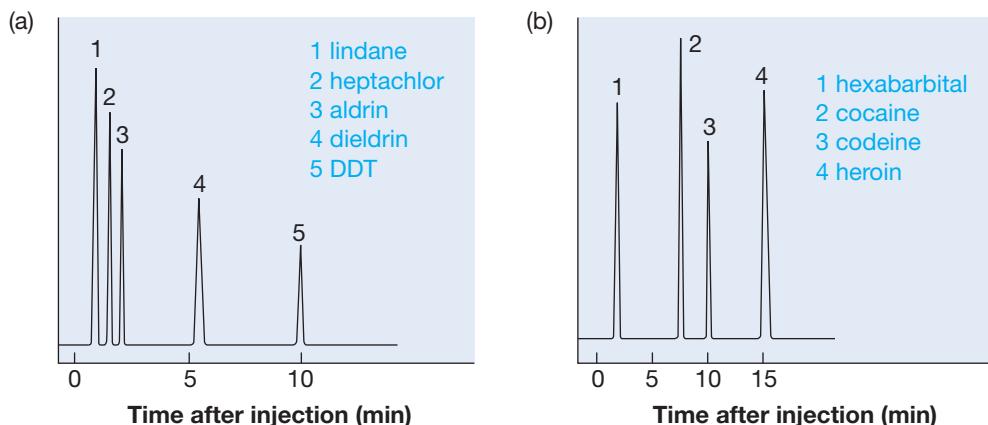
flame with a negatively charged electrode located just above it. No current flows through the detector circuit when just pure carrier gas is flowing through the detector, but when a component of the mixture flows into the detector, it is decomposed by the hot flame and produces some positive ions. These are collected by the negative electrode and so a small current flows through the detector circuit. This is amplified and displayed either on a recorder (older instruments) or on a computer screen (newer instruments). There are other detectors in use also, particularly for compounds that do not burn readily.



## Identifying compounds

Compounds are generally identified by the time (after injection) that they take to reach the detector (called the **retention time**) when conditions (such as oven temperature and gas flow rate) are carefully controlled. This means that pure samples of all likely compounds in the mixture must be available and their chromatograms run under the same conditions as to be used in the analyses and their retention times recorded. For quantitative work the instrument must be calibrated by measuring peak areas for known amounts of compound injected. If the peaks are sharp, peak height can be used instead of peak area.

Two typical gas chromatograms are shown in Figure 15.3.



ABOVE A typical gas chromatograph, showing the oven containing the column and how the sample is injected; during an actual analysis the oven door would be closed

FIGURE 15.2 Schematic separation of a mixture by GLC, showing how the chromatogram (recorder trace or computer display) is generated

FIGURE 15.3 Capillary column gas-liquid chromatograms for (a) some common pesticides (b) some commonly abused drugs

Because the separation is based upon the different solubilities of the substances being analysed in the stationary phase, the degree of separation

can often be improved by changing the polarity of the stationary phase. Consequently analysts generally have several columns available, with different liquids of different polarities coated on their internal surfaces. If one column does not bring about a complete separation of the components of the mixture, another column is tried.

## Forensic use of GLC

Gas–liquid chromatography is very sensitive; it can routinely detect microgram quantities of substances and in many cases quantities in the nanogram range. Hence it is widely used by forensic chemists to identify pesticide residues in foods, illegal drugs and steroids in athletes, trace pollutants in air and water and a wide variety of substances found at crime scenes. It is relatively quick and easy to perform (though great care is needed to avoid sample contamination), but the instruments are quite expensive.

## Terminology

The following terminology applies to both GLC and HPLC (next section). The technique is called *chromatography*, the instrument used is a **chromatograph**, and the plot of detector signal versus time is called a **chromatogram**.

## 15.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

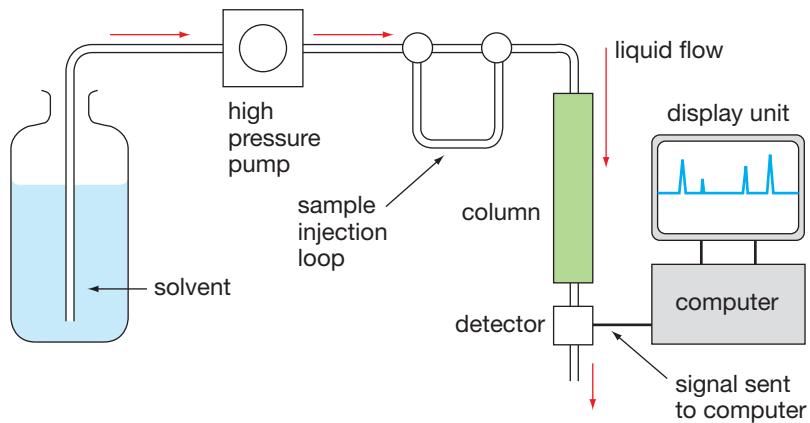
In high performance liquid chromatography, HPLC<sup>†</sup>, mixtures are separated based upon their differing solubilities in two liquids, one stationary and one moving.

## Basic arrangement

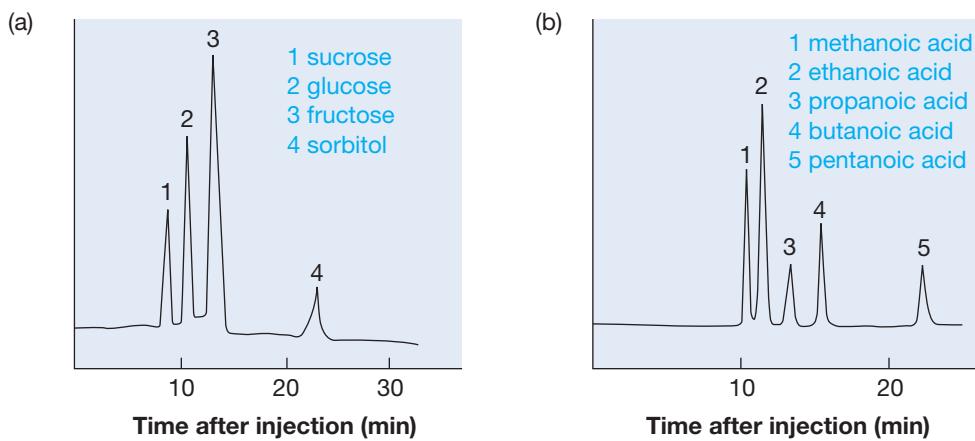
The column is usually a metal tube 15 to 30 cm long and about 3 to 10 mm internal diameter. It is packed with very small, uniformly sized synthetic silica spheres (10 to 20 µm diameter) on the surface of which is adsorbed a liquid (the stationary phase). A solution of the sample to be analysed is admitted to the top of the column, then a pump pushes solvent through the column at high pressure to wash the components of the sample down the column. High pressure is needed because of the high resistance to flow of the tightly packed small particles. A suitable detector such as a refractive index monitor or an ultraviolet light absorption cell detects the various components of the mixture as they come out the bottom of the column. It feeds its signal to a computer, which displays the signal as a function of time after the start of the analysis; the chromatogram forms in the same way as shown in Figure 15.2. Figure 15.4 is a schematic arrangement of such a chromatograph; typical HPLC chromatograms are shown in Figure 15.5.

As with GLC, substances are identified by the time taken to wash through the column (the *retention time*) under controlled conditions such as temperature and solvent flow rate or by comparison with standard known samples run under identical conditions. From the size (height or area) of the peak the actual amount of the substance can be estimated.

<sup>†</sup> Originally HPLC was high *pressure* liquid chromatography, a name that indicated its key feature. The name changed when marketers took over from the scientists.



**FIGURE 15.4**  
A schematic arrangement of a high performance liquid chromatograph



**FIGURE 15.5**  
Two typical HPLC chromatograms: (a) an analysis of apple juice for sugars (b) analysis of a mixture of alkanoic acids

## Basis of separation

In HPLC substances are separated on the basis of their *different solubilities in both the stationary and mobile phases*. A substance with a high solubility in the mobile phase and a low solubility in the stationary phase will move through the column at a greater rate than one that has a low solubility in the mobile phase and a high one in the stationary phase. As with GLC, because solubility depends upon polarity of the solvent, separations can often be improved by changing the stationary phase (changing the column). However HPLC has the added flexibility of being able to change the mobile phase also; it is more usual to change the solvent than to change the column.

## Forensic use of HPLC

High pressure liquid chromatographic analyses are usually performed at room temperature and, since they do not involve vaporising the sample, can be used for mixtures of non-volatile substances such as carbohydrates, fats and fatty acids.

As with GLC, HPLC is widely used by forensic chemists for a great variety of analyses such as the ones listed for GLC, but also for ones where high temperatures cannot be used such as detecting traces of explosives. HPLC is often used to analyse biological samples such as polypeptides from proteins.

As with GLC, the technique is quick and simple, but great care is needed to avoid contamination, and again instruments are expensive.

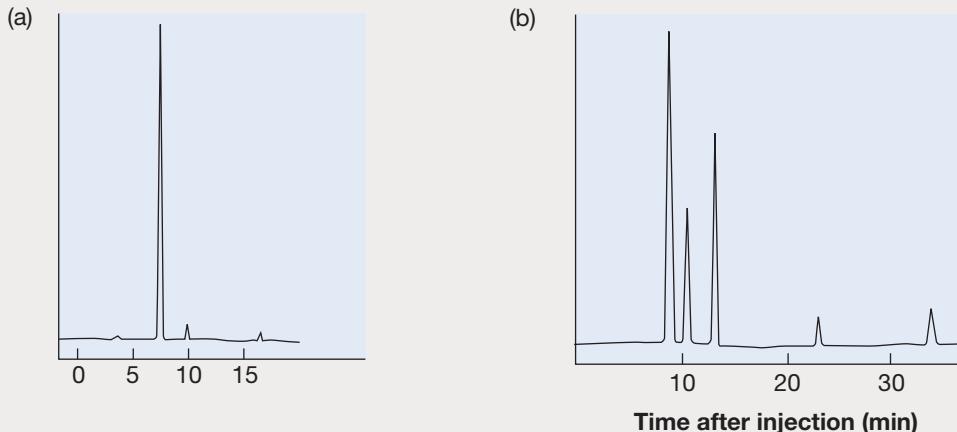


Both GLC and HPLC provide forensic chemists with ways of separating and identifying complex organic and biological samples. A major advantage of these techniques is that they first separate mixtures of complex substances into individual compounds, then provide a method of identifying them (via retention times, provided pure samples of the compounds involved are available). There are no other techniques that can analyse mixtures as effectively. Another advantage is that both techniques are extremely sensitive, being able to identify nanogram quantities. DNA analysis is more sensitive, but it can be applied to only a limited range of samples.

A high performance liquid chromatograph; the column is the white tube being held by the retort clamps. The inlet system is behind door (a); (b) and (c) are high pressure pumps (to supply a mixture of two solvents to the column from the large bottles), (d) is the display unit; the boxes behind the column contain the two detectors available on this instrument while above them is the overall controller for the unit

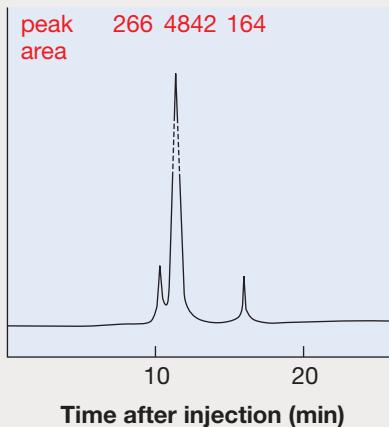
### Exercises

- 1** A mixture of pesticides was analysed by gas–liquid chromatography. The conditions used were as for Figure 15.3(a). The recorder trace showed a very large peak at a time of 1.6 minutes after sample injection, and small but definite peaks at 2.7 and 5.6 minutes. What do you conclude about the composition of the sample? Explain fully.
- 2** Solvent extraction was used to extract any likely drugs of addiction from a sample of the blood of a drug addict. The extract was then analysed by gas–liquid chromatography under the same conditions as were used for Figure 15.3(b). The result is shown at (a) below. What drug (if any) is present?



- 3** HPLC was used to check that a sample of apple juice had not been adulterated by the addition of some other substance(s). The resulting chromatogram, using the conditions of Figure 15.5(a) is shown at (b) above. Is the apple juice ‘pure’? If not, how many substances have been added to it? Identify some or all of them (if possible). Explain your reasoning fully.

- 4 A sample of acetic acid was analysed by HPLC to check for any contamination using the conditions of Figure 15.5(b). The chromatogram is shown below. What if any contaminants are present in the sample and what is their approximate percentage in the sample? Why are your percentages only approximate?



## 15.4 MASS SPECTROMETRY

**Mass spectrometry** is a technique that measures the masses and relative intensities of the positive ions formed when a sample is bombarded with electrons or irradiated with u.v. light. The instrument that does this is called a **mass spectrometer**.

One design of mass spectrometer is shown in Figure 15.6. It consists of an evacuated tube,  $AA$ , with a semicircular section located between the poles of a strong magnet,  $B$ . There is an ion source at one end and an ion collector at the other. A gaseous sample is admitted to the source and positive ions are produced by electron bombardment (at  $EB$ ): this is shown schematically in Figure 15.7.

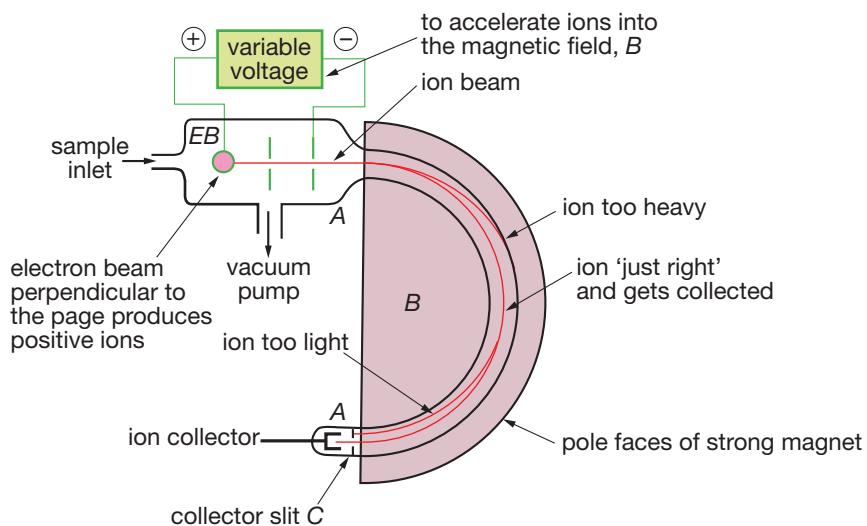
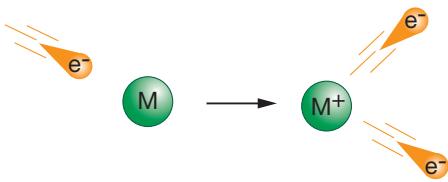


FIGURE 15.6  
A simple mass spectrometer

These positive ions are collimated into a fine beam and accelerated through an electric field into the magnetic field. Magnetic fields cause moving charges to follow circular paths. With fixed accelerating voltage,  $V$ , and magnetic field strength,  $B$ , the radius of the path is dependent upon the mass-to-charge ratio of the ion. If the values of  $V$  and  $B$  are such that the radius,  $r$ , for argon (say)

corresponds to that of the apparatus, then argon ions will pass through the collector slit,  $C$ , and reach the collector. Krypton atoms with greater mass will follow a path of greater radius and will not pass through the collector slit; neon, of lesser mass, will follow a path of smaller radius and again will not be collected.

**FIGURE 15.7**  
Formation of a positive ion by electron bombardment:  $M$  is an atom or a molecule

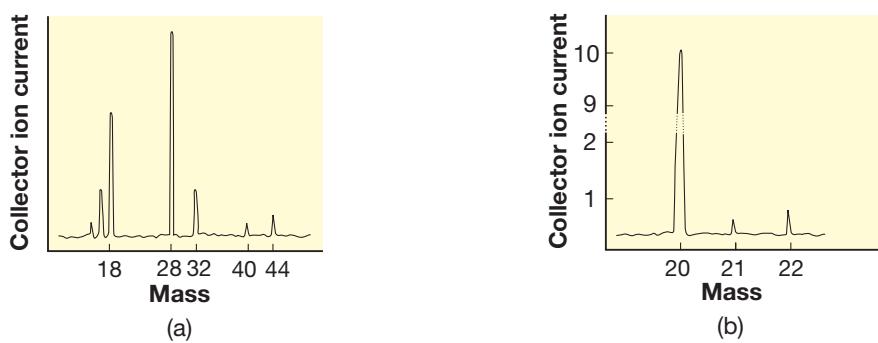


## Atomic masses and isotopes

By measuring  $V$ ,  $B$  and  $r$ , the value of the mass-to-charge ratio of the ion collected can be calculated, and if it is assumed that the charge is equivalent to one electron (the commonest situation), then the mass can be calculated. In this way, accurate atomic or molecular masses are obtained. Determination of atomic masses was the major use of mass spectrometry when the technique was first developed in the 1910s.

Today a mass spectrometer is used to produce what is called a mass spectrum. By varying the accelerating voltage,  $V$ , different ions can be focused onto the collector slit one at a time. *A record of the ion current (through the detector) as a function of accelerating voltage (that is, as a function of mass-to-charge ratio), as in Figure 15.8, is a mass spectrum.* The current through the detector is proportional to the number of ions of the mass being collected. A mass spectrum can be used to identify the components present in a simple gas mixture (such as air as in Figure 15.8(a)), or to determine the isotopes that make up an element.

**FIGURE 15.8**  
Typical mass spectra:  
(a) of residual air, showing peaks due to  $O^+$ ,  $OH^+$ ,  $H_2O^+$ ,  $N_2^+$ ,  $O_2^+$ ,  $Ar^+$  and  $CO_2^+$ , (b) of neon, showing three isotopes



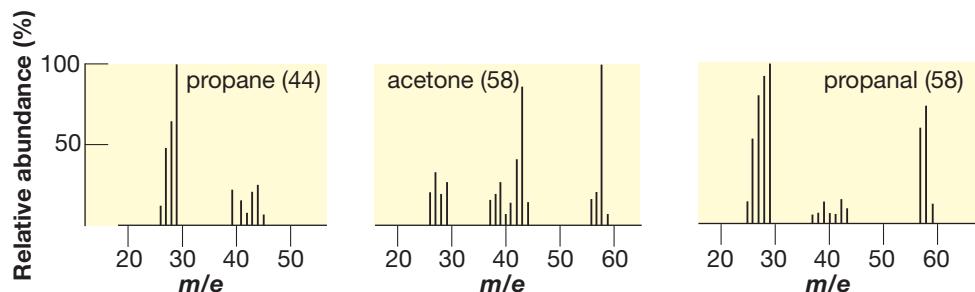
Francis Aston, in 1919, found that the mass spectrum of neon contained not just the one expected line at mass 20, but three lines (as shown from a modern instrument in Figure 15.8(b)). This directly demonstrated the existence of isotopes. In the next few years many elements were shown to be mixtures of two or more isotopes.

## 15.5 CRACKING PATTERNS

In the mass spectrum of air in Figure 15.8(a), water produces not just one peak at mass 18, but also peaks at 17 and 16. This occurs because the ion originally formed,  $H_2O^+$ , is unstable and some of it falls apart to form  $OH^+$  and then  $O^+$  (masses 17 and 16 respectively).

The mass spectra of molecular substances are generally quite complex: they contain peaks corresponding to many different masses as shown for propane,

acetone (propanone) and propanal in Figure 15.9. Multiple peaks appear from the one compound because the parent ion formed by direct electron bombardment of the molecule is generally unstable and breaks up in a variety of ways to form ions of smaller masses.

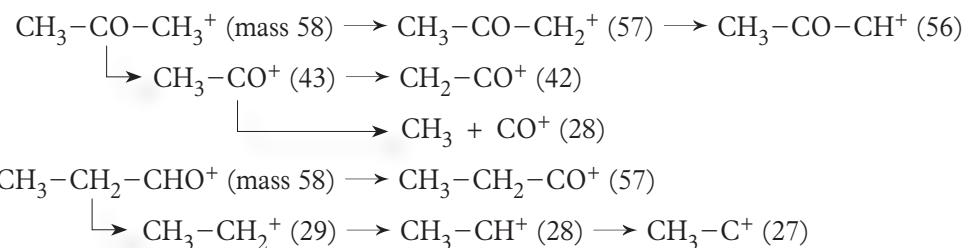


**FIGURE 15.9**  
Mass spectra of propane,  
acetone (propanone)  
and propanal; molecular  
weights are given in  
brackets

The peak with the largest mass to charge ratio in a mass spectrum is generally from the parent ion; it can give an estimate of the molecular weight of the compound. Often, however, it is not the most intense peak, and for some compounds there is no parent-ion peak at all, because the parent ion is so unstable that it breaks up almost as soon as it is formed.

When propane is admitted to the mass spectrometer, ion bombardment produces the parent ion,  $\text{CH}_3\text{---CH}_2\text{---CH}_3^+$  (mass 44, Fig 15.9). This easily loses one or two H atoms to form  $\text{CH}_3\text{---CH}_2\text{---CH}_2^+$  and  $\text{CH}_3\text{---CH}_2\text{---CH}^+$  (masses 43 and 42). In addition the parent ion can split off a  $\text{CH}_3$  group, forming  $\text{CH}_3\text{---CH}_2^+$  (mass 29) and by loss of further H atoms it forms masses 28 and 27.

The **cracking patterns** (as the collections of lines in mass spectra are called) for acetone ( $\text{CH}_3\text{--CO--CH}_3$ ) and propanal ( $\text{CH}_3\text{--CH}_2\text{--CHO}$ ) result from the following ion fragmentations:



These three compounds are relatively simple ones and lead to fairly simple mass spectra. As molecules become more complex, their mass spectra also become more complex because more and more fragmentation paths are possible. This means that there are more and more lines with differing relative intensities in the mass spectrum. As a result, compounds containing more than about 8 to 10 atoms have unique mass spectra. Consequently mass spectra can be used as ‘fingerprints’ for compounds.

# 15.6 FORENSIC USE OF MASS SPECTROMETRY

Because each compound (apart from very simple ones) has a unique mass spectrum, such spectra can be used to identify compounds. If a library of mass spectra is available, then the mass spectrum of an unidentified sample can be compared with those in the library and if an exact match is obtained, then

the sample can be confidently identified. Computers can be used to match unknowns with standards if the spectra are stored electronically. This is the major use of mass spectrometers by forensic chemists. There is one constraint: the operating conditions used to collect the mass spectrum of the unknown compound must be the same as those used to record the library spectra.

Even if the data bank of standard spectra contains no match for the sample being analysed, experienced operators are able to use the cracking pattern to deduce considerable information about the structure of the sample and often to identify it completely. This aspect of mass spectrometry is beyond the scope of this account.

## Solid and liquid samples

Although the analysis in a mass spectrometer occurs in the gas phase, solid and liquid samples can also be analysed. A solid or liquid sample is admitted into the high vacuum chamber of the mass spectrometer then slowly heated until some of the sample vaporises and drifts into the ionising electron beam. Microgram samples can be analysed in this way.

## Mixtures

Because individual compounds that contain more than about twenty atoms produce quite complex cracking patterns, mass spectra of mixtures (apart from very simple ones) are extremely complex and are generally too difficult to be resolved into individual compounds. Hence mass spectra are not very helpful for identifying the compounds in a mixture.

However if mixtures are first separated into individual compounds, for example by gas chromatography or high performance liquid chromatography, and then the pure compounds admitted to a mass spectrometer, the individual compounds can be identified by their cracking patterns. Today mass spectrometers are routinely coupled to gas chromatographs and high performance liquid chromatographs in order to identify the compounds as they emerge from the chromatographic column. This gives a more definite identification of the compounds than retention times alone: it is possible for two compounds to have the same retention time.

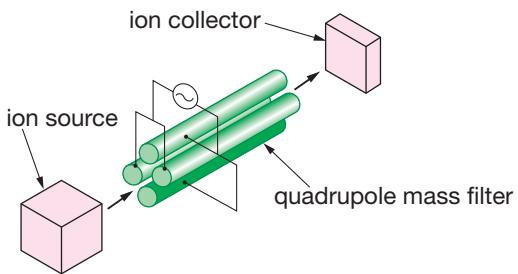
In order to work effectively in this way, the mass spectrometer needs to be able to scan the whole mass range (10 to 1000 or more) very quickly in order to process one chromatograph peak before the next one emerges. This requirement has led to the development of different designs of mass spectrometer.

## 15.7 OTHER DESIGNS OF MASS SPECTROMETERS

A wide variety of different designs for mass spectrometers is used today. The instrument described in Section 15.4 is a fairly old design: it uses a  $180^\circ$  sector magnetic separator (meaning that the ions travel through  $180^\circ$  in the magnetic field). Other designs use a  $60^\circ$  magnetic sector (ions travel through  $60^\circ$  only).

The part of the instrument that separates the ions according to mass is called the **mass filter**. Today several different types of mass filter are in use. A widely used one, called a quadrupole mass filter, is shown in Figure 15.10. This consists of four parallel metal rods with a direct voltage plus a radio-frequency voltage applied across opposite pairs. The ions oscillate down the space between the rods

and as the voltage is varied ions of different masses are able to get right through to the collector without hitting a rod and being lost.



Some mass spectrometers have two mass filters, one after the other. One is often a quadrupole and the other a magnetic sector filter.

Features that users desire are:

- high resolution (ability to separate ions of nearly identical mass)
- high scan speeds (ability to scan from masses 10 to 1000 in a few seconds)
- high sensitivity (ability to detect nanogram quantities).

Quadrupole mass spectrometers are able to scan large mass ranges very quickly and so are often used in conjunction with GLC and HPLC.

Mass spectrometry, often after chromatographic separation, is routinely used to analyse a wide range of industrial, environmental and forensic samples. For example prohibited performance-enhancing drugs in the urine of athletes are commonly detected in this way.

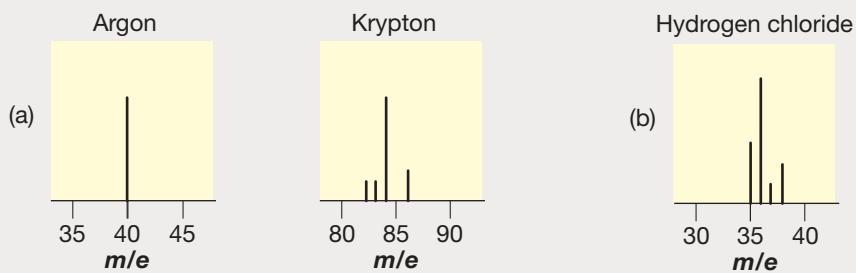
A quadrupole mass spectrometer; the black cylinder is the source where the sample is ionised and accelerated into the mass filter (inside the cream box); the filter is similar to the one in the inset

FIGURE 15.10  
A quadrupole mass filter



## Exercises

- 5 Portions of the mass spectra of argon and krypton are shown below in part (a). Explain why there is just one peak for argon but four for krypton.

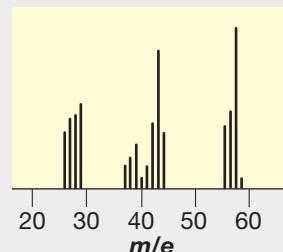


- 6 a Use a table of atomic weights to calculate the relative molecular mass of hydrogen chloride.  
 b The mass spectrum of hydrogen chloride has four peaks in the mass range 30 to 40 as shown in (b) above. Why is there no peak corresponding to the relative molecular mass calculated in (a)? Explain how this diagram establishes that there

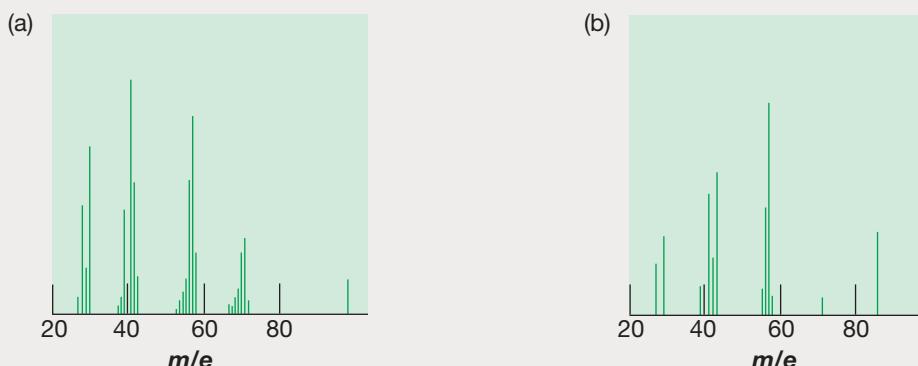
are two isotopes of chlorine. (*Hint:* we might reasonably expect the  $\text{HCl}^+$  ion to dissociate into H and  $\text{Cl}^+$ .) What are the mass numbers of the two isotopes?

What is their relative abundance? Explain how you decided this. Reconcile your conclusions here with your answer in (a).

- c The mass spectrum of chlorine contains peaks as mass to charge ratios of 70, 72 and 74 (as well as others between 30 and 40). Is this mass spectrum consistent with your conclusions from (b)? Explain. What peaks would you expect between masses 30 and 40?
- \*7 A chemist suspected that the laboratory supply of acetone was not pure so ran its mass spectrum. The result is shown below. Using the standard spectra in Figure 15.9, is the acetone pure or not? Why? If it is not pure what is the most likely contaminant?



- b A team of forensic chemists measured the mass spectra of two unidentified compounds under the same conditions as were used for recording the spectra in their data bank. The spectra of the unknowns are shown below while some of the spectra from their data bank are given in Figure 15.11. Identify the unknown compounds.



- 9 Mass spectrometers with low resolution are not able to separate the parent peaks of nitrogen gas, carbon monoxide and ethylene. Explain why. Would you expect a mass spectrometer capable of separating peaks with mass differences as small as 0.002 to be able to separate the parent peaks of these three compounds? Explain.

Before turning to atomic emission spectroscopy, the final instrumental technique to be discussed here, we need to consider electromagnetic radiation which is at the heart of that technique.

## 15.8 ELECTROMAGNETIC RADIATION

Electromagnetic radiation was briefly introduced in Section 7.9, but let us take a closer look at it.

Visible light is a form of radiation. Three of its properties are:

- 1 It can transfer energy from one point to another without there being any transfer of mass (for example a light bulb shining on a photoelectric (photovoltaic) cell).

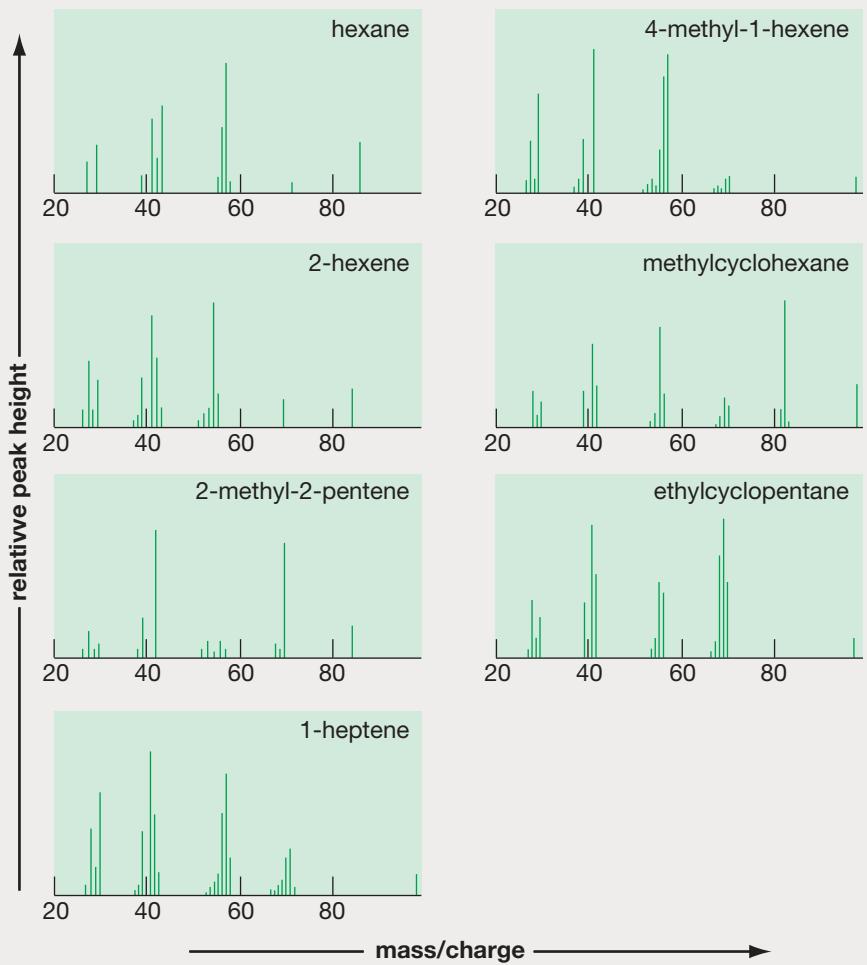


FIGURE 15.11  
Some standard mass spectra from a data bank

- 2** It can be transmitted through empty space (as when sunlight travels from the sun to Earth).
- 3** It travels with a speed of  $3.00 \times 10^8 \text{ m s}^{-1}$ .

There is actually a whole family of different types of radiation which have these same three characteristics: radio waves, microwaves, radiant heat or infrared (i.r.) radiation, visible light, ultraviolet (u.v.) light, X-rays and  $\gamma$ -rays. The general name used for all these types of radiation is **electromagnetic radiation**. The name arises because they all consist of oscillating electric and magnetic fields. Electromagnetic radiation is a type of wave motion. *The essential difference between the various forms of electromagnetic radiation is that they have different wavelengths or frequencies.*

Wavelength and frequency (measured in **hertz**, Hz, or cycles per second) are related by:

$$\lambda\nu = c \quad \dots (15.1)$$

where  $\lambda$  is the wavelength,  $\nu$  is the frequency and  $c$  is the speed of electromagnetic radiation (speed of light).

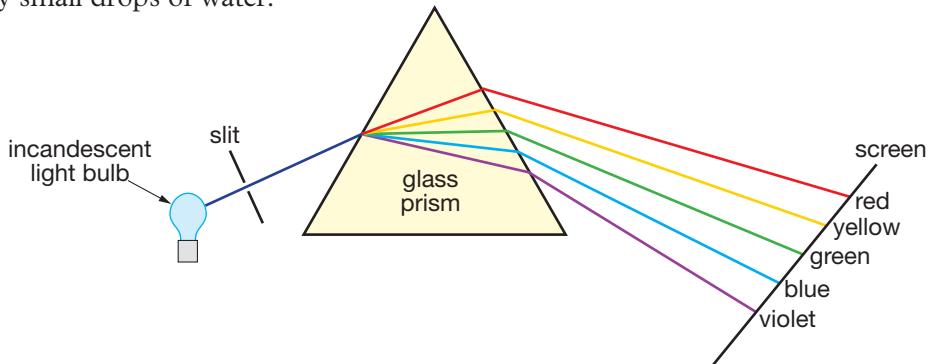
Each of the types of radiation listed above corresponds to a particular range of wavelengths (frequencies) as shown in Table 7.4 on page 244. Frequency of electromagnetic radiation is commonly used in connection with broadcast radio; each radio station transmits at a particular frequency (wavelength): AM in the range 500 to 1600 kHz and FM in the range 60 to 300 MHz.

## 15.9 SEPARATING LIGHT INTO ITS COMPONENTS

Isaac Newton showed in 1666 that light could be broken into its various wavelength components by passage through a glass prism as shown in Figure 15.12. The instrument used to do this is called a **spectroscope** (if observations are made by eye) or **spectrograph** (if photographic plates are used).

White light (from an incandescent light bulb) is a mixture of all wavelengths from blue to red (400 to 800 nm). When it passes through a prism, it separates into its various wavelength components and looks like a rainbow. In fact rainbows are formed by this same dispersion of light, brought about in that case by small drops of water.

FIGURE 15.12  
Dispersion of light by a prism



It is possible to use dispersion of light by such a prism to measure the wavelength of the light. That is, we can use a spectroscope or spectrograph to measure the wavelength(s) of light from a particular source.

In addition if we put a slit at an appropriate place on the dispersed light side of the prism (in addition to the one shown in Figure 15.12), we can select out light of a particular wavelength. An instrument which allows us to select particular wavelengths of light is called a **monochromator**. A prism is one type of monochromator. A monochromator was used in atomic absorption spectroscopy in Section 6.18 to select the required line (wavelength) from the emission lamp being used as the light source.

## 15.10 EMISSION OF LIGHT FROM ATOMS

Atoms whether in isolation or in compounds do not normally emit light. However if they are given extra energy, either by being heated to a high temperature or by being placed in an electric discharge, they can be made to emit light. This is the basis of atomic emission spectroscopy. It was briefly introduced in Section 6.17. You should re-read that section before proceeding.

If we excite electrons in an atom into higher energy levels, then as those electrons ‘fall back’ to their normal energy levels—called their ground states—energy is emitted as was shown in Figure 6.11 on page 224. This energy is emitted as electromagnetic radiation. There is a relationship between the energy released,  $\Delta E$ , and the wavelength of the radiation emitted:

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad \dots (15.2)$$

Therefore the greater the amount of energy to be released, the shorter the wavelength of the radiation emitted. Big jumps in energy release u.v. light, medium jumps visible light and small jumps i.r. radiation.

## Emission spectra

If a sample of an element is excited in a gas discharge tube and if the light emitted as the atoms fall back from excited states to ground states is examined (or photographed) through a spectroscope, we observe a series of bright (or coloured) lines on a black background. This is called an **emission spectrum** of the element or more precisely an **atomic emission spectrum**. The wavelengths of the emitted light from one element are different from those from any other element. Several emission spectra were shown in Figure 6.12.

If we look at a sample of an element in which some of the atoms have been excited (for example, in a discharge tube or in a flame), we observe a particular colour—yellow for sodium, red for neon, pink for hydrogen, green for copper<sup>†</sup>. We are then directly observing the radiation emitted by the excited electrons in atoms of those elements as they fall back to the ground state.

The question arises, then, why do elements emit light at different wavelengths?

### 15.11 EXPLAINING EMISSION SPECTRA

In order to find an explanation for emission spectra let us start with the simplest element, hydrogen and its spectrum. Figure 6.12 on p. 225 showed the visible portion of the hydrogen spectrum. Actually there are lines in the hydrogen spectrum extending from the u.v. region into the i.r. region. A more extensive form of the hydrogen spectrum is shown schematically at the top of Figure 15.13 on p. 526. Several series of lines have been identified in the figure.

The one electron in the hydrogen atom has available to it a large number of energy levels, labelled  $n = 1$  for the lowest energy state,  $n = 2$  for the next level up,  $n = 3$  for the next one and so on as shown in Figure 15.13. Normally the electron in hydrogen is in the ground state ( $n = 1$ ). When hydrogen is given energy in a discharge tube, the electron is excited into any one of these excited states or levels ( $n = 2$  and above).

When the electron falls from one of these excited states back to the ground state, the amount of energy released is large (corresponding to the lengths of the arrows in Figure 15.13(a)) so by Equation 15.2 the wavelength is short. These transitions produce lines in the u.v. region of the spectrum.

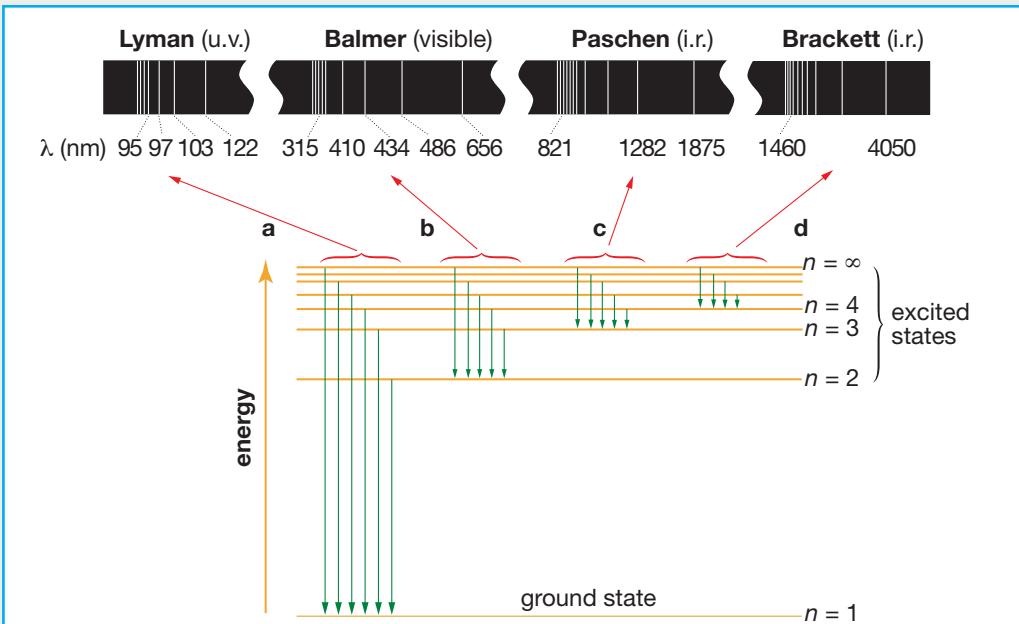
The electron does not necessarily fall back to the ground state in one drop. If the electron falls from higher energy states to the first excited energy state ( $n = 2$ ), then the energy differences are less (shorter arrows in the diagram) and so these transitions show up as lines in the visible region of the spectrum: (b) in the diagram. If the excited electron only drops down to the  $n = 3$  or  $n = 4$  states, then emissions appear in the i.r. region: (c) and (d) in the diagram.

Note that the energy that an electron can have is not continuously variable: there are only certain values of energy that the electron can have. We say that the energy is *quantised*, meaning that the energy that the electron can possess must be discrete whole number multiples of a basic ‘parcel’ of energy called a **quantum**.

In summary, the bright lines in the emission spectrum of an atom arise because electrons fall from various excited levels to lower energy levels.

<sup>†</sup> Do not look at discharge tubes without glasses or protective goggles; they emit considerable amounts of u.v. radiation that can damage eyes.

FIGURE 15.13  
The hydrogen emission spectrum and its interpretation in terms of energy levels available to the electron



## Why different elements have different spectra

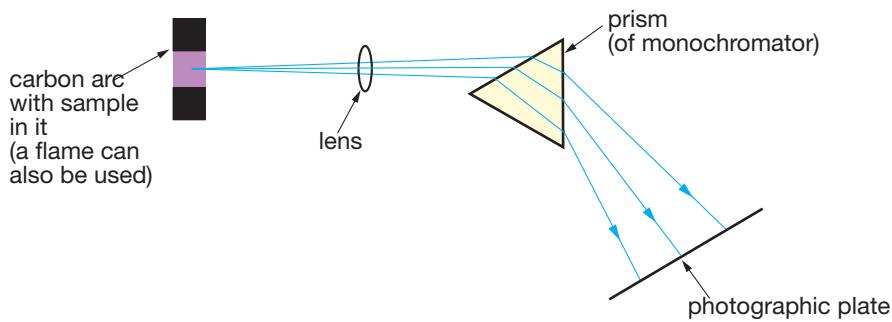
The electrons in atoms of all other elements have available to them a set of energy levels that is qualitatively similar to that for electrons in the hydrogen atom. However all the levels have slightly different energy values. Therefore transitions between pairs of levels involve different energy changes and so light emissions are at slightly different wavelengths. This means that the emission spectra of all elements are different from one another. We can use these differences in emission spectra as a method of analysing for different elements.

## 15.12 ATOMIC EMISSION SPECTROSCOPY

Because the emission spectra of elements are all different from one another, they can be used to identify the elements present in mixtures. This is called **atomic emission spectroscopy**. Emission spectra are used as a type of ‘fingerprint’ for the element: lines in a sample to be identified are matched with lines in the spectra of known elements.

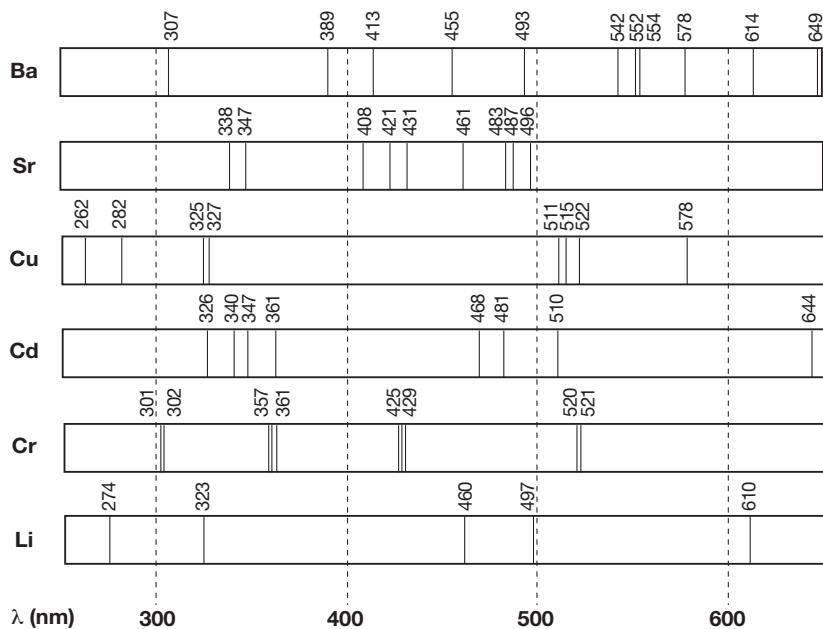
A typical experimental arrangement for atomic emission spectroscopy is shown in Figure 15.14. The sample to be analysed is heated to vaporise it and excite the electrons either in a flame or in a carbon arc (electric discharge across a pair of carbon electrodes quite close together). Emissions from the excited sample are concentrated with a lens then passed through some form of monochromator such as a prism which separates the emitted radiation into its different wavelengths. In older instruments a photographic plate was used to record the spectrum (as shown in the diagram). Later instruments generally used a fixed slit with a photomultiplier behind it as the detector and rotated the prism so that the different wavelengths of light fall on to the photomultiplier in turn. A photomultiplier is a sensitive device which converts light into an electrical current with the current being proportional to the intensity of the light. A recorder or computer was then used to draw a graph of intensity of light as a function of wavelength and this was the emission spectrum.

If the spectrum is recorded on a photographic plate or film, the instrument is called a *spectrograph*: if the spectrum is produced as a recorder or computer



graph, the instrument is usually called a *spectrometer*. As mentioned earlier, if the spectrum is observed by viewing through an eyepiece the instrument is called a *spectroscope*.

Figure 6.12 showed emission spectra of four elements; these were produced from discharge tubes. Figure 15.15 shows schematic spectra of six further elements; these were produced by exciting suitable compounds of the elements in flames or in carbon arcs. The spectra shown in Figure 15.15 are schematic in that they show the spectral lines as black stripes on a white background—a convenient way of drawing them. However it must be remembered that they appear in a spectroscope as coloured lines on a black background, or in a black and white photograph as white lines on a black background. Spectra in Figure 15.15 are really negatives (that is, reverses) of the true spectra.



By measuring the intensity of the emission lines, atomic emission spectroscopy can be used for the *quantitative* estimation of elements in samples, though until recent decades the technique has been more commonly used for *qualitative* analysis. For quantitative measurements atomic absorption spectroscopy has generally been preferred (Section 6.18).

## Emission spectra and flame colours

For some elements, there is one particular electron transition which occurs far more readily than any other. This means that the emission spectrum of such an

**FIGURE 15.14**  
Schematic layout of a traditional atomic emission spectrograph. In modern instruments, generally called spectrometers, the monochromator is a grating (mirror with very fine lines scratched on it, typically 400 per cm) and the detector is an array of microscopic solid-state photodiodes, called a charge coupled device, CCD; this is similar to the CCDs in digital cameras and video cameras

**FIGURE 15.15**  
Some further emission spectra (in reverse form); for others see Fig. 6.12 on p. 225

element has one extremely bright line corresponding to this transition. In such cases, the flame in which the excited atoms are produced takes on the colour of that particular line. This is the origin of the flame colours and the tests based upon them that were described in Section 6.14. You should revise that section before proceeding: flame tests are part of this HSC option.

## 15.13 USE OF EMISSION SPECTRA BY FORENSIC CHEMISTS

Atomic emission spectroscopy was developed towards the end of the nineteenth century, but was mainly a tool for scientists for a couple of decades. As the twentieth century progressed analytical chemists began to use it for qualitative (and to a lesser extent, quantitative) analysis of samples. One of its earliest applied uses was in the steel industry to monitor compositions of steels as they were being made: it was particularly good for the rapid measurement of relative amounts of various metals in such mixtures.

Forensic chemists have used atomic emission spectroscopy routinely for many decades. During the middle decades of the twentieth century the inconvenience of photographic plates and slowness of recorders attached to photomultipliers limited its use particularly for quantitative work. However in recent decades with the development of faster and more sensitive detectors, such as CCDs (Fig. 15.14), and powerful data processors (computers) its use has become much more common.

It is now widely used to monitor many elements simultaneously and quantitatively. Water authorities routinely use it to measure concentrations of up to twenty elements in the one sample. While atomic absorption spectroscopy measures concentrations more accurately, the need to use a different lamp for each element being measured makes it inconvenient for routine analysis of many elements.

Some forensic uses of atomic emission spectroscopy are:

- determining the origin of small chips of paint at a crime scene by analysing the chip and likely sources of the paint and comparing them
- testing a claim that a painting is by a famous long-dead artist by comparing the atomic emission spectrum of a small sample of a particular coloured paint with a similar sample from a known work of the artist (remember forensic chemistry is not just about law cases—see p. 454)
- determining the origin of small pieces of a metal or alloy or of fragments of coloured glass found at a crime scene by comparing the spectrum of the sample with spectra from likely sources
- determining the source of a soil sample by measuring the concentrations of less common elements in the soil (Section 13.5) and comparing them with known soil compositions from various areas.

In many newer atomic emission spectrometers a plasma is used to excite the atoms. A *plasma* (in physical and chemical contexts) is a highly ionised gas that has a distinct glow: it results from the gas being heated to a very high temperature (typically  $5000^{\circ}\text{C}$ ), for example by an electromagnetic induction furnace. Because of its very high temperature a plasma is able to excite a greater proportion of the atoms in a sample than a carbon arc is, and this increases the sensitivity of the instrument. This has made the technique even more useful for forensic purposes.

## A limitation

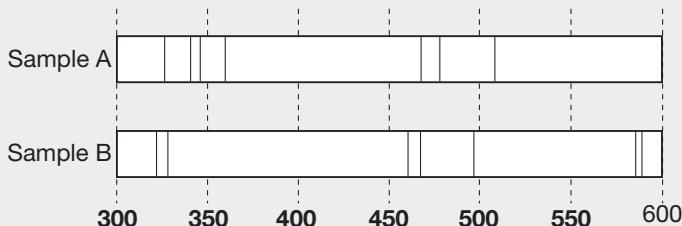
Emission spectra can be used to determine the elements present in the sample. However, because compounds have to be decomposed into gaseous atoms (by high-temperature flames or electrical discharges), emission spectra tell us nothing about the nature of the compounds in which the elements were present. Consequently atomic emission spectroscopy is of little use in identifying organic compounds, because they contain only five major elements (C, H, O, N, S).

An atomic emission spectrometer with a plasma source (in the top window); below it is the sample handling system (to pump sample solution into the plasma to atomise it and to excite the atoms; the monochromator and detector are behind the grey cover near the operator's face



### Exercises

- 10 A chemist had two samples of metal that were thought to be pure. In order to check the purity and to identify the samples the chemist volatilised a small portion of each sample in turn in a flame and recorded its emission spectrum between 300 and 600 nm. The spectra are shown below. Use Figures 6.12 and 15.15 to determine whether the samples are pure or not. If pure identify the element; if impure what elements are present? (Sometimes closely spaced lines are not completely resolved, and occasionally weak lines do not show up.)



- 11 The emission spectra in the region 350 to 600 nm of two unknown samples showed lines at:

- a 358, 361, 408, 421, 425, 427, 429, 496 and 521 nm
- b 361, 468, 481, 511, 515, 522 and 578 nm

Use the emission spectra in Figures 6.12 and 15.15 to determine which elements are present in the unknown samples. Note the warning at the end of Exercise 10.

- 12 A chemist prepared some lithium metal, and to check its purity determined its emission spectrum between 350 and 650 nm. Emission lines were observed at 610, 588, 497, 460 and 408 nm. Use Figures 6.12 and 15.15 to determine which, if any, impurities are present.
- 13 The five most intense emission lines for each of eight metals are shown (in nm) in the following table:



Iron	Cobalt	Nickel	Chromium	Manganese	Vanadium	Copper	Tungsten
358	341	341	358	261	309	282	362
372	344	349	359	279	318	325	387
373	345	352	361	280	411	327	401
382	350	357	425	403	438	522	407
386	357	362	427	404	439	578	430

The emission spectra were measured for three different alloys and they showed the following lines:

Alloy A: 318, 358, 372, 382, 386, 411, 438

Alloy B: 341, 345, 350, 358, 359, 372, 382, 386, 425

\*Alloy C: 325, 327, 341, 352, 357, 362, 522, 578

Which elements are present in each alloy? Note the warning at the end of Exercise 10.

- 14** A person had been stabbed to death. The blade of the knife used struck a bone and a small fragment of it broke off and was recovered by forensic scientists. It was possible that the knife could have been resharpened and the damage removed. Two suspects of the murder had knives that could have been the murder weapon. To try to identify the murder weapon the scientists performed atomic emission analyses (in the wavelength range 300 to 420 nm) on the fragment from the body and on the knives from the two suspects. After removal of spectral lines due to iron (all the blades were alloy steels), the remaining emission lines between 300 and 420 nm were as shown below. Using the table in the previous exercise, determine which knife, if either, the fragment found in the victim came from. What conclusion can you draw from this result?

*Murder weapon*                    309, 318, 341, 344, 345, 349, 350, 357, 362, 387, 407, 411 nm

*Knife from suspect 1*            341, 344, 345, 349, 350, 352, 357, 362, 387, 401, 407 nm

*Knife from suspect 2*            309, 318, 341, 349, 352, 357, 359, 361, 362, 411 nm

- 15** Which metals, in addition to iron, were in the alloys used to make the steels in the knives in Exercise 14?

## 15.14 CHEMICAL PROGRESS AND FORENSIC OUTCOMES

The increasing effectiveness of forensic investigations depends very much on new developments in analytical chemistry. Some examples will illustrate:

- There was little concern about mercury contamination of fish before about 1960, largely because small concentrations of mercury (below 1 ppm) could not easily be detected. After the development of atomic absorption spectroscopy in the 1950s (Section 6.18), it became possible to measure mercury concentrations well below the 1 ppm level and it was found that many species of fish were contaminated with low concentrations of mercury. This led to more stringent controls on releases of mercury to the environment and so to a diminution of the problem. More generally atomic absorption spectroscopy has led to better monitoring and control of all forms of heavy metal pollution.

- Before the development of spectroscopic methods such as those described in this chapter, the identification of an organic substance was a long and tedious process, involving a wide range of tests of which those described in Section 13.6 are the simplest. Unless samples were of gram quantities complete identification was rarely possible. Now with spectroscopic methods, samples as small as micrograms can generally be identified in less than an hour. Spectroscopic methods developed during the 1950s and 60s but have been refined almost continuously over the past four decades.
- Technological development in chromatography, such as capillary columns for gas chromatography and small uniformly sized spherical particles and high pressure pumps for liquid chromatography in the 1970s and 80s, led to more sensitive analyses for substances such as dioxin (a pollutant from garbage incineration and paper manufacture), pesticide residues in foods and illegal drugs in athletes. The development of techniques for coupling mass spectrometers to liquid and gas chromatographs further increased the ability of forensic chemists to detect smaller and smaller quantities of more complex substances. Gas chromatography coupled with mass spectrometry (GC-MS) is now widely used to screen athletes for prohibited performance-enhancing substances.
- The advance in chemistry (or biochemistry) that has most affected forensic investigations in the last decade is the development of methods of analysing DNA for identification of the source of a biological sample. As explained in Section 14.16 it is now possible to identify persons from very small DNA samples with an extremely high degree of certainty. This has greatly increased the ability of forensic scientists to identify the culprits of crimes. In addition it has allowed many persons convicted of crimes to prove their innocence even after ten or more years in jail (over 60 people in the US alone).

As a result of these and other advances in analytical chemistry, forensic chemists are today more likely to be able to solve crimes and other forensic problems than they were twenty to fifty years ago.

As progress is made in analytical methods, forensic chemists are quick to adopt them in order to solve the wide variety of problems they face in fields as diverse as solving crime, tracing sources of environmental pollution, contamination of products, detection of prohibited drugs in athletes and identification of bodies after disasters.

## Important new terms

You should know the meaning of the following terms.

atomic emission spectroscopy (p. 526)  
atomic emission spectrum (p. 525)  
chromatogram (p. 514)  
chromatograph (p. 514)  
cracking pattern (p. 519)  
destructive analysis (testing) (p. 511)  
electromagnetic radiation (p. 523)  
emission spectrum (p. 525)

hertz (p. 523)  
mass filter (p. 520)  
mass spectrometer (p. 517)  
mass spectrometry (p. 517)  
mass spectrum (p. 518)  
monochromator (p. 524)  
non-destructive analysis (testing) (p. 511)  
quantum (p. 525)  
retention time (p. 513)  
spectrograph (p. 524)  
spectroscope (p. 524)

## Test yourself

- 1 Explain the meaning of each of the items in the ‘Important new terms’ section above.
- 2 What problems does a requirement for non-destructive testing create for a forensic chemist? When is such a requirement likely to be made?
- 3 Describe the basic structure of a gas–liquid chromatograph.
- 4 Explain how high performance liquid chromatography differs from gas–liquid chromatography.
- 5 Explain how the chromatogram (that is, the graph of signal versus time after injection of the sample) is produced in GLC and HPLC.
- 6 How are compounds identified in GLC and HPLC?
- 7 Outline some forensic uses of gas–liquid and high performance liquid chromatography, including mention of situations where one technique is preferable over the other.
- 8 Explain how a magnetic sector mass spectrometer works (with a diagram).
- 9 Why is a mass spectrometer able to identify the isotopes in an element?
- 10 Why are there many lines (peaks) in the mass spectrum of an organic compound?
- 11 How does mass spectrometry help a forensic chemist identify substances?
- 12 List five types of electromagnetic radiation and explain why they are different from one another. Give common uses of them.
- 13 Describe the emission spectrum of an element such as hydrogen or mercury.
- 14 Explain why the emission spectrum of an element consists of a series of bright lines on a dark background.
- 15 What do we mean when we say that the energy of an electron is quantised?
- 16 In what way does the emission spectrum of one element differ from that of another element? Why do they differ in this way?
- 17 Explain how you can use emission spectra to identify the metals present in an alloy.
- 18 Why do certain elements impart particular colours to flames? List four elements that do this and state the colours they form.
- 19 What is the main limitation of atomic emission spectroscopy? As a consequence to what classes of compound is the technique of significant use?
- 20 Describe two scientific advances in the past thirty years that have been particularly useful for forensic scientists.

# EXTENDED RESPONSE EXAM-STYLE QUESTIONS FOR OPTION 3

OPTION  
**3**

Questions in this section are in a similar style to that currently being used in the extended response questions in the New South Wales HSC Chemistry examination: for more information see p. 93.

Marks (shown at the right-hand end of the question) are assigned to each question in order to indicate how much detail is required in your answer (that is, how much time you should spend on each question). The marks are on the HSC exam basis of 100 marks for three hours work (or 1.8 minutes per mark).

- |   | MARKS |
|---|-------|
| 1 Discuss the importance of accuracy in forensic chemistry relative to other branches of chemistry.   | 3     |
| 2 Explain how an atomic emission spectrum is generated and observed.  | 4     |
| 3 Outline the composition and structure of DNA.   | 6     |
| 4 Explain the chemical difference between reducing and non-reducing sugars and describe a test you have performed to determine whether a sugar is reducing or non-reducing.                               | 5     |
| 5 Discuss ethical issues that may need to be considered during an analytical investigation.   | 5     |
| 6 Evaluate the usefulness of atomic emission spectroscopy to forensic scientists.   | 5     |
| 7 Compare and contrast the chemical structures of glucose and deoxyribose.  | 4     |
| 8 Identify the chemical features a forensic chemist would concentrate on in order to determine the origin of a sample of soil and assess the usefulness of atomic emission spectroscopy for this purpose. | 4     |
| 9 Explain the effect upon the isoelectric point of adding an extra $-\text{NH}_2$ group or $-\text{COOH}$ group to an amino acid.   | 4     |
| 10 Summarise the uses of DNA analysis for forensic purposes.  | 4     |
| 11 Outline an experiment you have performed to separate a mixture of organic substances by chromatography and describe the chemical and/or physical principles underlying the separation.                 | 6     |
| 12 Discuss, with at least one example, how developments in analytical chemistry have led to improved outcomes in forensic investigations.   | 4     |
| 13 Evaluate the usefulness of mass spectrometry for forensic investigations.  | 4     |
| 14 Identify the main polysaccharides present in plants and animals and explain how they differ chemically from one another.   | 5     |
| 15 Explain why analysis of a DNA sample allows identification of the person the sample came from and why this identification is considered to be extremely accurate.                                      | 4     |
| 16 Outline the operating principles of gas–liquid chromatography and assess its usefulness and limitations for forensic purposes.   | 6     |
| 17 Compare and contrast the structures of nylon and proteins.   | 4     |

- 18** Describe two tests you could use to distinguish between classes of carbon compounds and assess the reliability of the conclusions you would draw from these tests. **6**
- 19** Using sucrose as an example, demonstrate the meaning of the terms condensation reaction and disaccharide. **4**
- 20** Justify the establishment of DNA data banks by law enforcement agencies and discuss some ethical issues associated with their establishment. **6**

# REVISION TESTS FOR OPTION 3: FORENSIC CHEMISTRY

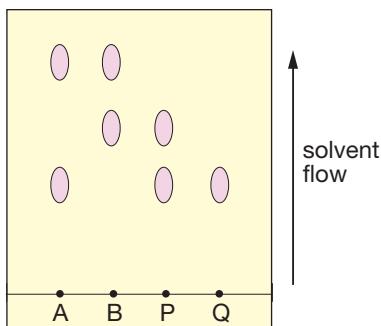
OPTION  
**3**

## TEST A

**Total marks: 25**

**Suggested time: 45 minutes**

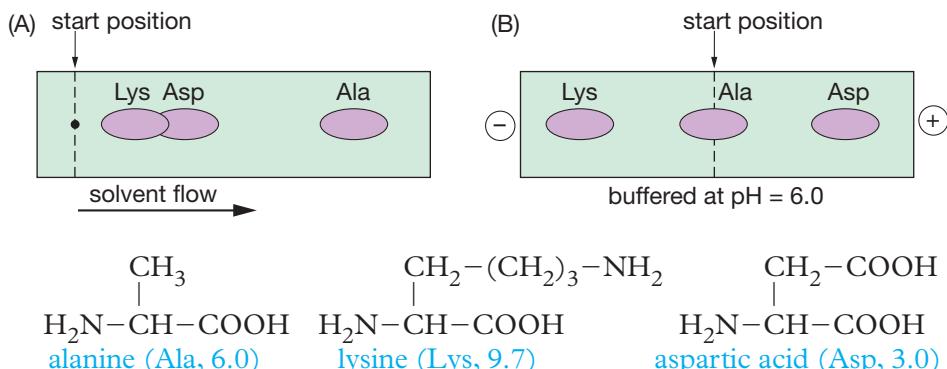
- |  | MARKS |
|--|-------|
| a i Describe how a mass spectrometer works.  | 3     |
| ii Explain why there are many peaks in the mass spectra of relatively simple compounds such as pentane.  | 1     |
| b i To identify the monosaccharides making up two disaccharides P and Q, a chemist completely hydrolysed them, then ran a paper chromatogram of the hydrolysed mixtures along with two reference samples. Reference sample A was completely hydrolysed sucrose (a mixture of glucose and fructose). Reference B was a mixture of fructose and galactose. The resulting chromatogram is shown below. Identify the monosaccharides present in P and Q. | 2     |



- |  |   |
|--|---|
| ii Explain the fact that the disaccharide Q produced only one monosaccharide. Q was a reducing sugar. Draw a possible structure for Q. What is the relevance of Q being a reducing sugar for doing this? Is this the only structure possible? Explain. | 3 |
| c Describe an experiment you have performed using electrophoresis and explain how it separated the substances in your mixture. Suggest methods for improving the separation of the components in your mixture.   | 5 |
| d i Demonstrate the meaning of the terms peptide bond, dipeptide and polypeptide.  | 3 |
| ii Identify the difference in the products formed when proteins are hydrolysed by enzymes and by strong acids.   | 2 |
| e Outline the basic principles of gas–liquid chromatography and high performance liquid chromatography and evaluate their roles in forensic investigations.  | 6 |

**TEST B****Total marks: 25****Suggested time: 45 minutes****MARKS**

- a**
- i Distinguish between destructive and non-destructive testing. **1**
  - ii Discuss the constraints that a requirement for non-destructive testing or very unobtrusive destructive testing places upon a forensic investigation. **3**
  - iii Outline steps forensic scientists take to avoid contamination of samples between their collection and the completion of all analyses. **3**
- b** Demonstrate the meaning of the terms monosaccharide, disaccharide, and polysaccharide. **3**
- c** In the diagram below, A is a paper chromatogram of a mixture of the three substances, alanine, aspartic acid and lysine. B is the result of an electrophoresis experiment in a buffer with a pH of 6.0 on this same mixture. Structures of the three substances, with their common abbreviations and their isoelectric points given in brackets, are shown below the diagram. **3**



- i** In A why is there a good separation between alanine and the other two, but only a poor separation between aspartic acid and lysine? **1**
- ii** Why is there a good separation between aspartic acid and lysine in the electrophoresis experiment? Draw structures to illustrate your explanation. **3**
- iii** Why has alanine hardly moved in the electrophoresis experiment? **1**
- d**
- i** Describe the procedure you would follow for carrying out flame tests in order to identify certain elements. **3**
  - ii** Explain why only some elements produce characteristic flame colours. **1**
- e** Assess the usefulness and reliability of DNA analysis in forensic investigations. **6**

# OPTION 3 AND THE NEW SOUTH WALES HSC SYLLABUS

This section allows you to check that *Conquering Chemistry* has covered all necessary material for the Forensic Chemistry option of the New South Wales Higher School Certificate HSC Course.

## Syllabus content

The following table lists (for Option 3) the items from the *students learn to* column of the HSC syllabus and shows where they are treated in *Conquering Chemistry (CCHSC)*.

Location of HSC Course material in *Conquering Chemistry* for Option 3 Forensic Chemistry

Syllabus reference <i>Students learn to</i>	Sections where found in CCHSC
<b>9.9.1 The job of the forensic chemist is to identify materials and trace their origin</b>	
■ outline precautions that may be necessary to ensure accuracy and prevent contamination of samples	13.1, 13.2
■ distinguish between organic and inorganic compounds	13.3
■ explain that there are different classes of carbon compounds including <ul style="list-style-type: none"><li>– hydrocarbons</li><li>– alkanols</li><li>– alkanoic acids</li></ul> which can be identified by distinguishing tests	13.6
■ explain that the inorganic chemical properties of soils and other materials may be useful evidence	13.5
■ discuss, using a recent example, how progress in analytical chemistry and changes in technology can alter the outcome of a forensic investigation	15.14
<b>9.9.2 Analysis of organic material can distinguish plant and animal material</b>	
■ identify that carbohydrates are composed of carbon, hydrogen and oxygen according to the formula: $C_x(H_2O)_y$	13.7
■ identify glucose as a monomer and describe the condensation reactions which produce: <ul style="list-style-type: none"><li>– sucrose as an example of a disaccharide</li><li>– polysaccharides including glycogen, starch and cellulose</li></ul>	13.7 to 13.9
■ describe the chemical difference between reducing and non-reducing sugars	13.10, 13.11
■ distinguish between plant and animal carbohydrates' composition in terms of the presence of: <ul style="list-style-type: none"><li>– cellulose</li><li>– starch</li><li>– glycogen</li></ul>	13.9

Syllabus reference Students learn to	Sections where found in CCHSC
<b>9.9.3 Because proteins are a major structural and metabolic component of all living organisms, the analysis of protein samples can be useful in forensic chemistry</b>	
■ distinguish between protein used for structural purposes and the uses of proteins as enzymes	14.1
■ identify the major functional groups in an amino acid	14.1
■ describe the composition and general formula for amino acids and explain that proteins are chains of amino acids	14.1, 14.4
■ describe the nature of the peptide bond and explain that proteins can be broken at different lengths in the chain by choice of enzymes	14.4, 14.5
■ compare the processes of chromatography and electrophoresis and identify the properties of mixtures that allow them to be separated by either of these processes	14.8 to 14.11
■ discuss the role of electrophoresis in identifying the origins of protein and explain how this could assist the forensic chemist	14.10
<b>9.9.4 DNA is an important compound found in all living things and is a most useful identification molecule</b>	
■ outline the structure and composition of DNA	14.12, 14.13
■ explain why analysis of DNA allows identification of individuals	14.15
■ describe the process used to analyse DNA and account for its use in: – identifying relationships between people – identifying individuals	14.16, 14.17
<b>9.9.5 Much forensic evidence consists of very small samples and sensitive analytical techniques are required</b>	
■ explain what is meant by the destructive testing of material and explain why this may be a problem in forensic investigations	15.1
■ identify, outline and assess the value of the following techniques in the analysis of small samples: – gas-liquid chromatography – high performance liquid chromatography	15.2, 15.3
■ outline how a mass spectrometer operates and clarify its use for forensic chemists	15.4 to 15.7
<b>9.9.6 All elements have identifiable emission spectra and this can be used to identify trace elements</b>	
■ describe the conditions under which atoms will emit light	15.10, 6.17
■ identify that the emission of quanta of energy as electrons move to lower energy levels may be detected by humans as a specific colour	15.10
■ explain why excited atoms in the gas phase emit or absorb only certain wavelengths of light	15.11

Syllabus reference	Sections where found in CCHSC
Students learn to	
■ account for the fact that each element produces its signature line emission spectrum	15.11
■ discuss the use of line emission spectra to identify the presence of elements in chemicals	15.12, 15.13

## Compulsory experiments

The table below lists the compulsory experiments for this option (from the right-hand column of the syllabus), along with the location of relevant information in this book.

### Compulsory experiments for Option 3 Forensic Chemistry

Experiment	Related material in CCHSC <sup>a</sup>
1 Perform a sequence of tests to distinguish between organic and inorganic compounds	Section 13.3
2 Perform tests to distinguish between reducing and non-reducing sugars and to identify starch	Sections 13.11 and 13.12 Exam-style Question 4
3 Perform a test to identify protein	Section 14.7 Exam-style Question 3
4 Separate a mixture of organic materials by chromatography	Sections 14.8, 14.9 Exam-style Question 11
5 Identify a range of solvents that may be used for chromatography	Sections 14.8, 14.9
6 Carry out electrophoresis on an appropriate mixture	Section 14.10 Revision Test A Question c
7 Perform flame tests or use a spectroscope to describe the emission spectra of a range of elements including Na and Hg	Sections 15.12, 6.14 Revision Test B Question d(i)
a Exam-style and Revision Test questions are listed here, because their answers at the back of the book often contain helpful information.	

## Location of material for other Option 3 Forensic Chemistry activities

Syllabus item	Relevant material in CCHSC
9.9.1 ■ solve problems ... discuss the importance of accuracy in forensic chemistry	Section 13.2
■ solve problems ... discuss ethical issues ... during an analytical investigation	Section 13.2
■ Experiment 1 (see previous table)	
■ gather ... information ... series of distinguishing tests to separate ...	Sections 13.4, 13.6

Syllabus item	Relevant material in CCHSC
<b>9.9.2</b>	<ul style="list-style-type: none"> <li>■ Experiment 2 (see previous table)</li> <li>■ ... using molecular model kits, computer simulations or other multimedia resources to compare the structure of organic compounds ...</li> </ul>
<b>9.9.3</b>	<ul style="list-style-type: none"> <li>■ ... molecular model kits ... composition and generalised structure of proteins</li> <li>■ Experiment 3 (see previous table)</li> <li>■ Experiment 4 (see previous table)</li> <li>■ Experiment 5 (see previous table)</li> <li>■ Experiment 6 (see previous table)</li> </ul>
<b>9.9.4</b>	<ul style="list-style-type: none"> <li>■ ... discuss the range of uses of DNA analysis... and ... ethics of maintenance of data banks of DNA</li> </ul>
<b>9.9.5</b>	<ul style="list-style-type: none"> <li>■ analyse ... information ... to discuss the ways in which analytical techniques may provide evidence about samples</li> </ul>
<b>9.9.6</b>	<ul style="list-style-type: none"> <li>■ Experiment 7 (see previous table)</li> <li>■ process ... information ... to ... identify individual elements present in a mixed emission spectrum and ... explain how such information can assist analysis of the origins of the mixture</li> </ul>

### Prescribed focus areas

Although the syllabus suggests that in this option the emphasis is on prescribed focus areas 3, 4 and 5 (p. 101), namely applications and uses of chemistry, the implications of chemistry for society and the environment, and current issues, research and developments in chemistry, considerable attention to area 2, the nature and practice of chemistry, is also needed; in fact this option introduces more new chemical concepts than either of the other two options treated in this book. For students at this level some quite complex chemistry is introduced, such as reducing and non-reducing sugars, amino acids and proteins and the structure of DNA. The basic principles of gas–liquid chromatography, high performance liquid chromatography, mass spectrometry and atomic emission spectroscopy, though more straight-forward, do constitute a considerable body of new concepts.

Nevertheless the main emphasis is on applications, the use of chemistry for forensic purposes. Bear in mind that forensic chemistry is concerned with a wide range of investigations such as detecting contaminants in products, monitoring content claims of other products and measuring pollutants in the environment, and not just with collecting evidence for criminal prosecutions.

The implications for society probably have more to do with the non-criminal aspects of forensic chemistry—quality control, truth in advertising and safety of products. The use of DNA for paternity testing also has social implications (as a 2005 case involving a senior politician very publicly demonstrated) as well as political ones (issues about paternal child-support payments). For the environment the availability of analytical techniques that are far more sensitive

than those of thirty years ago has far-reaching implications; it is now possible to monitor harmful substances at extremely low concentrations, thus providing better safeguards for people's health and wellbeing.

For current issues there is the question of forensic DNA data banks and the privacy questions involved. For research and developments in chemistry there have been the major improvements to chromatographic techniques. Although chromatography has been in widespread use for about seventy years, the developments in recent decades of capillary columns for gas–liquid chromatography and of high pressure pumps and uniform-sized micro-spheres for high performance liquid chromatography have greatly improved the sensitivity and versatility of these techniques. Added to this, developments in mass spectrometry that have led to high speed scans and direct coupling of chromatographs to mass spectrometers have resulted in even better compound identification methods. Although atomic emission spectroscopy has been in use for over one hundred years, the development in recent decades of plasma sources, CCD detectors and computer data processing have seen a re-emergence of this technique for analytical (and forensic) use.



# PERIODIC TABLE OF THE ELEMENTS

# RELATIVE ATOMIC MASSES (ATOMIC WEIGHTS) OF COMMON ELEMENTS

(arranged alphabetically by element name)

Element		Relative atomic mass	Element		Relative atomic mass
aluminium	Al	26.98	neon	Ne	20.18
antimony	Sb	121.75	nickel	Ni	58.71
argon	Ar	39.95	niobium	Nb	92.91
arsenic	As	74.92	nitrogen	N	14.01
barium	Ba	137.34	osmium	Os	190.2
beryllium	Be	9.01	oxygen	O	16.00
bismuth	Bi	208.98	palladium	Pd	106.4
boron	B	10.81	phosphorus	P	30.97
bromine	Br	79.90	platinum	Pt	195.09
cadmium	Cd	112.40	potassium	K	39.10
caesium	Cs	132.91	radium	Ra	226.03
calcium	Ca	40.08	rhenium	Re	186.2
carbon	C	12.01	rhodium	Rh	102.91
cerium	Ce	140.12	rubidium	Rb	85.47
chlorine	Cl	35.45	ruthenium	Ru	101.07
chromium	Cr	52.00	scandium	Sc	44.96
cobalt	Co	58.93	selenium	Se	78.96
copper	Cu	63.55	silicon	Si	28.09
fluorine	F	19.00	silver	Ag	107.87
gallium	Ga	69.72	sodium	Na	22.99
germanium	Ge	72.59	strontium	Sr	87.62
gold	Au	196.97	sulfur	S	32.06
hafnium	Hf	178.49	tantalum	Ta	180.95
helium	He	4.00	technetium	Tc	98.91
hydrogen	H	1.01	tellurium	Te	127.60
indium	In	114.82	thallium	Tl	204.37
iodine	I	126.90	thorium	Th	232.04
iridium	Ir	192.22	tin	Sn	118.69
iron	Fe	55.85	titanium	Ti	47.90
krypton	Kr	83.80	tungsten	W	183.85
lanthanum	La	138.91	uranium	U	238.03
lead	Pb	207.2	vanadium	V	50.94
lithium	Li	6.94	xenon	Xe	131.30
magnesium	Mg	24.31	yttrium	Y	88.91
manganese	Mn	54.94	zinc	Zn	65.38
mercury	Hg	200.59	zirconium	Zr	91.22
molybdenum	Mo	95.94			

# THE ELEMENTS AND THEIR SYMBOLS

(arranged alphabetically by symbol)

<b>Ac</b>	actinium	<b>Er</b>	erbium	<b>S</b>	sulfur
<b>Ag</b>	silver	<b>Es</b>	einsteinium	<b>Sb</b>	antimony
<b>Al</b>	aluminum	<b>Eu</b>	euroium	<b>Sc</b>	scandium
<b>Am</b>	americium	<b>F</b>	fluorine	<b>Se</b>	selenium
<b>Ar</b>	argon	<b>Fe</b>	iron	<b>Sg</b>	seaborgium
<b>As</b>	arsenic	<b>Fm</b>	fermium	<b>Si</b>	silicon
<b>At</b>	astatine	<b>Fr</b>	francium	<b>Sm</b>	samarium
<b>Au</b>	gold	<b>Ga</b>	gallium	<b>Tin</b>	tin
<b>B</b>	boron	<b>Gd</b>	gadolinium	<b>Sr</b>	strontium
<b>Ba</b>	barium	<b>Ge</b>	germanium	<b>Ta</b>	tantalum
<b>Be</b>	beryllium	<b>H</b>	hydrogen	<b>Tb</b>	terbium
<b>Bh</b>	bohrium	<b>He</b>	helium	<b>Tc</b>	technetium
<b>Bi</b>	bismuth	<b>Hf</b>	hafnium	<b>Te</b>	tellurium
<b>Bk</b>	berkelium	<b>Hg</b>	mercury	<b>Th</b>	thorium
<b>Br</b>	bromine	<b>Ho</b>	holmium	<b>Ti</b>	titantium
<b>C</b>	carbon	<b>Hs</b>	hassium	<b>Tl</b>	thallium
<b>Ca</b>	calcium	<b>I</b>	iodine	<b>Tm</b>	thulium
<b>Cd</b>	cadmium	<b>In</b>	indium	<b>U</b>	uranium
<b>Ce</b>	cerium	<b>Ir</b>	iridium	<b>V</b>	vanadium
<b>Cf</b>	californium	<b>K</b>	potassium	<b>W</b>	tungsten
<b>Cl</b>	chlorine	<b>Kr</b>	krypton	<b>Xe</b>	xenon
<b>Cm</b>	curium	<b>La</b>	lanthanum	<b>Y</b>	yttrium
<b>Co</b>	cobalt	<b>Li</b>	lithium	<b>Yb</b>	ytterbium
<b>Cr</b>	chromium	<b>Lr</b>	lawrencium	<b>Zn</b>	zinc
<b>Cs</b>	caesium	<b>Lu</b>	lutetium	<b>Zr</b>	zirconium
<b>Cu</b>	copper	<b>Md</b>	mendelevium		
<b>Db</b>	dubium	<b>Mg</b>	magnesium		
<b>Dy</b>	dysprosium	<b>Mn</b>	manganese		
		<b>Rn</b>	radon		
		<b>Ru</b>	ruthenium		

# USEFUL DATA

## Some fundamental constants

Avogadro constant  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Volume of one mole of gas at a pressure of 100.0 kPa:

at 0°C (273.2 K) 22.71 L mol<sup>-1</sup>

at 25°C (298.2 K) 24.79 L mol<sup>-1</sup>

## Conversion factors

0°C = 273.2 K

1 litre = 1000 millilitres (mL) = 1000 cubic centimetres (cm<sup>3</sup>)

1 cubic metre (m<sup>3</sup>) = 1000 litres

1 tonne (t) = 1000 kg = 10<sup>6</sup> g

## Some common prefixes

giga	$10^9$	deci	$10^{-1}$	micro	$10^{-6}$
mega	$10^6$	centi	$10^{-2}$	nano	$10^{-9}$
kilo	$10^3$	milli	$10^{-3}$	pico	$10^{-12}$

## Solubility of ionic compounds (TABLE 8.1 page 205 CCPQ)

### Compounds that are soluble

- Group 1 and NH<sub>4</sub><sup>+</sup> compounds
- nitrates
- acetates (ethanoates)
- chlorides, bromides and iodides  
(except Ag<sup>+</sup> and Pb<sup>2+</sup>)
- sulfates (except Ag<sup>+</sup>, Pb<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>)

### Compounds that are insoluble

- carbonates
  - sulfites
  - phosphates
  - hydroxides
  - oxides
  - sulfides
- } (except Group 1 and NH<sub>4</sub><sup>+</sup> compounds)
- } (except Group 1, NH<sub>4</sub><sup>+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>)
- } (except Groups 1, 2 and NH<sub>4</sub><sup>+</sup>)

## Tables of frequently used data

An activity series of metals, page 43

Common acids and the anions they form, Table 4.2 page 114

Common indicators and their pH ranges, Table 4.7, page 139

Common reduction half reactions and standard electrode potentials, Table 2.1, page 67

Tests used to identify cations, Tables 6.2 and 8.3, pages 208 and 281

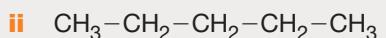
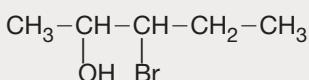
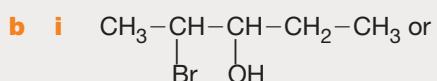
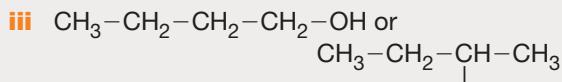
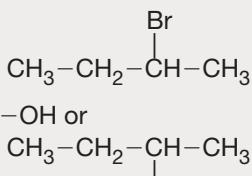
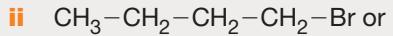
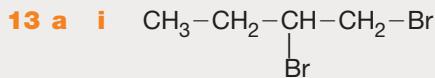
Tests used to identify anions, Table 6.3, page 214

# Answers to exercises

## Chapter 1

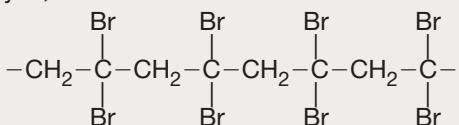
- 1 a i**  $C_{14}H_{30} \rightarrow C_8H_{18} + C_6H_{12}$
- b**  $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$   
octane  
 $CH_3-CH_2-CH=CH-CH_2-CH_3$   
(1- and 2-hexene are acceptable)
- 2**  $C_6H_{12} \rightarrow 2C_3H_6$ ;  $C_6H_{12} \rightarrow 3C_2H_4$
- 4** any one of:  
 $C_{16}H_{34} \rightarrow 8C_2H_4 + H_2$   
 $C_{16}H_{34} \rightarrow 2C_3H_6 + 5C_2H_4 + H_2$   
 $C_{16}H_{34} \rightarrow 4C_3H_6 + 2C_2H_4 + H_2$
- 5 a** Cool the mixture to about  $0^\circ C$  to condense the  $C_4$  to  $C_{12}$  compounds and remove the gaseous ethylene and propene; distil the liquid to remove the  $C_4$  and  $C_5$  alkenes, then add the remaining liquid  $C_6$  to  $C_{12}$  alkanes to the original gasoline fraction.
- b**  $C_{20}H_{42} \rightarrow C_{12}H_{26} + C_8H_{16}$  followed by  $C_8H_{16} \rightarrow C_5H_{10} + C_3H_6$   
There are many other possibilities.  
 $C_5H_{10} \rightarrow C_3H_6 + C_2H_4$
- 6 a**  $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$   
(or  $C_4H_{10} + 6\frac{1}{2}O_2 \rightarrow 4CO_2 + 5H_2O$ )
- b**  $2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O$   
(or  $C_6H_{14} + 9\frac{1}{2}O_2 \rightarrow 6CO_2 + 7H_2O$ )
- 7**  $C_4H_{10} + Cl_2 + u.v. \rightarrow C_4H_9Cl + HCl$   
two monosubstituted products:  
 $CH_3-CH_2-CH_2-CH_2-Cl$  and  
 $CH_3-CH_2-CH(Cl)-CH_3$
- 8 a**  $Br-CH_2-CH_2-Br$        $Br-CH(Cl)-CH_3$
- b** two;  $CBr_3-CH_3$  and  $CHBr_2-CH_2Br$

- 9 a**  $2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$   
(or  $C_3H_6 + 4\frac{1}{2}O_2 \rightarrow 3CO_2 + 3H_2O$ )
- b**  $2C_5H_{10} + 15O_2 \rightarrow 10CO_2 + 10H_2O$   
(or  $C_5H_{10} + 7\frac{1}{2}O_2 \rightarrow 5CO_2 + 5H_2O$ )
- 10 a i**  $CH_3-CH=CH_2 + H_2 \rightarrow CH_3-CH_2-CH_3$
- ii**  $CH_3-CH=CH_2 + Cl_2 \rightarrow$   
 $CH_3-CH(Cl)-CH_2-Cl$
- iii**  $CH_3-CH=CH_2 + HOBr \rightarrow$   
 $CH_3-CH(OH)-CH_2-Br$   
or  $CH_3-CH(Cl)-CH_2-OH$
- b i**  $CH_3-CH=CH-CH_3 + H_2 \rightarrow$   
 $CH_3-CH_2-CH_2-CH_3$
- ii**  $CH_3-CH=CH-CH_3 + Cl_2 \rightarrow$   
 $CH_3-CH(Cl)-CH(Cl)-CH_3$
- iii**  $CH_3-CH=CH-CH_3 + HOBr \rightarrow$   
 $CH_3-CH(OH)-CH(Cl)-CH_3$   
(only one possibility)
- 11 a**  $CH_3-CH=CH_2 + HCl \rightarrow$   
 $CH_3-CH_2-CH_2-Cl$  and  $CH_3-CH(Cl)-CH_3$
- b**  $CH_3-CH_2-CH=CH_2 + HCl \rightarrow$   
 $CH_3-CH_2-CH_2-CH_2-Cl$   
and  $CH_3-CH_2-CH(Cl)-CH_3$
- 12 a**  $CH_3-CH=CH_2 + H_2O \rightarrow$   
 $CH_3-CH_2-CH_2-OH$  and  $CH_3-CH(Cl)-CH_3$   
(1-propanol)  
 $CH_3-CH(Cl)-CH_2-OH$   
(2-propanol)

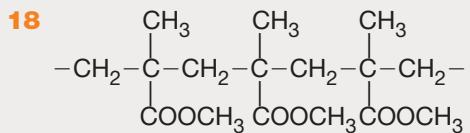
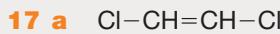


**14** A is octane; B is 1-hexene; C is octane

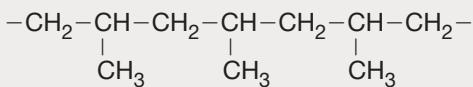
**15** yes;



**16 a** 1152      **b**  $8.3 \times 10^4$



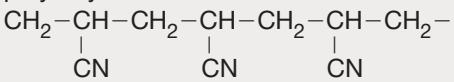
**19** polypropylene:



polytetrafluoroethylene:



polyacrylonitrile:



**20** polyethylene < PVC < polystyrene, because that

is the order of increasing size of the side groups,



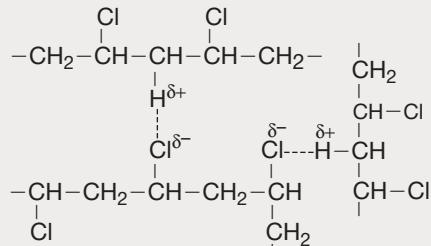
Most flexible, polypropylene, least styrene; because

as the chain gets stiffer (less able to flop about) the polymer becomes more rigid.

**21** See below

**22 a** dispersion forces

**b** dispersion forces plus dipole-dipole interactions



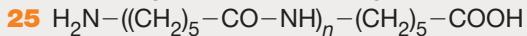
**23 a** LDPE; most easily crushed for recycling, or any polymer would do, so use the cheapest which is LDPE

**b** HDPE; want a material that will tolerate rough treatment and repeated use but without being brittle

**c** PVC or LDPE; both are quite flexible and easily blown into film for making raincoats (so too is HDPE but it makes more noise when it is crinkled and flexed)

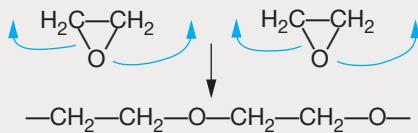
**d** polystyrene; can be made transparent and is rigid and tough

**24**  $4.86 \times 10^4$  g/mol (from  $300 \times \text{C}_6(\text{H}_2\text{O})_5$ ) or  
 $4.87 \times 10^4$  g/mol (from  $300 \times \text{C}_6\text{H}_{12}\text{O}_6 - 299 \times \text{H}_2\text{O}$ ); mass of glucose  $5.41 \times 10^4$  g



**26 a** See below

**b** the ring C–O bonds open out:

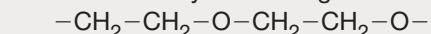


**27** See below

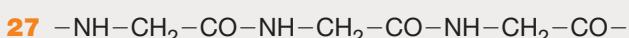
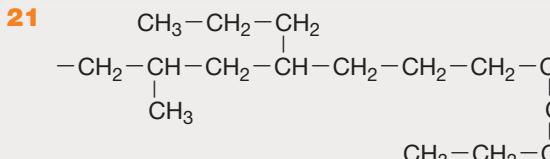
**28 a** two functional groups; they can be the same or different

**b i** no; only one functional group

**ii** yes; OH of one molecule can react with Cl of another by eliminating HCl and forming

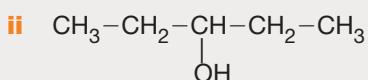
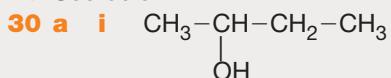


**iii** yes; but another compound is needed, for



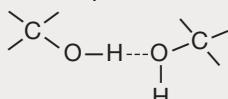
example  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$  or  
 $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{COOH}$

**29** See below

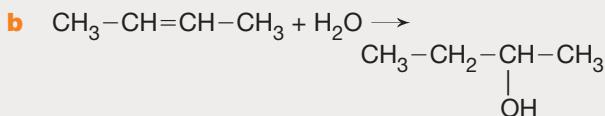
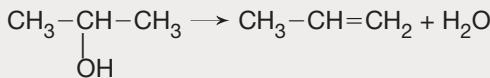
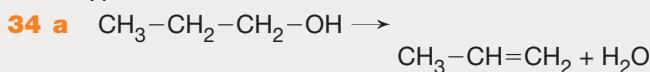
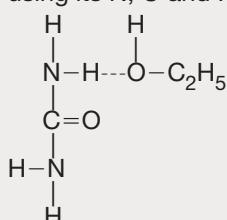


**b i** 1-pentanol      **ii** 2-butanol

**31** There is strong hydrogen bonding in ethanol but only weak dispersion forces in propane.



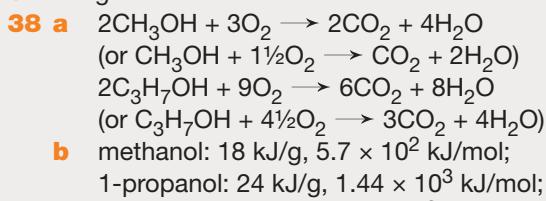
**33** Urea can form strong hydrogen bonds with ethanol using its N, O and H atoms and ethanol's O and H:



- 35 a** addition      **e** addition  
**b** dehydration      **f** dehydration  
**c** substitution      **g** hydration or addition  
**d** polymerisation

**36** 49 g; 3.6%

**37** 7.7 g



- 39 a** The heat absorbed by the Al container was less than 0.4 kJ compared with 63 kJ absorbed by the water: this is only about 0.5%: the other errors in the experiment greatly exceed this.  
**b** heat loss to the surroundings; incomplete combustion of the alcohol

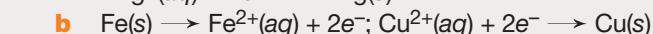
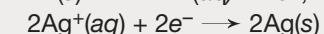
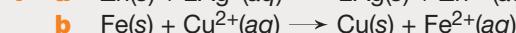
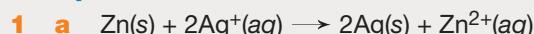
**40**  $\text{H}_2$ : 141 kJ/g; propane, 50 kJ/g; octane, 48 kJ/g; ethanol, 30 kJ/g

$\text{H}_2 > \text{propane} > \text{octane} > \text{coal} > \text{ethanol}$

Because we generally buy fuels by mass or volume, not by moles.

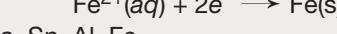
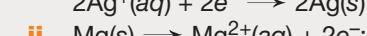
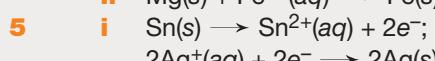
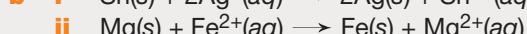
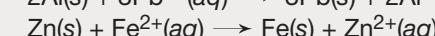
**41** Not as good: ethanol releases only about two-thirds of the energy per gram as hydrocarbons do.

## Chapter 2

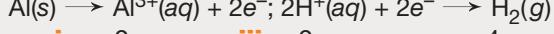
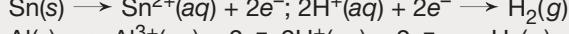


**3 a** any three of Mg, Al, Zn, Fe (Ca, Ba, Li would react with water much more rapidly than with Pb)

**b** Mg, Al, Zn



**6** Ca, Sn, Al, Fe



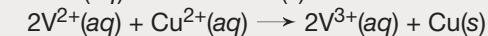
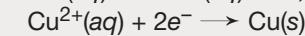
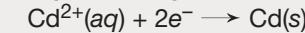
**8 a** oxidation; oxidation state (OS) has changed from +3 to +4

**b** oxidation; OS increases from -1 to 0

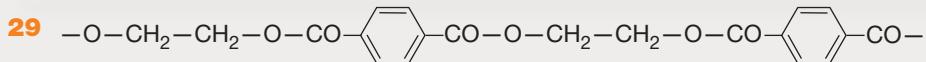
**c** oxidation; OS increases from +2 to +3

**d** neither; OS is unchanged, +3 in both

**e** reduction; OS decreases from 0 to -2



**10** It would drop to zero. The migration of ions from one beaker to the other, which is necessary to preserve electrical neutrality in both beakers, would cease and so the electrode reactions would cease.



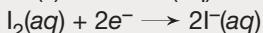
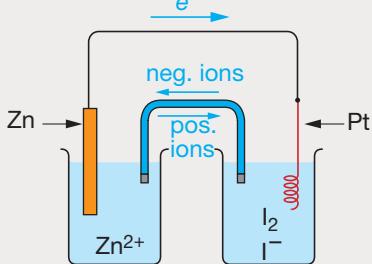
**11** for cell (a): see A below.

for cell (b): see B below.

**12** yes in all three cases, because both electrode reactions can still occur—the reactants  $\text{Cl}_2$  and Cu are still there—and there is an electrolyte to allow migration of ions to maintain electrical neutrality in the solution

**13** (b) and (c) could, because they are redox reactions  
(a) and (d) could not, because they are not redox reactions

**14**



c  $\text{I}^-$  ions migrate towards the  $\text{ZnSO}_4$  beaker while  $\text{Zn}^{2+}$  ions migrate towards the  $\text{I}_2$ ,  $\text{KI}$  beaker.

d Zn

**15 a** Cell would look like cell (a) in Answer 11 with Fe replacing Mg and Cu replacing Cd

**b** Again cell (a) in Answer 11, but with Al replacing Mg and Pb replacing Cd.

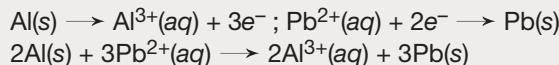
For (a) the activity series tells us than Fe would displace Cu; that is, Fe would go into solution as  $\text{Fe}^{2+}$  and copper deposit out (Cu would gain electrons). Hence Fe is the negative electrode and Cu the positive one. The electrode reactions would be:



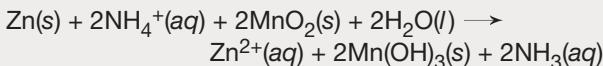
and the overall reaction:



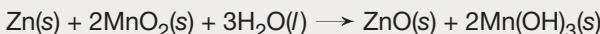
Similarly for (b) Al would displace Pb so Al would be the negative electrode (Al gives up electrons) and Pb the positive electrode. The electrode reactions and overall reaction are:



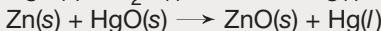
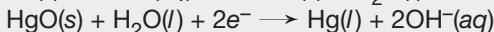
**16 Leclanché cell:**



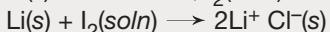
**Alkaline cell:**



**17 Mercury cell:**



**Lithium-iodine cell:**



**18 a** Because the zinc casing is thinner: it gets eaten away as the cell delivers electricity.

**b** It leaks sodium hydroxide paste which is very corrosive, whereas the Leclanché cell leaks a mixture of ammonia and ammonium chloride which is less corrosive.

**19** 6.9 g Li; 32.7 g Zn; 56.2 g Cd

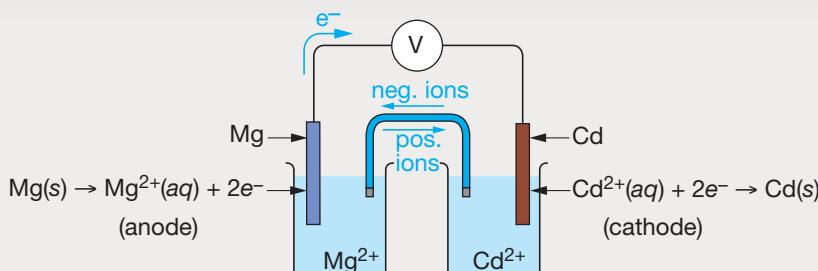
**20** As the cell discharges, changes occur to the electrodes ( $\text{PbO}_2 \rightarrow \text{PbSO}_4$  and  $\text{Pb} \rightarrow \text{PbSO}_4$ ), so to recharge the cell these changes must be reversed as well as replenishing the sulfuric acid solution; this can only occur by passing a current through the cell in the opposite direction.

**21 a**  $\text{CH}_3\text{OH(l)} + \text{H}_2\text{O(l)} \rightarrow \text{CO}_2(\text{g}) + 6\text{H}^+(\text{aq}) + 6\text{e}^-$   
$$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O(l)}$$

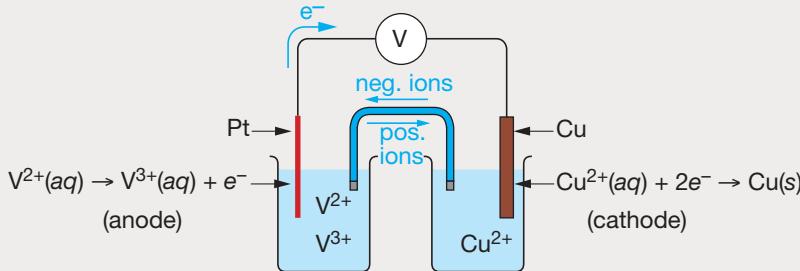
To get the overall reaction, multiply the first equation by 2 and the second by 3 (to balance electrons), then add.



**A**

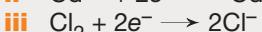
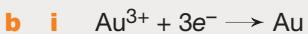


**B**



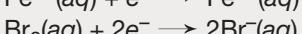
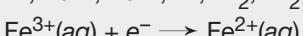
**22** Yes, because it can be recharged simply by replacing the spent vanadium solutions with fresh ones; the electrodes do not undergo any changes during discharge. It is also a rechargeable cell in that passage of current in the opposite direction restores the vanadium solutions to their initial states.

**23** a i +1.99 V ii -0.40 V iii 1.36 V



**24** b Zn,  $\text{Zn}^{2+}$ ; Ag,  $\text{Ag}^+$  etc

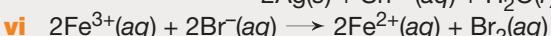
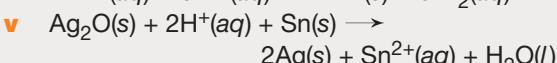
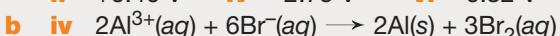
c Pt,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , Pt,  $\text{Br}_2$ ,  $\text{Br}^-$ ; Pt,  $\text{Sn}^{4+}$ ,  $\text{Sn}^{2+}$



(These are the reactions to which the electrode potentials apply: depending on the cell the electrode is present in, these reactions may occur in the reverse direction.)

**25** a i +0.60 V iii -2.50 V v +1.31 V

ii +0.40 V iv -2.75 V vi -0.32 V



c (i), (ii) and (v) as written; (iii), (iv) and (vi) in the reverse direction

**26** a 1.06 V (Ag positive)

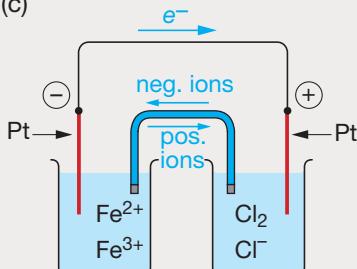
b 2.46 V (Ag positive)

c 0.59 V ( $\text{Cl}_2$  positive)

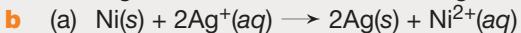
**27** a (a) like cell (a) in Answer 11 with Ni replacing Mg and Ag replacing Cd

(b) like cell (a) in Answer 11 with Al replacing Mg and Ag replacing Cd

(c)



This uses an aqueous chlorine electrode, a chloride solution saturated with  $\text{Cl}_2$ ; you could use a gaseous one like the one in Figure 2.5.



**28** a 1.60 V; 1.82 V; 1.26 V

b +0.49 V

## Chapter 3

**1** a  $^{12}\text{C}$  b  $^{32}\text{S}$  c  $^{37}\text{Cl}$  d  $^{127}\text{I}$

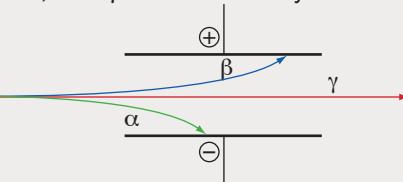
**2** a  $^{235}\text{Ra}$  b  $^{222}\text{Rn}$  c  $^{87}\text{Rb}$  d  $^{90}\text{Sr}$

**3** a  $^{239}\text{Pu} \rightarrow ^4_2\text{He} + ^{235}\text{U}$



**4** a Fr b Tl c Bi d Po e

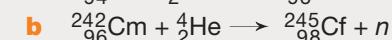
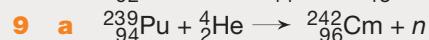
**5**  $\alpha$  is attracted to the negative electrode,  $\beta$  to the positive, and  $\gamma$  is unaffected by an electrical field



**6** a Decreases it, because it converts a neutron to a proton so in  $n/p$ ,  $p$  increases and  $n$  decreases: for example in Question (and answer) 2(d)  $n/p$  in Sr is 1.37 while in Y it is 1.31.

b Increases it, because the ratio of  $n$  to  $p$  lost is 2 : 2; whereas the  $n/p$  ratio in elements is normally greater than 1; taking 2 from top and bottom will increase the ratio: for example in Question (and answer) 2(a)  $n/p$  in Th is 1.66 while in Ra it is 1.67.

**7** unstable and  $\beta$  emitters: Ne, Ca, Pb; unstable but not  $\beta$  emitters: I, Ar (they emit positrons); stable: Ba and Si



**11** He and C nuclei are positively charged as are the nuclei they are bombarding, so high speed (energy) is needed to overcome the strong electrostatic repulsion that exists between bombarding particle and target. Neutrons have no charge so there is no electrostatic repulsion to overcome and so lower speeds (energies) are suitable.

**12** 6 half-lives = 48 days

**13** B, because it needs to be stored for 4 half-lives = 6000 years. (A needs to be stored for 10 half-lives but that is only 300 s.)

**14** because its half-life is so short: it decays quickly

**15** so that the same fraction of the total emissions is collected each time (decaying nuclei emit radiation in all directions: only some is collected by a detector)



**17**  $^{123}\text{I}$  has a short half-life (13.2 h), so it decays quickly and causes minimal damage to tissue after testing is complete.  $^{131}\text{I}$  has a much longer half-life (8 d); this means that it can irradiate the target tissue for longer times.

## Extended response exam-style questions for Module 1

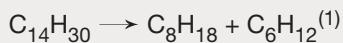
For answers for all the exam-style sets of questions the procedure will be as follows:

- A reference to the section of the book that treats the topic will be given.
- Then there will be some analysis of or commentary on what the question requires, such as what the main verb means in the context of the question, how much detail is warranted for the marks allotted, how to divide marks and time between different parts of the question and traps to watch out for.
- For some questions there will be a brief outline of the key points to treat; the amount of detail given here will depend on how directly the material in the section referred to relates to the question asked.
- For other questions a full answer will be given: in these answers there will be superscripted numbers such as (1) (2) (3) which count off the significant bits of information or marks for the answer. Answers quite different from these sample answers are possible and could equally well score full marks. However the sample answers are good guides for what to aim at. Sample answers are printed black while explanations and commentaries are blue.

The number of marks for a question determines the amount of time you should spend on it (100 marks for 3 hours work so 1.8 minutes per mark). Another guiding principle this author recommends, though you will not find it in any Board of Studies or HSC document, is that there should be at least one piece of significant and relevant information per mark. For a 5-mark question three significant bits of information is unlikely to score full marks, five pieces should, seven would be playing it very safe if you could do it in the nine minutes allowed, while ten would be foolhardy: too much time spent on the question at the expense of later questions (and you cannot get more than full marks on a question anyway).

- 1 See Section 1.1. There are two major reasons for cracking hydrocarbons: to balance the output of oil refineries to match demand, and to make the starting materials for various plastics (polymers). So you need to state these two reasons and explain why each is important. *Outline* means describe in general terms; that is, be brief, but not too brief. There are 4 marks or about seven minutes for this. You should also explain what cracking is (to convince an examiner that you know what you are talking about).

Cracking of hydrocarbons is the process in which large molecules are broken into two or more smaller ones, for example:



Cracking is important because it allows oil refineries to match their output of petrol and other

products to the relative demand for these products; this results in the most efficient use of crude oil<sup>(2)</sup> in that all of the oil is used to meet genuine demand without there being an excess of one product that has to be sold off cheaply to stimulate a false demand for it. Cracking is also important because it produces ethylene and propylene, which are the starting materials for the manufacture of many polymers (plastics) such as polyethylene and poly(vinyl chloride), PVC<sup>(3)</sup>; because there is a huge demand for such polymers to make a great variety of goods we use in our everyday lives, a cheap and readily available source of the starting materials is essential<sup>(4)</sup>.

- 2 See Section 2.1. *Demonstrate* means *show by example*. State what a displacement reaction is, give an example with an equation, then break it into half reactions, and finally show that electrons have been transferred.
- 3 See Section 3.3. There are 5 marks for this question so probably 2 for *distinguish between* and 3 for *outline*. *Distinguish* means *point out differences*; an example will help. *Outline* means *describe in general terms* (not too much detail).

Unstable (or radioactive) isotopes are ones that undergo nuclear decay—ones that emit  $\alpha$ ,  $\beta$  or  $\gamma$  rays (particles)—and so change into other isotopes<sup>(1)</sup>, for example radium and uranium. Stable isotopes are ones that do not undergo such decay, for example oxygen-16, nitrogen-14 and sodium-23<sup>(2)</sup>.

Scientists decide whether a particular isotope will be stable or not by comparing its neutron to proton ratio with a graph of this ratio against number of protons for all elements<sup>(3)</sup>. (Sketch the graph, Fig 3.1<sup>(4)</sup>.) If the isotope lies within the zone of stability, the isotope will be stable, but if it lies above or below this zone it will be unstable<sup>(5)</sup>.

- 4 See Section 1.13 and possibly 1.12. There are four bits to the question, structure, sources, uses and assess the potential, so there seem to be two possible ways of allocating marks: 2 marks for each bit (though examiners would probably allocate only 1 mark for sources), or alternatively 3 marks for structure, 1 for each of sources and uses and 2 for assess, so the safest approach would be to work on the basis of a 3, 1, 2, 2 distribution.

Cellulose is a polymer of glucose<sup>(1)</sup> with the glucose units strung together in a long unbranched chain<sup>(2)</sup>.

*Give a structure (diagram) such as structure (3) on p. 25 or the flat-ring one on p. 471 or the ‘molecular’ one on p. 23 (or if you are really stretched, a string of ovals joined together as in Figure 13.9 on p. 473 but with no branching)<sup>(3)</sup>.*

The main sources of cellulose are plants including trees<sup>(4)</sup>; cellulose is the structural material of all plants.

The main uses of cellulose are to make clothing and textiles (cotton and linen)<sup>(5)</sup> and paper and cardboard<sup>(6)</sup>.

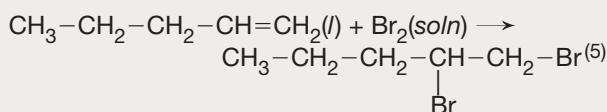
Cellulose shows considerable potential as a source of chemicals we currently get from oil such as ethylene and ethanol. However there are no processes for doing this on an industrial scale in operation at the moment: it is still in the developmental stage<sup>(7)</sup>. It is possible to hydrolyse cellulose into glucose (using either enzymes or strong acid as catalysts), and then glucose can be hydrolysed into ethanol, which is useful in itself (as a fuel and industrial solvent) but which can also be dehydrated to ethylene<sup>(8)</sup>. Ethylene is a starting material for making polyethylene, poly(vinyl chloride) (PVC) and other polymers. With six carbon atoms in a string, cellulose could be a source of more complex chemicals such as butenes for making synthetic rubber, but there are no practical processes in sight. (*The last two sentences are probably overkill.*)

- 5 See Section 1.19. Two major advantages and two disadvantages are listed in that section. *Discuss* means that you do have to talk about these four items, not just list them; the bits in brackets on p. 35 are therefore important. Marks will probably be distributed 3 for advantages and 2 for disadvantages or vice versa, so write as if there are 3 for each part.
- 6 See Section 3.12. *Demonstrate* means *use examples to show*. You need to consider both industry and medicine, so give at least one use for each. There are 2 or 3 marks for industry and 3 or 2 for medicine, so you need to give more than just a few words for each. Explain how the radioactive nature of the isotope is used. You could describe several uses very briefly or fewer uses in greater detail, but whichever you do, your answer must contain at least five significant bits of information.
- 7 See Sections 2.4 to 2.8. This is not exactly compulsory Experiment 4 or 5 (p. 100) but could be based on either, but before you rush in and use Experiment 4, note that you have to *explain* the flow of electrons and ions, so one of the cells from Experiment 5 may be easier to treat. Describe the cell (in words), 1 mark, and draw a diagram, 1 mark. To explain the flow of electrons and ions you will need to write the electrode reactions, 1 mark, and explain how these cause the electrons to flow in a particular direction through the external circuit (show it on your diagram), 1 mark, and the ions to migrate through the electrolytes of the cell (again show it on the diagram), 1 mark. Finally name the electrode which is the anode and which the cathode (preferably show on the diagram as well), 1 mark. The diagram in Answer 11 of Chapter 2 above is a good example of what is required.
- 8 See Sections 1.3, 1.4 and pp. 262–3 CCPC. *Compare and contrast* means that we must show

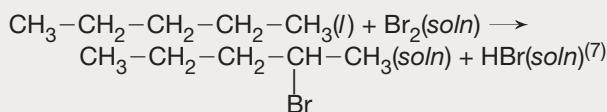
up similarities and differences. The main physical properties to consider are melting and boiling points, colour, density and solubility. The main chemical properties (reactions) are combustion, addition (for alkenes) and substitution (for alkanes).

The alkanes and alkenes have very similar physical properties. Both classes of compounds are colourless and have similar densities and they are both insoluble in water but soluble in non-polar solvents such as chloroform<sup>(1)</sup>. For compounds in the two classes with the same number of carbon atoms, the boiling and melting points are similar<sup>(2)</sup>.

For the two classes of compound some of their chemical properties are similar while others are quite different. Both alkanes and alkenes burn in oxygen to form carbon dioxide and water<sup>(3)</sup>. However their reactions with chlorine and bromine are quite different. Alkenes undergo addition reactions with chlorine and bromine in chloroform or hexachloroethane solution<sup>(4)</sup>, for example:



On the other hand alkanes do not react with chlorine or bromine in the dark, though they slowly undergo substitution reactions in the presence of u.v. light<sup>(6)</sup>, for example:



- 9 See Section 1.11. *Assess* involves making some judgement; in this case we have to decide whether there is a need, how important it is and how urgent it is. But first we should set out briefly the two cases (1) that there is a great need for alternative sources and (2) that there is no urgency about the matter, 2 marks, then make some judgement about how real or urgent the need is with some justification for that judgement, 2 marks.

Currently crude oil provides many of the important starting materials, such as ethylene and propene, that we need for the manufacture of a wide range of products such as polymers, synthetic rubber, paints, detergents and industrial solvents. It is expected that at the rate we are using up oil as a fuel, crude oil reserves will be exhausted within the next few decades. Therefore we need to develop alternative sources of the key starting materials<sup>(1)</sup>. An alternative argument is that as we use up oil reserves, the price will escalate until oil becomes too expensive to use as a fuel and so alternative fuel sources will be developed. This will leave the remaining oil as a raw material for these other industries<sup>(2)</sup>. Even on the basis of this second argument, new sources will eventually need to be

found, though we may have an extra few decades in which to do it.

There is a genuine need for alternative sources, because we really do need the products that are currently made from petrochemicals and oil will eventually be all used up<sup>(3)</sup>. However the time we have available in which to find alternative sources—a few decades or nearly a century—depends upon which of the arguments above will prove to be the most accurate. Hence the urgency of the need to find alternative sources is less clear cut<sup>(4)</sup>.

- 10** See Sections 2.10 and 2.11. Do not just describe the chemistry of the two cells but point out similarities and differences. Regardless of whether you use the vanadium redox cell or some other fuel cell (such as the hydrogen oxygen one), one similarity is that both use a reversible redox reaction to generate electricity, 1 mark, though the actual reactions are quite different; state them (either as an overall reaction or as half reactions), 2 marks. Both can be recharged by passing electricity through them in the opposite direction, 1 mark. In the lead–acid cell the electrodes undergo changes as the cell discharges ( $\text{Pb} \rightarrow \text{PbSO}_4$  and  $\text{PbO}_2 \rightarrow \text{PbSO}_4$ ) whereas in the other two cells the electrodes remain unchanged, 1 mark. Hence the vanadium redox cell or fuel cell can be recharged by replenishing the supply of chemicals whereas the lead–acid cell cannot, 1 mark.
- 11** See Section 3.12. *Outline* means describe without too much detail. Choose a use and a named isotope where you can identify the properties that make the particular isotope suitable for that use. The properties that usually decide which isotope to use are the type of radiation emitted, the energy or penetrating power of the radiation and the half-life. A good industrial use to treat would be a thickness gauge ( $^{137}\text{Cs}$  or  $^{90}\text{Sr}$ ): gamma ray emitter, moderate energy and penetrating power, reasonably long half-life) or a good medical use would be cancer treatment ( $^{60}\text{Co}$ , gamma ray emitter, moderately high energy or good penetrating power, moderately long half-life so source does not need frequent replacement).
- 12** See Section 2.3. Explain, give an example, then show how the example illustrates the explanation.
- 13** See Section 1.15. A reasonable mark allocation for the three parts of the question is production (including naming it and giving its structure), 3 marks, uses, 2 marks and evaluating its significance, 2 marks. Production and uses are in Section 1.15. For evaluate its significance:

Its significance lies in the facts that it is a polymer produced from a non-oil starting material, that it is biodegradable and that it shows another way of synthesising polymers (using biotechnology instead of oil and traditional industrial chemistry). Hence it has considerable significance for society<sup>(1)</sup>.

However these advantages are partly overshadowed by the facts that it is much more expensive than orthodox polymers and that it has not as yet achieved much market penetration. Consequently it has some significance for society but not an outstanding one<sup>(2)</sup>.

- 14** This is compulsory Experiment 3 on p. 100; see Section 1.20. Describe the experiment you performed, 3 marks, list two sources of error (heat losses to the surroundings, incomplete combustion of the alkanol, lack of sensitivity of the balance used to weigh the spirit burner before and after), 2 marks, and steps you took to minimise these, 2 marks. You probably minimised heat losses by putting a screen around the experiment to eliminate drafts, by using a highly polished aluminium container rather than a dark dull one and stirring with the thermometer and not a separate stirrer, and suspending the can above the burner with a wire or string handle instead of using a triangular stand or clamp. Errors from incomplete combustion are harder to minimise; about all you can do is locate the container just above the luminous zone of the flame—allowing adequate time (height) for near complete combustion but not too much space for excessive heat loss.
- 15** See Section 1.10. Two marks each for the two examples; choose examples where it is easy to relate uses to properties to structure.
- Low density polyethylene, LDPE, is used to make Cling Wrap, thin transparent film for wrapping sandwiches and other food items and for sealing salad bowls and other food containers. The properties that make LDPE suitable for this are its softness, flexibility and ability to stick to itself and to many other materials<sup>(1)</sup>. These properties arise because there is much chain branching which keeps the substance non-crystalline and therefore quite soft; the molecular chains are very floppy because the side groups are just small H atoms which do not introduce any chain stiffening into the molecule. This helps to keep the molecule soft and pliable<sup>(2)</sup>.
- Polystyrene is used for screwdriver handles. The properties that make polystyrene suitable for this are its hardness and rigidity and transparency<sup>(3)</sup>. These properties arise because there are large side groups, phenyl groups  $\text{C}_6\text{H}_5-$ , in the molecule; these stiffen the chain and stop it flopping around. In addition there is little chain branching in polystyrene. These properties combine to make polystyrene a very crystalline solid and so it forms hard, rigid and transparent objects<sup>(4)</sup>.
- (That is probably enough for 4 marks; to be safe you could include diagrams showing chain stiffening and chain branching.)*
- 16** See Section 1.5. Demonstrate means show by example, so we need examples; since there are 4 marks, four examples (reactions, preferably with equations) would seem to be required.

**17** See Section 3.13. Discuss in this context means point out the significance of the benefits and the seriousness of the problems or the adequacy of solutions to them; that is, do not just list the benefits and problems. With 6 marks you should include at least two benefits and two problems.

**18** See Sections 1.6 and 1.7. One mark for each structure and 1 mark for uses of each polymer; give more than one use if you can, to be on the safe side.

**19** See Section 2.9. Probably 3 marks for structure and chemistry (include a diagram and either the electrode reactions or the overall reaction) and 2 for assess its importance. For ‘assess its importance’:

In the first part of the twentieth century the ordinary dry cell was extremely important to society because it was an easily portable battery and so allowed the development of devices such as the common torch, battery-operated clocks and later portable radios and battery-operated toys<sup>(1)</sup>. While it is still widely used in devices that draw only small currents, it is less significant today, because we now have a wide range of other cells that are able to deliver greater currents and larger total amounts of electricity<sup>(2)</sup> for such devices as mobile phones, portable CD players, laptop computers and movie and digital cameras.

**20** See Section 1.19. Evaluate in this context means make some judgement about the correctness or accuracy of the claim. Hence state the basis for the claim, explain why the claim is or is not strictly valid, then make an overall evaluation of it.

Ethanol is regarded as a renewable fuel because it can be made by fermentation of substances (such as sugar and starch) that are made by photosynthesis from CO<sub>2</sub> and H<sub>2</sub>O<sup>(1)</sup> and when it is used as a fuel it is converted back to CO<sub>2</sub> and H<sub>2</sub>O<sup>(2)</sup>.

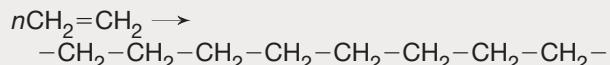
However it is not completely renewable because considerable amounts of non-renewable fossil fuel go into making it; energy from fossil fuel is used to make fertiliser that is needed to grow the plants and to drive the machinery used to cultivate and harvest the crops. Fermentation produces only about a 15% aqueous solution of ethanol and generally large amounts of fossil fuel are used to distil ethanol from this mixture. Hence when we use ethanol as a fuel we are effectively using considerable quantities of non-renewable fuel as well<sup>(3)</sup>.

The claim that ethanol is a renewable fuel would be close to the truth if the raw materials were wastes from other processes (for example, if cellulose could be used) and if solar energy were used to distil off the ethanol<sup>(4)</sup>. This means that overall the claim is only partly true; it could just be an oversimplification of the real situation or in some circumstances be decidedly incorrect<sup>(5)</sup>.

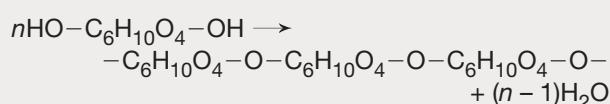
## Revision test for Module 1

- |          |   |          |   |          |   |          |   |           |   |
|----------|---|----------|---|----------|---|----------|---|-----------|---|
| <b>1</b> | a | <b>2</b> | b | <b>3</b> | d | <b>4</b> | c | <b>5</b>  | d |
| <b>6</b> | b | <b>7</b> | c | <b>8</b> | c | <b>9</b> | a | <b>10</b> | b |

**11** In addition polymerisation monomer molecules simply join to one another as when ethylene forms polyethylene:



In condensation polymerisation monomer molecules join together by eliminating a small molecule such as water, for example when glucose written as HO-C<sub>6</sub>H<sub>10</sub>O<sub>4</sub>-OH forms cellulose:



A water molecule is eliminated between each pair of glucose molecules.

- 12** **a** 8.5 × 10<sup>2</sup> kJ/mol  
**b** loss of heat to the surroundings, incomplete combustion of ethanol (forming soot or CO instead of CO<sub>2</sub>)
- 13** This is Experiment 5 from p. 100. See Sections 2.4 to 2.8. Describe the experiment, 2 marks, draw a fully labelled diagram as in Answer 11 in Chapter 2, 2 marks, and give two reasons (or more) why your voltage differed from the calculated one, 2 marks. The reasons are likely to be (1) the solutions were not 1.00 mol/L (Section 2.13), (2) the metals were not completely pure, (3) there were impurities in the electrolyte solutions.

- 14** **a**  $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3-\text{CH}_2-\text{OH}$   
Heat the ethylene under pressure with dilute sulfuric or phosphoric acid.  
 $\text{CH}_3-\text{CH}_2-\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$   
Heat the ethanol with concentrated sulfuric or phosphoric acid.  
**b** The first reaction is addition (or hydration); the second reaction is dehydration (or elimination). Another example of an addition reaction is the addition of bromine to propylene:  
$$\text{CH}_3-\text{CH}=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_3-\underset{\substack{| \\ \text{Br}}}{\text{CH}}-\text{CH}_2-\text{Br}$$

- 15** See Section 3.10. You certainly need two specific examples (isotopes) and preferably two methods: exposure to neutron bombardment in a nuclear reactor, for example molybdenum-99 which is the precursor of technetium-99m, 2 marks, and a cyclotron, for example fluorine-18 for positron emission tomography, 2 marks. Probably one method, the nuclear reactor with an equation for nuclear fission, would score 2 marks.

- 16** **a** (i) Our massive use of crude oil as a fuel could so deplete supplies that none would be left for making polymers: the starting materials for many polymers are ethylene and propylene obtained

from cracking crude oil.

(ii) Normal synthetic plastics (from oil-based reactants) are not biodegradable, so when discarded they stay in the environment indefinitely which can be a problem.

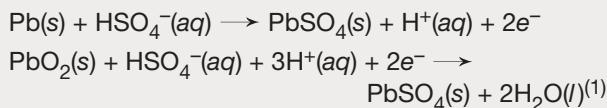
- b** One approach is to use non-oil based starting materials to make biodegradable polymers such as PHA (or PHB): see page 28.

**17** See Section 3.11. Describe the Geiger–Müller counter with a diagram. Alternatively describe a cloud chamber, again with a diagram. There is not enough information about scintillation counters in this book to warrant 3 marks so unless you have information from other sources avoid that instrument.

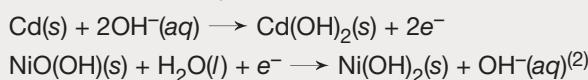
**18** This is Experiment 1 on p. 100. See Section 1.4. Describe the experiment you performed. Most likely you used an aqueous solution of bromine in which case you need two equations (see text); this is the reason for the *at least one equation* in the question. If you used bromine in hexachloroethane, only one equation is needed. If your account includes bromine in chloroform, you are signalling to the examiner that you probably did not do the experiment as chloroform is not allowed in school laboratories. Ensure that the alkane and alkene you use are C<sub>5</sub> or above; C<sub>4</sub> and below are gases and so not amenable to school laboratory testing. Remember that examiners are looking for evidence that you actually did the experiment.

**19** See Sections 2.9 to 2.12. You could compare one of the designated cells with an alkaline cell, a silver oxide cell or with a nickel–cadmium cell (the chemistry of the vanadium redox cell and the Gratzel cell is probably too complex for this question). Plan on 3 or 4 marks for the chemistry, 1 for uses and 1 or 2 for environmental impacts. Remember the question is *compare and contrast* so do not just *describe the chemistry, uses and impacts*. One sample answer follows.

Nickel–cadmium cell compared with the lead–acid cell: The lead–acid cell consists of a lead anode and a lead, lead dioxide cathode, both dipping into a solution of sulfuric acid. As the cell produces electricity the electrode reactions are:



The nickel–cadmium cell consists of a cadmium, cadmium hydroxide anode (negative electrode) and a nickel, nickel hydroxide, nickel oxyhydroxide cathode (positive electrode) with the electrolyte being a potassium hydroxide paste. As the cell produces electricity the electrode reactions are:



Both of these cells are rechargeable; if an electric current is passed through them, the electrode reactions are reversed.<sup>(3)</sup>

Although both of these cells use an unusual oxidation state of a metal (+4 for Pb in PbO<sub>2</sub> and +3 for Ni in NiO(OH)), their chemistry is quite different. In addition the Ni–Cd cell uses an alkaline electrolyte while the lead–acid cell uses an acidic one.<sup>(4)</sup>

**Uses:** Both of these cells are used where a rechargeable source of electricity is needed or desired. The main use of the lead–acid cell is in motor cars, while nickel–cadmium cells are generally used in more portable appliances such as electric drills, video cameras and CD players. Nickel–cadmium cells can be made in the same sizes and shapes as dry cells and alkaline cells, and so are often used as direct replacements for those cells.<sup>(5)</sup>

**Environmental impacts:** Both cells are potentially dangerous to the environment, because they contain lead and cadmium respectively, both of which are poisonous<sup>(6)</sup>. However the environmental impact of the lead–acid cell is quite minimal, because these cells are largely recycled; having one main use (motor cars) and being big, lead–acid cells are easy to collect and to recover lead from. On the other hand nickel–cadmium cells have more diverse uses, are smaller and so are harder to collect for recovery of the cadmium and so they have a more detrimental effect upon the environment.<sup>(7)</sup> (*The marking scheme here caters for all of the above suggestions.*)

## Chapter 4

- 1** acidic: Z, X; alkaline: Y, U: neutral: W, M; N is either neutral or alkaline: use bromothymol blue—if it goes blue the solution is alkaline, if green it is neutral
- 2** P, highly acidic; Q, slightly acidic; R, alkaline; S, highly alkaline; T, neutral; V could be slightly acidic, neutral or slightly alkaline. Test R with phenolphthalein: if colourless, R is slightly alkaline, if red, highly alkaline. Test V with bromothymol blue: if yellow, V is slightly acidic, if green, it is neutral, if blue, slightly alkaline.
- 3** **a** **i** H<sup>+</sup> (or H<sub>3</sub>O<sup>+</sup>) and Br<sup>-</sup>  
**ii** H<sup>+</sup>, NO<sub>3</sub><sup>-</sup>
- b** **i** Ba<sup>2+</sup>, OH<sup>-</sup>    **ii** Na<sup>+</sup>, OH<sup>-</sup>
- 4** **a** **i** HNO<sub>3</sub>(aq) + NaOH(aq) → NaNO<sub>3</sub>(aq) + H<sub>2</sub>O(l)  
**ii** 2HNO<sub>3</sub>(aq) + ZnO(s) → Zn(NO<sub>3</sub>)<sub>2</sub>(aq) + H<sub>2</sub>O(l)  
**iii** HNO<sub>3</sub>(aq) + NH<sub>3</sub>(aq) → NH<sub>4</sub>NO<sub>3</sub>(aq)
- b** **i** H<sub>2</sub>SO<sub>4</sub>(aq) + 2NaOH(aq) → Na<sub>2</sub>SO<sub>4</sub>(aq) + 2H<sub>2</sub>O(l)  
**ii** H<sub>2</sub>SO<sub>4</sub>(aq) + ZnO(s) → ZnSO<sub>4</sub>(aq) + H<sub>2</sub>O(l)  
**iii** H<sub>2</sub>SO<sub>4</sub>(aq) + 2NH<sub>3</sub>(aq) → (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>(aq)
- 5** **a** K<sub>2</sub>O(s) + 2H<sup>+</sup>(aq) → H<sub>2</sub>O(l) + 2K<sup>+</sup>(aq)  
**b** Al<sub>2</sub>O<sub>3</sub>(s) + 6H<sup>+</sup>(aq) → 3H<sub>2</sub>O(l) + 2Al<sup>3+</sup>(aq)  
**c and f** see Section 4.3

- 6** **a**  $\text{Mg}(\text{OH})_2(s) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{Mg}^{2+}(\text{aq})$

**b**  $\text{HNO}_3(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(l) + \text{NO}_3^-(\text{aq})$

**c**  $\text{H}_2\text{CO}_3(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{CO}_3^{2-}(\text{aq})$

**d**  $\text{H}_3\text{PO}_4(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow 3\text{H}_2\text{O}(l) + \text{PO}_4^{3-}(\text{aq})$

**7** **a**  $\text{KI}$

**b**  $\text{BaSO}_4$

**c**  $\text{Na}(\text{CH}_3\text{CO}_2)$  or  $\text{CH}_3\text{CO}_2\text{Na}$

**d**  $\text{K}_2\text{SO}_3$

**e**  $\text{AlCl}_3$

**f**  $\text{Zn}(\text{NO}_3)_2$

**8** **a** calcium fluoride, sodium chloride, potassium bromide, silver iodide, potassium sulfate, sodium sulfite, lead nitrate, sodium nitrite, calcium carbonate, sodium phosphate, magnesium formate (magnesium methanoate), silver acetate (silver ethanoate), potassium cyanide, zinc sulfide

**b** **i** silver bromide

**ii** ammonium carbonate

**iii** sodium sulfite

**iv** magnesium fluoride

**v** potassium nitrite

**vi** potassium phosphate

**9** **a** for 7(e): react  $\text{Al}(\text{OH})_3$  with  $\text{HCl}$ ; for 7(f): react  $\text{ZnO}$  with  $\text{HNO}_3$ ; for 8(b)(iv) react  $\text{MgO}$  or  $\text{Mg}(\text{OH})_2$  with  $\text{HF}$ ; for 8(b)(ix) react  $\text{Ca}(\text{OH})_2$  with acetic (ethanoic) acid; in all cases either evaporate the solution to dryness or concentrate it and then cool it to crystallise out the salt.

**b** for 7(e):

$$\text{Al}(\text{OH})_3(s) + 3\text{HCl}(\text{aq}) \rightarrow \text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(l)$$

$$\text{Al}(\text{OH})_3(s) + 3\text{H}^+ + 3\text{Cl}^- \rightarrow \text{Al}^{3+} + 3\text{Cl}^- + 3\text{H}_2\text{O}(l)$$

$$\text{Al}(\text{OH})_3(s) + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}(l)$$

for 8(b)(iv):

$$\text{MgO}(\text{s}) + 2\text{HF}(\text{aq}) \rightarrow \text{MgF}_2(\text{aq}) + \text{H}_2\text{O}(l)$$

$$\text{MgO}(\text{s}) + 2\text{H}^+ + 2\text{F}^- \rightarrow \text{Mg}^{2+} + 2\text{F}^- + \text{H}_2\text{O}(l)$$

$$\text{MgO}(\text{s}) + 2\text{H}^+ \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{H}_2\text{O}(l)$$

**10** **a**  $\text{B}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(l) \rightarrow 2\text{H}_3\text{BO}_3(\text{aq})$

$$\text{N}_2\text{O}_3(\text{g}) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_2(\text{aq})$$

$$\text{P}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(l) \rightarrow 2\text{H}_3\text{PO}_3(\text{aq})$$

$$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$$

$$\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O}(l) \rightarrow 2\text{HOCl}(\text{aq})$$

**b**  $2\text{NaOH}(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq})$

$$2\text{NaOH}(\text{aq}) + \text{SO}_3(\text{g}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq})$$

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

**b**  $\text{Na}_2\text{O}(\text{s}) + \text{SO}_2(\text{g}) \rightarrow \text{Na}_2\text{SO}_3(\text{s})$

**12** **a** The plot of solubility versus pressure is a straight line through the origin: this proves proportionality.  

$$3.26 \times 10^{-4} \text{ mol L}^{-1} \text{ kPa}^{-1} (\pm 0.02 \times 10^{-4})$$

**b** **i** 0.021 mol/L      **ii** 92 kPa

**c** **i** 0.081 mol/L      **ii** 169 kPa

**13** When the cap was replaced there was only a small pressure of  $\text{CO}_2$  in the air in the bottle, so  $\text{CO}_2$  comes out of solution until there is equilibrium between  $\text{CO}_2$  in the gas and in the solution. This significantly lowers the concentration of  $\text{CO}_2$  in the

solution (compared to that in the just opened bottle), so it tastes ‘flatter’ when the bottle is re-opened.

- 14 a** Vapour pressure increases as temperature increases, because by Le Chatelier's principle as temperature increases the equilibrium moves to counteract the rise and so moves in the endothermic (heat absorbing) direction: that is, towards vapour.

**15 a** Adding  $\text{HCO}_3^-$  decreases  $[\text{H}^+]$ , because it forces the equilibrium to the left in order to minimise the increase in  $[\text{HCO}_3^-]$ .

**b** Add  $\text{H}^+$  to remove  $\text{OH}^-$  and so drive the equilibrium towards the right (i.e. make the pool slightly acidic).

**16 a**  $\text{CH}_3\text{CO}_2\text{Ag(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$

**b** add an excess of  $\text{CH}_3\text{CO}_2^-$

**c** As  $\text{H}^+$  is added, the equilibrium in (c) of the question is forced towards the right: this lowers the concentration of  $\text{CH}_3\text{CO}_2^-$  so the equilibrium in (a) moves to the right to counteract this: in other words the precipitate dissolves.

**17** dinitrogen monoxide, nitrogen monoxide, nitrogen dioxide (see p. 81 CCPC)

**18**  $2\text{FeS(s)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{FeO(s)} + 2\text{SO}_2(\text{g})$

**19**  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$   
 $\text{SO}_3(\text{g}) + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4(\text{aq})$

**20**  $\text{SO}_2$  in polluted air is converted into sulfuric acid dissolved in water droplets; ammonia can react with this acid:  
 $2\text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{aq})$   
Ammonium carbonate could form similarly:  
 $2\text{NH}_3(\text{g}) + \text{H}_2\text{CO}_3(\text{aq}) (= \text{CO}_2 + \text{H}_2\text{O}) \rightarrow (\text{NH}_4)_2\text{CO}_3(\text{aq})$

**21** calcium sulfite;  $\text{CaO(s)} + \text{SO}_2(\text{g}) \rightarrow \text{CaSO}_3(\text{s})$

**22**  $2\text{HNO}_3(\text{aq}) + \text{CaCO}_3(\text{s}) \rightarrow \text{Ca}(\text{NO}_3)_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$   
 $\text{H}_2\text{SO}_4(\text{aq}) + \text{CaCO}_3(\text{s}) \rightarrow \text{CaSO}_4(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$   
(Calcium sulfate is sparingly soluble so dissolves at the low concentrations of sulfuric acid involved.)

**23**  $1.5 \times 10^{-5}$  mol/L;  $8.2 \times 10^{-10}$  mol/L

**24 a** 6.375 g  
**b** 11.9 L

**25** 0.93 L

**26** 0.082 L

**27** 1.53 L

**28** 2.26 kg

<b>29 a</b>	4.0	<b>c</b>	2.593	<b>e</b>	4.24
<b>b</b>	1.77	<b>d</b>	3.364	<b>f</b>	-0.11

**30** (all are in mol/L)

<b>a</b>	$1.0 \times 10^{-3}$	<b>d</b>	0.036	<b>g</b>	$4 \times 10^{-10}$
<b>b</b>	$1.4 \times 10^{-4}$	<b>e</b>	$3 \times 10^{-13}$	<b>h</b>	0.45
<b>c</b>	$2.5 \times 10^{-11}$	<b>f</b>	$1.5 \times 10^{-6}$	<b>i</b>	5.0

**31** for  $\text{pH} = 4.75$ ,  $[\text{H}^+] = 1.8 \times 10^{-5}$  mol/L; for  $\text{pH} = 3.75$ ,  $[\text{H}^+] = 1.8 \times 10^{-4}$  mol/L, so a decrease of one unit in pH increases  $[\text{H}^+]$  by a factor of ten

**32** A, 6 (6.0 to 6.2); B, 3.8; C, 7.6 to 8.0

**33** P, < 3.1; Q, 4.4 to 6.2; R, > 8; S, > 10; T, 7;  
V, 4.4 to 8.3

**34 a**  $\text{H}_2\text{SO}_4(l) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{HSO}_4^-(aq)$   
(goes to completion hence  $\rightarrow$ )  
 $\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$   
(comes to equilibrium; only some of the  $\text{HSO}_4^-$  ions ionise to  $\text{SO}_4^{2-}$ ; hence  $\rightleftharpoons$ )  
 $\text{HF}(g) \rightarrow \text{HF}(aq)$   
 $\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$

**b**  $\text{HClO}_4(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{ClO}_4^-(aq)$   
 $\text{HClO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}_2^-(aq)$

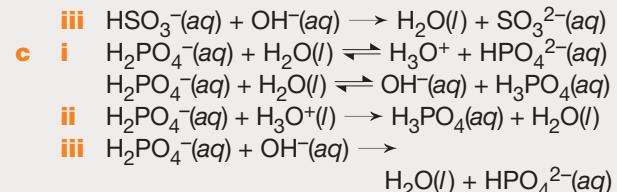
**35 a** 1.19      **b** 0.13 (or 13%)

**36** D < E < A < B < C; C is strong (because pH shows that  $[\text{H}^+]$  is 0.015 mol/L which is the total concentration of the acid in the solution)

**37 a** 3.34      **b** 32% ionised

## Chapter 5

- 1 a**  $\text{HClO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClO}_2^-(aq)$   
**b**  $\text{HOBr}(aq) + \text{H}_2\text{O}(aq) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OBr}^-(aq)$   
**f**  $\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$   
(You might like to precede this with  
 $\text{NaHSO}_4(aq) \rightarrow \text{Na}^+(aq) + \text{HSO}_4^-(aq)$ )
- 2 a**  $\text{CH}_3-\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3-\text{NH}_3^+(aq) + \text{OH}^-(aq)$   
**b**  $\text{N}_2\text{H}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{N}_2\text{H}_5^+(aq) + \text{OH}^-(aq)$   
**c**  $\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$
- 3** from Exercise 1: (a)  $\text{ClO}_2^-$  (b)  $\text{OBr}^-$  (f)  $\text{SO}_4^{2-}$   
from Exercise 2: (a)  $\text{CH}_3-\text{NH}_3^+$  (b)  $\text{N}_2\text{H}_5^+$  (c)  $\text{HCN}$
- 4 a** (first three and 7th)  $\text{HCOO}^-$ ,  $\text{OCN}^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$   
**b** (first, 3rd, 6th and last)  $\text{C}_6\text{H}_5\text{NH}_3^+$ ,  $\text{NH}_3\text{OH}^+$ ,  
 $\text{H}_3\text{PO}_4$ ,  $\text{OH}^-$ ,
- 5** CB = conjugate base; CA = conjugate acid
- a i** acid  $\text{NH}_4^+$ , CB  $\text{NH}_3$   
**i i** acid HCN, CB  $\text{CN}^-$
- b i** base  $\text{NH}_3$ , CA  $\text{NH}_4^+$   
**i i** base  $\text{CH}_3\text{O}^-$ , CA  $\text{CH}_3\text{OH}$
- 6 a**  $\text{KHCO}_3$       **b**  $\text{NH}_4\text{HSO}_4$       **e**  $\text{Li}_2\text{HPO}_4$
- 7 a** lithium hydrogen carbonate  
**b** zinc hydrogen sulfate
- d** ammonium hydrogen phosphate
- f** potassium dihydrogen phosphate
- 8 a**  $\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$   
 $\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq)$
- 9 a**  $\text{Ba}(\text{NO}_3)_2$ ; 7; neither ion reacts with water  
(hydrolyses)
- b**  $\text{HCOONa}$ ; >7;  
 $\text{HCOO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCOOH}(aq) + \text{OH}^-(aq)$
- c**  $\text{Na}_2\text{CO}_3$ ; >7;  
 $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$
- d**  $\text{NH}_4\text{NO}_3$ ; <7;  
 $\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq)$
- g**  $\text{NaCN}$ ; >7;  
 $\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$
- 10 a i**  $\text{HSO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_3^{2-}(aq)$   
 $\text{HSO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{SO}_3(aq)$
- ii**  $\text{HSO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l)$



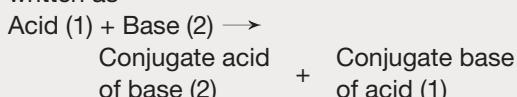
**11 a**  $\text{CaO}(s) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l)$   
(from HCl to  $\text{O}^{2-}$ )

**b**  $\text{Cu}(\text{OH})_2(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(aq) + 2\text{H}_2\text{O}(l)$   
(from  $\text{H}_2\text{SO}_4$  to the  $\text{OH}^-$  in  $\text{Cu}(\text{OH})_2$ )

**c**  $\text{NH}_3(aq) + \text{HNO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(aq)$   
(from  $\text{HNO}_3$  to  $\text{NH}_3$ )

**12**  $\text{Na}_2\text{SO}_3(s \text{ or } aq) + 2\text{HCl}(aq) \rightarrow 2\text{NaCl}(aq) + \text{H}_2\text{SO}_3(aq)$   
sulfur dioxide:  $\text{H}_2\text{SO}_3(aq) \rightarrow \text{SO}_2(g) + \text{H}_2\text{O}(l)$   
yes;  $\text{KHSO}_3(s \text{ or } aq) + \text{HCl}(aq) \rightarrow \text{KCl}(aq) + \text{H}_2\text{SO}_3(aq) (\rightarrow \text{SO}_2(g) + \text{H}_2\text{O})$

**13** yes; because the acid  $\text{HNO}_2$  has been converted to the salt  $\text{NaNO}_2$ . The acid HCN is much weaker than  $\text{HNO}_2$  so  $\text{CN}^-$  can be regarded as having removed the  $\text{H}^+$  of  $\text{HNO}_2$ . Neutralisation is sometimes written as



with conjugate base of acid (1) being a weaker base than base (2) and conjugate acid of base (2) being a weaker acid than acid (1).

**14** 57 kJ/mol; -57 kJ/mol

**15**  $\text{NH}_3(aq) + \text{H}^+(aq) \rightarrow \text{NH}_4^+(aq)$ ; -50 kJ/mol

**16** 0.187 (or 0.1866) mol/L; 0.101 mol/L; 17.3 g/L

**17** 0.165 mol/L

**18** Use Table 5.5.  $\text{Na}_2\text{CO}_3 + \text{HCl}$ : methyl orange, methyl red, bromocresol green or bromophenol blue. At the equivalence point we have a solution of  $\text{H}_2\text{CO}_3$  and  $\text{NaCl}$  and  $\text{H}_2\text{CO}_3$  makes the solution slightly acidic. Alternatively, the first stage of this titration (to  $\text{HCO}_3^-$ ) is strong acid + strong base, but the second stage ( $\text{HCO}_3^-$  to  $\text{H}_2\text{CO}_3$ ) is strong acid + weak base so needs one of the above indicators.

$\text{Ba}(\text{OH})_2 + \text{HCl}$ : bromothymol blue or phenol red – strong acid + strong base.

$\text{KH}(\text{C}_8\text{H}_4\text{O}_4) + \text{NaOH}$ : phenolphthalein or thymol blue – weak acid + strong base.

(For an explanation of the indicators recommended in Table 5.5 see Section 5.5.)

**19** 0.712 mol/L; 4.27%

**20** Wash the volumetric flask, pipettes and burette thoroughly with water; leave the volumetric flask wet with water.

Rinse the burette and pipettes with the solutions they are to dispense.

Fill the pipette carefully, taking great care that the meniscus sits exactly on the graduation mark; hold the pipette vertically at eye level and view it with a pale wall or white card as background to make the meniscus appear sharper.

Drain the pipette carefully; keep it vertical and at the end, touch the tip against the side of the flask and hold it there for the stated draining period (20 s); do not blow out the small volume of liquid that is intended to stay there.

Fill the volumetric flask with water carefully; use a Pasteur pipette (eye dropper) for the last few mL and get the meniscus sitting exactly on the graduation mark as for the pipette.

When filling the burette (after rinsing with the solution to be used), ensure there are no air bubbles trapped in the tip.

Read the starting and ending volumes of the burette carefully, using a white card behind it to make the meniscus appear sharper; write down the volumes immediately they are read.

Sit the titration flask on a white tile or card to make it easier to see the indicator colour change.

Use the correct indicator (phenolphthalein in this case) and use just enough indicator to give the solution a distinct colour; for this titration determine how many drops are needed by using an equal volume of slightly alkaline solution (since this indicator is colourless in acid solution); too much indicator makes the colour change harder to see.

After the first trial titration has given the approximate end point, dispense the sodium hydroxide solution from the burette slowly near the equivalence point, one drop at the time or for the last bit, a fraction of a drop, washing it off with a wash bottle.

If the first titration was larger than the subsequent ones, discard it as it probably overshot the equivalence point.

Repeat the titration until three titres agree to within 0.05 mL.

**21** 3.29 mol/L

**22** 3.20 mol/L; 314 g/L; 17.0 g

**23** 0.0178 mol/L; 0.133 g/100 mL

- 25 a** phenolphthalein or thymol blue (weak acid + strong base)  
**b** methyl orange, methyl red, bromocresol green or bromophenol blue (strong acid + weak base)  
**c** bromothymol blue, phenol red or litmus (strong acid + strong base)

**26 a** 0.254 mol/L

**b** 0.620 mol/L; 3.72%

**c** It is a weak acid, weak base titration. For these the change in pH at the equivalence point is quite small and not very sudden, so indicators do not give a sharp colour change: they slowly change colour over several millilitres. Hence it is not possible to determine the equivalence point accurately.

**27** The two salts are involved in the equilibrium,

- 35 c**  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CO—O—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$   
**d**  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CO—O—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$



The position of this equilibrium with approximately equal concentrations of the two anions present is such that pH is close to 7. If HCl is added:



that is, the equilibrium moves to the left and removes most of the added HCl and so pH does not fall much. If NaOH is added:

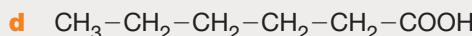
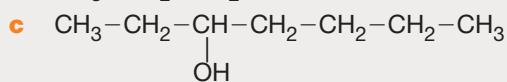
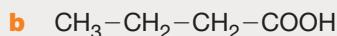
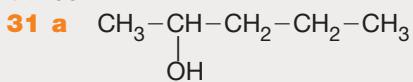


that is the equilibrium moves to the right and so keeps pH approximately constant.

**28 a** yes; comparable amounts of a weak acid and its conjugate base are present.

**c** no; nitric acid is a strong acid, meaning it is completely ionised regardless of how much nitrate is present, so there is no equilibrium to adjust.

**30** 65.4 L



**32 a** 3-pentanol      **c** 3-hexanol

**b** pentanoic acid      **d** octanoic acid

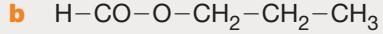
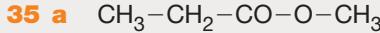
**33 a** The graphs show that boiling point increases as number of C atoms increases (for both classes of compound). Boiling point increases as the number of carbon atoms increases because with an increasing number of atoms there is an increasing number of electrons and the more electrons there are in the molecule the stronger are the dispersion forces; stronger intermolecular forces means higher boiling points.

The curve for alkanoic acids is displaced to higher temperatures relative to the alkanol curve. This is because there is stronger hydrogen bonding in alkanoic acids (two O atoms with an H on one of them) than in alkanols (just one O atom with an H atom attached).

**b** **i**  $(177 \pm 3)^\circ\text{C}$       **ii**  $(208 \pm 4)^\circ\text{C}$

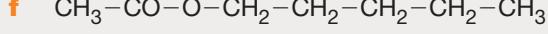
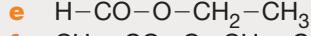
**34 a** ethyl methanoate      **c** propyl propanoate

**b** ethyl ethanoate      **d** methyl butanoate



**c** see below

**d** see below



water so it dissolves in the carbonate solution. Hence shake the ester with the carbonate solution, allow all bubbles of  $\text{CO}_2$  to disperse and the two layers to separate, then run off the lower (aqueous) layer. This will remove pentanoic acid from the ester.

- 43**

  - a** propyl acetate (ethanoate)  
 $\text{CH}_3\text{-COOH} + \text{HO-CH}_2\text{-CH}_2\text{-CH}_3 \rightarrow \text{CH}_3\text{-CO-O-CH}_2\text{-CH}_2\text{-CH}_3 + \text{H}_2\text{O}$
  - b** acetic acid; by dissolving it in water and in  $\text{Na}_2\text{CO}_3$  solution; acetic acid has some solubility in the ester, but the acetate is completely insoluble in it; add drops of water to the layers in the separating funnel and observe which layer they dissolve in (the bottom one); the small solubility of the ester in water means that both layers will smell of the ester; to form sodium acetate which is very soluble in water but insoluble in the ester
  - c**
    - i** see Figure 5.4
    - ii** see Figure 1.5 on p. 13 CCPC
  - d** Both reactants can form hydrogen bonds with water which makes them soluble in water, whereas the ester cannot.

## Extended response exam-style questions for Module 2

See p. 547 for some explanations about answers to extended response exam-style questions.

- 1 See Sections 4.7 and 4.8. State the principle, 1 mark, discuss the effect of pressure, 1 mark, and of hydrogen ion concentration, 2 marks, and summarise the usefulness of the principle, 1 mark.

Le Chatelier's principle states ...<sup>(1)</sup>†.

The solubility of carbon dioxide in water can be written as an equilibrium:

$$\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)$$

By Le Chatelier's principle, if we increase the pressure of  $\text{CO}_2$  above the solution, the equilibrium will adjust to try to minimise the increase. That means it will move to the right, so more  $\text{CO}_2$  dissolves in the water. That is, the solubility of  $\text{CO}_2$  in water increases<sup>(2)</sup>.

For the effect of pH we need to consider a second equilibrium:

$$\text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})^{\text{(3)}}$$

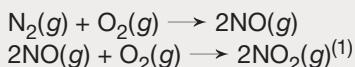
For this reaction Le Chatelier's principle tells us that if we decrease the concentration of  $\text{H}_3\text{O}^+$ —that is, increase pH—the equilibrium will move so as to minimise this decrease—that is, move to the right. This lowers the concentration of  $\text{H}_2\text{CO}_3$ , which means that the first equilibrium will move to the right (to try to minimise this decrease in  $\text{H}_2\text{CO}_3$ ). The net

Remember (from p. 547) superscripted numbers in brackets 'count' the marks awarded through the question.

result is that the total amount of  $\text{CO}_2$  in the solution increases; that is, the solubility of  $\text{CO}_2$  increases<sup>(4)</sup>. These two examples demonstrate that Le Chatelier's principle can be used to predict the effect of various changes upon equilibrium reactions; this is very useful for chemists<sup>(5)</sup>.

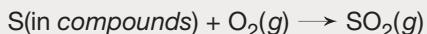
- 2** See Section 5.5. You need to explain that certain ions are weak bases or acids and so they produce hydrogen or hydroxide ions (give equations), 2 marks each, while other ions have no acid or base properties at all (and so produce neutral solutions), 1 mark.
- 3** This is Experiment 1 from p. 188. See Section 4.2. Describe the experiment you actually performed, 2 marks. Then 2 marks for the naming and stating the acidity of three everyday substances you tested. Substances you most likely tested were vinegar, lemon juice, soda water (all acidic) and cloudy ammonia (household cleaner), laundry washing powder, automatic dishwashing powder or liquid, drain cleaner, antacid tablet, bleach solution, washing soda (all alkaline). Stick to substances that are definitely acidic or alkaline and not near neutral, because you may not remember the exact pH range over which your indicator changed colour.
- 4** See Sections 4.9 to 4.11. There are three parts to this question: *outline*, *indicate* and *explain*. Assume 2 marks for each, though to be on the safe side you should proceed on the basis of 3 marks for *outline*—that is, give three significant bits of information for *outline*.

The oxides of nitrogen, NO and  $\text{NO}_2$ , are produced as by-products in combustion, particularly in power stations and transport (cars, trucks, trains aeroplanes). At the high temperatures involved nitrogen and oxygen in the air react as follows:



The human activity that produces nitrous oxide,  $\text{N}_2\text{O}$ , is the use of nitrogenous fertilisers; bacteria in the soil act on these to form  $\text{N}_2\text{O}$ <sup>(2)</sup>.

Sulfur dioxide is produced from combustion and from extracting metals from sulfide ores. Most fuels, particularly coal, contain small amounts of sulfur-containing compounds. When the fuel is burnt this sulfur is converted to  $\text{SO}_2$ :

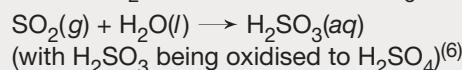
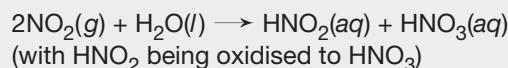


Sulfide ores form  $\text{SO}_2$  when roasted in air, the first step in extracting metals, for example:



Despite the large amounts emitted, there have been virtually no increases in the overall global concentrations of  $\text{NO}_2$  and  $\text{SO}_2$ <sup>(4)</sup>. However there has been about a 15% increase in overall global concentration of  $\text{N}_2\text{O}$  over the past one hundred years<sup>(5)</sup>.

The explanation for no increase in  $\text{NO}_2$  and  $\text{SO}_2$  concentrations is that these gases dissolve in water droplets in the atmosphere and so get washed out as rain; they dissolve in water to form acids:



The explanation for significant increases in  $\text{N}_2\text{O}$  concentration is that there is no effective mechanism for removing it from the atmosphere at the rate at which it is being produced<sup>(7)</sup>.

- 5** See Sections 4.14 to 4.18. Define pH and illustrate how much easier pHs are to write and say than hydrogen ion concentrations, 1 mark. You need to point out the usefulness of pH, 1 mark, then make some assessment about it for both chemistry and the world at large—that is, how important it is, 2 marks.

pH is defined by  $\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$ . This means that very small values of hydrogen ion concentration such as  $4.6 \times 10^{-5}$  mol/L, which are awkward to say and write, convert to quite simple numbers on the pH scale, 4.34 in this case<sup>(1)</sup>. The benefits of the pH scale are that it provides:

- simple numbers to represent very small hydrogen ion concentrations.
- simple numbers to represent alkaline solutions as well as acidic ones; a pH of 10 means an  $\text{OH}^-$  concentration of  $10^{-4}$  mol/L
- an easy way of giving 'order of magnitude' estimates of acidity or alkalinity—a pH of 3 or 4 represents a slightly acidic solution, a pH of 10 or 11 a slightly alkaline solution
- an easy way of indicating a factor of ten or a hundred change in hydrogen ion concentration: one unit of pH represents a factor of ten change in hydrogen ion concentration<sup>(2)</sup>. (Any two of these reasons would get the mark.)

The pH scale is of considerable use to chemistry as a convenience tool; it is not essential because chemists could still do everything they do with pH by just using hydrogen ion concentration instead<sup>(3)</sup>. pH is of considerably greater use to the world at large because it provides a method of giving semi-quantitative information about acidity or alkalinity, which is all that is usually required in the outside world, without the complication of the cumbersome numbers that otherwise represent hydrogen ion concentration<sup>(4)</sup>.

- 6** See Sections 5.13 and 5.14. Define what a buffer is, 1 mark. A good specific example from a natural system is the  $\text{H}_2\text{CO}_3$  (or  $\text{CO}_2 + \text{H}_2\text{O}$ ),  $\text{HCO}_3^-$  that occurs in many lakes and rivers and in home swimming pools, 1 mark. In explaining how it works consider adding both acid, 1 mark, and alkali, 1 mark, and use Le Chatelier's principle in your explanation, 1 mark.

- 7 See Sections 4.2 and 4.19. In this question *evaluate* means make a judgement on how useful a set of indicators is, with a reason. But first explain how each method is used to measure pH, 1 mark. Point out the advantages and disadvantages of each, 1 mark, then evaluate, 1 mark. Give one specific use, 1 mark.

To use a set of indicators to determine pH of a solution, drops of particular indicators are added to fresh small samples of the solution to be tested and their colours compared with a standard chart of indicator colours at different pHs. To use a pH meter, the sensing electrode is simply dipped into the solution to be tested and the reading on the meter noted<sup>(1)</sup>.

The advantage of the pH meter is that it is quick and it does not alter the composition of the solution being tested. The advantage of the indicator solutions is that they are much cheaper than the pH meter. A disadvantage is that some of the solution becomes contaminated by indicator solution and so the method uses up some of the solution to be tested<sup>(2)</sup>.

In most situations the use of indicator solutions to measure pH is less convenient and more time consuming than using a pH meter and the results are generally less accurate. However using indicator solutions has the advantage of being easily accessible to a wide range of people without having to go to the expense of a pH meter<sup>(3)</sup>.

An everyday example of using indicator solutions is the determining the pH of garden soils<sup>(4)</sup>. (*Another example is measuring the pH of home swimming pools.*)

- 8 See Sections 5.17 and 5.18, particularly Tables 5.7 and 5.8. For compounds of similar molecular weight, the melting and boiling points of alkanoic acids are higher than those of alkanols which in turn are higher than those of esters. Explain in terms of intermolecular forces, particularly hydrogen bonding. Probably 2 marks for the comparison and 3 for the explanation, so you need to explain fully *how* hydrogen bonding causes melting and boiling points to be higher, not just state it.

- 9 See Sections 4.9 and 4.10. You need to consider both localised and global increases in SO<sub>2</sub>, NO<sub>x</sub> and N<sub>2</sub>O. *Discuss* in this context means comment on the accuracy or reliability or extensiveness of the evidence about whether or not there have been increases; in particular comment on the sensitivity and accuracy of the direct analytical techniques available and on indirect evidence used. It is hard to work out a marking scheme in advance for this question, so make sure you include at least seven important bits of information and that you cover the whole scope of the question.

For sulfur dioxide the evidence is that in certain locations such as industrialised cities and mining

sites there have been considerable increases in its concentration in the atmosphere over the past 150 years. The evidence for this is both from direct chemical measurements and from the detrimental effects these increased concentrations have had on people and the environment<sup>(1)</sup>. This evidence is quite strong.

Similarly for nitric oxide and nitrogen dioxide, together called NO<sub>x</sub>, there is strong evidence for increases in atmospheric concentrations in localised areas such as in large cities and in locations where there are many fossil fuel burning power stations. Again the evidence for these increases is from direct chemical measurements and it is quite strong, because the high localised concentrations have made chemical measurement relatively easy<sup>(2)</sup>.

However globally the evidence is that there have been no significant long-term increases in the atmospheric concentrations of sulfur dioxide and NO<sub>x</sub>. There are often short-term increases in SO<sub>2</sub> concentrations following abnormal volcanic activity but the levels usually fall back to normal within a year or so. Both sulfur dioxide and nitrogen dioxide (and so effectively NO<sub>x</sub>) are washed out of the atmosphere because they dissolve in water droplets and fall out of the atmosphere as rain<sup>(3)</sup>.

The evidence for no increase in global SO<sub>2</sub> and NO<sub>x</sub> concentration is quite convincing for the past fifty years or so because over that period we have had sensitive and accurate measuring instruments such as infra-red spectroscopy that can measure concentrations in the ‘clean air’ range of 0.001 to 0.003 ppm<sup>(4)</sup>. The evidence for no increase over the past 100 to 150 years is more indirect and less convincing, because chemical analysis was not sufficiently sensitive to ensure accurate measurements<sup>(5)</sup>.

For nitrous oxide there are no localised increases in concentration. However there is quite strong evidence for about a 15% increase in the global concentration of N<sub>2</sub>O over the last 100 years or so. The evidence for an increase over the past 50 years since reliable and sensitive infra-red and other analyses has become available is quite strong<sup>(6)</sup>. The evidence for increases over the preceding 50 to 100 years is more indirect and less convincing, though based on what we now know about the release of N<sub>2</sub>O to the atmosphere, increases in that time period would have been expected<sup>(7)</sup>.

- 10 See Sections 4.10 (reactions of SO<sub>2</sub> and NO<sub>2</sub> with water), 4.11 (effects of acid rain) and 5.14 (role of natural buffers). There are three parts to the question: *causes, effects and explain*, so assume 2 marks each.

- 11 See Section 4.13, last subsection. Give two reasons with an example for each, preferably naming the acid used (citric acid added to drinks, acetic acid, as

- vinegar, added to preserved vegetables and pickles), 1 mark for each reason and for each example.
- 12** See Section 4.20. Just explain the meanings of the four terms; good examples to use are hydrochloric acid (strong) and acetic acid (weak).
- 13** See Sections 5.1 to 5.3. Give the definitions of Davy (contains replaceable hydrogen), Arrhenius (ionises to form  $H^+$ ) and Brönsted–Lowry (proton donor), 1 mark each, and show how each definition increased our understanding of the nature of acids, 1 mark each.
- 14** See Section 5.15. State the purpose of doing this (to neutralise spills of acids and alkalis), 1 mark, then comment on how effective it is (very effective, more so than any other possible procedure), 1 mark, and say why (at least three reasons), 2 marks.
- 15** See Section 5.2. Explain the concept, 1 mark, with an example of an acid forming its conjugate base and a base forming its conjugate acid, 1 mark each. Assess *its usefulness* means make some judgement about how useful the concept is with some reasons for your judgement, 2 marks. For the assessment:
- The concept is very useful, not just because it allows us to connect pairs of acids and bases together, but also because it allows us to relate strengths of conjugates to each other. The conjugate base of a strong acid is an extremely weak base, virtually no base properties at all ( $Cl^-$  from  $HCl$ ). The conjugate base of a moderately weak acid is a moderately weak base ( $NO_2^-$  from  $HNO_2$ ). The conjugate acid from a strong base is an extremely weak acid, virtually no acidic properties at all ( $H_2O$  from  $OH^-$ )<sup>(1)</sup>.
- The concept of conjugates is also useful because it allows us to see the hydrolysis of salts as simple acid–base reactions: the cations that hydrolyse, such as the ammonium or acetate ions, are weak acids or weak bases<sup>(2)</sup>.
- 16** This is Experiment 7 from p. 189. See Sections 5.8 to 5.12. There are two parts to the question: *describe the experiment and outline the measures*. A reasonable mark distribution would be 3 or 4 marks for the *describe* and 4 or 3 for the *outline*, so answer on the basis of 4 marks for each part. Describe the experiment you actually performed; mention that you had previously standardised the solution of sodium hydroxide against a primary standard such as oxalic acid or potassium hydrogen phthalate (Exercises 17 and 26 in Chapter 5). Include mention of the indicator used (and why), that you repeated the titration several times and that you discarded the first titration because, not knowing the approximate equivalence point, you had overshot it. For the measures you took to ensure that your results were accurate, see the answer to Exercise 19 in Chapter 5. The marks (and time allowed) do not justify including all twelve of the measures listed there, so the main ones to include (to score 4 marks)
- are (1) repeating the titration until three successive titres agreed to within 0.05 mL, (2) rinsing the pipette and burette with the solution to be dispensed by them, (3) taking care to fill the pipette and read the burette carefully (using the bottom of the meniscus), and (4) using the correct indicator (phenolphthalein), the right amount of it and placing the titration flask on a white tile or card to make it easy to see the colour change.
- 17** See the subsection ‘Reproducibility and accuracy’ in Section 6.16 and Sections 5.8 to 5.12. Two marks for defining the two terms and 2 for proposing reasons; you need a reason for the results being reproducible as well as a reason for them being inaccurate.
- ‘Very reproducible’ means that they got very close to the same answer every time they repeated the titration<sup>(1)</sup>; ‘not accurate’ means that the answer they got differed significantly from the true value<sup>(2)</sup>.
- They got very reproducible results because they took care to use the same procedure each time they performed the titration—filled the pipette carefully, titrated to the right point (same partial colour change in the indicator) each time and read the burette accurately<sup>(3)</sup>. The most likely reason for their results not being accurate is that there had been an error in the standardisation of the sodium hydroxide solution they were using, so they were using a wrong concentration for it in their calculations<sup>(4)</sup>.
- 18** This is Experiment 5 from p. 188. See Sections 5.4, 5.5 and 4.19. You would have used a pH meter for this experiment; indicator solutions would not be accurate enough for many of the salts likely to be used. Describe the experiment you performed (mention some of the salts you used, including some neutral ones such as  $NaCl$ ,  $KNO_3$ ,  $Na_2SO_4$ ), 3 marks. Then 1 mark for precautions (rinsing the electrode carefully between measurements, stirring it gently in the solution being tested, waiting 30 s or more to make sure the reading is stable and ensuring very pure water was used to make up the solutions). Then 1 mark each for your three examples. Good examples to use are  $NaHSO_4$  and  $NH_4Cl$  ( $pH < 7$ ),  $Na_2CO_3$ ,  $Na_3PO_4$ ,  $NaCH_3COO$ ,  $NaNO_2$  ( $pH > 7$ ).
- 19** See Section 5.18 and p. 13 CCPC. Don’t just define the two terms: explain how they differ, 2 marks. Include diagrams similar to Figure 5.4 and Figure 1.5 on p. 13 CCPC, 2 marks.
- Refluxing and distillation both involve heating a mixture with a cooling condenser attached. In refluxing the condenser is attached in such a way that the condensed liquid runs back into the heated vessel; refluxing is used to bring about a reaction at moderately high temperatures without losing a volatile reactant or product as in the synthesis of esters<sup>(1)</sup>.
- In distillation the condenser is positioned so that the condensed vapour runs into a separate

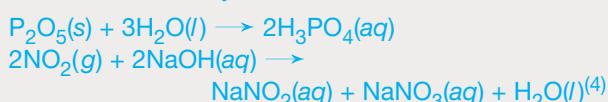
collection vessel and not back into the original vessel. Distillation is used to separate the volatile substance from a mixture<sup>(2)</sup>.

- 20** See Section 4.5. You could treat each oxide separately or you could group them into the three categories and then treat each category; the 'category' approach would lead to less repetition of words, but you still need an equation or reason for each of the five oxides. Essentially there is one mark for each oxide, so you need to give both the category and the equation or reason to get the mark.

Magnesium oxide and copper oxide are basic oxides<sup>(1)</sup>, because they react with acids:



Diphosphorus pentoxide and nitrogen dioxide are acidic oxides<sup>(3)</sup>, because they react with water to form acids and they react with bases:



Nitric oxide, NO, is a neutral oxide, because it does not react with either acids or bases<sup>(5)</sup>.

## Revision test for Module 2

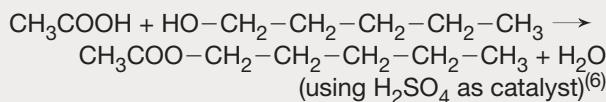
- 1** c    **2** b    **3** d    **4** b    **5** d  
**6** a    **7** b    **8** d    **9** c    **10** a

- 11** a P, between 5.4 and 6.8; Q, 8.8; R, >10; S, 3.7 (or 3.8)  
**b** A; 20 times greater  
**12** see Section 5.13;  
 $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$   
 $\text{H}_2\text{CO}_3(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)} + \text{HCO}_3^-(\text{aq})$   
**13** This is Experiment 8 from p. 189. See Section 5.18. Outline means describe briefly, without too many details. However you must mention the catalyst. You probably prepared an ester that was not very soluble in water, such as pentyl or hexyl acetate (ethanoate) (to make it easy to separate the final ester from the reaction mixture). Assume that there are 3 (possibly 4) marks for the description, 1 for the diagram, 1 for the equation, 1 for stating which reactant was in excess and 1 for why (maybe only 1 for which and why).

We prepared pentyl acetate by refluxing a mixture of 1-pentanol and acetic acid with a few drops of concentrated sulfuric acid as catalyst<sup>(1)</sup>. Refluxing, shown in the diagram, was necessary to prevent loss of the volatile product<sup>(2)</sup>. (Draw a diagram similar to Figure 5.4.<sup>(3)</sup>) We heated the mixture for about 20 minutes, then cooled it and transferred it to a separating funnel. We used a small excess of acetic acid<sup>(4)</sup>. This was removed by slowly adding sodium carbonate solution to the mixture to convert it to sodium acetate which readily dissolved in the aqueous solution which was separated off.

After washing and drying, the ester was distilled<sup>(5)</sup>. (You may have just washed and dried the ester and not distilled it; this is quite acceptable.)

The equation is:

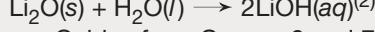


We used acetic acid in excess because it is easier to separate from the product than propanol would have been, because its anion is very soluble in water and insoluble in the ester<sup>(7)</sup>.

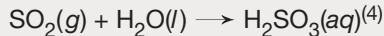
- 14** a 0.0120 mol  
**b**  $2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$ ; 0.0240 mol  
**c** triprotic; number of moles of citric acid used was  $8.00 \times 10^{-3}$  whereas the number of moles of H<sup>+</sup> present was 0.0240  
**15** a i 2-butanol ii propanoic acid  
iii methyl ethanoate (acetate)  
**b** (ii) and (iii) because they have the same molecular formula, C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>

- 16** See Section 4.5. Demonstrate means show by example. Because of elements, plural, you need at least two examples of each acidic and basic oxides. Probably one equation for each acidic and basic oxides will suffice (but give two each if you have time). One mark for naming two basic oxides and 1 for an equation; similarly for acidic oxides.

Oxides of Groups 1 and 2, such as lithium oxide, Li<sub>2</sub>O, and calcium oxide, CaO, from the left-hand side of the Periodic Table are basic oxides<sup>(1)</sup> because they react with acids; for example:



Oxides from Groups 6 and 7, such as sulfur dioxide, SO<sub>2</sub>, and chlorine monoxide, Cl<sub>2</sub>O, from the right-hand side of the Periodic Table are acidic<sup>(3)</sup> because they react with water to form acids; for example:



- 17** a It absorbs CO<sub>2</sub> from the air so may not be pure; it absorbs water so its mass changes as it is being weighed.  
**b** It is easily obtained in very pure form; it is very stable and does not absorb water from the air so can be weighed out accurately.  
**c** see Using a burette on pp. 163–4  
**d** 0.203 mol/L  
**18** a HP,  $5.0 \times 10^{-4}$  mol/L; HQ, 0.050 mol/L  
**b** HQ is strong because it is completely ionised into H<sup>+</sup> and Q<sup>-</sup>; HP is weak because only some of its molecules have ionised.  
**c** Degree of ionisation of HP is 1%.

- 19** See Section 5.7. Justify means present an argument to support a claim. The best way to justify this claim is to present all possible combinations of weak and strong acids and bases and show that there is a

proton transfer in every case. One mark per equation plus pointing out the proton transfer.

That neutralisation is a transfer of a proton from an acid to a base can be shown by writing equations for neutralisation involving all combinations of weak and strong acids and bases:

Weak acid + strong base:



Weak base + strong acid:



Strong acid + strong base:  $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$

Weak acid + weak base:  $\text{HNO}_2(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq})$

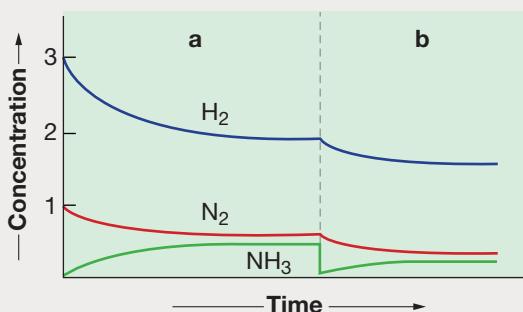
In all these cases there is a transfer of a proton from the acid to the base: from HCOOH to OH<sup>-</sup>, from H<sub>3</sub>O<sup>+</sup> to NH<sub>3</sub>, from H<sub>3</sub>O<sup>+</sup> to OH<sup>-</sup> and from HNO<sub>2</sub> to NH<sub>3</sub>.

This shows, then, that neutralisation is a transfer of a proton from an acid to a base for all combinations of weak and strong acids and bases.

- 20** See Sections 4.9 to 4.11. Assess in this question means make a judgement on how good or bad and how significant the impacts upon the environment are. But first you need to describe the human sources and their impacts. And you will need to consider both the local environment and the global one. The sources are burning fossil fuels and extracting metals for SO<sub>2</sub> (1 mark) and high temperature combustion (N<sub>2</sub> + O<sub>2</sub>) for NO<sub>2</sub>, again with an equation (1 mark). The environmental impacts are first localised pollution and its detrimental health effects, particularly for SO<sub>2</sub> (1 mark), but only minimal impact globally (1 mark) and then acid rain, with one or two equations and its detrimental effects for fish, forests and buildings (1 mark). Finally assessment (all impacts bad, localised air pollution can be quite severe, acid rain also very damaging) (2 marks).

## Chapter 6

- 1 a** Equation 6.2

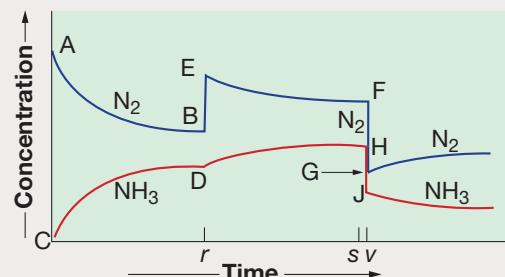


At equilibrium there will be 0.4 mol NH<sub>3</sub>, 0.6 mol N<sub>2</sub> and 2.8 mol H<sub>2</sub>.

- b** With most of the NH<sub>3</sub> removed, the equilibrium will move further to the right; more ammonia will

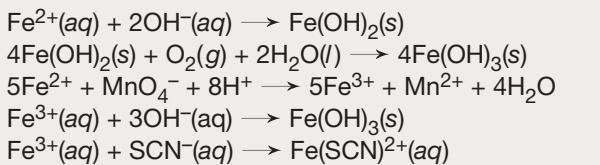
form. Approximately 40% of the nitrogen left at the end of (a) will convert to ammonia in (b).

**2**



Adding extra N<sub>2</sub> at r causes the equilibrium 6.2 to move to the right (form more NH<sub>3</sub>) to counteract the change (Le Chatelier's principle). Doubling the volume halves the total pressure (N<sub>2</sub> drops from F to G, NH<sub>3</sub> drops from H to J), so the equilibrium moves in the direction which increases the pressure: that is, from right to left (2 mol → 4 mol).

- 3** **a** i L → R  
ii L → R  
iv R → L  
v R → L  
**b** i R → L  
iii R → L  
iv L → R  
v L → R  
**d** i no change  
iii L → R  
iv L → R  
v no change  
**4** none; adding an inert gas does not affect the concentration (or pressure) of any reactant or product and so has no effect upon the equilibrium  
**5** a Use excess O<sub>2</sub> and a high pressure.  
c Use excess steam, remove CO as it forms (if possible); lower the pressure  
**6** a i reaction has reached equilibrium  
ii same amount of NO in smaller volume increases the concentration  
iii reaction re-establishes equilibrium  
iv at t the pressure of the mixture is increased; this causes equilibrium to move to the right, but it does not go far enough to lower [NO] to its AB value.  
**7** endothermic; by Le Chatelier's principle reactions move in the endothermic direction when temperature is increased (because that is the direction that absorbs heat and so opposes the change)  
**8** Pb<sup>2+</sup>(aq) + 2Cl<sup>-</sup>(aq) → PbCl<sub>2</sub>(s)  
Pb<sup>2+</sup>(aq) + 2I<sup>-</sup>(aq) → PbI<sub>2</sub>(s)  
Ba<sup>2+</sup>(aq) + SO<sub>4</sub><sup>2-</sup>(aq) → BaSO<sub>4</sub>(s)  
Ca<sup>2+</sup>(aq) + SO<sub>4</sub><sup>2-</sup>(aq) → CaSO<sub>4</sub>(s)  
Ca<sup>2+</sup>(aq) + 2F<sup>-</sup>(aq) → CaF<sub>2</sub>(s)  
Cu<sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq) → Cu(OH)<sub>2</sub>(s)  
Cu(OH)<sub>2</sub>(s) + 4NH<sub>3</sub>(aq) → Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq)



- 9** **a** Add  $\text{Cl}^-$ ; if a white precipitate forms the compound is lead nitrate.
- b** Add  $\text{OH}^-$ ; both produce a precipitate, one blue the other brown. Add excess ammonia solution; if blue precipitate dissolves to form a deep blue solution then the compound was copper sulfate; if precipitate does not dissolve the compound is iron(II) sulfate.
- c** Add  $\text{OH}^-$ ; if it produces a brown precipitate, the compound is  $\text{FeCl}_3$ . If the  $\text{CaCl}_2$  solution was reasonably concentrated it would produce a white precipitate. Alternatively add  $\text{SCN}^-$  solution: if it produces a red colour the compound is  $\text{FeCl}_3$ . Or add fluoride: if a white precipitate forms, the compound is  $\text{CaCl}_2$ .
- 10** A is  $\text{Ca}^{2+}$ ; B is  $\text{Fe}^{3+}$  confirm by adding  $\text{SCN}^-$  to a fresh sample; this forms a red colour with  $\text{Fe}^{3+}$ ; C is  $\text{Cu}^{2+}$  (confirm by seeing whether the precipitate dissolves in excess ammonia)
- 11** no, because all the cations produce a precipitate with carbonate
- 12** **a**  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$  and possibly  $\text{Ba}^{2+}$  also
- b**  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$
- c**  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$
- 13** could contain  $\text{Ca}^{2+}$ ; add  $\text{F}^-$ : if a precipitate forms,  $\text{Ca}^{2+}$  is present
- 14** B and C; C because  $\text{BaSO}_4$  and  $\text{BaCO}_3$  are insoluble while  $\text{Ba}(\text{OH})_2$  is soluble. C could also be correct, because, depending on concentrations used,  $\text{Ca}^{2+}$  could precipitate with sulfate and not with hydroxide as both  $\text{CaSO}_4$  and  $\text{Ca}(\text{OH})_2$  are sparingly soluble;  $\text{CaCO}_3$  is quite insoluble and will precipitate at virtually all concentrations. A is definitely wrong, because  $\text{Pb}^{2+}$  would form a precipitate with hydroxide.
- 15** P contains  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$ ; Q contains  $\text{Ba}^{2+}$  and  $\text{Fe}^{3+}$ ; R contains  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ .
- 16** **a**  $\text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $$\text{SO}_4^{2-}(\text{aq}) + \text{Ba}^{2+}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$$
- $$\text{SO}_4^{2-}(\text{aq}) + \text{Pb}^{2+}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s})$$
- $$2\text{PO}_4^{3-}(\text{aq}) + 3\text{Ba}^{2+}(\text{aq}) \rightarrow \text{Ba}_3(\text{PO}_4)_2(\text{s})$$
- $$\text{PO}_4^{3-}(\text{aq}) + \text{Mg}^{2+}(\text{aq}) + \text{NH}_4^+(\text{aq}) \rightarrow \text{Mg}(\text{NH}_4)\text{PO}_4(\text{s})$$
- $$\text{Cl}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{AgCl}(\text{s})$$
- $$\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq}) + \text{Cl}^-(\text{aq})$$
- b** because it would precipitate with  $\text{Ag}^+$  in the  $\text{Cl}^-$  test and with  $\text{Ba}^{2+}$  in the phosphate test
- 17** **a** Add  $\text{Ba}(\text{NO}_3)_2$ : white precipitate with sulfate, not with chloride.
- b** Make alkaline then add  $\text{Ba}^{2+}$ : white precipitate with phosphate, none with chloride.
- c** Add HCl: bubbles of colourless gas with carbonate, not with hydroxide.

- 18** **a**  $\text{SO}_4^{2-}$       **b**  $\text{CO}_3^{2-}$       **c**  $\text{PO}_4^{3-}$
- 19** Use a fresh sample for each of the following tests.  
Add drops of permanganate; if they decolorise,  $\text{Fe}^{2+}$  is present. Add one or two drops of fluoride; if a white precipitate forms,  $\text{Ca}^{2+}$  is present. Acidify, then add barium nitrate solution; if a white precipitate forms sulfate is present. If there is no sulfate, acidify and add silver nitrate solution; a white precipitate means chloride is present.
- 20** A is  $\text{Cl}^-$ , B is  $\text{CO}_3^{2-}$
- 21** P:  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ; Q:  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$   
R:  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$
- 22** **a**  $\text{Ba}^{2+}$       **b**  $\text{Ca}^{2+}$   
**c**  $\text{Cu}^{2+}$ ; see Answer 8 for equations
- 23** **a** lilac flame:  $\text{K}^+$ ; red flame:  $\text{Li}^+$ ; compounds of K and Li are all soluble  
**b**  $\text{H}^+$ ; measure pH or add  $\text{Na}_2\text{CO}_3$  and observe bubbles of gas
- 24** **a** flame test: Sr, red; Ba, green  
**b** flame test: Na, yellow; K, lilac; nitric acid, no colour
- 25** **a** Solid would be pale blue: dissolve some of it in water. Add  $\text{NH}_3$  dropwise: first a blue precipitate then it dissolves to form a deep blue solution: this proves  $\text{Cu}^{2+}$ ; acidify a fresh sample of the solution then add  $\text{Ba}(\text{NO}_3)_2$ : a white precipitate proves sulfate.  
**b** white solid soluble in water. Add  $\text{Ag}^+$  to a portion of the solution: a white precipitate indicates  $\text{Cl}^-$  (but we still need to eliminate  $\text{SO}_4^{2-}$ ). Acidify a fresh portion of the solution and add  $\text{H}_2\text{SO}_4$ : a white precipitate indicates  $\text{Ba}^{2+}$  (but it could be lead or silver). If the cation has to be barium, lead or silver, then the anion cannot be sulfate (sulfates of Ba, Pb, Ag are insoluble); so the anion is chloride. If the anion is chloride, the cation cannot be lead or silver (they have insoluble chlorides). Hence the substance must be barium chloride.
- c** bluish-yellow solid readily soluble in water. If drops of  $\text{SCN}^-$  added to a portion of the solution produce a red colour, the cation is  $\text{Fe}^{3+}$ . Acidify, then add  $\text{Ba}^{2+}$ ; a white precipitate shows that sulfate is present.
- d** white solid insoluble in water. Add some of the solid to an HCl solution: if effervescence, anion is carbonate. Test the resulting solution for  $\text{Ca}^{2+}$ : add  $\text{F}^-$ : white precipitate indicates calcium. Confirm by a flame test (brick red).
- 26** **a**  $\text{FeCl}_2$       **b**  $\text{CuSO}_4$   
**c**  $\text{BaCl}_2$       **d**  $\text{K}_3\text{PO}_4$
- For equations see answers 8 and 16.
- 27** 45.7%; 15.3%
- 28** **a** Did not fill pipette accurately each time, did not drain it properly, were careless in reaching the equivalence point (approached it too quickly and

sometimes overshot it), were careless in reading initial and final volumes in the burette.

- b** Made an error in standardising the sodium carbonate solution. For example, used impure sodium carbonate, did not dry it properly, were careless in weighing it out, spilt some of it in transferring it to the volumetric flask, did not fill the volumetric flask accurately, did not mix the solution thoroughly before using it.

**29 a** 0.117% (w/v)

- b** **i** to minimise solubility losses when precipitating  $Mg(OH)_2$   
**ii** so that the precipitate would form as coarse crystals which would filter easily

**30**  $7.46 \times 10^{-3}$  mol; 3.34%; labelling is justified

**31** 5.99% (w/v); discarded the second mass because it is an ‘outlier’ (there was probably a mistake in that experiment) and averaged the other three.

**32** no; because the light source for the analysis is an emission line of lead, and copper and barium do not absorb at the emission wavelengths of lead—only at their own emission wavelengths which are different.

**33** A, 16.4 ppm; B, 23.6 ppm; C, 10.8 ppm;  
D, 2.9 ppm

**34** A, 6.7 ppm; B, 4.3 ppm; C, 5.4 ppm; it may be difficult to get all the lead into solution with dilute  $HNO_3$ , the jam is very heterogeneous and the lead may be unevenly distributed between solid fruit and liquid syrup.

**35** A, 6.3 ppm; B, 3.1 ppm; C, 0.44 ppm; D, 0.40 ppm  
Copper is being slowly leached from the household pipes overnight; when the tap is first turned on in the morning, copper concentration in the water is quite high. As the water is flushed out of the pipes the concentration of copper falls eventually reaching background levels. There is a leaching problem in the pipes in the houses.

## Chapter 7

**1** 0.0350%; 0.0018%; 0.00005% ( $5 \times 10^{-5}\%$ );  
 $2 \times 10^{-6}\%$

**2 a** 0.0403 mol/L

**b**  $1.41 \times 10^{-5}$  mol/L

**3 b** Pressure decreases exponentially as altitude increases. Mass of gas in a given volume depends upon the pressure, so most of the mass of the gas is where the pressure is relatively high which is below 15 km.

**5** Diesel engines produce much less CO, because the high air to fuel ratio means that there is more  $O_2$  to bring about more complete combustion (to  $CO_2$ ). Diesel engines produce more NO (and  $NO_2$ ), because there is more air in the combustion chamber (higher concentrations of  $N_2$  and  $O_2$ ) and so the rate of reaction between  $N_2$  and  $O_2$  to form NO will be greater.

- 7 a** because hydrocarbons and  $NO_x$  are emitted when the intensity of sunlight is low  
**b** reducing hydrocarbon emissions: this slows down conversion of NO to  $NO_2$ , an essential first step in ozone formation; it is the ratio of  $NO_2$  to NO that affects the ozone concentration, not the actual amounts

- 8 a** no net chemical change; conversion of light energy into heat energy  
**b** exothermic: because it involves the formation of a new chemical bond; no prediction is possible for  $O_3 + NO$  because it involves both breaking a bond and making a bond and we cannot predict which involves more energy

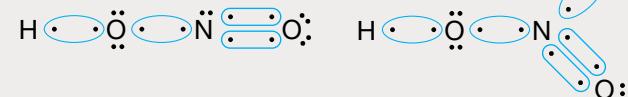


because the end N atom does not have a noble gas electron configuration (has only 6 electrons around it)

Let the lone pair on the central N atom form a coordinate covalent bond between the two N atoms: all three atoms then have noble gas configurations



**10**



(coordinate covalent bond to the extra O atom)



Coordinate covalent bonds are formed between each  $Cl^-$  or  $CN^-$  and the central  $Zn^{2+}$  ion forming tetrahedral complexes:



**12 a** 3-bromohexane

**b** 1,2-dichlorobutane

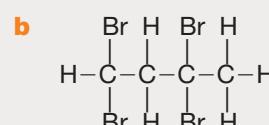
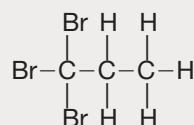
**c** 1,1,2,2-tetrachloro-1,2-difluoroethane

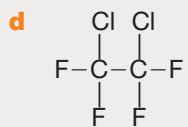
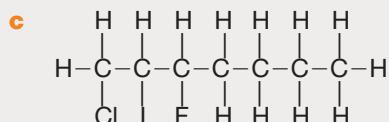
**d** 1,1,1,2-tetrabromo-4,4-dichloropentane

**e** 1,3-dibromo-1,2,3-trichloro-1,2,3-trifluoropropane

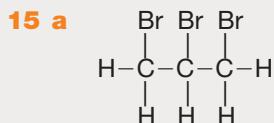
**f** 1,2,2-tribromo-1,1,2-trifluoroethane

**13 a**

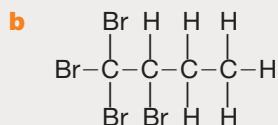




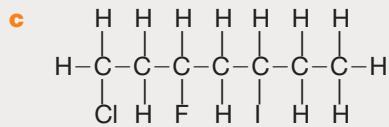
- 14 In 12: (a)  $\text{C}_6\text{H}_{13}\text{Br}$  (b)  $\text{C}_4\text{H}_8\text{Cl}_2$   
 (c)  $\text{C}_2\text{F}_2\text{Cl}_4$  (d)  $\text{C}_5\text{H}_6\text{Cl}_2\text{Br}_4$   
 (e)  $\text{C}_3\text{F}_3\text{Cl}_3\text{Br}_2$  (f)  $\text{C}_2\text{F}_3\text{Br}_3$   
 In 13: (a)  $\text{C}_3\text{H}_5\text{Br}_3$  (b)  $\text{C}_4\text{H}_6\text{Br}_4$   
 (c)  $\text{C}_7\text{H}_{13}\text{FClI}$  (d)  $\text{C}_2\text{F}_4\text{Cl}_2$



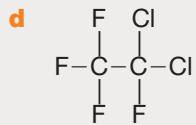
1,2,3-tribromopropane (1,1,2- 1,2,2- and 1,1,3- also possible and they are the only other possibilities)



1,1,1,2-tetrabromobutane (there are ten other possibilities)

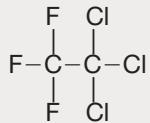


1-chloro-3-fluoro-5-iodoheptane (there are many other possibilities)



2,2-dichloro-1,1,1,2-tetrafluoroethane (the only possibility)

- 17 one (2,2,2-trichloro-1,1,1-trifluoroethane);



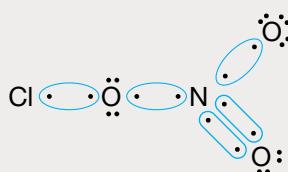
- 18 a
- $$\text{H} \cdot \ddot{\text{O}} \cdot \ddot{\text{O}} \cdot \ddot{\text{Cl}}: \quad \cdot \ddot{\text{O}} \cdot \ddot{\text{O}} \cdot \ddot{\text{Cl}}: \quad \text{or} \quad \cdot \ddot{\text{Cl}} \cdot \ddot{\text{O}} \cdot \ddot{\text{O}} \cdot$$

There is an unpaired electron on the O atom.

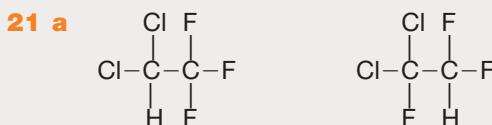
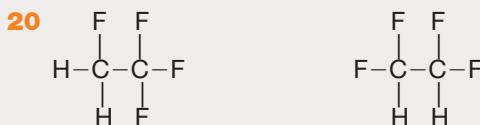
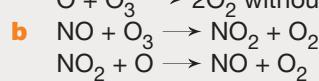
- b because they each have an unpaired electron (on the N atom)



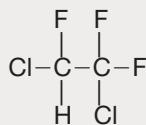
- c Both have an unpaired electron: these can combine to form a bond:



- 19 a because they are regenerated in Equations 7.5 and 7.6; that is, they speed up the reaction  
 $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$  without being consumed by it



1,1-dichloro-2,2,2-trifluoroethane      1,1-dichloro-1,2,2-trifluoroethane



1,2-dichloro-1,1,2-trifluoroethane

- c  $\text{CH}_2\text{F}_2$ ; difluoromethane no isomers

## Chapter 8

- 1 because a litre is only approximately 1 kg (ppm = mg per kg, mass/mass)

- 2 a  $2.1 \times 10^{-4}$  mol/L;  $9.7 \times 10^{-6}$  mol/L

- b 10.1 ppm; 9.9 ppm

- 3 1.13% suspended solids;  $7.6 \times 10^{-2}\%$  dissolved solids

- 4 b i 8.7 mg/L ii 12.0 mg/L iii 14.1 mg/L (iii) is less accurate than (i) or (ii) because it involves an extrapolation whereas the others involve interpolation

- c i 2.5°C ii 28.5°C

- d  $2.7 \times 10^{-4}$  mol/L

- 5 a 88% saturation b 62%

- c 62% d 85%

- 6 a 6.6 ppm; some turbidity and discolouration but no serious change to aquatic life; further downstream there would be negligible effects apart from some small increases in total dissolved solids and nutrients

- b zero; after dilution this waste can use up 11 ppm  $\text{O}_2$  but there is only 9 ppm present; serious pollution—smell, discolouration, destruction of most aquatic life, sediments

- c** In (a) the river would have completely recovered, but in (b) the river would still be seriously polluted: after complete destruction, aquatic life comes back only very slowly.
- 7 a** 125 ppm    **b** 500 ppm
- 8**  $1.47 \times 10^{-4}$  mol I<sub>2</sub>;  $7.3 \times 10^{-5}$  mol O<sub>2</sub>; 7.8 ppm (using a volume of 302 mL; using 312 mL gives 7.5 ppm, which is acceptable)
- 9** BOD is 5.8 ppm; slightly polluted; sewage, run-off from poultry farms, cattle feed-lots or food processing factory, urban stormwater run-off
- 10 a** **i** A and E    **ii** B  
**iii** C, D and F (based on TDS values)
- b** A and F (high BOD and high coliform counts); C is probably contaminated from run-off from animal farms
- c** A, C and F (quite hight coliform counts)
- d** B, D and E (low BODs and coliform counts), though D is not safe to drink without treatment
- 11 a** the four O atoms at the end of the carboxyl groups, –COO<sup>–</sup> and the two N atoms: they all have lone pairs of electrons that can be used to form coordinate covalent bonds with Mg<sup>2+</sup> and Ca<sup>2+</sup> ions
- b** The N atoms are bases (like NH<sub>3</sub>) so as pH falls they tend to become protonated (as NH<sub>3</sub> does to form NH<sub>4</sub><sup>+</sup>): if a proton is attached to the N atom it cannot form a bond with the metal ion.
- 12 a**  $5.4 \times 10^{-4}$  mol/L  
**b** 46 mg/L
- 13** 83 mg/L; because hardness is expressed in terms of CaCO<sub>3</sub>: we just need the total number of moles of Mg<sup>2+</sup> and Ca<sup>2+</sup> then convert that to mass of CaCO<sub>3</sub>
- 14** A ( $0.054 \pm 0.002$ ) ppm; B ( $0.136 \pm 0.004$ ) ppm; C ( $0.182 \pm 0.006$ ) ppm; D ( $0.010 \pm 0.001$ ) ppm; no; because the calibration curve is linear, there are no extra errors in extrapolating to the small extents involved here
- 15** 2 ppm < [Cl<sup>–</sup>] < 20 ppm; 0.5 ppm < [SO<sub>4</sub><sup>2–</sup>] < 5 ppm
- 16 a** **i** measure coliform bacteria: if more than 30 CFU/L, sewage pollution,    **ii** measure BOD: if > 50 ppm, sewage pollution    **iii** add Na<sub>2</sub>S: if a precipitate, heavy metal pollution
- b** measure pH: if < 6, acid drainage pollution
- c** measure DO: if > 7 ppm, no threat, if between 5 and 7, marginal
- 17** add Ag<sup>+</sup> to test for Cl<sup>–</sup>: measure as per Table 8.2; or measure TDS: if >5000 seawater has encroached
- 18** measure coliform bacteria, BOD, TDS, heavy metals; disease causing agents and oxygen demanding wastes are the main problems from sewage discharge; even well treated sewage can increase TDS; sewage from big cities often contains heavy metals which are poisonous and not completely removed by sewage treatment.
- 19** [Cl<sup>–</sup>] > 20 ppm; add 1 drop  $1 \times 10^{-4}$  mol/L AgNO<sub>3</sub> to 100 mL to decide whether [Cl<sup>–</sup>] is greater than 200 ppm or between 20 and 200
- 20 a** Acidify and add Na<sub>2</sub>S: if a precipitate forms, Pb<sup>2+</sup> is present; if not it is Cr<sup>3+</sup>.
- b** Add NaOH solution slowly: if white precipitate forms and does not dissolve in excess, Cd<sup>2+</sup> is present; if white precipitate forms and dissolves in excess, Zn<sup>2+</sup> is present. Alternatively acidify and add Na<sub>2</sub>S: if a precipitate forms cadmium is present, otherwise it is zinc.
- 23 a** measure phosphate concentration in both;  
**i** >0.1 ppm    **ii** >0.05 ppm; because there is likely to be more water movement in the stream: moving water is less likely to develop an algal bloom
- b** because phosphate is more often the limiting factor for algal blooms, and because it is much easier to remove phosphate (precipitate it with lime, Ca(OH)<sub>2</sub>)
- 24** A is contaminated from partly treated sewage or from run-off from a poultry farm or animal feedlot (low DO, moderate BOD and high phosphate). B is probably affected by soil erosion from farmland or forest clearing (turbidity high and BOD and phosphate a little high). C is contaminated with a factory effluent (high pH, though other parameters are within the normal ranges). D is polluted with one or more heavy metals (positive Na<sub>2</sub>S/H<sup>+</sup> test), probably from a factory or metals processing plant rather than from mining, because turbidity is so low.
- 25 a** FeCl<sub>3</sub>(aq) + 3OH<sup>–</sup>(aq) → Fe(OH)<sub>3</sub>(s) + 3Cl<sup>–</sup>(aq)
- b** Al<sup>3+</sup>(aq) + 3OH<sup>–</sup>(aq) → Al(OH)<sub>3</sub>(s)  
(the Al<sup>3+</sup> generally comes from alum, KAl(SO<sub>4</sub>)<sub>2</sub>)
- c** because they are extremely insoluble: precipitate forms as very small particles which have a very large surface area for adsorbing impurities, and very little of the Fe<sup>3+</sup> and Al<sup>3+</sup> ions remain in solution after filtration

## Extended response exam-style questions for Module 3

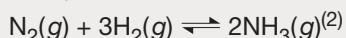
See p. 547 for some explanations about answers to extended response exam-style questions.

- 1** See Section 6.4. Assess means that you need to include a judgement in your answer (*how important* is collaboration?). Three marks means that you need at least three significant bits of information: (1) chemistry is such a broad discipline today that no one chemist can be an expert in all branches of it. (2) problems in the real world often involve several branches of chemistry and cannot be solved by a specialist in one branch only. Hence (3) collaboration between chemists is extremely important for solving problems in the everyday world. Including an example of the need for collaboration would really ensure full marks.
- 2** See Section 7.4. Ozone in the stratosphere is beneficial because it absorbs short wavelength

u.v. radiation which is harmful to people and other life forms. It is dangerous in the lower atmosphere because it is poisonous to humans at very low concentrations. That is the essence of the question in just two bits of information. However there are 3 marks for the question so you need to expand on this for the third mark. Either explain which u.v. ozone absorbs, what happens to ozone when it absorbs u.v., why short wavelength u.v. is harmful to people, or how ozone is harmful to people.

- 3 See Section 6.7. *Outline* means describe without too much detail. Assume 4 or 5 marks for *outline* and 4 or 3 for *list*. To be safe work on the basis of 5 plus 4.

Ammonia is made by passing a stoichiometric mixture of nitrogen and hydrogen gases at high pressure and elevated temperature over an  $\text{Fe}_3\text{O}_4$  catalyst<sup>(1)</sup>:



About 30 to 40% of the  $\text{N}_2$  is converted to ammonia. This is condensed out by cooling then the unreacted gases are recycled through the reactor<sup>(3)</sup>. (*Draw a diagram—a simplified version of Fig. 6.2*<sup>(4)</sup>.) Because conditions that favour a high equilibrium yield make the reaction very slow and conditions that favour a high rate produce a low equilibrium yield, compromise conditions are used to produce a moderate yield moderately rapidly<sup>(5)</sup>.

Designers would need to consider the equilibrium reaction between hydrogen and nitrogen (and how to force it in the desired direction) and the rate of the reaction (including what catalyst and temperature to use) and how to balance these two factors to maximise yield (in terms of tonnes of ammonia produced per day)<sup>(1)</sup>. They would need to choose the cheapest raw materials (generally methane or a hydrocarbon fraction from crude oil as the source of hydrogen and air for nitrogen)<sup>(2)</sup> and design the plant to minimise heating costs by using the heat of reaction to pre-heat reactants<sup>(3)</sup>. The operators of the plant would need to monitor the process carefully (temperature, pressure, state of catalyst) to ensure yields remain as high as possible<sup>(4)</sup>.

- 4 See Section 6.14. *Evaluate* in this question means make a judgement on *how useful* flame tests are and give your reasons for your evaluation. At least one example should be included.

Flame tests are sometimes useful in identifying elements, mainly metals, in samples. They are useful for distinguishing between calcium (red) and barium (green), particularly as it is often difficult to distinguish between these by precipitation tests<sup>(1)</sup>. They are also useful for distinguishing between lithium (red), sodium (yellow) and potassium (light purple), three elements for which there are no simple precipitation tests<sup>(2)</sup>.

Apart from these five elements (and Cu and Sr) there are few other elements that have characteristic

flame tests. This restricts the usefulness of flame tests<sup>(3)</sup>. In addition flame colours are often quite fleeting (due to the volatility of the compounds being used) and sodium impurity can easily mask other colours.

Overall then, flame tests are of some use for identifying certain elements in samples, but they do not have widespread applications and are not an essential part of any analytical scheme<sup>(4)</sup>.

- 5 This is Experiment 3 from p. 306. See Sections 8.2 to 8.10. Describe the experiments that you actually performed. For 7 marks, if you measured temperature, pH, total dissolved solids and dissolved oxygen by ‘immerse and read’ instruments, you would probably need to describe two to four other experiments, at least one of which should be quantitative. (Although pH, DO and TDS by instruments are ‘quantitative’, they do not involve much work or skill.) Suitable quantitative experiments could be dissolved oxygen by titration (though it is difficult for students to get good results), hardness by EDTA titration (easy), turbidity (turbidity tube or Secchi disc) or suspended solids. Qualitative tests you may have performed are tests for anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) and cations ( $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , etc.) or a general test for heavy metals (addition of  $\text{Na}_2\text{S}$  to acidified samples followed by making the mixtures alkaline).

- 6 See Section 6.7. *Evaluate* in this context means make a judgement on how important or valuable was their work and give reasons for your judgement. Note that there are two periods over which to make the evaluation, when they actually developed the process (1908 to 1914) and over the next one hundred years. Four marks means that you need four significant pieces of information. In an exam you need to convince the examiner that you know what you are talking about, so state what the work of Haber and Bosch actually was.

Fritz Haber and Carl Bosch developed a process for the commercial manufacture of ammonia from nitrogen and hydrogen gases<sup>(1)</sup>. This work was of critical importance, both to Germany at the time they developed the process and to the world at large over the next one hundred years<sup>(2)</sup>.

Before this process Chile saltpetre, sodium nitrate, was the main artificial nitrogenous fertiliser and the starting point for the manufacture of nitric acid and explosives. During World War I supplies of this were cut off from Germany; this would have had disastrous consequences for German agriculture and munitions manufacture had not the Haber process become available to supply ammonia for agriculture. So the work of Haber and Bosch at that time was of critical importance to the German war effort<sup>(3)</sup>.

In subsequent decades their work was of critical importance to agriculture throughout the world.

- Naturally occurring nitrate deposits were insufficient to meet the growing needs of expanding agriculture (needed to feed growing world populations). The availability of ammonia from the Haber process and its conversion to ammonium sulfate and ammonium nitrate provided synthetic fertilisers that could meet these demands. Expanded world agriculture, and probably expanded world populations are due largely to the development of the Haber process<sup>(4)</sup>.
- 7 See Sections 7.6 and 7.7, particularly Table 7.3. Because of the compare you should take properties one at a time and state how the two substances are similar or different. A reasonable distribution of marks would be 2 for physical properties and 1 each for chemical reactivity, molecular structure (electron dot structures of both molecules) and for interpretation. Physical properties to mention are smell, density, boiling point and possibly colour when liquid (three properties for 2 marks).
- 8 See Section 6.19 (and possibly 6.18). Assess in this question means make a judgement about how big or important the impact was, and give reasons for your assessment. Being an exam, you should explain very briefly what atomic absorption spectroscopy and trace elements are (1 mark each).
- Atomic absorption spectroscopy, AAS, is a technique in which gaseous atoms are irradiated with light of a wavelength they are known to absorb; the fraction of the incident light absorbed is measured and converted to a concentration of the element in the sample<sup>(1)</sup>.
- Trace elements are elements that are required by living organisms in very small amounts, such as Zn, Co, Cu and Ni<sup>(2)</sup>.
- Because of its very high sensitivity, AAS was able to detect trace elements in plants and animals where other less sensitive analytical techniques had failed to find them. AAS was used to show that these trace elements were essential to the good health of the organism<sup>(3)</sup>.
- Because it determined their existence and helped work out what their functions in organisms were, AAS has had an enormous impact upon the study of trace elements<sup>(4)</sup>.
- 9 See Section 6.5 and p. 286 CCPC. The most obvious process to describe is combustion with CO<sub>2</sub> and CO and maybe soot being the products formed under different conditions. An alternative is the reaction of ethylene with oxygen, with a catalyst and limited oxygen to form ethylene oxide and without a catalyst and excess oxygen to form CO<sub>2</sub>, 1 mark. You should give two equations for whichever example you use, 2 marks. To ensure production of the maximum amount of the desired products you would monitor the products of the reaction, 1 mark, and change reaction variables (such as concentration of oxygen) to favour the required product, 1 mark.
- 10 See Section 8.11. Since this question is about town water supplies, we can assume that pollution is not the main issue here, but rather the pathway from rain to storage dam (surface run-off, underground aquifer, or deep bore), whether there are other towns further upstream using the water, the nature of the catchment (heavily wooded or open grasslands or rocky terrain), the nature and amount of human activity in the catchment (roads, forestry, farming). Explanation of how these four factors affect ion concentrations would probably score 4 marks. Brief mention could be made of possible pollution and leaching from rubbish tips.
- 11 See Section 7.3. Identify in this context simply means name, though to be safe you should give the chemical formula where appropriate. 1 mark for each pollutant and its source. The five 'big ones' are carbon monoxide, oxides of nitrogen, hydrocarbons and other volatile organic compounds, sulfur dioxide and particulates, though ozone, airborne lead and carcinogenic compounds such as benzene, vinyl chloride and dioxins would be acceptable.
- 12 See Section 8.14. Three marks for comparisons (describe actual structure of each and compare filtering methods) and 1 mark for each of two advantages (any two of definite size cut-off, faster filtering, filtering can be speeded up by using pressure, can be back-washed for longer life).
- 13 See Section 7.13. Assess in this question means make a judgement about how successful international agreements have been—very, moderately, marginally or not successful at all, 1 mark, and give your reasons for this assessment, 2 marks. You should start with a brief summary of what the international agreements are (1 mark).
- 14 See Section 8.12. Evaluate in this question means make a judgement about how effective or successful monitoring phosphate for this purpose is. Explain briefly what algal blooms are, 1 mark, and what causes them, 1 mark, and why monitoring phosphate concentration is considered an effective way of predicting their occurrence, 1 mark. Then make your evaluation, 1 mark, and give your reasons, 1 mark. Remember that there is often not a right or wrong evaluation; any evaluation you give will get the marks as long as you give valid arguments in support of it.
- It might be tempting to answer this question by just saying that monitoring phosphate concentrations is very effective for predicting the likelihood of algal blooms because algal blooms occur when there is excess nutrient in the water body and phosphate is generally the nutrient present in least amount. This would certainly score 3 marks but there are 5 marks for the question so more than this is required.
- Algal blooms are excessive growths of algae and other aquatic organisms that cover water bodies

with a green sludge<sup>(1)</sup>. They are caused by excessive concentrations of nutrients in the water<sup>(2)</sup>. Because in Australia the nutrient in least amount is generally phosphate, monitoring phosphate concentrations is widely used as a method of predicting the likelihood of algal blooms<sup>(3)</sup>. Monitoring phosphate is only moderately effective for this purpose<sup>(4)</sup>, because there are many other factors that influence the occurrence of algal blooms such as water temperature, amount of sunlight, depth of water and flow rate of the water<sup>(5)</sup>. If phosphate concentration is very low, say <0.02 ppm, an algal bloom is most unlikely and if it is very high, say >1 ppm then one is highly probable, but if phosphate concentration is around the more usual values of 0.1 ppm level, predictions are much less certain.

- 15** See Sections 7.11 and 7.12. *Explain* in this question means describe the chemical processes that lead to the destruction of ozone. In the stratosphere short wavelength u.v. radiation splits off a Cl atom from a CFC molecule (give an equation), 1 mark. Cl atoms catalyse the destruction of ozone, 1 mark; give the two equations, 1 mark. This is a chain reaction so one CFC molecule can destroy thousands of ozone molecules, 1 mark. Other reactions lead to the formation of HCl and chlorine nitrate, 1 mark. In the cold Antarctic winter HCl and ClONO<sub>2</sub> combine to form chlorine (give an equation), 1 mark, so when the sun comes up in spring there is an extra source of Cl atoms (Cl<sub>2</sub> + u.v.), so there is increased destruction of ozone, 1 mark.

- 16** See Section 8.13. Again assess, so you need to make a judgement. But first explain briefly what the procedures are. If you do not know how your local water supply is treated, use the general method described in the text (HSC examiners will not know where you come from!). The procedure for clarification is flocculation (with adsorption of impurities on the precipitate as it forms) followed by sand filtration, 1 mark. For sanitisation it is usually chlorination (though the use of ozone is increasing), 1 mark. The procedures are very effective, though not perfect, 1 mark; with reasonable quality raw water, they do produce very clear water, and they remove the vast majority of bacteria and viruses, 1 mark. They are not perfect because some parasites such as *Giardia* and *Cryptosporidium* can pass through the procedure, 1 mark. Note that fluoridation is not part of clarification and sanitisation.

- 17** See Section 6.7. *Outline* means describe briefly, so just state the benefits and shortcomings and illustrate them with the nitrogen plus hydrogen reaction.

The benefits of Le Chatelier's principle are that it allows us to predict conditions that will maximise the equilibrium yield for a chemical reaction<sup>(1)</sup>. For example for the exothermic reaction



it tells us that we should use a high pressure and a low temperature<sup>(2)</sup>. The shortcomings are that it tells us nothing about how fast the reaction will reach equilibrium<sup>(3)</sup>. We have to determine rate experimentally. In this case the low temperature that maximises equilibrium yield produces an extremely slow reaction; reaction rates generally decrease as temperature decreases<sup>(4)</sup>. You could add: Hence we have to use a moderate temperature and a catalyst (to get a moderate yield in a reasonable time).

- 18** See Section 7.14. *Evaluate* in this question means make a judgement on whether the current methods are very effective, moderately effective or not particularly effective, 1 mark, and give your reason (they provide reliable data to decide the extent of the ozone hole each year—profiles at particular locations and global contour maps, 1 mark—and to determine whether it is increasing or decreasing year by year, 1 mark), but first state what the current methods are (vertically pointing spectrophotometers, a satellite and high altitude balloons (two will suffice), 1 mark).
- 19** See Section 6.18. There could be 2 marks for each part, though 3 for (a) and 1 for (b) is a possibility so take both possibilities into account in writing your answer (hence 5 marks in the following answer).

In atomic absorption spectroscopy, AAS, a different lamp is used for each element, because this is the way that the high sensitivity of the technique is achieved<sup>(1)</sup>. If the sample is irradiated with light of the exact wavelength that a particular element absorbs, then the fraction of the light absorbed is high and can be determined accurately, and so small concentrations of that element can be measured<sup>(2)</sup>. Using such a lamp means that other elements present in the sample will not absorb any of that light and so they will not interfere with the measurement<sup>(3)</sup>.

AAS does not provide information about the compound in which the element being measured is present, because it decomposes the compound into atoms in a flame in order to make measurements<sup>(4)</sup>. This decomposition is necessary in order to be able to use atomic absorption (absorption by atoms—compounds absorb at completely different wavelengths)<sup>(5)</sup>.

- 20** See Section 7.13. State what HCFCs and HFCs are, 1 mark, assess their individual effectiveness (that is, make judgements), 1 mark each, and give your reasons, 1 mark each.

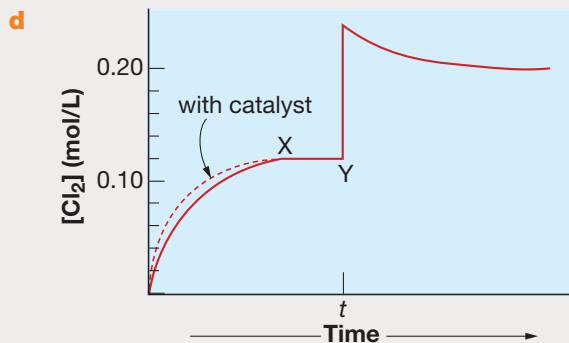
HCFCs are compounds that contain hydrogen, chlorine, fluorine and carbon, for example C<sub>2</sub>HCl<sub>2</sub>F<sub>3</sub>, while HFCs contain hydrogen, fluorine and carbon and no chlorine, for example C<sub>2</sub>H<sub>2</sub>F<sub>4</sub><sup>(1)</sup>. HCFCs were only moderately successful in minimising damage to the ozone layer<sup>(2)</sup>. Because they contained hydrogen they were more easily destroyed in the lower atmosphere and so smaller proportions of

them diffused into the stratosphere; however once there, they did lead to ozone destruction<sup>(3)</sup>. HFCs are extremely effective in minimising damage to the ozone layer<sup>(4)</sup>, because the small proportions of them that diffuse into the stratosphere have no effect on ozone, because HFCs contain no chlorine so there can be no Cl + O<sub>3</sub> reaction<sup>(5)</sup>.

### Revision test for Module 3

- 1** c    **2** c    **3** d    **4** b    **5** a  
**6** a    **7** d    **8** c    **9** b    **10** c

- 11 a** N<sub>2</sub>(g) + 3H<sub>2</sub>(g)  $\rightleftharpoons$  2NH<sub>3</sub>(g); iron or magnetite, Fe<sub>3</sub>O<sub>4</sub>
- b** i to drive the equilibrium to the right (4 vol  $\rightarrow$  2 vol; Le Chatelier's principle)  
ii high temperature would reduce the % conversion to ammonia; low temperature would make the reaction too slow
- c** after passing the reactant mixture over the catalyst, the ammonia is condensed out and the unreacted gas recirculated back over the catalyst to convert more N<sub>2</sub> and H<sub>2</sub> to NH<sub>3</sub>
- 12 a** see Section 7.6
- b** NO<sub>2</sub> + sunlight  $\rightarrow$  NO + O; O + O<sub>2</sub>  $\rightarrow$  O<sub>3</sub>
- 13** This is Experiment 2 from p. 306. See Section 6.16, Example 1. Describe the experiment you performed; 2 or 3 marks for the description and 1 for the equation, then 3 or 4 marks for sources of error and how to overcome them. Probably three sources of error and how to overcome them would suffice here. Several possible sources are listed in *Experimental difficulties* immediately following Example 1, along with procedures to minimise them. Good ones to treat (because you can describe ways of minimising them) are (1) impurities adsorbing on the precipitate, (2) small particles passing through the filter or clogging the filter and slowing down the filtration and (3) leaving some of the precipitate in the beaker or flask in which the precipitate was formed.
- 14 a** The reaction has reached equilibrium and equilibrium corresponds to not all the PCl<sub>5</sub> being converted to PCl<sub>3</sub>.
- b** Increasing the volume means that concentration decreases (same mass in larger volume).
- c** Equilibrium adjusts: it moves in the direction that counteracts the change which means that it moves from left to right (1 vol  $\rightarrow$  2 vol). It reaches a new equilibrium position at W so [Cl<sub>2</sub>] is constant between W and V.



- e** dotted line in the above diagram; equilibrium is reached more quickly, but it is the same equilibrium position
- 15 a** see Sections 7.11 and 7.12
- i** Cl and ClO are recycled
- ii** compounds need to have a C–Cl or a C–Br bond: C–F bonds are too strong to be broken by u.v. in sunlight; compounds with C–H bonds are destroyed in the troposphere
- iii** see Section 7.12
- b** See Section 7.13. State how the world is trying to solve this problem, 1 mark, give your assessment of how effective it is, 1 mark, and give a reason for your assessment, 1 mark.

The world is trying to solve this problem by banning the manufacture and use of CFCs and replacing them with hydrochlorofluorocarbons (HCFCs) or preferably with hydrofluorocarbons (HFCs), compounds that have much less or zero effect upon stratospheric ozone<sup>(1)</sup>. This approach is proving reasonably effective<sup>(2)</sup> in that many countries are reporting significantly reduced CFC emissions; however the concentration of CFCs in the troposphere has hardly fallen yet (though it has at least stopped increasing which is seen as a sign of success)<sup>(3)</sup>.

- 16 a** Pb<sup>2+</sup> (white precipitate with HCl) and Cu<sup>2+</sup> (blue precipitate with OH<sup>-</sup> which dissolves in NH<sub>3</sub>) Any two of:
- Pb<sup>2+</sup>(aq) + SO<sub>4</sub><sup>2-</sup>(aq)  $\rightarrow$  PbSO<sub>4</sub>(s)  
Cu<sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq)  $\rightarrow$  Cu(OH)<sub>2</sub>(s)  
Cu(OH)<sub>2</sub>(s) + 4NH<sub>3</sub>(aq)  $\rightarrow$  Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>(aq) + 2OH<sup>-</sup>(aq)
- b** CO<sub>3</sub><sup>2-</sup> (bubbles of gas with H<sup>+</sup>), Cl<sup>-</sup> (precipitate with Ag<sup>+</sup>) and PO<sub>4</sub><sup>3-</sup> (precipitate with Ba<sup>2+</sup> in alkaline solution but not in acid)
- 17 a** See Sections 8.1 to 8.10. Probably 3 marks for the six properties and 4 marks for the ways various forms of pollution affect four of these properties. The properties could be any six of those listed on p. 263 (apart from temperature and pH, which the question excludes). For the second part of the question good properties to treat are (1) turbidity or suspended solids (sewage, erosion from land clearing, run-off from

farm land and mining all increase this), (2) total dissolved solids (irrigation, deforestation, soil erosion and discharge of treated sewage increase TDS), (3) dissolved oxygen, (4) BOD, (5) disease-causing agents (pathogens) (sewage, food processing wastes, run-offs from poultry farms and cattle feedlots and urban storm water run-off decrease DO and increase the other two) (6) nutrients such as phosphate and nitrate (treated sewage, farmland run-off and urban stormwater run-off increase these), (7) heavy metals (mining, minerals processing and various industries can increase their concentrations).

- b  $2.6 \times 10^{-3}$  mol/L; 19 kPa; need to add another 12 kPa O<sub>2</sub> and so another 48 kPa N<sub>2</sub> on top of the 100 kPa already there

# Chapter 9

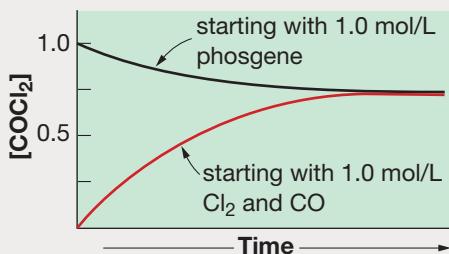
- 1** **a** see below  
**b** see below  
**c** see below

**2** **a**  $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$

**b**  $T_2$ ;  $T_2$  because reaction rate increases as temperature increases

**c** The final values are different from 1.0 mol/L because the reaction comes to equilibrium: it does not go to completion. The final concentrations are different in the two experiments because the reaction proceeds to different extents at the two temperatures.

**d** exothermic;  $T_2 > T_1$  and the reaction moves to the left as temperature increases ( $T_1 \rightarrow T_2$ ), so to the left must be the endothermic direction (Le Chatelier's principle) and so as written the reaction is exothermic.



- 1 a**

$$-\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-$$

**b**

$$\text{CH}_2=\overset{\text{Cl}}{\underset{|}{\text{C}}}-\text{CH}=\text{CH}_2$$

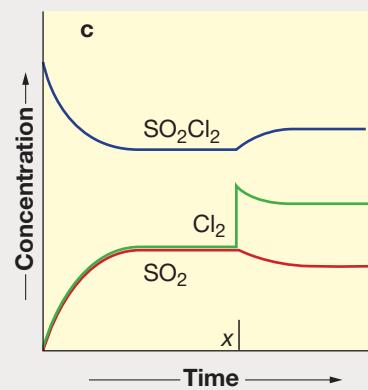
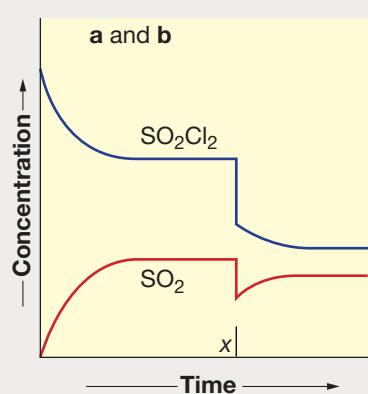
$$-\text{CH}_2-\overset{\text{Cl}}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{Cl}}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{Cl}}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{Cl}}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-$$

**c**

$$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-$$

The same equilibrium concentration of  $\text{COCl}_2$  is reached, because we are just approaching equilibrium from the opposite direction (using 1.0 mol/L  $\text{COCl}_2$  instead of 1.0 mol/L CO and  $\text{Cl}_2$ ).

- 3** **a** **i** L → R  
**ii** L → R  
**iii** R → L  
**iv** R → L  
**v** R → L  
**c** **i** R → L  
**ii** R → L  
**iii** R → L  
**iv** L → R  
**v** L → R



- b** The equilibrium reaction is  
 $\text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g)$   
Increasing the volume from 100 to 150 mL decreases the concentration of each substance

by 33%. This causes a decrease in pressure in the reaction vessel. By Le Chatelier's principle the reaction moves in the direction which increases pressure; that is, from left to right (1 mole  $\rightarrow$  2 moles).

- c** When the concentration of chlorine is increased, the reaction moves in the direction that decreases it (Le Chatelier's principle)—that is, from right to left—so more  $\text{SO}_2\text{Cl}_2$  is formed.
- 5 a** The pump pushing water from trough to tank represents the forward reaction and the flow of water from tank to trough the reverse reaction (or vice versa). The constant water levels in tank and trough represent constant equilibrium concentrations of products and reactants.
- b** Temperature increases the rates of reactions. Increasing pump speed simulates increasing the rate of the forward reaction; if temperature increases the rate of the forward reaction more than it increases the rate of the reverse reaction, there will be an increase in concentration of products (an increased height of water in the tank). This in turn will increase the rate of the reverse reaction (flow of water out of the tank) until the two rates are again equal and then the concentrations of products and reactants will again be constant (heights of water in tank and trough again constant).

- 6 a**  $\frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = K$
- b**  $\frac{[\text{ICl}]^2}{[\text{I}_2][\text{Cl}_2]} = K$
- c**  $\frac{[\text{HCOOH}][\text{CH}_3\text{OH}]}{[\text{HCOOCH}_3][\text{H}_2\text{O}]} = K$
- d**  $\frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = K$

- 7 a** 0.056 mol/L    **b**  $25 \text{ (mol/L)}^{-1}$

- 8**  $6.2 \text{ (mol/L)}^{-1}$

- 9**  $4.0 \times 10^4 \text{ mol/L}$

- 10**  $1.05 \times 10^{-5} \text{ mol/L}$

- 11** 3.9

- 12**  $0.600 \text{ (mol/L)}^{-2}$ ; none

- 13** 1.6

- 14 a** (ii)    **b** (i)    **c** (iii)    **d** (i)    **e** (iii)

- 15 a** no; will move to the left

- b** no; will move to the right

- 16 a** no; will move to the left; because the reaction quotient,  $Q$ , is greater than  $K$ , so the equilibrium adjusts to bring the value of  $Q$  down to  $K$ : to lower  $Q$  the reaction moves to the left

- b** no; will move to the right

- 17 a** 0.27 mol/L    **b** 0.13 mol/L

- 18 a** 5.06    **b** 0.14 mol/L

- 19 a**  $[\text{PCl}_3] = 0.084 \text{ mol/L}$ ;  $[\text{PCl}_5] = 0.17 \text{ mol/L}$

- b** 0.063 mol/L

- 20 a**  $\text{R} \rightarrow \text{L}$ ; decreases it; it decreases

- b**  $\text{L} \rightarrow \text{R}$ ; increases it; it increases
- c** For an exothermic reaction  $K$  decreases as temperature increases; for an endothermic reaction  $K$  increases as temperature increases.

- 21 a** and **c** decreases    **b** and **d** increases

- 22 a** **i**  $5.7 \times 10^{-3} \text{ mol/L}$     **ii** 0.47 mol/L

- b** yes; Le Chatelier's principle shows that increasing the concentration of  $\text{O}_2$  forces the equilibrium to the right: that is what the calculations show also.

- 23** because excess  $\text{O}_2$  is being used: recycling with some additional reactant mixture would build up higher and higher relative pressures (concentrations) of  $\text{O}_2$ ; to make recycling work would need to use a stoichiometric mixture of  $\text{SO}_2$  and  $\text{O}_2$

- 25** 0.3%

- 26 a**  $78 \text{ (mol/L)}^{-1/2}$

- b**  $2.6 \times 10^{-3} \text{ mol/L}$ ; 19 kPa; need to add another 12 kPa  $\text{O}_2$  (approx) and so 48 kPa  $\text{N}_2$  on top of the 100 kPa already there

- 27 a** 1.96 t (= tonne)    **b** 21.6 t

- 28**  $5.4 \times 10^6 \text{ kJ}$ ; 16 t

- 29** for  $\text{HCl}$ : 3.76; for  $\text{HNO}_3$ : 1.50; yes, because in each case there is sufficient  $\text{H}_2\text{O}$  to react with all the acid

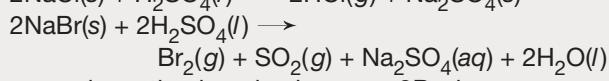
- 30 a** 10.4°C

- b** 1.1°C (both cases take the volume of the solution as 105 mL)

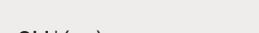


$\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$   
 $\text{HSO}_4^-$  is a moderately weak acid so does not ionise at all in concentrated solution, but ionises extensively in 0.01 mol/L solution.

- 32** with  $\text{NaCl}$ ,  $\text{HCl}$ ; with  $\text{NaBr}$ ,  $\text{Br}_2$



- 33 a**  $2\text{Ag}(s) + \text{H}_2\text{SO}_4(l) + 2\text{H}^+(aq) \rightarrow$



**b**  $\text{S}(s) + 2\text{H}_2\text{SO}_4(l) \rightarrow 3\text{SO}_2(g) + 2\text{H}_2\text{O}(g)$   
the  $\text{S}(s)$  has been oxidised to  $\text{SO}_2$  while the S in  $\text{H}_2\text{SO}_4$  has been reduced to  $\text{SO}_2$

- 34**  $\text{Mg}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{MgSO}_4(aq) + \text{H}_2(g)$

(or  $\text{Mg}(s) + 2\text{H}^+(aq) \rightarrow \text{Mg}^{2+}(aq) + \text{H}_2(g)$ )

yes; Mg loses 2 electrons and  $2\text{H}^+$  gains 2 electrons

- 35**  $2\text{NaNO}_3(s) + \text{H}_2\text{SO}_4(l) \rightarrow 2\text{HNO}_3(g) + \text{Na}_2\text{SO}_4(s)$

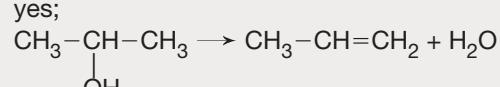
no; there has been no electron transfer—just a proton transfer (from sulfate to nitrate)

- 36 a**  $\text{HCOOH}(l) \rightarrow \text{H}_2\text{O}(l) + \text{CO}(g)$

with  $\text{H}_2\text{SO}_4(l) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq)^*$

- b** **i** no

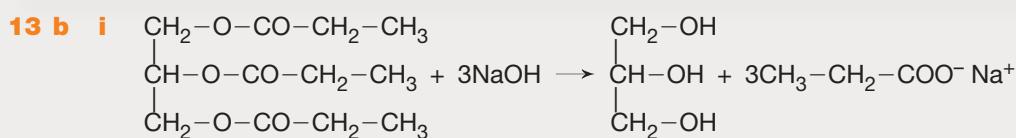
- ii** yes;



with equation \* from (a)

## Chapter 10

- 1 a** 11 mol/L; 87 mol/L  
**b i** 76 g/100 mL    **ii** 19 mol/L
- 2 a**  $2\text{NaOH}(\text{aq}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{Na}_2\text{S}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$   
 $2\text{NaOH}(\text{aq}) + \text{SO}_2(\text{g}) \rightarrow \text{Na}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
Bubble the gas through the solution in a flask or in a proper gas bubbler jar (such as A in Figure 1.9 on p. 17 of CCPC).
- c** LiOH has a smaller molar mass (23.9 g/mol compared with 40 for NaOH) so a smaller mass is required to absorb a given quantity of  $\text{CO}_2$ .
- 3 a** endothermic; by Le Chatelier's principle as temperature falls, reaction moves in the direction that releases heat: if R  $\rightarrow$  L is exothermic then the reaction as written is endothermic  
**b** Adding acid would effectively lower  $[\text{OH}^-]$  by removing it by reaction; again by Le Chatelier's principle lowering  $[\text{OH}^-]$  causes reaction to move to the left (that is, to precipitate  $\text{Al(OH)}_3$ ); because it uses up NaOH which would need to be replenished in order to use the solution again.  
**c**  $2\text{Al(OH)}_3(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l})$
- 4 a** at the anode:  
 $4\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) + 4\text{e}^-$   
at the cathode:  
 $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$   
This is electrolysis of water because the overall reaction is:  
 $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$   
(Double the cathode reaction, add to the anode one, then cancel  $2\text{H}_2\text{O}$ )  
**b** because it does not conduct electricity; if there is no current there can be no electrolysis
- 5 a**  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$   
 $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$   
overall reaction:  $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$   
**b**  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$   
 $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$   
overall reaction:  
 $4\text{Ag}^+(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Ag}(\text{s}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq})$   
**c** same as in (a)  
**d**  $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$   
 $4\text{OH}^-(\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^-$   
overall reaction:  $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
- 6 a** by mass,  $\text{NaOH} : \text{Cl}_2 : \text{H}_2 = 40 : 35 : 1$ ; no, all cells involve the same overall reaction  
**b** Adjust prices: lower the price of the low-demand product and so increase demand for it, and increase the price of the high-demand product and so reduce demand for it: do this until demands balance. Production of hydrogen is not a major purpose of such plants so the price is set at the 'going rate' just to off-load it.
- c** No, because they are produced in fixed proportions by the one electrolysis process.
- 7 a** 310 L    **b** 310 L
- 8 a** 0.02 mol  $\text{OH}^-$  has diffused into the NaCl compartment and 0.04 mol  $\text{Cl}^-$  has diffused from the NaCl compartment into the NaOH one (a total of 0.25 mol  $\text{Na}^+$  has migrated from the NaCl compartment to the NaOH one); in the NaOH compartment there is 0.18 mol NaOH and 0.04 mol NaCl  
**b** 0.20 mol of each ( $\text{OH}^-$  and  $\text{Cl}^-$  cannot diffuse through the membrane in this cell)
- 9** The high concentration of NaOH in the solution lowers the solubility of NaCl in this solution to well below its pure water value.
- 10 a**  $\text{H}-\text{COO}-\text{CH}_2-\text{CH}_3 + \text{OH}^- \rightarrow$   
 $\text{H}-\text{COO}^- + \text{CH}_3-\text{CH}_2-\text{OH}$   
**b**  $\text{CH}_3-\text{CH}_2-\text{COO}-\text{CH}_3 + \text{OH}^- \rightarrow$   
 $\text{CH}_3-\text{CH}_2-\text{COO}^- + \text{CH}_3-\text{OH}$
- 11 a** because hydrogen bonding is possible (between  $-\text{OH}$  of alcohol and water)  
**b** Ions, including carboxylate anions, are generally soluble in water; the acid as a neutral molecule has low solubility particularly if the hydrocarbon chain is more than two or three carbons long.
- 12 a**  $\text{CH}_3-(\text{CH}_2)_4-\text{COO}-(\text{CH}_2)_3-\text{CH}_3 + \text{OH}^- \rightarrow$   
 $\text{CH}_3-(\text{CH}_2)_4-\text{COO}^- + \text{CH}_3-(\text{CH}_2)_3-\text{OH}$   
**b** A is 1-butanol because it is a liquid with a low solubility in water (and so separates out); B is hexanoic acid because it is a solid with a low solubility in water, but it forms a soluble carboxylate anion in aqueous sodium hydroxide solution (and so is in the aqueous phase after saponification).  
**c** Add a few drops of water to the layers in a separating funnel and see which layer they dissolve in: that is the aqueous layer.  
**d** to convert the hexanoate anion (in (a)) to hexanoic acid
- 13 a** **i** structure at the left in the equation in (b)(i)  
**b** **i** see below
- 15 a** **i**  $\begin{array}{c} \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3 \\ | \\ \text{CH}-\text{O}-\text{CO}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3 \\ | \\ \text{CH}_2-\text{O}-\text{CO}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3 \end{array}$   
**b** **i** 3    **ii** 6  
**c** monounsaturated: one double bond per carboxylate unit  
polyunsaturated: more than one double bond per carboxylate unit

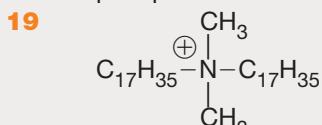


It is not possible. This highlights an inadequacy in this nomenclature.

- 16 a** i and ii stearic acid  
b i one mole ii 2 moles

**17** so that they will spread out as a thin film of liquid over the whole surface: if their surface tension is too high, they roll up into small drops and do not cover the surface

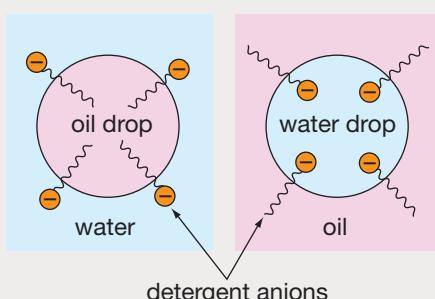
- 18 a** can form many hydrogen bonds with water: from each O and from terminal –OH  
b It does not have an anionic group to form a precipitate with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ .



Repulsion between the anionic ‘heads’ of the surfactant ions and the negative charges on the glass surface helps remove the dirt particle from the surface: this is in addition to the solubility of the anionic ‘heads’ in the water.

- c** because the cationic centres are attracted to the negative charges on the glass; similarly the positive surface charges on plastics hold anionic surfactants strongly and so they do not wash off easily

**22**



- 23 a**  $\text{C}_{15}\text{H}_{31}-\text{COO}^-(\text{aq}) + \text{Ca}^{2+}(\text{aq}) \rightarrow (\text{C}_{15}\text{H}_{31}-\text{COO})_2\text{Ca}(\text{s})$   
**b**  $\text{Na}_2\text{CO}_3(\text{aq}) + \text{Mg}^{2+}(\text{aq}) \rightarrow \text{MgCO}_3(\text{s}) + 2\text{Na}^+(\text{aq})$

**24** There would be no precipitate to settle on the clothes being washed.

**25** 16%

**26** The value of the equilibrium constant for the first reaction is sufficiently high for this reaction to go to completion (Section 9.6). However the value for the second reaction is much less than 1 which means that this equilibrium lies well to the left: that is it hardly goes at all.

**27** yes; the overall reaction is Equation 10.9: it goes by having ammonia involved but ammonia is not used up by the reaction.

**28** 1.05 t; 3.5 t

**29** 0.202 t

**30** 2.94 t

**31** 0.63 kg

**32 a**  $2.95 \times 10^5 \text{ L (295 m}^3)$

**b**  $2.34 \times 10^5 \text{ L}$ ; because the formula weights of the two compounds are different. One mole of  $\text{CO}_2$  produces 1 mol  $\text{NaHCO}_3$  and 1 mol  $\text{Na}_2\text{CO}_3$ , but 1 t of each compound is a different number of moles.

**33** 2.70 t

**34** 3.9 t; danger of an accidental spill, corrosion of the transport vehicle; locate the plant near the source of the brine because limestone is easier to transport and the quantity to be transported is smaller

**35** For all three sites with construction of a good access road, a suitable workforce should be available from the nearby city and/or holiday town. Being close to a big city, adequate energy supplies are probably available. If the market is to be solely the local glass factory then all three sites are roughly equal in terms of getting the product to market, assuming a connecting road to the major highway network is built. If major markets are to be in distant cities then A has a significant advantage in that a rail spur from the existing line to the factory could easily be built. If export markets are being sought, then all three sites are probably equally suitable; they would all have to truck the product to the harbour, though A with the possibility of a rail link would have a slight advantage.

It is in access to raw materials, suitable disposal sites for wastes and requirements about air pollution that the three sites differ.

A has good access to limestone but would need to transport brine considerable distances through urban areas, which is a decided disadvantage. B and C have good access to brine (seawater), though would require transport of limestone over considerable distances and again through urban areas. Smaller quantities of limestone than of brine are required and limestone is less hazardous to transport, so on access to raw materials B and C are roughly equivalent and superior to A.

A, being remote from the ocean and close to the city’s water supply dam, presents problems for disposal of waste calcium chloride. Solutions would need to be evaporated to dryness and the solid shipped to a suitable disposal site, an expensive procedure. B has easy access to the ocean for disposal of  $\text{CaCl}_2$ , while C has reasonable access to the ocean (assuming disposal into Peach Bay will not be allowed), though local opposition from the holiday towns would be expected.

The main air pollution concern will be dust from handling and crushing limestone. Licensing authorities would place less stringent air pollution controls on A because it is downwind of the city, moderate controls on B and quite severe ones on C, being close to the city on the upwind side. Overall none of the sites is ideal for a Solvay plant.

On the information available, B would probably be the best choice, with A marginally better than C.

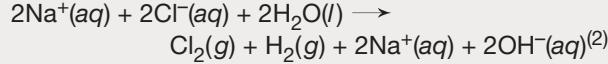
- 36 a  $\text{Na}_2\text{CO}_3(\text{aq}) + 2\text{HNO}_3(\text{aq}) \rightarrow 2\text{NaNO}_3(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- 37 a  $\text{Na}_2\text{CO}_3(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaHCO}_3(\text{aq or s})$
- b 358 L; 2.46 kg
- 38 a  $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$   
The  $\text{CO}_2$  blankets the fire and prevents oxygen getting to it and so smothers it.
- b  $\text{NaHCO}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- c for  $\text{NaHCO}_3$ : 120.5 g chemicals produce 1 mole (24.8 L)  $\text{CO}_2$   
for  $\text{Na}_2\text{CO}_3 + \text{HCl}$ : 179 g chemicals produce 1 mole (24.8 L)  $\text{CO}_2$
- 39 a  $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)(\text{aq}) + \text{NaHCO}_3(\text{aq}) \rightarrow \text{NaK}(\text{C}_4\text{H}_4\text{O}_6)(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- b  $\text{Ca}(\text{H}_2\text{PO}_4)_2(\text{aq}) + 2\text{NaHCO}_3(\text{aq}) \rightarrow \text{Ca}^{2+} + 2\text{Na}^+ + 2\text{HPO}_4^{2-} + 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
- 40 a  $\text{Na}_2\text{CO}_3(\text{s}) + \text{SO}_2(\text{g}) \rightarrow \text{Na}_2\text{SO}_3(\text{s}) + \text{CO}_2(\text{g})$
- b 42.7 kg

## Extended response exam-style questions for Option 1

- 1 See Section 9.1. There are eight factors listed in that section. You need to choose one example that illustrates as many of these as possible. With 4 marks your example should involve at least four factors. Good examples are rubber (increasing demand, inability of natural sources to meet demand (initially because of interruption by war), escalating price of natural product (after the war), increasing availability of starting materials for the synthetic product (by-product from increasing use of oil), decreasing price of the synthetic product, greater reliability of supply), soap (increasing demand, competition for the natural resource from other sources, inability of natural sources to keep up with demand, increasing availability of starting material for the synthetic (by-product from rapidly expanding oil refining), decreasing price of the synthetic), and wool (similar list).
- 2 See Section 9.9. With 5 marks you can assume 2 for each of two uses and 1 for the third, so your third use could be briefer than your first two. Notice that it says *describe*, not just list. Because of *with chemical equations where appropriate* you should include at least one use where you can write a chemical equation (for example manufacture of fertiliser, ammonium nitrate or superphosphate, or synthesis of ethanol from ethylene).
- 3 See Sections 10.4 to 10.8. *Outline* means describe without too much detail, so you do not have to describe each of the three cells used; emphasis is on the chemistry. A reasonable allocation of marks would be 3 for *outline* and 3 for *identify potential hazards*.

Sodium hydroxide is produced industrially by the electrolysis of concentrated aqueous solutions of sodium chloride<sup>(1)</sup>. The electrode reactions are:  
 $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$   
 $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{aq}) + 2\text{e}^-$

leading to the overall reaction



There are three cells currently in use for doing this: the diaphragm cell and the membrane cell, which differ only in the nature of the porous partition used to separate anode and cathode compartments, and the mercury cell in which the chemistry is somewhat different but in which the overall reaction is the same as the one above<sup>(3)</sup>.

The hazards associated with this procedure are:

- the safe collection and handling of the gases formed: chlorine (which is an extremely poisonous and corrosive substance) and hydrogen (which can form explosive mixtures with air)<sup>(4)</sup>, both of which are sold<sup>(4)</sup>
  - the safe handling of sodium hydroxide solutions and solid; this is also an extremely corrosive substance and is produced as both concentrated solutions and pure solid<sup>(5)</sup>
  - pollution of the environment, particularly of water, and particularly from the mercury cell, which tends to lose a small amount of this poisonous metal no matter how carefully the plant is managed<sup>(6)</sup>.
- 4 See Section 10.2 and perhaps 2.4. There are 4 marks for this question, so more than just a brief account of the difference is required. Describe what galvanic and electrolytic cells are, that galvanic cells use a spontaneous chemical reaction to produce electrical energy while in electrolytic cells electrical energy is used to bring about a chemical reaction that otherwise does not occur. To be sure of full marks give simple examples (the  $\text{Cu}(\text{s}) + \text{Ag}^+(\text{aq})$  reaction can be made produce electricity while energy is needed to electrolyse  $\text{CuCl}_2$ ).

- 5 See Sections 9.7 and 9.8. Compare, so point out the similarities and the differences: both can be used to predict the effect of changing the concentration of one species involved in the reaction, 1 mark, and both can predict the effect of changing the pressure or volume of an equilibrium mixture (though for the equilibrium expression the effects have to be translated into how they affect individual concentrations), 1 mark. The equilibrium expression can make quantitative predictions whereas Le Chatelier's principle provides only qualitative ones, 1 mark. On the other hand Le Chatelier's principle provides predictions for changing temperature whereas the equilibrium expression does not, 1 mark.

- 6 This is Experiment 7 from p. 388. See Section 10.13.

Describe the experiment you performed. The simplest experiment is this.

We half filled a test tube with hot water, then added some cooking oil to it, then shook the tube vigorously and allowed it to settle. We noted that the oil formed a separate layer sitting on top of the water<sup>(1)</sup>. We made a solution of soap in water then added a few drops of this to the water and oil in the test tube, then shook the tube vigorously for about a minute; then we allowed it to stand until most of the bubbles had broken up<sup>(2)</sup>. We noticed that the mixture now appeared homogeneous (no separate layers) though it had a cloudy appearance; an emulsion of invisibly small oil droplets dispersed through the water had formed. This demonstrated that soap can act as an emulsifier, a substance that can help form an emulsion between two normally immiscible liquids<sup>(3)</sup>.

- 7 See Section 10.17. Discuss in this question means comment on how difficult or easy and how effective or how expensive the ways are; do not just list the ways. The main issue to treat is disposal of calcium chloride, probably 2 marks, then two other issues, 1 mark each (two of ammonia losses, waste heat, mining and dust management at the plant from handling and crushing limestone).
- 8 See Section 9.12. Sulfur dioxide is needed to make sulfuric acid; extraction of metals such as copper, lead and zinc from sulfide ores produces sulfur dioxide, 1 mark (give an equation for this, 1 mark). Obtaining sulfur dioxide from a metals-extraction plant is much cheaper than using imported elemental sulfur, 1 mark. Metals-extraction plants are no longer allowed to discharge their SO<sub>2</sub> to the atmosphere, so selling this SO<sub>2</sub> to sulfuric acid plants offsets the costs of trapping the SO<sub>2</sub> out of their flue gases, 1 mark. Hence there are great benefits to both parties.
- 9 This is Experiment 2 from p. 388. See Sections 9.2, 4.7 and 4.8. A common experiment is the following.

The equilibrium reaction we analysed was:



Fe<sup>3+</sup> and SCN<sup>-</sup> solutions are colourless while Fe(SCN)<sup>2+</sup> has a blood red colour.

We mixed equal volumes of moderately concentrated solutions of iron(III) nitrate and potassium thiocyanate; a blood red colour formed. We diluted this solution by a factor of 50, then put equal volumes of it in six test tubes. We kept one test tube as a reference<sup>(2)</sup>. We then added drops of the original Fe<sup>3+</sup> solution to the second test tube; compared with the reference tube, the solution went darker (more complex formed). To the third test tube we added drops of the original SCN<sup>-</sup> solution; again the solution in the test tube went darker<sup>(3)</sup>. Both of these experiments showed that increasing the concentration of reactant in an equilibrium reaction pushes the equilibrium towards products;

this is what we had expected from Le Chatelier's principle<sup>(4)</sup>.

We heated the solution in the fourth tube and the solution went paler; we cooled the solution in the fifth tube and it went darker. These two experiments showed that the equilibrium moves to the left as temperature increases<sup>(5)</sup>; Le Chatelier's principle applied to these results shows that the reaction is exothermic.

To the sixth tube we added drops of a sodium fluoride solution; fluoride removes Fe<sup>3+</sup> from solution by forming a very stable FeF<sub>3</sub> complex; the solution went colourless. This again demonstrates Le Chatelier's principle by showing that removal of a reactant drives the equilibrium towards reactants; that is, to the left. (*You would probably have obtained the 5 marks without this last paragraph.*)

- 10 See Sections 10.15 and 10.16. To answer this question adequately you need to recognise that the word *detergent* has two meanings: surfactant and washing mixture (surfactant, phosphate builder, fluorescers, perfumes, etc.). Another key word is *current-day*. In the 1960s and '70s there were problems with the detergents (surfactants) then in widespread use; they were only very slowly biodegradable and their discharge into streams led to lots of froth and foam in the waterways. Also note the verb is *discuss*, so you need to comment on how extensive or serious the various impacts are and not just list them.

Most current-day detergents, meaning surfactants, and soaps have very similar environmental impacts which are quite small, because both classes of compounds are biodegradable and so break down fairly quickly<sup>(1)</sup>. Cationic detergents in high concentrations, being biocides, can interfere with the efficient operation of sewage treatment works (by killing many of the organisms that break down organic wastes), so they have significantly greater impacts; however cationic detergents are not as widely used as anionic and non-ionic ones<sup>(2)</sup>.

The word *detergent* is also widely used to mean a cleaning mixture such as a laundry powder or liquid, dishwashing liquid or floor cleaner; these detergents are mixtures of several ingredients of which one is the surfactant and another is phosphate. Phosphate is added to improve the cleaning power of the mixture. Phosphate presents a significant environmental problem<sup>(3)</sup>, because it is a plant nutrient and is the one that is usually present in least concentration. Hence discharge of large amounts of phosphate from washing products into waterways can lead to increasing concentrations of phosphate, which in turn can lead to algal blooms that cause considerable damage to the stream or dam and seriously reduce the usefulness of the water body for humans<sup>(4)</sup>.

*(You could mention the fact that first generation detergents (surfactants) were much less biodegradable and this led to problems, but strictly it is not relevant because of the current-day in the question.)*

- 11** See Sections 10.4 to 10.8. Demonstrate means use an example to illustrate a concept or statement. The improvements in the technology of manufacturing sodium hydroxide were from the diaphragm cell (asbestos diaphragm, some contamination of the product with sodium chloride and some environmental pollution from asbestos), 1 mark, to the mercury cell (which produced a much purer product and which was originally thought to be free of pollution but which, despite the best efforts of operators, always led to small amounts of mercury contamination of nearby water bodies), 1 mark, to the membrane cell (current technology that has successfully overcome both problems), 1 mark. The scientific advances that lead to these improvements were the discovery of the different cathode reaction that occurs with a mercury cathode, 1 mark, and the development of synthetic ion-exchange membranes that can let  $\text{Na}^+$  ions through but not any other ions, 1 mark.
- 12** See Sections 10.10 and 10.11. Again demonstrate means use an example to illustrate. Define the terms, soap and fats and oils, with chemical structures, 2 marks. Explain that soap is made by the saponification of fats and oils and write an equation showing how a fat or oil forms three soap anions and a glycerol molecule, 1 mark. Raw materials are fatty wastes from abattoirs and butcher shops and common oils such as coconut and palm oils, 1 mark.
- 13** This is Experiment 4 on p. 388. See Section 10.3. Describe the experiment you actually performed. Note *products* and *solutions* (plural) so the question is wanting your experiment to include both concentrated and dilute solutions, because they lead to different products. And you need to describe how you determined what the products were.

We electrolysed a concentrated solution of sodium chloride by immersing a pair of graphite (or stainless steel) electrodes in it and connecting them to a power supply. (*Draw a diagram.*) We adjusted the voltage to produce a gentle stream of bubbles at each electrode. The gas formed at the positive electrode had a strong smell while the one at the negative electrode had hardly any smell at all<sup>(1)</sup>. After about ten minutes we switched off the power supply and tested the solutions near the electrodes. We added drops of phenolphthalein to the solution near the negative electrode; the solution there turned red indicating that alkaline solution had been produced. From this we deduced that the gas formed there was hydrogen<sup>(2)</sup>. (*You may have been able to collect some of this gas and perform a ‘pop’ test to confirm that it was hydrogen.*) We dipped a piece of pH

paper into the solution near the positive electrode; it indicated a near-neutral pH. We then added drops of colourless iodide solution near the positive electrode and it turned brown, indicating that chlorine had been produced there (chlorine reacts with iodide to form brown iodine)<sup>(3)</sup>. (*Alternatively you may have used a solution of o-tolidine from a swimming pool test kit.*)

The reactions occurring at the electrodes were therefore:

at the negative electrode:



at the positive electrode:



We then repeated the experiment using a dilute solution of sodium chloride. Again gases formed at both electrodes, though neither gas had a strong smell. After the electrolysis we tested the solution near the negative electrode with phenolphthalein and got the red colour again, showing that the same product, hydrogen, had been formed there<sup>(5)</sup>. When we tested the solution near the positive electrode with pH paper it gave a decidedly acidic reading. When we tested that solution with iodide solution we got only a faint brown colour, indicating that chlorine was not the major product. The low pH suggested that the product was  $\text{O}_2$ , a conclusion that was also consistent with the lack of a strong smell. The reaction at the positive electrode in the dilute solution was:



- 14** See Section 9.10. Outline means describe briefly. Describe the method and include a diagram, 3 marks. For explain how, the relevant properties are melting point (meaning that the sulfur will melt at temperatures to which superheated water can be heated), 1 mark, and lack of solubility in water (so when the mixture cools solid sulfur separates out), 1 mark.
- 15** See Sections 10.4 to 10.7. Describe the impacts of the three cells and point out similarities and differences.

Apart from traces of chlorine in the brine returned to the ocean, there are no significant environmental impacts of the membrane cell<sup>(1)</sup>. This contrasts with the earlier two cells. With the original membrane cell the brine being returned to the ocean contained small concentrations of hydroxide as well as chlorine<sup>(2)</sup>; both of these have minor detrimental effects upon the environment. In addition there was some release of asbestos to the air and water<sup>(3)</sup>. In the mercury cell the main environmental impact was a small but significant release of mercury to the ocean; mercury is quite poisonous. Although in theory no mercury should have been released, it seemed impossible to prevent it<sup>(4)</sup>. The brine returned to the ocean in the mercury cell also contained small concentrations of chlorine.

- 16** See Section 10.17. Describe the experiment you performed. Note that risk assessment is an important part of this question: 3 marks for description, 2 marks for hazards and their minimisation.

The step we carried out was the formation of sodium hydrogen carbonate by the reaction

$$\text{NaCl(aq)} + \text{CO}_2(g) + \text{NH}_3(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow \text{NaHCO}_3(\text{s}) + \text{NH}_4\text{Cl(aq)}^{(1)}$$

We dissolved sodium chloride in commercial concentrated ammonia solution to produce a near-saturated solution<sup>(2)</sup>. We then set up a carbon dioxide generator by adding dry ice to a flask containing a quantity of water; the flask was fitted with a plastic delivery tube. The water warmed up the dry ice, which evaporated into gaseous carbon dioxide. This was bubbled through our NaCl + NH<sub>3</sub> solution and a white precipitate of NaHCO<sub>3</sub> formed. We filtered this off<sup>(3)</sup>.

Some of the hazards in this experiment and how we minimised them were as follows:

Ammonia is a dangerous gas so to avoid exposure to it we performed the experiment in a fume cupboard, wore plastic gloves and kept a cover on the flask containing the ammonia solution whenever possible<sup>(4)</sup>. There is the possibility of excessive pressure build-up in our dry ice evaporator; to minimise this we plugged the stopper into the flask not too firmly and took care not to kink the delivery tube<sup>(5)</sup>. In addition we did not use too large quantities of dry ice. Carbon dioxide can be suffocating if so much of it is released that it displaces oxygen, so we took care not to use more dry ice than was necessary and to keep the excess in its cold container. (*This third hazard is playing it safe; two should score the marks.*)

- 17** See Sections 10.12 and 10.13. In your explanation, 2 marks, include a diagram similar to the right-hand one in Figure 10.5. Two marks for four everyday situations (for example mayonnaise and salad dressings, many cosmetics such as cold creams and moisturising lotions, sunscreens and garden insecticide sprays).

- 18** See Section 9.18. Assess in this question means make some judgement about how effective each procedure is. With 4 marks, four safety procedures (of the eight listed) with an assessment of each is probably sufficient, though give more if time allows. The most effective procedures to assess are diluting by adding acid to water, storing it in small bottles, wearing protective goggles and clothing and working where running water and sodium hydrogen carbonate are close by.

- 19** See Sections 10.17 and 10.18. Describe where Solvay plants are commonly located (for example the Penrice plant at Osborne near Adelaide) and explain why such locations are used (availability of raw materials, easy disposal of wastes, availability

of energy, workforce and markets and suitability of environmental controls). At least four criteria should be treated.

- 20** This is Experiment 6 from p. 388. See Section 10.13. Describe the experiment you performed. You may have used cream as your emulsion. Common properties to study are viscosity (how easily it pours) and stability (how easy it is to separate the two components, using shaking, heating or adding acid).

## Revision tests for Option 1

### Test A

- a i and ii increases it  
iii and iv decreases it

Explain in terms of Le Chatelier's principle, Sections 4.7 and 9.2.

- b i See Section 9.13. It is an environmental issue (limitations placed on the amount of SO<sub>2</sub> that can be released to the atmosphere) that leads to the current reactor design in which SO<sub>3</sub> is condensed out of the equilibrium reaction mixture and the unreacted gases sent back over a further batch of catalyst to convert more of the SO<sub>2</sub> to SO<sub>3</sub>.  
ii See Section 9.17. Reactions you are likely to have performed or to have seen are oxidation of colourless bromide to brown bromine or colourless iodide to purple iodine and the dehydration of sucrose (to carbon) by concentrated sulfuric acid. Give equations for one oxidising reaction and the dehydrating reaction. Because there are 5 marks for this, to be safe you could give two oxidising reactions, one of the above and oxidation of carbon or sulfur.

- c i See Section 10.7. Describe the cell. The equations are on Figure 10.6 and in Section 10.4.  
ii very pure product (not contaminated with NaCl), no mercury or asbestos pollution

- d See Section 10.17, particularly the subsection *The chemistry*.  
e See Section 10.14, particularly Table 10.4.

### Test B

- a See Section 9.11.

- b i See Section 10.3.

- ii See Sections 10.5 and 10.6. Assess, so make some judgement about how significant or how real the benefits were. There are 4 marks, so include some detail.

The benefits of replacing the diaphragm cell with the mercury cell were the production of a purer product (no contamination by chloride from its diffusion through the diaphragm)<sup>(1)</sup> and no asbestos pollution in the waste water or the air (from the diaphragm that separates the anode and cathode compartments in the

diaphragm cell)<sup>(2)</sup>. Although these benefits were quite significant and worth gaining<sup>(3)</sup>, it turned out that the mercury cell had a big disadvantage that was not apparent until plants using it had been in operation for considerable time. This was the virtually unavoidable loss of mercury from the cell into the spent brine that was being returned to the ocean, so overall the benefits of replacing the diaphragm cell with the mercury cell were not particularly great<sup>(4)</sup>.

- c** **i** This is Experiment 5 on p. 388. See Section 10.11. You probably saponified a fat or oil into a soap. Describe the experiment you performed and give an equation for it.
- ii** See Section 10.11. For 3 marks you need to mention three differences.
- d** **i**  $\frac{[\text{NO}]^2 [\text{Br}_2]}{[\text{NOBr}]^2} = K$
- ii**  $4.3 \times 10^{-4}$
- iii**  $K$  increases
- e** See Section 10.18. Assess means that you need to make a judgement about which of the two sites is the better. List the advantages and disadvantages of each site, make a judgement and give a reason for it. It does not matter which site you choose, as long as you give valid arguments for preferring it.

The advantages of site A are that raw materials are easily available (limestone from A and brine from bores in Dry Lake), that there is a convenient disposal site for the calcium chloride solution (let it evaporate in Dry Lake; the accumulation of solid calcium chloride over time will not be a problem) and good rail and road transport to Bigtown and other cities is close at hand<sup>(1)</sup>. The disadvantages are that water and energy supplies are quite distant and that a small town will need to be built to house a workforce because Bigtown is about sixty kilometres away, too far for daily commuting<sup>(2)</sup>.

The advantages of site B are that one raw material is easily available (brine from the ocean), there is a good disposal site for waste calcium chloride solution (the open ocean), water and energy are readily available and a workforce would also be readily available within easy commuting distance<sup>(3)</sup>. Its disadvantages are that one raw material would need to be transported in from a quite a distance (80 km), it would not have easy access to rail transport and, being close to a big city, more stringent control of emissions to the air (dust and ammonia leaks) would be required<sup>(4)</sup>.

Site B is the better location for the plant because its disadvantages of no rail link, long-distance trucking of limestone and control of air pollution are probably less costly than those of A, establishing a new town with reasonable community facilities for a relatively small workforce and bringing in energy and water<sup>(5)</sup>.

## Chapter 11

- 1** 0.606 mol of positive charge per L; 0.606 mol of negative charge per L
- 2** **a** % (w/v):  $\text{Na}^+$ , 1.08;  $\text{K}^+$ , 0.039;  $\text{Mg}^{2+}$ , 0.13;  $\text{Ca}^{2+}$ , 0.040;  $\text{Cl}^-$ , 1.95;  $\text{SO}_4^{2-}$ , 0.27  
ppm:  $\text{Na}^+$ ,  $1.08 \times 10^4$ ;  $\text{K}^+$ ,  $3.9 \times 10^2$ ;  $\text{Mg}^{2+}$ ,  $1.3 \times 10^3$ ;  $\text{Ca}^{2+}$ ,  $4.0 \times 10^2$ ;  $\text{Cl}^-$ ,  $1.95 \times 10^4$ ;  $\text{SO}_4^{2-}$ ,  $2.7 \times 10^3$
- b** Add up all the percentages to get a total concentration of all ions: 3.51%.
- 3** 1.29 kg
- 4** Mn, Zn; they would deposit near the ridges as insoluble sulfides; Ca and Mg would disperse through the ocean as soluble compounds
- 5** **a** **i**  $2\text{Mg(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{MgO(s)}$   
**ii**  $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2(\text{g})$   
**iii**  $2\text{Na(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$   
**iv**  $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow 2\text{Ag(s)} + \text{Zn}^{2+}(\text{aq})$   
**b** O is oxidation, R is reduction  
**i**  $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-(\text{O})$   
 $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}(\text{R})$   
**ii**  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-(\text{O})$   
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{R})$   
**iii**  $\text{Na(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{e}^-(\text{O})$   
 $2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) (\text{R})$   
**iv**  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-(\text{O})$   
 $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag} (\text{R})$
- 6** **a** no; it is a direct reaction between Na and  $\text{H}_2\text{O}$ ; no migration of ions through an electrolyte is required. (For some reactions such as rusting to be discussed in the next chapter a migration of ions is required and they go more rapidly in salt water because of its greater electrical conductivity.)  
**b** no; same reason as in (a)
- 7** Being endothermic, this equilibrium moves towards the left as the reaction mixture is cooled, so  $\text{Fe}_3\text{C}$  decomposes to Fe and C. If the mixture is cooled very quickly so that the equilibrium does not have time to adjust before the reaction rate becomes extremely slow (at low temperature), then most of the  $\text{Fe}_3\text{C}$  will still be present as  $\text{Fe}_3\text{C}$ . So the end product is iron containing dissolved cementite rather than graphite.
- 8** The high temperature and high concentration of oxygen causes the carbon to burn off:  
 $\text{C} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
- 9** pure iron, 1535°C; 1% C, 1450°C; 3% C, 1250°C; melting point decreases as concentration of impurity increases
- 10** See p. 102 CCPC.
  - a** tungsten
  - b** chromium (10 to 20%) and nickel
  - c** silicon
  - d** chromium (2 to 4%)

- 11 a** Zn; Zn has the lower (more negative) standard electrode potential, so it oxidises more readily; corrosion in this context is oxidation of the metal
- b** Al; Al has the lower  $E^\circ$ , so it oxidises more easily
- 12 a** Sn; Cu. Tin has the greater tendency to oxidise, because it has an algebraically lower  $E^\circ$  than Cu. Therefore tin gives up electrons to the external circuit and that makes it the negative electrode. At the positive electrode, copper, the reaction that takes the electrons from the external circuit is
- $$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$
- b** Zn has the greater tendency to oxidise (lose electrons) because it has the lower  $E^\circ$ .
- c** It has a higher voltage, approximately 1.1 V (combining oxidation of Zn with reduction of O<sub>2</sub>) compared with 0.5 V for the tin, copper cell.
- 13** A will corrode more readily than the mild steel, B less readily. Because A was the negative electrode of the cell, it must have been giving up electrons to the external circuit, so oxidation of A occurs more readily than oxidation of mild steel. Conversely with B, the mild steel gives up electrons (oxidises or corrodes) more readily than B.
- 14 a**  $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$   
 $ZnO(s) + CO_2(g) \rightarrow ZnCO_3(s)$   
 $ZnO(s) + H_2O(l) \rightarrow Zn(OH)<sub>2</sub>(s)$   
similar reactions for Pb
- b** Its carbonate and hydroxide are soluble in water so are easily washed away and provide no protection.
- 15** passivating. Its highly negative  $E^\circ$  (comparable to Al) shows that Ti readily oxidises to Ti<sup>2+</sup> which means that it is a reactive metal, so its lack of reactivity must be because it passivates.
- 16 a** at cathode, Cu; at anode, Br<sub>2</sub>;  
 $Cu^{2+} + 2e^- \rightarrow Cu$ ;  $2Br^- \rightarrow Br_2 + 2e^-$   
 $Cu^{2+}(aq) + 2Br^-(aq) \rightarrow Cu(s) + Br_2(aq)$
- b** at cathode, H<sub>2</sub>; at anode, Cl<sub>2</sub>;  
 $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ ;  
 $2Cl^- \rightarrow Cl_2 + 2e^-$   
 $2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$
- c** at cathode, H<sub>2</sub>; at anode O<sub>2</sub>;  
 $2H^+ + 2e^- \rightarrow H_2$ ;  
 $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ ;  
 $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
- d** at cathode: H<sub>2</sub>; at anode: O<sub>2</sub>  
 $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$   
 $4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$   
(these are the alkaline forms of the electrode reactions in (c))  
overall reaction as in (c)
- e** at cathode: H<sub>2</sub>; at anode: O<sub>2</sub>  
 $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$   
 $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$   
overall reaction as in (c)

- 17** cathode; oxygen;  
 $K^+ + e^- \rightarrow K$ ;  $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$   
 $4K^+(l) + 4OH^-(l) \rightarrow 4K(l) + O_2(g) + 2H_2O(g)$
- 18** positive electrode; H<sub>2</sub>; see Answer 16(c)
- 19**  $Cu^{2+} + 2e^- \rightarrow Cu(s)$        $E^\circ = +0.34\text{ V}$   
 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O(l)$        $E^\circ = +1.23\text{ V}$   
When comparing two half reactions the one with the algebraically smaller  $E^\circ$  has the greater tendency to go in the reverse (oxidation) direction, so in this case Cu has the greater tendency to oxidise than water has. With gold  
 $Au^+ + e^- \rightarrow Au(s)$        $E^\circ = +1.69\text{ V}$   
so comparing water with Au, the water reaction has the lower  $E^\circ$  so it has the greater tendency to occur in the oxidation direction. Hence water will be oxidised, not gold.
- 20 a**  $Ag^+ + e^- \rightarrow Ag(s)$ ; the reduction half reaction with the higher  $E^\circ$  has the greater tendency to occur, so silver is reduced in preference to copper; the voltage is not high enough for copper to be reduced.
- b** Both metals would deposit on the electrode together, because the voltage is high enough.
- 21** iodine. The iodine, iodide half reaction has a lower  $E^\circ$  than the bromine, bromide one, so it has the greater tendency to occur in the oxidation direction. That is, iodide will oxidise at a lower voltage than bromide.
- 22** H<sub>2</sub>; Ni; at pH = 0  
 $2H^+ + 2e^- \rightarrow H_2(g)$        $E^\circ = 0$   
 $Ni^{2+} + 2e^- \rightarrow Ni(s)$        $E^\circ = -0.26\text{ V}$   
The hydrogen reaction has the higher  $E^\circ$  so hydrogen forms preferentially. At pH = 7 the non-standard electrode potential for the hydrogen reaction is -0.41 V; the nickel reaction now has the higher  $E^\circ$  so it occurs preferentially; that is, nickel deposits at pH around 7.
- 23** no. The difference in  $E^\circ$  values (1.23 V versus 0.54 V) is too great for a change in concentration to alter which of the two  $E^\circ$ 's is the greater. For O<sub>2</sub> and Cl<sub>2</sub> the difference in  $E^\circ$  values is much smaller (1.23 V versus 1.36 V) and so a change in concentration can alter which of these two  $E^\circ$ 's is the larger.
- 24** Their mistake was to keep the current constant. There is only one factor that affects the rate of electrolysis and that is the current that flows: the greater the current, the greater the rate of electrolysis. If we use a constant voltage, then using bigger electrodes or moving the electrodes closer together increases the current (by increasing the conductivity of the cell) and so increases the rate of electrolysis. Had they used a constant voltage they would have found that the rate of electrolysis increased when they increased the size of the electrodes and when they decreased the spacing between the electrodes.

## Chapter 12

- 1 a** Ni; has the lower  $E^\circ$
- b i** less; copper is a less reactive metal
- ii** less; nickel corrodes more easily if a less reactive metal is attached to it to act as a cathode, in the same way as iron rusts more rapidly when attached to copper or tin
- 2 a** around the edge of the drop because that is where  $O_2$  comes into contact with the  $e^-$ s that are moving through the iron and away from the oxidation site which is under the drop
- 3** The dirt cuts off the supply of  $O_2$  to the iron underneath it (as did the water in the previous question): this facilitates formation of an anodic site there while the exposed areas of the tool are good cathodic sites: hence rusting is speeded up; rust forms on the uncovered part of the tool; pitting occurs under the dirt.
- 4 a** Steel has greater structural strength and so ships made of it can carry heavy loads and withstand rough seas.
- b** Aluminium is much lighter and less corrosive and so more convenient for personal use where structural strength is less of a consideration.
- 5** 0.85 V; zero; disconnect the two metals and measure the voltage between them, but even then the voltage would not be very close to 0.85 V because  $Fe^{2+}$  is not 1.00 mol/L and the oxygen pressure is much less than 100 kPa (that is, conditions are not the standard ones)
- 6** in moist atmospheres (both oxygen and water present); Ni because it is the more active metal
- 7 a** The aluminium would corrode away from the nail and the guttering would come loose. This is because as the iron rusts Al converts  $Fe^{2+}$  back to Fe, itself being oxidised to  $Al^{3+}$  which gets washed away.
- 8** 0.31 V, Fe positive; 1.21 V, Fe positive
- 9**
- 
- $Mg \rightarrow Mg^{2+} + 2e^-$
- $Fe^{2+} + 2e^- \rightarrow Fe$

- 10** Al; because Al is more reactive than Mn (Al has the algebraically lower  $E^\circ$ ); Zn is less reactive than Mn (higher  $E^\circ$ ) so would facilitate oxidation of Mn
- 11** With its negative terminal connected to the car body the battery tends to push electrons into the car body. This prevents the formation of  $Fe^{2+}$  ions (or if any form it converts them back to Fe). If the positive of the battery is connected to the body,

it tends to pull electrons out of the metal and so accelerates corrosion.

- 12** 0.3 g (assuming the product is Fe(II)) or 0.2 g (assuming the product is Fe(III))
- 13** Cd, because Cd has the more negative electrode potential and so more easily reduces any  $Fe^{2+}$  formed; Zn would be better than both because it has a more negative electrode potential than both; nickel plating, being shiny and smooth, looks better while cadmium plating is easier to do than Zn plating (Cd has the higher electrode potential)
- 14** The solubilities of the gases in the figures are for a 100 kPa pressure of each gas above the solution whereas the values in Table 12.1 are for the actual pressures of the gases in the atmosphere: 20 kPa for  $O_2$ , 80 kPa for  $N_2$  and 35 Pa for  $CO_2$ . Solubility of a gas is proportional to pressure.
- 15 a** (all in g/100 mL)  $O_2$ ,  $9.0 \times 10^{-4}$ ;  $N_2$ ,  $1.6 \times 10^{-3}$ ;  $CO_2$ ,  $6.2 \times 10^{-5}$
- b** (all in ppm)  $O_2$ , 9.0;  $N_2$ , 16;  $CO_2$ , 0.62
- 16 b i** 0.139      **ii** 0.117
- iii** 0.089 all in mol/L and all  $\pm 0.001$  (possibly  $\pm 0.002$ )
- c i** 11.8°C
- ii** 28.0°C both  $\pm 0.2^\circ C$  (possibly  $\pm 0.4^\circ C$ )
- d** 0.0345 mol/L; 0.403 mol/L
- e** It increases, because  $H_2S$  reacts with  $OH^-$  and the resulting  $HS^-$  ion is much more soluble than the molecular  $H_2S$ :  
 $H_2S(aq) + OH^-(aq) \rightarrow H_2O(l) + HS^-(aq)$
- 17 b i** 30 g/100 g
- ii** 47.5 g/100 g (both  $\pm 0.5$  g/100 g)
- c i** 66°C
- ii** 26°C (both  $\pm 1^\circ C$ )
- d** 70°C; 15.5 g
- e** Impurities will remain in the solution, because their concentrations are not great enough to exceed their solubilities; hence the crystallised KCl will be significantly purer than the starting material. This process of crystallisation is a common method of purifying substances.
- 18**  $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe(OH)_2(s)$   
 $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$   
 $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$
- 20** The reduction reaction that occurs preferentially is the one with the larger  $E^\circ$ . 0.99 V is larger than  $-0.24$  V so it is reduction of oxygen that occurs, not reduction of  $H^+$ .
- 21 a** The rate of oxidation of iron is increased if there is a good cathodic surface available for reduction of  $O_2$  to  $OH^-$ ; copper in contact with iron is a good cathodic surface for this and so accelerates the corrosion of the iron. Copper itself does not easily corrode because it becomes covered with an impervious layer of mixed hydroxide and carbonate. The asbestos was to insulate the copper from the iron: without good electrical contact copper cannot act as a

cathodic surface for corrosion of iron.

- 22** Copper accelerates the corrosion of iron (previous answer) with the corrosion being worst near the join between the two metals. Paint the pipe either side of the join with a strongly bonding and tough paint or plastic coating, or use a plastic connector between the two metals so that there is no electrical contact.
- 23 a** the more reactive Al reduces  $\text{Ag}^+$  to Ag and so converts  $\text{Ag}_2\text{S}$  back to Ag:  
 $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$ ;  $\text{Ag}_2\text{S} + 2\text{e}^- \rightarrow 2\text{Ag} + \text{S}^{2-}$
- b** so that the reduction occurs uniformly over all the tarnished surface
- c** no, just as long as there is electrical contact between each object and the Al so that the  $\text{e}^-$ s released can flow to the  $\text{Ag}_2\text{S}$
- d** because it does not remove silver from the object as abrasive cleaners do
- 24** Acidify a sample and add silver nitrate solution; a white precipitate or turbidity indicates the presence of chloride.
- 25** use a similar approach to that used for restoring silver in Section 12.18
- 26 a**  $\text{FeCl}_3(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{Fe(OH)}_3(\text{s}) + 3\text{Cl}^-(\text{aq}) + 3\text{H}^+(\text{aq})$
- The released  $\text{H}^+$  and  $\text{Cl}^-$  makes the surface moisture layer on the object quite conducting so that normal corrosion of iron is speeded up (compare with iron objects in sea water). In addition, iron corrodes more rapidly in acid solution (Section 12.13).
- Keeping the object in  $\text{NaOH}$  solution means that  $\text{Fe(OH)}_3$  forms without the solution becoming acidic and so retards corrosion; in addition, formation of  $\text{Fe(OH)}_3$  in alkaline solution creates a protective coating over the iron and prevents  $\text{O}_2$  reaching bare iron. The surface deposit is more likely to be the mixed oxide,  $\text{Fe}_3\text{O}_4$  ( $= \text{Fe}_2\text{O}_3 + \text{FeO}$ ) or hydrated iron(III) oxide,  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  rather than simple  $\text{Fe(OH)}_3$ .
- b**  $\text{Fe(OH)Cl}(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{Fe(OH)}_2(\text{s}) + \text{Cl}^-(\text{aq})$   
 $\text{Fe(OH)}_2 + \text{OH}^- \rightarrow \text{Fe(OH)}_3 + \text{e}^-$ ;  
 $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$   
 $2\text{Fe(OH)}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Fe(OH)}_3(\text{s}) + \text{H}_2(\text{g})$
- 27** Gold is very resistant to oxidation (high  $E^\circ$ ), so the deposits on the gold coin will just be encrustations formed by bacterial action or chemical precipitation; none of the gold will have reacted to form them. Hence dissolving them or chipping them off will not lose any of the gold or any engravings on it.
- 29** See answer to Exercise 26 in Chapter 1.

## Extended response exam-style questions for Option 2

- 1** See Section 11.1, particularly Table 11.1. List the six ions, 2 marks, and *outline* (describe without much detail) leaching and hydrothermal vents (but you

must do more than just name them), 2 marks.

- 2** See Section 11.4 and pp. 100–7 CCPC. Remember that Preliminary Course material is examinable if it relates to HSC course material. *Discuss* in this question means describe with examples. For dependence upon composition, 4 marks and upon heat treatments, 2 marks. For composition good added elements to discuss are carbon (more taken away than added), tungsten, manganese, silicon and chromium (alone at low concentrations and at higher concentrations with nickel). Heat treatments are quenching and annealing.
- 3** See Section 11.3. In this question *evaluate* means make a judgement about how important each person's contribution was and give a reason for it, but make sure you mention what their contributions were. Probably 2 marks each for Davy and Faraday and 1 for Volta.

Volta's contribution to science was the development of a source of direct current that Davy and Faraday and others were able to use to electrolyse substances. While this was important to science generally, it did not contribute very significantly to our understanding of electron-transfer reactions<sup>(1)</sup>.

Davy, using Volta's pile, introduced electrolysis as a way of decomposing compounds and isolating many new elements<sup>(2)</sup>. His contribution to our understanding of electron-transfer reactions was very important, because he brought about many chemical reactions that are electron-transfer ones, though the concept did not exist at that time<sup>(3)</sup>.

Faraday showed that mass changes in electrolysis were related to the quantity of electricity involved<sup>(4)</sup>. When the electron was discovered and the ionic nature of electrolytes was recognised, this relationship was very important in developing full understanding of electron-transfer reactions<sup>(5)</sup>.

Davy and Faraday provided valuable information that later scientists were able to use to develop a full understanding of what became known as electron-transfer reactions.

- 4** See Sections 12.1 to 12.3. In this question *identify* means list the conditions (presence of both oxygen and water, though you could mention one or two conditions that accelerate the rate of rusting), 2 marks. *Explain the chemistry* means that you will have to give equations; a diagram may help. There are 4 marks for this part so give sufficient detail to justify them.

- 5** See Sections 10.3 and 11.8. Remember that Sections 10.2 and 10.3 are also part of this option. *Demonstrate* means show by using examples. There are probably 3 marks for the part you answer best and 2 for the other part, and for these marks you will need to include electrode reactions, not just name the different products. For (a) use dilute and concentrated sodium chloride solution and for

- (b) copper sulfate solution with inert and copper electrodes (though silver nitrate with inert and silver electrodes is equally good).
- 6 This is Experiment 3 from p. 450. Describe the experiment that you performed. To decide on how much detail to give you need to estimate how many marks there are likely to be for the description and how many for the assess *the suitability*—probably 4 for experiment and 3 for the assessment. In describing the experiment make sure you explain how you determined the amount of corrosion on each sample, and include metals and alloys that you could use in the assessment part. Good examples would be mild steel, stainless steel, copper, aluminium, bronze, three metals and two alloys. In assessing suitability, cost as well as chemical and physical properties can be factors.
- 7 See Section 12.20. Two marks for major problems (fragility due to loss of cellulose, saturated with water and salts), and 4 for procedures (store in sea water in the dark until restoration starts, clean carefully to remove silt etc., replace water and salts by soaking in or spraying with increasingly concentrated aqueous solutions of polyethylene glycol, finally air dry, then coat with a wax). For 4 marks in the procedures you need four key pieces of information.
- 8 See Sections 12.9, 12.11 and 12.12. Although the verb is *discuss* there is little more that you can do than *describe* the effect, which was to change our understanding of corrosion at great ocean depths.
- When the wreck of the *Titanic* was discovered in 1985, it was found to be much more corroded than scientists had expected<sup>(1)</sup>. This caused them to revise completely their theory of corrosion at great depths in oceans<sup>(2)</sup>.
- Before the discovery of the wreck of the *Titanic*, scientists had expected that at great ocean depth there would be only limited corrosion, because oxygen concentrations are very low at depths below 1000 m and the temperature was also very low. Both of these factors would slow down the rate of corrosion<sup>(3)</sup>.
- Analysis of rusted samples recovered from the *Titanic* gave evidence that much of the rust had been produced by a bacterial corrosion process. There are certain anaerobic bacteria that obtain their energy by reducing sulfate ions in seawater to sulfide and hydroxide ions<sup>(4)</sup>:
- $$\text{SO}_4^{2-}(\text{aq}) + 5\text{H}_2\text{O(l)} + 8\text{e}^- \rightarrow \text{HS}^-(\text{aq}) + 9\text{OH}^-(\text{aq})$$
- And in the process they oxidise Fe to  $\text{Fe}^{2+}$ , leading to increased deposits of insoluble  $\text{FeS}$  and  $\text{Fe(OH)}_2$ , which were major components of rust from the *Titanic*. The discovery of the wreck of the *Titanic* was of considerable scientific importance, because it showed that there is a significant bacterial contribution to deep ocean rusting which had not been recognised before<sup>(5)</sup>.
- 9 See Sections 11.4 and 12.6. Assess in this question means make a judgement about how important the developments were. For 6 marks you should talk about at least three developments. Because of the vagueness of *other alloys*, you need not confine yourself to ferrous alloys. Some key developments were the removal of sulfur and phosphorus (which made steel brittle) after the 1940s, 1 mark (very important, for example *Titanic* and liberty ships, 1 mark), the ability soon after that to produce steels containing carefully controlled concentrations of many other metals to give steels specific properties for specific purposes, 1 mark, and more recently the development of surface alloys similar to stainless steel, 1 mark. Stainless steel had been developed in the first half of the twentieth century but was not of great importance for shipbuilding (used in equipment and in many fittings but not for hulls because it was too expensive), 1 mark. Non-ferrous alloys such as bronze (propellers) and alloys of aluminium (of some importance to shipbuilding for superstructures and fittings but not for hulls, except in recent years for some quite sizeable catamarans) could also be included.
- 10 See Sections 11.8 and 11.9. The electrode reactions are the same for both salts. *Describe what happens* means say that bubbles of colourless gas form at each electrode. For *explain why*, include the electrode reactions (half-equations) and add them up to show that the net result is electrolysis of water.
- 11 See Section 12.10. *Outline* means describe without too much detail. Briefly describe the four factors, 1 mark each, then compare the concentrations (9 ppm at the surface, less than 2 ppm at great depths).
- 12 See Section 12.12. The following minimum explanation would probably score 3 marks.
- Certain anaerobic bacteria reduce sulfate to sulfide and hydroxide (*give the half reaction*, Equation 12.4) and oxidise iron to  $\text{Fe}^{2+}$  which leads to the formation of  $\text{Fe(OH)}_2$  and  $\text{FeS}$ . These are major constituents of rust under these conditions.
- For full marks you would need to give the other half reaction plus equations for formation of  $\text{FeS}$  and  $\text{Fe(OH)}_2$  or alternatively the overall equation and perhaps name the family of bacteria.
- 13 This is Experiment 5 on p. 450. See Sections 12.1 to 12.3. Describe the experiment you performed, which probably involved using steel nails. Be careful to explain how you compared the relative rates (amounts) of corrosion. You probably did it just by visual observation of the amount of rust formed. However, if you used potassium ferricyanide solution (which produces an intense blue precipitate in the presence of  $\text{Fe}^{2+}$  ions), note that this prevents the formation of rust;  $\text{Fe}^{2+}$  is converted to  $\text{KFeFe(CN)}_6(\text{s})$ , though it does not interfere with the oxidation of iron to  $\text{Fe}^{2+}$ . Testing with this solution at the end of

the experiment is not particularly helpful as virtually all the  $\text{Fe}^{2+}$  will be tied up as rust and so will not be detected. Note that the question says *materials*, plural, so you should have used some other metal as well as steel, for example zinc or magnesium; there is not much point in using copper as it would not show any corrosion in any of the conditions of this experiment. However if you used only steel then just describe the experiment you actually performed.

One suggestion for improving the accuracy would be to wait a longer period before making your observations, say two to three weeks instead of just a few days. Another suggestion could be to weigh the pieces of materials used (nails), before and after they had been allowed corrode and express the mass loss as a percentage. Care would be needed to wash off the rust completely and dry the nails thoroughly (in an oven), and probably you would need to let the experiment stand for more than a week to get a significant mass loss.

- 14 See Section 11.7. You need at least two examples of passivating metals, say Al, Zn, Cr. Cu is not a good example because it is not a particularly active metal in the first place though it does form a protective coating. Two marks for the explanation, 1 for two examples and 1 for an equation. For your equation  $4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)}$  would suffice; alternatively use



- 15 See Sections 12.6 to 12.8. The common methods are painting and sacrificial anodes, though perhaps you could consider the newer methods of surface alloys and pyroaurite paints, though these are perhaps not yet all that common. *Evaluate* means that you have to make a judgement about how effective the methods are and give your reasons. There are 3 marks for each method, so describe it, evaluate it and give a reason for your evaluation.

- 16 This is Experiment 6 on p. 450. See Section 12.13. Three marks for description and 1 for a suggestion for improving the reliability (after explaining what it is). You probably compared the rusting of steel nails in pure water and in an acetic acid, sodium acetate buffer (pH 4 to 5) and compared the amount of rusting by visual observation over several days. This buffer was used to reproduce the approximate pH that could be found in acidic sea water. Using dilute hydrochloric acid would produce an unrealistically low pH or if a sufficiently low concentration was used to produce a pH of about 4, it could easily change as rusting progressed and so invalidate the experiment. For the reliability part of the question:

Reliability means reproducibility, that is, getting the same results when we repeat the experiment. To improve the reproducibility of this experiment we could allow a longer time before making our observation of how much rusting had occurred

so that the difference between the two solutions would be greater and the risk of making a wrong assessment would be less. (*Alternatively we could ensure that the same volume of water and buffer solution was used in any particular experiment and in the solutions for repeat experiments, and use nails from the same batch and clean them until they looked exactly the same.*)

- 17 See Section 12.6, last subsection. The newer methods are surface alloys and pyroaurite paints. For each method, 1 mark for the description and 1 for the assessment of its effectiveness compared with more traditional methods (ordinary paint and sacrificial anodes).
- 18 See Sections 12.14 to 12.19. Because there are 6 marks for this question you need to choose a metal or alloy for which you can provide at least six important facts; silver and iron would probably be the best. A total of 6 marks suggests 2 marks for each of three steps in the procedure (dissolving or chipping off concretions, electrolysis to reduce the metal ions in insoluble corrosion products and to remove residual chloride from fine pores in the object, and coating with a suitable wax or lacquer to prevent further corrosion). There would be 1 mark for describing the step and one for evaluating how effective the step was in the restoration process, perhaps compared to alternative methods.
- 19 See Sections 12.7 and 12.8. Describe, with chemical equations, how galvanising and either a sacrificial anode or an applied voltage works. Probably 2 marks for each, leaving 3 for the evaluation for which a suitable answer would be:

In principle galvanising should be very effective in protecting the hulls of ships from corrosion, but there are problems arising from the large size of ships. It is not possible to coat the completed hull with zinc, either by dipping it in molten zinc or by electrolysing zinc on to it. If the hull is made by welding together sheets of galvanised steel then the welding would vaporise the zinc coating and leave the joins unprotected<sup>(1)</sup>. Galvanising is not a very effective way of protecting the hulls of ships<sup>(2)</sup>, even ignoring its high cost. On the other hand sacrificial electrodes protect hulls very effectively. Several blocks of zinc or magnesium are bolted on to the hull, particularly in corrosion-prone regions such as near the propeller. These get eaten away over a period of years as they do their jobs and need to be replaced, but that becomes part of the normal maintenance of the ship<sup>(3)</sup>.

- 20 See Section 12.18. Make sure you answer all three parts of the question.

Silver sulfide forms as a black deposit on silver coins in shipwrecks, because silver is attacked by the hydrogen sulfide<sup>(1)</sup> that is produced by reduction of sulfate by certain bacteria.



This silver sulfide forms as a tightly bound and impervious layer on the coin and so prevents the bulk of the coin from being converted to sulfide<sup>(3)</sup>. This sulfide layer is of considerable value in protecting the rest of the coin.

This sulfide layer could be removed from salvaged coins by abrasive cleaners, but that would destroy any engravings on the coin. A much better approach is to use electrolysis to convert the silver sulfide back to metallic silver<sup>(4)</sup>. This is done by making the coin the cathode in an electrolytic cell containing dilute hydroxide solution as electrolyte and an inert anode (such as platinum)<sup>(5)</sup>. The cathode reaction is:



In this way the silver is deposited back where it came from and the coin is very closely restored to its original form.

## Revision tests for Option 2

### Test A

- a**
- i**  $E^\ominus$  for Y must be negative
  - ii** yes, because if any of X oxidises to  $X^{2+}$ , Y would react with it and convert it back to metal because Y with the algebraically smaller  $E^\ominus$  oxidises more readily than X does
- b** This is Experiment 2 on p. 450. See Section 11.10. With only 4 marks for describing what is a fairly long experiment, you need to be brief. You need to state all your results fairly precisely, even though the number of marks for it do not seem enough. Although there is only 1 mark for improvements, try to give at least two ways (because it's ways, not way).

**i** We electrolysed solutions of copper sulfate for a measured period of time, using copper electrodes<sup>(1)</sup>. The electrode reactions were:  
at the anode:  $\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2\text{e}^-$   
at the cathode:  $\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)^{(2)}$

We determined the rate of electrolysis by measuring the mass of copper that transferred from the anode to the cathode in the set time period; we did this by measuring the mass of the electrodes before and after electrolysis<sup>(3)</sup>. We performed a series of experiments in which we changed the following factors one at a time while keeping the others constant: applied voltage, surface area of the electrodes, separation between the electrodes and concentration of the copper sulfate solution<sup>(4)</sup>.

**ii** We found that with electrodes of constant surface area, with constant separation and with constant electrolyte concentration, the rate of electrolysis increased as the applied voltage increased. With constant voltage, the rate of electrolysis increased with surface area of the electrodes, with decreasing separation of the electrodes and with increasing concentration of the electrolyte.

**iii** When we compared results from different groups of students, results differed quite significantly; that is, they were not very reproducible. One method of improving the reliability of our experiment would have been to use a longer period of electrolysis, say an hour instead of the twenty minutes we used; that would have given us larger mass differences to measure. Another way would have been to have taken greater care in washing and drying the electrodes after electrolysis, and perhaps to have just used the mass loss of the anode rather than the average change in mass of both electrodes, because we tended to lose some of the deposited copper on the cathode when washing and drying it.

*(Some of the information included here is not to answer the specific question, but to convince the examiner that you actually did the experiment.)*

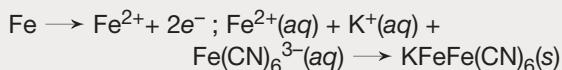
- c** See Section 11.3. Assess means you need to make some judgement about how important the work of each person was and give a reason, but first you need to outline what their contributions were. Assume 2 marks for each person, 1 for the contribution and 1 for its importance and why.

Volta developed the first sources of electric current, the so-called Volta's pile<sup>(1)</sup>. This was of critical importance to our understanding of electrolysis because without a source of current there can be no electrolysis<sup>(2)</sup>.

Davy used Volta's pile to bring about many electrolysis reactions. He demonstrated that electrolysis could be used to decompose many compounds such as water into elements and he used electrolysis to isolate many new elements<sup>(3)</sup>. Davy's work was very important because it introduced electrolysis into chemistry and showed how broad its scope could be<sup>(4)</sup>.

Faraday put electrolysis on a quantitative basis by showing that the mass of a substance formed was proportional to the quantity of electricity that flowed and that the masses of different elements formed were related to their atomic weights<sup>(5)</sup>. His contribution to our understanding was also extremely important in that it showed that there was a connection between mass and electricity, a connection we later discovered was due to electrons<sup>(6)</sup>.

- d**
- i** The blue colour forms because Fe oxidises to  $\text{Fe}^{2+}$ , which then forms a deep blue precipitate with ferricyanide:



The pink colour develops because oxygen is being reduced there to form hydroxide, which sends the pH above 9 and so turns phenolphthalein pink:



Iron tends to oxidise at points of stress in its crystal structure. This means at sharp corners and at points; hence it occurs at both ends of the nail. At other parts of the nail reduction of O<sub>2</sub> occurs; hence the pink colour occurs along the body of the nail.

- ii** Any Fe<sup>2+</sup> that forms is converted back to Fe by Mg so there is no Fe<sup>2+</sup> ion in solution to form a precipitate with ferricyanide:



Electrons are still released at the oxidation site (the anodic site) and so O<sub>2</sub> is still reduced along the body of the nail and so the pink colour still forms.

- iii** Cu in contact with iron is a very good cathodic site and so accelerates the corrosion of iron. More Fe<sup>2+</sup> forms at the anodic sites (and so more blue colour) and more O<sub>2</sub> is reduced all along the copper wire.
- iv** Ions diffuse through aqueous solution much more quickly than through an agar gel so if aqueous solution were used, the ions would quickly mix and we would not see regions of separate colour. Use of an agar gel makes diffusion of ions slower than the corrosion reactions and so we see the separate colours.

- e** See Sections 12.15 and 12.16. In this question *evaluate* means that you need to make some judgement about how efficient or successful the methods are, and give reasons for your judgements. But first you need to explain what leaching is and how electrolysis removes chloride.

Leaching is a process in which unwanted substances are removed from objects by immersing them in clean water and letting the unwanted substance such as sodium chloride diffuse out of the object and into the water. The water is replaced periodically as the salt concentration builds up in it<sup>(1)</sup>. Leaching is moderately effective in removing salt from artefacts recovered from long-submerged shipwrecks. It is not completely effective because the chloride is often present as insoluble hydroxy chlorides such as Fe(OH)Cl and Cu(OH)Cl, and insoluble substances have to dissolve before they can diffuse out of fine pores in objects<sup>(2)</sup>.

Electrolysis can be used to remove chloride from such artefacts by making the artefact the anode. Dissolved chloride will migrate towards the cathode (and so out of the fine pores in the object). In addition insoluble hydroxy chlorides will be decomposed at the cathode:

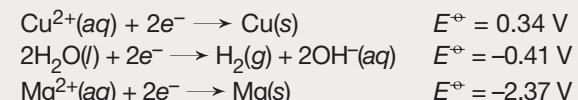


The chloride ion is now in solution and so is free to migrate to the cathode and out of the object. Because it converts the insoluble chloride compound into soluble chloride ion which readily migrates away from the anode, electrolysis is

very effective at removing chloride from artefacts recovered from shipwrecks<sup>(4)</sup>.

### Test B

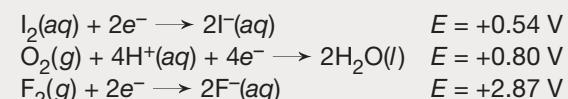
- a i** When comparing two reduction half reactions, the one with the higher electrode potential occurs in preference to the other<sup>(1)</sup>. For the three reduction half reactions involved here, the electrode potentials in neutral solution are:



Hence because +0.34 is greater than -0.41, the first half reaction will occur in preference to the second; that is, copper will be formed at the cathode rather than hydrogen.

When comparing the second and third half reactions, because -0.41 is greater than -2.37, hydrogen will form in preference to magnesium<sup>(2)</sup>.

- ii** A consequence of the first sentence above is that the half reaction with the lower electrode potential has the greater tendency to occur in the oxidation direction<sup>(1)</sup>. For the three half reactions involved here, the electrode potentials in neutral solution are:



Because 0.54 is smaller than 0.80, iodide will be oxidised to iodine in preference to water being oxidised to oxygen. However, comparing the second and third half reactions, water will be oxidised to oxygen in preference to fluoride being oxidised<sup>(2)</sup>.

- b** This is Experiment 4 on p.450. See Sections 12.6 and 12.7. The experiment described below uses the minimum number of coatings that would get full marks. If you used others, include them. Although there are only 3 marks for this description, you do have to give sufficient detail to make it clear what you did and to convince the examiner that you actually did the experiment. In (ii) ways is plural so you need to mention at least two ways; three possibilities are given below.

- i** We placed several nails with different protective coatings on them in individual test tubes containing salt water; the amount of water was such as to cover about two-thirds of the length of the nail. We used three plain steel nails. One was left bare, whereas the other two had been painted; we scratched the paint on one of these to expose some bare metal. In addition we used two galvanised (zinc coated) nails of a similar size; on one of these we scratched some of the galvanising off to expose bare steel. We observed these nails daily over a period of a week, noting by visual inspection the amount of corrosion that had occurred. At the end of the experiment we

- ranked the coatings from the least effective to the most effective in preventing corrosion. The order was no coating, scratched paint, scratched galvanising, then unscratched paint and unscratched galvanising equally effective (on the time scale of our experiment). (*It is probably not necessary to give the results of your experiment; that is, the last sentence is probably not needed.*)
- i** One way of improving the accuracy of the experiment would have been to have made our observations over a longer time period, so that the differences in extent of corrosion would have been more noticeable. Another way would have been to have set up several duplicates of the experiment and averaged the observations from each set. A better way, but a much more difficult one, would have been to have determined the amount of corrosion quantitatively, for example by collecting all the rust from each test tube and nail and analysing for iron, say by atomic absorption spectroscopy.
- c** See Section 11.4 and pp. 100–7 CCPC.  
*Demonstrate* means *show by example*, so in this question you need to give the (qualitative) composition of several steels and state the particular properties those steels have. For 4 marks you should mention four (possibly five) different types of steel. Include carbon steels and point out that the properties of the steel depend upon the percentage carbon in it (hardness increases as carbon content increases). Other good steels to include are tungsten steel (hard at high temperatures), chrome steel (2 to 4% chromium) (hard and shock resistant), silicon steel (good magnetic properties), stainless steel (10 to 20% Cr plus Ni) (stain resistant and capable of taking a high polish).
- d**
- i** See Section 12.2. Give three bits of information: (1) the oxidation half reaction, (2) the reduction half reaction and (3) the migration plus precipitation reaction.
  - ii** Increasing depth should slow down the rate of rusting, because at great depths the concentration of dissolved oxygen is much less than at the surface and oxygen is needed for rusting to occur. In addition the low temperatures at great depths should also slow down the rate of rusting.
  - iii** There were significant amounts of corrosion brought about by certain anaerobic bacteria. These bacteria obtain their energy by reducing sulfate in seawater to sulfide and hydroxide and in doing this they oxidise Fe to  $\text{Fe}^{2+}$ . The  $\text{Fe}^{2+}$  combines with sulfide and hydroxide to form insoluble  $\text{FeS}$  and  $\text{Fe(OH)}_2$ , which are constituents of the rust found on the *Titanic*.
- e** See Sections 12.15 to 12.20. Note that the question refers to *Australian* projects. Three suitable ones from this book are the restoration of iron cannons from the *Endeavour*, restoration of silver coins from Dutch shipwrecks on the west coast and restoration of wood from the *Batavia* (photo in Section 12.20). You could choose any two of these. The question is *compare and contrast* so do not just describe the techniques. To get full marks you need to show that you know how the artefacts were conserved and restored, and point out similarities and differences in the techniques used for the two chosen artefacts. The restoration and conservation techniques for the three projects were as follows. For the cannon: remove encrustations (by chipping), restore corroded iron and remove chloride (electrolysis) and preserve (coat with wax). For the coins: remove encrustations (dissolve in dilute acid, because it does not affect silver), restore corroded silver (electrolysis), preservation (coat with lacquer, but not really necessary if the air is clean). For the timber: remove silt (spray with water and gently brush), remove salt and stabilise the fragile structure of the wood from which much of the cellulose has been removed by bacteria (displace salt water with polyethylene glycol oil), preserve (coat with a polyethylene wax).

## Chapter 13

- 1** C is organic (it burns and contains C and H). B is inorganic (contains no C). C is organic (contains C and Cl and other elements: that means it is organic; halogenated compounds often do not burn).
- 2**
- $$2\text{CH}_3-\text{COOH}(l) + \text{Na}_2\text{CO}_3(aq) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l) + 2\text{Na}^+(aq) + 2\text{CH}_3-\text{COO}^-(aq)$$
- $$2\text{CH}_3-\text{OH}(l) + 2\text{Na}(s) \rightarrow \text{H}_2(g) + 2(\text{CH}_3\text{O}^- \text{Na}^+)(soln)$$
- $$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 + \text{Br}_2 \rightarrow \begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ | \quad | \\ \text{Br} \quad \text{Br} \end{array}$$
- $$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 + \text{Br}_2 + u.v. \rightarrow \begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{Br} \end{array} + \text{HBr}$$
- $$\text{CH}_3-\text{COO}-\text{CH}_2-\text{CH}_3 + \text{Br}_2 + u.v. \rightarrow \begin{array}{c} \text{Br}-\text{CH}_2-\text{COO}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{Br} \end{array} + \text{HBr}$$
- (or  $\text{CH}_3-\text{COO}-\text{CH}_2-\text{CH}_2-\text{Br}$  or other possibilities)
- 3**
- a** In the absence of u.v. light add drops of bromine solution to samples of each. One substance decolorises the bromine: that is 1-hexene; the other substance has no effect: that is hexane.
  - b** Carefully dry samples of both liquids by letting them stand over a small lump of calcium chloride for ten minutes then add a small piece

of sodium to each. In one liquid colourless bubbles of gas form (hydrogen): that is 2-butanol; there is no reaction in the other liquid: that is pentane. See below for equation.

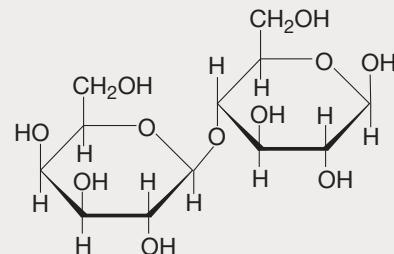
- c** Add drops of sodium carbonate solution to each liquid. One liquid forms bubbles of colourless gas ( $\text{CO}_2$ ): that is propanoic acid; there is no reaction in the other liquid: that is 2-propanol. (Note that both of these liquids would form bubbles of gas with sodium.)  

$$2\text{CH}_3\text{CH}_2\text{COOH}(l) + \text{Na}_2\text{CO}_3(aq) \rightarrow 2\text{CH}_3\text{CH}_2\text{COO}^-(aq) + \text{Na}^+(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$$
- d** Heat each white solid strongly over a Bunsen burner. The one that decomposes (goes black) or burns is glucose. The one unaffected by heating is sodium sulfate.
- 4 a** Add drops of sodium carbonate solution to samples of each liquid. The one that forms bubbles of colourless gas ( $\text{CO}_2$ ) is propanoic acid. Add drops of bromine in hexachloroethane solution to fresh samples of the remaining two liquids: the one that quickly decolorises the bromine is 2-pentene. The other is 1-hexanol. 1-hexanol reacts with bromine if water is present so this test may not give a clear result. In that case dry fresh samples of the two liquids and add small pieces of sodium to each: the one that forms bubbles of colourless gas is 1-hexanol. There is no reaction with 2-pentene.
- Equations: propanoic acid +  $\text{Na}_2\text{CO}_3$ —see Answer 3(c); 2-pentene +  $\text{Br}_2$ —similar to Answer 3(a); 1-hexanol + Na—similar to Answer 3(b).
- 5** P is butanol and Q is pentene; however there is not enough information in either case to determine whether it is the 1- or the 2- compound.
- 6**  $\text{CH}_2\text{O}$ ; yes; molecular formula would be  $(\text{CH}_2\text{O})_x$  or  $\text{C}_x\text{H}_{2x}\text{O}_x$  which is the formula for a carbohydrate
- 7 a i**  $\text{C}_5\text{H}_{10}\text{O}_5$       **ii**  $\text{C}_5\text{H}_{10}\text{O}_4$   
**b i**  $\text{CH}_2\text{O}$       **ii**  $\text{C}_5\text{H}_{10}\text{O}_4$
- 8 a i**  $\text{C}_6\text{H}_8\text{O}_6$       **ii**  $\text{C}_3\text{H}_4\text{O}_3$   
**b** double bond, 4 alcohol groups, ester group  
**c** no; its formula cannot be written as  $\text{C}_x(\text{H}_2\text{O})_y$ . However it is generally considered to be a carbohydrate: see the footnote on page 465.
- 9** In most organic compounds there are only weak intermolecular forces, and so these substances are liquids or soft solids with low melting and boiling points, and they are generally insoluble in water because they are not very polar. However carbohydrates contain many OH groups and so there is extensive hydrogen bonding in these compounds. These strong intermolecular forces mean that the compounds need to be heated to high temperatures in order to break these

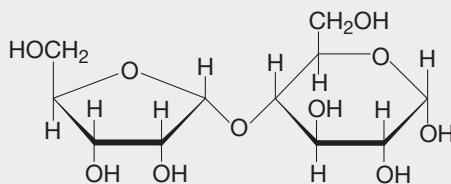
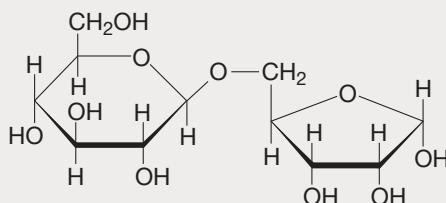
hydrogen bonds and melt the compound and as a result these compounds often decompose before melting. Because extensive hydrogen bonding can form between carbohydrates and water, these compounds are soluble in water.



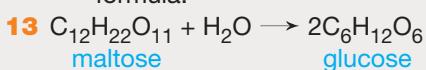
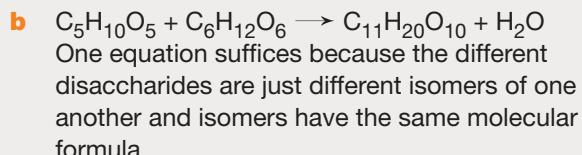
**11**



**12 a**

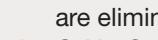


Others are possible: you need to join the carbonyl OH of one molecule to any OH of the other molecule.



**14** fucose,  $\text{C}_6\text{H}_{12}\text{O}_5$ ; lyxose,  $\text{C}_5\text{H}_{10}\text{O}_5$

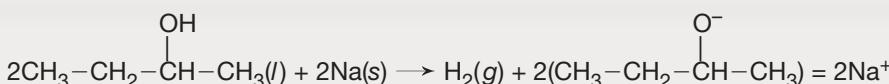
- 15 a**  $\text{C}_6\text{H}_{10}\text{O}_5$  (strictly  $\text{C}_{6000}\text{H}_{10002}\text{O}_{5001}$ )  
**b** not really; the numbers are too large for 1 in 500 or 1 in 5000 to be significant  
**c** One  $\text{H}_2\text{O}$  is eliminated between each pair of glucose molecules: for 1000 glucose molecules this means that 999 water molecules are eliminated.



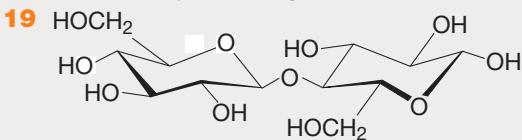
**16**  $4.86 \times 10^4$

**17** 49.3%

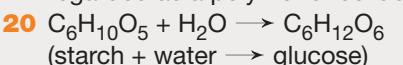
**3 b**



**18** Because each pair of glucose units is joined as in maltose, starch could be made by joining maltose molecules together. For sucrose, no, because there is no carbonyl OH on sucrose to form a normal polysaccharide bond with another sucrose molecule. (This is because sucrose was formed by joining the two carbonyl OHs in glucose and fructose.)



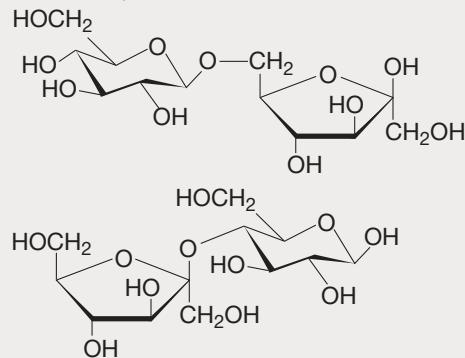
The bonding between glucose molecules is the same in both compounds; in fact cellulose can be regarded as a polymer of cellobiose.



$(C_6H_{10}O_5)_{100} + 99H_2O \rightarrow 100C_6H_{12}O_6$   
No, because it has 599 O atoms and 1198 H atoms on the left and 600 Os and 1200 Os on the right.  
This is because  $C_6H_{10}O_5$  is only an approximate formula for starch; it assumes the loss of one  $H_2O$  per glucose unit whereas there will always be one fewer water molecules lost than glucose molecules joined together.

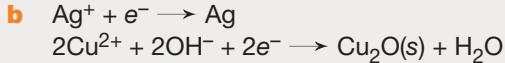
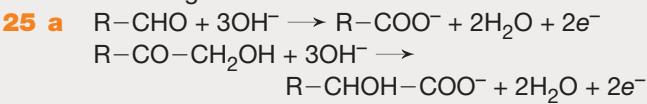
**21** Both are reducing sugars.

**22** yes; by joining the carbonyl OH of one molecule to an ordinary alcohol OH on the other; for example



Others are possible.

**23** In Answer 12(a), both, but you may have drawn a non-reducing one



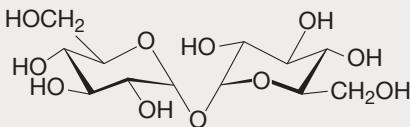
**26** yes; if the two glucose molecules are joined through the carbonyl carbons of both molecules

**27 a i** Q; galactose is a reducing sugar and is not starch  
**ii** S; sucrose is not a reducing sugar and it is not starch  
**iii** P; starch gives a positive test with iodine and is not a reducing sugar  
**b** Heat it with hydrochloric acid for a few minutes, then re-test. It would then give a positive Tollens'

test (both the hydrolysis products, glucose and fructose, are reducing sugars).

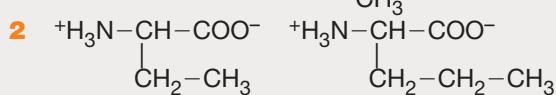
**c** R; the positive iodine test shows starch is still present, while the positive Tollens' test shows that the sample contains a reducing sugar; glucose, the hydrolysis product, is a reducing sugar

**28** two molecules of glucose joined through both carbonyl OHs

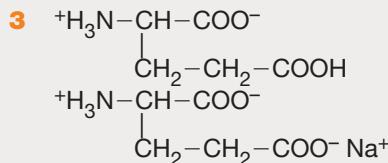


$\alpha\alpha$  linkage shown here:  $\alpha\beta$  and  $\beta\beta$  are also acceptable

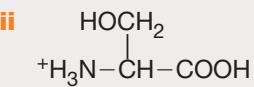
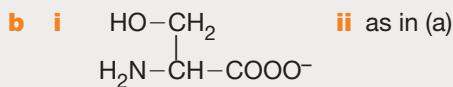
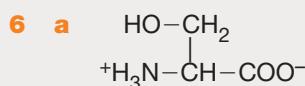
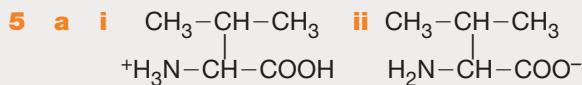
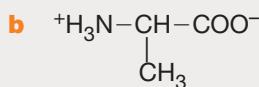
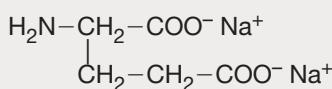
## Chapter 14



(non-ionic forms are acceptable)



because it would be possible to have disodium glutamate by having another  $Na^+$  with the other carboxylic acid group:



- 7** because it can act both as an acid and as a base and so remove added  $\text{H}^+$  or  $\text{OH}^-$ :

$${}^+\text{H}_3\text{N}-\text{CH}_2\text{COO}^- + \text{H}_3\text{O}^+ \rightleftharpoons {}^+\text{H}_3\text{N}-\text{CH}_2-\text{COOH} + \text{H}_2\text{O}$$

$${}^+\text{H}_3\text{N}-\text{CH}_2\text{COO}^- + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{H}_2\text{N}-\text{CH}_2\text{COO}^-$$

**9 a**  $\text{H}_2\text{N}-\text{CH}_2-\text{CO}-\text{HN}-\underset{\substack{| \\ \text{CH}_3-\text{CH}-\text{CH}_3}}{\text{CH}}-\text{COOH}$

**b**  $\text{H}_2\text{N}-\underset{\substack{| \\ \text{CH}_3-\text{CH}-\text{OH}}}{\text{CH}}-\text{CO}-\text{HN}-\underset{\substack{| \\ \text{CH}_3}}{\text{CH}}-\text{COOH}$

**10** yes;  $\text{H}_2\text{N}-\underset{\substack{| \\ \text{CH}_3-\text{CH}-\text{CH}_3}}{\text{CH}}-\text{CO}-\text{HN}-\text{CH}_2-\text{COOH}$

$\text{H}_2\text{N}-\underset{\substack{| \\ \text{CH}_3}}{\text{CH}}-\text{CO}-\text{HN}-\underset{\substack{| \\ \text{CH}_3-\text{CH}-\text{OH}}}{\text{CH}}-\text{COOH}$

**11 a**  $\text{H}_2\text{N}-\underset{\substack{| \\ \text{CH}_3-\text{CH}-\text{CH}_3}}{\text{CH}}-\text{CO}-\text{HN}-\underset{\substack{| \\ \text{CH}_2-\text{OH}}}{\text{CH}}-\text{COOH}$

**12 a** See below

**c** See below

**13 a**  $\text{C}_4\text{H}_9\text{N}_2\text{O}_3^+ + \text{H}_3\text{O}^+ \rightarrow 2\text{C}_2\text{H}_6\text{NO}_2^+$

**c**  $\text{C}_6\text{H}_{13}\text{N}_2\text{O}_4^+ + \text{H}_3\text{O}^+ \rightarrow \text{C}_3\text{H}_8\text{NO}_3^+ + \text{C}_3\text{H}_8\text{NO}_2^+$

**14 a** HOOC-CH<sub>2</sub>      CH<sub>2</sub>-

H<sub>2</sub>N-CH-CO-HN-CH-COOH

**b** HOOC-CH<sub>2</sub>      CH<sub>2</sub>-

|

H<sub>2</sub>N-CH-CO-HN-CH-COOCH<sub>3</sub>

**c** C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>

**d** The dipeptide hydrolyses into the two amino acids and so loses its sweetness.

**15** A is a protein or peptide, B is starch, C is an amino acid

**16** Add ninhydrin to samples of each solution: the one that develops a purple colour contains protein. Add iodine solution to fresh samples of the other three: the one that develops a deep blue solution is starch. Add Tollens' reagent to fresh samples of the remaining two solutions: the one that forms a precipitate of silver (either as a silver mirror or as black particles) contains glucose. The remaining solution is (d). Instead of Tollens' reagent you could have used Benedict's or Fehling's solution in which case (c) would have produced a reddish-brown precipitate of copper(II) oxide.

**17 a i** purple colour      **ii** no reaction  
**iii** no reaction

**b i, ii, iii** no reaction      **ii** deep blue colour

**c i** and **iii** no reaction      **ii** and **iii** no reaction

**d i** purple colour      **ii** and **iii** no reaction

**18 a** Boil gently with hydrochloric acid solution (to hydrolyse sucrose if present), then test with Tollens' reagent; no precipitate of silver will form if both sucrose and glucose are absent from the original sample.

**b** Add silver nitrate and barium chloride solutions to separate samples: if a precipitate formed with  $\text{AgNO}_3$  but not with  $\text{BaCl}_2$  the solution contained chloride but not sulfate or carbonate.

**19** glycine, alanine, leucine

**20** X contains alanine, serine and aspartic acid; Y contains leucine, alanine and lysine

**22 a i**  ${}^+\text{H}_3\text{N}-\text{CH}_2-\text{COOH}$

**ii**  ${}^+\text{H}_3\text{N}-\text{CH}_2-\text{COO}^-$

**iii**  $\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$

**c i**  ${}^+\text{H}_3\text{N}-\underset{\substack{| \\ \text{CH}_2-\text{SH}}}{\text{CH}}-\text{COOH}$

**ii**  $\text{H}_2\text{N}-\underset{\substack{| \\ \text{CH}_2-\text{SH}}}{\text{CH}}-\text{COO}^-$

**iii**  $\text{H}_2\text{N}-\underset{\substack{| \\ \text{CH}_2-\text{SH}}}{\text{CH}}-\text{COO}^-$

**23 a i** All three migrate towards the negative electrode because at pH less than the isoelectric point a species is protonated as in Answer 22(a)(i).

**ii** glycine the greatest, phenylalanine the least; all three have one positive charge so the smallest molecule (ion) travels the fastest and the largest the slowest.

**b i** towards the negative electrode

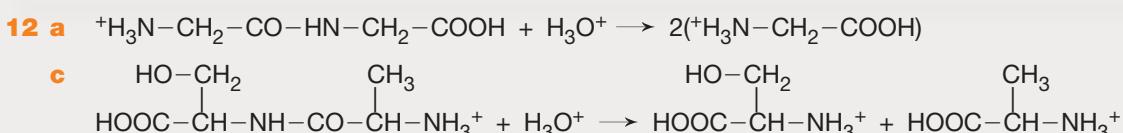
**ii** does not migrate at all

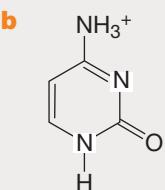
**iii** and **iv** towards the positive electrode

**c** The distance travelled at pH 11 would be greater than at pH 8, because at pH 11 aspartic acid has two negative charges on the ion compared with one at pH 8.

**24 a** cysteine, because the experiment shows that the isoelectric point is 5.0.

**26 a** They contain ammonia-like groups such as  $-\text{NH}_2$ . (The  $=\text{N}-$  are extremely weak as bases as are the NHs beside C=O groups: the latter are amides which are neutral.)

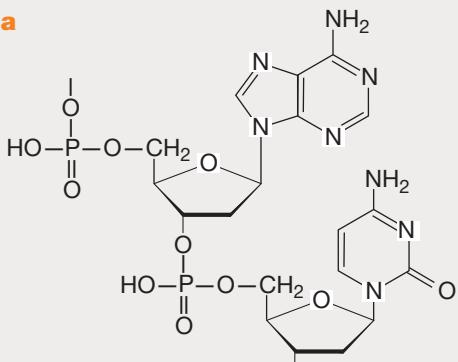




- 27 a A, C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>; C, C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>O; G, C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>O; T, C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>

b for the nucleotides incorporating:  
adenine, C<sub>10</sub>H<sub>12</sub>O<sub>5</sub>N<sub>5</sub>P; cytosine, C<sub>9</sub>H<sub>12</sub>O<sub>6</sub>N<sub>3</sub>P;  
guanine, C<sub>10</sub>H<sub>12</sub>O<sub>6</sub>N<sub>5</sub>P; thymine, C<sub>10</sub>H<sub>13</sub>O<sub>7</sub>N<sub>2</sub>P  
To get an approximate empirical formula for DNA, average these four formulae and round to the nearest integer: C<sub>10</sub>H<sub>12</sub>O<sub>6</sub>N<sub>4</sub>P

- 28 a



- 30 6; deoxyribose, phosphoric acid, adenine, cytosine, guanine, thymine

- 31 -P-D-P-D-P-D-P-D-P-
- |   |   |   |   |
|---|---|---|---|
| + | C | G | A |
|---|---|---|---|

- 32 1.15 × 10<sup>-8</sup> (4<sup>30</sup>)

- 34 contamination of the sample, or mixing up or deliberate swapping of samples from different people: the actual analysis if competently done has virtually no chance of identifying the wrong person

- 35 The blood on suspect 1's clothes was his own and he did not have sex with the victim. Both suspects 2 and 3 had sex with the victim. The blood on suspect 2's clothes was the victim's.

- 36 female; the profile is: 14, 15; 17, 18; 23, 24; 13, 13; 25, 30; 15, 19; 11, 11; 10, 11. (Use the two 100 to 340 scales to align the peaks in the sample with peaks in the same colour zone in the standard.)

## Chapter 15

- 1 The pesticide was mainly heptachlor with small amounts of aldrin and dieldrin. This was determined by measuring the retention times of the known compounds in Figure 15.3 and comparing those of the unknowns with them.
- 2 Cocaine is present.
- 3 Sucrose and one other substance had been added to it. That sucrose had been added was determined by comparing the height of the sucrose peak relative to the fructose and glucose peaks in the standard

and suspect chromatograms. The other substance added had a retention time of thirty-five minutes but insufficient information is available to identify it.

- 4 methanoic acid, 5.0% and butanoic acid, 3.1%. Percentages are only approximate, because they are based on peak areas alone, assuming that the sensitivity of the instrument is the same for all compounds, which is not strictly correct. Normally the chromatograph is calibrated for each substance.

- 5 just one isotope for argon but four for krypton (at masses 82, 83, 84, 86)

- 6 a 36.5

b Because there is no molecule with a relative molecular mass of 36.5. This mass is the weighted average of the different isotopic forms of the molecule. Of the four peaks the one at the lowest mass must be the lightest Cl<sup>+</sup> isotope, that is 35. The highest mass must be the HCl<sup>+</sup> peak with the highest Cl isotope, meaning that the mass 38 peak indicates a chlorine-37 isotope. If there are two Cl isotopes of masses 35 and 37, then we would expect four peaks—at masses 35 and 37 for Cl<sup>+</sup> and at 36 and 38 for HCl<sup>+</sup>. This is what is observed.

The ratio of peak heights of 35 to 37 should equal that for 36 to 38 (same isotopic ratio in Cl<sup>+</sup> and in HCl<sup>+</sup>). Both of these ratios are 3:1 so the abundances are 75% <sup>35</sup>Cl and 25% <sup>37</sup>Cl. The average molecular weight of HCl will therefore be  $0.75 \times 35 + 0.25 \times 37 = 36.5$ .

- c yes; we would expect peaks corresponding to <sup>35</sup>Cl<sup>35</sup>Cl, <sup>35</sup>Cl<sup>37</sup>Cl and <sup>37</sup>Cl<sup>37</sup>Cl; 35 and 37

- 8 a 1-heptene

- b hexane

- 9 all three have approximate molecular weights of 28; yes, because the more accurate molecular weights of these compounds are: CO, 28.01; N<sub>2</sub>, 28.02; C<sub>2</sub>H<sub>4</sub>, 28.06

- 10 A is Cd; B contains Na and Li (Calculate the wavelengths in the given spectra and compare them with values listed in Figures 6.12 and 15.15.) (Na has a line at 330 nm which is off the scale in Figure 6.12)

- 11 a Cr, Sr b Cd, Cu

- 12 Na and Sr impurities are present

- 13 A: V and Fe; B: Fe, Co, Cr

- 14 Neither knife is the murder weapon. Comparing the murder weapon with each suspect's knife in turn, there are lines in the murder knife spectrum that are not in the spectrum from the suspect's knife (309, 318, 411 for knife 1 and 344, 345, 350, 387, 407 for knife 2).

- 15 murder weapon: V, Ni, Co, W

knife from suspect 1: Ni, Co, W

knife from suspect 2: V, Ni, Cr

## Extended response exam-style questions for Option 3

- 1 See Section 13.2. *Discuss* means talk about the issue and give arguments for and against, though it does not require you to make a judgement in favour of one argument over another.

It is often argued that there is a greater need for accuracy in forensic chemistry than in other branches of chemistry, because inaccurate forensic evidence could convict an innocent person and take away their freedom<sup>(1)</sup>, or because faulty analyses could result in a person or company having to pay massive fines or suffer large commercial losses by having to withdraw an allegedly faulty product from the market. These are very legitimate reasons for accuracy<sup>(2)</sup>. However the need for accuracy is strong in all branches of chemistry; inaccurate measurements can mislead other chemists, faulty research results can send colleagues on time-consuming and expensive tasks trying to establish the correctness of the reported findings, while inaccurate quality control analysis can cause manufacturers great expense in having to reprocess or throw away products that actually meet specifications. Accuracy must be a prime goal of all chemists<sup>(3)</sup>.

- 2 See Sections 6.17 and 15.10 to 15.12. *Explain* in this question means *describe*. In outline: electrons in atoms are excited into higher energy levels, they fall back to the ground state and in so doing emit energy in the form of radiation. This is broken into its different wavelength components that then fall onto different locations on a focusing screen, for example in a hand spectroscope, and are observed visually as a series of bright lines on a black background (draw a diagram). Alternatively the separated wavelengths can fall onto a photographic plate or electronic detector and be observed as a photograph or on a computer screen, 2 marks plus 1 for a diagram. The lines occur at different wavelengths because in the one element different electrons get excited into different energy levels and in different elements the energy levels are different, 1 mark.

- 3 See Section 14.13. Note *composition* in the question, so state that DNA (give its full name at least once) is a compound made from the elements, C, H, O, N and P, 1 mark. There are 5 marks for *structure* so a fair amount of detail is required. DNA is a polymer (molecular weight of the order of a billion) containing alternate phosphate and deoxyribose groups with one of four bases attached to the ribose, 1 mark. Draw a schematic structure such as Figure 14.10(a), 1 mark, and give the full structure of one nucleotide, 1 mark. Explain the double helix structure, 1 mark, with hydrogen bonding between the two separate strands, 1 mark, with adenine joined to thymine and cytosine joined to guanine.

- 4 See Section 13.11. This question includes Experiment 2 on p. 539. For explaining the difference (sugars that are easily oxidised; they contain –CHO or –CO–CH<sub>2</sub>OH in the open-chain form), 2 marks, and for the test (including one equation or at least formulae of oxidised and reduced forms of the sugar and the test reagent), 3 marks.
- 5 See Section 13.2. *Discuss ethical issues* means describe what the issues are and indicate how significant and/or important they are. For 5 marks describing three issues and commenting about them should score full marks.
- 6 See Sections 15.12 and 15.13. *Evaluate* in this question means make a judgement about how useful the technique is. But first you need to explain briefly what the technique is (show the examiner you know what you are talking about).

Atomic emission spectroscopy is a technique in which a sample is converted to atoms, electrons in the atoms are excited into higher energy levels, then as these electrons return to the ground state and emit the released energy as radiation<sup>(1)</sup>, this radiation is separated into its different wavelengths and the wavelengths and intensities of the emission recorded<sup>(2)</sup>.

Atomic emission spectroscopy is extremely useful to forensic scientists because it can analyse very small samples and determine the elements that are present in the sample and do this quantitatively without one element interfering with the determination of another<sup>(3)</sup>. It can be used to characterise soil samples or paint from a suspected artwork forgery, or to check for suspected contaminants in fertiliser or other products or to simultaneously monitor several metal ions in water supplies<sup>(4)</sup>. One limitation is that atomic emission spectroscopy can only determine the elements present in a sample; it gives no information about which compounds are in the sample (because it decomposes compounds in making its measurements)<sup>(5)</sup>.

- 7 See Section 13.7. Draw structures of each molecule, 2 marks, then comment on similarities and differences. Similarities: they are both carbohydrates, both have a ring structure, both are reducing sugars, 1 mark. Differences: glucose has six C atoms, deoxyribose has five, deoxyribose has a smaller proportion of O atoms than glucose, and glucose has a six-membered ring, deoxyribose, a five-membered one, 1 mark. Not all these similarities and differences are required for the marks.
- 8 See Section 13.5. In this question *identify* means name or list, while *assess* means make a judgement (with a reason) about how useful the technique is. Assume 2 marks for *identify* and 2 for *assess*.

If a sample of soil cannot be identified from its overall appearance, texture and colour, or if the sample is too small for this, then the soil will

generally be identified by determining which of the less common elements, such as Mo, Mn, Zn, Cu or B<sup>(1)</sup>, are present in it and at what concentrations<sup>(2)</sup>.

Atomic emission spectroscopy is ideally suited to this purpose<sup>(3)</sup> because it can handle small samples, it allows several elements to be determined simultaneously and it just gives the total concentration of each element, regardless of the compound it is in<sup>(4)</sup>.

- 9 See Section 14.10 and Table 14.1. First explain what the isoelectric point is, then explain how the named groups would affect it.

The isoelectric point of an amino acid is the pH at which the molecule is neutral<sup>(1)</sup>. For example the isoelectric point of glycine is the pH at which it has the structure

$\text{H}_3\text{N}-\text{CH}_2-\text{COO}^-$ . At lower pH it will be positively charged,  $\text{H}_3\text{N}-\text{CH}_2-\text{COOH}$ , while at higher pH it will be negative,  $\text{H}_2\text{N}-\text{CH}_2-\text{COO}^-$ <sup>(2)</sup>.

If an extra  $-\text{NH}_2$  group is in the molecule, as in lysine, that group will have to be present as  $-\text{NH}_2$  and not as  $-\text{NH}_3^+$  for the overall molecule to be neutral; a higher pH (a more alkaline solution) is needed to stop that  $-\text{NH}_2$  group from protonating, so the isoelectric point will be higher<sup>(3)</sup>. If an extra  $-\text{COOH}$  group is present, as in aspartic acid, that group will have to be present as  $-\text{COOH}$  and not as  $-\text{COO}^-$  for the molecule to be neutral; a lower pH (more acidic solution) is needed to stop  $-\text{COOH}$  ionising to  $-\text{COO}^-$  and so the isoelectric point will be lower<sup>(4)</sup>.

- 10 See Section 14.17. Summarise means describe briefly. Just give the four uses listed in that section.

- 11 This is Experiment 4 on p. 539. See Sections 14.8 and 14.9. Assume 4 marks for the description and 2 for describing the principle. You probably used paper chromatography to separate food dyes from Smarties or coloured inks from felt-tipped pens. Describe the experiment you actually performed and draw a diagram of the set-up you used (be careful to show the solvent level below the drops of mixture on the paper) and of the final chromatograph. In explaining the principle of the separation make sure you mention both the differing solubilities in the mobile phase and the differing strengths of attachment to the paper.

- 12 See Section 15.14. In this question discuss means list some developments and show how they have led to improved forensic outcomes. In doing this remember that forensic investigations apply to more than just criminal trials; they are also concerned with monitoring the environment for pollutants, checking products to see that they comply with their stated claims and with any legal requirements, and monitoring sportspeople to check on prohibited drug use. Good examples of developments in analytical chemistry would be the introduction of atomic absorption spectroscopy, the development of

HPLC, the coupling of gas chromatography to mass spectrometry and the development of DNA analysis. Examples could be the ability to monitor mercury in fish (mercury is dangerous to people at quite low concentrations), or dioxins in air (dioxins are extremely poisonous), to detect anabolic steroids in sportspeople and to use DNA to identify the source of biological samples at crime scenes.

- 13 See Sections 15.5 and 15.6. Evaluate means make a judgement on how useful it is. But first summarise briefly what the technique is.

Mass spectrometry is a technique in which a substance is bombarded with electrons to produce positive ions, which are then sorted according to mass and a graph of ion intensity versus mass is produced; this is called a mass spectrum<sup>(1)</sup>. Because the ion initially formed readily breaks up into a large number of smaller ions, the mass spectrum of a compound comprises a series of different lines (called a cracking pattern). Because of this, mass spectrometry is very useful for identifying compounds (by comparing the mass spectrum of unknowns with standard spectra of known compounds)<sup>(2)</sup>. However it is only moderately useful for forensic investigations<sup>(3)</sup>. It can identify pure compounds in very small quantities, but generally forensic samples are mixtures and mass spectrometry is not particularly good at identifying compounds present in mixtures (because of the complexity of several individual cracking patterns being mixed together)<sup>(4)</sup>. When it is coupled with gas chromatography, mass spectrometry is very useful for forensic science, because the chromatograph separates the mixture into individual compounds and then the mass spectrometer identifies them as they emerge from the column<sup>(5)</sup>.

- 14 See Section 13.9. In this question identify means name and explain means point out their differences and is best done by using chemical structures. The differences: cellulose has  $\beta$  linkages between glucose units while starch and glycogen have  $\alpha$  ones (draw structures or partial structures to show what this means), cellulose and one form of starch (amylose) have unbranched chains while glycogen and the other form of starch (amylopectin) have branched chains (show what this means by schematic drawings such as Figure 13.9(b)).

- 15 See Sections 14.15 to 14.17. The marks could be split 2 and 2 or 3 and 1 for identification and why ... extremely accurate. It would be safest to answer on the basis of 3 plus 2. Just saying because each person's DNA is unique would not get 2 marks: some detail is needed.

Although most of the genetic coding parts of DNA are similar in all people, the non-coding sequences, called introns, differ from one person to another, so a person's DNA is unique<sup>(1)</sup>. DNA analysis for forensic purposes focuses on the intron region; it

measures the length of particular intron sequences (in terms of the number of short tandem repeats)<sup>(2)</sup> and compares these lengths in the unidentified sample with those in samples from known people. When all the lengths match, the person from whom the unidentified sample came is determined<sup>(3)</sup>.

By measuring the lengths in nine different intron regions and requiring that all the measured lengths in the unknown and known samples match, it can be shown that there is less than one chance in ten billion of a coincidental match, and so there is no chance of a false identification<sup>(4)</sup>. Because of the PCR amplification used in DNA analysis, clear results can be obtained from extremely small samples. These two reasons are the basis for the extreme accuracy of using DNA for identifying the person from whom a biological sample came<sup>(5)</sup>.

- 16** See Sections 6.2 and 15.2. In this question *outline* means describe without too much detail, and *assess* means make a judgement about how useful it is and how serious are its limitations. Assume 4 marks for *outline* and 2 for *assess*. Note that the question is *outline the operating principles*, so concentrate on them rather than details of the instrument.

The separation is based upon the different solubilities of compounds in the stationary phase (liquid adsorbed on the walls of a capillary column or on small solid particles in packed columns) and on their volatility back into the gas phase.

GLC is very useful for forensic purposes because it can analyse very small samples, the samples can be mixtures, and GLC can detect small concentrations of impurities in substances (give examples), 1 mark. It does have some limitations: samples must be able to be vaporised at operating temperatures, and for identification of compounds, pure samples of all likely compounds in the mixture must be available (unless the GC is coupled to a mass spectrometer which can identify compounds as they emerge from a GC). These limitations restrict the usefulness of GLC for forensic purposes, but not too severely, 1 mark.

- 17** See Sections 1.12 and 14.4. Exam questions do not have to be confined to just the one module or option. *Compare and contrast* means that you need to point out similarities and differences. Draw structures, 1 mark each, and mention similarities (both are non-branched polymers, they both use the peptide (amide) linkage), 1 mark, and differences (nylon basically uses just the one monomer unit while a protein uses up to twenty-three different monomers (amino acids), 1 mark.

- 18** See Section 13.6, particularly Table 13.1. In this question *assess the reliability* means comment on the possibility of getting a false result; that is, of a different class of compound giving a positive result. Assume 3 marks for each test, 1 for describing it, 1 for an equation and 1 for an assessment. The best

tests to choose would be two of the carbonate test for carboxylic acids, the sodium test for alcohols or the bromine test for alkenes. The carbonate test is extremely reliable; no other compounds (that we are dealing with) react that way and the test is easy to perform. The sodium test is quite reliable, provided the carbonate test has been done first (because carboxylic acids react the same way); however the need for great care in drying the sample first does reduce the reliability of the test (water gives the same reaction). The bromine test is very reliable if a non-aqueous solvent is used, though the test should be done in subdued light to avoid the reaction of alkanes with bromine in the presence of u.v. light. Testing with aqueous bromine is less reliable, because the decolorisation is less easily observed and because many alcohols also decolorise aqueous bromine.

- 19** See Section 13.8. Define the two terms, 1 mark each, then write an equation showing glucose plus fructose undergoing a condensation reaction (elimination of a water molecule), 1 mark, to form sucrose (give its structure), 1 mark.
- 20** See Section 14.18. In this question *justify* means give arguments to support the establishment of DNA data banks (but explain what they are first), and *discuss* means comment on how important and/or valid the issues are and how they should be accommodated.

A DNA data bank is a collection of DNA profiles (lengths of particular segments in the intron region), mainly from identified people, but also from the scenes of unsolved crimes<sup>(1)</sup>. The reasons for establishing a DNA data bank are that it allows police to compare DNA samples from crime scenes with profiles in the bank and possibly identify the culprit of the crime or to eliminate suspects if the DNA profiles do not match or to determine that the same culprit committed two or more unsolved crimes<sup>(2)</sup>. Police argue that such data banks are very strong weapons in their fight against crime<sup>(3)</sup>.

The main ethical issues are the matters of civil liberties and privacy: should convicted people or suspects be forced to provide samples for such a data bank (currently they are the only people who have to), and is the collection of a DNA profile an invasion of privacy?<sup>(4)</sup> The arguments are similar to the ones used decades ago to oppose data banks of fingerprints, and since collecting DNA profiles is no more invasive of privacy than collecting fingerprints, the argument would seem to be already lost, particularly as authorities have accommodated it by confining compulsory collection to people convicted of crimes<sup>(5)</sup>.

These civil liberties and privacy issues were also accommodated by abandoning earlier suggestions of establishing data banks of actual DNA samples, because such samples could provide information

about genetic disorders that could be used by employers or insurance companies to disadvantage people who had these disorders. The DNA profiles stored in DNA data banks in Australia provide absolutely no genetic information.

Overall these arguments show that the establishment of DNA data banks of this type is justified<sup>(6)</sup>.

## Revision tests for Option 3

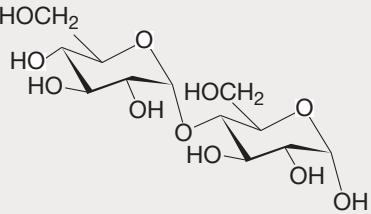
### Test A

a See Sections 15.4 and 15.5.

- i Use a diagram with your description.
- ii Include the term, cracking pattern.

b i P contains galactose and glucose; Q contains only glucose.

ii The disaccharide consisted of two glucose molecules joined together. The fact that Q is a reducing sugar means that the carbonyl OH of one glucose unit is not involved in forming the disaccharide. A possible structure is:



Other structures are possible with the left-hand glucose molecule joined to one of the three other ordinary alcohol OHs of the right-hand molecule (but not to the carbonyl OH).

c This is Experiment 6 on p. 539. See Section 14.10. Describe the actual experiment you performed, and if you separated a mixture of colourless substances such as amino acids, mention how you made your spots or bands visible. Methods of improving the separation could be using a higher voltage to have the compounds travel greater distances and so increase the separation, use a different buffer solution to change the charge on one or more ions, and change from paper (if you used paper) to a gel or use a different gel.

d See Sections 14.4 and 14.5.

- i Demonstrate means show by using an example. Give the structure of a dipeptide and mark the peptide bond. For a polypeptide either draw an open-ended structure with at least three amino acids in it or draw a structure like the one just before the start of Section 14.5.
- ii Here identify means state or describe the differences.

Proteins are polypeptides. In hydrolysing proteins a particular enzyme breaks the peptide bond adjacent to one particular amino acid, so the products of hydrolysis by enzymes will be a mixture of polypeptides; for example a

particular enzyme may break the bond adjacent to lysine, so it will break the protein into short polypeptides, each starting with lysine<sup>(1)</sup>.

Strong acids generally break all the peptide bonds and so the product will be a mixture of amino acids; under carefully controlled conditions, acid hydrolysis can produce a mixture of polypeptides but the bond breaking will be random and so there will be no particular pattern in the polypeptides formed<sup>(2)</sup>.

- e See Sections 15.2 and 15.3. Outline means describe without too much detail (but you must explain how each technique actually separates components of mixtures—that's what *basic principles* means). In this question evaluate means make a judgement about how useful or how effective the techniques are in forensic investigations, with some mention of what their roles are (that is, what they are used for), preferably with a couple of examples (such as pesticide residues in food, prohibited drugs in athletes, dioxins in air or carcinogens in water, all at sub-ppm concentrations). A reasonable mark distribution would be 2 marks for each description and 2 marks for the evaluation with reasons for it. For evaluation: both are extremely valuable, because they can analyse very small samples, they work well on mixtures and they can analyse for complex organic substances that forensic chemists are often concerned with.

### Test B

a See Sections 15.1 and 13.1.

- i Distinguish between means describe the difference between.

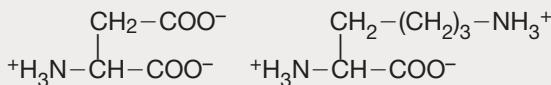
ii Non-destructive testing requires techniques beyond the scope of this book. The constraints that unobtrusive destructive testing places upon forensic scientists are that they must work with extremely small samples (and hence need to use very sensitive instruments) and that they may not be allowed to take samples from the most useful locations. To discuss these constraints, use an example.

b See Sections 13.7 to 13.9. Demonstrate means show by example. Good examples to use here are glucose, maltose and starch (though sucrose and cellulose are equally acceptable). For full marks you need to give structures of the compounds you use.

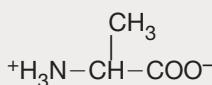
c See Sections 14.8 to 14.11.

- i Alanine is not very polar whereas aspartic acid and lysine are strongly polar. Hence alanine moves rapidly in chromatography (using a polar stationary phase and non-polar mobile phase), whereas the other two move slowly and at similar rates (they tend to stay attached to the polar stationary phase).

- ii because at pH 6.0 aspartic acid is negatively charged while lysine is positively charged



- iii because pH 6.0 corresponds to its isoelectric point, meaning that it is a neutral species (zwitterion):



- d i This is Experiment 7 from p. 539. See Section 6.14. Note the need to clean the wire thoroughly before doing the test.
- ii See Section 15.12, last subsection.

When elements are heated to very high temperatures in flames, electrons in the atoms are excited into higher energy levels and then fall back to the ground state and emit the extra energy as radiation; this radiation constitutes the emission spectrum of the element. For some elements there is one particular electron transition that occurs far more readily than any other. In such cases the flame in which the excited atoms are produced takes on the colour of this transition. Elements for which this is the case and which therefore produce distinctive flame colours include Na, K, Li, Ba, Ca, Sr and Cu.

- e See Sections 14.15 to 14.17. In this question assess means make a judgement about how useful and how reliable DNA analysis is, but because this is an exam, you need to state very briefly what DNA analysis is (to convince the examiner you know what you are talking about). Assume 2 marks for explaining what DNA analysis is, 2 marks for assessing its usefulness and 2 for its reliability (with reasons in both cases).

In DNA analysis multiple copies are made of selected segments of DNA (using the polymerase chain reaction, PCR) in the non-genetic-coding or intron regions where there are the greatest differences between the DNA from different people<sup>(1)</sup>. These segments are then separated by electrophoresis and their lengths determined. By comparing the lengths of these segments (nine are used in Australia) in a forensic sample and the corresponding segments from known people, the person from whom the forensic sample came can be identified<sup>(2)</sup>.

DNA analysis is extremely useful in forensic investigations, because it can unequivocally identify the person from whom the sample came, and because it is extremely sensitive<sup>(3)</sup> (because of the PCR amplification quite minute samples can give clear results). The one limitation is that it is applicable only to biological samples<sup>(4)</sup>.

DNA analysis is also extremely reliable, meaning that it is virtually impossible for it to identify the

wrong person. This is because with nine segments being amplified and measured there is less than one chance in ten billion of two people producing the same DNA profile<sup>(5)</sup>. In addition contamination of the sample or sloppy laboratory work would show up as an obvious mixture (contamination) or as too many or too few fragments in the analysis or as an inability to identify the person who produced the sample, and not lead to a wrong identification<sup>(6)</sup>.