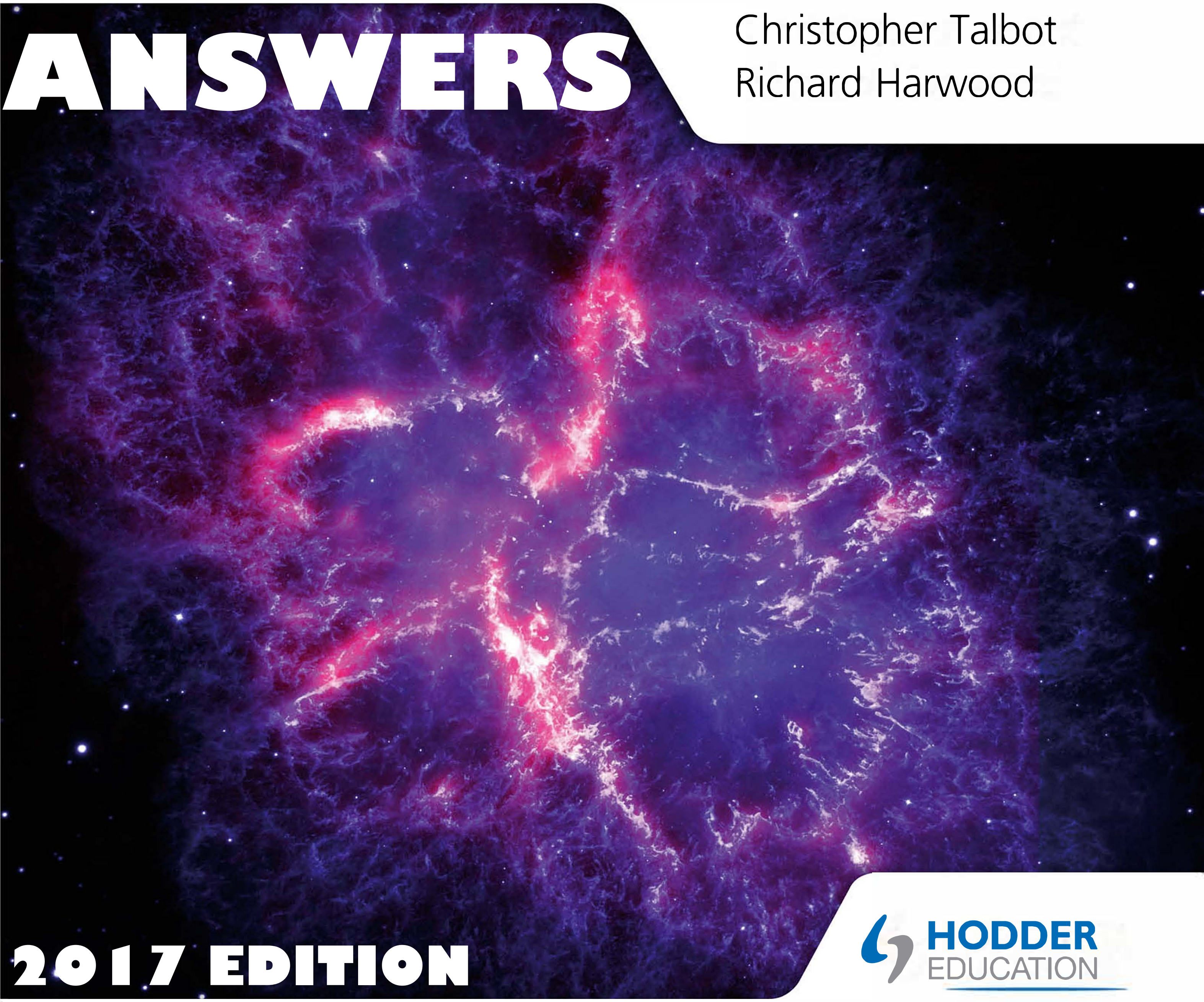
FOR THE
IB DIPLOMA

Chemistry

Study and Revision Guide

ANSWERS

Christopher Talbot
Richard Harwood



2017 EDITION

HODDER
EDUCATION

Answers

Topic 1 Stoichiometric relationships

Quick check questions

1

Substance	Type of substance	Nature of mixture
Smoke	Mixture	Homogeneous
Mercury	Element	
Bronze	Mixture	Homogeneous
Sucrose	Compound	
Dry ice	Compound	
Carbonated (fizzy) drink	Mixture	Homogeneous
Magnesium iodide	Compound	
Distilled water	Compound	
Air	Mixture	Homogeneous
Magnesium and sulfur powders	Mixture	Heterogeneous
Petrol and water	Mixture	Heterogeneous
Chalk and water	Mixture	Homogeneous

2 **Z** is a compound.

3 $3Cl_2(g) + 6NaOH(aq) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$

$MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$

$2Cs(s) + 2H_2O(l) \rightarrow 2CsOH(aq) + H_2(g)$

$3CuO(s) + 2NH_3(g) \rightarrow 3Cu(s) + N_2(g) + 3H_2O(l)$

$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

4 $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$

$Na_2CO_3(s) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l) + 2Na^+(aq)$

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

5 $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$; redox

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$; precipitation (double decomposition)

$O^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l)$; acid-base

6 $238.03\,g\,mol^{-1}$

$146.07\,g\,mol^{-1}$

$207.2\,g\,mol^{-1}$

$132.17\,g\,mol^{-1}$

7 1.204×10^{24}

2.408×10^{23}

8 2723 mg

9 7.64×10^{-23} g

10 0.800 mol; 28.36 g; 4.816×10^{23}

11 $40.00\,g\,mol^{-1}$

12 39.9728

13 1.44 g

14 4.21 g

15 239 g

16 CH, CH_2, PH_3, BH_3, NO_2, Fe_2O_3 and CH

17 $K_2Cr_2O_7$

18 CuS

19 $C_6H_{12}O_6$

20 $ZnSO_4$

21 CH_4O

22 $3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$

CuO is the limiting reagent; NH_3 is present in excess

23 The reaction is reversible, side reactions leading to formation of other products, mechanical losses during purification, insufficient time for reaction to reach completion

24 $0.08\,mol\,dm^{-3}$; $3.20\,g\,dm^{-3}$

25 $0.004\,dm^{-3}$ Al^{3+} and $0.006\,mol\,dm^{-3}$ SO_4^{2-}

26 0.79 g

27 $138\,g\,mol^{-1}$

28 $12.20\,mol\,dm^{-3}$; potassium

29 18%

30 88%

The sodium hydroxide solution absorbs water and carbon dioxide from the air if left to stand for a period of time and is therefore not an accurate standard. The concentration of the solution decreases with time.

31 $0.534\,mol\,dm^{-3}$

32 $25.00\,cm^3$

33 $0.906\,mol\,dm^{-3}$

34 10.6 g; $0.46\,mol\,dm^{-3}$; 10 321 ppm

35 34%; 100%. The electrolytic method is far more efficient.

36 pressure increases; pressure decreases; pressure increases

37 250 kPa

38 $79.0\,cm^3$

39 **a** 11.7 kPa

b $40.4\,g\,mol^{-1}$

40 $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

41 $18\,cm^3$ hydrogen and $64\,cm^3$ nitrogen

42 $6\,dm^3$ ($4.8\,dm^3$ of NO_2 and $1.2\,dm^3$ O_2)

43 $500\,cm^3$ O_2 needed and $1000\,cm^3$ of SO_2 produced

44 $5.675\,dm^3$ and $34.05\,dm^3$

45 45

46 72

47 $64\,g\,mol^{-1}$

48 Gas molecules do not exert attractive forces on each other. Gas molecules are in constant motion in an overall random direction and they frequently collide with each other elastically. The total energy of the molecules in the system remains constant. The average kinetic energy of the molecules is proportional to the absolute temperature of the gas. Any two gases at the same temperature will have molecules with the same average kinetic energy.

49 Gas pressure is the result of collisions between molecules and the walls of their container and is proportional to the number of molecules per unit volume of gas. Decreasing the volume of a given amount of gas increases the number of molecules per unit volume and hence its collision rate. Hence, at constant temperature the pressure of a gas is inversely proportional to its volume.

50 Gases behave ideally at low pressure and high temperature. At high temperature, the gas molecules possess high amounts of kinetic energy and this is greater than the intermolecular forces of attraction. At low pressure, the molecules of gas (in average) are relatively far apart and hence the intermolecular attractive forces are very small.

51 Hydrogen would behave the most ideally because it consists of small non-polar molecules with low London (dispersion) forces of attraction. Hydrogen fluoride would show the greatest deviation from ideal behaviour because although HF molecules are smaller than F_2 molecules, they are very polar and form strong hydrogen bonds. Fluorine molecules have stronger London forces then hydrogen molecules due to the greater number of electrons present.

Topic 2 Atomic structure

Quick check questions

1 a

Sub-atomic particle	Proton (p)	Neutron (n)	Electron (e)
Position within atom	Nucleus	Nucleus	Energy levels (shells)
Relative mass (amu)	1	1	Very small
Relative charge	+1	0	–1

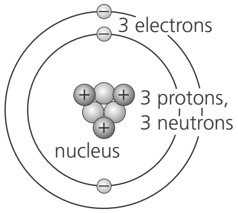
b Protons and neutrons are nucleons.

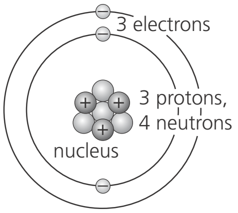
2 8, 8, 8; 8, 8, 9; 8, 8, 10; 8, 10, 8; 8, 2, 9; 16, 16, 16; 16, 15, 20

3 $^{19}_{9}F^-$

4 a Isotopes are atoms of the same element having the same number of protons (atomic number) but different numbers of neutrons (mass or nucleon numbers).

b





5 melting point, boiling point, density and rate of diffusion

6 a ^{121}Sb =55.2% and ^{123}Sb=44.8%

b carbon-12 ($^{12}_{6}C$)

7 a $^{28}_{14}Si^+$, $^{29}_{14}Si^+$, $^{30}_{14}Si^+$

b Relative atomic mass of silicon = (28 × 92.20%) + (29 × 4.70%) + (30 × 3.10%) = 28.11

8 63.5

9 $^{35}Cl^{37}Cl$; $^{35}Cl^{35}Cl$ and $^{37}Cl^{37}Cl$

10 Red – higher wavelength; blue – lower wavelength; red – lower frequency; blue – higher frequency; red – lower energy; blue – higher energy.

11 a $5.08 \times 10^{14}\,s^{-1}$

b 522 nm; green

12 UV-B radiation has shorter wavelength (or higher frequency); hence UV-B radiation / photons has higher energy.

Or UV-A radiation has longer wavelength (or lower frequency); less energy (in its photons or rays).

13 An atom is in the ground state when all the electrons in the atom are in the lowest energy levels. This is the most stable state for atom. An atom is in an excited state when one or more of the electrons in the atom are promoted to higher energy levels. An atom in an excited state rapidly emits photons and the excited electrons transition back to the lower energy levels.

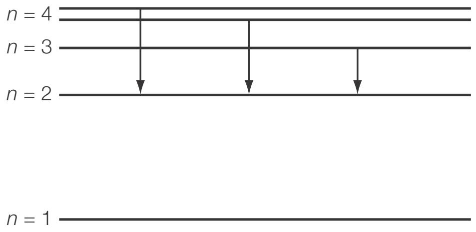
14 a $4.55 \times 10^{-8}\,m$, $4.38 \times 10^{-18}\,J\,mol^{-1}$

b $3.32 \times 10^{-19}\,J$

15 A continuous spectrum is a spectrum that consists of all electromagnetic wavelengths across a range of wavelengths. A line spectrum consists of electromagnetic radiation of specific wavelengths.

16 a Electrons in an atom are quantized and can only exist in specific energy levels. When an atom has absorbed energy corresponding to the difference in energy levels, an electron is excited to the higher energy level. This is an unstable excited state and the electron will undergo a transition to a lower energy level emitting radiation / light / photon of a specific energy corresponding to the difference in the two energy levels. A line spectrum is produced because the electrons in atom have discrete values of energy. Each line represents a specific frequency / wavelength / energy.

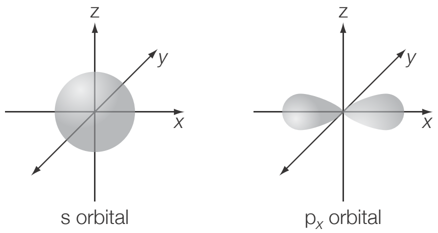
b



17 Discrete or quantized energy levels; the energy gap or difference in energies between quantum shells (main energy levels) decreases; the distance between adjacent quantum shells (main energy levels) becomes smaller as the distance from the nucleus increases; the energy levels converge at high frequency.

18 An orbital is a region of space around the nucleus of an atom in which there is a high probability of finding an electron of a specific energy is a maximum.

19 a

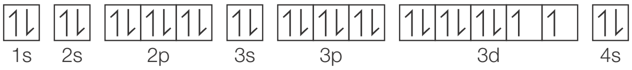


b The 2s and 3s orbitals are like all other s orbitals and can be described as spherically symmetrical. A 3s orbital is larger than a 2s orbital. An electron in a 3s orbital has more energy than an electron in a 2s orbital. The electron density is more diffuse in a 3s orbital.

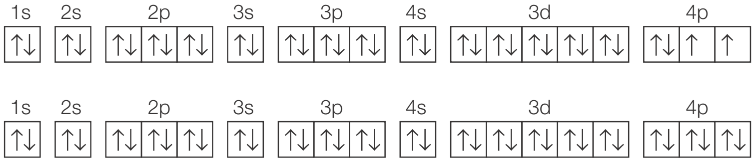
20 50, 3, 6, 10 and 14

21 a The Aufbau principle states that the order of electron filling sub-levels is from the orbital which has the lowest energy. Hund's rule states when electrons are placed in degenerate orbitals (same energy), the electrons must occupy them with parallel spins before they can occupy the orbitals in spin pairs.

b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$



22



$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$

[Ar] $3d^{10}\ 4s^2\ 4p^4$; [Ar] $3d^{10}\ 4s^2\ 4p^6$

23 a Electronic configuration according to Aufbau principle: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$

Electronic configuration determined by experiment: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

b Completely filled 3d orbitals ($3d^{10}$) or half-filled orbital ($3d^5$) are relatively stable compared with partially filled orbitals.

24 Chromium; $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

25 [Ar]$3d^3\ 4s^2$ (or [Ar]$4s^2\ 3d^3$); [Ar]$3d^3$; [Ar]$3d^2$ and [Ar]$3d^1$

Topic 3 Periodicity

Quick check questions

1 They have the same outer shell electron configuration and the same number of valence electrons. These are the electrons that take part in chemical reactions and hence the elements undergo similar reactions.

2 arsenic: 5 valence electrons, p block, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$; group 2 and period 4

calcium: 2 valence electrons, s block, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$; group 15 and period 4

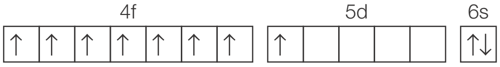
3 period 2, p block, group 15

period 3, p block, group 18

period 3, s block, group 2

period 4, d block, group 5

4 a



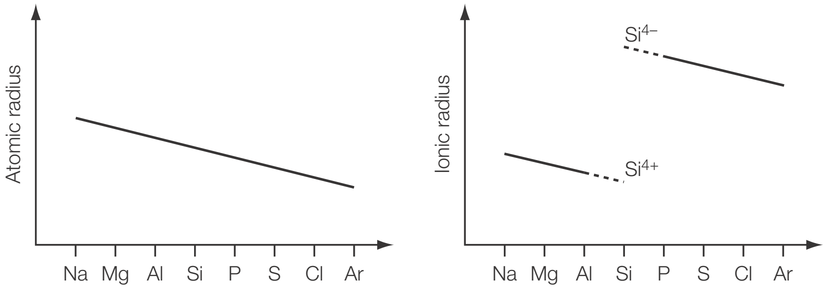
b Good thermal conductor; good electrical conductor; shiny (lustrous); cation formation; basic oxide

5 Periodicity of elements refers to the chemical, physical and atomic properties of the elements that recur periodically when these elements are arranged in increasing order of their proton number (atomic number).

6 The atomic radius decreases across a period due to the increase in effective nuclear charge as the proton number increases in each atom of the element across a period. The nuclear charge increases rapidly but the shielding (electron–electron repulsion) increases more slowly, since the additional electrons enter the same shell (main energy level). Consequently, all electrons are pulled closer to the nucleus.

The size of atoms increases down a group due to the presence of additional electron shells (main energy levels). The nuclear charge increases due to the presence of additional protons, but this effect is more than outweighed by the presence of additional electrons shells with all shells located further away from the nucleus.

7 a



b Atomic radius decreases across the period because of rapidly increasing nuclear charge (due to additional protons) and a small increase in shielding (electron–electron repulsion) since the electrons enter the same shell. All the electrons are more strongly attracted to the nucleus and therefore atomic radii decreases. Cationic radii and anionic radii decrease across the period because of increased nuclear charge and a small increase in shielding (electron–electron repulsion). However, the anionic radius is much larger than the cationic radius because of electron–electron repulsion as additional electrons enter the valence shell.

8 $A1^{3+} < Mg^{2+} < Na^+$

They are isoelectronic ions, having the same electronic configuration of $1s^2\ 2s^2\ 2p^6$. The proton numbers, however, increase from sodium to aluminium. Since the number of electrons in the ions remains constant the radius of the ions decreases with increasing nuclear charge, as all the electrons are more strongly attracted to the nucleus.

$Mg^{2+} < C1^- < S^{2-}$

Mg^{2+} has the electron configuration $1s^2\ 2s^2\ 2p^6$. S^{2-} and Cl^- are isoelectronic ions (with the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$). S^{2-} is large than Mg^{2+} because it has an additional shell of electrons. Cl^- is smaller than S^{2-} due to a higher effective nuclear charge in Cl^-.

9 Magnesium has stronger metallic bonding than sodium because has magnesium has smaller atomic / metallic / ionic radius; hence stronger electrostatic attraction between the nucleus and the delocalized valence electrons. Magnesium has the electron configuration $[Ne]3s^2$, while sodium has the electron configuration $[Ne]3s^1$; hence each sodium atom donates one delocalized electron per atoms, while magnesium donates two.

Silicon has a giant covalent structure / giant three-dimensional network; strong Si–Si covalent bonds extending through the entire structure; many or all these strong bonds need to be overcome during melting. Sulfur, S_8, has a simple molecular / simple covalent structure with weak London (dispersion) forces operating between non-polar molecules. A small amount of thermal energy is needed to overcome them and cause melting.

10 a The first ionization energy is the minimum energy required for the removal of 1 mole of outermost electrons from 1 mole of gaseous atoms in its ground state to form 1 mole of gaseous unipositive cations.

b $K(g) \rightarrow K^+(g) + e^-$

c K: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ and K^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

11 a Evidence for the existence of main levels: highest values (peaks) for noble gases (group 18) / lowest values (troughs) for alkali metals (group 1) / general increase across periods 2 and 3; (evidence for sublevels); decrease in first ionization energy from beryllium to boron / magnesium to aluminium / group 2 to group 13; decrease in first ionization energy from nitrogen to oxygen / phosphorus to sulfur / group 15 to group 16.

b Aluminium has a lower value of first ionization energy compared to magnesium because the electron removed is from the 3p orbital which is of a higher energy level than the 3s orbital from which the valence electron of magnesium is removed from. Since the 3p electron is less strongly held, and experiences more shielding (electron–electrons repulsion) less energy is required to remove it. Sulfur has a lower value of first ionization energy compared to phosphorus because the electron removed is from a spin pair which experiences greater electron–electron repulsion. Since the electron is more easily removed, less energy is required to ionize the atom.

12 a Electronegativity is the ability of an atom / element to attract a pair of electrons towards itself in a covalent bond. Electron affinity is the amount of energy released or absorbed when 1 mole of gaseous atoms accepts 1 mole of electrons to form a mole of gaseous uninegative ions.

b $F(g) + e^- \rightarrow F^-(g)$; $F^-(g) + e^- \rightarrow F^{2-}(g)$

c The first electron affinity is exothermic: the energy released by attraction between the incoming electron and the nucleus is greater than the repulsion between incoming electron and the electrons in the atom (neutral). The second electron affinity is endothermic because of repulsion between the electrons and the negatively charged fluoride ion – this is greater than the electrostatic attraction between the incoming electron and the nucleus.

d Electronegativity decreases because the atomic radii of the halogen atoms increases (additional electron shells) and hence less attraction for the bonding pairs of electrons due to the greater distance and increase in shielding. Electron affinity decreases for the same reason except the attraction is for an incoming valence electron.

13 a An amphoteric oxide reacts with acids and bases.

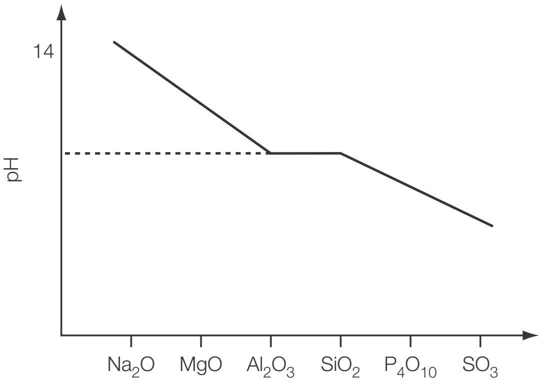
b $Ga_2O_3(s) + 6HCl(aq) \rightarrow 2GaCl_3(aq) + 3H_2O(l)$

$Ga_2O_3(s) + 2KaOH(aq) + 3H_2O(l) \rightarrow 2KGa(OH)_4(aq)$

14 $N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(aq)$;

hydrolysis; no change in oxidation state

15 a



b $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ pH 12 or 14

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ pH 1 or 2

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ pH 1 or 2

16 $2Cs(s) + 2H_2O(l) \rightarrow 2CsOH(aq) + H_2(g)$

$2Cs(s) + F_2(g) \rightarrow 2CsF(s)$

$4Cs(s) + O_2(g) \rightarrow 2Cs_2O(s)$

$Cs_2O(s) + H_2O(l) \rightarrow 2CsOH(aq)$

17 Reactivity increases as a result of an increased ease of ion formation as we move down the group. The effective nuclear charge decreases due to the significant increase of the shielding effect (electron–electron repulsion) over nuclear charge (increase in proton number). Atomic radius increases and the valence electrons are less strongly attracted due to a greater distance from the nucleus, so less energy is required to remove the valence electron resulting in the decrease in the first ionization energy.

18 a $Br_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Br^-(aq)$

b Br_2 is an oxidizing agent; I^- is a reducing agent

c A yellow precipitate of silver(I) iodide will be observed when added to colourless iodide ions.

Topic 4 Chemical bonding and structure

Quick check questions

1 lithium atom (Li) $1s^2\ 2s^2$; fluorine atom (F) $1s^2\ 2s^2\ 2p^5$

The ionic bond in lithium fluoride is formed by the transfer of an electron from a lithium atom to a fluorine atom. When these two elements react, a lithium atom loses an electron from the 2s orbital to form the lithium ion, Li^+. The electronic configuration of the lithium ion is the same as that of the noble gas helium.

$Li\ (1s^22s^1) \rightarrow Li^+\ (1s^2) + e^-$

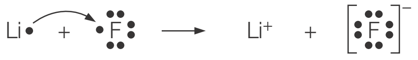
lithium atom lithium ion

The electron that has been lost by a lithium atom is now gained by a fluorine atom to form a fluoride ion, F^-, which has the electronic configuration of the noble gas, neon (Ne).

$F\ (1s^22s^22p^5) + e^- \rightarrow F^-\ (1s^22s^22p^6)$

fluorine atom fluoride ion

The positive lithium ions, Li^+, and the negative fluoride ions, F^-, attract one another because they have opposite charges. It is the electrostatic attraction between two oppositely charged ions that is ionic bonding.



The curved arrow indicates the transfer of an electron from the 2s orbital of lithium atom (Li) to the 2p orbital of the fluorine atom (F). The formula is LiF [$Li^+\ F^-$] which is electrically neutral.

2 Na_2O, MgO, Al_2O_3, Mg_3P_2, NaCl, $MgCl_2$, $AlCl_3$, $CrCl_3$, Cu_2O, Fe_2S_3 and Al_2S_3

3 covalent, ionic, covalent, covalent, covalent, covalent, ionic and ionic

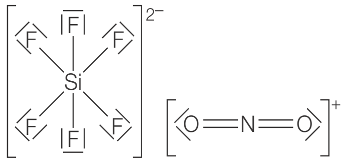
4 sodium sulfate, Na_2SO_4, sodium hydroxide, NaOH, sodium hydrogen sulfate, $NaHSO_4$, sodium carbonate, Na_2CO_3, sodium hydrogencarbonate, $NaHCO_3$, sodium phosphate, Na_3PO_4, magnesium nitrate, $Mg(NO_3)_2$, magnesium phosphate, $Mg_3(PO_4)_2$, aluminium hydroxide, $Al(OH)_3$, aluminium phosphate, $AlPO_4$ and ammonium sulfate, $(NH_4)_2SO_4$

5 a Lithium fluoride has low volatility which is a consequence of having a relatively high melting and boiling point. This is due to the strong attractive electrostatic forces of attraction operating between oppositely charged ions in the lattice. Large amounts of thermal energy are required to break down the lattice.

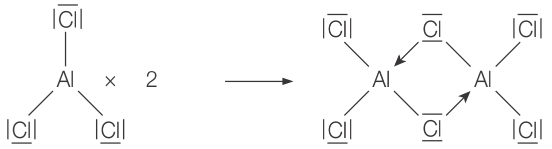
b Lithium fluoride is a non-conductor in the solid state: the ions are not free to move when a voltage is applied. It becomes an electrical conductor when melted or when an aqueous solution is formed. The electrical conductivity is due to the presence of mobile lithium and fluoride ions.

c Lithium fluoride is soluble in water (a polar solvent) because both ions are hydrated by the water molecules. The polar water molecules hydrate the lithium and fluoride ions via ion-dipole forces. The attraction between water molecules and ions is energetically favourable to break up the lattice and release hydrated ions.

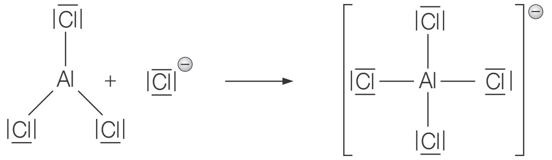
6



7

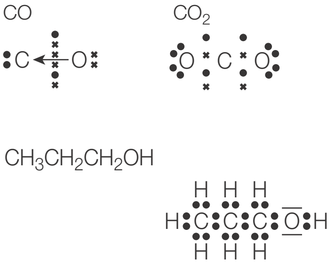


Aluminium is the acceptor; chlorine is the donor



Aluminium is the acceptor, chlorine is the donor

8 a

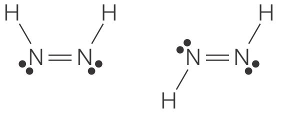


b CO < CO_2 < C_3H_7OH. Triple bonds are shorter than double bonds which are shorter than single bonds. The greater the number of shared pairs of electrons between the two nuclei the stronger the electrostatic attraction so the shorter the bond.

9 $^{+\delta}O{-}F^{\delta-}$; $^{+\delta}B{-}F^{\delta-}$; $^{+\delta}C{-}Cl^{\delta-}$; P–H (least polar – same electronegativities);

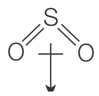
$^{\delta+}C{=}O^{\delta-}$; $^{\delta-}O{-}H^{\delta+}$; $^{\delta+}H{-}Br^{\delta-}$ and $^{\delta+}H{-}F^{\delta-}$ (most polar)

10



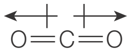
polar form non-polar form

11 SO_2:



Correct representation of the bent / non-linear / V-shape **and** for showing the net dipole moment, or explaining it in words (unsymmetrical distribution of bond dipole moments).

CO_2:



Correct representation of the linear shape **and** for showing the two equal but opposite dipole moments or explaining it in words (symmetrical distribution of bond dipole moments).

Allow either an arrow or an arrow with bar for the representation of dipole moment / correct partial charges instead of the representation of the vector dipole moment.

12 ionic, covalent, polar covalent, ionic and polar covalent

13 The sodium ion, Na^+, has a low charge density so therefore it has a low polarizing power. Therefore, sodium compounds will be essentially ionic. However, the oxide ion, O^{2-}, is a larger and more highly charged ion than the fluoride ion, $F^{-.}$ Therefore, its electron cloud can be more easily distorted and polarized towards the Na^+ ion. Hence, Na_2O has a higher degree of covalent character than NaF.

14 Carbon dioxide, CO_2, is simple molecular covalent with a linear structure; silicon dioxide, SiO_2, is giant three-dimensional solid/network solid/macromolecular structure with repeating tetrahedral units.

Covalent bonds are present in CO_2 and SiO_2. Carbon dioxide has double bonds: C=O and silicon dioxide has single bonds: –O–Si–O– bonds.

15 Diamond: three-dimensional array / network / lattice involving tetrahedral bonded carbons / each carbon atom joined to four other carbon atoms (except at surface) by single covalent bonds;

Graphite: multi-layer structure involving trigonal (triangular) planar carbon atoms / with each carbon atom joined to three others / with hexagonal (six-membered) rings of carbon atoms;

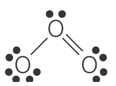
C_{60} fullerene: truncated icosahedron; or cage of carbon atoms with 32 faces, of which 12 are pentagons (isolated) and 20 are hexagons.

Diamond: covalent bonds between carbon atoms; **graphite**: covalent bonds between carbon atoms and the separate layers held together by (weak) London (dispersion) forces; **fullerene-60, C_{60}**: covalent bonds between carbon atoms and the approximately spherical cages are attracted to one another by (weak) London (dispersion) forces.

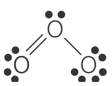
16 **Diamond-like form of BN**: Extremely hard, insoluble in water, very high melting and boiling point, electrical insulator.

Graphite-like form of BN: Soft, slippery, electrically conducting across layers and lower melting and boiling points.

17 a



and

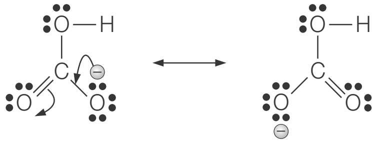


Bond angle is 117° (but accept between 115 to 119°).

b The two pi electrons in the ozone molecules are delocalized over the three oxygen atoms. The pi electrons are **equally** shared by all three oxygen atoms, hence giving two oxygen–oxygen bonds that are equal in length.

18 a Resonance occurs when two (or more) valid Lewis (electron dot) structures need to be used to describe a molecule or ion (with pi bonds). The actual structure (hybrid) is a blend (50% contribution from each) of both them with intermediate values of bond length/bond strength (bond enthalpy).

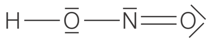
b



19 Order: $PH_2^- < PH_3 < PH_4^+$

Between lone (non-bonding) pairs of electrons, there is a greater repulsion than bonding (shared) pairs thus, the bond angle decreases with increasing number of lone pairs.

20 a



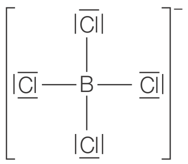
The N=O bond is the shorter of the two.

b 102 to 105°; lone / non-bonding pairs on the oxygen occupy more space and hence repel more than a bonding / shared pair, hence decreasing the H–O–N bond angle (from 109.5°)

21

α	β	θ
104.5°	120°	109.5°

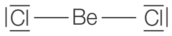
22



Lewis structure of BCl_4^-

tetrahedral bond angle =109.5°

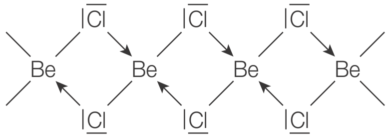
23 a



A $BeCl_2$ molecule

b beryllium in the $BeCl_2$ molecule is electron deficient – it has four valence electrons

c



bond angle approximately 109°

24 For the molecules H_2S, H_2Se and H_2Te, as the molecular size and mass increases, London (dispersion) forces increase in strength (and the boiling point increases). H_2O experiences hydrogen bonding which is stronger than London (dispersion) forces.

25 CCl_4 is non-polar molecule and therefore insoluble in water (because it forms only weak London forces with water molecules), whereas CH_3CH_2OH forms hydrogen bonds with water molecules and readily dissolves in water.

Methanoic acid is soluble in water as it forms hydrogen bonds with water molecules and undergoes ionization. However, octanoic acid is much less soluble in water despite the presence of the carboxylic acid functional group that hydrogen bonds with water molecules because of the long hydrophobic non-polar alkyl chain (C_7H_{15}) that does not interact with the solvent water molecules (and the long alkyl chain also disrupts the hydrogen bonding that is present in water).

26 Lattice of cations (positive caesium ions); delocalized or mobile 'sea' of valence electrons; electrostatic attraction between the two; electrons move when a voltage (potential difference) is applied.

27 Aluminium is malleable as the lattice planes can slide over each other without the metallic bonding being disrupted. In the alloy, the movement of planes of aluminium atoms is prevented by the presence of the impurity copper alloying atoms. The electrical conductivity is due to the presence of delocalized valence electrons which are supplied by both the aluminium and copper atoms in the alloy.

28 a In potassium, only one valence electron contributes to the metallic bonding (electron 'sea'), in calcium, two and in titanium, more than two, because the electrons in both 3d and 4s sub-levels are used for the formation of metallic bonds and hence the number of valence electrons per atom increases from potassium to titanium.

Also, from potassium to titanium (across period 4), the atomic radius decreases. Hence, the strength of metallic bonding increases. The density increases because the relative atomic mass increases and the atomic size decrease and the increase in nuclear charge is greater than the shielding effect.

b In going down (ascending) group 2, the boiling and melting points of the metals are expected to decrease. This is because the strength of the metallic bonding is inversely proportional to the metallic radius (size of cation). On going down group 2 the metallic radius increases and shielding increases, hence the metallic bonding becomes weaker and hence the boiling point and boiling points are expected to decrease.

The melting point increases because the strength of metallic bonding increases. The strength of metallic bond is proportional to the number of valence (delocalized electrons per metal atom) / metallic radius.

29 a CH_3CN and CHI_3 are both polar molecules and hence dipole–dipole interactions / forces operate between molecules.

b CH_3CN can dissolve in water because it can form hydrogen bonds with water molecules via the lone-pair on the nitrogen atom and the hydrogen atom of water molecules.

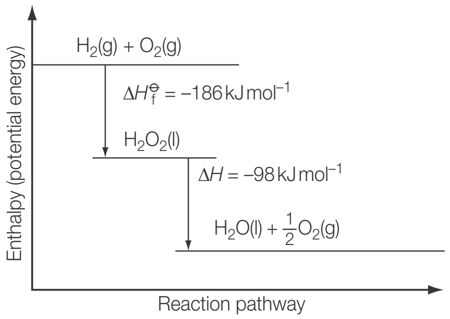
30 Ca_3N_2 has a giant ionic structure held together by strong electrostatic attraction between Ca^{2+} and N^{3-} ions. S_4N_4 has a simple molecular structure held together by weak London (dispersion) forces. Hence, more thermal energy is required to overcome the strong electrostatic attractions in Ca_3N_2 accounting for the higher boiling point.

Topic 5 Energetics / thermochemistry

Quick check questions

1 exothermic; exothermic: endothermic; exothermic; endothermic

2



3 282 kJ

4 1.43×10^6 kJ

5 $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$

$H_2(g) + S(s) \rightarrow H_2S(g)$

6 $-222.5\,\text{kJ mol}^{-1}$

7 $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

$2K(s) + \frac{1}{2}O_2(g) \rightarrow K_2O(s)$

$C_2H_4(g) + 2.5O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

$C_6H_6(g) + 7.5O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$CH_3OH(l) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

8 0.498 g

9 $5058\,\text{kJ mol}^{-1}$

10 a $C_3H_7COOH(aq) + NaOH(aq) \rightarrow C_3H_7COONa(aq) + H_2O(l)$

b Some of the heat released released from the neutralization is used to break the –O–H bond in the propanoic acid molecules and release hydrogen ions.

11 6.4 °C

12 $-56.8\,\text{kJ mol}^{-1}$

13 $+5.23\,\text{kJ mol}^{-1}$

14 450 J

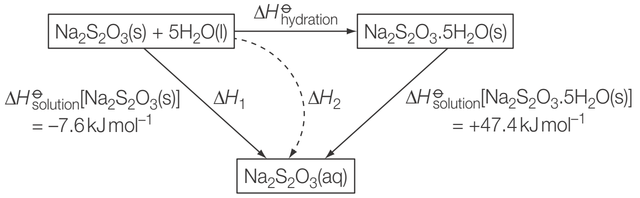
15 $\dfrac{2.5 \times 1.0 \times 4.18 \times 40.0}{1000} = 0.418\,\text{kJ mol}^{-1}$

16 a $620\,\text{kJ mol}^{-1}$

b heat loss to the surroundings / incomplete combustion; determine the heat capacity of calorimeter and take the heat absorbed by the calorimeter into account / improve thermal insulation / measure temperature against time and extrapolate graph to compensate for heat loss

17 $\Delta H^\ominus = (y - x)\,\text{kJ mol}^{-1}$

18



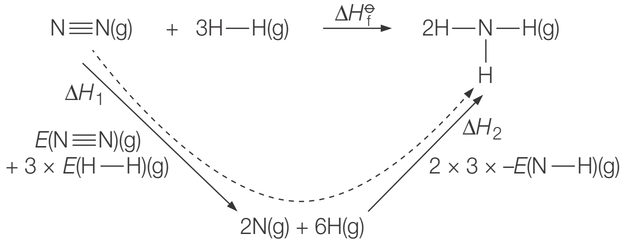
$\Delta H_1 = \Delta H_2$

$(-7.6\,\text{kJ mol}^{-1}) = \Delta H^\ominus_{hydration} + (+47.4\,\text{kJ mol}^{-1}) = -55.0\,\text{kJ}$

19 Cyclohexane has localized single bonds (bond order 1) of the same length and same strength. Benzene exists as a resonance hybrid and contains delocalized bonds intermediate in length and strength between single and double bonds (bond order 1.5). Bond enthalpies can be used for cyclohexane but not benzene.

20 The energy change to break one mole of bonds in a molecule in the gaseous state; averaged over similar or related compounds; the I–I bond is only present in one molecule, I_2.

21



enthalpy of reaction = −92 kJ (enthalpy of formation of ammonia = $-46\,\text{kJ mol}^{-1}$

22 $-10\,\text{kJ mol}^{-1}$

23 a −1080 kJ mol^{-1}

b The three nitrogen–nitrogen single bonds in the trinitramide molecule are longer than the nitrogen–nitrogen triple bond in the nitrogen molecule; the bond in N_2 is shorter because there are three electron pairs versus one electron pair in the N–N bonds in trinitramide; resulting in greater electrostatic attraction between the two nuclei and the bonding pairs.

Topic 6 Chemical kinetics

Quick check questions

1 B

2 1.00×10^{-3} mol dm^{-3} s^{-1}

3 a five times (5×) as fast

b rate of appearance of Br_2 is half (0.5×) that of the disappearance of H^+ ions.

4 a follow the volume of oxygen gas produced (gas syringe), or loss in mass from flask

b follow the disappearance of I_2 using a colorimeter, or by titration with sodium thiosulfate

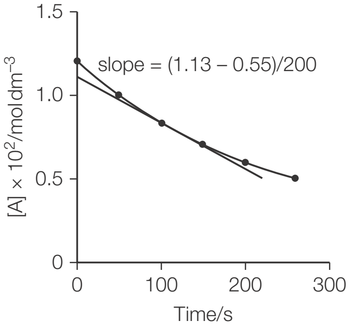
c follow the disappearance of NaOH by titration with acid

d follow the disappearance of OH^- by titration with acid, or the change in conductivity or pH

5 a the reaction has stopped

b 2.8×10^{-5} mol dm^{-3} s^{-1}

c and **d** graph of [A] against time; then draw tangent at 100 s



$$\text{slope of tangent} = \frac{(1.13 - 0.55) \times 10^{-2}}{200} = 2.90 \times 10^{-5}$$

instantaneous rate at 100 s = 2.90×10^{-5} mol dm^{-3} s^{-1}

average rate for 0 to 100 s = 3.28×10^{-5} mol dm^{-3} s^{-1}

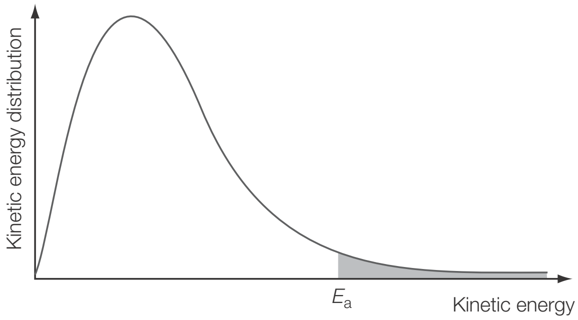
note that the instantaneous rate has a lower value as the reaction is slowing down.

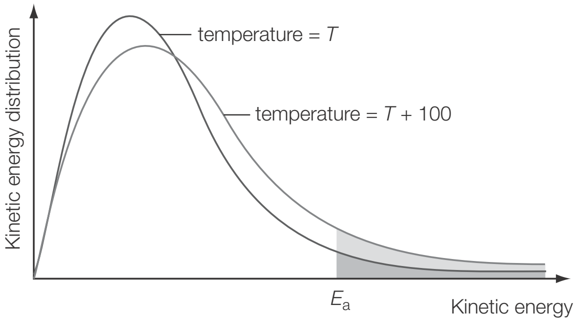
6 D

7 B

8 A

9 At higher temperature the particles have more kinetic energy and therefore move faster. This means that they collide more frequently. However, this has only a relatively small effect on the reaction rate. The major effect arises from the fact that a greater proportion of the collisions will involve particles whose total kinetic energy is greater than the activation energy for the reaction. The Maxwell–Boltzmann distribution shows that at the higher temperature more particles have kinetic energy greater than, or equal to, E_a.





Topic 7 Equilibrium

Quick check questions

1 D

2 **a** $K_c = [[Fe(SCN)]^{2+}(aq)] / [Fe^{3+}(aq)] [SCN^-(aq)]$

b $K_c = [SO_3(g)]^2 / [SO_2(g)]^2 [O_2(g)]$

c $K_c = [NO(g)]^4 [H_2O(g)]^6 / [NH_3(g)]^4 [O_2(g)]^5$

d $K_c = [CO_2(g)] [H_2(g)]^4 / [CH_4(g)] [H_2O(g)]^2$

3 C

4 $K_c = \frac{1}{4}$ or 0.25

5 **a** $K_c = 5.8 \times 10^{-5}$

b $K_c = 2.89 \times 10^8$

6 The change in pressure has lowered the proportion of products in the reacting mixture. Therefore, to reach equilibrium again and the same value of K_c, the system must shift to the right towards products.

7 **a** The equilibrium position will shift to the right (favouring the products) in order to lower the concentration of Fe^{2+} ions again.

b No effect, the addition of water will lower all the concentrations equally.

8 a i will shift equilibrium position to the left (in the exothermic direction), favouring the reactants

ii will shift equilibrium position to the right (in the endothermic direction), favouring the products

iii no effect

iv will shift equilibrium position to the left (to lower the hydrogen concentration again), favouring reactants

b i will lower K_c

ii will increase K_c

iii no change

iv no change

9 a i will shift equilibrium position to the left (in the direction of that side of the equation involving fewer moles of gas molecules), favouring the reactants

ii no change as both sides of the equation involve the same number of moles of gas molecules

b i will shift equilibrium position to the right (in the direction of that side of the equation involving more moles of gas molecules), favouring the products

ii will shift equilibrium position to the right (in the direction of that side of the equation involving more moles of gas molecules), favouring the products

10 a will shift equilibrium position to the left (in the endothermic direction), favouring the reactants; K_c value lowered

b will shift equilibrium position to the right (in the endothermic direction), favouring the products; K_c value increased

c will shift equilibrium position to the left (in the endothermic direction), favouring the reactants; K_c value lowered

Topic 8 Acids and bases

Quick check questions

1 It is not an acid–base reaction (under Arrhenius theory) because HCl(g) does not contain H^+ ions and $NH_3(g)$ does not contain OH^- ions. There is no water present so no ions are released into aqueous solution.

2 An amphiprotic species is both a proton donor (Brønsted–Lowry acid) and a proton acceptor (Brønsted–Lowry base).

$HSeO_4^-(aq) + H^+(aq) \rightarrow H_2SeO_4(aq)$

$HSeO_4^-(aq) \rightarrow H^+(aq) + SeO_4^{2-}(aq)$

3 Acids: $HClO_2(aq)$ and $HCOOH_2^+(aq)$

Bases: $ClO_2^-(aq)$ and HCOOH(aq)

4 Acid – a proton donor; base – a proton acceptor

Reaction	Acid	Conjugate base	Base	Conjugate acid
I	$H_2O(l)$	$OH^-(aq)$	$NH_3(aq)$	$NH_4^+(aq)$
II	$HCO_2H(aq)$	$HCOO^-(aq)$	$C_6H_5O^-(aq)$	$C_6H_5OH(aq)$

Stronger base in reaction II: phenoxide ion, $C_6H_5O^-$ – K_c value is large – equilibrium favours forward reaction; product favoured – better proton / hydrogen ion acceptor / stronger affinity for protons/hydrogen ions.

5 Equation that shows accepting a proton, e.g. reacting with hydrochloric acid.

$CH_3NH_2(aq) + HCl(aq) \rightarrow CH_3NH_3^+(aq) + Cl^-(aq)$ / *accept* CH_3NH_3Cl;

$CH_3NH_2(aq) + H_2O(l) \rightarrow CH_3NH_3^+(aq) + OH^-(aq)$

6 H_2O is the acid; OH^- is the conjugate base

NH_3 is the base; NH_4^+ is the conjugate acid

7 F^-, NO_3^-, SO_4^{2-}, HS^- and N_2H_4

8 NH_3, H_3O^+, PH_4^+, $C_2H_5OH_2^+$, H_2O and HCOOH

9 Colourless and odourless gas released; heat released to surroundings; colourless solution formed; magnesium consumed / used up / reacted

$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

10 The hydrogen gas would be released at a slower rate / rate of reacting of magnesium will be slower, since the concentration of hydrogen ions (protons) is less/acid partially dissociates or ionizes.

11 Any three from: $2CH_3COOH(aq) + Ca(s) \rightarrow (CH_3COO)_2Ca(aq) + H_2(g)$

$2CH_3COOH(aq) + CaCO_3(s) \rightarrow (CH_3COO)_2Ca(aq) + CO_2(aq) + H_2O(l)$

$CH_3COOH(aq) + KOH(aq) \rightarrow CH_3COOK(aq) + H_2O(l)$

$2CH_3COOH(aq) + 2Na(s) \rightarrow 2CH_3COONa(aq) + H_2(g)$

12 lithium hydroxide and nitric acid; sodium sulfate; neutralization / acid–base reaction / proton transfer; exothermic.

13 $[H^+](aq) = 10^{-pH}$; $[H^+(aq)]_{HNO_3} = 10^{-2}$ (mol dm^{-3})

and

$[H^+(aq)]_{HCN} = 10^{-6}$ (mol dm^{-3})

10 000 / 10^4 : 1

14 Amount of NaOH = 0.05 dm^3 × 0.50 mol dm^{-3} = 0.025 mol

Amount of HCl = 0.20 dm^3 × 0.10 mol dm^{-3} = 0.02 mol

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

Excess NaOH is 0.005 mol in 250 cm^3 of solution; concentration of NaOH = 0.02 mol dm^{-3}

$pOH = -\log_{10}[OH^-(aq)] = 1.69 = 1.7$; $pH = 14.0 - 1.7 = 12.3$

15 10^4

16 pH = 0.43

17 pH = 0.90

18 $NaHCO_3(s) + HCOOH(aq) \rightarrow HCOONa(aq) + H_2O(l) + CO_2(g)$

$[H^+] = 3.7 \times 10^{-3}$ mol dm^{-3}

19 Increases by one pH unit

20 pH = 11.64

21 0.40 g

22 12.7 and 12.7

23

$[H^+(aq)]$	$[OH^-(aq)]$	Type of solution
0.1	1×10^{-13}	Acidic
1×10^{-3}	1×10^{-11}	Acidic
1×10^{-5}	1×10^{-9}	Acidic
1×10^{-7}	1×10^{-7}	Neutral
1×10^{-9}	1×10^{-5}	Alkaline
1×10^{-11}	1×10^{-3}	Alkaline
1×10^{-13}	0.1	Alkaline

24 $[OH^-] = 2.0 \times 10^{-13}\,mol\,dm^{-3}$

25 Monoprotic: one proton donated per molecule of acid in aqueous solution.

Strong acid completely dissociated / ionized **and** weak acid partially dissociated / ionized.

$H_2O(l) + HClO_4(aq) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$

$H_2O(l) + HCN(aq) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

26 $0.20\,mol\,dm^{-3}$ $H_2SO_4(aq) < 0.20\,mol\,dm^{-3}$ $HCl(aq) < 0.020\,mol\,dm^{-3}$ $HCl(aq)$, $< 0.020\,mol\,dm^{-3}$ CH_3CH_2COOH, $< 0.002\,mol\,dm^{-3}$ $CH_3CH_2COOH < 0.0020\,mol\,dm^{-3}$ $NH_3(aq) < 2.0\,mol\,dm^{-3}$ $NH_3(aq) < 2.0\,mol\,dm^{-3}$ $NaOH(aq)$

27 HCl/A is strong and CH_3COOH/C is weak;

HCl/A is fully dissociated and CH_3COOH is slightly dissociated;

$[H^+]$ is greater in HCl/A than in CH_3COOH/C; by a factor of 100

28 Bubbling/ effervescence/ dissolving of CO_2 / colourless and odourless gas released (do not accept CO_2 produced). The rate of release is faster with sulfuric acid and the time taken for completion of the reaction is less.

29 Normal rainwater has a pH less than 7.0 because of dissolved carbon dioxide and other acidic gases from natural sources.

Acid rain (deposition) is rainwater that is below pH 5.6.

30 Limestone is a mineral form of calcium carbonate; this reacts with acid, as do all carbonates, to produce a salt, water and carbon dioxide. So the limestone is eroded away over time.

31 $N_2(g) + O_2(g) \rightarrow 2NO(g)$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Nitrogen(IV) oxide reacts with water in the air to produce a mixture of nitric(III) acid and nitric(V) acid.

$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$

A further reaction in the presence of water can convert nitrogen(IV) oxide to nitric(V) acid by oxidation; the reaction involving oxygen directly.

$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$

Topic 9 Redox processes

Quick check questions

1 $2H_2O_2 \rightarrow 2H_2O + O_2$; −1, −2 and 0; is a redox reaction in which both oxidation and reduction of the same species occurs (in this example, oxygen).

2 $2N_2H_4(g) + N_2O_4(g) \rightarrow 3N_2(g) + 4H_2O(l)$; hydrogen is oxidized, nitrogen reduced.

3 $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$; ammonia is oxidized; oxygen reduced.

4 $Li \rightarrow Li^+ + e^-$ (oxidation)

$H_2 \rightarrow 2H^+ + 2e^-$ (oxidation)

$4e^- + 2O \rightarrow 2O^{2-}$ (reduction)

$Cu^+ \rightarrow Cu^{2+} + e^-$ (oxidation)

$e^- + Cr^{3+} \rightarrow Cr^{2+}$ (reduction)

$e^- + Fe^{3+} \rightarrow Fe^{2+}$ (reduction)

$Al \rightarrow Al^{3+} + 3e^-$ (oxidation)

$2Cl^- \rightarrow Cl_2 + 2e^-$ (oxidation)

5 $-3, 0, -3, -2, -2, +2, +1, +3, +5, +3, +5, -3, +5, +3, \frac{-1}{3}, -1$

6 Element–element (homopolar) bonds are ignored in terms of oxidation state and hence the terminal sulfur atom is regarded as S=S and hence each sulfur atom has an oxidation state of zero.

The central sulfur atom is less electronegative than oxygen and hence assigned a positive oxidation state – it forms four bonds with oxygen – the bond to sulfur is not counted.

7 Cr^{6+} refers to a hypothetical ion formed by the loss of six valence electrons from a chromium atom; the +6 oxidation state refers to the idea that oxidation numbers assign the more electronegative atom the electrons in the bonds – and chromium is forming two Cr=O bonds and two $Cr–O^-$ bonds; oxygen is more electronegative than chromium.

8 +5, –2, –1; +1, –1, +3, –2; +1, –2; +1, –1; +7, –2; +1, –1; +2, –3; and +1, –1.

9 a $4K(s) + O_2(g) \rightarrow 2K_2O(s)$

b K: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$ and O: $1s^2\,2s^2\,2p^4$; K^+: $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ and O^{2-}: $1s^2\,2s^2\,2p^6$

c Oxygen is reduced since it has gained electrons / reduced since the oxidation number has decreased (from 0 to –2).

10 a potassium sulfate(IV), sodium sulfate(VI), iron(III) nitrate, iron(II) nitrate, copper(II) sulfate, copper(I) oxide, chromium(III) oxide, copper(I) sulfate, manganese(VII) oxide and manganese(IV) oxide.

b $NaOCl$, Fe_2O_3, $CsNO_3$, PCl_3, SCl_4 and $NaClO_3$

11 +3, +2, +2 and +1

12 $2FeI_2 + I_2 \rightarrow 2FeI_3$

(Iron in) FeI_2 is oxidized because its oxidation number increases / changes from +2 to +3; iodine reduced because it gains electrons / $I_2 + 2e^- \rightarrow 2I^-$ and its oxidation number/state decreases / changes from 0 to –1

13 no change in oxidation number; precipitation (double decomposition)

14 a silver(I) nitrate or silver(I) ions

b oxidation or replacement; $Pb\ (s) \rightarrow Pb^{2+}(aq) + 2e^-$

c silver solid forms; silver atoms produced as the silver ions gain electrons and are reduced: $Ag^+ + e^- \rightarrow Ag$

15 $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(g) + Br_2(aq)$

There is a change in oxidation number / electron transfer occurs.

A pale green gas and colourless solution becomes an orange brown solution.

16 $Cr_2O_7^{2-}(aq) + 3SO_2(aq) + 2H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$

17 $Ti^{3+}(aq) + e^- \rightarrow Ti^{2+}(aq)$

$Ag(s) \rightarrow Ag^+(aq) + e^-$

$Ti^{3+}(aq) + Ag\ (s) \rightarrow Ti^{2+}(aq) + Ag^+(aq)$

18 Copper(II) ions are an oxidizing agent and iodide ions are a reducing agent.

It is a redox reaction because there is a change in oxidation number in iodine and copper.

19 $3I_3^- + 3H_2O \rightarrow IO_3^- + 8I^- + 6H^+$

20 $n(Cr_2O_7^{2-}) = (21.50/1000)\,dm^3 \times 0.100\,mol\,dm^{-3} = 0.00215\,mol$

$n(Fe^{2+})$ in 25.00 cm^3 = 0.00215 mol × 6 = 0.0129 mol

$n(Fe^{2+})$ in 250.00 cm^3 = (0.0129/25.00) × 250.00 = 0.129 mol

mass of iron in iron ore = 0.129 mol × 55.85 g mol^{-1} = 7.20 g

% mass of iron in iron ore = 7.20/12.25 × 100% = 58.81% or 58.8%

21 a $HOCl(aq) + 2I^-(aq) + H^+(aq) \rightarrow Cl^-(aq) + I_2(aq) + H_2O(l)$

b Amount of sodium thiosulfate/thiosulfate ions = (16.85/1000) dm^3 × 0.152 mol dm^{-3} = 0.0025612 mol

Amount of iodine = 0.0025612 mol/2 = 0.0012806 mol

c Amount of NaOCl in original bleach solution = $\dfrac{0.0012806\,mol \times 250}{20}$ = 0.0160075 mol

Mass of NaOCl = 0.0160075 mol × 74.44 g mol^{-1} = 1.19159 g

Concentration of NaOCl = 1.19159 / 0.025 = 47.6 g dm^{-3}

22 $n(S_2O_3^{2-}) = (12.5/1000)\,dm^3 \times 0.00200\,mol\,dm^{-3} = 0.000025\,mol$

$n(I_2)$ = (0.000025/2) mol = 0.0000125 mol

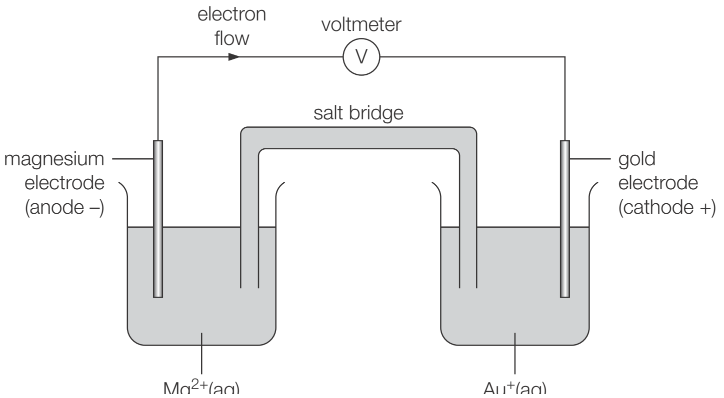
$n(Mn(OH)_3)$ = 2 × 0.0000125 mol = 0.000025 mol

$n(O_2)$ = (0.000025/4) mol = 0.00000625 mol

mass of O_2 in 24.50 cm^3 = 0.00000625 × 32.00 = 0.0002 g

mass of O_2 in 1000 cm^3 = $\left(\dfrac{0.0002}{24.5}\right) \times 1000$ = 0.00816 g dm^{-3} = 8.16 mg dm^{-3} or ppm

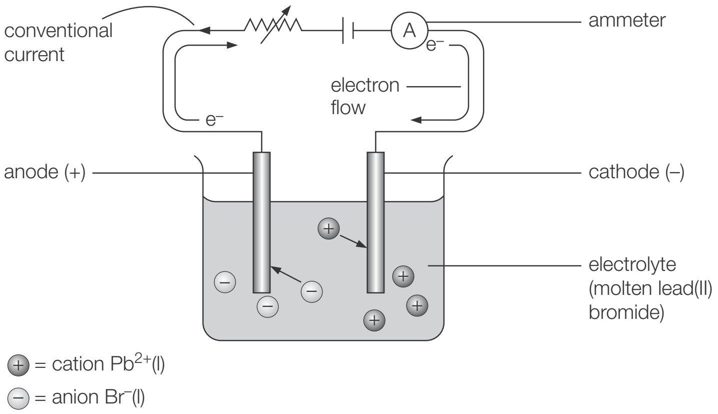
23 a



b Cathode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$; anode: $Au^+(aq) + e^- \rightarrow Au(s)$

c Allows cations and anions to flow through it / to complete the circuit / to maintain electroneutrality. KCl/KNO_3/$NaNO_3$

24 a



b Electrons flow through connecting wires in the external circuit and ions move in the molten electrolyte to their respective electrodes and lose / gain electrons on the surfaces.

c $Pb^{2+}(l) + 2e^- \rightarrow Pb\ (s)$; $2Br^-(l) \rightarrow Br_2(l) + 2e^-$.

d It means energy has to be supplied to make the electrolytic processes occur. Electrical to chemical energy. Mobile ions are able to move under the influence of an applied voltage.

25 a electrical energy to chemical energy

b The electrolysis only occurs in the molten state as the ions present must be able to move laterally. In the solid the only motion of the ions taking place is vibration about a fixed point.

c Cathode: $Sr^{2+}(l) + 2e^- \rightarrow Sr(l)$; reduction

Anode: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$; oxidation (also accept $2Br \rightarrow Br_2$)

d To prevent the re-oxidation of hot strontium by oxygen (air).

Topic 10 Organic chemistry

Quick check questions

1 D

2 a $CH_3CH_2COOCH_3$

b $CH_3CH_2CHCHCH_3$

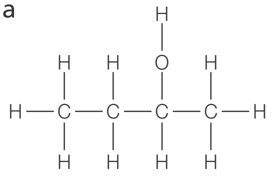
c $CH_3CH_2CH(OH)CH_3$

d $(CH_3CH_2)_3N$

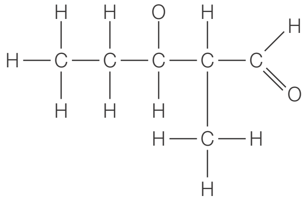
e $CH_3CH_2COCH_3$

f $CH_3CH_2CONH_2$

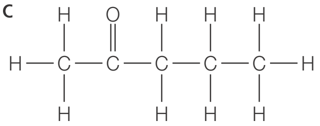
3 a



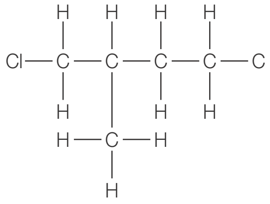
b



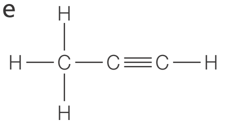
c



d



e



4 a 3; $CH_2CHCH_2CH_3$; $CH_3CHCHCH_3$; $CH_2C(CH_3)_2$

b 4; $CH_3CH_2CH_2CH_2Br$; $CH_3CH_2CHBrCH_3$; $CH_3CH(CH_3)CH_2Br$; $CH_3CBr(CH_3)CH_3$

c 6; $CH_3CH_2CH_2CH_2OH$; $CH_3CH_2CH(OH)CH_3$; $CH_3CH(CH_3)CH_2OH$; $CH_3C(OH)(CH_3)CH_3$; $CH_3CH_2OCH_2CH_3$; $CH_3OCH_2CH_2CH_3$

5 a butanamide

b ethyl propanoate

c diethylamine

d ethyl ethanoate

e ethyl methanoate

f ethyl-1-methylethanoate

g 2,2-dimethylpropanenitrile

h pentanenitrile

6 a propane

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$2C_3H_8 + 7O_2 \rightarrow 6CO + 8H_2O$

butane

$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

$2C_4H_{10} + 9O_2 \rightarrow 8CO + 10H_2O$

b ethanol

$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

7 a $CH_3CH_2CH_2OH(l) + CH_3COOH(l) \rightarrow CH_3COOCH_2CH_2CH_3(l) + H_2O(l)$

b $CH_3CH_2CH_2CH_2OH(l) + HCOOH(l) \rightarrow HCOOCH_2CH_2CH_2CH_3(l) + H_2O(l)$

c $CH_3CH_2COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3CH_2COOCH_2CH_3(l) + H_2O(l)$

8 $CH_3CH_3(g) + Cl\bullet(g) \rightarrow CH_3CH_2Cl(g) + \bullet CH_3CH_2(g)$

$\bullet CH_3CH_2(g) + Cl_2(g) \rightarrow CH_3CH_2Cl(g) + Cl\bullet(g)$

9 a	partial oxidation:	propanal	CH_3CH_2CHO
	complete oxidation:	propanoic acid	CH_3CH_2COOH
b	complete oxidation:	propanone	CH_3COCH_3
c	no oxidation as this is a tertiary alcohol		
d	partial oxidation:	butanal	$CH_3CH_2CH_2CHO$
	complete oxidation:	butanoic acid	$CH_3CH_2CH_2COOH$

10 50:50 mixture of concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4); the active electrophile is $^{+}NO_2$, the nitronium ion (note the positive charge is on the nitrogen atom)

Topic 11 Measurement, data processing and analysis

Quick check questions

1 a yes

b no

2 Precision refers to how close the experimental measurements of the same physical quantity are to each other. Accuracy refers to how close an individual reading is to the true, accepted or literature value.

3 5 s.f.; 4 s.f.; 1 s.f.; 6 s.f.; 3 s.f.; 6 s.f.; 1 s.f.; 6 s.f.

4 a $13.5\,\text{m}^3$ (3 s.f.)

b $1900\ \text{g J mol}^{-1}$ (2 s.f.)

c $1.02\,\text{g cm}^{-3}$

d $2.00\,\text{J mol}^{-1}$ (3 s.f.)

5 a $\Delta G = -766 - \left(\frac{376 \times 19.6}{1000}\right) = -733\,\text{kJ mol}^{-1}$

Absolute uncertainty of $\Delta G = \pm\left(20 + \left[\left(\frac{0.5}{373} + \frac{0.7}{19.6}\right) \times \frac{373 \times 19.6}{1000}\right]\right) = \pm 20.3$

$\approx 30\,\text{kJ mol}^{-1}$ (rounding up)

$\Delta G = (-773 \pm 30)\ \text{kJ mol}^{-1}$

b $\%\ \text{error} = \frac{[-773 - (-785)]}{-785} \times 100\% = 1.528\% = 1.53\%$

6 a Amount of HCl = $(24.40/1000) \times 0.140 = 3.416 \times 10^{-3}\,\text{mol}$

Amount of KOH = 3.416×10^{-3} mol

b Concentration of KOH(aq) = $0.140 \times 24.40/20.00 = 0.171\,\text{mol dm}^{-3}$

c % error in volume of HCl = $(0.04/24.40) \times 100 = \pm 0.16\%$

% error in concentration of HCl = $(0.002/0.140) \times 100 = \pm 1.43\%$

% error in volume of KOH = $\pm 0.2\%$

% error in concentration of KOH = $0.17\% + 1.43\% + 0.2\% = 1.79\% = \pm 1.9\%$

Concentration of KOH = $0.171 \pm 0.003\,\text{mol dm}^{-3}$

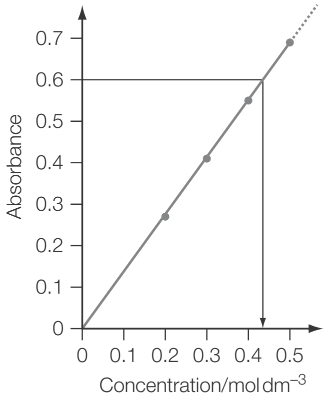
7 magnesium does react directly with water, but very slowly; magnesium may have been oxidized due to the large surface area; heat is lost to the surroundings and not accounted for in calculation; assumption that the density of solution is $1\,\text{g cm}^{-3}$ and specific heat capacity is the same as that of pure water; heat is absorbed by the apparatus and thermometer repeating the experiment many times and using only precise and temperature changes for averaging

$\Delta q = 2080\left(\frac{\Delta \text{m}}{\text{m}} + \frac{(\Delta \text{T})}{\text{T}}\right)$ or $= 2800\left(\frac{0.10}{50.0} + \frac{1.0}{10.0}\right) = 212.16 = 220\,\text{J}$

8 $\%\ \text{error} = \frac{(1367 - 855)}{1367} \times 100 \approx 37.5\%\ (37.45427\%)$

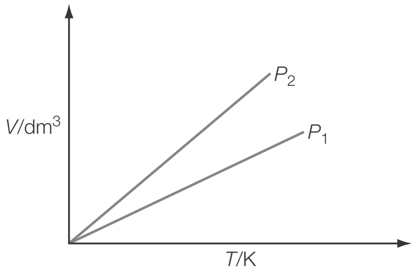
The heat (thermal energy) gained by the copper container is not taken into account (via knowing its specific heat capacity) / the burning wick may not transfer all the heat to the water/ incomplete combustion (soot formation)

9

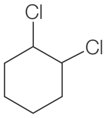


concentration = $0.44\,\text{mol dm}^{-3}$

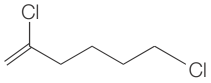
10



11 IHD = (14 − 12)/2 = 1



or



and many more

12 IHD values = 2, 1, 3, 2, 3 and 2

13 $[CH_3CH_2CHO]^+ \rightarrow \underset{m/z\,=\,29}{[CH_3CH_2]^+} + \bullet CHO$ or $\rightarrow CH_3CH_2\bullet + \underset{m/z\,=\,29}{[CHO]^+}$

$[CH_3CH_2CHO]^+ \rightarrow \underset{m/z\,=\,57}{[CH_3CH_2CO]^+} + H\bullet$ or $\rightarrow CH_3CH_2CO\bullet + \underset{m/z\,=\,1}{H^+}$

14 A: $C_2H_5{}^{35}Cl^+$ and $C_2H_5{}^{37}Cl^+$;

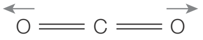
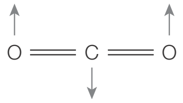
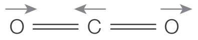
B: $C_2H_4{}^{79}Br_2{}^+$, $C_2H_4{}^{81}Br_2{}^+$, $C_2H_4{}^{79}Br^{81}Br^+$;

$C_2H_5{}^+$

15 Cyclohexane

16 The bond angle (H–P–H) changes as bending occurs. The lengths of the P–H bonds change as stretching occurs. The dipole moment of the phosphine molecule changes.

17

Mode of vibration			
IR active or IR inactive	IR inactive	IR active	IR active

18 Infrared waves have a smaller frequency and less energy and a lower wavenumber but longer wavelength than red light waves.

19 4.08×10^{-7} m; 7.353×10^{14} s^{-1}; 2.45×10^{6} m^{-1}

20 Carbon–carbon triple bond is stronger / shorter / more energy needed to vibrate it / cause resonance.

21 Ethene 1610–1680 cm^{-1} (>C=C<)

Ethane-1,2- diol 3200–3600 cm^{-1} (–O–H)

Ethane-1,2-dioic acid 2500–3300 cm^{-1} (–O–H in carboxylic acids) or 1700–1750 cm^{-1} (>C=O)

22 **two** wavenumber ranges common to the IR spectrum of both compounds:

(>C=O) 1680 to 1750 (cm^{-1});

(C–O) 1050 to 1410 (cm^{-1});

(C–H) 2840 to 3100 (cm^{-1});

one wavenumber range found only in the spectrum of one compound:

(–OH) 2500 to 3300 cm^{-1} (in methyl propanoic acid only)

23 It is a complicated region with many absorptions due to the large number of molecular vibrations. This part of the infrared spectrum is totally unique to a particular molecule and so can be used to identify and distinguish between compounds.

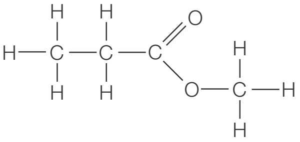
24 An alkyne (hex-1-yne); C≡C and C–H

25 1, 3, 2, 1, 2

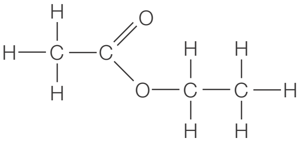
26 1, 3, 2, 5, 8

27 a Number of signals: the number of different hydrogen or proton environments. Integration trace: the relative numbers or ratio of hydrogen / protons in each environment. Chemical shift: effect of the neighbouring atoms, e.g. oxygen atom shifts the proton / hydrogen atoms signal downfield (due to its high electronegativity).

b



methyl propanoate



ethyl ethanoate

28 a number of signals in ^{1}HNMR spectrum. 3; ratio of signals in ^{1}H NMR spectrum. 2:3:3; radio waves

b *m*/*z* 57: $[CH_3CH_2CO]^+$; *m*/*z* 43: $[CH_3CO]^+$

Topic 12 Electrons in atoms

Quick check questions

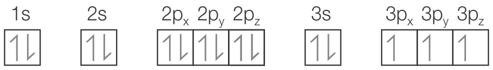
1 The two species are isoelectronic. Both have the same electronic configuration in the valence shell: $3s^2\ 3p^3$. As $S^+(g)$ has a higher nuclear charge (due to a greater number of protons in the nucleus), the valence electrons in the $S^+(g)$ species will experience a greater attractive force. Hence sulfur's second ionization energy is larger than the first ionization energy of phosphorus.

2 a Each letter represents an orbital orientated along the *x*-, *y*- or *z*-axis.

b The p orbitals are arranged mutually at right angles.

c Electrons are placed singly in degenerate orbitals before pairing occurs in one orbital (to form a spin pair with electrons of opposite spin). This is known as Hund's rule.

3 The '4p' orbitals should be labelled '3p'. Hund's rule states that electrons will occupy degenerate orbitals singly before any orbital is doubly filled (with a spin pair).



4 a $He(g) \rightarrow He^+(g) + e^-$

b 380 kJ mol^{-1} (±20 kJ mol^{-1})

c The noble gas atoms have the smallest radii (for their period) and the valence electrons experience the highest effective nuclear charge.

d The group 1 metal atom has the largest radius (for their period) and has the smallest effective nuclear charge in that period.

e Each new energy level (shell) means a larger radius (less attraction for the valence electron) and provides a greater shielding effect and hence reduced attraction by the nucleus.

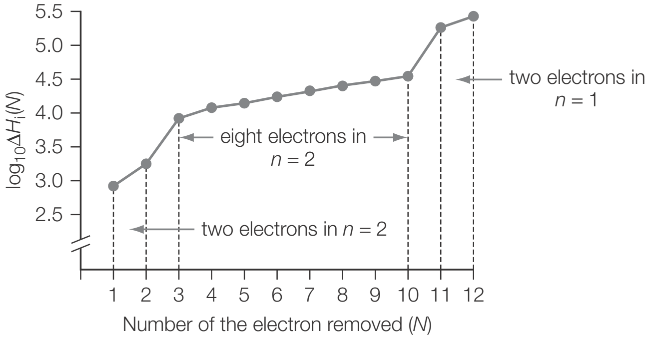
There is a rapid increase in nuclear charge and the slight decrease in atomic radius from lithium to neon atoms makes the attraction of the nucleus for outer electrons greater. The effective nuclear charge increases across the period.

f A beryllium atom has the configuration $1s^22s^2$ but a boron atom has the configuration $1s^22s^22p^1$. The valence electron in the boron atom is in a higher energy sub-level, further away from the nucleus and more effectively shielded.

The electron removed from oxygen during ionization is from a spin pair in the 2p sub-level. This experiences more repulsion than removal of the electron in a singly occupied 2p orbital from nitrogen.

5 Group 13. The first large change is between the third and the fourth ionization energies.

6



As the electrons are successively removed from a gaseous atom, the protons increasingly outnumber the remaining electrons. The effective nuclear charge experience by the remaining electrons increase and they are all pulled closer to the nucleus.

7 a Ti: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$, from the 3d sub-level

b The 5th electron is removed from 3p sub-level compared to the 4th electron from the 3d sub-level. The electrons in the 3p sub-level are closer to the nucleus than the 3d sub-level, hence the 4th electron experiences weaker forces of electrostatic attraction.

The 11th electron is removed from 3s sub-level compared to the 10th electron which is from the 3p sub-level which is further away from the nucleus, hence the 10th electron experiences weaker forces of electrostatic attraction.

8 6.604×10^{-7} m

9 1312.9 kJ mol $^{-1}$

10 2.04×10^2 kJ mol $^{-1}$

11 4.87×10^{14} s $^{-1}$; 9×10^9 m; 3.23×10^{-19} J

12 493 nm

13 74.42 nm; ultraviolet

14 a $n = 1$ to $n = 4$; $n = 3$ to $n = 4$

b III, I, II

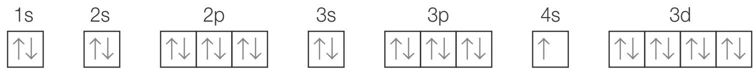
Topic 13 The periodic table – the transition metals

Quick check questions

1 Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

Ti^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

Ti^{4+}: $1s^2 2s^2 2p^6 3s^2 3p^6$

2 

Copper is a d-block element because it has 3d electrons in its outer main energy level. It is a transition element because the copper(II) ion has unpaired 3d electrons; it has the configuration d^9.

3 Scandium can form compounds with cations with an incompletely filled d sublevel; zinc only forms Zn^{2+} with the 3d sublevel filled (d^{10}).

4 5; 4; 2 and 0.

5 $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + 4H_2O(g) + Cr_2O_3(s)$

$Cr_2O_7^{2-}$: +6 and Cr^{3+}: +3 and NH_4^+: −3 and N_2: 0

6 a $Ti(g) \rightarrow Ti^+(g) + e^-$; $Ti^{3+}(g) \rightarrow Ti^{4+}(g) + e^-$

b 4th electron removed from 3d sublevel and 5th electron removed from the 3p sublevel; electrons removed from lower energy level / energy level closer to nucleus and are attracted more strongly.

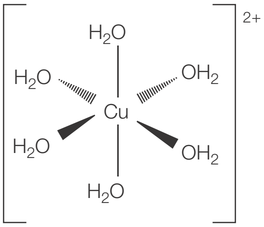
7 The calcium atom will lose two 4s electrons to form the calcium cation, Ca^{2+}, resulting in a stable ion with a noble gas configuration. A third ionization energy would involve the removal of an electron in an inner 3p sublevel much closer to the nucleus which would be energetically unfavourable. Transition metals are capable of forming a range of stable cations due to the presence of 4s and 3d electrons, whose energy levels are relatively close in energy.

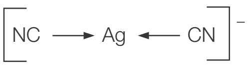
8 Paramagnetic; the copper(II) ion, Cu^{2+}, contains an unpaired electron in its 3d orbitals ($3d^9$ configuration). Diamagnetic: the zinc ion, Zn^{2+}, does not contain any unpaired 3d electrons (d^{10} configuration).

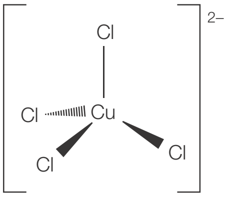
9 Typical properties of transition metals are variable oxidation states, form complex ions with ligands, have coloured compounds and display catalytic and magnetic properties. Iron forms compounds with different oxidation states: +2 and +3. Magnesium only forms compounds with an oxidation state of +2. Iron forms coloured compounds: iron(II) compounds are often pale green; iron(III) compounds are often reddish-brown. Magnesium forms colourless compounds (unless the anion is coloured). Iron forms many complex ions and complexes with well-defined stoichiometry with ligands, but magnesium does not. Iron and its compounds often show catalytic behaviour, but magnesium and its compounds do not. Iron(II) and iron(III) compounds are paramagnetic, due to the presence of unpaired electrons. Magnesium and its compounds are diamagnetic (due to the presence of spin pairs of electrons).

10 V^{3+}; [Ar] $3d^3$ and Zn^{2+} [Ar] $3d^{10}$; V^{3+} not it in highest oxidation state (+5; +4 also stable) and can be oxidized (by an oxidizing agent); Zn^{2+} in its highest oxidation state and cannot be oxidized (to a higher oxidation state).

11 +7,+2 and +2 and +3; MnO_4^- and Fe^{2+}

12 





13 a $[Ti(H_2O)_6]^{3+}$; 3+

b $[CuCl_4]^{2-}$; 2−

c $[CoI_4]^{2-}$; 2−

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

e $[Fe(SCN)(H_2O)_5]^{2+}$; 2+

f $[Cu(CN_2)_2]$; 0

g $[Fe(CO)_5]$; 0

14 a Hydroxide ion, OH^- and choride ion, Cl^-, oxidation state of chromium is +3

b Cr^{3+} has the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$; 3 unpaired electrons

15 $[Co(H_2O)_6]^{2+} + 6Cl^- \rightarrow [CoCl_6]^{2-} + 6H_2O$

$[Fe(H_2O)_6]^{3+} + SCN^- \rightarrow [Fe(H_2O)_5SCN]^{2+} + H_2O$

There is no change in oxidation number.

16 a 6; +2

b molecules or anions with at least one lone pair of electrons; ligands use their lone pair of electrons to form a coordinate covalent bond with the empty 3d and 4s orbitals of the Cu^{2+} ion

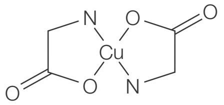
c hexaquacopper(II) ion and pentaaquabromocopper(II) ion

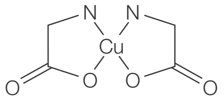
17 $[Ni(NH_3)_6]^{2+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightarrow [Ni(H_2NCH_2CH_2NH_2)_3]^{2+}(aq) + 6NH_3(aq)$

There is an increase in the number of ions on the right. The ammonia will form ammonium ions.

18 bidentate; bidentate and bidentate

19

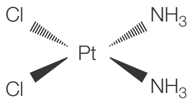




20 Optical isomerism / enantiomerism / stereoisomerism

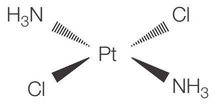
Both will rotate plane-polarized light to the same extent / degree / angle but in opposite directions.

21 a Diamminedichloroplatinum(II)



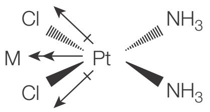
cisplatin

and



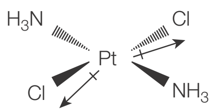
transplatin

b



cisplatin

and



M = 0
transplatin

cis: polar and *trans*: non-polar

c X-ray crystallography / diffraction of X-rays

22 $[Cu(H_2O)_6]^{2+} \rightarrow [Cu(H_2O)_5OH]^+ + H^+$

The copper(II) ion is relatively small with +2 charge and hence has some polarizing power. It will polarize a water molecule and cause the loss of a proton and retention of a hydroxide ion.

23 $[Ti(H_2O)_6]^{3+}$appears violet because it absorbs yellow light / rays / complementary colour

24 It has partially filled 3d orbitals and the d sublevel splits into two energy levels (d–d*) in the presence of ligands, allowing a d electron from the lower energy 3d orbital to absorb energy from the visible spectrum and be excited to the higher energy 3d orbital. The colour observed is complementary to the colour absorbed.

25 The ammonia ligand, NH_3, causes a greater degree of d–d splitting resulting in a larger energy gap between the two sets of d orbitals; hence the wavelength absorbed is shorter (blue) whereas the water ligands, H_2O, cause a smaller degree of d–d splitting and radiation (light) of a longer wavelength (orange) is absorbed.

26 The electronic configuration of Zn^{2+} is [Ar] or [Ar] $3d^{10}$ / fully filled d sub-level. Hence, there d–d transitions cannot occur as all the d orbitals are fully occupied with spin pairs of electrons.

27 Fe^{3+} (because of its greater positive charge) pulls the water ligands closer (to the central cation); the energy levels of the two sets of 3d orbitals are split wider with a larger energy gap; d electrons absorb higher frequency / energy / violet light when then undergo a transition from lower energy level to higher energy level.

28 The gaseous reactants molecules are adsorbed on the surface / increases surface concentration / bonds weakened / products formed and desorb. The catalyst lowers the activation energy barrier by providing an alternative pathway or mechanism for reaction.

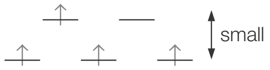
29 **a** $2I^-(aq) + S_2O_8{}^{2-}(aq) \rightarrow I_2(aq) + 2SO_4{}^{2-}(aq)$

b The uncatalysed reaction involves a step involving two anions, which experience repulsion.

c $2Fe^{2+}(aq) + S_2O_8{}^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4{}^{2-}(aq)$

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

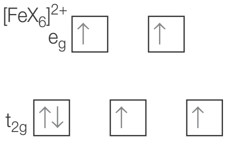
30 $CrF_6{}^{4-}$ contains Cr^{2+} (d^4)

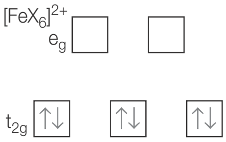


The fluoride ion, F^-, must be a weak field ligand to produce high-spin configuration.

31 **a** Nature / identity of metal ion (cation); oxidation state / oxidation number charge of metal ion (cation); nature of ligands; molecular geometry of complex ion / coordination number of metal ion (cation).

b





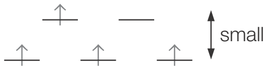
$CrF_6{}^{4-} \rightarrow Cr^{2+}$ (d^4)

The fluoride ion, F^-, must be a weak field ligand to produce high-spin configuration.

Y since the coordination number is 6 but with 3 ligands; hence each ligand forms 2 coordinate bonds with the iron(II) cation.

c X < Y < Z; complex ion with ligand X absorbs light at longest wavelength hence smallest ΔE in complex / Complex with ligand Z absorbs light at shortest wavelength hence largest ΔE in complex / Complex with ligand X is paramagnetic which implies a small value of ΔE thus maximum spin while in Z, ΔE is large hence minimal spin.

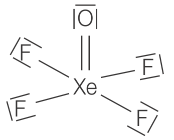
d



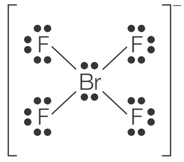
Topic 14 Chemical bonding and structure

Quick check questions

1



square pyramidal, 90°



square planar, 90°

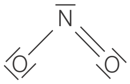
2 Number of electron domains is five: four bonding pairs and one lone pair, $n = 1$.

3 linear, 180°; bent / V-shaped / non-linear, between 90° and 109°

4

linear

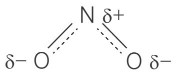
5 a



Bent/V-shaped/ angular; 109.5° < θ < 120°;

b Bond angle: 109.5° < θ < 120°; less than 120° because of the added repulsion of the lone pair

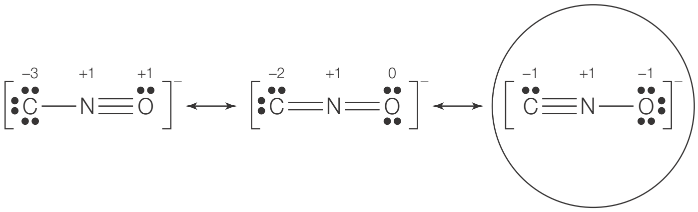
Resonance structures:



6 a Electron domain geometry; molecular shape: trigonal pyramidal and O–Cl–O bond angle.

b In Lewis structure **I**, the FC of Cl is 0 while O is −1; in Lewis structure **II**, the FC of Cl is −1 while O is 0. Structure **II** does not obey the octet rule, but chlorine is in period 3 (row 3) of the Periodic Table and can accommodate an expanded valence shell.

7 a



b The circled structure is more stable; Δ formal charge is closest to zero.

8 

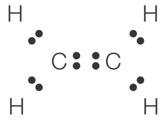
Formal charge (FC) on nitrogen: 0 and formal charge (FC) on oxygen: 0

9 Sigma bonds are formed by end on / axial overlap of orbitals with electron density between the two carbon atoms / nuclei; pi bonds are formed by sideways overlap of parallel p orbitals with equal regions of electron density above **and** below the inter-nuclear axis / sigma bond.

10 a mixing / joining together / combining / merging of atomic orbitals to form the same number of molecular orbitals / new orbitals / orbitals of equal energy / identical shape

b sp hydridized; one sigma and two pi (bonds).

11 12 sigma bonds; 2 pi bonds

12 a 

b sp^2; 5 σ bonds and 1 π bond

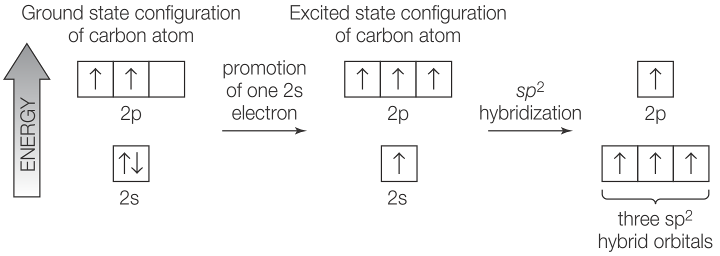
c the sigma bond is formed by head-on overlap and merging of hybridized sp^2–sp^2 of the two carbon atoms / sp^2 hybridized orbitals of carbon and 1s hydrogen orbitals along the inter-nuclear axis; a pi bond is formed by the side-on overlap and merging of parallel p-orbitals

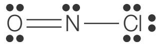
13 a Conjugation refers to a system of alternating carbon–carbon double (triple) and carbon–carbon single bonds. Delocalization refers to molecules or ions that have p orbitals extending over three or more atoms with delocalized pi electrons;

b sp^2 hybridization

c longer than the C=C bond but shorter than the C-C bond / between 0.134 to 0.154 nm

d 4 pi electrons are delocalized / resonance.



14 a 

b bent; V-shaped, non-linear; bond angle: between 119° and 107°

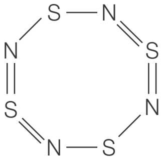
c Hybridization refers to the mixing and merging of atomic orbitals (to form the same number of new bonding/molecular orbitals); nitrogen is sp^2 hybridized and chlorine is sp^3 hybridized.

15 sp^3, sp^2 and sp^2

16 a 8 sigma bonds, 10 lone pairs, 4 pi bonds

b 104° (accept from 103 to 106°)

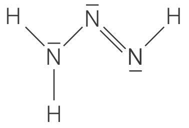
c sp^2 hybridization; nitrogen has 3 electron domains.

d 

17

molecule	**sp hybridized**	**sp^2 hybridized**	**sp^3 hybridized**
Butanal $CH_3(CH_2)_2CHO$		1	3
Pentane, C_5H_{12}			5
Ethylbenzene, C_6H_5-C_2H_5	0	6	2

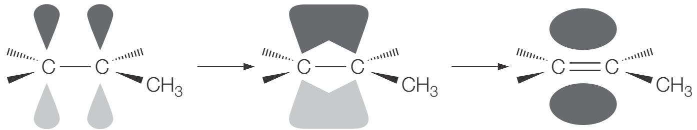
18



Trigonal planar, <109˚, sp^3, sp^2 and sp^2, 5 sigma bonds and 1 pi bond

19 a 8 sigma bonds and 1 pi bond

b



c The two p orbitals overlap sideways to form one localized pi bond over two carbon atoms. The bond is localized as the electron cloud is just over the two bonded atoms.

20 a $2O_3(g) \rightarrow 3O_2(g)$

b $O\bullet + NO\bullet \rightarrow NO_2$ *or* $O_3 + NO \rightarrow NO_2 + O_2$

$NO_2 + O_3 \rightarrow 2O_2 + NO$ *or* $NO_2 + O_3 \rightarrow NO + 2O_2$

21 a O=O bond = 498 kJ mol^{-1}

= 498 000 J; 1 mol = 6.02×10^{23}

Energy of O=O bond = 498 000 J /(6.02×10^{23} mol^{-1});

$E = hv$ and $c = v\lambda$, therefore $\lambda = hc/E$;

$$\lambda = 6.63 \times 10^{-34}\,\text{mol}^{-1} \times 3.00 \times 10^{8}\,\text{m s}^{-1} \times \frac{1}{498\,000} \times 6.02 \times 10^{23}\,\text{mol}^{-1}$$

$$= 2.40 \times 10^{-7}\,\text{m} = 240\,\text{nm}$$

b Bond order in ozone (1.5) is lower than oxygen (2); the lower bond order and hence weaker bonding in ozone is due to the delocalization of pi electrons (or resonance).

22 $Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$,

$ClO\bullet + O_3 \rightarrow Cl\bullet + 2O_2$,

Overall equation: $2O_3 \rightarrow 3O_2$;

The chlorine atom / radical *Cl•* is a catalyst as it is consumed and regenerated in the process.

Topic 15 Energetics/thermochemistry

Quick check questions

1 Work has to be done (energy absorbed) to pull the ions away from each other and overcome the attractive electrostatic forces.

2 $MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$

$AlF_3(s) \rightarrow Al^{3+}(g) + 3F^{-}(g)$

$K_2S(s) \rightarrow 2K^{+}(g) + S^{2-}(g)$

$Na_2O_2s) \rightarrow 2Na^{+}(g) + O_2^{2-}(g)$

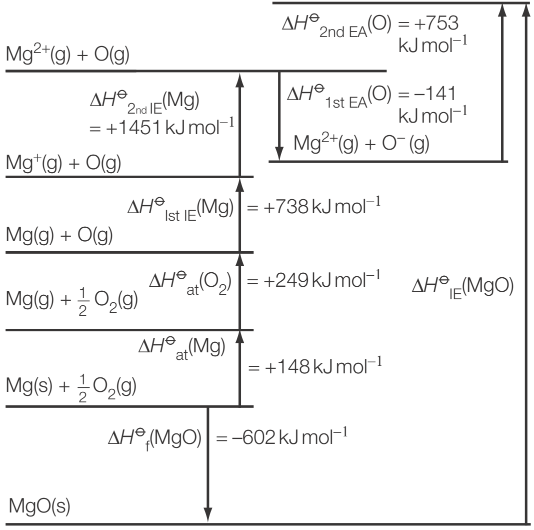
3 a $\frac{1}{2}N_2(g) \rightarrow N(g)$; $Ba(s) \rightarrow Ba(g)$; $\frac{1}{2}I_2(g) \rightarrow I(g)$; $Sc(s) \rightarrow Sc(g)$

b It is zero for neon because it exists in the form of gaseous atoms under standard conditions.

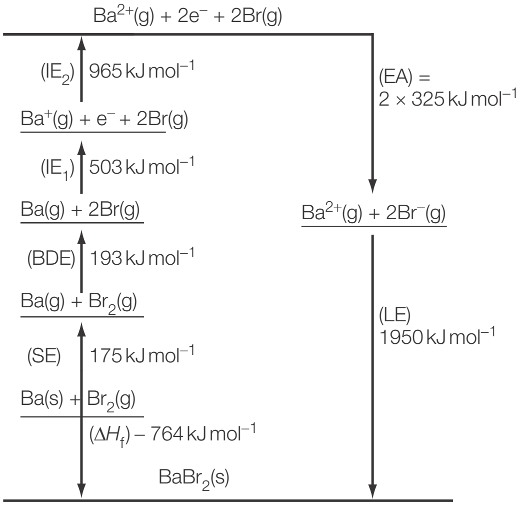
4 a The lattice enthalpy is the energy required to convert one mole of ionic solid into gaseous ions.

b Enthalpy of atomization for M: $M(s) \rightarrow M(g)$; enthalpy of atomization for X: $X(s) \rightarrow X(g)$; first ionization energy of M: $M(g) \rightarrow M^+(g) + e^-$; first electron affinity of X: $X(g) + e^- \rightarrow X^-(g)$ and enthalpy of formation of MX: $M(s) + X(s) \rightarrow MX(s)$.

5



6 a



b Lattice enthalpy = $[2 \times (-325)] + 965 + 503 + 193 + 175 - (-764) = 1950\,kJ\,mol^{-1}$

7 a Enthalpy of formation of $AuCl_2(s)$ = $+368 + 890 + 1980 + 242 + 2(-349) - 2180$
= $602\,kJ\,mol^{-1}$

b This large positive formation enthalpy means that $AuCl_2(s)$ is energetically unstable.

8 The charges remain constant, but there is an increase in ionic size from fluoride to iodide. The larger ions have smaller charge densities, which reduce the attraction to the sodium ions and hence reduces the lattice enthalpy.

9 Size of ions and charge of ions; the charge on the calcium ion Ca^{2+} is twice that of the potassium K^+ ion; the size of Ca^{2+} is smaller than of the K^+ ion. Therefore, the lattice enthalpy of potassium chloride, KCl will be less endothermic compared to that of calcium chloride, $CaCl_2$.

10 $-123 + (1650) + (-2255) = -728$

$\Delta H_{hydration}\ Cl^-(g) = -728/2 = -364\,kJ\,mol^{-1}$

11 The chloride ion has a smaller radius than the bromide ion and hence its charge / size ratio is greater. Water molecules are polar and therefore chloride ions interact with the partially positive hydrogen atoms in the water molecules. This interaction (ion–dipole attraction) with chloride ions is stronger than the interactions between water molecules and bromide ions. Hence more energy is released to the surroundings by chloride ions compared to bromide ions.

12 Solubility depends on the balance of energy required to destroy the solid structure, the lattice energy (enthalpy) and the energy released when ions are hydrated by water molecules (hydration enthalpy). So a compound like M_2O_3 is expected to have a significantly larger lattice energy due to its higher charges: (3+)(2−) versus (1+)(1−) in MX. This will make the enthalpy for dissolution likely much more positive and unfavorable.

13 A spontaneous process occurs by itself, whereas a non-spontaneous process requires a continuous input of energy to make it occur. It is possible to cause a non-spontaneous process to occur, but the process stops once the energy source is removed. A reaction that is spontaneous at one temperature, may become spontaneous at a different temperature.

14 The low molar entropy of ice indicates that the structure is very organized into a regular, repeating lattice; in water there is less structure and no long range organization in the structure and the much higher value for steam because of a very disordered and constantly changing random arrangement of molecules.

15 **a** decrease

b increase

c decrease

d decrease

e increase

f increase

g decrease

h increase

i decrease

16 **a** 16

b 1/16

c 87.5%

17 The entropy is low at the start because the water molecules are arranged into a regular repeating lattice in the form of ice crystals and so there is a relatively small number of ways to arrange the molecules and a relatively small number of ways to distribute quanta within the molecule. As the ice melts, the water cools, and any given water molecule can be found anywhere in the glass. Now there are many more ways to arrange the molecules and distribute their quanta in energy levels due to the broadening of temperature. The entropy is now much higher and is maximized once equilibrium is achieved.

18 $\Delta S_{\text{surroundings}} = -\Delta H/T = -17\,800\,\text{J mol}^{-1} / 300\,\text{K} = -593.3\,\text{J K}^{-1}\,\text{mol}^{-1}$

$\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}} = -593.3\,\text{J K}^{-1}\,\text{mol}^{-1} + 160.4\,\text{J K}^{-1}\,\text{mol}^{-1} = -433\,\text{J K}^{-1}\,\text{mol}^{-1}$

The reaction is not spontaneous at 300 K.

$\Delta S_{\text{surroundings}} = -\Delta H/T = -17\,800\,\text{J}/1200\,\text{K} = -148.3\,\text{J K}^{-1}\,\text{mol}^{-1}$

$\Delta S_{\text{total}} = \Delta S_{\text{surroundings}} + \Delta S_{\text{system}} = -148.3\,\text{J K}^{-1}\,\text{mol}^{-1} + 160.4\,\text{J K}^{-1}\,\text{mol}^{-1} = +12.1\,\text{J K}^{-1}\,\text{mol}^{-1}$

The reaction is spontaneous at 1200 K.

19 **a** The two gases gradually diffuse into each other until the concentrations of each gas are the same at all points in both bulbs.

b $\Delta H = 0$, ΔS is positive and ΔG is negative.

c Yes, it is consistent.

20 $\Delta G = -T\Delta S_{\text{universe}}$ and the second law of thermodynamics states that all spontaneous reactions involve an overall increase in entropy. If $\Delta S_{\text{universe}}$ is positive then $-T\Delta S_{\text{universe}}$ must be negative.

21 Non-spontaneous under standard conditions, therefore $\Delta G > 0$

22 Steam condenses to water when $\Delta G < 0$; $\Delta H = T\Delta S$;

$\Delta S = 189 - 70 = 119\,\text{J K}^{-1}\,\text{mol}^{-1}$; $\Delta H = 373 \times 119 = 44\,\text{kJ mol}^{-1}$

23 diamond → graphite $\Delta S = +3\,\text{J K}^{-1}\,\text{mol}^{-1}$ since $\Delta H < 0$, ΔG is always < 0 kinetics: large activation energy, E_a, makes reaction extremely slow: kinetically hindered

24 $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

$\Delta S = 90 - (214 + 40) = -164\,\text{J K}^{-1}\,\text{mol}^{-1}$

$\Delta G = \Delta H - T\Delta S$

and to be spontaneous $\Delta G < 0$.

Temperature at which $-T\Delta S > 178$ is 1085 K.

25 a $\Delta G = \Delta H - T\Delta S$; $\Delta H = c$ and $(-)\Delta S = m$ / ΔH and ΔS are constants; ΔH is the intercept, and $(-)\Delta S$ is the slope / gradient

b because the entropy change / ΔS is positive / $T\Delta S$ becomes larger/ $-T\Delta S$ becomes more negative

c not feasible / unfeasible / not spontaneous

26 $\Delta G^{\ominus} = \Delta G_f^{\ominus}\,(CuO(s)) - \Delta G_f^{\ominus}\,(H_2O(g)) = (-129.7\,\text{kJ mol}^{-1}) - (-228.6\,\text{kJ mol}^{-1})$

$\Delta G^{\ominus} = 98.9\,\text{kJ mol}^{-1}$; the positive sign indicates that the reaction is non-spontaneous; that is, the reverse reaction is spontaneous.

27 because bromine is a liquid under standard thermodynamic conditions

28 $\Delta G^{\ominus} = -RT\ln K = -\,(8.31\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times (\ln 1.8 \times 10^{-5}) = 2.7 \times 10^{4}\,\text{J mol}^{-1}$ or $2.7 \times 10^{1}\,\text{kJ mol}^{-1}$

29 2.22×10^{6}

30 An equilibrium constant less than 1 indicates the equilibrium mixture contains very little product. The reaction is not spontaneous in the forward direction and ΔG is a relatively large positive value.

31 A large negative value for ΔG indicates that the reaction is spontaneous and goes almost to completion. The equilibrium mixture will contain a high concentration of product, so $K_c > 1$. The reaction quotient, Q, depends on initial conditions, not equilibrium conditions, so its value cannot be predicted from ΔG.

32 The equilibrium position; ΔG

Topic 16 Chemical kinetics

Quick check questions

1 A

2 C

3 Plot gives a straight line passing through the origin / shows a directly proportional relationship between rate and $[I^-(aq)]$ / reaction is first order with respect to $[I^-(aq)]$

4 a Plot of rate against $[H_2O_2(aq)]$ gives a straight line / the reaction is first order with respect to $[H_2O_2(aq)]$

b gradient of the line = rate constant $k = 7.4 \times 10^{-4}\,\text{s}^{-1}$

5 a first order / second order / third order overall

Rate = k [A] [B]^2

b $k = 1.21 \times 10^{-2}\,\text{dm}^6\,\text{mol}^{-2}\,\text{s}^{-1}$

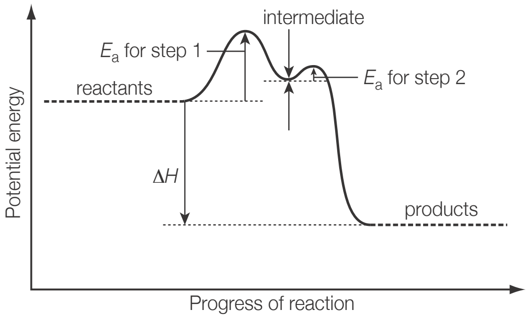
c rate = $8.65 \times 10^{-6}\,\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$

6 rate = $k[\text{NO}]^2\,[\text{O}_2]$

$k = 71.1\,\text{dm}^6\,\text{mol}^{-2}\,\text{s}^{-1}$

7 a rate = k [NO]^2

b



8 $H_2O_2 \rightarrow 2OH$

9 a $C + B_2 \rightarrow BC + B$

$A + B \rightarrow AB$

b $A + B \rightarrow AB$

$A + AB \rightarrow A_2B$

c $NO + H_2 \rightarrow H_2O + N$

$NO + N \rightarrow N_2 + O$

$H_2 + O \rightarrow H_2O$

10 43 kJ mol^{-1}

11 41.6 kJ mol^{-1}

12 a A small amount of catalyst greatly increase the rate of reactions; undergoes no permanent chemical change or change in mass; the catalyst provides an alternative reaction pathway of lower activation energy; the catalyst does not increase the equilibrium constant, but equilibrium is reached faster.

b The catalyst and reactants are in the same physical state.

c +1 and 4

d The presence of a lone pair of electrons on the phosphorus atom.

e $C_6H_{10} + H_2 \rightarrow C_6H_{12}$

f Bubble through bromine – if there is no loss of colour or reduction in intensity then the reaction has gone to completion.

g The ability of transition metals to interconvert between two or more stable cations via redox reactions.

Topic 17 Equilibrium

Quick check questions

1 a $K_c = [\text{NH}_3(g)]^2 / [\text{N}_2(g)]\,[\text{H}_2(g)]^3$

b $K_c = 2.09$

2 a $K_c = [NO]^2[Cl_2] / [NOCl]^2$ or $K_c = [NO(g)]^2[Cl_2(g)] / [NOCl(g)]^2$

b at 503 K: $K_c = 4.5 \times 10^{-3}$

at 738 K: $K_c = 9.2 \times 10^{-2}$

c The value of K_c is greater at 738 K; K_c increases with temperature, with the forward reaction being favoured to increase the proportion of products in the equilibrium mixture. This suggests that the forward reaction is endothermic.

3 a $CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$

b $K_c = [H_2]\,[CO_2] / [CO]\,[H_2O]$ or $K_c = [H_2(g)]\,[CO_2(g)] / [CO(g)]\,[H_2O(g)]$

$K_c = 1.84$

4 $K_c = 33$

5 $[CH_3OH(g)] = 2.4 \times 10^{-3}\,mol\,dm^{-3}$

6 $[H_2(g)] = 5.2 \times 10^{-7}\,mol\,dm^{-3}$

7 $\Delta G^{\ominus} = -33.3 = kJ\,mol^{-1}$

8 a $\Delta G^{\ominus} = 0$

b $\Delta G^{\ominus} = +69.73\,kJ\,mol^{-1}$

9 a $K = e^{-1.79} = 0.166$

b The equilibrium constant value is less than 1.00 and so the equilibrium is well to the reactants side of the equation.

Topic 18 Acids and bases

Quick check questions

1 Water acts as a base in both reactions; HBr is a Brønsted–Lowry base / proton acceptor; $Fe^{3+}(aq)$ is a Lewis base / electron pair donor.

2 Brønsted–Lowry base: a substance that accepts a proton (H^+); Lewis base: a substance that donates an electron pair to form a coordinate bond.

3 Boric acid acts as a Lewis acid because it accepts an electron pair from the hydroxide ion released by the water molecule. It is not a Brønsted–Lowry acid because it does not donate a proton to the water molecule; it acts as a hydroxide ion acceptor.

4 $B(CH_3)_3$ (electrophile), OH^- (nucleophile), $HOCH_3$ (nucleophile), CN^- (nucleophile) $CH_3CH_2O^-$ (nucleophile) $C_6H_5{-}CH_2^+$ (electrophile) and HI (electrophile).

5 CH_3COO^-, Cl^- and NH_3 are Lewis bases in **a**, **b** and **c** respectively.

6 $K_b = 10^{-4.75} = 1.78 \times 10^{-5}$; $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$ $/[OH^-(aq)] = \sqrt{(K_b[NH_3])}$

$[OH^-(aq)] = \sqrt{(1.78 \times 10^{-5} \times 0.121)}$; pOH = 2.83; pH = 14.00 − 2.83 = 11.17

7 4.5×10^{-4}

8 1.77×10^{-5}

9 $9.8 \times 10^{-3}\,mol\,dm^{-3}$; 2.01

10 $4.30 \times 10^{-3}\,mol\,dm^{-3}$

11 HClO and $C_6H_5NH_2$

12 R > Q > P > S

13 $[H^+] = \sqrt{(5.0 \times 10^{-10} \times 0.2)} = 10^{-5}\,mol\,dm^{-3}$

14 $[OH^-(aq)] = 1.0 \times 10^{-2}\,mol\,dm^{-3}$; $1.0 \times 10^{-2} = \sqrt{(K_b \times 0.15)}$; $K_b = 6.7 \times 10^{-4}$

15 $K_w = 5.60 \times 10^{-13}\,mol^2\,dm^{-6} = [H^+][OH^-]$; $pH = -\log_{10}\sqrt{(5.60 \times 10^{-13})} = 6.13$

16 $[H^+] = 5.60 \times 10^{-13}/0.100 = 5.60 \times 10^{-12}\,mol\,dm^{-3}$; pH = 11.3

17 The ionization / dissociation of water to H^+ / H_3O^+ and OH^- / $H_2O \rightleftharpoons H^+ + OH^-$;

$2H_2O \rightleftharpoons H_3O^+ + OH^-$; the forward reaction is an endothermic process due to –O–H bond cleavage;

By applying Le Châtelier's Principle, raising the temperature will shift the position of equilibrium to the right, resulting in a higher concentration of H_3O^+/H^+ and OH^-; neutral because for water, $[H^+] = [OH^-]$

18 Amount of KOH = $0.05\,dm^3 \times 0.50\,mol\,dm^{-3} = 0.025\,mol$

Amount of HCl = $0.20\,dm^3 \times 0.10\,mol\,dm^{-3} = 0.02\,mol$

0.005 mol of excess KOH/OH^- present in $250\,cm^3$ of solution

Concentration of KOH = $0.02\,mol\,dm^{-3}$

$pOH = -\log_{10}[OH^-(aq)] = 1.69 = 1.7$; $pH = 14.0 - 1.7 = 12.3$

19 1.90; 12.10

20 11.6; 2.4

21 $K_b = \dfrac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$; $10^{-3.35} = \dfrac{[OH^-]^2}{0.500}$

$[OH^-] = 0.0149\,mol\,dm^{-3}$; pOH = 1.83 ; pH = 12.17

22 $[NH_4Cl] = 53.30\,g/53.50\,g\,mol^{-1} = 1.00\,mol\,dm^{-3}$; amount of NH_3 = $14\,mol\,dm^{-3} \times 0.4\,dm^3$
= 6 mol; $[NH_3] = 5.60\,mol\,dm^{-3}$

23 A buffer solution is one that resists changes in pH when a small amount of acid or base is added to it; the conjugate base, CH_3COO^- removes the added acid by reacting with it: $CH_3COO^- + HCl \rightarrow CH_3COOH + Cl^-$ or $CH_3COO^- + H^+ \rightarrow CH_3COOH$; the ethanoic acid molecules remove the added KOH by reacting with it: $CH_3COOH + KOH \rightarrow CH_3COO^-K^+ + H_2O$ or $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$.

24 **a** $20.00\,cm^3$

b at the half-equivalence point of $10.00\,cm^3$, pH = pK_a; pK_a is 4.75 hence the acid is ethanoic acid

c Owing to negative inductive effect of chlorine (relatively electronegative atom) the ionization of chloroethanoic acid increases and its K_a value is higher than ethanoic acid.

25 basic; neutral; basic; basic; acidic; neutral

26 Potassium ions have only a +1 charge and a relatively large size and hence low charge density with low polarizing power. They are unable to polarize the O–H bond in the water ligand strongly enough to release H^+ ions (protons) in solution.

27 Slightly acidic due to hydrolysis / polarizing effect of Cu^{2+} which has a charge density sufficient to dissociate water molecules.

$[Cu(H_2O)_6]^{2+}(aq) + H_2O(l) \rightarrow [Cu(OH)(H_2O)_5]^+(aq) + H_3O^+(aq)$

neutral; $Ba(NO_3)_2$ is formed from a neutralization reaction involving a strong base $Ba(OH)_2$ and a strong acid (HNO_3) and the ions of the salt do not undergo hydrolysis; alkaline because HCO_3^- is a weak base: and undergoes hydrolysis with water molecules:

$HCO_3^-(aq) + H_2O(l) \rightarrow H_2O(l) + CO_2(aq) + OH^-(aq)$ / $HCO_3^-(aq) + H_2O(l) \rightarrow H_2CO_3(aq) + OH^-(aq)$

28 $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$;

colour A colour B

in presence of acid / H^+, equilibrium shifts to the left, colour A predominates;

in presence of base / OH^-, equilibrium shifts to the right, colour B predominates;

bromophenol blue / bromocresol green / methyl red

29 yellow, colourless and green (yellow and blue)

30 orange (a mixture of red, yellow and colourless)

Topic 19 Redox processes

Quick check questions

1 Platinized platinum electrode; H_2 gas at 100 kPa; $[H^+(aq)]$ = 1 mol dm^{-3} HCl/0.5 mol dm^{-3} H_2SO_4; temperature = 298 K / 25 °C

2

A	A solution of $ReO_4^-(aq)$ at 298 K and 1 mol dm^{-3}
B	Platinum electrode (coated with a layer of rhenium)
C	Salt bridge
D	Hydrogen gas at 209 K and 100 kPa
E	$H^+/HCl/H_3O^+$ at 1 mol dm^{-3}

From SHE to the rhenium half cell (left to right); to complete the circuit / allows movement of anions and cations between electrolytes / maintain electroneutrality; saturated aqueous potassium nitrate/potassium chloride

3 When an aluminium half-cell which consists of an aluminium electrode in contact with a 1 mol dm^{-3} aqueous solution of $Al^{3+}(aq)$ connected to the SHE, the potential difference measured will be +1.66 V. Aluminium atoms have a higher tendency to lose electrons than hydrogen molecules. Electrons will flow from the aluminium half-cell to the SHE: $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$.

When a copper cell is connected to a SHE, the electrode potential measured is −0.34 V and the electrons will flow from the SHE to the copper half-cell. Hydrogen molecules have a greater tendency to lose electrons than copper atoms: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

4 silver(I) ions, $Ag^+(aq)$

5 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; $2e^- + Pb^{2+}(aq) \rightarrow Pb\ (s)$

$2e^- + 2H^+(aq) \rightarrow H_2(g)$; $Ca\ (s) \rightarrow Ca^{2+}(aq) + 2e^-$

6 $Al(s)\ |\ Al^{3+}(aq)\ ||\ Ag^+(aq)\ |\ Ag(s)$; $Al(s) + 3Ag^+(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$

$E^\ominus = (1.66\ V) + (0.80\ V) = +2.46\ V$

7 $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$

$Pt(s)\ |\ Fe^{2+}(aq), Fe^{3+}(aq)\ ||\ MnO_4^-(aq), Mn^{2+}(aq)\ |\ Pt(s)$

8 $E^\ominus_{cell} = 0.77\ V - (-0.26\ V) = 1.03\ V$: yellow/brown to green at Fe^{3+}/Fe^{2+} half-cell; nickel electrode decreases in mass / size; nickel ion concentration increasing;

$2Fe^{3+} + Ni \rightarrow 2Fe^{2+} + Ni^{2+}$

9 $E^\ominus_{cell} = +1.56\ V$; $\Delta G^\ominus = -\ (2)\ (9.65 \times 10^4\ C\,mol^{-1})\ (+1.56\ V) = -301\ kJ\,mol^{-1}$

10 3.2

11 $VO_2^+(aq)$; species most readily gains electrons (in aqueous solution) to form $VO^{2+}(aq)$ and $H_2O(l)$ / most positive $E^\ominus$ value; $Zn(s)$; species most readily loses electrons (in aqueous solution) to form zinc ions, $Zn^{2+}(aq)$; $Zn(s) + 2VO_2^+(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + 2VO^{2+}(aq) + 2H_2O(l)$; a positive cell potential implies a spontaneous reaction and hence a negative value of negative $\Delta G^\ominus$ due to the relationship: $\Delta G^\ominus = -nFE^\ominus$.

12 $E^\ominus_{cell} = (+0.77\ V) - (0.00\ V) = +0.77\ V$; electrons will flow from the hydrogen half-cell to the Fe^{3+}/Fe^{2+} half-cell through the external circuit. $H_2(g) + 2Fe^{3+}(aq) \rightarrow 2H^+(aq) + 2Fe^{2+}(aq)$; when the concentration of the Fe^{3+} ion is increased the reaction will be shifted towards the right hand side, making the cell potential more positive (> 0.77 V).

13 Mn^{2+} is a weaker oxidizing agent than H_2O and H^+ will be discharged to form H_2, in preference to Mn^{2+}.

14 Dilute sodium chloride: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

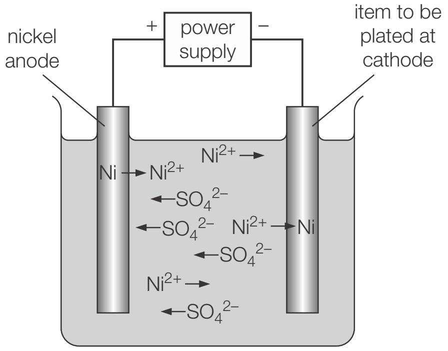
Concentrated sodium chloride: $2Cl^- \rightarrow Cl_2 + 2e^-$

15 Sulfuric acid is formed which results in a decrease in pH: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

16 Anode: Ag (s) → Ag^+(aq) + e^-; cathode: Ag^+(aq) + e^- → Ag (s)

17 Molten sodium chloride releases mobile Na^+ and Cl^- ions; Na^+ migrates towards the cathode and undergoes reduction: $Na^+ + e^- \rightarrow Na$. In aqueous sodium chloride, since the $E^\ominus$ H^+/H_2 > $E^\ominus$ Na^+/H_2, it is hydrogen gas which is produced at the cathode: $2H^+ + 2e^- \rightarrow H_2$.

18



19 a Electrode X

b Electrode X: Cr^{3+}(aq) + $3e^-$ → Cr (s); Electrode Y: Cr (s) → Cr^{3+}(aq) + $3e^-$;

c because H^+ ions are discharged / H_2 gas is produced instead / standard reduction potential of aluminium is relatively negative

20 Anode: $Cu \rightarrow Cu^{2+} + 2e^-$; cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

$Q = 2.40\,A \times (25 \times 60)\,s = 3600\,C$

Amount of electrons = $3600\,C/96\,500\,C\,mol^{-1} = 3.73 \times 10^{-2}\,mol$

Mass of copper = $(\frac{3.73 \times 10^{-2}}{2}) \times 63.58\,g\,mol^{-1} = 1.186\,g$

21 2:2:1

22 1:4

23 Ag^+(aq) + e^- → Ag (s); amount of silver atoms = $0.200\,g/107.87\,g\,mol^{-1} = 0.00185\,mol$; amount of electricity needed to deposit 0.00185 mol of Ag = $96\,500\,C\,mol^{-1} \times 0.00185\,mol = 178.53\,C$; $178.53\,C = I \times 1200\,s$; $I = 0.149\,A = 149\,mA$

Topic 20 Organic chemistry

Quick check questions

1 a Polar aprotic solvents will not interact with the attacking nucleophile forming a 'solvent shell'. The nucleophile remains 'naked'. A nucleophile with a solvent shell is going to be slower in attacking the target molecule. By using an aprotic solvent and allowing the nucleophile to react all of the time, we are greatly speeding up the reaction. S_N2 reactions performed with nucleophiles in polar aprotic solvents occur about 1000 times faster than those in regular protic solvents.

b DMF is a better solvent for this reaction as it is a polar aprotic solvent whereas water is a polar protic solvent which will shield the nucleophile by forming a solvent shell. Water has hydrogen atoms that are attached to a highly electronegative element, oxygen.

2 a $CH_3CHBrCH_2CH_3$

b Cl is more electronegative than Br, so the Cl will be δ– and the Br δ+

$CH_3CH_2CHBrC(CH_3)_2Cl$

3 a butan-1-ol

b 3-methylbutan-2-ol

4 a Reduction with $LiAlH_4$ in diethyl ether; reflux; add dilute acid to complete reaction.

b Not a possible route.

c Reaction with bromine vapour (or in an organic solvent) in sunlight (UV light).

d Reaction with chlorine or bromine in an organic solvent (in dark).

e Heat with concentrated sulfuric acid and then add water.

f Reaction under reflux (50 °C) with a nitrating mixture of concentrated nitric acid and concentrated sulfuric acid.

g Reflux with tin and concentrated hydrochloric acid.

h Warm with sodium dichromate(VI)/concentrated sulfuric acid in distillation apparatus.

5 **but-1-ene** → (react with HBr) → **2-bromobutane** → (react with NaOH solution) → **butan-2-ol** → (oxidation with $Na_2Cr_2O_7$ / concentrated H_2SO_4) → **butanone**

or

but-1-ene → (react with conc. H_2SO_4 /add water) → **butan-2-ol** → (oxidation with $Na_2Cr_2O_7$ / concentrated H_2SO_4) → **butanone**

The second method may give the greater yield as it involves fewer stages

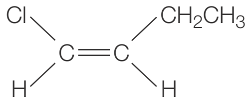
6 **1-chlorobutane** → (react with NaOH solution) → **butan-1-ol** → (oxidation with $Na_2Cr_2O_7$ / concentrated H_2SO_4 under reflux) → **butanoic acid**

$CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH$

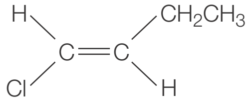
$CH_3CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2COOH + H_2O$

7 **a** and **c** show *cis–trans* isomerism, **b** does not

1-chlorobut-1-ene

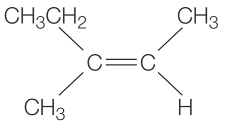


Z-form

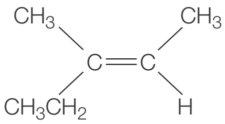


E-form

3-methylpent-2-ene



Z-form



E-form

8 five

9 D

10 In each case decide the priority of the different groups attached to the carbon atoms making the carbon–carbon double bond

A is the *E*-isomer as the high-priority groups are on different sides of the molecule (different carbon atoms of the two forming the double bond).

B is the *E*-isomer as the high-priority groups are on different sides of the molecule.

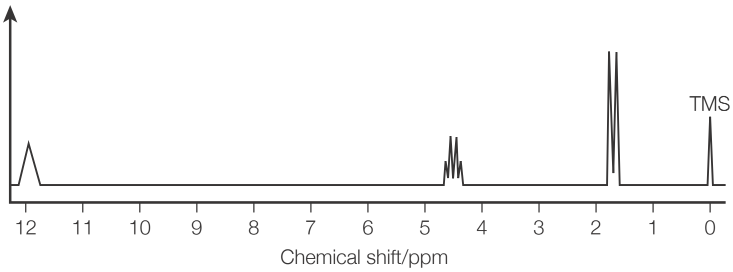
C is the *Z*-isomer as the high-priority groups are on the same side of the molecule (attached to the same carbon atom of the two forming the double bond).

Topic 21 Measurement and analysis

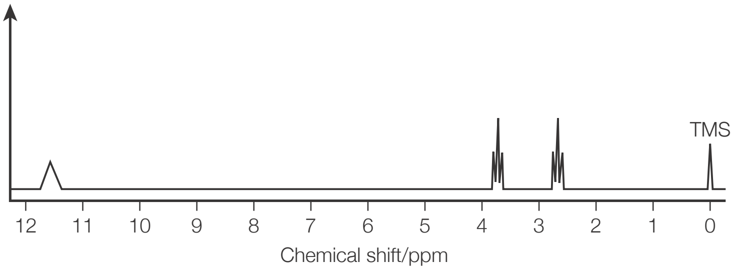
Quick check questions

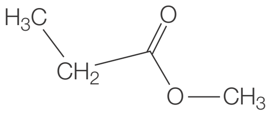
1 A doublet and a quartet and a sextet

2 High-resolution ^{1}H NMR spectrum for 2-chloropropanoic acid, $CH_3CHClCOOH$



High-resolution ^{1}H NMR spectrum for 3-chloropropanoic acid, $CH_3CHClCOOH$



3 

three types of hydrogen / proton environments

two $-CH_3$ groups (peak area 3) and one $-CH_2-$ group (peak area 2)

one of the $-CH_3$ groups is next to an electronegative oxygen (at 4.1 ppm), proton/hydrogen most deshielded / downfield signal

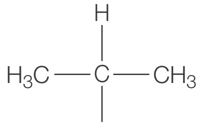
one of the $-CH_3$ groups is adjacent to a carbon atom (at 0.9 ppm), proton / hydrogen atom most shielded / upfield

the $-CH_2-$ group next to >C=O at 2 ppm, signal is in between the two extremes one of the $-CH_3$ groups, has no neighbouring protons / hydrogen atoms produces a singlet

one of the $-CH_3$ groups next to $-CH_2-$ (2+1) produces a triplet

the $-CH_2-$ next to $-CH_3$ / $-C_2H_5$ (3+1) produces a quartet

4 The IHD is zero which means that the compound contains no rings or double bonds. Six equivalent hydrogen atoms usually implies two methyl groups. This is a doublet, so the six hydrogen atoms have one neighbouring hydrogen atom which is logical since the other hydrogen atom is a septet (seven peaks, six hydrogen atom neighbours). This gives the following partial structure meaning the compound is 2-iodopropane.



5 tetramethysilane / TMS

strong single peak (as there are 12 hydrogen atoms (protons) in identical chemical environment); absorbs upfield / away from most other hydrogen atoms (protons);

low boiling point / bp / volatile (so easily removed from sample by evaporation);

non-toxic / unreactive / does not interfere or react with sample;

6 It does not contain hydrogen atoms (protons) that will give rise to signals in the NMR spectrum.

7 Empirical formula is $C_4H_{10}O$; M_r is 74; mass spectrum gives peak of 74; IR spectrum indicates presence of an –OH group, which is C_4H_9OH (3300 cm^{-1}) as well as $-CH_3$ and $-CH_2-$ groups. NMR spectrum has four peaks showing hydrogen atoms are present in four different environments. $\delta = 0.9$ for $R-CH_3$ (integration trace of 3), $\delta = 1.4$ for $R-CH_2-R$ (integration trace of 4), $\delta = 2.2$ for $R-CH_2-O$ (integration trace of 2) and $\delta = 3.6$ for R–OH (integration trace of 1); this confirms the structure as $CH_3CH_2CH_2CH_2OH$.

8 Non-invasive; low-energy radiation / no tissue damage

Magnetic resonance imaging (MRI) gives a three-dimensional view of organs in the human body; protons (hydrogen atoms) in water molecules(/ lipids / carbohydrates) in human cells give different signals depending upon their chemical environment

9 An aromatic compound containing a benzene ring would give rise to the six equivalent sets of rings. The slight 'humps' on two of these are hydrogen atoms, and the three large sets of circles are the iodine atoms as they have a larger number of electrons. The last set of circles attached to a carbon atom is an oxygen atom as it is slightly larger than the carbon atoms (contains more electrons) and the slight 'hump' on it is a hydrogen atom, giving the –OH group.

Topic 22 Option A Materials

Quick check questions

1 $Si_2O_8^{8-}$, SiO_4^{4-} and SiO_5^{6-}

2 Ceramics have ionic bonding and covalent structures; no delocalized electrons. Metals contain fixed lattice of positive ions / cations in 'sea' of delocalized (or mobile) valence electrons.

3 ionic bonding / ionic bonding with covalent character; giant covalent bonding

4 Ductility, excellent electrical and thermal conductivity and malleability describe metals. Ceramics can be characterized as being electrically and thermally insulating and brittle.

5 polar covalent, ionic, metallic, metallic, metallic, polar covalent and covalent

6 100% covalent, 0% ionic; 48–52% ionic, 48–52% covalent; 32–38% ionic, 62–68% covalent

7 Difference in electronegativity = 2.0 − 1.3 = 0.7

Average = $\frac{2.0 + 1.3}{2}$ = 1.65

Ionic character approx. 15%

Metallic bonding

8 $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$

$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$

9 limestone / $CaCO_3$;

air (enriched with hydrocarbons, such as methane)

coke / C / carbon

contains too much carbon / 4% carbon by mass; (and so it is) brittle / has low malleability

10 **a** $3Fe + Sb_2S_3 \rightarrow 2Sb + 3FeS$

b $Fe \rightarrow Fe^{2+} + 2e^-$

c $2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2$

d Sulfur dioxide is used to make sulfuric acid.

11 Charge passed = 3.60×10^4 C; amount of electrons = 0.373 mol; $Al^{3+} + 3e^- \rightarrow Al$; amount of aluminium atoms = 0.124 mol; mass of aluminum = 3.35 g

12 Mass of manganese = [54.94 g mol^{-1} × 0.235 A × (250 × 60) s]/ [(2 × 96 500 C mol^{-1}) = 1.00 g

13 **a** The electrolysis can be carried out at a much lower temperature; its presence lowers the melting point of aluminium oxide (a physical effect).

b $2O^{2-} \rightarrow O_2 + 4e^-$

c Oxygen produced at the anode reacts with the hot carbon electrode to form carbon dioxide: $C + O_2 \rightarrow CO_2$.

d Aluminium oxide (alumina) reacts with sodium hydroxide to form a soluble product (sodium aluminate); basic impurities, such as iron(III) oxide, do not react and dissolve.

e High electrical and thermal conductivity; resistance to corrosion; low density; high tensile strength

f Aluminium has a greater affinity for oxygen compared to carbon / aluminium is more reactive than carbon / higher up the reactivity or activity series

14 A homogeneous mixture of metals, or of a metal and a non-metal (for example carbon).

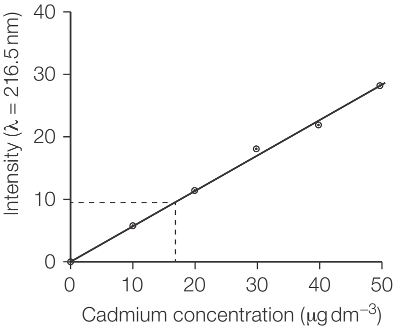
15 When these two metals form alloys with each other, the metallic bonding is weakened because of their slightly different atomic and ionic radii and different ionization energies. This weaker metallic bonding means that the melting points of the alloys are lower than those of the pure metals.

16 FeO, paramagnetic; unpaired electrons present, so magnetic moments do not cancel out; ZnO; diamagnetic; no unpaired electrons / all electrons are paired, so magnetic moments cancel out

17 The purpose of the plasma in ICP-OES is to atomize the sample and produce excited state atoms.

18 It has a dual role of aerosol generation and droplet selection.

19 a



b cadmium concentration = 17.0 ppb ($\mu g\,dm^{-3}$)

20 a It is a heterogeneous catalyst: the reactants (gas) are in a different physical state from the catalyst (solid).

b Reactant gas molecules adsorbed onto the catalyst surface; covalent bonds broken in reactants due to interactions with surface; new covalent bonds form; product molecules released / diffuse away from surface.

c Lead particles are irreversibly adsorbed onto surface and occupy active sites, instead of reactant molecules.

21 Pores / cavities / channels / holes / cage-like structures in zeolites have specific fixed shape / fixed size or act as molecular sieves; only reactants with appropriate size / geometry fit inside and are activated / reacted.

22 Rapid uptake by living organisms, unknown distribution pathways, unknown interactions with living organisms, high reactivity, ability to penetrate cells and rapidly spread in the body including along nerve cells.

23

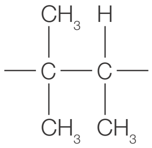
	Crystalline solid	Nematic phase liquid crystal	Pure liquid
Positional order of particles	Yes	No	No
Directional order of particles	Yes	Yes	No

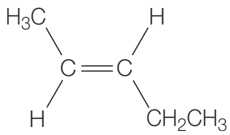
24 The nitrile (cyanide) functional group –CN group make the molecule polar; the alignment/ orientation of molecules can be controlled by electric field / voltage is applied across a sample of molecules. A liquid crystal is thermotropic if the order of its components is determined or changed by temperature.

25 Liquid crystal molecules work over a limited temperature range; ability of liquid crystal molecules to transmit light depends on molecular orientation of polar liquid crystal molecules controlled by applying voltage (electric field) across a small section; areas of the material / display that are dark and light can be controlled.

26 Isotatic and atactic / isotactic – chains exhibit greater stereoregularity ('more regular'); chains pack together more effectively; stronger attractive forces operating between chains; chains do not move past each other easily, so the fibre is stronger.

27 Addition polymerization





28 The orientation of the monomer units along the chain (head-to-tail, head-to-head, random) and the orientation of the methyl groups with respect to the polymer backbone (tacticity).

29 Thermosets are more rigid, brittle, capable of operating at higher temperatures, and cannot be re-melted.

30 LDPE has a branched structure and is amorphous. HDPE is linear and highly crystalline. These differences account for HDPE having higher density, stiffness and melting point.

31 Plasticizer molecules fit between the PVC chains / plasticizer molecules prevent chains from forming crystalline regions (crystallites) / plasticizer molecules keeps PVC strands / chains / PVC molecules separated / plasticizer molecules increase space / volume / distance between PVC chains; weakens intermolecular / dipole–dipole / London / dispersion / instantaneous induced dipole–induced dipole / van der Waals.

32 Polar C–Cl bonds in PVC leading to formation of dipole–dipole forces; stronger intermolecular forces (than weaker London (dispersion) forces in polythene)

33 Iron does not rust / undergo corrosion

low density; thermal insulator / poor conductor of heat (thermal energy); electrical insulator / poor conductor of electricity

(wood) easily moulded or decomposed; non-biodegradable / does not rot; low density

34 The main cylinder is made only from hexagons of sp^2 hybridized carbon atoms (graphene), with pentagons required to close the structure at the ends; single- or multiple-walled tubes made from concentric carbon nanotubes can be formed; bundles of the aligned nanotubes have high tensile strength; other substances (elements, small molecules, metal oxides, etc.) can be inserted inside the nanotubes; strong two-dimensional covalent bonding / no weak bonds; the behaviour of the delocalized π electrons depends on the length, diameter and arrangement of hexagons of a nanotube and hence some forms are metallic conductors and some are semiconductors.

35 iron (clusters) or iron(0) pentacarbonyl / $Fe(CO)_5$; high temperature (1050 °C); high pressure (30–100 atm); single-walled carbon nanotubes

36 possible toxicity of the cores of small airborne particles; unknown long-term health effects; small particle size and hence large surface area may increase reactions rates; immune system / allergy concerns; uncertain impact on the environment

37 Complete combustion of substances of PVC needs a very high temperature to vaporize them into a gas and overcome surface area limitations; relatively large amounts of air and hence oxygen are required; many fires take place in closed houses. PVC will decompose before melting and release hydrogen chloride.

38 $C_2H_3Cl + 2\frac{1}{2}O_2 \rightarrow 2CO_2 + H_2O + HCl$ or

$2C_2H_3Cl + 5O_2 \rightarrow 4CO_2 + 2H_2O + 2HCl$

HCl is produced when PVC is thermally decomposed; HCl is toxic and acidic in the presence of water when hydrochloric acid is formed; no toxic products when polyethene is combusted.

39 Phthalates are highly lipophilic (fat soluble and non-polar). When used in PVC plastic, DEHP is weakly interacting with the PVC chains and readily leaches into blood or other lipid-containing solutions in contact with the plastic. It is chemically stable and accumulates within the body.

40 Collisions between the delocalized valence electrons and positive ions (cations) in the lattice. Collisions with impurities present in the metal also contribute to resistance.

41 The loss of magnetism that a superconductor displays when cooled to its transition temperature in a magnetic field; the magnetic flux is excluded when it is in a superconducting state, except for a thin layer at the surface.

42 $Y_2O_3 + 4BaO + 6CuO \rightarrow 2YBa_2Cu_3O_{6.5}$

43 perovskite; type 2 superconductor

44 They have opposite spins and opposite momenta.

45 Mercury is a superconductor; passing electrons deform the mercury lattice / displace positive ions / cations and couple / form Cooper pairs / condense with other electrons; energy propagates along the mercury lattice as waves (phonons); Cooper pair / electron condensate moves through lattice freely; phonons (vibrational quanta) are perfectly elastic / cause no energy loss / transfer.

46 a $d = n\lambda/2 \sin\theta = (1 \times 154\,\text{pm})/(2 \sin (10.91°)) = 407\,\text{pm}$

b $d = \lambda/2 \sin$; $(1 \times 154\,\text{pm})/(2 \sin 14.22) = 313\,\text{pm} = 3.13 \times 10^{-10}\,\text{m}$

47 monochromatic X-rays / X-rays of known frequency / wavelength / energy single crystal / powder; sample rotated; X-rays diffracted by electrons in samples atoms; detected / recorded on (photographic) film

48 a For a body-centred cubic lattice with one atom per lattice point, there are two atoms per unit cell.

b For this type of lattice the atoms are in contact along a body diagonal and $4r = a\sqrt{2}$, where r is the metallic radius and a is the edge length of the cell. Thus, $r = 0.433a = 0.433 \times 343\,\text{pm} = 149\,\text{pm}$.

49 There are 4 uranium ions and 8 oxide ions per unit cell, and a U:O ratio of 4:8. The chemical formula is therefore UO_2.

50 Determine the volume of the unit cell (in cm³).

Volume = $l^3 = (4.09 \times 10^{-10}\,\text{m} \times 1\,\text{cm}/10^{-2})^3 = 6.842 \times 10^{-2}\,\text{cm}^3$

Determine the mass of the unit cell (in g).

Mass of unit cell = $10.5\,\text{g}\,\text{cm}^{-3} \times 6.842 \times 10^{-23}\,\text{cm}^3 = 7.184 \times 10^{-22}\,\text{g}$

Deduce the number of atoms per unit cell.

4 atoms.

Determine the molar mass of X and the identify of X.

$(7.184 \times 10^{-22}\,\text{g}/ 4\ \text{atoms}) = (1.796 \times 10^{-22}\,\text{g/atom}) \times 6.02 \times 10^{23}\ \text{atoms} = 108\,\text{g}\,\text{mol}^{-1}$; X is silver.

51 Cubic closest packed structures have an *abcabc* . . . pattern, and hexagonal closest packed structures have an *abab*… pattern.

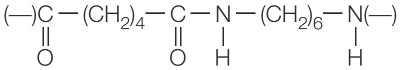
52 Volume of silver unit cell = $(408.7\,\text{pm})^3 = 6.83 \times 10^{-23}\,\text{cm}^3$

Mass of 4 Ag atoms = $107.87\,\text{g}\,\text{mol}^{-1}/6.02 \times 10^{23}\,\text{mol}^{-1} = 7.167 \times 10^{-22}\,\text{g}$; density $= 7.167 \times 10^{-22}\,\text{g}/6.83 \times 10^{-23}\,\text{cm}^3 = 10.5\,\text{g}\,\text{cm}^{-3}$

53 The rock salt (NaCl) structure has coordination number = 6, while the CsCl has coordination number = 8.

54 Perovskite = 1 × Ti = Ti at centre; 8 Ca × 1/8th = 1 Ca; 6O × ½ = 3 O. Thus $CaTiO_3$.

55 hexane-1,6-diamine or 1,6-diaminohexane or 1,6 hexan(e)diamine

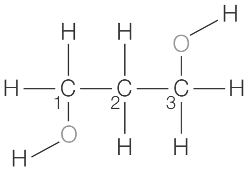


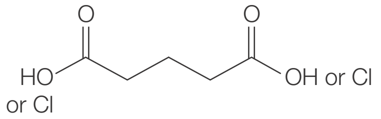
$(-)\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-(CH_2)_6-\underset{\underset{H}{|}}{N}(-)$

56 Addition polymerization: unsaturated monomers containing >C=C< monomers with reactive π bonds that add together without elimination / removal of any atoms (to form an addition polymer)

Condensation polymerization: monomers have two reactive functional groups / are bifunctional and produce a larger molecule with elimination / removal of a smaller molecule, such as water or hydrogen chloride.

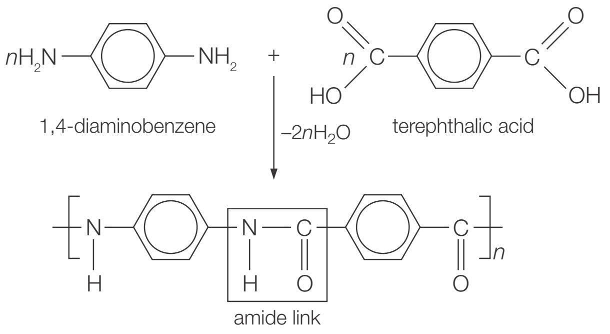
57





Condensation polymerization

58 polyester: terylene / PET; polyamide: Kevlar (or aromatic nylon); hydrogen bonding in second polymer between amide linkages; stronger than dipole–dipole forces in the first polymer



59 a bullet-proof vests and cords to reinforce the walls of car tyres

b Hydrogen bonds form between adjacent chains from –NH– of one chain to >C=O of the next chain, which were aligned into a crystalline fibre.

60 a The –NH– groups are protonated; disrupting the hydrogen bonds between adjacent Kevlar chain; there is flexibility in the carbon chain in nylon, but not in the benzene ring in Kevlar.

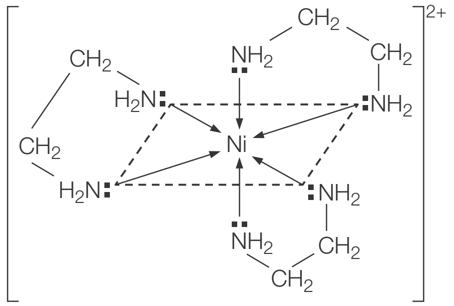
b The fibres of nylon can be stretched more easily without breaking bonds; it will therefore be more elastic.

61 Polyamide link can be hydrolysed; polyalkenes cannot be hydrolysed.

OH^- attacks polyamide link or electron deficient $C^{\delta+}$; poly(ethene) is non-polar

62 Adsorption is the physical interaction between heavy metal ions and an inert solid surface (for example, a zeolite or carbon) and the removal of the ions from solution.
Chelation is the reaction between a heavy metal ion and a multidentate ligand (chelating agent) to form an insoluble complex.

63



64 $AlPO_4 \rightleftharpoons Al^{3+}(aq) + PO_4^{3-}(aq)$ $K_{sp} = [Al^{3+}][PO_4^{3-}]$

$BaSO_4 \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$CdS \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$ $K_{sp} = [Cd^{2+}][S^{2-}]$

65 The K_{sp} expression is: $K_{sp} = [Ce^{4+}][IO_3^-]^4$

There is a 1:4 ratio between the concentrations of the cerium(IV) ion and the iodate(V) ion. There is a 1:1 ratio between the molar solubility and the cerium(IV) ion's concentration. Therefore: $K_{sp} = (1.80 \times 10^{-4})\,(7.20 \times 10^{-4})^4 = 4.84 \times 10^{-17}$

66 The K_{sp} expression is: $K_{sp} = [Mg^{2+}]^3\,[PO_4^{3-}]^2$. There is a 3:1 ratio between the concentration of the magnesium ion and the molar solubility of the magnesium phosphate. There is a 2:1 ratio between the concentration of the phosphate ion and the molar solubility of the magnesium phosphate. Therefore: $K_{sp} = (1.071 \times 10^{-5})^3\,(7.14 \times 10^{-6})^2 = 6.26 \times 10^{-26}$.

67 Convert to grams per 1000 cm³, then moles per cubic decimetre:

$2.97 \times 10^{-10}\,\text{g}/100\,\text{cm}^3 \times (10/10) = 2.97 \times 10^{-9}\,\text{g}/1000\,\text{cm}^3$

$2.97 \times 10^{-9}\,\text{g}\,\text{dm}^{-3}$ divided by $90.77\,\text{g}\,\text{mol}^{-1} = 3.27 \times 10^{-11}\,\text{mol}\,\text{dm}^{-3}$

When NiS dissolves, it dissociates: $NiS\ (s) \rightleftharpoons Ni^{2+}\ (aq) + S^{2-}\ (aq)$

The K_{sp} expression is: $K_{sp} = [Ni^{2+}]\,[S^{2-}]$

There is a 1:1 ratio between NiS and Ni^{2+} and there is a 1:1 ratio between NiS and S^{2-}. This means that, when 3.27×10^{-11} mole per cubic decimetre of NiS dissolves, it produces 3.27×10^{-11} moles per cubic decimetre of Ni^{2+} and 3.27×10^{-11} moles per decimetre of S^{2-} in solution.

$K_{sp} = (3.27 \times 10^{-11})\,(3.27 \times 10^{-11}) = 1.07 \times 10^{21}$

68 EDTA is a chelating (multidentate) ligand that forms very stable complexes by bonding its six Lewis base groups to a cation. The Cu^{2+} in a solution containing EDTA is not toxic to phytoplankton because the Cu^{2+} ion is fully complexed by the EDTA molecule.

69 $Fe^{3+} + \bullet O_2^- \rightarrow Fe^{2+} + O_2$; $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$

Topic 23 Option B Biochemistry

Quick check questions

1 Catabolism – the breakdown of complex molecules into simpler molecules; with the release of energy

Anabolism – the synthesis of more complex molecules from simpler precursor molecules - requiring energy

Photosynthesis – catabolic

Respiration – anabolic

2 a ethanol and carbon dioxide

b lactic acid

3 $2C_3H_8O_3 + 7O_2 \rightarrow 6CO_2 + 8H_2O$

$2C_{18}H_{34}O_2 + 51O_2 \rightarrow 36CO_2 + 34H_2O$

4 $2H_2O_2\ (aq) \rightarrow 2H_2O\ (l) + O_2\ (g)$; catabolic; since it involves the decomposition of one molecule into two smaller molecules

5 $3C_6H_{12}O_6 \rightarrow C_{18}H_{32}O_{16} + 2H_2O$

By boiling with dilute aqueous acid; or reacting with the appropriate enzyme

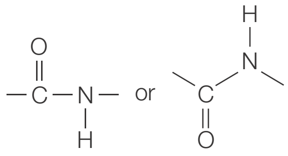
6 a Alanine is in the zwitterion form in the solid state ($^+H_3NCH(CH_3)COO^-$) and is therefore essentially an ionic solid with relatively strong electrostatic forces between the ionic forms.

b At around neutral pH alanine is in the zwitterionic form and is soluble in a polar solvent such as water.

7 a the amino group, NH_2

b a peptide bond / amide link

c



d hydrogen bonding between peptide link regions of the backbone of the protein chain

e **secondary:** folding of backbone of the chain into α-helix and/or β-pleated sheet

tertiary: folding of the polypeptide chain involving non-covalent interactions between the R-groups of the amino acid residues

quaternary: folding and assembly of multiple subunits of a protein

8 a $H_2NCHRCOOH$

b Ala-Gly and Gly-Ala

$H_2NCH(CH_3)CONHCH_2COOH$ and $H_2NCH_2CONHCH(CH_3)COOH$

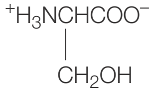
water (H_2O)

c six

9 a concentrated HCl(aq); heat in a sealed tube for 6 hours (or overnight) the peptide bonds (amide links) are hydrolysed

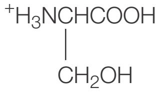
b A buffer solution is used as the electrolyte in electrophoresis. The amino acid molecules are charged and move in an applied electric field, and separate predominantly according to the charge on the molecules. The net charge on the amino acid depends on the pH of the buffer. An amino acid will be positively charged if the pH of the running buffer is below its isoelectric point, and negatively charged if the pH is above its isoelectric point.

10



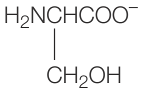
$^{+}H_3NCH(CH_2OH)COO^{-}$

in the solid state and in solution at pH 5.7



$^{+}H_3NCH(CH_2OH)COOH$

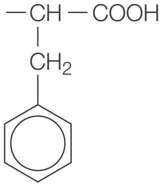
at pH 1



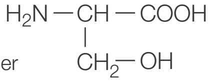
$H_2NCH(CH_2OH)COO^{-}$

at pH 14

11 Look closely at the R-groups along the chain; the sequence is Phe-Ser-His-Ala

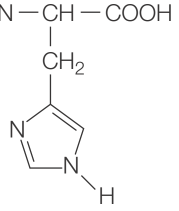


Phe

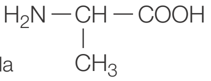


Ser

$H_2N-CH(CH_2-OH)-COOH$



His



Ala

$H_2N-CH(CH_3)-COOH$

12 see Figure 23.22

13 Maintain internal / core body temperature / thermal insulation (around organs and under the skin); energy / respiratory source (during starvation); to transport and store fat-soluble vitamins (A, D, E and K); phospholipids in cell membranes; maintain skin and hair

14 a 57 carbon atoms

b mol iodine = 7.61 / 253.8 = 0.03 mol

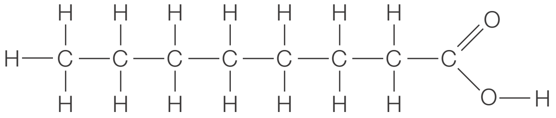
molar ratio iodine : oil = 0.03:0.01 = 3:1

An average of **three C = C double bonds** in a molecule of the oil.

15 a $CH_2OH–CHOH–CH_2OH$

b carboxyl group; –COOH

$CH_3(CH_2)_6COOH$



c Saturated fatty acids contain only carbon–carbon single bonds in the chain; unsaturated fatty acids contain at least one carbon–carbon double bond in the chain.

d Degree of unsaturation is determined by finding the iodine number of the oil or fat / the fat or oil is reacted with a solution of iodine in a non-polar solvent (ethanol, for example) of known concentration / the iodine number is the mass of iodine reacting with 100 g of the fat or oil.

16 a Mol iodine reacting = $0.5 \times 19 / 1000 = 9.5 \times 10^{-3}$ mol

Mass of iodine = $9.5 \times 10^{-3} \times 253.8 = 2.41$ g

Iodine number = $(100 / 25) \times 2.41 = 96.4$

b Mol vegetable oil = $2.5 / 865 = 2.89 \times 10^{-3}$ mol

Molar ratio of iodine : oil (to nearest whole number) = 3:1

An average of **three C=C double bonds** in a molecule of the oil.

c The vegetable oil will contain a mixture of different long-chain acid molecules

17 a i stearic acid

ii oleic acid

b i To prevent the chocolate manufactured melting too readily in the hotter climate.

ii They are likely to be made of longer chains and have a higher proportion of saturated fats.

18 a soya bean oil, highest proportion of unsaturated fats and with a high proportion of linoleic acid

b soya bean oil: 6.1 / olive oil: 5.7 / beef fat: 0.69

c soya bean oil, highest proportion of unsaturated fats

19 a an alkenyl group and a ketone carbonyl group

b the four fused rings of the steroid ‘nucleus’

c Such steroids have medical uses in the treatment of growth disorders and muscle wasting conditions / their production has medical benefit.

20 ketone = **B**; aldehyde = **A** and **C**; triose = **C**; pentose = **A**; hexose = **B**

21 a Both contain just carbon, hydrogen and oxygen and have the general formula $C_x(H_2O)_y$.

b **P** is an aldose (has an aldehyde group); **Q** is a ketose (has a ketone group).

22 a $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

b M_r glucose = 180.18 g mol^{-1}

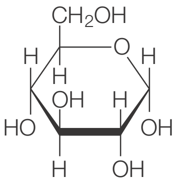
amount of glucose = 15.0 / 180.18 = 0.083 mol

energy produced = $0.083 \times 2803 = 233$ kJ

23 a α-1,4 and α-1,6 glycosidic links

b hydrolysis

c α-glucose

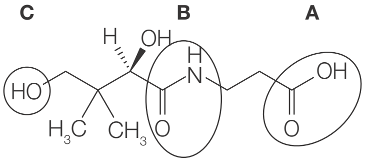


d amylopectin

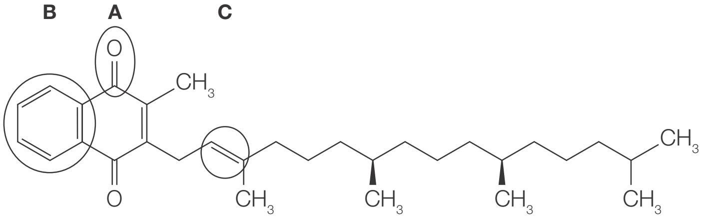
e The polymer contains many glucose molecules which are not able to react while they are 'stored' in the polymer, whereas the monomer is readily able to react.

24 Starch contains α-glycosidic links which enzymes present in humans are able to hydrolyse – hence starch is a useful dietary source of energy; cellulose contains β-glycosidic links and humans do not have enzymes capable of hydrolysing such bonds. Cellulose is useful in human diet as 'dietary fibre'.

25 a i X



ii Y



b X is water-soluble; Y is fat-soluble

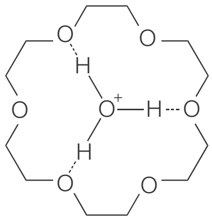
26 Vitamin C undergoes oxidation in the air, and it is soluble in water where it undergoes oxidation and hydrolysis.

27 a A vitamin is an organic compound and a vital nutrient that an organism requires in limited amounts.

b It is fat soluble because of the presence of a long hydrophobic alkyl chain and a benzene ring.

c The process of adding vitamin K to foods to increase its content.

28 The oxonium ion fits into the crown ether interior and the attractive interactions are maximised.



29 a heating, dissolving in water, lowering the pressure

b The atoms are too small to interact strongly and they escape as gas.

c London (dispersion) forces

30 **advantage:** the packaging is biodegradable / the packaging is made from a renewable resource

disadvantage: the packaging is not chemically resistant / packaging is relatively fragile

31 a Atom economy = (total mass of desired product formed / total mass of all products) × 100

Method 1: atom economy = (120.16 / 620.49) × 100 = 19.4%

Method 2: atom economy = (120.16 / 138.18) × 100 = 86.9%

b Consider: the use of highly corrosive chemicals such as sulfuric acid or the ease of availability of any catalyst.

32 Enzymes lower the activation barrier of the reaction.

The free-energy difference between the initial and the final states is not affected.

The energy source is the binding energy, i.e. the energy released from enzyme-substrate interactions.

33 a The presence of an enzyme behaves as a catalyst in providing an alternative reaction pathway – via the ES intermediate – that has a lower activation energy than the uncatalysed reaction.

The substrate binds to the enzyme at the active site and the interactions between the enzyme and substrate facilitate the chemical reaction(s) that need to take place – mention the 'lock and key' and/or induced-fit hypothesis.

b **Competitive inhibition:** the inhibitor (resembles the substrate in shape) competes with the substrate for active sites on the enzyme thus slowing the rate of reaction / the rate will eventually reach the same plateau value (V_{max}) as that achieved without inhibitor.

Non-competitive inhibition: the inhibitor binds to a site on the enzyme other than the active site, altering the conformation of the enzyme and reducing its activity / the rate will not reach the same plateau value (V_{max}) as the uninhibited enzyme.

34 a $K_a = 1.74 \times 10^{-5} = 0.250 \times [H^+] / 0.200$

$[H^+] = (1.74 \times 10^{-5}) \times 0.200 / 0.250 = 1.39 \times 10^{-5}$

$pH = -\log_{10}(1.39 \times 10^{-5}) = \mathbf{4.86}$

b $pH = pK_a + \log_{10}([base]/[acid]) = 7.21 + \log_{10}(0.045/0.055)$

$pH = 7.21 - 0.09 = \mathbf{7.12}$

c $pH = pK_a + \log_{10}([base]/[acid]) = 8.30 + \log_{10}(0.750/0.650)$

$pH = 8.30 + 0.06 = \mathbf{8.36}$

35 $pH = pK_{a2} + \log([anionic\ form]/[zwitterion])$

$pH = 9.1 + \log(0.2/0.8) = 9.1 + \log 0.25$

$pH = 9.1 + (-0.6) = \mathbf{8.5}$

36 a Concentration = $A/\varepsilon = 0.31/500 = 6.4 \times 10^{-4}\ mol\ dm^{-3}$

b Concentration $A/\varepsilon = 0.23/63.5 = 3.6 \times 10^{-3}\ mol\ dm^{-3}$

37 The phosphate groups of the backbone of the DNA molecule are negatively charged.

38 a Hydrogen bonds play a part in the recognition of the possible base pairs that can form / A always pairs with T, and G with C / AT pairing involves two hydrogen bonds whereas GC pairing involves three.

b After replication the daughter molecules contain one parent strand and one new strand / each new molecule contains one old strand and one new strand.

c **i** hydrogen bonding (and London forces referred to as 'base stacking')

ii phosphodiester links

39 a RNA contains the sugar, ribose / DNA the sugar, deoxyribose

RNA contains the base, uracil / DNA contains thymine

(RNA is single stranded / DNA is double stranded)

b i purine: adenine or guanine

pyrimidine: cytosine or thymine

ii I is a purine (with two rings); II is a pyrimidine (with one ring).

40 a The position of the phosphate groups on the inside of the structure would have led to the chains repelling each other as under cellular conditions the phosphate groups would carry negative charges.

b The hydrogen bonds between the nitrogenous bases in the two chains break so that the chains can part.

41 Separate red blood cell DNA from other material (by centrifugation).

Cut DNA up (using restriction enzymes).

Separate DNA fragments by gel electrophoresis.

Method of detection (e.g. UV, radioactive probe, X-ray (autoradiograph)).

42 a i an RNA virus / the structure contains the base, U (uracil), not T (thymine)

ii single-stranded / the % composition of the bases in the structure do not correspond to those expected for a double helical structure: $A \neq U$ and $G \neq C$

b 5′ ACUGUGCGACAGU 3′

Since the sequence is a palindrome, it will form a double-strand RNA hairpin structure.

43 a A food from an animal or plant in which the DNA / genetic material has been altered by artificial means.

Foods where biotechnology has been used to modify the plants used in food production. Inter-species DNA transfer has been used and a wide range of genetically modified foods, GM foods, are possible. The genetic modification may have been used to add a gene to yield a new product, inactivate a gene to remove an undesired property or modify a gene for higher yields of its protein.

b From the following lists

Benefits of GM foods:

- longer shelf-life
- improved flavour, texture and nutritional value
- increased resistance to diseases and pests, reducing the use of pesticides
- produce a supply of substances such as vitamins and vaccines
- increased crop yields
- tolerance of a wider range of growing conditions, such as drought resistance.

Concerns:

- lack of information about long-term effects
- changes to the natural ecosystem through cross-pollination
- possible links to increased allergies
- risk of altering natural composition of food
- concerns of breeding species that are resistant to control
- escape of modified genes into the environment; potential harm to natural ecosystem.

44 Bromine, Br_2, reacts with the double bonds / the number of double bonds in the conjugated system decreases as the bromine reacts / the absorbed energy shifts towards the violet end of the spectrum / a higher energy in the visible region is absorbed; resulting in complementary yellow colour.

45 Benzene absorbs strongly in the UV region, but not at all in the visible region. The light absorbed by benzene is lower in energy than the light absorbed by most non-conjugated molecules, but it is still higher in energy than visible light. The degree of conjugation determines the actual energy difference between the ground and excited states. The more highly conjugated the system the lower the energy difference and the lower the required energy of light needed to excite the electrons. Hence the pi transitions for pentacene are in the visible region.

46 a structure involves extensive conjugation

b water soluble since there are several hydroxyl groups (capable of hydrogen bonding) and charged regions of the structure which will interact with the polar solvent, water

47 pH 2 – absorbs in the blue / green region so the solution will be red / orange

pH 11 – absorbs in the red / orange region so solution will be blue / green

48 a increased temperature – less oxygen binds

decreased pH (increased acidity) – less oxygen binds

higher levels of carbon dioxide – less oxygen binds

presence of carbon monoxide – CO binds more strongly, and irreversibly, to hemoglobin instead of oxygen

b Fetal hemoglobin is a different form of hemoglobin only present in the blood of the developing fetus. It has a higher affinity for oxygen than maternal hemoglobin (which replaces it after birth). This adaptation allows the efficient transfer of oxygen from the mother's blood to the fetal blood in the placenta.

49 **A** is D-form / **B** is L-form / **C** is D-form.

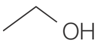
50 a isomerism

b The several hydroxyl groups can all participate in hydrogen bonding with the water molecules.

c **A** is α-glucose as the –OH on carbon-1 is on the opposite side of the plane of the ring to the carbon-6 / **C** is β-glucose.

51 a i $C_{20}H_{28}O$

ii Add the following to end of the molecule; the aldehyde group –CHO is converted to a primary alcohol grouping $-CH_2OH$

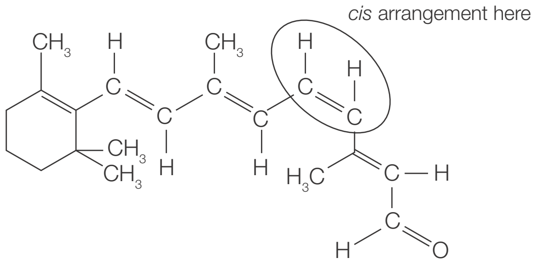


iii A C = C double bond.

iv Heat alcohol with sodium dichromate(IV) / concentrated sulfuric acid in distillation apparatus so that the aldehyde distils over as soon as formed; use an excess of the alcohol to the oxidizing agent.

v 5 mol

b i

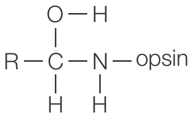


11-*cis*-retinal

ii primary amine group ($-NH_2$)

iii condensation reaction

iv



$$R-\overset{\overset{\large O-H}{|}}{\underset{\underset{\large H}{|}}{C}}-\underset{\underset{\large H}{|}}{N}-\text{opsin}$$

Topic 24 Option C Energy

Quick check questions

1 Specific energy = 7434 kJ mol^{-1} ÷ 156.31 g mol^{-1} = 47.56 kJ g^{-1}

Volume of one mole of undecane = 156.31 g ÷ 0.740 g cm^{-3} = 211.23 cm^3 = 0.2113 dm^3

Energy density = 7434 kJ ÷ 0.2133 dm^3 = 34 852 kJ dm^{-3}

2 a Specific energy = 2021.06 kJ mol^{-1} ÷ 60.11 g mol^{-1} = 33.62 kJ g^{-1}

Volume of one mole of propan-1-ol = 60.11 g ÷ 0.803 g cm^{-3} = 74.86 cm^3 = 0.07486 dm^3

Energy density = 2021.06 kJ ÷ 0.07486 dm^3 = 26997 kJ dm^{-3}

b $2CH_3CH_2CH_2OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)$

3 mol of CO_2 produced per mole of propan-1-ol

3 The amount of carbon dioxide released on complete combustion is equivalent to the amount of carbon dioxide absorbed from the atmosphere by photosynthesis.

4 Different solutions / approaches / statistical data / dependent data, e.g. efficiencies can be compared / combined or best ideas / solution / best practices can be shared to arrive at global / national / local solutions or acceleration of pace or rate of research or discoveries and findings become available to all scientists and engineers or improved confidence in validity / reproducibility of results if many scientists with engineers / research groups are involved in a similar project or money / resources / time is not wasted duplicating work other scientists and engineers have already done

5 a $2C(s) + O_2(g) \rightarrow 2CO(g)$; $S(s) + O_2(g) \rightarrow SO_2(g)$

b Liquid fuel can be pumped; easy to mix with air and react with oxygen; easier to control the rate of combustion.

6 a boil / vaporize the crude oil (petroleum); (vapours / gases) rise up the fractionating column or tower; vapours / gases condense / liquids form at different heights; the heights depend on the boiling points which varies with the size of molecule

b residue / bitumen; refinery gas; gas oil; naphtha

7 In winter more volatile components are incorporated into the petrol, so it vaporizes more readily. However, in hot weather you do not want a large proportion of volatile components. There will be loss of petrol from the petrol tank by evaporation.

8 a calculate the weighted averages of the three components:

$[(90/100) \times 100] + [(5/100) \times 0] + (5/100 \times 114)] = 95.7$; the fuel mixture has an octane rating of about 96

b to increase the octane number; to favour complete combustion and hence release of more heat (thermal energy)

9 a $C_{16}H_{34} \rightarrow C_{11}H_{24} + C_2H_4 + C_3H_6$

b $C_{12}H_{26} \rightarrow C_8H_{18} + C_4H_8$

c $C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$

10 a Catalytic cracking produces a mixture of alkanes and alkenes; hydrocracking produces alkanes only.

b $C_7H_{16} \rightarrow C_7H_{14} \rightarrow C_7H_8 + 4H_2$

11 $2C(s) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g)$ or $3C(s) + 2H_2O(g) \rightarrow CH_4(g) + 2CO(g)$

12 a $9C(s) + 10H_2(g) \rightarrow C_9H_{20}(l)$

b $19H_2(g) + 9CO(g) \rightarrow C_9H_{20}(l) + 9H_2O(l)$

13 4000 tonnes × 0.746 tonne carbon/tonne of coal = 2984 tonnes of carbon
Mass of carbon dioxide = 2984 tonnes of carbon × (44.01 ÷ 12.01) = 10 935 tonnes CO_2/day

14 Gamma, beta and alpha

15 a ${}^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He}$

b ${}^{49}_{21}\text{Sc} \rightarrow {}^{48}_{22}\text{Ti} + {}^{0}_{-1}\text{e} + {}^{1}_{0}\text{n}$

c ${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$

16 a ${}^{1}_{1}\text{H} + {}^{15}_{7}\text{N} \rightarrow {}^{12}_{6}\text{C} + {}^{4}_{2}\text{He} + {}^{0}_{0}\gamma$

b In radioactive decay, there is no bombardment, no collisions; transmutation involves the collision of two particles.

17 The mass defect is the difference between the mass of the nucleus of an isotope and the sum of the masses of the individual nuclear particles that make up that isotope. The binding energy is the energy released when individual nucleons combine to form the nucleus of an isotope.

18 $\Delta m = 8.45946 \times 10^{-26}\,\text{kg} - [(23 \times 1.67262 \times 10^{-27}\,\text{kg}) + (28 \times 1.677493 \times 10^{-27}\,\text{kg}]$

$= -7.737 \times 10^{-28}\,\text{kg}$

$\Delta E = -7.737 \times 10^{-28}\,\text{kg} \times (3.00 \times 10^{8}\,\text{m}\,\text{s}^{-1})^{2}$

$= 6.96 \times 10^{-11}\,\text{J}$

19 Similarity – some mass is converted to energy

Differences – (fission) one heavy / large nucleus / atom becomes two (or more) lighter ones; (fusion) two light nuclei / atoms become one heavier nucleus

20 ${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow {}^{95}_{37}\text{Rb} + {}^{A}_{Z}\text{X} + 3{}^{1}_{0}\text{n}$

Applying the law of conservation of mass, $A = 138$, and applying the law of conservation of charge $Z = 55$. Hence the nuclide is ${}^{138}_{55}\text{Cs}$.

21 $c = f \times \nu$; $3 \times 10^{8}\,\text{m}\,\text{s}^{-1} = f \times 587.562 \times 10^{-9}\,\text{m}$; $\nu = 5.10584 \times 10^{14}\,\text{Hz}$

$E = h\nu$; $E = 6.63 \times 10^{-34}\,\text{J}\,\text{s} \times 5.10584 \times 10^{14}\,\text{Hz} = 3.3852 \times 10^{-19}\,\text{J}$

$E = (3.3852 \times 10^{-19}\,\text{J}/1000) \times 6.02 \times 10^{23}\,\text{mol}^{-1} = 203.6\,\text{kJ}\,\text{mol}^{-1}$

22 $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

chlorophyll in chloroplasts

23 Ethanol may be too volatile to be used on its own in a hot country and the engine may not be 'tuned' to work on pure ethanol; ethanol and the molecules in petrol can interact with each other and there is an increase in entropy upon mixing.

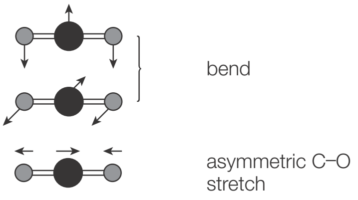
24 0, unsaturated; 1 unsaturated and 2 unsaturated.

25 $CH_3COOCH_3 + HOCH_2(CH_2)_8CH_3$ and $2 \times CH_3COOCH_3 + HOCH_2CH_2OH$

26 methanol or ethanol, concentrated sulfuric acid (H^+) / concentrated sodium hydroxide (or other strong base)

27 $CO_2(g) + H_2O(l) \rightleftharpoons H^+\,(aq) + HCO_3^-(aq)$ or $CO_2(g) \rightleftharpoons CO_2(aq)$ and $CO_2(aq) + H_2O(l) \rightleftharpoons H^+\,(aq) + HCO_3^-(aq)$; with decreasing levels of carbon dioxide the equilibrium will shift to the left and the pH increases.

28



29 lower energy / lower frequency / longer wavelength / infrared radiation reflected from the Earth greenhouse gases absorb / retain / trap this energy as vibrational energy within the bonds of the molecule

30 Voltage is the potential difference between the two electrodes; a measure of the energy carried by each electron.

Power is the total quantity of electricity available; the product of the voltage and current.

Voltage is affected by the materials used to form the electrode.

Power is affected by the quantity of materials used.

31 a $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$;

$PbO_2 + 2H^+ + H_2SO_4 + 2e^- \rightarrow PbSO_4 + 2H_2O$

b positive because reduction occurs / electrons gained; decrease in oxidation number

32 a Cathode: $H^+ (aq) + NiO(OH)(s) + e^- \rightarrow Ni(OH)_2 (aq)$

Anode: $Cd (s) \rightarrow Cd^{2+} (aq) + 2e^-$

b These NiCad cells can be recharged because the products of the discharge half reactions remain in contact with the electrodes in a convertible form.

33 A hybrid vehicle uses a relatively cheap fuel (gasoline or petrol) in the internal combustion engine and has good fuel economy but releases carbon dioxide. A hydrogen fuel-cell vehicle does not release carbon dioxide (the reaction produces water) but requires a more expensive and explosive fuel (hydrogen gas); current battery technologies incorporate materials that are still very expensive and bulky.

34 $E^{\ominus}\text{ cell} = 1.10\,V - \frac{0.0592}{2}\log_{10}\frac{0.050}{5.00} = 1.16\,V$

35 a A concentration cell is one whose emf is generated solely because of a concentration difference. In a standard voltaic cell the emf is generated because of a difference in the reduction potentials of two electrodes.

b +0.0888 V

36 Let the rate of diffusion of oxygen be $r(O_2) = r_1$; the rate of diffusion of the unknown gas $r(x) = 4r$

$$\frac{r(O_2)}{r(x)} = \sqrt{\frac{M(x)}{M(O_2)}}$$

or

$$\frac{r_1}{4r_1} = \sqrt{\frac{M(x)}{32}}$$

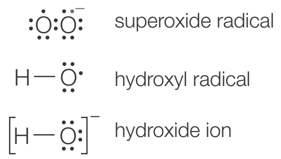
Squaring on both sides,

$$\frac{1}{16} = \frac{M(x)}{32}$$

$$M(x) = \frac{32}{16} = 2$$

Gas is hydrogen, H_2.

37 a



b They both contain an unpaired electron in their outer energy levels.

38 $Al(g) \rightarrow Al^+(g) + e^-$; $Si(g) \rightarrow Si^+(g) + e^-$; aluminium

39 a group 13 element / Ga / In has three outer (valence) electrons; p-type semiconductor / forms electron holes; group 5 element / As / P / Sb has five outer (valence) electrons; n-type semiconductor / forms mobile electrons

b sunlight / photons interacts with the semiconductor surface to release electrons

40 a Light energy excites dye molecules

(excited) dye molecules inject electrons into TiO_2 layer or
dye $\rightarrow$ dye$^+$ + e$^-$

Oxidized dye molecules oxidized / convert I^- to I_3^-; or 2 dye$^+$ + $3I^-$ $\rightarrow$ I_3^- + 2dye, or dye$^+$ + e$^-$ $\rightarrow$ dye and $3I^- \rightarrow I_3^- + 2e^-$

Electrons flow through external circuit back to the counter electrode
Electrons reduce / convert I_3^- ions to I^- (at the counter electrode) or $I_3^- + 2e^- \rightarrow 3I^-$

b Dye-sensitized cells can use light of lower energy / lower frequency / longer wavelength than silicon cells; the advantage of nanoparticles is that they provide a large surface area.

Topic 25 Option D Medicinal chemistry

Quick check questions

1 oral – by mouth / swallowing pills/powders / drinking liquids/mixtures;

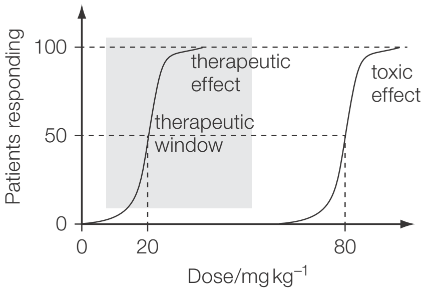
inhalation – administering drugs into respiratory tract / inhaling gases/vapours/sprays/powders;

rectal – introducing drugs into the rectum/colon via the anus / using suppositories/enemas;

transdermal – diffusion through the skin / skin patches / ointments / therapeutic baths

2 drug design / discovery (often from plant extracts) / screening / identifying lead compound / rational drug design process using computer studies of receptor; preparation of analogues through combinatorial chemistry; characterization of the new compound / *in vitro* testing / drug formulation / delivery / stability studies; pre-clinical (toxicology and pharmacokinetics) tests / tests on animals / bacteria / cell cultures / determination of LD_{50} with test animals; clinical tests/tests on humans; determination of ED_{50} to show improvements over existing drugs

3 a Therapeutic index = 80/20 = 4;



b The second drug has a higher therapeutic index hence the probability of toxicity / risk of adverse effects due to over-dosage is not high.

4 a Z; X and Y; X

b the range of dosages between the minimum amounts of the drug that produced the desired effect and a medically adverse effect; a biologically inert substance used as a control when testing a drug clinically

5 a solubility in water

b how easily it is absorbed through the cells / membranes of the intestinal wall; susceptibility to hydrolysis or being broken down by enzymes in the gut and liver and formulation of the tablets.

6 esterification or condensation (addition–elimination)

7 Aspirin prevents the synthesis of enzyme prostaglandin synthase / cyclooxygenase (COX) and hence interferes with the production of prostaglandins (‘local hormones’ / autacoids); this stops the transmission of nerve impulses / action potentials from the site of the injury to the brain.

8 preventing (recurrence of) heart attacks / strokes / reduces blood clotting / thins the blood / anti-inflammatory

9 increases solubility in aqueous solution blood plasma; higher proportion of drug dosage reaches target cells

solubility in water; increases how easily it is absorbed through the cells / membranes of the intestinal wall; though converted back to un-ionized form in the stomach

10 (secondary) amide group / –CONH– / peptide; ring is strained / bond angles less than 109°; ring breaks / hydrolyses easily so (the two fragments similar to cysteine and valine) then bond(s) covalently to the enzyme (*trans* peptidase) that synthesizes the bacterium cell wall (so blocking its action)

11 resistant to penicillinase enzyme / more resistant to bacteria breaking it down / effective against bacteria that are genetically resistant (to penicillin G); resistance to breakdown by stomach acid / hydrochloric acid (so it can be taken orally)

12 irregular / interrupted treatment allows more bacteria to be selected for and survive (and mutate) / failure to complete full course; surviving bacteria develop / pass on genetic resistance to the antibiotic

13 $(CH_3CO)_2O$; CH_3COOH; or CH_3COCl and HCl; or CH_3COOH and H_2O

14 Morphine has two hydroxyl / hydroxyl groups and diamorphine (heroin) has two ester / ethanoate functional groups; morphine is more polar than diamorphine / heroin; diamorphine / heroin crosses the blood–brain barrier more easily due to its lower polarity; morphine is more soluble in blood plasma (aqueous solution) and diamorphine / heroin is more soluble in lipids (lipophilic).

15 increasing amounts / doses needed to produce same effect; increasing amounts cause damage / death

16 Both molecules have a tertiary amine group, a phenylethylamine structure and a benzene ring; they have different shapes and different rigidities.

17 Mass of $Mg(OH)_2$ = 0.960 g; amount $Mg(OH)_2$ = 0.01646 mol; amount of HCl = 0.03292 mol; volume of HCl neutralized = 220 cm^3

18 a ionic and covalent

b kill bacteria / microorganisms; provides an acidic medium so enzymes for digestion can work

c $Mg_2Si_3O_8(s) + 4HCl(aq) \rightarrow 3SiO_2 (s) + 2H_2O(l) + 2MgCl_2(aq)$

The silicon dioxide is inert and dense and will prevent the acid from undergoing reflux.

19 Other factors to consider when deciding an antacid's effectiveness include the neutralizing action of the antacid over a prolonged period (30 minutes or 1 hour, for example), and whether or not the antacid upsets the acid/ion balance in the stomach's gastric juice. The presence and nature of food in the stomach may also affect the neutralization reaction. Furthermore, some brands claim to have a coating action on the stomach wall which might be unrelated to the neutralizing action. There may also be side effects.

20 $HCO_3^-(aq) + H_3O^+(aq) \rightarrow CO_2(g) + 2H_2O(l)$

21 Acid / gastric juice from the stomach rises into the oesophagus and damages the cells.

22 Both compounds relieve symptoms of acid reflux / heartburn / indigestion / both raise the pH of gastric juice; both may cause diarrhoea; omeprazole stops the production of hydrogen ions / protons / hydrochloric acid; inhibits the action of the proton pump; the antacid neutralizes the excess hydrogen ions / protons / hydrochloric acid in the gastric juice; omeprazole takes longer than metal hydroxide-based antacids to provide relief; omeprazole is used to treat gastric ulcers while metal hydroxide-based antacids are not. Omeprazole can prevent long-term damage to the stomach lining and oesophagus from over-production of acid; metal hydroxide based antacids do not. The magnesium ions affect the ionic/electrolyte balance in the body fluids and omeprazole does not.

23 Ranitidine is a competitive, reversible inhibitor of the action of histamine at the histamine H_2 receptors found in gastric parietal cells.

24 a Carbonic acid removes hydroxide ions from an alkali:

$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$;

hydrogen carbonate ion removes protons / hydrogen ions from an acid:

$HCO_3^- + H^+ \rightarrow H_2CO_3$

b $\text{pH} = \text{p}K_a + \log\frac{\text{salt}}{\text{acid}}$ / $7.4 = 6.1 + \log\frac{[\text{hydrogencarbonate}]}{[\text{carbonic acid}]}$;

$\frac{[\text{hydrogencarbonate}]}{[\text{carbonic acid}]} = 10^{1.3} = 20$

Since the concentration of hydrogencarbonate ions is 20 times greater than the carbonic acid concentration, the buffer is better at resisting the effects of acids rather than alkalis.

25 $n(\text{NaOH}) = 20.00\,\text{g} / 40.00\,\text{g mol}^{-1} = 0.500\,\text{mol}$; ratio of HEPES to NaOH is 1:1 $n(\text{HEPES})$ consumed = 0.500 mol; n(anion) = 0.500 mol; n(HEPES) in original solution = 1.00 mol; n(HEPES) left = 0.500 mol; since $[\text{anion}] = [\text{HEPES}]_{\text{remaining}}$; $\text{pH} = \text{p}K_a$; pH = 7.5.

26 To catalyse the formation of double stranded DNA from single stranded viral RNA.

27 block enzyme activity within host cell / block reverse transcriptase;

alter host cell's genetic material;

prevent virus from multiplying / replicating;

alter virus's binding site on cell wall / prevent virus binding with cell wall; prevent virus from entering / leaving cell

28 prevents virus from binding to host cell membrane; prevents the uncoating process (loss of viral capsid) and thus the injecting of genetic material (DNA or RNA) into cell / inhibit activity of enzyme in formation of new viral particles (viruses) / prevents virus from leaving host cell

29 bacteria multiply by cell division / binary fission / (mitosis);

viruses insert DNA / RNA / genetic material into cells;

viruses lack a cellular structure and they can only replicate within the host cell; they mutate at a high rate; antiviral agents must inhibit the host cell without damaging the host cells.

30 HIV virus mutates rapidly; HIV metabolism linked to that of host cell / HIV uses host cell; retroviral drugs harm host cell as well as HIV / difficult to target HIV without damaging host cell.

31 Leads to genetically determined bacterial resistance of antibiotics; antibiotics less effective; increased side effects due to larger doses; proportion of genetically resistant bacteria increases; kill useful / beneficial symbiotic bacteria replaced by more harmful (pathogenic) bacteria; genetically resistance bacteria transfer the genes for resistance to the next generation of bacteria.

32 **a** $2CH_2Cl_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O + 2Cl_2$

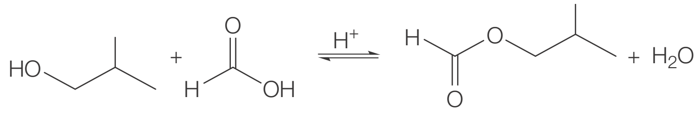
$CH_2Cl_2 + O_2 \rightarrow CO_2 + 2HCl$

b contamination of soil and ground water; stored in body fat and concentrated as they move up food chain; toxic and often carcinogenic

33 low-level waste: short half-life; low activity

high-level waste: long half-life; high activity

34



M_r (alcohol) = 74.0: M_r (methanoic acid) = 46.0; M_r (ester) = 102; M_r (H_2O) = 18.0

$\%\ \text{atom economy} = \frac{102.0}{(74.0 + 46.0)} \times 100\% = 85.0\%$

35 the number of steps in the synthesis; the type of waste (toxicity (if chemical) / half-life activity (if nuclear) produced in the synthesis; the amount of energy needed in the synthesis and the nature of any solvents needed.

36 Less land used; faster due to high rate of bacterial binary fission; simpler extraction process from bacteria; solvents not needed for extraction.

37 Not all pollution may be cleared up; energy will be wasted producing unwanted products; it is better not to produce hazardous materials at all then there is no danger of them entering the environment.

38 Using a catalyst (or more efficient catalyst) may mean that the process can be carried out at a lower temperature, which saves energy. (It may also increase the yield of one product over that of another, unwanted one.)

39 a ovarian, lung and breast cancers

b Production of the drug starts with a compound isolated from a natural source but the rest of the steps in the production of Taxol uses organic chemistry synthesis conversions.

40 This means 50% of rats (in a large test sample) would die if Taxol concentrations in the body tissues were 35.2 mg of Taxol for 1000 g of rat tissue.

41 One enantiomer may have a therapeutic effect; the other enantiomer may have no therapeutic effect or have a harmful effect.

42 A chiral molecule is bonded to a non-chiral starting reagent to produce a chiral intermediate. The presence of the auxiliary follows the reagent in the next stage of the synthesis and forces the reaction to follow a path that produces one of the possible enantiomers. Chemical removal of the chiral auxiliary follows to give a single enantiomer.

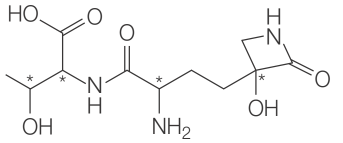
43 cheap to synthesize and readily available in both enantiomeric forms; easily attached; induce stereochemistry; chemically inert; easily removed

44 need a point of attachment (limits structures); need a stoichiometric amount of the chiral auxiliary; extra steps – installation and removal of chiral auxiliary.

45 equimolar mixture of a pair of enantiomers / 50% each of a pair of enantiomers

46 a refluxing of dried plant material; solvent extraction

b



$2^4 = 16$

c polarimeter; pass plane polarized light through a sample; analyser / second polarizer determines the angle of rotation of the plane of polarized light

d each enantiomer will rotate the plane of plane polarized light in opposite directions by the same angle (under the same experimental conditions)

47 a ${}^{60}_{27}\text{Co} \rightarrow {}^{59}_{28}\text{Ni} + {}^{0}_{-1}\text{e} + \gamma$;

b A method for delivering a beam or of high-energy X-rays or ionizing radiation to a patient's tumour. Beams are generated outside the patient and are targeted at the tumour site.

48 the use of a carrier substance used to transport particular radioisotopes directly to cancer cell which are killed by alpha radiation

${}^{225}_{89}\text{Ac} \rightarrow {}^{221}_{87}\text{Fr} + {}^{4}_{2}\text{He}$; short path length and highly ionizing

49 Targeted alpha therapy targets cancer cells by using monoclonal antibodies; monoclonal antibodies can be made to target the cell surface proteins of a specific type of cancer cell and can be labelled with an α-emitting radioisotope; the antibody reaches and interacts with the target cancer cell carrying the α radioisotope with it.

50 Cancer patient given non-radioactive boron-10 atoms (in the form of a compound) at targeted cancer cells; irradiation of patient with a neutron beam from outside the body; boron-10 atoms (in boron compound) capture neutrons to form boron-11 atoms which undergo fission to produce α particles and lithium nuclei.

51 a $^{177}_{71}\text{Lu} \rightarrow ^{177}_{72}\text{Hf} + ^{0}_{-1}\text{e}$; $\lambda = \ln 2/t_{½} = 0.103\ \text{day}^{-1}$; $N/N_0 = e^{-\lambda t} = 0.559$

b mass of lutetium-177 = 0.0559 × 20 = 1.118 mg

52 Strontium has a similar electronic structure to calcium – both have an s^2 valence configuration. The Ca^{2+} and Sr^{2+} ions have the same charges and similar ionic radii.

53 Traditional radiotherapy – healthy tissues receive a similar dose of kinetic energy to cancerous tissues; proton beam therapy – doctors can control the energy distribution of the protons directed and deposited in tissue volumes in a three-dimensional pattern from each beam used. Greater control and precision of the radiation.

54 $^{99}_{42}\text{Mo} \rightarrow ^{99}_{43}\text{Tc} + ^{0}_{-1}\text{e}$

55 Appropriately short half-life allows time for production of nuclide, administration to patient, and for it to accumulate in the tissue of interest. Activity is high enough to give good quality image with small amount of nuclide. It is a gamma emitter – highly penetrating radiation that can be detected outside the body and is not damaging to human tissue as it is non-ionizing. Its chemical properties allow it to be incorporated into molecules that will be absorbed by the organs to be investigated.

56 skin and nail damage; nausea; fatigue; sterility

57 risk versus benefit to the patient and the environment (and society); providing adequate information and informed consent to patients about risks, doses and including likely side effects; security concerns if radioactive material was acquired by terrorists (conventional explosion involving nuclear material); cultural resistance / superstition; lack of education and scientific awareness; potential exposure of health workers and technicians to ionizing radiation; proper training in handling / disposal and storage of radioactive materials not given; proper disposal of radioactive material.

58 a The vapour pressure is the pressure exerted by a vapour (or mixture of vapours) over a liquid when they are in dynamic equilibrium.

b temperature / the composition of the mixture

59 Liquid X will have the higher vapour pressure at 50 °C as it has a lower boiling point than Y. Liquid X is more volatile than liquid Y.

60 $P_A = P°_A \times X_A = P°_A\,(1 - X_B)$

$X_B = (P°_A - P_A)/P°_A = (30 - 28)/30 = 0.067$

61 Only a mixture containing hexane and heptane will obey Raoult's law as the interaction between heptane molecules will be similar to those between hexane molecules.

62 a Ketone (carbonyl), alkenyl and hydroxyl; $C_{18}H_{26}O_2$

b increase in muscle mass, strength and stamina

c The chemicals are extracted from the urine sample then separated into various components by gas chromatography (GC). Each band / component as it leaves the gas chromatography column is passed directly into a mass spectrometer (MS) where it is analysed. The mass spectra obtained are matched with a database to identify the compound.

63 Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Oxidation: $C_2H_5OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$ or $C_2H_5OH + H_2O \rightarrow CH_3CHO + 2H^+ + 2e^-$