

Answers to examination questions in Chapters 1 to 21

1 Stoichiometric relationships

Paper 1

- | | |
|------|------|
| 1 D | 14 A |
| 2 B | 15 D |
| 3 D | 16 C |
| 4 C | 17 B |
| 5 D | 18 D |
| 6 D | 19 A |
| 7 D | 20 B |
| 8 C | 21 B |
| 9 B | 22 D |
| 10 D | 23 A |
| 11 B | 24 D |
| 12 D | 25 A |
| 13 B | 26 D |

Paper 2

- 1 a $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ [2]
 b Carbon dioxide produced = 20 cm^3
 Oxygen remaining = 10 cm^3 [2]
- 2 a $\text{Zn}(\text{s}) + \text{I}_2(\text{s}) \rightarrow \text{ZnI}_2(\text{s})$ [1]
 b Amount of zinc = $\frac{100\text{ g}}{65.37\text{ g mol}^{-1}} = 1.530\text{ mol}$
 Amount of iodine = $\frac{100\text{ g}}{253.8\text{ g mol}^{-1}} = 0.3940\text{ mol}$
 The reacting molar ratio is 1 : 1 therefore the zinc is present in excess. [3]
 c Amount of zinc iodide = amount of iodine used
 Amount of zinc iodide = $\frac{100}{253.8} = 0.3940\text{ mol}$
 Mass of zinc iodide = $\frac{100}{235.8} \times (65.37 + 253.8)$
 = 125.8 g [1]
- 3 a $\frac{V_1}{T_1} = \frac{V_2}{T_2}$; $\frac{955\text{ cm}^3}{278\text{ K}} = \frac{V_2}{303\text{ K}}$; $V_2 = 1041\text{ cm}^3$
 The balloon will burst. [3]
 b The increase in temperature increases the average kinetic energy of the nitrogen molecules and hence increases their average speed. They collide more frequently and energetically with each other and the walls of the balloon. [2]

- 4 a Amount of hydrochloric acid
 = $\frac{13.95\text{ dm}^3}{1000} \times 2.00\text{ mol dm}^{-3} = 0.0279\text{ mol}$ [1]
 b Amount of sodium carbonate in 20.00 cm^3 of solution = 0.01395 mol [1]
 c Concentration of sodium carbonate
 = $\frac{1000\text{ dm}^3}{20} \times 0.01395\text{ mol} = 0.6975\text{ mol}$ [1]
 d Molar mass of hydrated sodium carbonate
 = $\frac{200.00\text{ g}}{0.6975\text{ mol}} = 286.74\text{ g mol}^{-1}$ [1]
 e Molar mass of anhydrous sodium carbonate,
 $\text{Na}_2\text{CO}_3 = (22.99 \times 2) + 12.01 + (3 \times 16.00)$
 = 105.99 g mol^{-1}
 Molar mass of water = $286.74\text{ g mol}^{-1} - 105.99\text{ g mol}^{-1}$
 = 180.75 g mol^{-1}
 Hence, $n = \frac{180.75\text{ g mol}^{-1}}{18.02\text{ g mol}^{-1}} = 10$ [2]
- 5 a $3\text{Ag}^+(\text{aq}) + \text{XO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{XO}_4(\text{s})$ [1]
 b i Amount of silver ions =
 $0.2040\text{ mol dm}^{-3} \times 0.04118\text{ dm}^3 = 8.401 \times 10^{-3}\text{ mol}$ [1]
 ii Amount of $\text{Ag}_3\text{XO}_4 = \frac{1}{3} \times 8.401 \times 10^{-3}\text{ mol}$
 = $2.800 \times 10^{-3}\text{ mol}$ [1]
 iii $2.800 \times 10^{-3}\text{ mol}$ of Ag_3XO_4 weighs 1.172 g .
 Hence one mole weighs
 $\frac{1.172\text{ g}}{2.800 \times 10^{-3}\text{ mol}} = 418.6\text{ g mol}^{-1}$ [2]
 iv $(3 \times 107.87) + X + 4(16.0) = 418.6$;
 hence $X = 30.99$ and X is phosphorus (P). [2]
- 6 $11\text{ mg} \times \frac{(1\text{ g})}{(1000\text{ mg})} = 0.0011\text{ g}$
 $\text{ppm} = \frac{\text{mass of solute (g)}}{\text{mass of solvent and solute (g)}} \times 10^6\text{ ppm}$
 = $\frac{0.011\text{ g}}{(2000\text{ g} + 0.011\text{ g})} \times 10^6\text{ ppm/1} = 5.5\text{ ppm}$ [2]
- 7 $\text{IO}_3^-(\text{aq}) + 5\text{I}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{I}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$
 Amount of $\text{KIO}_3/\text{IO}_3^- = \frac{0.6125\text{ g}}{214.00\text{ g mol}^{-1}} = 0.00286\text{ mol}$
 in 250 cm^3
 Amount of $\text{KIO}_3/\text{IO}_3^-$ in $25.00\text{ cm}^3 = 0.000286\text{ mol}$
 Amount of $\text{I}_2 = 8.58 \times 10^{-4}\text{ mol}$
 $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$
 Amount of $\text{S}_2\text{O}_3^{2-}(\text{aq}) = 1.716 \times 10^{-3}\text{ mol}$ in 24.50 cm^3
 Concentration of $\text{Na}_2\text{S}_2\text{O}_3 = \frac{1000 \times 1.716 \times 10^{-3}}{24.50}$
 = 0.07 mol dm^{-3}

2 Atomic structure

Paper 1

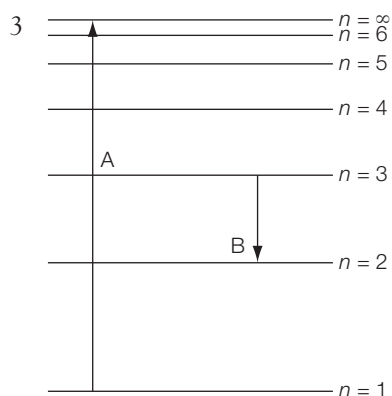
- | | |
|------|------|
| 1 D | 12 B |
| 2 C | 13 D |
| 3 A | 14 D |
| 4 D | 15 D |
| 5 C | 16 A |
| 6 D | 17 A |
| 7 C | 18 B |
| 8 A | 19 A |
| 9 C | 20 D |
| 10 C | 21 C |
| 11 A | 22 A |

Paper 2

1 a [3]

	An atom of ^{79}Br	An ion of $^{81}\text{Br}^-$
Protons	35	35
Neutrons	44	46
Electrons	35	36

- b ^{79}Br because its relative isotopic mass is closer to 79.90. [1]
- 2 a Atoms of the same element but with different mass numbers and hence different number of neutrons. [1]
- b 47 protons, 46 electrons and 60 neutrons. [2]
- c Carbon-12 (^{12}C). [1]



- a Line starting at $n = 1$;
Line finishing at $n = \infty$ (not above ∞);
Upward arrow [2]
- b Line from $n = 3$ to $n = 2$;
Arrow pointing downward (in any transition) [2]
- 4 The emission spectrum consist of a series of sharp or discrete coloured lines on a black background. [1]
- The lines converge together at high energy (high frequency). The lines are generated when excited

electrons move from high energy levels to lower energy levels. Light of a particular frequency is released during this process. [2]

- 5 a Weighted average mass of naturally occurring isotopes of an element compared to $\frac{1}{12}\text{g}$ of carbon-12. [1]
- b Diagram of mass spectrometer containing in the correct sequence:
vaporization/vaporized sample;
ionization/electron gun;
acceleration/oppositely charged plates;
deflection/magnetic field;
detection [5]
- c $63x + 65(1 - x) = 63.55$
 $^{63}\text{Cu} = 72.5\%$ and $^{65}\text{Cu} = 27.5\%$ [2]
- d Cobalt-60 (^{60}Co), iodine-131 (^{131}I) or iodine-125 (^{125}I) [1]

3 Periodicity

Paper 1

- | | |
|------|------|
| 1 A | 13 C |
| 2 D | 14 A |
| 3 A | 15 B |
| 4 C | 16 B |
| 5 C | 17 D |
| 6 B | 18 D |
| 7 B | 19 B |
| 8 A | 20 C |
| 9 A | 21 B |
| 10 A | 22 B |
| 11 C | 23 C |
| 12 C | 24 D |

Paper 2

- 1 a i The minimum energy required for the removal of a mole of electrons from a mole of gaseous atoms to form a mole of unipositive gaseous ions. [2]
- ii $\text{Al(g)} \rightarrow \text{Al}^+(\text{g}) + \text{e}^-$ [1]
- b The magnesium atom has a greater nuclear charge due a higher number of protons. Consequently, the atomic radius is smaller and there is a stronger attraction for the electrons by the nucleus. [3]
- c $2\text{Li(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{LiOH(aq)} + \text{H}_2(\text{g})$

There will be effervescence: release of gas at the surface. Bubbles of a colourless gas will be observed. The lithium moves around the surface and is converted into a soluble product. Heat and sound energy are released. [3]

- 2 a i The bromine atom has a greater number of protons and hence a greater nuclear charge: 35+ versus 34+. Hence the outer or valence electrons are attracted more strongly. The bromide ion is formed by the addition of one electron to the bromine atom; the selenide ion is formed by the addition of two electrons to the selenium atom. The additional electrons cause electron-electron repulsion which increase radii. The effect is highest in the selenide ion. [2]
- ii The electronegativity is the ability of atom to attract a bonding pair of electrons in a covalent bond. Fluorine has a smaller radius and hence the electrons are closer to a nucleus in a lower energy level. The electrons are repelled by fewer inner electrons and there is a decreased shielding effect. [3]
- b i Brown solution formed; $\text{Cl}_2 + 2\text{KI} \rightarrow \text{I}_2 + 2\text{KCl}$; $\text{Cl}_2 + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{Cl}^-$ [2]
- ii A cream or off-white precipitate (solid) is formed: $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$ [2]
- c The reaction in (i) is redox. The chlorine is reduced/gains electrons/decreases its oxidation number. The iodide ion is oxidized/loses electrons/increases its oxidation number. [4]
- The reaction in (ii) is not redox. There is no electron transfer/change in oxidation number.
- 3 a The size of an atom is determined by the attraction of the nucleus for electrons and the shielding of outer electrons from the nucleus by inner shells of electrons. [3]
- b i This is because the sodium ion, Na^+ , has one less shell of electrons compared to the sodium atom. Consequently, there is a decrease in shielding and an increase in the nuclear charge experienced by each electron. [2]
- ii This is because with increasing proton number, each successive positive ion contains an additional shell of electrons. The additional screening or shielding effect outweighs the effect of increased nuclear charge. [2]
- c The magnesium ion has 12 protons and 10 electrons; the sodium ion has 11 protons and 10 electrons. The nuclear charge of the magnesium ion (+12) is greater than the sodium ion (+11). Consequently, all the electrons in the magnesium ion will experience a greater force and be located nearer to the nucleus. [2]
- d i $\text{N} < \text{N}^{3-}$ [1]
- ii $\text{Fe}^{3+} < \text{Fe}^{2+} < \text{Fe}$ [1]

- 4 The ions formed across period 3 would be Na^+ , Mg^{2+} , Al^{3+} and P^{3-} , S^{2-} and Cl^- .

There is a decrease in ionic radii from Na^+ to Al^{3+} : all the ions have the electron arrangement of 2, 8 (i.e. they are isoelectronic); however, there is a progressive increase in the nuclear charge due to the additional protons: the sodium ion has 11 protons, the magnesium ion has 12 protons and the aluminium ion has 13 protons. All of the electrons experience a higher effective nuclear charge and the electrons in the two shells are pulled progressively towards the nucleus.

There is a decrease in ionic radii from P^{3-} , S^{2-} to Cl^- : all the ions have the electron arrangement of 2, 8, 8 (i.e. they are isoelectronic); however, there is a progressive increase in the nuclear charge due to the additional protons: the phosphide ion has 15 protons, the sulfide ion has 16 protons and the chloride ion has 17 protons. (All of the electrons experience a higher effective nuclear charge and the electrons in the three shells are pulled progressively towards the nucleus.) [6]

- 5 a Ionization energy increases.

Nuclear charge increases/electron is closer (on average) to the nucleus/atomic radius decreases. [2]

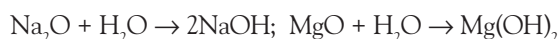
- b Aluminium is lower than expected; sulfur is lower than expected.

In aluminium the electron removed is in a p sub-shell/at a higher energy than in magnesium.

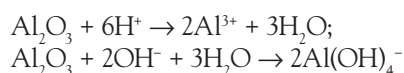
The s electron removed is in an orbital that contains a second electron that repels it/change to a half-filled p sub-shell. [4]

- 6 Across period 3 of the periodic table, the oxides of the elements change from basic to amphoteric to acidic in nature due to the increasingly electronegativity of the elements, which gradually changes the bonding from ionic to covalent.

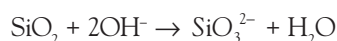
Sodium and magnesium oxide react to form hydroxide ions:



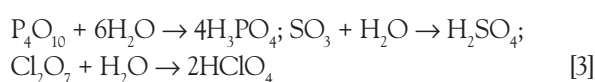
Aluminium oxide is amphoteric and reacts with both acids and bases:



Silicon dioxide is an acidic oxide and reacts with hot, concentrated alkali:



The highest oxides of the remaining non-metallic elements react with water to form strongly acidic solutions:



4 Chemical bonding and structure

Paper 1

- | | |
|------|------|
| 1 A | 15 A |
| 2 A | 16 B |
| 3 B | 17 D |
| 4 B | 18 C |
| 5 A | 19 D |
| 6 C | 20 A |
| 7 D | 21 A |
| 8 C | 22 A |
| 9 B | 23 B |
| 10 C | 24 A |
| 11 D | 25 A |
| 12 D | 26 A |
| 13 B | 27 A |
| 14 A | 28 A |

Paper 2

- 1 Sodium, magnesium and aluminium are metallic and hence are good electrical conductors due to the presence of delocalized valence electrons. From sodium, magnesium to aluminium, the atomic and ionic size decrease and the number of valence electrons available for delocalization increases from one to three. Thus, the metallic bonding strength increases and hence the melting point increases since more heat energy is required to break the metallic bonding. In addition, with more valence electrons for delocalization, the electrical conductivity also increases. [3]

Silicon has a giant covalent structure with strong silicon–silicon single bonds. A large amount of heat energy is required to break all these bonds and hence it has a high melting point. Phosphorus (P_4), sulfur (S_8), chlorine (Cl_2) and argon (Ar) are simple molecular covalent substances and hence are held together in the solid state by London (dispersion) forces. A small amount of thermal energy is required to break these intermolecular forces and hence their melting points are low. The strength or extent of London (dispersion) intermolecular forces increases with molecular size (number of electrons). Thus, sulfur has the highest melting point followed by phosphorus, chlorine and then argon. [3]

- 2 a Electron dot structures for N_2 and F_2 : [2]



The triple bond in the nitrogen molecule is stronger and hence harder to break. [1]

- b The C–Cl bond is more polar than the N–Cl bond. Nitrogen is more electronegative than carbon. NCl_3 is polar; CCl_4 is polar. The NCl_3 molecule is not symmetrical and dipole moments do not cancel; CCl_4 is symmetrical and the four dipole moments cancel. [5]

- 3 Ethanol and water are miscible in each other due to the formation of hydrogen bonding. The ethane molecule is non-polar and is not able to form hydrogen bonds with water molecules. [2]

Ethane molecules can only form weaker London (dispersion) forces with water molecules. Cholesterol has a polar alcohol group; however, it behaves as a non-polar molecule due to the relatively large size of the hydrocarbon group. [2]

- 4 a Potassium metal has a lattice of unipositive ions (cations) in fixed positions with a ‘sea’ of delocalized or mobile valence electrons that are free to move through the lattice. The metal is held together by attraction between the nuclei of the positive ions and the delocalized electrons. [4]

- b Lewis structure for fluorine: [2]



The bonding within a fluorine molecule is a single covalent bond. This consists of a shared pair of valence electrons. [1]

The bonding between molecules arises from London (dispersion) forces. These involve the attraction between dipoles temporarily set up by electron polarization. [1]

- c The potassium atom has the configuration 2, 8, 8, 1. [1]

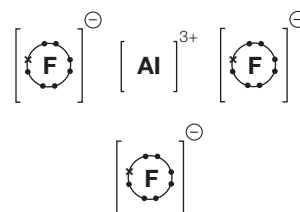
The fluorine atom has the configuration 2, 7. [1]

Potassium’s outer electron is transferred to the outer shell of the fluorine atom. [1]

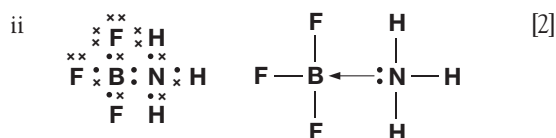
Oppositely charged ions are formed (with complete octets of electrons) which attract each other due to electrostatic forces of attraction. [1]

- d The ions are not free to move in the solid state. However, they can move in the molten state under the influence of a voltage. [1]

- 5 a Boron trifluoride is a simple molecular substance and aluminium fluoride is ionic. [6]



- b i A coordinate covalent bond. Both electrons are supplied by the nitrogen atom of ammonia which has a lone pair of electrons. [2]



5 Energetics/thermochemistry

Paper 1

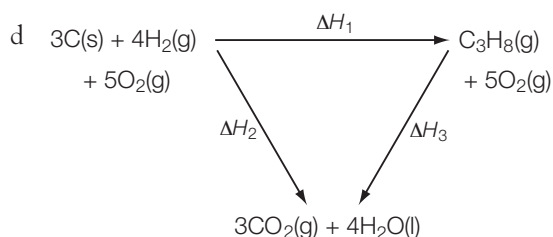
- | | |
|-----|------|
| 1 C | 10 A |
| 2 D | 11 A |
| 3 D | 12 D |
| 4 D | 13 A |
| 5 A | 14 C |
| 6 B | 15 A |
| 7 B | 16 D |
| 8 A | 17 C |
| 9 D | |

Paper 2

- 1 a i The energy needed to break one mole of a particular covalent bond in a molecule in the gaseous state and form gaseous atoms.
The value is averaged using those from similar compounds. [3]
- ii It is an element and is the only species with a F-F bond. [1]
- b i Sum of bonds broken = 412 + 158 = 570 kJ
Sum of bonds formed = 484 + 562 = 1046 kJ
 $\Delta H = -476 \text{ kJ mol}^{-1}$ [3]
- ii
- | | $\text{CH}_4 + \text{F}_2$ |
|----------|-----------------------------------|
| enthalpy | $\text{CH}_3\text{F} + \text{HF}$ |
- [2]
- iii About the same since the same number and type of bonds are being broken and formed. [2]
- 2 a It is exothermic because heat is released to the surroundings and the temperature rises. [1]
- b To make any heat loss as small as possible, so that all the heat will be given out very rapidly. [1]
- c Heat released = mass \times specific heat capacity \times temperature increase
Amount of LiOH or HCl used =
 $0.500 \text{ dm}^3 \times 0.050 \text{ mol dm}^{-3} = 0.025 \text{ mol}$
Heat released = $100 \text{ g} \times 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1} \times 3.5^\circ\text{C}$
 $= 1463 \text{ J} = 1.463 \text{ kJ}$
 $\Delta H = (1.463 \text{ kJ}) \div 0.025 \text{ mol} = -58.5 \text{ kJ mol}^{-1}$ [4]

- d Significant heat loss to the surroundings. Insulate the reaction vessel and use a lid. Draw a temperature versus time graph and extrapolate to calculate the rise in temperature. [2]
- e The temperature change would be the same, namely, 3.5°C . This occurs because the amount of lithium hydroxide reacted would be the same. The excess hydrochloric acid would not react; lithium hydroxide is the limiting reagent. [2]

- 3 a The enthalpy change that occurs when one mole of a pure compound is formed under standard thermodynamic conditions from its elements in their standard states. [2]
- b The enthalpy change that occurs when one mole of a pure compound undergoes complete combustion in the presence of excess oxygen under standard conditions. [2]
- c Hess's law states that the total enthalpy change for a reaction is independent of the route taken. It depends only on the initial and final states. [1]



According to Hess's law, $\Delta H_1 = \Delta H_2 - \Delta H_3$

$$\Delta H_1 = \Delta H_f^\ominus [\text{C}_3\text{H}_8(\text{g})]$$

$$\Delta H_2 = 3 \times \Delta H_c^\ominus [\text{C}_{\text{graphite}}] + 4 \times \Delta H_c^\ominus [\text{H}_2(\text{g})]$$

$$\Delta H_2 = 3 \times (-393 \text{ kJ mol}^{-1}) + 4 \times (-286 \text{ kJ mol}^{-1})$$

$$= -2323 \text{ kJ mol}^{-1}$$

$$\Delta H_3 = \Delta H_c^\ominus [\text{C}_3\text{H}_8(\text{g})] = -2220 \text{ kJ mol}^{-1}$$

Hence,

$$\Delta H_f^\ominus [\text{C}_3\text{H}_8(\text{g})] = (-2323 \text{ kJ mol}^{-1}) - (-2220 \text{ kJ mol}^{-1})$$

$$= -103 \text{ kJ mol}^{-1}$$
 [4]

6 Chemical kinetics

Paper 1

- | | |
|-----|-----|
| 1 A | 5 D |
| 2 B | 6 A |
| 3 C | 7 C |
| 4 C | |

Paper 2

- 1 a i Carbon dioxide, CO_2 [1]
- ii $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ [2]

- b 800 cm^3 ; 8 minutes [2]
- c i The collision frequency between carbonate and hydrogen ions is greatest at the start, but decreases with time. The concentrations of the two reactants is highest at the start of the reaction. However, as the chemicals react the number of reacting ions decreases the concentrations and hence the collision rate decreases. [2]
- ii The mass of calcium carbonate may be less in Y and hence greater in X. [1]
- The concentration of hydrochloric acid may be less in Y and hence higher in X. [1]
- 2 a i 30 cm^3 [1]
- ii 19 cm^3 [1]
- iii 9 cm^3 [1]
- b As the reaction proceeds the surface area of the magnesium (the limiting reagent) decreases. The magnesium is being used up, and hence the rate decreases. The acid remains in excess and its concentration remains relatively constant. [2]
- c The reaction has stopped; all of the magnesium has been consumed. [1]
- d Plot an accurate graph of the results: labelling the axes, plotting points carefully, and drawing a curve of best fit. [3]
- Parts i and ii; draw tangents to your curve and estimate the slopes at the two points. [4]
- e i Initial rate increased [1]
- ii Initial rate decreased [1]
- iii Initial rate increased [1]
- f i Final volume of gas increased [1]
- ii Final volume of gas unchanged [1]
- g i Use to measure one of the following: gas pressure, motion or change in mass using a balance connected to computer. [2]
- Could not use: light sensor. [1]
- ii Give a brief description of one use: pressure sensor fitted to sealed flask detecting increase in pressure with time; motion sensor detecting movement of gas syringe barrel with time; balance detecting loss in mass of flask and contents with time. [3]
- 3 a i Increasing the concentration of H_2O_2 will increase the rate of reaction as the frequency of collisions will increase as there are more particles present. [2]
- ii This will have no effect; the concentration of NaI does not depend on the size of the crystals used to make the solution, just the mass used. [2]

- b The rate of a reaction increases with temperature as the particles are moving faster (have greater kinetic energy) and therefore collide more frequently [1]
- The colliding particles are more likely to have combined kinetic energy greater than the activation energy of the reaction and so more collisions produce a reaction. [1]
- The second of these factors is the more significant/important of the two. [1]

7 Equilibrium

Paper 1

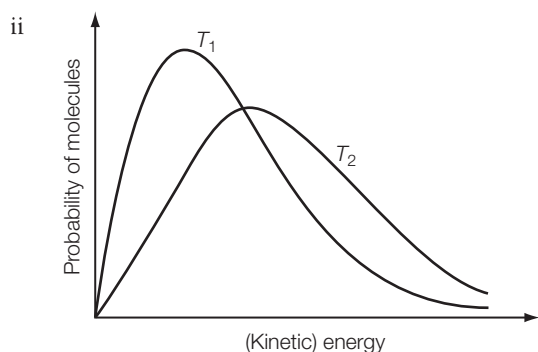
- | | |
|-----|------|
| 1 A | 8 A |
| 2 D | 9 B |
| 3 A | 10 A |
| 4 D | 11 D |
| 5 C | 12 C |
| 6 D | 13 B |
| 7 B | |

Paper 2

- 1 a Any one of the following statements: [1]
- Rate of forward process/reaction = rate of backwards/reverse process/reaction
- Rate of vaporization/evaporation = rate of condensation;
- Concentrations of reactants and products remain constant;
- There is no change in macroscopic properties in a closed system;
- Do not accept concentration of reactants and products are equal.*
- Accept constant colour of Br_2 vapour/liquid.
- b i $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$ [1]
- ii Two or three correct [1]; four or five correct [2]; all correct [3]

	Position of equilibrium	Value of K_c
Decrease in temperature	Shifts to right/products	Increases
Increase in pressure	Shifts to right/products	No effect
Addition of catalyst	No effect	No effect

- c i Minimum/least/smallest energy needed (by reactants/colliding particles) to react/start/initiate a reaction. [1]
- Allow energy difference between reactants and transition state.*



The x-axis label: (kinetic) energy; the y-axis label: probability/fraction of molecules/particles/probability density.

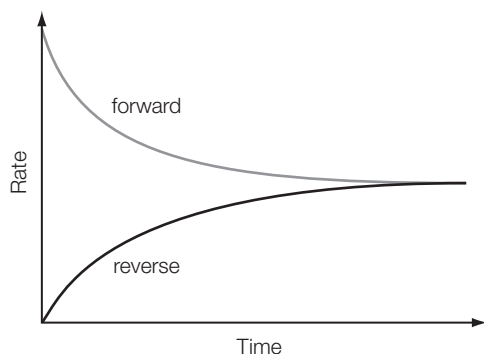
Allow number of molecules/particles for y-axis.

Correct shape of a typical Maxwell–Boltzmann energy distribution curve;

Do not award mark if curve is symmetric, does not start at zero or if it crosses x-axis.

Two curves represented with second curve for $T_2 > T_1$ to right of first curve, peak maximum lower than first curve and after the curves cross going to the right, T_2 curve needs to be above T_1 curve as illustrated. [2]

- 2 a $K_c = \frac{[HI]^2}{[H_2][I_2]}$ [1]
- b Concentration of product / HI greater (than $[H_2]$ and $[I_2]$) [1]
- c It will have no effect. [1]
- d As the reaction is endothermic, increasing the temperature will shift the equilibrium position to the right (more product formed). [1]
- 3 a Two curves – one labelled ‘forward’ starting up high up y-axis and one labelled ‘reverse’ starting from zero. The curves merge and become horizontal.



- i Forward reaction – highest concentration, thus rate high to begin with. As the reaction proceeds, the concentrations decrease, as does the rate.
- ii Reverse reaction – zero rate initially at $t = 0$ (since no products present). The rate increases as concentration of products increases.

Equilibrium established when rate of forward reaction = rate of reverse reaction. [7]

- b Reaction is endothermic [1]
 K_c increases with (increasing) temperature [1]
 the forward reaction favoured/heat is used up. [1]

- 4 a 200°C [1] and 600 atm [1]. [2]

(Allow the ‘highest pressure and the lowest temperature’.)

- b i Yield increases/equilibrium moves to the right/more ammonia. [1]

4 (gas) molecules \rightarrow 2/decrease in volume/fewer molecules on right-hand side. [1]

- ii Yield decreases/equilibrium moves to the left/less ammonia; exothermic reaction. [2]

- c High pressure expensive/greater cost of operating at high pressure/reinforced pipes, etc. needed.

Lower temperature: greater yield, but lowers rate. [2]

(Do not award a mark for simply saying ‘compromise’.)

- d $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ [1]

- e i Artificial fertilizers/increasing crop yields; production of high explosives for mining [1 max]. [1]

- ii Fe/iron (allow magnetite/iron oxide). [1]

The claim is not valid since catalysts do not alter the yield/position of equilibrium they only increase the rate of reaction. [1]

8 Acids and bases

Paper 1

- | | |
|------|------|
| 1 D | 14 B |
| 2 C | 15 D |
| 3 A | 16 B |
| 4 C | 17 D |
| 5 D | 18 D |
| 6 A | 19 A |
| 7 A | 20 A |
| 8 D | 21 C |
| 9 B | 22 A |
| 10 D | 23 C |
| 11 B | 24 B |
| 12 A | 25 B |
| 13 D | |

Paper 2

- 1 a i Acid X [1]
 ii A factor of 10 [1]
 iii Y, Z and X [1]
 Conductivity increases with ion concentration.
 As the pH value decreases the concentration of hydrogen ions increases. [1]
- 2 a A strong acid is fully ionized or dissociated in solution. [1]
 $\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ [1]
 A weak acid is partly ionized or dissociated in solution. [1]
 $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ [1]
 or
 $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$
- b Universal indicator: hydrochloric acid – red; carbonic acid – yellow/orange. [1]
 Electrical conductivity: hydrochloric acid – high; carbonic acid – low
 or
 Reaction with metal/metal carbonate: hydrochloric acid – vigorous; carbonic acid – slow. [1]
- c 10000:1 or $10^4:1$ or $0.1:0.00001$ or $10^{-1}:10^{-5}$ [2]
- d i Base: HCO_3^- ; conjugate acid: H_2CO_3 [1]
 Acid: HCl; conjugate base: Cl^- [1]
 ii Brønsted-Lowry [1]
- 3 a Both solutions have an excess of hydroxide ions, which can accept protons to form water molecules. [1]
 b The pH of potassium hydroxide solution would be higher. This is because it is a stronger base than ethylamine. It hence undergoes greater dissociation. [3]
 c $\text{C}_2\text{H}_5\text{NH}_2(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$ [1]
 OH^- is a base/conjugate base and $\text{C}_2\text{H}_5\text{NH}_3^+$ is a conjugate acid/acid [1]
 d $\text{C}_2\text{H}_5\text{NH}_2(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{Cl}^-(\text{aq})$ [1]
 e It is a strong acid and hence corrosive. [1]
- 4 a Proton (H^+) donor [1]
 b $\text{HSO}_3^-(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$ [1]
 c Nitric(v) acid, HNO_3 [1]
 d Leaching of minerals into freshwater lakes; killing of young fish [2]
 e $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$;
 $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$ [3]
 $\text{H}_2\text{SO}_3(\text{aq}) \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{SO}_3^{2-}(\text{aq})$

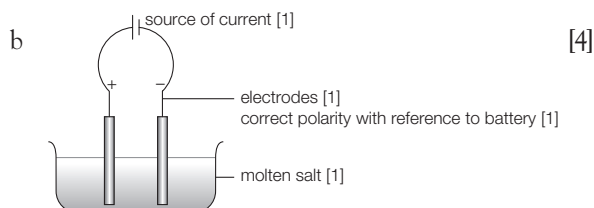
9 Redox processes

Paper 1

- | | |
|-----|------|
| 1 A | 10 D |
| 2 D | 11 D |
| 3 D | 12 C |
| 4 A | 13 B |
| 5 A | 14 C |
| 6 B | 15 B |
| 7 D | 16 D |
| 8 D | 17 A |
| 9 B | |

Paper 2

- 1 a i Magnesium (Mg), iron (Fe), copper (Cu), and gold (Au). [1]
 ii The loss or removal of electrons from a chemical species. [1]
 Iron atoms lose electrons during their reaction with copper(II) ions:
 $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$ [1]
 iii Reduction involves a decrease in oxidation number. [1]
 Copper(II) ions gain electrons during their reaction with iron atoms:
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ [1]
 iv Magnesium (Mg) is the strongest reducing agent. [1]
 It reduces Fe^{2+} ; Fe reduces Cu^{2+} ; Cu reduces Au^+ . [1]
 v Gold ions, Ag^+ [1]
 Every metal present can reduce gold ions to gold atoms. [1]
 vi Does not react. [1]
 It is too low in the reactivity series and hence is less reactive than magnesium. [1]



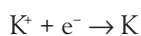
- c At the cathode (negative electrode):
 electrons are given to the cations (positive ions) [1]
 electrons are removed from the anions (negative ions). [1]

At the anode (positive electrode):

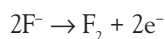
copper atoms formed (at the cathode) [1]

chlorine molecules formed (at the anode). [1]

2 a At the negative electrode (cathode):



At the positive electrode (anode):



Electrons flow through the external circuit or wires and the ions move through the electrolyte to the electrodes where they gain or lose electrons. [4]

b 0.2 mol since the K to F_2 molar ratio is 2:1. [2]

c i Sodium atoms lose electrons and undergo reduction. Aluminium ions (in aluminium chloride) gain electrons and undergo oxidation. [2]

ii Reactants: sodium metal: 0; aluminium in aluminium chloride: 3
Products: aluminium metal: 0; sodium in sodium chloride: +1 [2]

3 a i $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$
ii $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
iii $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

b i Amount of $\text{MnO}_4^- = \frac{11.6}{1000} \times 0.0200$
 $= 2.32 \times 10^{-4} \text{ mol}$

ii Amount of $\text{Fe}^{2+} = 5 \times 2.32 \times 10^{-4}$
 $= 1.16 \times 10^{-3} \text{ mol}$

iii Mass of $\text{Fe}^{2+} = 55.85 \times 1.16 \times 10^{-3}$
 $= 6.48 \times 10^{-2} \text{ g}$

$$\% \text{ of } \text{Fe}^{2+} \text{ in tablet} = \left(\frac{6.48 \times 10^{-2}}{1.43} \right) \times 100$$

$$= 4.53\%$$

b Molar mass of empirical formula = 71. [1]

Molecular mass = 142; therefore molecular formula = $2 \times$ empirical formula.

Molecular formula of hydrocarbon = $\text{C}_{10}\text{H}_{22}$ [1]

c i $2\text{C}_{10}\text{H}_{22} + 31\text{O}_2 \rightarrow 20\text{CO}_2 + 22\text{H}_2\text{O}$ [2]

ii $2\text{C}_{10}\text{H}_{22} + 21\text{O}_2 \rightarrow 20\text{CO} + 22\text{H}_2\text{O}$ [2]

Could also have an equation where C is produced.

d i C_4H_{10} [1]

ii C_5H_{10} [1]

2 a i % Oxygen = 36.4

Empirical formula is $\text{C}_2\text{H}_4\text{O}$ [3]

ii Molar mass of empirical formula = 44.

Molecular formula = $2 \times$ empirical formula
 $= \text{C}_4\text{H}_8\text{O}_2$ [2]

b i Empirical formula is CH_2O

ii Molar mass of empirical formula = 30. [2]

Molecular formula = $2 \times$ empirical formula
 $= \text{C}_2\text{H}_4\text{O}_2$ [2]

3 a Full or condensed structures:

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, butane / $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$, 2-methylpropane. [4]

b A: $\text{CH}_3\text{CH}_2\text{COOH}$ / $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ propanoic acid.

B or C: $\text{CH}_3\text{COOCH}_3$ methyl ethanoate.

C or B: $\text{HCOOCH}_2\text{CH}_3$ ethyl methanoate. [6]

c i A forms hydrogen bonds with water. [1]

A ionizes/dissociates to give H^+ ions. [1]

ii $\text{C}_2\text{H}_5\text{COOH} + \text{NaOH} \rightarrow \text{C}_2\text{H}_5\text{COONa} + \text{H}_2\text{O}$ [1]

iii No C=C bond. [1]

d A has the highest boiling point as the acid molecules have the capability of hydrogen bonding together; B and C have similar boiling points as they are both esters, their boiling points are lower than that of A as they cannot take part in intermolecular hydrogen bonding. [2]

e i Ester [1]

Flavourings/plasticizers/solvents/perfumes [1]

ii Carboxylic acid/alkanoic acid [1]; alcohol/alkanol [1]; water [1]. [3]

f Any feasible formula containing C=C (e.g. $\text{CH}_3\text{CHC}(\text{OH})_2$ or $\text{HOCH}=\text{C}(\text{OH})\text{CH}_3$). [1]
Addition [1]

Mixture is decolorized/colour change is from yellow/orange to colourless. [1]

4 a i Same general formula/differ by $-\text{CH}_2-$ /similar chemical properties/gradual change in physical properties. [3]

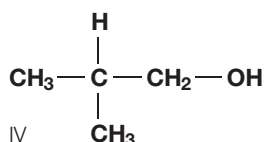
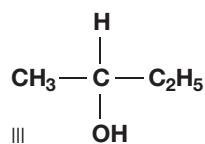
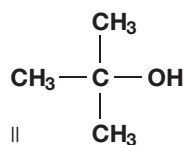
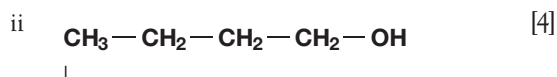
10 Organic chemistry

Paper 1

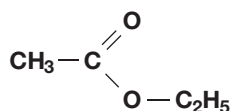
- | | |
|-----|------|
| 1 D | 7 D |
| 2 B | 8 C |
| 3 B | 9 D |
| 4 A | 10 B |
| 5 C | 11 A |
| 6 B | 12 C |

Paper 2

1 a Molar ratio = 1:2.2. [1]
Therefore empirical formula is C_5H_{11} [1]



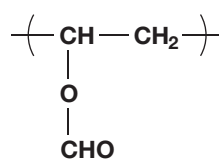
- b i Esterification / condensation $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$



Ethyl ethanoate [4]

- ii Catalyst; lowers activation energy (by providing an alternate pathway) [2]
- iii Flavouring agents / in plasticizers / in solvents / in perfumes [1]
- c i II reacts with bromine / contains $\text{C}=\text{C}$ / II is an alkene / has unsaturated R group. [2]
- I contains only saturated R groups. [2]

- ii Addition polymerization



- 5 a i Propan-2-ol [1]
- ii Propan-1-ol [1]
- iii 2-Methylbutan-2-ol [1]
- iv Ethane-1,2-diol [1]
- b i Secondary [1]
- ii Primary [1]
- iii Tertiary [1]
- iv Primary [1]
- c i Propanone, CH_3COCH_3 [2]
- ii Propanoic acid, CH_3COOH [2]
- iii No oxidation [1]
- iv Ethane-1,2-dioic acid, $\text{HOOCCH}_2\text{CH}_2\text{COOH}$ [2]

- 6 a i Number of moles of carbon = $\frac{73.99}{12.01} = 6.161$
- Number of moles hydrogen = $\frac{6.55}{1.01} = 6.49$
- Number of moles nitrogen = $\frac{9.09}{14.01} = 0.649$
- Number of moles oxygen = $\frac{10.37}{16.00} = 0.648$
- C:H:N:O molar ratio is 9.5:10:1:1
- Empirical formula is $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$ [3]
- ii M_r of empirical formula = actual M_r
- Molecular formula is $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2$ [1]
- iii (0.5) $(40 - 20 - 2) = 9$ [1]
- b A is carboxamide (amide); B is phenyl; C is carboxyl (carboxy); D is hydroxyl. [2]

11 Measurement and data processing

Paper 1

- | | |
|-----|------|
| 1 B | 8 B |
| 2 D | 9 D |
| 3 C | 10 C |
| 4 B | 11 C |
| 5 C | 12 B |
| 6 A | 13 C |
| 7 B | |

Paper 2

- 1 a i The actual volume of sodium hydroxide will be lowered, and the calculated concentration of hydrochloric acid will be higher. [2]
- ii If there was water in the burette, the sodium hydroxide would be diluted, lowering the amount of sodium hydroxide and the concentration of hydrochloric acid. [2]
- iii This will make the concentration of the hydrochloric acid appear greater than it is. [1]
- iv The end point will not be accurate, causing random errors. [1]
- b i Systematic error. [1]
- ii Measure the pH of a buffer solution of known pH value. [1]
- 2 a Mass of copper (dependent), time (independent) and current (controlled variable). [3]
- b Directly proportional. [1]
- c Rate = $\frac{\text{mass of copper (g)}}{\text{time (min)}} = \frac{1.24 \text{ g}}{15 \text{ min}} = 0.08 \text{ g min}^{-1}$ [2]
- d Interpolation, area under the graph and extrapolation. [2]

3 a Percentage uncertainty in length = $\left(\frac{1}{298}\right) \times 100$
 = 0.336% [1]

b Percentage uncertainty in width = $\left(\frac{1}{210}\right) \times 100$
 = 0.476% [1]

c Area = 298 mm × 210 mm = 62 580 mm² [1]
 Percentage uncertainty in area = $\frac{1}{298} + \frac{1}{210} \times 62\,580 = 508 \text{ mm}^2$
 Area = 62 580 mm² ± 508 mm² [2]

- 4 a The bond angle (H–S–H) changes as bending occurs. [1]
 The lengths of the S–H bonds change as stretching occurs. [1]
 The dipole moment of the molecule changes. [1]

- b i Absorptions in NMR are due to transitions between different spin states in the nucleus (when an external magnetic field is applied). [1]
 IR absorptions are due to bond vibrations. [1]

The nuclear transitions are at a much lower energy than bond vibrations. [1]

There is an inversely proportional relationship between frequency and energy. [1]

- ii The bond in both molecules vibrates and stretches; only the stretching in the hydrogen bromide, H–Br, causes a change in dipole moment. [2]

c wavenumber = $\frac{1}{\text{wavelength (cm)}}$;
 energy = $\frac{\text{Planck's constant} \times \text{velocity}}{\text{wavelength}}$;
 wavenumber = $\frac{\text{energy}}{\text{Planck's constant} \times \text{velocity}}$ [2]

- d Atomic masses increase from chlorine to iodine. [1]
 Heavier atoms vibrate more slowly and hence the stretching frequency decreases. [1]

- 5 a P: ⁺CH₃, Q: ⁺C₂H₅ and R: ⁺C₃H₇ [3]

b

Information	Analytical technique
Relative atomic mass of an element	Mass spectrometry
Functional groups and strength of bonds present in an organic molecule	Infrared spectroscopy
Potassium ions in a sample of blood serum	Atomic absorption spectroscopy and inductively-coupled plasma spectroscopy
Detailed structure of an organic molecule (without degrading the sample)	Nuclear magnetic resonance

[3]

- 6 a Both 1-fluorobutane and 2-fluorobutane have four peaks:

(ratio of areas or integration traces in)

1-iodobutane: 3 : 2 : 2 : 2

(ratio of areas or integration traces in)

2-iodobutane: 3 : 1 : 2 : 3 [4]

- b 1-fluoro-2-methylpropane has three peaks:

(ratio of areas or integration traces in)

1-iodobutane: 2 : 1 : 6 [3]

12 Atomic structure

Paper 1

- | | |
|-----|------|
| 1 A | 9 A |
| 2 A | 10 A |
| 3 C | 11 B |
| 4 B | 12 C |
| 5 A | 13 C |
| 6 D | 14 D |
| 7 B | 15 D |
| 8 C | 16 B |

Paper 2

- 1 a The first ionization energy is the minimum energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of unipositive gaseous ions (under standard thermodynamic conditions). [2]
- b In a group 2 element (C) the electron (for the first ionization energy) is removed from a spin pair in an s sub-shell. For D, a Group 13 element, the electron (for the first ionization energy) is removed from a 3p sub-shell further away from the nucleus. The 3p sub-shell also experiences more shielding. Hence there is a decrease in first ionization energy when moving from C to D. The increase in nuclear charge accounts for the increase from E (np² to F np³). In addition C cannot be in Group 15 (the other group after which there is a slight decrease) because there is a steady rise for the next 3 elements (D to E to F) indicating the filling of a p sub-shell. [4]
- c As you move down group 2 the first ionization energies decrease. As you descend the group the nuclear charge increases due to the presence of additional protons, but the shielding effect progressively increases due to the presence of an extra electron shell as you move from one period to the next. The effect of the extra protons is compensated for by the effect of the extra electrons. The only factor left is the additional distance between the outer electron and the nucleus. That lowers the first ionization energy. [3]
- d C is in period 3 since in period 2 the Group 2 element would have the higher ionization energy while in period 4 the Group 2 element would have a lower ionization energy. This can be accounted for by the progressively increasing average distance the

valence electron is from the nucleus. C cannot be in the first period (He) as p-orbitals are being filled, it cannot be in the fourth period (Ca) as $(x + 8)$ would not bring you back to Group 2 again. [3]

- e There is a slight decrease from F to G due to the presence of a spin pair in the np sub-shell for G. The resulting electron–electron repulsion is greater than the effect of the increase in nuclear charge and reduces the ionization energy of G^+ . [2]

- 2 a The energy needed to remove one mole of valence electrons from a mole of (neutral) atoms; in the gaseous state:



- b The electron removed (from aluminium) is in a p sublevel/sub-shell while that from magnesium is in an s sub-level/sub-shell.

The p sub-level is of higher energy/further from nucleus (than the s sub-level)/experiences greater shielding from nucleus. [2]

- c The third electron is more difficult to remove because it is taken from a positively charged ion and from a (main) energy level closer to nucleus / from second energy level/ $n = 2$ while the first electron comes from the third energy level/ $n = 3$. [1]

- d $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2; 4s$ [2]

- 3 a $4p$ [1]

- b $\text{Ge}^+(\text{g}) \rightarrow \text{Ge}^{2+}(\text{g}) + \text{e}^-$ [1]

- c The germanium atom contains four valence electrons: $4s^2$ and $4p^2$. There is a steady increase in ionization energy. Upon reaching the fifth ionization energy an electron must be removed from a completely filled inner 3d sub-shell. Once filled these act as core electrons and this is reflected in the large increase in ionization energy. [2]

13 The periodic table – the transition metals

Paper 1

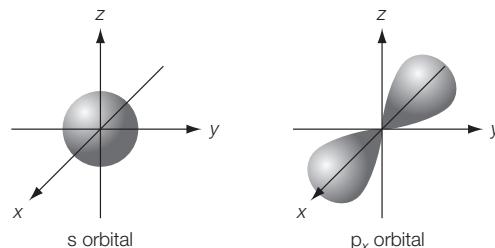
- | | |
|-----|------|
| 1 A | 9 A |
| 2 A | 10 A |
| 3 B | 11 D |
| 4 B | 12 D |
| 5 A | 13 D |
| 6 A | 14 A |
| 7 A | 15 C |
| 8 B | 16 D |

Paper 2

- 1 a Ester functional group. [1]

- b Coordinate covalent bond. [1]

- c i [2]



- ii 16 [1]

- d $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^6$ [1]

- e

↑↓

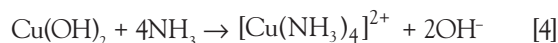
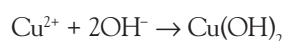
↑↓	↑↓	↑↓
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↑↓

↑	↑	↑	↑
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 [1]
3s 3p 4s 3d

- 2 a A pale blue precipitate of hydrated copper(II) hydroxide, $\text{Cu}(\text{OH})_2$. The precipitate reacts with excess ammonia to form a solution containing a deep blue complex ion:



- b i $4\text{H}^+ + 3 \text{MnO}_4^{2-} \rightarrow 2 \text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$ [2]

- ii +6, +7 and +4 [3]

- iii Catalysis [1]

- c The zinc ion, Zn^{2+} has a $3d^{10}$ electron configuration (fully occupied 3d-orbitals). Hence it is not possible to have d–d transitions and it is thus colourless. [2]

- 3 a +3 and +2 [2]

- b Six cyanide ligands are coordinated octahedrally to a central iron(II) ion. [2]

- c A transition metal is a metal that forms compounds in which the metal has a partially filled 3d sub-shell. [1]

- d Hemoglobin is an iron-containing protein found inside red blood cells. The iron forms a complex with oxygen, known as oxyhemoglobin, when the oxygen concentration is high. At low oxygen concentrations the oxygen is released and hemoglobin is re-formed. [2]

- 4 $E = \frac{hc}{\lambda}$; so the larger the wavelength, the smaller the energy, so $Z > Y > X$. [3]

- 5 $E = \frac{hc}{\lambda}$; $E = (6.63 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}) \times 1 \times 10^{-9} \text{ m} \times 1/1000 \times 6.02 \times 10^{23} = 163 \text{ kJ mol}^{-1}$ [4]

- 6 a +3 [1]

- b $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^6$ [1]

- c 4 [1]

- d Octahedral



[5]

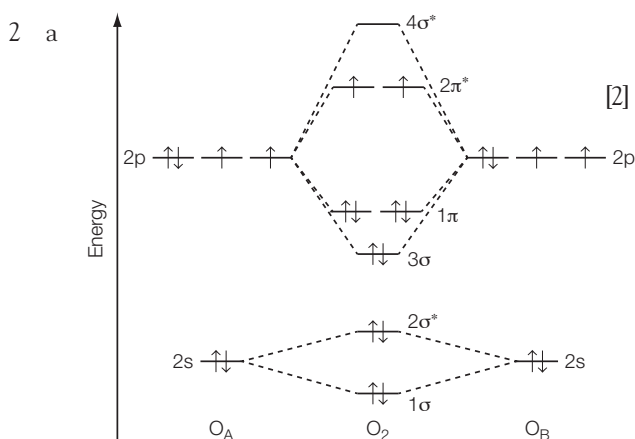
14 Chemical bonding and structure

Paper 1

- | | |
|------|------|
| 1 A | 11 C |
| 2 B | 12 D |
| 3 C | 13 C |
| 4 D | 14 D |
| 5 A | 15 B |
| 6 C | 16 C |
| 7 C | 17 C |
| 8 D | 18 A |
| 9 B | 19 A |
| 10 B | 20 B |

Paper 2

- 1 a The left-hand one. [1]
 b +2 and 0 [2]
 c The right-hand one. [1]



- b $2s(O_A)$ and $2s(O_B)$ combine to form 1σ and $2\sigma^*$.
 $2p_z(O_A)$ and $2p_z(O_B)$ combine to form 3σ and $4\sigma^*$. [2]
- c $2p_x(O_A)$ and $2p_x(O_B)$ combine to form one pair of 1π and $2\pi^*$.
 $2p_y(O_A)$ and $2p_y(O_B)$ combine to form one pair of 1π and $2\pi^*$. [2]
- d $(1\sigma)^2 (2\sigma^*)^2 (3\sigma)^2 (1\pi)^4 (2\pi^*)^2$. [1]
- e Paramagnetic. Paramagnetic refers to the magnetic state of an atom, ion or molecule with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. [2]
- f Two [1]
- g If four electrons are added to O_2 , the bond order will be reduced to zero. This will generate two oxide anions: $O_2 + 4e^- \rightarrow 2O^{2-}$. [2]

- 3 a Each correct structure (with non-bonding electron pairs where relevant)

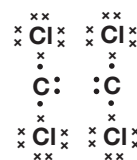
C_2H_2 linear/straight

Angle 180°



C_2Cl_4 (trigonal) planar

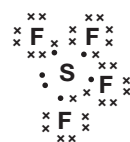
Angle 120°



SF_4 K-shaped/based on trigonal bipyramid/see-saw

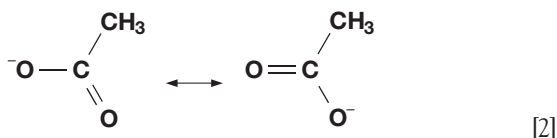
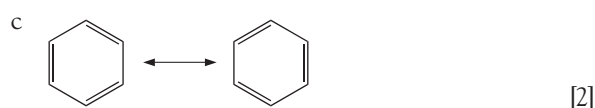
Angle 90°

Angle 120°



[10]

- b sp (C_2H_2) [2]
 sp^2 (C_2Cl_4) [2]

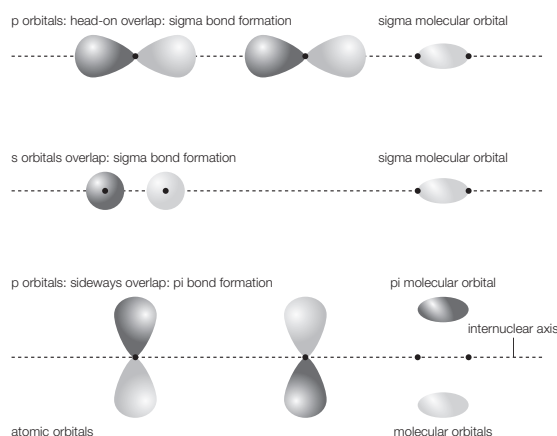


- 4 a Sigma bonds involve an overlap of orbitals end-on/along the molecular axis (it has axial symmetry around axis joining the two nuclei) overlap of s orbitals.

Pi bonds result from overlapping of parallel p orbitals/sideways overlap.

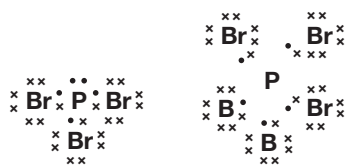
Double bond: a sigma bond and a pi bond.

Triple bond: a sigma bond plus two pi bonds. [4]

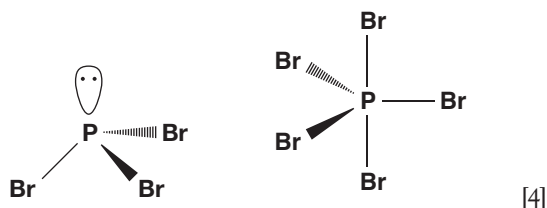


- b Delocalization: when pi electron pairs are not confined to two adjacent bonding atoms but extend over **three or more atoms**. [2]

- 5 a Lewis electron dot structures for PBr_3 and PBr_5 :



Molecular shapes for PBr_3 and PBr_5 :



- b The bond angles present in PBr_5 are 90° and 180° , respectively.

The bond angle in PBr_3 is approximately 107° since a lone pair of electrons (due to its more diffuse nature) produces more repulsion than a bonding pair, hence the bond angle is reduced below the tetrahedral bond angle of $109^\circ 28'$. [4]

Ion	$[\text{PBr}_4]^+$
Number of electrons in valency shell of central phosphorus atom	$(5 + 4 - 1) = 8$ (adjusting for ionic charge)
Number of electron pairs contributing to basic molecular shape	4
Molecular shape	Tetrahedral

- d The hybridizations of the phosphorus in phosphorus(III) bromide and the oxygen in water are sp^3 and sp^3 , respectively. [2]

Paper 2

- 1 a i ΔH_f^\ominus is the standard enthalpy change of formation of a substance. [1]

It is the heat change (absorbed or released under constant pressure) when a mole of a compound is formed from its elements in their standard states. [1]

S^\ominus represents the standard or absolute entropy. [1]

It is related to the disorder or randomness of particles. [1]

Related to standard conditions or 298 K (or 25°C) and one atmosphere pressure. [1]

- ii Δ was not included because S^\ominus has absolute values; S^\ominus values can be experimentally measured. [1]

- iii $\Delta H_f^\ominus(\text{Cu}) = 0$ (by definition an element is in its standard state) [1]

- b i $\Delta H_f^\ominus \text{ reaction} = \Sigma \Delta H_f^\ominus \text{ products} - \Sigma \Delta H_f^\ominus \text{ reactants}$ [1]

$$\Delta H_f^\ominus \text{ reaction} = ([4 \times (-242) + (-1084)] - [-2278])$$

$$= +226 \text{ kJ mol}^{-1} \quad [1]$$

An endothermic process or reaction needs heat energy. [1]

- ii $\Delta S^\ominus \text{ reaction} = \Sigma \Delta S^\ominus \text{ reactants} - \Sigma \Delta S^\ominus \text{ products}$
 $= (4 \times (189) + (150)) - (305)$ [1]

$$\Delta S^\ominus \text{ reaction} = 601 \text{ J K}^{-1} \text{ mol}^{-1} \text{ or } 0.601 \text{ kJ K}^{-1} \text{ mol}^{-1} \quad [2]$$

(+) sign/value, thus products more disordered than reactants. [1]

- iii Gibbs free energy (ΔG). [1]

Units: kJ mol^{-1} [1]

- c i At 25°C , $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
 $\Delta G^\ominus = (+226) \text{ kJ mol}^{-1} - (25 + 273) \text{ K} \times \frac{601}{1000} \text{ kJ mol}^{-1} \text{ K}^{-1}$ [2]

$$\Delta G^\ominus = +46.9 \text{ kJ mol}^{-1} \quad [1]$$

As the value of the Gibbs free energy change, ΔG^\ominus , is positive at 25°C , the forward reaction is not spontaneous. However, this implies that the backward reaction is spontaneous. Hence, at 25°C , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s})$ is the thermodynamically more stable compound. [2]

- ii When both compounds have equal thermodynamic stabilities, the Gibbs free energy change will be zero, ie, $\Delta G = 0$.

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

15 Energetics/thermochemistry

Paper 1

- | | |
|-----|------|
| 1 C | 8 B |
| 2 D | 9 D |
| 3 B | 10 C |
| 4 B | 11 A |
| 5 A | 12 C |
| 6 B | 13 A |
| 7 D | 14 C |

$$0 = (+226 \text{ kJ mol}^{-1}) - T \frac{601}{1000} \text{ kJ K}^{-1} \text{ mol}^{-1} \quad [1]$$

$$T = \frac{226 \text{ kJ mol}^{-1}}{0.601 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 376 \text{ K (103}^\circ\text{C)} \quad [1]$$

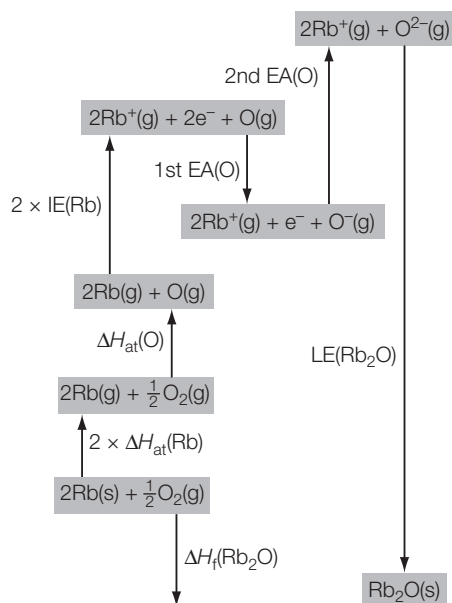
Hence, $\text{CuSO}_4 \cdot \text{H}_2\text{O(s)}$ is more thermodynamically stable above 103°C . [1]

- 2 a The lattice enthalpy is the energy needed to break down one mole of ionic solid into gaseous ions (separated to a infinite distance) under standard thermodynamic conditions (1 atm and 25°C). [2]

- b The greater the charge on the ions, the higher the value of the lattice enthalpy. Larger charges produce greater electrostatic forces of attraction between oppositely charged ions. [1]

The smaller the ionic radius, the higher the value of the lattice enthalpy. Smaller ions can approach each other more closely and hence experience greater electrostatic forces of attraction. [1]

- c Born-Haber cycle for rubidium oxide, Rb_2O : [2]



$$(2 \times 80.9) + 249.2 + (2 \times 403.0) - 146.1 + 795.5 + -\Delta H_{\text{lattice}}(\text{Rb}_2\text{O}) = -339.0$$

$$-\Delta H_{\text{lattice}}(\text{Rb}_2\text{O}) = -339.0 - (1866.4) = -2205.4 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{lattice}}(\text{Rb}_2\text{O}) = -2205.4 \text{ kJ mol}^{-1} \quad [2]$$

- d The ionic model is a good model for rubidium oxide – the bonds have very little covalent character. The ionic model is not a good model for silver bromide – the bonds are polar covalent. [2]
- e The sodium ion is smaller than that of rubidium. It can therefore approach the oxide ion more closely and exert higher electrostatic forces of attraction. [2]

$$\begin{aligned} 3 \quad a \quad \Delta H^\ominus &= [-394 + (-558) - (-1219)] = +267 \text{ kJ mol}^{-1} \\ \Delta S^\ominus &= [214 + 70] - [112] = +172 \text{ kJ mol}^{-1} \\ \Delta G^\ominus &= 267 - (298 \times (0.172)) = +216 \text{ kJ mol}^{-1} \end{aligned} \quad [6]$$

- b Non-spontaneous as ΔG^\ominus is positive. [1]

$$c \quad \Delta G^\ominus = \Delta H^\ominus - T \Delta S^\ominus; 267/0.172; 1552 \text{ K}$$

The factor $T\Delta S^\ominus$ predominates and ΔG^\ominus becomes negative; $T\Delta S^\ominus$ must be greater than ΔH for ΔG^\ominus to be negative. [4]

16 Chemical kinetics

Paper 1

- | | |
|-----|-----|
| 1 C | 5 D |
| 2 C | 6 D |
| 3 C | 7 D |
| 4 D | |

Paper 2

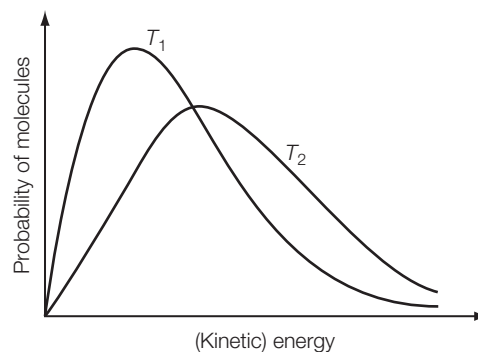
- 1 a The factor A is indicative of frequency of collisions **and** the probability that collisions have the proper orientation to react. [1]

$$b \quad k = \exp[(-87.0 \times 1000 / 8.31 \times 298) + \ln(2.10 \times 10^{11})] = 1.2 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

These units are chosen as this is an S_N2 reaction which implies it is second order. [2]

- 2 a i Change in concentration of reactant/product with time *or* rate of change of concentration. [1]
- ii Concentration; particle size / surface area; light; pressure. [2]
- iii (Measuring electrical) conductivity / (measuring) pH. [1]
- b i Minimum/least/smallest energy needed (by reactants/colliding particles) to react/start/initiate a reaction [1]

- ii [3]



- 3 a i $k = \ln 2 / t_{1/2} = 0.693 / (1.62 \times 10^4)$
 $= 4.28 \times 10^{-5} \text{ s}^{-1}$ [1]
- ii $\ln k = \ln A - E_a/RT = \ln 25 - E_a/(8.31 \times 1107)$
 Therefore: $E_a/(8.31 \times 1107) = \ln 25 - \ln k$
 $= \ln 25 - \ln (4.28 \times 10^{-5})$
 $E_a = (8.31 \times 1107)(\ln 25 - \ln (4.28 \times 10^{-5}))$
 $= 122\,167 \text{ J mol}^{-1}$
 $E_a = +122.17 \text{ kJ mol}^{-1}$ [2]
- 4 a Step 1 since it is the slowest. [1]
- b Step 1 is the slowest step, therefore it has a higher activation energy relative to step 2. [2]
- c $\text{Rate} = k[\text{NO}_2][\text{F}_2]$ [1]

17 Equilibrium

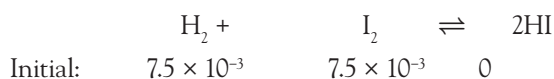
Paper 1

- 1 A 5 D
 2 A 6 C
 3 D 7 A
 4 B 8 B

Paper 2

1 a $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$ or $K_c = \frac{[\text{HI}]}{[\text{H}_2]^{1/2} [\text{I}_2]^{1/2}}$ [1]

b Initial $[\text{H}_2] = \text{initial } [\text{I}_2] = \frac{1.50 \times 10^{-2}}{2}$
 $= 7.5 \times 10^{-3} \text{ mol dm}^{-3}$



Equilibrium: $(7.5 \times 10^{-3} - x)$ $(7.5 \times 10^{-3} - x)$ $2x$

Therefore $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

$$53 = \frac{(2x)^2}{(7.5 \times 10^{-3} - x)^2}$$

Equilibrium concentrations: $[\text{H}_2] = [\text{I}_2]$
 $= 1.62 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{HI}] = 1.18 \times 10^{-2} \text{ mol dm}^{-3}$

See pages 595 and 596 for examples of this type of calculation [4]

- c Hydrogen bonding (dipole–dipole interactions) and London dispersion forces. [1]

2 [3]

Change	Shift	Reason
Increase in temperature	Equilibrium position shift to left	Since forward reaction is exothermic (ΔH is negative)
Increase in pressure	Equilibrium position shift to right	Since there are fewer gas molecules on right hand side
Addition of catalyst to mixture	No change in equilibrium position	A catalyst affects the rate of forward and reverse reactions equally

- 3 a i There will be no change in pressure. [1]
- ii The pressure will decrease. [1]
- b i The temperature will increase. [1]
- ii The methanol concentration will increase. [1]
- c i $K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$ [1]

ii

	$\text{CO(g)} + 2\text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$	
Initial amount:	1.00 2.00 0	
Amount at equilibrium/mol:	1.00 – 0.85 2.00 – 1.70 0.85	[1]
Equilibrium concentration:	0.15/0.45 0.30/0.45 0.85/0.45	[1]
	$= 0.333 \text{ mol} = 0.667 \text{ mol} = 1.889 \text{ mol}$	[1]

$$K_c = \frac{1.888}{0.333 \times (0.667)^2} = 12.7$$
 [1]

- iii Side reactions or leaks in the system or not operating under equilibrium conditions or operating at a higher temperature or the product might be collected before equilibrium is reached. [1]

- iv No effect on K_c (it just speeds up the reaction). [1]

- 4 a A; E [2]

- b i After 15 s (product) = 0.37 (mol dm⁻³);
 rate = 0.37 mol dm⁻³ / 15 s = 0.025 mol dm⁻³ s⁻¹ [3]

- ii At equilibrium/rates of forward and reverse reactions are equal/ $\Delta G = 0$. [1]

18 Acids and bases

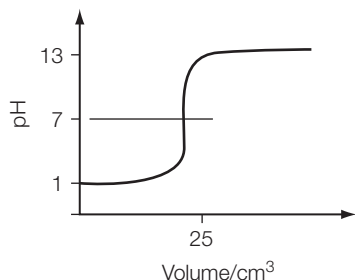
Paper 1

- 1 C 10 A
 2 B 11 D
 3 B 12 A
 4 A 13 C
 5 D 14 B
 6 B 15 C
 7 A 16 D
 8 C 17 C
 9 C

Paper 2

- 1 a i $\text{pH} = -\log [\text{H}^+(\text{aq})]$ [1]

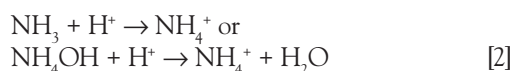
- ii The curve should include the following:
starting pH = 1; equivalence point: 25.0 cm^3
of NaOH; pH at equivalence point = 7; pH to
finish = 12–13. [4]



- iii $K_a = 10^{-4.76} = 1.74 \times 10^{-5}$;
 $K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{CH}_3\text{COOH}]} / 1.74 \times 10^{-5}$
$$= \frac{[\text{H}^+(\text{aq})]^2}{0.100}$$

 $[\text{H}^+(\text{aq})] = 1.32 \times 10^{-3} (\text{mol dm}^{-3})$
Starting pH = 2.88;
pH at equivalence point: 8–9 [5]

- b i HIn is a weak acid:
 $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$ and two colours indicated:
In acid the equilibrium moves to the left or *vice versa*. [3]
- ii Phenolphthalein / phenol red / bromothymol blue; the colour change of indicator occurs within the range of pH at the equivalence point / on vertical part of graph. [2]
- c i Specific examples of weak base and its salt / specific strong acid and weak base, e.g. NH_3 and NH_4Cl . [1]
- ii pH changes very little / most of the acid is neutralized by base, for example:



- d Brønsted–Lowry acid is a proton donor; a Lewis acid is an electron pair acceptor;
 $\text{HI}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{I}^-(\text{aq})$;
 $\text{N}_2\text{H}_4(\text{g}) + \text{H}^+(\text{g}) \rightarrow \text{N}_2\text{H}_5^+(\text{g})$
- e It will be acidic due to a hydrolysis reaction between the aluminium ion and water molecules;
 $[\text{Al}(\text{H}_2\text{O})_6]^{3+} \rightarrow [\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}^+(\text{aq})$
- 2 a A buffer solution is an aqueous solution that resists a change in pH when a small amount of a strong acid or base is added.

A buffer contains a weak acid (HA) and its conjugate base (A^-) or a weak base and its conjugate acid.

If hydrogen ions, $\text{H}^+(\text{aq})$, are added, these will react with the base of the buffer. The hydrogen ions are removed as they combine with A^- and the equilibrium shifts to the left.

Hence, there is only a very small change in the concentrations of HA and A^- . The strong acid (H^+) is replaced by a weak acid, HA. [5]

$$\text{b Amount of sodium benzoate} = \frac{7.2\text{ g}}{144\text{ g mol}^{-1}} = 0.05\text{ mol}$$

The calculation assumes that all of the anion concentration is derived from the salt only (as that from the acid is too small to consider). It also assumes that the ionization of the acid is so small it can be ignored. Standard conditions (1 atm and 298 K) are also assumed. [3]

$$10^{-5}\text{ mol dm}^{-3} \times 6.3 \times 10^{-5} = \frac{[\text{H}^+(\text{aq})] \times 0.05}{0.03}$$

$$[\text{H}^+(\text{aq})] = 3.78 \times 10^{-5}\text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}[\text{H}^+(\text{aq})] = 4.42 \quad [2]$$

- c A weak acid is partially or incompletely ionized or dissociated. A monoprotic acid donates one hydrogen ion per molecule. [2]

- 3 a Acidic because it is a hydrogen ion donor and basic because it is a hydrogen ion acceptor. Such substances are described as amphoteric. [2]

- b Oxide ion, O^{2-} . [1]

- c pH is the negative logarithm to the base ten of the hydrogen ion concentration. $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$.
pH of pure water = 7 [2]

- d i $K_w = [\text{H}^+(\text{aq})] \times [\text{OH}^-(\text{aq})]$ [1]

- ii Water is more dissociated or ionized at a higher temperature. Le Châtelier's principle implies that endothermic reactions are favoured by increases in temperature, hence the dissociation or ionization of water is endothermic. [3]

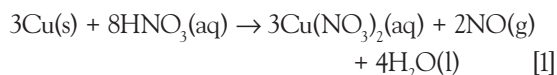
19 Redox processes

Paper 1

- | | |
|-----|------|
| 1 D | 9 B |
| 2 C | 10 B |
| 3 B | 11 B |
| 4 C | 12 A |
| 5 D | 13 B |
| 6 B | 14 A |
| 7 A | 15 B |
| 8 A | |

Paper 2

- 1 a Oxidation number of copper on left hand side is 0; oxidation number of nitrogen on right hand side is +5. [2]
- Oxidation number of copper on right hand side is +2; oxidation numbers of nitrogen on right hand side are +5 and +2. [2]



- b i The two electrodes must be dipping into aqueous solutions of their ions. The two electrodes must be connected via a salt bridge and an external circuit consisting of wire and a voltmeter. [3]
- ii Hydrogen gas at 1 atm pressure passed over a platinum electrode. The temperature of all chemicals is 298 K and all solutions have a concentration of 1 mol dm⁻³. [3]
- c i $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni(s)}; \text{Mn(s)} \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{e}^-$ [2]
Manganese is oxidized. [1]
Manganese(II) ions are the oxidizing agent. [1]
- ii Manganese is the anode. [1]
The electron flow is from manganese to nickel. [1]
- iii $E^\ominus_{\text{cell}} = (-0.23 \text{ V}) + (1.18 \text{ V}) = +0.95 \text{ V}$ [1]
 ΔG is negative. [1]
- d Gold is formed at the cathode (negative electrode). [1]
Oxygen is formed at the anode (positive electrode). [1]
- 2 a Cathode (negative electrode):
 $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$ [1]
Anode (positive electrode):
 $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$ [1]
- b There is no change in the intensity of colour since the rate of removal of copper(II) ions at the cathode is balanced by the rate of formation of copper(II) ions at the anode. [1]
There is no change in the pH since hydrogen and hydroxide ions are not involved in the discharge reactions. [1]
- c $2\text{H}_2\text{O(l)} \rightarrow \text{O}_2\text{(g)} + 4\text{H}^+(\text{aq}) + 4\text{e}^-$ [2]
- d Charge passed = $0.360 \text{ A} \times 600 \text{ s} = 216 \text{ C}$ [1]
Amount of electrons = $216 \text{ C} \div 96\,500 \text{ C mol}^{-1} = 2.24 \times 10^{-3} \text{ mol}$ [1]
2 moles of electrons are required for the discharge of one mole of copper atoms. [1]
Mass of copper deposited
= $0.50 \times 63.55 \text{ g mol}^{-1} \times 0.224 \times 10^{-3} \text{ mol} = 0.071 \text{ g}$ [1]
- 3 a i $2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$ [1]
 $2\text{e}^- + 2\text{H}^+ + \text{OCl}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$ [1]
 $2\text{H}_2\text{O} + \text{SO}_2 + 2\text{e}^- + 2\text{H}^+ + \text{OCl}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$ [1]
 $\text{H}_2\text{O} + \text{SO}_2 + \text{OCl}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} + 2\text{H}^+$ [1]

Element	Initial oxidation number	Final oxidation number
Chlorine	+1	-1
Sulfur	+4	+6

[1]

[1]

- b i The emf of a cell in which an electrode is connected to a standard hydrogen electrode/SHE ($\text{H}^+(\text{aq})/\text{H}_2(\text{g})$). The gas pressure is 101 kPa, the temperature of the solution is 298 K and the concentration of H^+ is 1.00 mol dm⁻³. [1]
- ii $2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O(l)} \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^-; E^\ominus = -1.36 \text{ V}$
 $\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O(l)}; E^\ominus = +1.49 \text{ V}$
 $E^\ominus_{\text{cell}} = +0.13 \text{ V}$; it is energetically feasible since the cell voltage is positive. [1]
Hence the Gibbs free energy change is negative and the forward reaction is spontaneous. [1]

20 Organic chemistry

Paper 1

- | | |
|-----|------|
| 1 C | 6 A |
| 2 D | 7 B |
| 3 A | 8 D |
| 4 A | 9 C |
| 5 C | 10 C |

Paper 2

- 1 a Mechanism showing: arrow from C=C double bond towards I; arrow from I-Cl bond to Cl; carbocation showing I on first carbon and positive charge on second carbon; arrow from Cl^- to carbon with positive charge and structure of product (see page 686 for this type of mechanism). [4]
- b 1-Chloro-2-iodobutane / 2-iodo-1-chlorobutane; formed via primary carbocation, which is less stable than the secondary carbocation; free electron-releasing alkyl groups / positive charge spread out less. [3]
- 2 a Electrophilic substitution [1]
- b Mechanism showing: curly arrow from delocalized electrons to Cl^+ ; structure of intermediate showing Cl attached to ring, positive charge and the remaining four electrons in the benzene ring; curly arrow showing C-H bond fission and electrons moving into benzene ring (see Figure 20.38b, page 689). [3]
- c J: $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$; K: $\text{C}_6\text{H}_5\text{CHCl}_2$; L: $\text{C}_6\text{H}_5\text{CCl}_3$ [3]

- d Free radical substitution [1]
- e $\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$; sunlight / UV light [2]
- f $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{Cl}\cdot \rightarrow \text{C}_6\text{H}_5\text{CHCl}\cdot + \text{HCl}$
 $\text{C}_6\text{H}_5\text{CHCl}\cdot + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CHCl}_2 + \text{Cl}\cdot$ [2]
- g $\text{C}_6\text{H}_5\text{CCl}_2\cdot + \text{Cl}\cdot \rightarrow \text{C}_6\text{H}_5\text{CCl}_3$ [1]
- 3 a i Show structure with the Hs on the different carbon atoms diagonally opposite each other (the *trans* form). [1]
- ii There is restricted rotation around the axis of the carbon–carbon double bond, so one form cannot be transformed into the other / the presence of the pi electron cloud makes the molecule rigid. [2]
- iii Hex-2-ene [1]
- b i Electrophilic addition [1]
- ii $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}_2\text{CH}_3$; the third carbon atom in the chain is a chiral centre as it has four different substituents attached to it (note that the alternative structure with the Br attached to the second carbon atom is also possible and also shows optical isomerism). [2]
- iii Mechanism involving carbocation formation (see page 686). [4]
- iv In this case there are two possible secondary carbocations that could be formed and Markovnikov's rule cannot distinguish between them. [2]
- 4 a The isomers are: **A** 1-bromobutane;
B 2-bromobutane; **C** 2-bromo-2-methylpropane;
D 1-bromo-2-methylpropane. [4]
- b i **C**; $\text{S}_{\text{N}}1$: Substitution/Nucleophilic/unimolecular. [2]
- ii $\text{RBr} \rightarrow \text{R}^+ + \text{Br}^-$; heterolytic fission to form the carbocation intermediate. [2]
- iii **A**; see Figure 20.3, page 673. [4]
- c Mechanism b(i): no change in rate; mechanism b(iii): rate doubles. [2]
- d The rate of reaction with 1-bromobutane is faster than for 1-chlorobutane as the C–Br bond is weaker than the C–Cl bond; Br^- is a better leaving group than Cl^- . [2]
- e **B** shows optical isomerism as the molecule contains a carbon atom with four different groups attached. Solutions of the two isomers will rotate the plane of plane-polarized light in opposite directions and this is detected in a polarimeter (see page 709). The polarimeter is set up with water to align the filters to obtain maximum extinction of light. The solutions of the two isomers of the same concentration are then tested – one will rotate the plane to the right, the other to the left by the same amount. The physical and chemical properties of the two isomers are the same. [5]

- 5 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). [9]

Chapter 21 Measurement and analysis

Paper 1

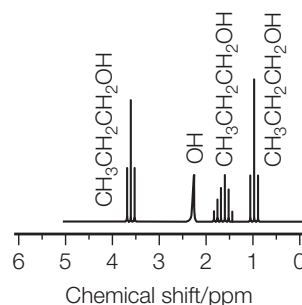
- | | |
|-----|-----|
| 1 A | 4 A |
| 2 C | 5 D |
| 3 B | 6 D |

Paper 2

- 1 a There is a stationary phase and a mobile phase. [1]
- The components of the mixture dissolve, absorb, or partition to differing extents between the two phases. [1]
- b i A [1]
- ii B [1]
- iii No, the two 'oranges' are different substances since they have different R_f values. [2]
- iv $R_f \text{ value} = \frac{9}{22} = 0.41$ [1]
- c i $R_f \text{ value of compound 1} = \frac{1.6}{12.6} = 0.13$ [1]
- $R_f \text{ value of compound 2} = \frac{9.2}{12.6} = 0.73$ [1]
- Compound 1 has a greater affinity for the thin layer than compound 2. Since the thin layer is composed of silica gel, compound 1 is more polar than compound 2. [1]
- ii TLC is faster than paper chromatography. The thin layer may be made from a variety of different solids. Hence, a range of mixtures can be separated by using different stationary and mobile phases. [1]
- 2 a By measuring the difference in time between the injection of the sample and the centre of the peak for a component. [1]
- b The areas under the peaks represent the amounts of the components in the mixture. [1]
- c i Hexan-1-ol [1]
- ii Ethanol [1]

- d Flow rate of the carrier gas; temperature of the column; length and diameter of the column; the nature of column surface and the volatility of the solute. [1]
- e i The two compounds have relatively high melting points and are involatile. [2]
 ii HPLC. [1]
- 3 a 3350 cm^{-1} due to O–H bond; 2900 cm^{-1} due to C–H bond. [2]
Award [1] if both bonds given but not linked to correct absorption.
- b Comparison of fingerprint regions/comparison with library, database or known spectra. [1]
- c Same molecular ion/parent ion (M) due to $\text{C}_4\text{H}_9\text{OH}^+/\text{C}_4\text{H}_{10}\text{O}^+$. [1]
- d i $(m/z = 57) \text{C}_4\text{H}_9^+ / (\text{CH}_3)_3\text{C}^+$.
 ii $(m/z = 45) \text{C}_2\text{H}_5\text{O}^+ / \text{CH}_3\text{CHOH}^+ / \text{C}_2\text{H}_4\text{OH}^+$. [2]
Penalize missing charge once only in (c) and (d).
- e i Four peaks because four different hydrogen environments/four different types of proton/OWTTE; 6:2:1:1. [2]
 ii $(\text{CH}_3)_3\text{COH}$ /more detailed formula. [1]

- 4 It has four hydrogen environments and there will be splitting of the methyl group and both sets of methylene ($-\text{CH}_2-$) protons. In the high resolution ^1H NMR spectrum the methyl group ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) is a triplet at approximately 1 ppm and the alcohol or hydroxyl group ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) is a broad singlet at approximately 2.3 ppm. Of the two methylene groups, the one next to the highly electronegative oxygen atom of the $-\text{OH}$ group is most downfield at approximately 3.6 ppm. This methylene group ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) is split into a triplet. The methylene group adjacent to the methyl group appears as a sextet.



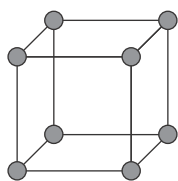
[5]

Answers to examination questions in Chapters 22 to 25 (Options A to D)

22 Option A Materials

- 1 a Coordination number is six. [1]

Each unit cell has eight atoms. The corner atoms belong to eight unit cells, thus $\frac{1}{8}$ of each corner atom belongs to the unit cell; $\frac{1}{8} \times 8 = 1$. [1]



b i $a = \frac{n\lambda}{2 \sin \theta} = \frac{1 \times 154.05 \times 10^{-12} \text{ m}}{2 \sin(10.89^\circ)}$
 $= 4.076 \times 10^{-10} \text{ m} = 4.076 \times 10^{-8} \text{ cm}$ [1]

ii Volume of unit cell $= a^3 = (4.076 \times 10^{-10})^3$
 $= 6.770 \times 10^{-29} \text{ m}^3 = 6.770 \times 10^{-23} \text{ cm}^3$ [1]

iii Number of unit cells present within 1.000 cm^3
of gold $= \frac{1.000}{6.770 \times 10^{-23}} = 1.477 \times 10^{22}$ [1]

iv Number of gold atoms present within 1.000 cm^3
of gold $= 1.477 \times 10^{22} \times 4 = 5.908 \times 10^{22}$ [1]

c i Mass of one atom of gold $= \frac{196.97 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}}$
 $= 3.27 \times 10^{-22} \text{ g}$ [1]

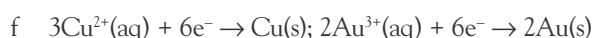
ii Mass of the unit cell of gold $= 3.27 \times 10^{-22} \text{ g} \times 4$
 $= 1.31 \times 10^{-21} \text{ g}$ [1]

d Density of gold $= 1.470 \times 10^{22} \times 1.31 \times 10^{-21}$
 $= 19.3 \text{ g cm}^{-3}$ [1]

- e i At low temperatures the positive ions (cations) in the lattice are attracted to a passing electron, distorting the lattice slightly. [1]

A second electron with opposite spin is attracted to this slightly positively charged deformation and a coupling of the electrons occurs (to form Cooper pairs). [1]

- ii Higher catalytic activity; higher stability; some nanocatalysts have charged sites that can help break bonds; increased selectivity. [2]



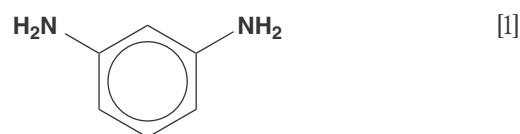
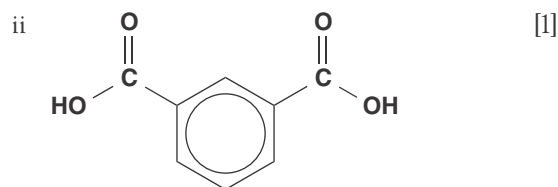
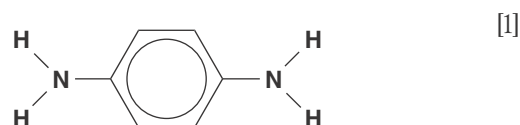
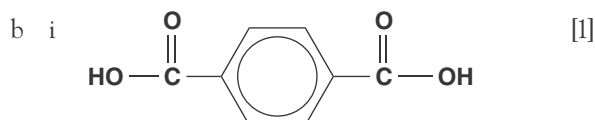
Amount of copper atoms $= \frac{0.965 \text{ g}}{63.55 \text{ g mol}^{-1}}$
 $= 0.015 \text{ mol}$

Amount of electrons $= 0.015 \times 2 = 0.030 \text{ mol}$
(Faradays) [1]

Amount of gold atoms $= \frac{0.03}{0.3} = 0.01 \text{ mol}$ [1]

Mass of gold atoms $= 0.01 \text{ mol} \times 196.67 \text{ g mol}^{-1}$
 $= 1.96 \text{ g}$ [1]

- 2 a They contain benzene rings (containing delocalized pi electrons). [1]



- c Hydrogen bonding/hydrogen bonds. [1]

- d Nomex has a lower tensile strength than Kevlar because the chains cannot be aligned as closely for maximizing hydrogen bonding interactions between adjacent chains. [2]

- e The carbonyl groups become protonated (at the nitrogen atoms) due to the sulfuric acid acting as a proton donor; disrupting the hydrogen bonding. [1]

The sulfuric acid molecules then solvate the protonated chains. [1]

- f During addition polymerization, no atoms are lost. [1]

During condensation polymerizations atoms in the form of small molecules are lost. [1]

- g It is composed of long rigid and extended molecules. [1]

- h A composite material is a solid material which consist of a combination of two or more constituents [1], in which the individual components retain their separate identities. [1]

3 a [2]

Compound	Chromium(III) oxide	Cadmium sulfide
Electronegativity difference	1.70	0.90
Average electronegativity	2.55	2.15

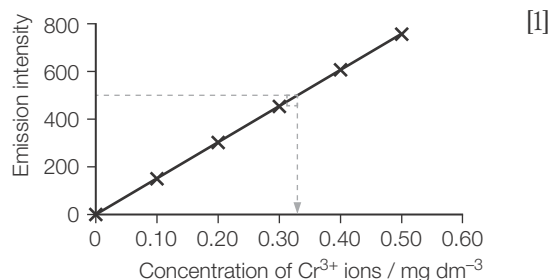
b [2]

Compound	Chromium(III) oxide	Cadmium sulfide
Bond type	Ionic	Polar covalent
%covalent character	15–20	60–58

- c i For example, 1000 cm^3 of the standard solution contains 5.00 mg of Cr^{3+} ions, so 2.0 cm^3 contains $\left(500 \times \frac{2.0}{1000}\right)\text{ mg} = 0.010\text{ mg}$ of Cr^{3+} ions; this was diluted in 100 cm^3 so the resulting solution had a concentration of 0.10 mg dm^{-3} .

The other concentrations are 0.20 , 0.30 , 0.40 and 0.50 mg dm^{-3} . [2]

ii



- iii The concentration is approximately 0.35 mg dm^{-3} . [1]

- iv 1000 cm^3 of the waste water would contain $\left(0.35 \times \frac{1000}{50}\right)\text{ mg} = 7.0\text{ mg}$ of $\text{Cr}^{3+}(\text{aq})$ ions; concentration = 7.0 mg dm^{-3} . [1]

- d $\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$, let x be the solubility of Ag_2CrO_4 in mol dm^{-3}
 $[\text{Ag}^+(\text{aq})] = 2x\text{ mol dm}^{-3}$; $[\text{CrO}_4^{2-}(\text{aq})] = x\text{ mol dm}^{-3}$ [1]
 $K_{\text{sp}} = [\text{Ag}^+(\text{aq})]^2[\text{CrO}_4^{2-}(\text{aq})] = (2x)^2(x) = 4x^3$
 $4x^3 = 4 \times 10^{-12}$; $x = 1 \times 10^{-4}\text{ mol dm}^{-3}$ [1]

- 4 a i $\text{Sc}: 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ [1]
 $\text{Sc}^{3+}: 1s^2 2s^2 2p^6 3s^2 3p^6$ [1]

- ii Scandium metal is paramagnetic because of the presence of an unpaired $3d$ electron. [1]
 Scandium(III) compounds are diamagnetic because all the electrons are paired. [1]

- iii $[(\text{Sc}^{3+})_3 \text{C}_{82}^{9-}]$ [1]

- b i Helium is an excellent coolant; and provides an inert and non-oxidizing environment. [1]

- ii Mixture of carbon containing compound and inert dilutant in gas/vapour phase [1] passed over a heated metal catalyst [1].

- iii The C_{82} molecule has larger number of atoms and hence a greater number of polarizable electrons available for temporary dipole formation and hence stronger London (dispersion) forces. [2]

- c i All sp^2 [1]

- ii There is a poor delocalization of π electrons within the C_{60} molecules because of the curved surface reducing p orbital overlap; these electrons are unable to transfer between adjacent C_{60} molecules (high energy band). [1]
 There is excellent delocalization of π electrons within the flat graphene sheet and these electrons readily move when a voltage is applied. [1]

- d The particles may be toxic/hazardous/carcinogenic. [1]

The human immune system may not mount a defence against nanoparticles. [1]

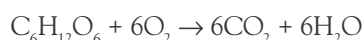
- e i Silicon and oxygen. [1]

- ii $\text{Sc}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{Sc}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$ [1]
 $2\text{Sc}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) \rightarrow 2\text{Sc}(\text{s}) + 3\text{CO}_2(\text{g})$ [1]

- iii Higher tensile strength/greater corrosion resistance/ to achieve properties not present in pure metals/alter properties, for example, melting point and malleability. [2]

23 Option B Biochemistry

- 1 M_r of glucose = 180.18 g mol^{-1}
 Number of moles of glucose per day = $\frac{135}{180.18}$
 = 0.75 mol [1]

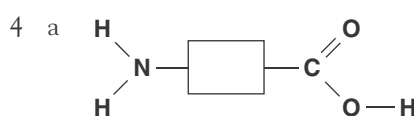


- From equation for respiration: 1 mol of glucose produces 6 mol of carbon dioxide
 $0.75\text{ mol glucose} \rightarrow 4.5\text{ mol CO}_2$ [1]

- Mass of $\text{CO}_2 = 4.5 \times 44.01 = 198.05\text{ g}$ [1]

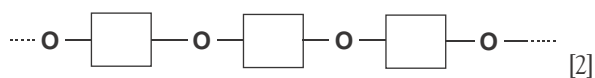
- 2 Anabolic pathways are metabolic pathways in which compounds are broken down [1], whereas catabolic pathways involve the synthesis of molecules [1].

- 3 Hydrolysis is the breaking of covalent bonds by a reaction involving the addition of water ($\text{H}-$ and $-\text{OH}$) to the breakdown products [1]; in condensation reactions molecules are joined together with the elimination of water as the bonds are made [1].

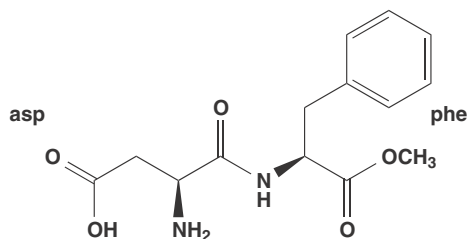


Draw this molecule and a similar one with the box shaded to match one of the examples in the question. [2]

b



- 5 The structure of aspartame is shown here – made up of aspartic acid (asp) as the N terminus of the dipeptide, and phenylalanine (phe) as the C terminus. Note the peptide link in the centre and the fact that the —COOH of the phenylalanine has been esterified with methanol (the —CH_3 group on the right). [3]



- 6 a i The amino acids will be in the zwitterion form [1]; but one will have an extra positive charge on the amino group in the side-chain, while another will have an extra negative charge on the R-group because of the ionization of the extra acid group [1].

Sketch a diagram showing three spots: one will remain at the centre (Val), one will have moved to the right because of the extra negative charge (Asp), and one will have moved to the left because of the extra positive charge (Lys) [1].

- ii At pH 12 two of the amino acids will move together to the right because they have a single negative charge on them (Val and Lys) [1]; the other amino acid (Asp) will move further to the right as it has a double negative charge [1].

- b Amino acids such as valine and isoleucine are non-polar and hydrophobic – the protein will tend to fold so that these amino acids are internal to the structure and away from exposure to water [1]. Amino acids such as glutamic acid and lysine have charged groups in their R-groups, capable of participating in ionic interactions and hydrogen bonding [1] – these will tend to be on the outer 'surface' of the protein structure where they can interact with water (they are hydrophilic) [1].

- 7 a The retention factor is the ratio of the distance moved by the sample to the solvent front. [1]
 b 0.4 and 0.7 [1]
 c 0.4, 0.5 and 0.8 [1]
 d Arg, His, Asn, Cys, Pro, Thr, Gly, Glu, Asp, Met, Leu [2]

- e Electrophoresis (or isoelectric focusing, or ion exchange chromatography) [1]

- 8 a See Figures 23.68 and 23.84 for comparison; note that in a triglyceride all three ester links to the central glycerol molecule are taken by long-chain fatty acid molecules whereas in a phospholipid a phosphate group is present. [3]

- b i In a saturated fat all the long-chain fatty acids contain saturated hydrocarbon chains – there are no $\text{C}=\text{C}$ double bonds; in an unsaturated fat at least one of the long-chain fatty acids has a hydrocarbon chain containing at least one $\text{C}=\text{C}$ double bond. [1]

- ii A mono-unsaturated fat contains hydrocarbon chains with one $\text{C}=\text{C}$ double bond. [1]

- iii *Cis-trans* isomerism; octadec-*cis*-9-enoic acid [2]

- 9 a Unsaturated fats in the fish oil / $\text{C}=\text{C}$ double bonds in the long hydrocarbon chains. [1]

- b Rancid (resulting from oxidative rancidity) [1]

- c Light promotes the formation of oxygen free radicals. [1]

- d The curcumin molecule contains a number of $\text{C}=\text{C}$ double bonds that absorb the free radicals, acting as an alternative target. [1]

- 10 a The structure contains groups such as —NH_2 , which can form hydrogen bonds with water molecules; and also carboxylic acid groups (—COOH) which can hydrogen bond and also ionize. [1]

- b i Night-blindness / xerophthalmia (a cause of blindness) [1]

- ii Vitamin A is fat-soluble, and if the intake of fat in the diet is insufficient the vitamin A from the livers cannot be absorbed and used by the body. [1]

- 11 a Atom economy

$$= \left(\frac{\text{total mass of desired product formed}}{\text{total mass of all products}} \right) \times 100$$
 [1]

Method 1: atom economy = $\left(\frac{120.16}{620.49} \right) \times 100$
 = 19.4% [1]

Method 2: atom economy = $\left(\frac{120.16}{138.18} \right) \times 100$
 = 86.8% [1]

- b Consider: the use of highly corrosive chemicals such as sulfuric acid or the ease of availability of any catalyst. [2]

- 12 a pK_a glycine = 2.34

$$\text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{base}]}{[\text{acid}]}} \right) = 2.34 + \log_{10} \left(\frac{0.20}{0.12} \right)$$

$$\text{pH} = 2.34 + 0.22 = 2.56$$
 [3]
 b
$$\text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{base}]}{[\text{acid}]}} \right) = 2.34 + \log_{10} \left(\frac{0.20}{0.121} \right)$$

$$\text{pH} = 2.34 + 0.218 = 2.56$$

$$\text{c } \text{pH} = \text{pK}_a + \log_{10} \left(\frac{[\text{base}]}{[\text{acid}]} \right) = 2.34 + \log_{10} \left(\frac{0.21}{0.12} \right)$$

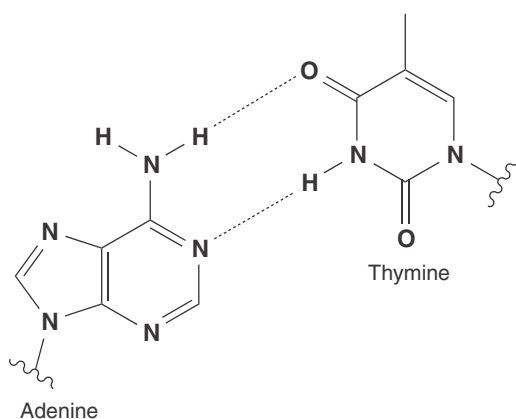
$$\text{pH} = 2.34 + 0.243 = 2.58$$

- 13 a The position of the phosphate groups on the inside of the structure would have led to the chains repelling each other [1] as under cellular conditions the phosphate groups would carry negative charges. [1]

- b The hydrogen bonds between the nitrogenous bases in the two chains break so that the chains can part. [1]

- 14 a Thymine is linked to a hydroxyl group of the sugar, deoxyribose which in turn has a phosphate group attached to another hydroxyl group; a nucleotide consists of a base-sugar-phosphate grouping. [2]

- b Thymine is able to hydrogen bond to the base, adenine, in the other chain of the DNA double helix / there is specific recognition, or base pairing, as the AT pairing involves two hydrogen bonds (the alternative pairing GC involves three hydrogen bonds). [3]



- c The sequence of the four bases along a strand of DNA provides the message coding for the synthesis of a specific amino acid sequence in a protein chain; each amino acid is coded for by a triplet code of bases; some amino acids have more than one triplet code but there is no ambiguity. [2]
- d Restriction enzymes are able to break DNA at very specific places (sequences) and therefore they give rise to very specific fragmentation patterns that are characteristic of an individual's DNA/ the fragmentation patterns can be analysed by gel electrophoresis. [2]
- 15 a White light is a mixture of colours of varying wavelength / anthocyanin colours the berries blue by absorbing light in the red to green regions of the spectrum thus allowing just the blue region of the spectrum to be seen. [2]
- b Low pH and low temperature. [1]

- 16 a Place an asterisk on the carbon atom at the bottom of the ring structure – see Figure 20.71 in text book. [1]

- b The isomers (enantiomers) are optically active / the (+)-form will rotate the plane of plane-polarised light to the right; the (–)-form to the left. [1]

- c The R/S convention is based on the priority rules (CIP rules) of Cahn, Ingold and Prelog – see Figure 20.68 – where substituent groups are assigned a priority based on complexity; the structure shown is R-(+)-limonene. [2]

- 17 a i $\text{C}_{20}\text{H}_{28}\text{O}$ [1]

- ii Add the following to end of the molecule: the aldehyde group $-\text{CHO}$ is converted to a primary alcohol grouping $-\text{CH}_2\text{OH}$



- iii A $\text{C}=\text{C}$ double bond. [1]

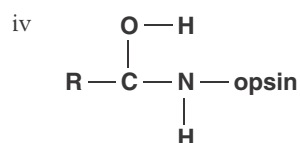
- iv Heat [1] alcohol with sodium dichromate(IV) / concentrated sulfuric acid [1] in distillation apparatus so that the aldehyde distils over as soon as formed [1]; use an excess of the alcohol to the oxidising agent [1].

- v 5 mol [1]

- b i See the structure on the left in Figure 23.264. [1]

- ii Primary amine group ($-\text{NH}_2$) – see Figure 23.267 [1]

- iii Condensation reaction [1]



24 Option C Energy

1 [3]

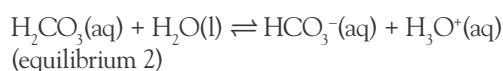
	Advantages	Disadvantages
Coal fires in homes	Coal is widely available and easily stored <i>in situ</i>	Health problems arising from particulate emissions Very inefficient – lots of heat goes up chimney
Coal for electricity generation	Coal has fewer other uses (i.e. oil can be used for manufacturing plastics, rather than as fuel) Less pollution in populated areas – easier to process emissions in large scale plants More efficient way of extracting maximum energy from coal	Emission of CO_2 (greenhouse gas) Emission of SO_2 (from sulfur impurities; acid rain) Electricity infrastructure is required – not always available in poorer countries

- 2 a 47.6 MJ kg^{-1} [2]
 b $476\,500 \text{ MJ}$ ($4.76 \times 10^{12} \text{ J}$) [2]
- 3 a $10\text{C(s)} + 11\text{H}_2\text{(g)} \rightarrow \text{C}_{10}\text{H}_{22}\text{(l)}$ [2]
 b $21\text{H}_2\text{(g)} + 10\text{CO(g)} \rightarrow \text{C}_{10}\text{H}_{22}\text{(l)} + 10\text{H}_2\text{O(l)}$ [3]
- 4 a $^{235}_{92}\text{U} + ^1_0\text{n} \rightarrow ^{137}_{54}\text{Xe} + ^{99}_{38}\text{Sr}$; Strontium-99 [2]
 b $^{137}_{54}\text{Xe} \rightarrow ^0_{-1}\beta + ^{137}_{55}\text{Cs}$; $^{137}_{55}\text{Cs} \rightarrow ^0_{-1}\beta + ^{137}_{56}\text{Ba}$ [2]
 c 1.6% [2]
 d High solubility makes it likely to enter ground water; solubility means it is likely to be taken up by organisms (plants and animals). [2]
- 5 a Alpha – beta – beta – alpha – alpha [5]
 b 3715 years [2]
 c Gases are likely to be breathed in. Alpha sources have a very short range in air but are very dangerous if they enter the body. [2]
- 6 a Advantages: (i) lower net greenhouse emissions than fossil fuels (as the plants absorb CO_2 when they grow); use of biofuels preserves fossil fuel reserves for other uses (e.g. plastics manufacture); existing infrastructure and car designs can be used with minimal modification.
 Disadvantages: production of biofuels is energy intensive (high embodied energy); commercial production of biofuels impacts on biodiversity; commercial production of biofuels might displace necessary food production. [4]
 b [3]

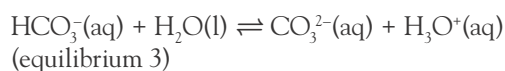
	Advantages	Disadvantages
Ethanol	Easily mixed with gasoline and usable in engines without modification	Lower specific energy Absorbs moisture so might damage engines
Palm oil biodiesel	Higher specific energy	Requires processing (transesterification) to lower viscosity

- c Vegetable oils are too viscous (especially at lower temperatures) so they need pre-warming or additional processing (transesterification) to make them usable. [2]
 d Transesterification involves reacting the triglyceride (oil) with methanol or ethanol, producing three molecules of methyl or ethyl esters and glycerol. This mixture has a similar energy density to the original oil but lower viscosity and lower boiling point. [2]
 e $(\text{C}_{17}\text{H}_{33}\text{COO})_3\text{CH}(\text{CH}_2)_2 + 3\text{CH}_3\text{OH} \rightleftharpoons 3\text{C}_{17}\text{H}_{33}\text{COOCH}_3 + \text{CH}_2\text{OHCHOHCH}_2\text{OH}$ [2]
- 7 As carbon dioxide dissolves in the oceans it forms carbonic acid, H_2CO_3 .
 $\text{CO}_2\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{CO}_3\text{(aq)}$ (equilibrium 1)

Carbonic acid is a weak diprotic acid, which dissociates to form first hydrogen carbonate ions (HCO_3^-)



The hydrogen carbonate ion then dissociates (to a smaller extent) to form carbonate ions (CO_3^{2-})



Both these reactions generate H_3O^+ . The solution becomes more acidic and the pH falls.

An increase in the concentration of dissolved carbon dioxide will lead to an increased concentration of carbonic acid in equilibrium (1). Increasing the concentration of carbonic acid in equilibrium (2) leads to a shift to the right and therefore more hydrogen carbonate and oxonium (H_3O^+) ions. More hydrogen carbonate ions in equilibrium (3) causes a shift towards more oxonium ions again.

Increased carbon dioxide concentrations in the atmosphere will lead to more carbon dioxide in the oceans and an increase in the oceans' acidity. This may kill sea creatures with calcium carbonate shells, an effect which will then move through the entire food chain. In addition, the larvae or eggs of sea creatures may be unable to survive.

A further effect may be the loss of coral. As the pH of the ocean falls, the loss of calcium carbonate may occur more quickly than the corals can replace. [5]

- 8 a Visible light, (near) infrared, (near) ultraviolet [3]
 b This radiation is absorbed by the Earth's surface, warming it. The surface emits infrared radiation which warms the atmosphere. [2]
 c Infrared radiation is absorbed by carbon dioxide as its frequencies match the vibrational frequencies of the molecule. The molecules then re-radiate infrared, with some of it radiated downwards towards the surface. [3]
 d GWP is a factor which combines the abundance of a gas in the atmosphere, their ability to absorb radiation, and their lifetime in the atmosphere before chemical processes remove them. [4]
 e Methane has much lower abundance than carbon dioxide, but it absorbs infrared much more efficiently. [2]
 f Outcomes might include: ocean acidification, drought, flooding, sea-level rise, glacier retreat, changing patterns of agriculture. [4]
- 9 a i The platinum catalyst on the anode splits the hydrogen molecules into hydrogen ions and electrons. The platinum on the cathode catalyses the reaction of oxygen gas and water forming hydroxide ions.

- ii The electrolyte completes the electrical circuit. The sodium hydroxide electrolyte reacts with the hydrogen ions carrying out a neutralisation reaction forming water. [4]
- b The polymer membrane allows the use of much less platinum. The polymer membrane has a lower resistance than the liquid electrolyte. [1]
- c Anode: $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$ (oxidation) – negative terminal
Cathode: $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ (reduction) – positive terminal [4]
- d Hydrogen is not readily available (it must be extracted, for example, from seawater). Hydrogen is a gas and must be stored under pressure. [1]
- 10 a A secondary cell is a voltaic cell in which the cell reaction can be reversed by passing a current through it. [1]
- b [4]

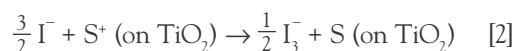
	Nature of electrolyte	Charge carrier
Lithium-ion battery	Polymer film	Lithium ion
Nickel–cadmium battery	Potassium hydroxide paste	Hydroxide ion

- c Lithium-ion battery half-equations:
Anode: $2\text{Li}(\text{graphite}) \rightarrow 2\text{Li}^+(\text{electrolyte}) + 2\text{e}^-$
Cathode: $2\text{CoO}_2(\text{s}) + 2\text{e}^- + 2\text{Li}^+(\text{electrolyte}) \rightarrow 2\text{Co}_2\text{O}_3(\text{s}) + \text{Li}_2\text{O}(\text{s})$
Nickel–cadmium battery half-equations:
Anode: $\text{Cd}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cd}(\text{OH})_2(\text{s}) + 2\text{e}^-$
Cathode: $2\text{Ni}(\text{OH})_3(\text{s}) + 2\text{e}^- \rightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq})$ [8]
- d Lithium-ion battery advantages: High energy density – lithium-ion batteries are light and powerful; Minimal memory effect – lithium-ion batteries are more tolerant of incomplete charge–discharge cycles.
Nickel–cadmium battery advantages: High number of charge–discharge cycles possible (thousands); Long storage time – can retain a charge ‘on the shelf’ for months. [4]
- 11 a Methanol has higher energy density than hydrogen; methanol is a liquid and is more easily stored. [2]
- b i –2 [1]
ii +4 [1]
iii $\text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CO}_2(\text{g}) + 6\text{H}^+(\text{aq}) + 6\text{e}^-$ [2]
iv $\text{O}_2(\text{g}) + 2\text{e}^- + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ [2]
- c Carbon in ethanol: -2 ; $\text{CH}_3\text{CH}_2\text{OH}(\text{l}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{CO}_2(\text{g}) + 12\text{H}^+(\text{aq}) + 12\text{e}^-$ [3]

- 12 a $\Delta G = -872 \text{ kJ mol}^{-1}$; $\Delta H = -874 \text{ kJ mol}^{-1}$; efficiency = 99.8%. [2]
- b They produce useful energy from a waste product; they help to clean up waste water by removing organic pollutants; they decrease the demand for expensive catalysts such as platinum. [2]
- 13 a i Fission; 0.18614 amu; 169.2 MeV
ii Fusion; 0.01894 amu; 17.6 MeV
iii Fission; 5.14×10^{-3} amu; 4.79 MeV
iv Fission; 0.22194 amu; 206.7 MeV [12]
- b $1.673 \times 10^{10} \text{ kJ mol}^{-1}$; very high value (a million times larger than a typical enthalpy of combustion of a fuel). [3]
- 14 a The graph has a very steep upwards curve, levelling off to Fe (mass = 56) and then a shallow slope across to heavy transuranic elements (250+ amu). [3]
- b The binding energy depends on the difference between two forces: the strong nuclear force and the electrostatic repulsion within the nucleus. For light elements (up to around ^{16}O) the increase in nuclear size causes a large increase in the strong nuclear force, but a relatively small increase in the electrostatic repulsion of the protons within the nucleus. During the approximately horizontal portion of the graph the increase in strong nuclear force is balanced by the increase in the electrostatic repulsion. For the heavier elements (beyond ^{56}Fe) the increase in electrostatic repulsion exceeds the increase in the strong nuclear force. [3]
- c For small elements undergoing fusion, the binding energy of the fusion product (in this case, helium) is greater than the binding energy of the hydrogen nuclei, so there is an energy output during fusion. [2]
- d For heavier elements, the total binding energy of the smaller nuclei produced during fission (barium and krypton) is greater than the binding energy of the uranium nucleus which undergoes fission. [2]
- 15 a Naturally occurring uranium contains insufficient fissionable nuclei to sustain a chain reaction. [1]
- b i $\text{UO}_2 + 4\text{HF} \rightarrow \text{UF}_4 + 2\text{H}_2\text{O}$; neutralization reaction [3]
ii $\text{UF}_4 + \text{F}_2 \rightarrow \text{UF}_6$; oxidation reaction [3]
iii Enrichment by effusion or centrifugation relies on the uranium compound being in the gas state. UF_6 is a gas whereas UO_2 is a solid. [2]
- c i 1.004 ($^{235}\text{UF}_6$ effuses at 1.004 times the rate of $^{238}\text{UF}_6$) [2]
ii $0.7 \times (1.004)^x = 90$; 1217 stages [2]
iii $0.7 \times (1.3)^x = 90$; 19 stages [1]

- 16 a $\text{H}_2\text{O} + \text{HO}^\bullet \rightarrow \text{HO}^\bullet + \text{H}_2\text{O}$ [1]
- b i $\text{H}^\bullet + \text{O}_2 \rightarrow \text{HOO}^\bullet$ [2]
- ii $\text{H}-\ddot{\text{O}}-\ddot{\text{O}}^\bullet$ [1]
- c $\cdot\ddot{\text{O}}:\ddot{\text{O}}^\bullet$ [1]
- d Radicals can collide and react with DNA molecules causing mutations. [2]
- 17 a i Neptunium-237 [1]
- ii Use $\lambda = \frac{\ln 2}{t_{\frac{1}{2}}}$
- $$\lambda = \frac{0.693}{432} = 1.605 \times 10^{-3} \text{ y}^{-1};$$
- $$\text{Use } N = N_0 e^{-\lambda t}$$
- $$N_0 = 0.29 \mu\text{g}; t = 20 \text{ y}; N = 0.28 \mu\text{g}$$
- [3]
- b i $\lambda = \frac{0.693}{23400 \text{ y}} = 2.962 \times 10^{-5} \text{ y}^{-1}$ [2]
- ii Use $t_{\frac{1}{2}} = t \frac{\ln 2}{\ln\left(\frac{N_0}{N}\right)}$
- $$\frac{N_0}{N} = \left(\frac{1 \text{ g}}{1 \text{ mg}}\right) = 0.001;$$
- $$t = 23400 \times \left(\frac{\ln(1000)}{\ln 2}\right) = 233200 \text{ y}$$
- [2]
- c i Praseodymium-144 [1]
- ii Use $\lambda = \frac{\ln 2}{t_{\frac{1}{2}}}$
- $$\lambda = \frac{0.693}{285} = 2.432 \times 10^{-3} \text{ d}^{-1}$$
- $$\text{Use } \frac{N}{N_0} = e^{-\lambda t}$$
- $$\frac{N}{N_0} = e^{-2.432 \times 10^{-3} \times 84} = 0.82$$
- 81% of the cerium remains untransmuted so 19% has transmuted. [2]
- 18 a A conjugated series of double and single bonds. [1]
- b i The titanium dioxide is a semi-conductor that transfers electrons from the dye to the external circuit. [1]
- ii To maximise the area of the dye exposed to light. [2]
- c i The iodide / triiodide electrolyte gains an electron (which has come from oxidation of the dye):
- $$\frac{1}{2} \text{I}_3^- + e^- \rightarrow \frac{3}{2} \text{I}^-$$
- [2]

- ii The dye (S) is reduced by electrons from the iodide ions:



- d A homemade DSSC is likely to use finely divided TiO_2 powder. The best DSSCs use TiO_2 nanoparticles which have a much larger surface area for dyes and more pathways for electron flow.
- A homemade DSSC uses fruit juice or plant dyes to absorb light. The best DSSCs use specially-designed dyes which optimise the absorption of light. [3]

25 Option D Medicinal chemistry

- 1 a An antibiotic is a synthetic or semi-synthetic substance that kills bacteria. [1]
- b Prevents deactivation by stomach acid/more resistant to stomach acid. [1]
- Prevents deactivation by the enzyme penicillinase (produced by bacteria) increases resistance/tolerance to penicillinase. [1]
- c Broad spectrum – effective against many types/strains of bacteria; narrow spectrum – effective only for certain type of bacteria. [1]
- d Penicillin interferes with the cell wall formation. [1]
- Cells can expand/burst/disintegrate/bacteria die. [1]
- e Makes penicillin less effective; destroys useful/beneficial bacteria; allows resistant population to build up. [1]
- f Failure to complete a course of antibiotics favours the selection of antibiotic-resistant bacteria. [1]
- g The strain within the four-membered ring structure increases the reactivity of the amide. [1]
- The ring structure opens so that the penicillin becomes covalently bonded to the enzyme [1] that synthesizes the bacterial cell walls (blocking its action). [1]
- h Pharmaceuticals, for example, penicillins and cephalosporins; analgesics, for example, codeine; anticonvulsants; beta-blockers, X-ray media and chemotherapy drugs and anabolic steroids. [3]
- 2 a Esterification or condensation. [1]
- b *Difference:* aspirin shows two strong peaks in the carbonyl ($>\text{C}=\text{O}$) stretching region ($1700\text{--}1800 \text{ cm}^{-1}$) since it has two carbonyl groups; the higher frequency peak at about 1750 cm^{-1} can be assigned to the acetyl ($-\text{O}-(\text{C}=\text{O})-\text{CH}_3$) group. [1]
- Similarity:* A strong peak near 1700 cm^{-1} due to the stretching of the $>\text{C}=\text{O}$ bond of the carboxylic

- acid group; peaks near 1605 cm^{-1} due to a skeletal vibration of the benzene ring; both have strong peaks from $1050\text{--}1410\text{ cm}^{-1}$ for C–O in alcohol/phenol; both have broad peaks (because of hydrogen bonding) from $2500\text{--}3000\text{ cm}^{-1}$ for –OH in carboxylic acid. [1]
- c Three peaks in a ratio of 4 : 3 : 1. [1]
All singlets. [1]
- d Reaction with potassium hydroxide produces an ionic salt:

$$\text{C}_6\text{H}_4(\text{OH})(\text{COOH}) + \text{KOH} \rightarrow \text{C}_6\text{H}_4(\text{OH})(\text{COOK}) + \text{H}_2\text{O}$$
 [1]
 Increases aqueous solubility for transport/uptake. [1]
 Higher proportion of drug/dosage reaches target region/cells. [1]
- e Any one of the following beneficial effects: used to treat mini-strokes; prevents heart attacks / reduces risk of heart attack / thins the blood / anticoagulant; relieves symptoms of rheumatologic diseases / anti-inflammatory; reduces fever. [1]
 Any one of the following side effects: stomach bleeding; allergic reaction; Reye's syndrome; hearing loss; tinnitus (ringing in the ears); gastrointestinal irritation (e.g. heartburn, nausea). [1]
- f Prostaglandins are involved in the transmission of pain impulses to the brain; when the enzyme controlled production of prostaglandins is suppressed, the pain impulses are reduced or do not reach the brain. [1]
- 3 a Mild analgesics intercept pain at the source/interfere with the production of substances that cause pain. [1]
 Strong analgesics bond to receptor sites in the brain/prevent the transmission of pain impulses. [1]
- b Amide [1]
 Tertiary (amine) [1]
- c –OH/alcohol/phenol/hydroxyl [1]
 Esterification/condensation [1]
 Water/ H_2O [1]
- d i Ether/alkene (carbon–carbon double bond); (tertiary) amine [2]
 ii *Main effect*: relief from strong pain. [1]
Side effect: constipation. [1]
- e i LD_{50} is the drug dosage that kills half the population of test animals. [1]
 ii Heroin [1]
- f TD_{50} is the dose at which toxicity occurs in 50% of humans in a test sample of a drug. [1]
- The ED_{50} of a drug is the dose required to produce the desired effect in 50% of test animals or patients. [1]
- g The ionic salt structure increases the drugs solubility in water due to the formation of strong ion–dipole interactions and therefore increase the drugs distribution in the body. [2]
- 4 a $\text{Mg}(\text{OH})_2 + 2\text{HCl} \rightarrow \text{MgCl}_2 + 2\text{H}_2\text{O}$
 $\text{Al}(\text{OH})_3 + 3\text{HCl} \rightarrow \text{AlCl}_3 + 3\text{H}_2\text{O}$ [2]
 b Aluminium hydroxide, $\text{Al}(\text{OH})_3$ [1]
 c Corrosive to body/tissue / strong base/alkali. [1]
 d Heartburn occurs when gastric juice from the stomach rises into the esophagus/gullet. [1]
 e Dimethicone is added as an anti-foaming agent to prevent flatulence (passing of wind) and hence reduce pain. [1]
 Provide a neutralizing layer on top of the stomach contents/to prevent acid rising up the esophagus/to prevent heart burn. [1]
 f Production of carbon dioxide gas, CO_2 [1]
 g $\frac{\text{H}^+(\text{aq})}{\text{HCl}(\text{aq})} = 10^{-2} = 0.1\text{ mol dm}^{-3}$
 Mass of HCl in $1\text{ dm}^3 = 0.1\text{ mol dm}^{-3} \times 36.46\text{ g mol}^{-1} = 3.646\text{ g}$
 Mass of HCl in $1.000\text{ cm}^3 = 3.646 \times 10^{-3}\text{ g} = 3.646\text{ mg}$ [2]

$$4.28\text{ g}$$

 h Amount of $\text{NH}_4\text{Cl} = \frac{4.28\text{ g}}{53.50\text{ g mol}^{-1}} = 0.08\text{ mol}$
 Concentration of $\text{NH}_4\text{Cl} = 0.08\text{ mol} \times \left(\frac{[1000]}{[250]} \right) = 0.32\text{ mol dm}^{-3}$ [1]

$$\text{pOH} = \text{pK}_b - \log_{10} \left(\frac{[\text{base}]}{[\text{salt}]} \right)$$

$$= 4.75 - \log_{10} \left(\frac{[0.50]}{[0.32]} \right) = 4.56$$

$$\text{pH} = 14.00 - 4.56 = 9.44$$
 [1]
 i $4.5 = 4.76 - \log_{10} \left(\frac{0.1}{x} \right)$, where x = concentration of CH_3COONa

$$x = 0.055\text{ mol dm}^{-3}; x = 0.055\text{ mol dm}^{-3} \times 82.03\text{ g mol}^{-1} = 4.512\text{ g dm}^{-3}$$
 [1]
 Mass of CH_3COONa required $= \frac{500}{1000} \times 4.512\text{ g dm}^{-3} = 2.256\text{ g}$ [1]
 j Molecules of ranitidine (Zantac) bind to the histamine receptors/ H_2 -histamine receptors of the parietal cells in the gastric lining reducing hydrochloric acid secretion. [1]
 Molecules of omeprazole reduce hydrochloric acid production by binding and inhibiting the gastric

- proton pump/ H^+K^+ ATPase pump located on the surface of gastric parietal cells. [1]
- 5 a Alcohol, ether, primary amine, amide and alkene. [2]
The $-OH$ groups allow it to hydrogen bond with water molecules. [1]
- b Intramuscular: into the muscles; intravenous: into veins; subcutaneous: into fat; anal: via the anus and inhalation. [1]
Intravenous since the drug is circulated and transported quickly via the bloodstream (to various parts of the body). [1]
- c Placebo [1]
- d A side effect is an effect produced as well as the one intended and is an unwanted or undesired effect. [1]
- e A synergistic effect is a cumulative effect of two drugs which together is greater than the sum of each drug's individual effect. [1]
- f The therapeutic window is an index for an estimation of drug dosage which can treat disease effectively while remaining within the safe dosage range. [1]
The use of this index can help to avoid most of the potential side effects of drug usage. [1]
- g Viruses undergo rapid mutation; viruses are not affected by antibiotics; it is difficult to destroy viruses without damaging cells; there are only a limited number of metabolic functions that can be targeted by antivirals. [1]
- h Viruses are acellular and hence have no ribosomes, cytoplasm or cell wall and cell membrane; viruses are smaller than bacteria and are not motile (able to move). [1]
Bacteria replicate via asexually via binary division. This occurs outside cells. Virus particles are synthesized and assembled within the host cells. [1]
- 6 a Oxidizing agent/accepts electrons [1]
Orange to green [1]
- b Gas-liquid chromatography and infrared spectroscopy [2]
- c Stomach bleeding [1]
- d A sample of blood, hair or urine is injected into a GC or HPLC column; the components are separated according to their volatility (GC) or solubility (HPLC) and affinity to the stationary phase. [1]
The presence of an anabolic steroid in the body can be detected by its retention time and confirmed by mass spectroscopy; the sample with the substance is vaporized and ionized to form cations. [1]
The cations are accelerated by an electric field and deflected by a magnetic field according to their mass to charge ratios. [1]
Each substance produces a unique pattern of fragment ions, which can be detected and compared (by a computer search) with a library of known anabolic steroids (and their degradation products). [1]