1.1 Atomic structure

1.1.1 Structure of the atom and isotopes

1 (a) A and D
(b) C and F
(c) B and E
(d) A and C

2

Symbol for atom or ion	Number of protons	Number of neutrons	Number of electrons
$^{3}_{1}H$	1	2	1
$^{18}_{8}O^{2-}$	8	10	10
$^{24}_{12}Mg^{2+}$	12	12	10
$^{14}_{7}N^{1}_{1}H_{3}$	10	7	10
$^{14}_{7}N^{2}_{1}H^{+}_{4}$	11	11	10

1.1.2 Mass spectrometry and relative masses of atoms, isotopes and molecules

1 Relative atomic mass refers to the weighted mean (average) mass of an atom in a mixture of isotopes.
Relative isotopic mass refers to the mass of a single isotope.

2 The mass calculated is an average mass of more than one isotope with different masses and the relative abundances of these are rarely whole numbers.

3. $(24 \times 0.786) + (25 \times 0.101) + (26 \times 0.113) = 24.3$ (to 3 significant figures).

4. $$\frac{63.0x + 65.0(100 - x)}{100} = 63.5$$
$63.0x + 6500 - 65.0x = 6350$
$2x = 150$
$x = 75$
copper-63: 75%; copper-65: 25%

5 (a) 79 and 81
(b) 158 = $^{79}Br_2^+$
160 = $^{79}Br^{81}Br^+$
162 = $^{81}Br_2^+$
(c) Relative abundance of the two isotopes is 50:50 or 1:1 (heights of 79 and 81 peaks are the same).
Chance of two ^{79}Br atoms combining are ½ × ½ = ¼
Chance of a ^{79}Br and a ^{81}Br atom combining is ½ × ½ × 2 = ½
Chance of two ^{81}Br atoms combining are ½ × ½ = ¼
This gives a ratio of 1:2:1 for the peaks' heights, corresponding to an *m/z* of 158, 160 and 162.

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1.1.3 Atomic orbitals and electronic configurations

1 (a) Hund's rule states that electrons will occupy the orbitals singly before pairing takes place.

The Pauli Exclusion Principle states that two electrons cannot occupy the same orbital unless they have opposite spins.

(b) (i) The arrows indicate the spin that the electron has. The letters x, y and z refer to the Cartesian axis on which the orbital exists.

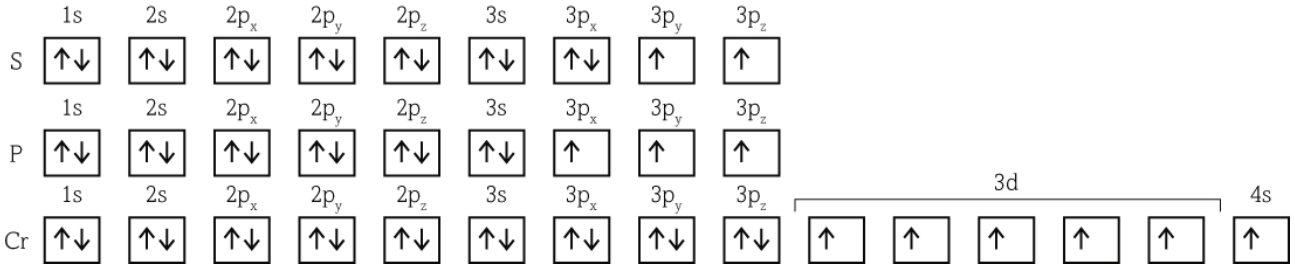
(ii) Two electrons in a single orbital would increase the electron-electron repulsion and the orbital energies of the electrons. The preferred electronic configuration is the one of lowest energy.

(iii) The s-orbitals are spherical and the p-orbitals are elongated (in the shape of a dumbbell).

(c) (i)

(ii)

(iii)



1.1.4 Ionisation energies

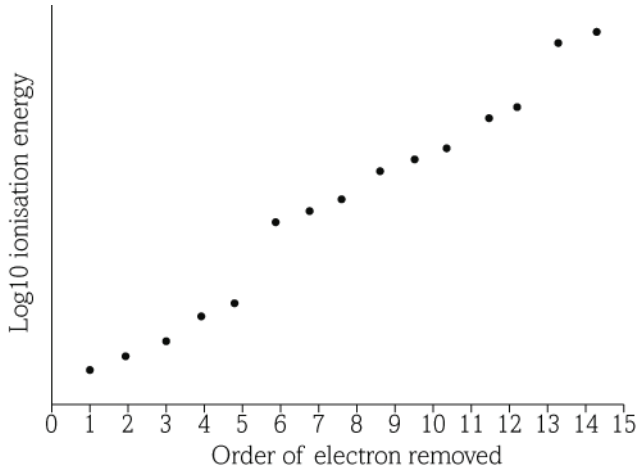
1 The three factors are: the energy of the electron (distance of electron from nucleus is often accepted, although this is not always correct), nuclear charge and electron-electron repulsion (also known as shielding or screening).

2 (a) $Na(g) \rightarrow Na^+(g) + e^-$

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

(c) $C^{3+}(g) \rightarrow C^{4+}(g) + e^-$

3



4 (a) B and D. B is magnesium and D is beryllium. In both cases, there is a large jump from the second ionisation energy to the third, so both elements are in Group 2.

It is possible that C and E are in the same group, but this cannot be confirmed without the fifth ionisation energy.

(b) Group 3. There is a large jump from the third ionisation energy to the fourth.

(c) E. The sum of the first two ionisation energies is the lowest.

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5 (a) After the first electron has been removed, the remaining electron in this orbital experiences less repulsion and so its orbital energy drops.

(You may also answer this question by stating that the remaining electron has moved closer to the nucleus and is therefore more strongly attracted to the nucleus.)

(b) The third electron to be removed is in a different quantum shell of lower energy.

1.2 The Periodic Table

1.2.1 The Periodic Table

1 (a) The highest energy electron is in an s-orbital.

(b) The highest energy electron is in a p-orbital.

2 The outer electronic configurations of the atoms are identical, with one electron in an s-orbital.

3 The outer electronic configuration of arsenic is $4s^2 4p^3$. Arsenic is in Group 5 so its outer electronic configuration is s^2p^3. It is also in Period 4, so its outer electrons are in the fourth quantum shell.

1.2.2 Periodicity

1 (a) A giant lattice structure.

(b) Whether it conducts electricity when solid. If it does, then it is likely to be metallic.

2 The helium atom has a higher nuclear charge. This offsets the increase in repulsion that occurs between the two electrons when a second electron is added to the 1s orbital.

3 The outer electron of a lithium atom is in a different quantum shell (the second) of much higher energy.

4 Lower. The outer electron of the gallium atom is in a 4p orbital, so the orbital energy of this electron is greater than that of the outer electron of a calcium atom, which is in a 4s orbital.

5 The neon atom has the highest nuclear charge of all the atoms of the elements in Period 2. The amount of shielding the outer electron experiences is similar to that for the other elements of Period 2. The orbital energy of the outer electron is therefore lower than that of any other element in Period 2. You could also score the last point for stating that the neon atom is the smallest, so the outer electron is closest to the nucleus and therefore most strongly attracted to it.

1 Answers to Exam-style questions

1 (a) Isotopes are atoms of the same element that have different masses (1).

(b) ^{3}He has one neutron; ^{4}He has two neutrons (1).

(c) (i) ^{12}C (1).

(ii) $(3 \times 0.00992) + (4 \times 0.99008)$ (1) = 3.99 (1).

(d) (i) The energy required to remove one electron from each atom (1) in a mole of atoms (1) in the gaseous state (1).

(ii) $He(g) \rightarrow He^+(g) + e^-$ (2)

(iii) H $1s^1$ He $1s^2$

A helium atom has two electrons in the *s*-orbital and this increases the shielding effect (1).

However, the greater nuclear charge of a helium nucleus more than compensates for this and hence the energy of the outer electron of helium is lower than that of hydrogen (1).

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2 (a) Group 3 (1).

There is a very large increase between the third and fourth ionisation energies indicating that a boron atom as three electrons in its outermost quantum shell (1).

(b) B (1).

(c) The first electron removed is from a 2p orbital.

The second electron removed is from a 2s orbital (1).

Electrons in a 2s orbital have a lower energy than those in a 2p orbital (1).

(d) $1s^2\ 2s^2\ 2p^1$ (1).

(e) p-block (1). The highest energy electron is in a p-orbital (1).

(f) Be $1s^2\ 2s^2$ B $1s^2\ 2s^2\ 2p^1$

Although the nuclear charge of the boron atom is higher than that of the beryllium atom, the outer electron has a higher energy since it is in a 2p orbital as opposed to the 2s orbital for beryllium (1). In addition, the 2p electron in boron experiences greater electron-electron repulsion (i.e. greater shielding) since there are two inner electron shells as opposed to only one in the beryllium atom (1).

3 (a) A repeating pattern in property across a period of the Periodic Table (1).

(b) There is an increase in nuclear charge across the period (1).

Electrons are added to the same quantum shell so the increase in shielding is minimal (1)

The increase in nuclear charge is more significant than the increase in shielding, so the energy of the outer electrons decreases (1).

(c) The atomic radii decreases across Period 3 (1) as the number of protons in the nucleus increases so does the nuclear charge (1).

This results in an increase in the attractive force between the nucleus and the outer electrons.

This increase in attractive force offsets the increase in electron-electron repulsion (1) as the number of electrons in the outer quantum shell increases (1).

(d)

Symbol of element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
melting temperature /^{o}C	98	650	660	1410	44	119	–101
bonding	metallic	metallic	metallic	(polar) covalent	covalent	covalent	covalent
structure	giant	giant	giant	giant	simple molecular	simple molecular	simple molecular

4 (a)

Particle	**Relative charge**	**Relative mass**
proton	+1	1
neutron	0	1
electron	–1	1/1840

(b) (i) ^{16}O has 8 neutrons; ^{17}O has 9 neutrons (1).

(ii) ^{24}Mg has 12 electrons; $^{24}Mg^{2+}$ has 10 electrons (1).

(iii) $^{39}K^{+}$ has 19 protons; $^{40}Ca^{2+}$ has 20 protons (1).

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5 (a) A region within an atom that can hold up to two electrons with opposite spins (1).

(b) (i) *s*-orbital



(ii) *p*-orbital



(c) (i) Two (1).

(ii) Six (1).

(d) (i) Na $1s^2\ 2s^2\ 2p^6\ 3s^1$ (1).

(ii) O^{2-} $1s^2\ 2s^2\ 2p^6$ (1).

(iii) Mg^{2+} $1s^2\ 2s^2\ 2p^6$ (1).

(iv) Cl $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ (1).

(e) **A** (1) [NH_4^+ has 10 electrons; the others have 18 each]

6 (a) 70 – $^{35}Cl_2^+$ (1); 72 – $^{35}Cl^{37}Cl^+$ (1); 74 – $^{37}Cl_2^+$ (1).

(b) *m/z* of 35 – $^{35}Cl^+$ (2)

m/z of 37 – $^{37}Cl^+$ (2)

Relative abundance – $^{35}Cl^+$: $^{37}Cl^+$ is 3 : 1 (1).

7 (a) Na $1s^2\ 2s^2\ 2p^6\ 3s^1$ Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$

The sodium atom has a lower nuclear charge than the magnesium atom (1).

The orbital energy of the electron in the 3s orbital in the sodium atom is therefore lower than that in the magnesium atom (1).

(b) Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ Al Mg $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

The outer electron in the aluminium atom has a higher energy since it is in a 3p orbital as opposed to the 3s orbital for magnesium (1). In addition, the 3p electron in aluminium experiences greater electron-electron repulsion (i.e. greater shielding) since there are three inner electron shells as opposed to only two in the magnesium atom (1).

(c) Mg^+ $1s^2\ 2s^2\ 2p^6\ 3s^1$ Al^+ $1s^2\ 2s^2\ 2p^6\ 3s^2$

The Al^+ ion has a higher nuclear charge than the Mg^+ ion (1).

Since there are two electrons in the 3s orbital of the Al^+ ion each electron experiences greater electron-electron repulsion (i.e. greater shielding) but this in offset by the higher nuclear charge (1).

(d) Al^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^1$ Al^{3+} $1s^2\ 2s^2\ 2p^6$

The outer electrons in the Al^{3+} ion have a lower energy (1) since they are in a 2p orbital as opposed to a 3s orbital in the Al^{2+} ion (1).

8 (a)

Isotope	Number of protons	Number of neutrons	Number of electrons
^6Li	3	3	3
^7Li	3	4	3

(2)

(b) (i) Mass spectrometer (1)

(ii) The mass of an atom of the isotope compared to 1/12th the mass of an atom of carbon-12 (1), which has a mass of 12 (1).

(iii) $(6 \times 0.0759) + (7 \times 0.9241)$ (1) = 6.92 (1).

(c) (i) $1s^2\ 2s^1$ (1).

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(ii) The highest energy electron is in an *s*-orbital (1).

(iii) Yes (1). They have the same electronic configurations (1).

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2.1 Giant structures

2.1.1 Metallic bonding

1 Metallic bonding is the electrostatic force of attraction between the positively charged metal cations and delocalised electrons.

2 Melting temperatures:

The melting temperature of a metal is dependent on the strength of its metallic bonding, i.e. the magnitude of the electrostatic force of attraction between the positively charged metal cations and delocalised electrons.

The aluminium ion (Al^{3+}) has a greater charge than the magnesium ion (Mg^{2+}), and the magnesium ion has a greater charge than the sodium ion (Na^{+}). In addition, aluminium has three delocalised electrons per ion, magnesium has two and sodium has only one.

The strength of the metallic bonding therefore increases in the order Na < Mg < Al.

The stronger the metallic bonding, the larger the amount of energy required to overcome it, leading to a higher melting temperature.

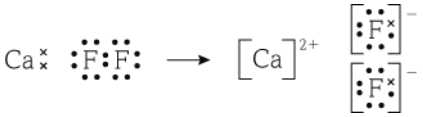
Electrical conductivity:

The electrical conductivity of a metal depends on the number of delocalised electrons per unit volume of metal. This is equal to the number of ions per unit volume multiplied by the number of valence electrons in each atom. The size of the ions decreases in the order $Na^{+} > Mg^{2+} > Al^{3+}$ so in the lattice structures the number of ions per unit volume increase in the order $Na^{+} < Mg^{2+} < Al^{3+}$. Na has only 1 delocalised electron per ion, whereas Mg has 2 and Al has 3. So the number of delocalised electrons per unit volume increases in the order Na < Mg < Al. This makes Al the best electrical conductor and Na the worst of the three metals.

2.1.2 Ionic bonding

1 Ionic bonding is the electrostatic force of attraction between oppositely charged ions in an ionic lattice.

2



3 (a) The force of attraction between the ions depends on the product of the charges on the ions and the radii of the ions. The charges on the ions are the same in each compound, but the Na^{+} ion is smaller than the K^{+} ion and so the forces of attraction between the oppositely charged ions are greater in sodium fluoride.

(b) The calcium ion (Ca^{2+}) has double the charge of the potassium ion (K^{+}). Also, the oxide ion (O^{2-}) has double the charge of the fluoride ion (F^{-}). The sum of the ionic radii is very similar for both (0.239 nm for CaO and 0.269 nm for KF), so the distances between the ions are very similar. The electrostatic forces of attraction between oppositely charged ions are directly proportional to the product of the charges.

2×2 is four times greater than 1×1.

4 (a) The number of electron shells decrease from Ca^{2+} to Mg^{2+} to Be^{2+}.

(b) The three ions are isoelectronic, but the nuclear charge increases by one each time from Cl^{-} to S^{2-} to P^{3-}. The electrons are therefore attracted most strongly in P^{3-} and least strongly in Cl^{-}.

2.1.3 Covalent bonding

1 The bond lengths increase in the order C—C < Si—Si < Ge—Ge. The electrostatic attraction between the nuclei and the bonding electrons decreases as the distance between them increases. This factor is more significant than the increases in nuclear charge from C to Si to Ge.

2 The non-bonding (lone) pairs of electrons on the two fluorine atoms are very close to each other. They therefore repel each other quite strongly and so reduce the bond strength. This is one of the reasons why fluorine is such a reactive element.

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3 The high area of electron density of a sigma (σ) bond is largely located directly between the two nuclei, producing a relatively large force of attraction between the nuclei and the bonding pair of electrons.

In a pi (π) bond, the high areas of electron density are situated above and below the electrons in the sigma bond. This reduces the force of attraction between the nuclei and these bonding electrons as they are further from the nuclei.

N.B. Another explanation of the relative strengths of these two bonds would be the extent to which the orbitals overlap in each case. There is a greater degree of orbital overlap with a σ bond than with a π bond. The greater the orbital overlap the stronger the bond.

2.1.4 Electronegativity and bond polarity

1 The nucleus of the fluorine atom is closer to the bonding electrons and so the force of attraction for the bonding pair is greater. This factor is more significant than the difference in nuclear charge between fluorine and chlorine.

2 (a) (i) Ionic bonding is the electrostatic force of attraction between oppositely charged ions.

Example: sodium chloride, Na^+Cl^-

(ii) Covalent bonding is the electrostatic force of attraction between the nuclei of two atoms and a pair of electrons in two overlapping atomic orbitals, one from each atom.

Example: chlorine, Cl—Cl

(b) Hydrogen chloride, H—Cl

The electronegativity of Cl (3.0) is greater than that of hydrogen (2.1). The electron cloud of the bonding electrons is therefore polarised and a dipole is created. The chlorine end of the molecule becomes slightly negative (δ−), while the hydrogen end of the molecule becomes slightly positive (δ+). The bond therefore has some ionic character.

3 C—F > C—Cl > C—Br > C—I

The greater the difference in electronegativity between the two atoms, the more polar the bond.

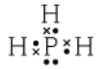
2.2 Discrete molecules

2.2.1 Bonding in discrete molecules

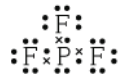
1 (a)



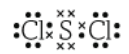
(b)



(c)



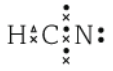
(d)



(e)



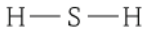
(f)

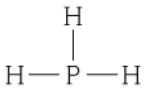


(g)

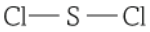


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2 (a) 

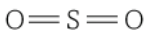
(b) 

(c) 

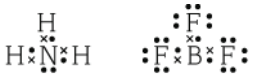
(d) 

(e) 

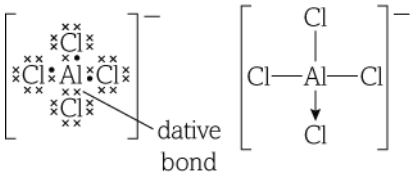
(f) 

(g) 

2.2.2 Dative covalent bonds

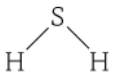
1 (a) 

(b) 

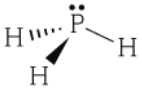
2 

3 

2.2.3 Shapes of molecules and ions

1 (a) (i) 

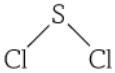
(b) V-shaped

(ii) 

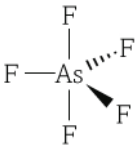
Trigonal pyramidal

(iii) 

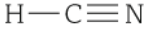
Trigonal pyramidal

(iv) 

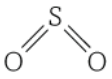
V-shaped

(v) 

Trigonal bipyramidal

(vi) 

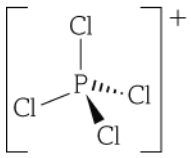
Linear

(vii) 

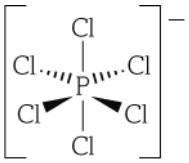
V-shaped

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2 (a) and (b)

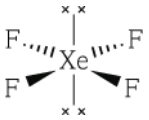


109.5°



90° and 180°

3



is likely to be the preferred arrangement.

Since lone pair–lone pair repulsion is greater than bond pair–bond-pair repulsion, the lone pairs are likely to take up positions as far away from one another as possible.

2.2.4 Non-polar and polar molecules

1 (a) A dipole exists in a bond when one atom acquires an excess of negative charge so that it carries a slightly negative charge (δ−). This is because one of the atoms has a higher electronegativity than the other. The second atom acquires a slightly positive charge (δ+). The charge separation creates the dipole.

(b) C—Cl, O—H, C—O, C—N and N—H will possess a dipole.

C—Cl	O—H	C—O	C—N	N—H
δ+ δ−	δ− δ+	δ+ δ−	δ+ δ−	δ+ δ−

2 (a) H_2S is polar. The H—S bonds possess a dipole and the molecule is V-shaped so the dipoles reinforce one another.

(b) CH_4 is non-polar. The C—H bonds possess a dipole but the molecule is tetrahedral and so the dipoles are symmetrically arranged and cancel out one another.

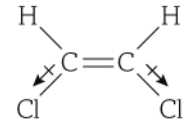
(c) SO_2 is polar. The S═O bonds possess a dipole and the molecule is V-shaped so the dipoles reinforce one another.

(d) SO_3 is non-polar. The S═O bonds possess a dipole but the molecule is trigonal planar and so the dipoles are symmetrically arranged and cancel out one another.

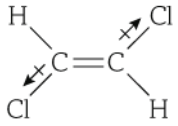
(e) $AlBr_3$ is non-polar. The Al—Br bonds possess a dipole but the molecule is trigonal planar and so the dipoles are symmetrically arranged and cancel out one another.

(f) PBr_3 is polar. The P—Br bonds possess a dipole and the molecule is trigonal pyramidal so the dipoles reinforce one another.

3. In the *cis* isomer the dipoles reinforce each other. In the *trans* isomer they cancel out each other.



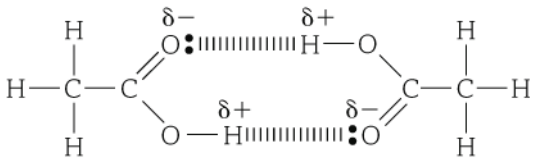
cis-dichloroethene



trans-dichloroethene

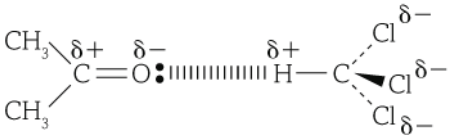
2.2.5 Intermolecular interactions

1



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2 The hydrogen atom in trichloromethane is made significantly δ+ by the highly electronegative chlorine atoms for it to be able to form a relatively strong hydrogen bond to the δ− oxygen atom of propanone.



3 The two intermolecular interactions present in methoxymethane are London forces (instantaneous dipole–induced dipole interactions) and Keesom forces (permanent dipole–permanent dipole interactions).

Both of these interactions are present in ethanol, but hydrogen bonding is also present. This extra interaction results in an overall increase in the total attraction among the molecules in ethanol.

2.2.6 Intermolecular interactions and physical properties

1 The only intermolecular interactions in each case are London forces. London forces of attraction increase with increasing number of electrons in the molecule. Larger instantaneous and induced dipoles are created, owing to larger fluctuations in electron density throughout the molecules.

The number of electrons per molecule increase in this order: $CH_4 < SiH_4 < GeH_4 < SnH_4$

As the London forces of attraction increase, the amount of energy required to separate the molecules increases, so the boiling temperatures increase.

2 In the bulk of a liquid, each molecule is pulled equally in every direction by neighbouring liquid molecules, resulting in a net force of zero. The molecules at the surface do not have other molecules on all sides of them and therefore are pulled inwards to compensate. This creates an effect known as surface tension.

The surface tension of water is particularly high because of the high attraction that water molecules have for one another, owing to the relatively strong hydrogen bonds.

3 The number of electrons in each molecule is similar, so the strength of the London forces should be similar, since the molecules also have similar shapes and similar chain lengths. (In fact, the chain length of butane is slightly greater than that of propanone.)

However, the propanone molecule is polar, whereas the butane molecule is non-polar. So, there are also Keesom forces (permanent dipole–permanent dipole interactions) acting between molecules of propanone. This extra intermolecular interaction increases the overall intermolecular attraction.

(Do not fall into the trap of stating that the Keesom forces in propanone are stronger than the London forces in butane. The London force in propanone contributes approximately 77% to the total intermolecular force of attraction. The Keesom force is small by comparison.)

4 The energy supplied by the hydration of the separate Mg^{2+} and Cl^- ions formed on breaking up the lattice is greater than 2494 kJ mol^{-1}

$Mg^+(g) + aq \rightarrow Mg^{2+}(aq) \quad \Delta H = 1920$ kJ mol^{-1}

$2Cl^-(g) + aq \rightarrow 2Cl^-(aq) \quad \Delta H = 728$ kJ mol^{-1}

$1920 + 728 = 2648$ kJ mol^{-1}

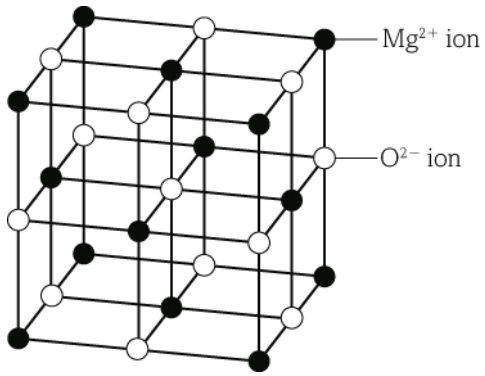
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2.3 Physical properties related to structure and bonding

2.3.1 Solid lattices

1 (a)



(b) The electrostatic force of attraction between Mg^{2+} and O^{2-} ions is greater than that between Na^+ and Cl^- ions because of the greater charge and smaller size on the ions.

(Mg^{2+} is smaller than Na^+ and O^{2-} is smaller than Cl^-.)

The amount of energy required to overcome the forces of attraction in magnesium oxide, and so break down the lattice structure, is therefore greater than that for sodium chloride.

2 (a) In an ionic compound, the charge carriers are ions. In solid magnesium chloride, the ions are not free to flow, so the solid does not conduct electricity.

In a metal the charge carriers are electrons. Magnesium has delocalised electrons that are free to flow when a potential difference is applied across the ends of the metal.

(b) White phosphorus has a molecular structure consisting of discrete molecules of formula P_4. In order to melt white phosphorus, it is only necessary to overcome the weak intermolecular forces of attraction. Relatively little energy is required to do this.

Silicon has a giant covalent structure. In order to melt the solid it is necessary to break a very large number of relatively strong covalent bonds. This requires a large amount of energy.

3 The lubricating properties of both materials depend on the ability of the layers to easily slide over one another.

The layers in graphite only slide easily over one another when gas molecules are adsorbed on the surface of the layers. In a vacuum, no gas molecules are present, so in these conditions graphite has very poor lubricating properties.

The lubricating properties of hexagonal boron nitride do not depend on the adsorption of gas molecules. The layers can slide over one another because of the weak London forces between the layers.

2.3.2 Structure and properties

1 **A** – metallic bonding and giant structure

B – covalent bonding and discrete (simple) molecular

C – covalent bonding and giant structure

D – ionic bonding and giant structure

2 (a) **P** – ionic and giant structure. The anomalous property is its ability to conduct electricity when solid. Since it produces ammonia when reacted with water, it is likely to be a nitride. Since it produces an alkaline solution when reacted with water, it is likely to be a group 1 metal compound. Substance **P** is lithium nitride, Li_3N.

(b) **Q** – covalent and giant structure. The anomalous property is its semi-conducting properties when solid. Substance **Q** is silicon.

(c) **R** – metallic and giant structure. The anomalous property is its low melting temperature. Since an alkaline solution and hydrogen gas are produced on reaction with water, **R** is likely to be an alkali metal. Substance **R** is sodium.

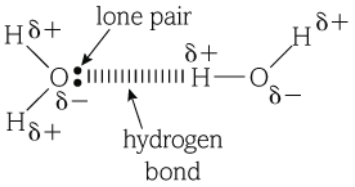
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2 Answers to Exam-style questions

1 (a) The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H (1), and an atom in the same or a different molecule, in which there is evidence of bond formation (1).

(b) (1) for bond shown between O of one molecule and H of the other.

(1) for lone pair and relevant dipoles shown.



(c) Any two from:

- melting/boiling temperature is higher than expected
- density of ice is greater than that of water at 0 ºC
- surface tension is greater than expected

(1) for each.

2 (a) The electrostatic force of attraction between metal cations (1) and delocalised electrons (1) (in a lattice structure).

(b) The delocalised electrons are able to flow when potential difference is applied (1).

(c) The magnesium ion is smaller than the sodium ion and there are two delocalised electrons per ion in magnesium, as opposed to only one per ion in sodium (1).

Hence there are more delocalised electrons per unit volume in magnesium (1).

(d) Lithium **should** be the better electrical conductor. Although the number of delocalised electrons per ion is the same (1), the lithium ion is smaller than the sodium ion so there should be fewer delocalised electrons per unit volume (1).

[Interestingly, sodium is the better electrical conductor of the two metals. The expected trend exists from sodium to caesium, with the electrical conductivity decreasing down the group.]

3 **A** – covalent; giant lattice (1). Poor conductor when solid; high melting temperature (1).

B – ionic; giant lattice (1). Poor conductor when solid, but good in aqueous solution; fairly high melting temperature (1).

C – metallic, giant lattice (1). Good conductor when solid; high melting temperature (1).

D – covalent; simple molecular (1). Poor conductor when solid; low melting temperature (1).

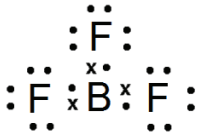
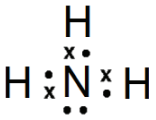
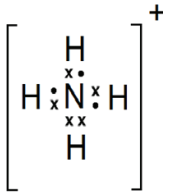
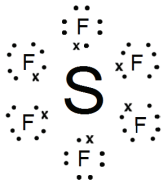
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4 (a) The shape of a molecule/ion is determined by the number of pairs of electrons surrounding the central atom (1).

The electron pairs repel one another and arrange themselves in space so that they are as far apart from one another as is possible (1).

Lone pair–lone pair repulsion > lone pair–bond pair repulsion > bond pair–bond pair repulsion (1).

(b)

(i) BF_3	(ii) NH_3	(iii) NH_4^+	(iv) SF_6
			
(1)	(1)	(1)	(1)

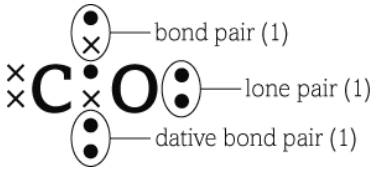
(c) BF_3 – trigonal planar, 120º (1)

NH_3 – trigonal pyramidal, 107º (1)

NH_4^+ – tetrahedral, 109.5º (1)

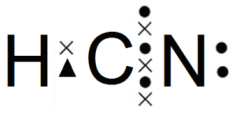
SF_6 – octahedral, 90º and 180º (2)

5 (a)



(b) (i) Contain the same number of electrons (1).

(ii)



(2)

(iii) N≡N is stronger than either H−C, C≡N or C≡O **OR** N≡N is non-polar, whilst HCN and CO have polar bonds (1).

6 (a) (i) Ethanol: London forces (1); dipole – dipole forces (Keesom forces) (1); hydrogen bonding (1).

(ii) Methoxymethane: London forces (1); dipole – dipole forces (1).

(b) *Solubility*

Ethanol can form strong hydrogen bond with water (1)

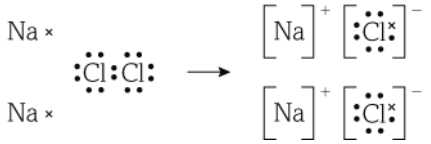
The dipole – dipole bonds formed between methoxymethane and water are not as strong as the hydrogen bonds between water molecules (1).

Boiling temperatures

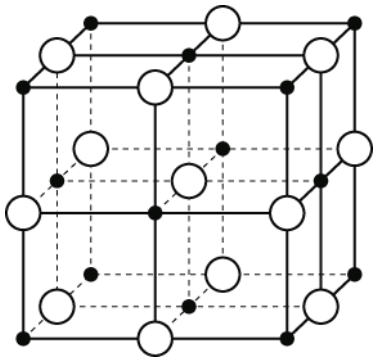
The London forces and dipole – dipole forces are likely to be similar in each case (1). Ethanol, however, has significant hydrogen bonding in addition, so the overall intermolecular forces if attraction are greater.

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7 (a)



(b)



(1) for alternating sodium and chloride ions (1) for all ions shown.

(c) (i) The forces of attraction between the ions are relatively strong (1).

There are a very large number of forces of attraction to overcome (1).

A large amount of energy is required to overcome these forces (1).

(ii) Energy is required to overcome the forces of attraction between the ions (1)

so that the lattice breaks down and the ions are separated (1).

This energy is supplied by the hydration of the ions by water molecules (1).

(iii) The ions are locked into fixed positions in the lattice and are not free to flow throughout the solid (1).

When molten, the lattice is broken down and the ions are able to flow when a potential difference is applied (1).

8 (a) The only forces of attraction between methane molecules and London forces (1) These are very weak and hence methane has a very low boiling temperature since very little energy is required to overcome them (1)

In addition to London forces, water molecules have intermolecular dipole – dipole forces and hydrogen bonds. The hydrogen bonds in particular are much stronger than London forces and so the overall intermolecular attraction are greater in water than in methane (1).

(b) As the chain length increase the number of points of contact between the molecules increases (1).

There are therefore more London forces the longer the chain, resulting in increase in the overall intermolecular forces of attraction (1).

(c) Because of the branching of the chain, there are fewer points of contact between methylpropane molecules than between butane molecules (1). Hence the overall intermolecular forces of attraction are weaker (1) so the boiling temperature will be lower (1).

9 (a)

Formula of molecule	H_2O	NH_3	CH_4	BCl_3
Number of bonding pairs	2	3	4	3
Number of non-bonding pairs	2	1	0	0

(b) (i) A polar bond exists when there is a charge separation between one end of the bond and the other. That is, one end of the bond possesses a partial positive charge (δ+) while the other possesses a partial negative charge (δ–) (1).

The polarity arises when one atom involved in the bond formation has a greater electronegativity than the other (1). This results in a distortion of the electron cloud producing higher electron density at the end of the bond where the more electronegative element is situated (1).

(ii) In ammonia, the three dipoles created by the three polar N–H bonds are acting in the same direction (1) and so the they reinforce one another (1).

In boron trichloride, the three dipoles cancel out since the molecule in symmetrical (1).

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3.1 Oxidation and reduction in terms of electrons

3.1.1 Electron loss and gain

1 (a) Zn is oxidised; Cu^{2+} is reduced

(b) $Zn \rightarrow Zn^{2+} + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu$

2 (a) Al – oxidised

(b) Ti^{4+} – reduced

(c) Ag^+ – neither

(d) Br^- – oxidised

(e) Cu^{2+} – neither

(f) Mn^{4+} – reduced

3 (a) Fe: lost two electrons to become Fe^{2+}

(b) Na: lost one electron to become Na^+

(c) Cu^{2+}: lost one electron to become Cu^+

(d) Fe^{2+}: lost one electron to become Fe^{3+}

(e) Zn: lost two electrons to become Zn^{2+}

3.2 Oxidising agents and reducing agents

3.2.2 Calculating oxidation numbers

1 $\underline{S}O_2$ +4 $\underline{S}O_3$ +6 $H_2\underline{S}$ −2 $\underline{S}O_3^{2-}$ +4 $\underline{S}O_4^{2-}$ +6 $\underline{S}_2O_3^{2-}$ +2

$\underline{Cr}O_4^{2-}$ +6 $\underline{Cr}_2O_7^{2-}$ +6 $\underline{Mn}O_4^{2-}$ +6 $\underline{Mn}O_4^-$ +7 $\underline{V}O^{2+}$ +4 $\underline{V}O_2^+$ +5

$\underline{Cl}O^-$ +1 $\underline{Cl}O_2^-$ +3 $\underline{Cl}O_3^-$ +5 $\underline{Cl}O_4^-$ +7 $[\underline{Cu}Cl_4]^{2-}$ +2 $[\underline{V}(H_2O)_6]^{2+}$ +2

$H_2\underline{O}_2$ −1 $\underline{O}F_2$ +2 $Na\underline{H}$ −1 $Ba\underline{O}_2$ −1

Note: The oxidation number of S in $S_2O_3^{2-}$ is a mean value of two. One S has an oxidation number of +6 while the other has an oxidation number of −2.

3.2.2 Recognising reactions using oxidation numbers

1

Equation	Redox reaction (✓ or ✗)	Disproportionation (✓ or ✗)	Element oxidised	Element reduced
$Mg + 2HCl \rightarrow MgCl_2 + H_2$ 0 +1 −1 +2 −1 0	✓	✗	Mg	H
$CaO + H_2O \rightarrow Ca(OH)_2$ +2 −2 +1 −2 +2 −2 +1	✗	✗	none	none
$2H_2O_2 \rightarrow 2H_2O + O_2$ +1 −1 +1 −2 0	✓	✓	O	O
$2SO_2 + O_2 \rightarrow SO_3$ +4 −2 0 +6 −2	✓	✗	S	O
$KOH + HNO_3 \rightarrow KNO_3 + H_2O$ +1−2+1 +1+5−2 +1+5−2 +1−2	✗	✗	none	none
$Cl_2 + H_2O \rightarrow HCl + HClO$ 0 +1−2 +1−1 +1+1−2	✓	✓	Cl	Cl

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3.2.3 Use of oxidation number in nomenclature

1 (a) Phosphorus(III) chloride
(b) Phosphorus(V) chloride
(c) Vanadium(V) oxide
(d) Sodium chlorate(I)
(e) Sodium chlorate(V)

2 (a) Nitrate(V)
(b) Nitrite(III)
(c) Chlorate(VII)
(d) Vanadate(IV)
(e) Vanadate(V)

3 (a) Cu_2O
(b) CuO
(c) $Cr_2(SO_4)_3$
(d) PbI_4
(e) $Co(NO_3)_3$

4 Sodium is a Group 1 element and has only one oxidation number in its compounds, +1.
Magnesium is a Group 2 element and has only one oxidation number in its compounds, +2.

3.2.4 Writing full equations from ionic half-equations

1 (a) $Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
(b) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
(c) $MnO_4^-(aq) + 8H^+(aq) + 5Ce^{3+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Ce^{4+}(aq)$
(d) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$
(e) $2FeO_4^{2-}(aq) + 16H^+(aq) + 3C_2O_4^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 8H_2O(l) + 6CO_2(g)$

2 (a) $3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 4H_2O(l) + 2NO(g)$
(b) $Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l) + 2NO_2(g)$
(c) $3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(g) + 3H_2O(l)$

3 Answers to Exam-style questions

1 (a) (i) +1 (1).
(ii) Chlorate(I) ion (1).
(b) $Cl_2(aq) + H_2O(l) \rightarrow ClO^-(aq) + Cl^-(aq) + 2H^+(aq)$ (1)
Oxidation number of chlorine changes from 0 in Cl_2 to +1 in ClO^- and –1 in Cl^- (1)
Chlorine has undergone disproportionation since it has been both oxidised and reduced in the same reaction (1).
(c) Oxidation number changes from +5 in $KClO_3$ to +7 in $KClO_4$ (1) and –1 in KCl (1).
Chlorine has undergone disproportionation (1).

2 (a) (i) Oxidation is the loss of electrons; reduction is the gain of electrons (1).
(ii) Chlorine (1). It is gaining electrons **OR** it is causing bromide ions to lose electrons (1).
(b) $2H_2O(l) + 2Cl^-(aq) \rightarrow Cl_2(aq) + 2OH^-(aq)$
All formulae correct and no electrons (1) correctly balanced (1).

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3 (a) (i) 0 (1)

(ii) +1 (1).

(b) Oxidation number of Cl in ClO_2 is +4 (1).

Oxidation number of Cl in $NaClO_2$ is +3 (1).

Chlorine has been reduced since its oxidation number has decreased (1).

(c) **C** +5 to –1 (1).

4 (a) $S_2O_3^{2-}$ +2 (1) SO_4^{2-} +6 (1) $S_4O_6^{2-}$ +2.5 (1).

(b) Chlorine has the greater oxidising power (1) since it oxidises the sulfur to a higher oxidation number (1).

(c) Oxidation number of Fe in $FeCl_3$ is +3 (1).

Oxidation number if Fe in FeI_2 is +2 (1).

Chlorine has oxidised the iron to a higher oxidation number, so the reactions support that statement made in (b) (1).

5 (a) $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$

All formulae correct with no electrons (1) correctly balanced (1).

(b) $4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$

All formulae correct and balanced (1) state symbols (1)

(c) **Stage 1:** Yes. Fe has been oxidised (0 to +2); O has been reduced (0 to –2) (1)

Stage 2: No. No change in oxidation number occurs (1).

Stage 3: Yes. Fe has been oxidised (+2 to +3); O has been reduced (O to –2) (1).

6 (a) (i) $V_2O_5 + SO_2 \rightleftharpoons V_2O_4 + SO_3$ (1).

(ii) $V_2O_4 + ½O_2 \rightleftharpoons V_2O_5$ (1).

(b) $2VO^{2+}(aq) + SO_2(g) \rightleftharpoons 2VO^{2+}(aq) + SO_4^{2-}(aq)$

All formulae correct and no electrons (1)

Balanced equation and H^+ ions H_2O molecules correctly cancelled out (1).

(c) (i) **A** $Mn^{2+}(aq)$ (1).

(ii) Mn changes from +7 to +2 (1).

Fe changes from +2 to +3 (1).

Ratio of Fe^{2+} to MnO_4^- is 5:1 (1).

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4.1 Group 2

4.1.1 Trends in the Group 2 elements

1 $Be(g) \rightarrow Be^{+}(g) + e^{-}$
$Ba^{+}(g) \rightarrow Ba^{2+}(g) + e^{-}$

2 Beryllium is less reactive than barium because more energy is needed to remove the electrons in beryllium (than in barium) during a reaction. This is because, even though the nuclear charge of beryllium is less than that of barium (which decreases the ionisation energy), the electron being removed from beryllium is closer to the nucleus than in barium. Also, there is only one filled shell of electrons in beryllium (compared with five filled shells in barium) to repel the electron being lost. The last two factors outweigh the first, so the ionisation energy of beryllium is higher than that of barium.

4.1.2 Reactions of the Group 2 elements

1 (a) $2Ca + O_2 \rightarrow 2CaO$
(b) $Sr + Cl_2 \rightarrow SrCl_2$
(c) $Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$

2 Magnesium and water react at high temperatures to form hydrogen, which would make the fire worse.

4.1.3 Reactions of the Group 2 oxides and hydroxides, and trends in solubility

1 There is carbon dioxide in the air and this would also react with limewater.

2 Barium nitrate forms other white precipitates (especially barium carbonate) and using an acid removes carbonate ions from the solution so that they do not interfere with the test.

4.1.4 Thermal stability of Group 2 compounds, and the comparison with Group 1

1 (a) Brown fumes and a white solid.
(b) No visible change, no decomposition.

2 (a) $2KNO_3 \rightarrow 2KNO_2 + O_2$
(b) $SrCO_3 \rightarrow SrO + CO_2$

4.1.5 Flame tests and the test for ammonium ions

1 It is used to convert the metal compound being tested into a chloride, because chlorides are usually volatile and so more likely to produce a better flame colour.

2 The energy released when electrons in the excited state of the species return to the ground state corresponds to radiation in the visible region of the spectrum in the case of barium compounds, but not in the case of magnesium compounds.

4.2 Group 7

4.2.1 General trends in Group 7

1 Bromine has more electrons and a bigger electron cloud than chlorine, so the London forces between bromine molecules are stronger than those between chlorine molecules.

2 For the number of protons in its nucleus, it has a very small distance between the nucleus and the electrons in the outer energy level and the lowest shielding effect due to only two electrons in the innermost energy level.

4.2.2 Redox reactions in Group 7

1 (a) $Cl_2 + 2KI \rightarrow I_2 + 2KCl$
(b) $Br_2 + 2At^{-} \rightarrow At_2 + 2Br^{-}$

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2 (a) $Br_2 + 2NaOH \rightarrow NaBr + NaBrO + H_2O$

(b) $3Br_2 + 6NaOH \rightarrow 5NaBr + NaBrO_3 + 3H_2O$

4.2.3 Reactions of halides with sulfuric acid

1 Sulfuric acid would act as an acid, not as an oxidising agent because fluoride ions have a very low reducing power and cannot reduce sulfuric acid.

2 $2I^- \rightarrow I_2 + 2e^-$

and

$H_2SO_4 + 8H^+ + 8e^- \rightarrow 4H_2O + H_2S$

giving

$8I^- + H_2SO_4 + 8H^+ \rightarrow 4H_2O + H_2S$

4.2.4 Other reactions of halides

1 (a) $Ag+(aq) + Br–(aq) \rightarrow AgBr(s)$

(b) $AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$

2 (a) They react to form a white solid.

(b) Ammonium bromide

$NH_3(g) + HBr(g) \rightarrow NH_4Br(s)$

4 Answers to Exam-style questions

1 (a) Magnesium oxide – MgO (1).

Magnesium nitride – Mg_3N_2 (1).

(b) (i) $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$

Formulae correct and balanced (1). State symbols (1).

(ii) Reactivity increases down the group (1).

Outer electrons in quantum shell of increasingly higher energy as new quantum shell is added (1).

Outer electrons more easily removed / takes less energy to remove the outer electrons (1)

(iii) The solubility of the hydroxides increases down the group (1).

(c) All the carbonates of the Group 2 metals are white solids. When heated, they do not melt, but all will decompose to produce the metal oxide and carbon dioxide (1). The carbonate anion changes into the smaller, more stable oxide ion, which combines with the stable cation to form the metal oxide(1). Decomposition gets increasingly difficult going down the group (1) as smaller cations affect the anions more.

(d) $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

Formulae correct (1) and balanced (1).

2 (a) (i) Silver, shiny solid (1).

(ii) Black solid (1).

(b) Astatine will be less reactive than iodine (1).

The reactivity of the halogens decreases as you go down the group (1) as the shielding effect and distance between the nucleus and the bonding electrons increases (1).

(c) $H_2 + At_2 \rightarrow 2HAt$ (1).

(d) $Ra + Cl_2 \rightarrow RaCl_2$ (1).

(e) **D** (Radium hydroxide and 12) (1).

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3 (a) (i) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (1).

$3NaBr + 4H_2SO_4 \rightarrow 3NaHSO_4 + HBr + Br_2 + SO_2 + 2H_2O$ (1).

(ii) HBr is a more powerful reducing agent than is HCl (1)

HCl cannot reduce H_2SO_4 (1)

but HBr reduces the H_2SO_4 (S +6) to SO_2 (S +4). HBr (Br –1) is oxidised to Br_2 (Br 0) (1).

(iii) $NH_3(g)$ reacts with HCl(g) (1) to produce a white solid of ammonium chloride, NH4Cl(s) (1).

(b) (i) $HBr(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Br^-(aq)$ (1).

(ii) The solution turns methyl orange red/pink (1).

The solution is acidic (1) because of the presence of H_3O^+ ions (1).

(c) Add dilute nitric acid followed by aqueous silver nitrate (1).

Add an excess of dilute aqueous ammonia and filter (1).

Add dilute nitric acid to the filtrate and a white precipitate appears. This shows the presence of chloride ions in the original solution (1).

Add concentrated aqueous ammonia to the residue. The solid does not dissolve showing the presence of iodide ions in the original solution (1).

4 (a) (i) The reaction was exothermic (1).

(ii) Calcium hydroxide solution / limewater (1). pH = 10 to 14 (1).

(iii) $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$ (1) balanced equation (1) state symbols.

(b) (i) $Ca + ½O_2 \rightarrow CaO$ (1).

$Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + ½O_2$ (1).

(ii) As the group is descended, the decomposition temperature increases (1).

The charge density of the cations decreases as the ions become larger (1).

The polarising power of the cations decreases (1) so there is subsequently less polarisation of the nitrate ion (1).

5 (a) $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO^{3-} + 3H_2O$ (1) all formulae correct (1) balanced

(b) Oxidation number changes from 0 in Cl_2 to –1 in Cl^- (1) and to +5 in ClO_3^- (1).

The chlorine is undergoing disproportionation (1).

(c) $Cl_2(g/aq) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$

All formulae correct (1) balanced (1).

6 (a)

Reagents	**An aqueous solution containing chloride ions**	**An aqueous solution containing bromide ions**	**An aqueous solution containing iodide ions**
chlorine, Cl_2	no reaction	Cl^- and Br_2	Cl^- and I_2
bromine, Br_2	no reaction	no reaction	Br^- and I_2
iodine, I_2	no reaction	no reaction	no reaction

(1) for each correct horizontal row.

(b) $Cl_2(aq) + 2At^-(aq) \rightarrow 2Cl^-(aq) + At_2(s)$

(c) Add dilute nitric acid followed by aqueous silver nitrate (1).

A cream precipitate (of silver bromide) is formed (1).

Divide the precipitate in two and add dilute aqueous ammonia to one, and concentrated aqueous ammonia to the other (1).

The precipitate is insoluble in dilute aqueous ammonia but soluble in concentrated aqueous ammonia (1).

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7 (a) (i) **X** is magnesium hydroxide / $Mg(OH)_2$ (1).

Y is barium hydroxide / $Ba(OH)_2$ (1).

(ii) **X** – 8 to 10 (1)

Y – 12 to 14 (1)

(iii) Barium hydroxide is more soluble in water (1) and so the concentration of hydroxide ions will be greater (1).

(b) Ca $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$ balanced equation (1) state symbols (1).

(c) Magnesium oxide – no colour (1).

Barium oxide – pale green / apple-green (1).

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5.1 Empirical and molecular formulae

5.1.1 Empirical formulae

1

	Ca	N	O
% of element	24.4	17.1	58.5
Relative atomic mass	40.1	14.0	16.0
Division by A_r	0.61	1.22	3.66
Ratio	1	2	6

Empirical formula is CaN_2O_6

2 Mass of carbon = $\frac{4.33 \times 12.0}{44.0} = 1.18$ g

Mass of hydrogen = $\frac{1.77 \times 2.0}{18.0} = 0.197$ g

Mass of oxygen = 2.16 − (1.18 + 0.197) = 0.783 g

	C	H	O
Mass of element	1.18	0.197	0.783
Relative atomic mass	12.0	1.0	16.0
Division by A_r	0.0983	0.197	0.0489
Division by smallest	2.01	4.03	1
Ratio	2	4	1

Empirical formula is C_2H_4O

5.1.2 Molecular formulae

1 $n = \frac{pV}{RT} = \frac{103 \times 10^3 \times 1.26 \times 10^{-3}}{8.31 \times 328} = 0.0476$ mol

$M = \frac{m}{n} = \frac{2.82}{0.0476} = 59.2$ g mol^{-1}

2

	C	H	O
% of element	40.0	6.7	53.3
Relative atomic mass	12.0	1.0	16.0
Division by A_r	3.33	6.7	3.33
Ratio	1	2	1

Empirical formula is CH_2O

$n = \frac{pV}{RT} = \frac{98 \times 10^3 \times 69.5 \times 10^{-6}}{8.31 \times 336} = 0.00244$ mol

$M = \frac{m}{n} = \frac{0.146}{0.00244} = 59.8$ g mol^{-1}

The 'mass' of the empirical formula is 12.0 + (2 × 1.0) + 16.0 = 30.0

As this is half the value of the molar mass, the molecular formula is double the empirical formula.

So, the molecular formula is $C_2H_4O_2$

5.2 Amount of substance

5.2.1 Calculations using moles and the Avogadro constant

1 (a) 8.0 ÷ 32.1 = 0.249 mol

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(b) $8.0 \div 64.1 = 0.125$ mol

(c) $8.0 \div 96.1 = 0.0832$ mol

2 (a) $n = \frac{2.0}{32.1} = 0.0623$ mol

Number of particles = $0.0623 \times 6.02 \times 10^{23} = 3.75 \times 10^{22}$

(b) $n = \frac{4.0}{64.1} = 0.0624$ mol

Number of particles = $0.0624 \times 6.02 \times 10^{23} = 3.76 \times 10^{22}$

(c) $n = \frac{8.0}{96.1} = 0.0623$ mol

Number of particles = $0.0832 \times 6.02 \times 10^{23} = 5.01 \times 10^{22}$

5.2.2 Writing chemical equations

1 $Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow S(s) + SO_2(g) + 2NaCl(aq) + H_2O(l)$

2 The full equation is:

$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O + 2NH_3$

Replacing formulae by ions where appropriate gives:

$2NH_4^+ + SO_4^{2-} + 2Na^+ + 2OH^- \rightarrow 2Na^+ + SO_4^{2-} + 2H_2O + 2NH_3$

Omitting common ions gives:

$2NH_4^+ + 2OH^- \rightarrow 2H_2O + 2NH_3$

This can be simplified to:

$NH_4^+ + OH^- \rightarrow H_2O + NH_3$

5.2.3 Calculations using reacting masses

1 $NH_3 + HNO_3 \rightarrow NH_4NO_3$

$n(NH_4NO_3) = \frac{20 \times 1000}{80.0} = 250$ mol $= n(NH_3)$

$m(NH_3) = 250 \times 17.0 = 4250g = 4.25$ kg

2 $n(Fe) = \frac{4.35}{56.0} = 0.0777$ mol and $n(H_2O) = \frac{1.86}{18.0} = 0.103$ mol

Fe:H_2O ratio is 0.0777:0.103 or 3: 4

Equation is $Fe_3O_4 + H_2 \rightarrow 3Fe + 4H_2O$

5.2.4 Avogadro's law and gas volume calculations

1 H_2O and S should be ignored as they are not gases.

Reaction ratio is 2:1

All H_2S reacts, so none left.

Half of the SO_2 reacts, so there is $0.5dm^3$ left.

2 H_2O should be ignored as it is not a gas.

Reaction ratio is 1:5:3

All oxygen reacts, so none left.

$30cm^3$ of propane reacts, so $20cm^3$ is left.

$90cm^3$ of carbon dioxide is formed.

Final volume = $0 + 20 + 90 = 110$ cm^3

5.2.5 Molar volume calculations

1 $n = \frac{2}{58} = 0.0345$ mol

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2 $n(CuO) = \frac{10.0}{79.5} = 0.126$ mol

$n(H_2) = n(CuO) = 0.126$ mol

Volume of hydrogen = $24\,000 \times 0.126 = 3024$ cm^3

5.3 Equations and calculations

5.3.1 Concentrations of solutions

1 $n(NaOH) = \frac{50.0}{40.0} = 1.25$ mol

$c = \frac{1.25}{1.50} = 0.833$ mol dm^{-3}

2 $n(Pb(NO_3)_2) = 0.125 \times 0.150 = 0.01875$ mol

$n(PbI_2) = 0.01875$ mol

$m(PbI_2) = 0.01875 \times 461.0 = 8.64$ g

5.3.2 Making standard solutions

1 (a) The amount of sulfamic acid in the volumetric flask will be less than that weighed out, so the concentration of the solution will be lower.

(b) The amount of sulfamic acid in the volumetric flask will be the same, but the volume of solution will be greater, so the concentration of the solution will be lower.

2 $n = \frac{5.164}{106.0} = 0.0487$ mol

$c = \frac{0.0487}{0.500} = 0.0974$ mol dm^{-3}

5.3.3 Doing titrations

1 When the tap is opened, the first volume of solution enters the space between the tap and the tip but does not enter the conical flask at this time. The initial reading is correct but the final reading will be too high. So, the value of the titre will be greater than it should be.

2 This will increase the amount of the substance in the conical flask, so that it is more than the value calculated using the 25.0 cm^3 from the pipette. This means that the volume of substance added from the burette will be greater, so the titre will be greater.

5.3.4 Calculations from titrations

1 The first mistake is that all the readings are recorded to 0.1 cm^3 instead of to 0.05 cm^3.

The second mistake is that the average titre has been calculated using titres that are not within 0.10 cm^3 of each other.

2 $n(H_2SO_4) = 0.0618 \times 0.01983 = 0.0123$ mol

$n(KOH) = 2 \times 0.0123 = 0.0246$ mol

$c = \frac{0.0246}{0.0250} = 0.984$ mol dm^{-3}

5.4 Errors and uncertainties

5.4.1 Mistakes, errors, accuracy and precision

1 The student has made a mistake by using in incorrect piece of apparatus. As the measuring cylinder is much less accurate than using the pipette, this is likely to also introduce a systematic error.

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2 Student 1's titres are all concordant and the average titre is 27.67 cm^3, so they are precise but not accurate because they are too far away from the correct value.

None of Student 2's titres are concordant and the average titre is 26.48 cm^3, so they are not precise but the average titre is accurate because it is very close to the correct value.

Student 3's titres are all concordant and the average titre is 26.45 cm^3, so they are precise and accurate.

5.4.2 Measurement errors and measurement uncertainties

1 (a) 0.10 cm^3

(b) The atmospheric pressure and temperature could have changed from one day to the next, causing a slight change to the volume of the liquid in the burette. This would introduce a random error.

(c) Systematic errors could be due to a poorly calibrated burette, either in its measurement scale or its dimensions.

2 The pipette error is 0.12 cm^3 for two uses. The burette error is 0.10 cm^3 for two readings, so the burette is better.

5.4.3 Percentage measurement uncertainty

1 The balance error is 0.05 g, but you have to count it twice (once for the calibration to zero, and once for the measurement), so the percentage error is:

$$\frac{2 \times 0.05 \times 100}{2.8} = 3.6\%$$

2 The thermometer error is 1 ºC for each of the two readings. The percentage error is:

$$\frac{2 \times 1 \times 100}{13} = 15.4\%$$

5.5 Yield and atom economy

5.5.1 The yield of a reaction

1 $n(CuO) = \frac{4.68}{79.5} = 0.0589 \text{ mol} = n(CuSO_4.5H_2O)$

$m(CuSO_4.5H_2O) = 0.0589 \times 249.5 = 14.7 \text{ g}$

$\text{Percentage yield} = \frac{7.85 \times 100}{14.7} = 53.4\%$

2 $n(CH_3OH) = \frac{50\,000}{32} = 1562.5 \text{ mol} = n(CH_3COOH)$

$m(CH_3COOH) = 1562.5 \times 60 = 93.75 \text{ kg}$

$\text{Percentage yield} = \frac{89.2 \times 100}{93.75} = 95.1\%$

5.5.2 Atom economy

1 100%

2 $\text{Percentage yield} = \frac{28.0 \times 100}{46.0} = 60.9\%$

5.6 Types of reaction

5.6.1 Displacement reactions

1 $Fe(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Fe(NO_3)_2(aq)$

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$Fe(s) + 2Ag^+(aq) + 2NO_3^-(aq) \rightarrow 2Ag(s) + Fe^{2+}(aq) + 2NO_3^-(aq)$
$Fe(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Fe^{2+}(aq)$

2 $Zn(s) + CuO(s) \rightarrow Cu(s) + ZnO(s)$
$Zn(s) + Cu^{2+}(s) + O^{2-}(s) \rightarrow Cu(s) + Zn^{2+}(s) + O^{2-}(s)$
$Zn(s) + Cu^{2+}(s) \rightarrow Cu(s) + Zn^{2+}(s)$

5.6.2 Precipitation reactions

1 (a) $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Ba^{2+}SO_4^{2-}(s)$
(b) $Ag^+(aq) + Cl^-(aq) \rightarrow Ag^+Cl^-(s)$

2 $n(KI) = 0.005 \times 1.0 = 0.005$ mol
$n(Pb(NO_3)_2) = 0.0035 \times 1.0 = 0.0035$ mol
$n(PbI_2) = 0.0035$ mol
$n(KNO_3) = 0.00175$ mol

5.6.3 Reactions of acids

1 (a) $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
(b) $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

2 (a) $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$
(b) $Mg^{2+}CO_3^{2-} + 2H^+ \rightarrow Mg^{2+} + H_2O + CO_2$

5 Answers to Exam-style questions

1 (a) Magnesium disappears (1) bubbles of gas/fizzing/effervescence (1).
(b) (i) $(1.215 \div 24.3) = 0.050$ (1).
(ii) $(0.060 \times 2.00) = 0.120$ (1).
(iii) 0.050 mol of require 0.100 mol of HCl (1)
0.120 > 0.100 (1)
(c) 0.050 mol Mg → 0.050 mol H_2 (1).
0.050 mol × 24.0 dm^3 mol^{-1} = 1.20 dm^3 (1).

2 (a) Oxidation number of N in NH_3 is –3 (1).
Oxidation number of N in HNO_3 is +5 (1).
(b) (i) $n(NH_3) = (0.025 \times 2.00) = 0.050$ mol (1).
Vol. of $HNO_3 = ((0.050 \times 1000) \div 0.500) = 100$ cm^3 (1).
(ii) Leave the solution to evaporate / crystallise by cooling from a hot concentrated solution (1).
(c) (i) $n(NH_4NO_3) = (4.00 \div 80.0)$ (1) = 0.050 mol (1).
(ii) Vol. of $N_2O = (0.050$ mol × 24.0 dm^3 $mol^{-1}) = 1.20$ dm^3 (1).
(iii) $N_2O(g) \rightarrow N_2(g) + ½O_2(g)$ correct equation (1) state symbols (1).

3 (a) The formula that shows the number of atoms of each element present in one molecule (1).
(b) $P_4 + 10Cl_2 \rightarrow 4PCl_5$ (1).
(c) $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5H^+(aq) + 5Cl^-(aq)$ correct equation (1) state symbols (1).
[Accept $5HCl(aq)$ for $5H^+(aq) + 5Cl^-(aq)$]
(d) (i) P $(30.39 \div 31.0) = 0.980$; Cl $(69.61 \div 35.5) = 1.96$ (1).
0.980 : 1.96 = 1 : 2 (1)
Compound is P_2Cl_4 (1)
(ii) (di)phosphorus(II) tetrachloride (1).

4 (a) (i) $n(H_2) = n(M) = (0.230$ $dm^3 \div 24.0$ dm^3 $mol^{-1}) = 0.00958(3)$ mol (1)
Molar mass of M = 0.24 g ÷ 0.00958(3) mol = 25.0 g mol^{-1} correct answer (1) units (1)
(ii) Magnesium (1) 25.0 is closer to 24.3 than to the molar mass of any other Group 2 metal (1).
(b) (i) Loss of gas before the bung is replaced (1).

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(ii) Place the acid in a small container and put this into the flask along with the metal. Put the bung into place and then tilt the flask so that the acid makes contact with the metal (1).

(c) (i) Balance – ((±0.005 ÷ 0.24) × 100) = 21% (1)

Measuring cylinder – ((±1.0 ÷ 230) × 100) = 0.43% (1)

(ii) Use a three decimal place balance (1)

The measurement uncertainty would then be ±0.0005 g (1).

5 (a) Oxidation number of W changes from +6 to 0 (1).

Oxidation number of H changes from 0 to +1 (1).

W has been oxidised; H has been reduced (1).

(b) $WO_3 \rightarrow W$

1 mol of WO_3 = 232 g → 1 mol of W = 184 g (1)

2 tonnes → ((184 ÷ 232) × 2) (1) = 1.59 tonnes (1).

6 (a) B (36 dm^3)

(b) (i) $NaN_3 \rightarrow Na$

65.0 g → 23.0 g (1).

3.25 g → ((23.0 ÷ 65.0) × 3.25) = 1.15 g (1).

(ii) n(Na) = 1.15 ÷ 23.0 = 0.05 mol (1); conc of NaOH = (0.05 × 1000) ÷ 25.0 = 2.0 mol dm^{-3} (1).

(c) (i) Good conductor of heat (1).

(ii) Highly reactive (1).

7 **C** (C_3H_8)

8 (a) Yellow at the beginning; orange at the end (1).

(b) Results that are within 0.1 cm^3 of one another (1)

(c) 25.0 cm^3 of *y* mol dm^{-3} Na_2CO_3 ≡ 17.80 cm^3 of 0.100 mol dm^{-3} HCl

Na_2CO_3 ≡ 2HCl (1)

y = 0.0356

Concentration of sodium carbonate = 0.0356 mol dm^{-3} (1).

(d) Mass of Na_2CO_3 in 250 cm^3 = ((0.0356 × 106) ÷4) = 0.943 g (1).

Purity = ((0.943 × 100) ÷ 1.00) = 94.3% (1).

(e) (i) Volumetric flask – ((0.30 × 100) ÷ 250) = 0.12% (1).

Pipette = ((0.060 × 100) ÷ 25.0) = 0.24% (1).

Burette = ((0.10 × 100) ÷ 17.78) = 0.56% (1).

Total measurement uncertainty = 0.92% (1).

(ii) 0.92% of 94.3 = 0.87

Therefore exact degree of purity could be between 93.4% and 95.2%.

The manufacturer's claim is justified since both values are within the range quoted (1).

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6.1 Introduction to organic chemistry

6.1.1 What is organic chemistry?

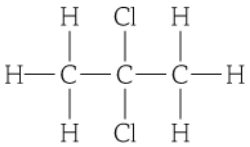
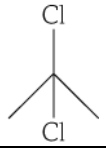
1 10

2 (a) It is not easy to decide – it contains carbon, so could be an organic compound, but it does not contain hydrogen, so perhaps it is an inorganic compound!

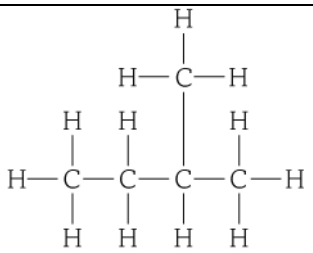
(b) It is unsaturated. Each carbon forms four bonds, so allowing for the C–C bond there are another six atoms that could be joined to these two. As there are only four F atoms, then there must be a C=C double bond.

6.1.2 Different types of formulae

1

Type of formula	Formula
Displayed formula	
Structural formula	$CH_3CCl_2CH_3$
Skeletal formula	
Molecular formula	$C_3H_6Cl_2$
Empirical formula	$C_3H_6Cl_2$

2

Type of formula	Formula
Displayed formula	
Structural formula	$CH_3CH_2CH(CH_3)_2$
Molecular formula	C_5H_{12}
Empirical formula	C_5H_{12}

6.1.3 Functional groups and homologous series

1 $C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$

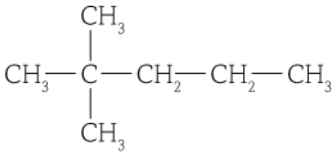
2 HCHO and CH_3CHO

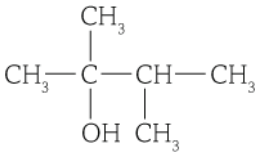
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6.1.4 Nomenclature

1 1,2-dibromopropane
1-bromopropan-2-ol

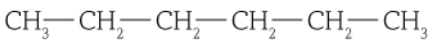
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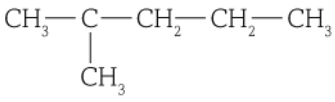


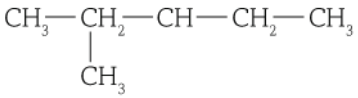


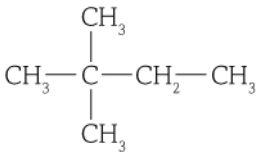
6.1.5 Isomerism

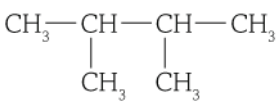
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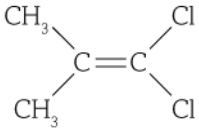




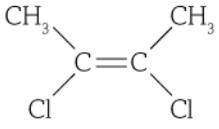




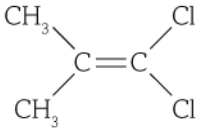
2



1, 1-dichloro-2-2methylpropene



cis-2,3-dichlorobut-2-ene



trans-2,3-dichtorobut-2-ene

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6.2 Hydrocarbons

6.2.1 Alkanes from crude oil

1 In two molecules of ethene there are four carbon atoms. The alkane formed must contain 12 − 4 = 8 carbon atoms. Two molecules of ethene contain 8 hydrogens, so the alkane formed must be C_8H_{18}.

2 There are four carbon atoms in two molecules of ethene and five carbon atoms in one molecule of pentane. The alkane being cracked has 4 + 5 = 9 carbon atoms, so it must be C_9H_{20}.

6.2.2 Alkanes as fuels

1 Complete combustion – carbon dioxide and water

Incomplete combustion – carbon and carbon monoxide

2

Substance	Product
unburned hydrocarbons	carbon dioxide and water
carbon monoxide	carbon dioxide
oxides of nitrogen	nitrogen

6.2.3 Alternative fuels

1 Hydrogen does not occur naturally, so it has to be manufactured. This uses energy, some of which comes from burning fossil fuels.

2 The plants from which biofuels are obtained may need fertilising and pesticides produced from organic chemicals, and are then harvested, transported and processed using energy from fossil fuels.

6.2.4 Substitution reactions of alkanes

1 $Br_2 \rightarrow Br\bullet + Br\bullet$

$Br\bullet + CH_4 \rightarrow HBr + CH_3\bullet$

$CH_3\bullet + Br_2 \rightarrow CH_3Br + Br\bullet$

$Br\bullet + Br\bullet \rightarrow Br_2$

$Br\bullet + CH_3\bullet \rightarrow CH_3Br$

$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$

2 (a) Termination, because two radicals become a molecule.

(b) Termination, because two radicals become a molecule.

(c) Propagation, because there is a radical on both sides of the equation.

6.2.5 Alkenes and their bonding

1 It is a cyclic structure, so it has two fewer hydrogen atoms than the corresponding non-cyclic compound.

2 $2C_3H_6 + 7O_2 \rightarrow 6CO_2 + 6H_2O$

6.2.6 Addition reactions of alkenes

1 (a) $CH_3CHCHCH_3 + H_2 \rightarrow CH_3CH_2CH_2CH_3$

(b) $CH_3CHCHCH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_3$

(c) $CH_3CHCHCH_3 + HCl \rightarrow CH_3CH_2CHClCH_3$

2 (a) The product is an alkane with four carbon atoms, so it is butane.

(b) The product has no multiple bonds, so ends in –ane. There are bromine atoms on carbons 2 and 3 in the chain of four, so it is 2,3-dibromobutane.

(c) The product has no multiple bonds, so ends in –ane. There is a chlorine atom on carbon 2 (counting from the right) in the chain of four, so it is 2-chlorobutane.

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6.2.7 The mechanisms of addition reactions

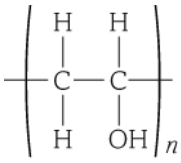
1 (a) Radical substitution

(b) Electrophilic addition

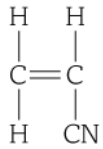
2 There are two possible products in this reaction. The major product is the one formed via the more stable carbocation. In this case, the more stable carbocation is the secondary one, so the chlorine becomes attached to the second carbon in the chain. So 2-chlorobutane is the major product.

6.2.8 Polymerisation reactions

1



2



6.2.9 Dealing with polymer waste

1 They can be made in many different shapes and with different physical properties. They are lighter in weight. They do not corrode or rot.

2 Advantages: very little solid waste formed, saves landfill, can produce useful energy.

Disadvantage: toxic pollutants may be formed.

6.3 Halogenoalkanes

6.3.1 Halogenoalkanes and hydrolysis reactions

1 (a) 2-chloro-2-methylbutane tertiary

(b) 2-bromobutane secondary

(c) 1-iodo-2-methylpropane primary

2 Fluorine is more electronegative than chlorine, so the C—F bond is more polar than the C—Cl bond. This means that the C in the C—F bond has a greater δ+ charge than the C in the C—Cl bond and so attracts nucleophiles more strongly.

6.3.2 Comparing the rates of hydrolysis reactions

1 2-iodopropane is hydrolysed more quickly because the C—I bond is weaker than the C—Br bond and so breaks more easily.

2 Hydrolysis involves the breaking of the C—X bond. As the C—F bond is stronger than the C—Cl bond, the C—Cl bond needs less energy to break and so breaks, while the C—F bond does not.

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6.3.3 Halogenoalkane reactions and mechanisms

1 (a) methylamine

(b) ethanenitrile

2 (a) Nucleophilic substitution

(b) Elimination

There are two products in (b) because the hydrogen that is removed can come from the first or the third carbon atom in the chain, so the double bond that forms is between the first and second carbon atoms or between the second and third carbon atoms.

6.4 Alcohols

6.4.1 Alcohols and some of their reactions

1 $C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$

2 The OH group removed in the dehydration comes from the carbon atom in the middle of the molecule. The hydrogen atom removed comes from the next carbon in the chain. Whether it comes from the carbon before or after the C—OH, the double bond is next to the middle carbon atom, so the only product is pent-2-ene.

6.4.2 Oxidation reactions of alcohols

1 but-1-ene $CH_2=CH—CH_2–CH_3$

butanal $CH_3–CH_2–CH_2–CHO$

butanoic acid $CH_3–CH_2–CH_2–COOH$

2 pent-1-ene $CH_2=CH–CH_2–CH_2–CH_3$

pent-2-ene $CH_3–CH=CH–CH_2–CH_3$

pentan-2-one $CH_3–CO–CH_2–CH_2–CH_3$

6.4.3 Purifying an organic liquid

1 Distillation can be done without a thermometer as it is needed to measure the temperature of the vapour passing into the condenser, which helps to check which liquid is distilling over. A change in the temperature of the vapour indicates that a different substance is distilling over.

2 The boiling temperature of a pure compound should match the correct value shown in a data book. Sometimes the thermometer used will give an incorrect reading, so if it reads 2 °C too high but still matches the data book value of the boiling temperature, you might think that the liquid is pure when it is not.

6 Answers to Exam-style questions

1 (a) C_8H_{18} (1).

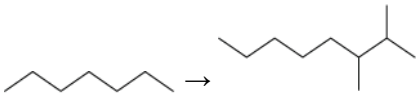
(b) (i) As the chain length increase the number of points of contact between the molecules increases (1). There are therefore more London forces the longer the chain, resulting in increase in the overall intermolecular forces of attraction (1).

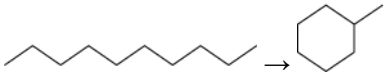
(ii) Any value between 418 and 428 K (1).

(c) (i) $C_{10}H_{22} \rightarrow C_8H_{18} + C_2H_4$ (1).

(ii) $C_2H_4 + H_2O \rightarrow C_2H_5OH$ (1)

350 ºC (1); 60 to 70 atm pressure (1); phosphoric(V) acid catalyst (1).

(d) (i)  (1)

(ii)  for heptane (1) for methylcylohexane (1)

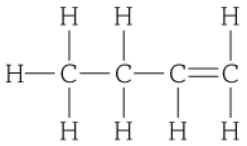
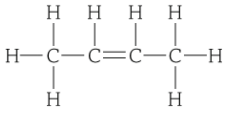
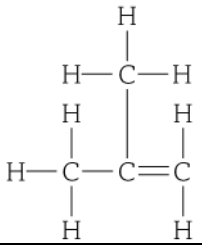
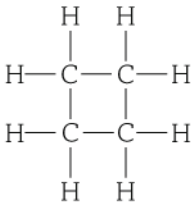
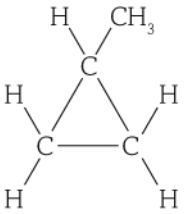
(iii) To produce more efficient burning petrol (1).

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2 (a) (i) C (85.7 ÷ 12.0) = 7.14; H (14.3 ÷ 1.0) = 14.3 (1)
7.14 : 14.3 = 1 : 2
Empirical formula = CH_2 (1)

(ii) Empirical formula mass = 14
56 ÷ 14 = 4 (1).
Therefore molecular formula = C_4H_8

(b)

Isomer 1	Isomers 2 and 3	Isomer 4	Isomer 5	Isomer 6
				
but-1-ene	but-2-ene (*cis* and *trans*)	methylpropene	cyclobutane	methylcyclopropane

(1) for each combination of correct structure with correct name.

(c) Compound **Y** contains a C=C since it undergoes an addition reaction with steam (1).
Since a primary unbranched-chain alcohol is formed, the C=C is at the end of the molecule.
Compound **Y** is therefore but-1-ene (1).
[$CH_3CH_2CH{=}CH_2 + H_2O \rightarrow CH_3CH_2CH_2OH$]

3 (a) (i) $Cl_2 \rightarrow Cl\bullet + Cl\bullet$ (1).

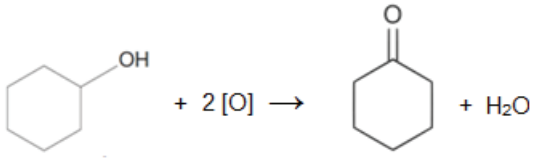
(ii) Ultraviolet radiation (1).

(iii) $C_6H_{12} + Cl\bullet \rightarrow \bullet C_6H_{11} + HCl$ (1).
$\bullet C_6H_{11} + Cl_2 \rightarrow C_6H_{11}Cl + Cl\bullet$ (1)

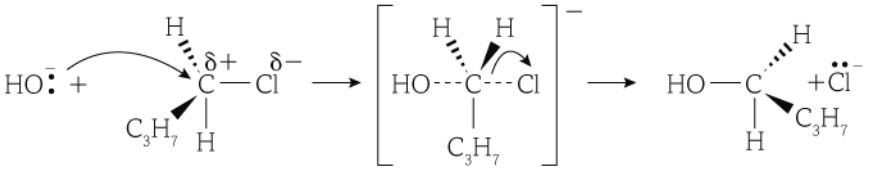
(b) (i) Solvent **W** is water (1).

(ii) Solvent **X** is ethanol (1).

(c) (i) Acidified potassium dichromate(VI) (1).

(ii) 

cyclohexanone (1), balanced equation (1).

4 (a) 

Arrow from lone pair on HO^- to correct C atom (1).
Arrow head form C–Cl bond to Cl atom (1).
Correct products (1).
[N.B. correct stereochemistry not essential]

(b) The C–Br bond is weaker than the C–Cl bond (1).
The activation energy is lower with 1-bromobutane (1).
More collisions per second result in reaction (1).

(c) **B**

(d) **C**

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5 (a) (i) $C_{10}H_{18}O$ (1).

(ii) alkene (1) (primary) alcohol (1).

(b) (i) Add acidified potassium dichromate(VI) to lavandulol (1), and distil out the product as it forms (1).

(ii) Heat under reflux (1) with an excess of acidified potassium dichromate(VI) (1).

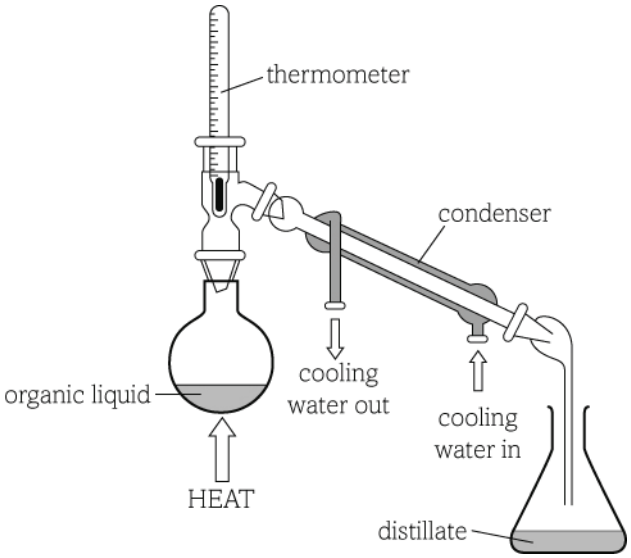
(iii) Add Fehling's solution and heat (1).
Compound **X** produces a red precipitate; compound **Y** gives no observable change (1).

6 (a) Concentrated hydrochloric acid is corrosive (1), therefore protective gloves must be worn (1).

(b) To remove the unreacted hydrochloric acid (1).

(c) To remove water from the organic liquid (1).

(d)



Labels: flask containing organic liquid (1); bulb of thermometer opposite exit to condenser (1); condenser with water in at bottom and out at top (1); correct method of collection (i.e. open, not sealed) (1).

(e) 74.0 g $C_4H_{10}O$ gives 92.5 g of C_4H_9Cl (1)
7.40 g $C_4H_{10}O$ gives 9.25 g of C_4H_9Cl (1)
((7.82 ÷ 9.25) × 100) = 84.5% (1).

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7.1 Mass spectrometry

7.1.1 Mass spectrometry in organic compounds

1 A small proportion of carbon atoms in an organic compound are ^{13}C isotopes instead of the much more common ^{12}C isotopes. This means that some of the molecular ions have a slightly higher relative molecular mass than that of the normal molecular ion.

2 $(CH_3—CH_2—CH_2—CH_3)^+ \rightarrow (CH_3—CH_2—CH_2)^+ + CH_3$

7.1.2 Deducing structures from mass spectra

1 $(CH_3—CH_2—CH_2—CH_2—CH_3)^+ \rightarrow (CH_3—CH_2)^+ + CH_3—CH_2—CH_2$

2 C $(CH_3—CH_2—CH_2—OH)^+ \rightarrow (CH_2—OH)^+ + CH_3—CH_2$

D $(CH_3—CH(OH)—CH_3)^+ \rightarrow (CH_3—CH(OH)^+ + CH_3$

7.2 Infrared spectroscopy

7.2.1 Infrared spectroscopy

1 Only polar molecules absorb infrared radiation. Hydrogen fluoride contains a polar H–F bond and so absorbs, but the bond in fluorine (F–F) is not polar so does not absorb.

2 The broad absorption at 2850 cm^{-1} suggests the presence of OH in a carboxylic acid, and the sharp absorption at 1710 cm^{-1} suggests a C=O bond in a carboxylic acid, so the compound is almost certainly a carboxylic acid

7.2.2 Using infrared spectra

1 The bonds in propan-1-ol and propan-2-ol are the same – they are C–C, C–H, C–O and O–H, so the absorptions are very similar.

2 If it has the structure $(CH_3)_2CO$ it will have a sharp absorption in the range 1700–1680 cm^{-1}

If it has the structure $CH_3C(OH)=CH_2$ it will not have this absorption but will have a broad absorption in the range 3750–3200 cm^{-1} and an absorption in the range 1689-1645 cm^{-1}.

7 Answers to Exam-style questions

1 (a) Butanoic acid (1).

Absorption between 3300 and 2500 indicates O–H stretching in a carboxylic acid (1).

Absorption between 1725 and 1700 indicates C=O stretching in an alkyl carboxylic acid (1).

(b) $CH_3CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2COOH + H_2O$

correct formulae (1) balanced equation (1).

2 (a) Continuous evaporation and condensing of the reactant liquid (1).

(b) No absorbance in the region 3750 to 3200 corresponding to O–H stretching in alcohols (1).

(c) Add bromine water and shake (1), bromine is decoloured (1).

3 Spectrum A is pentan-2-one (1).

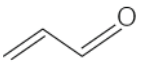
Spectrum B is pentan-3-one (1).

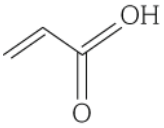
Peak at 43 in spectrum A is CH_3CO^+ and peak at 71 is $CH_3CH_2CH_2CO^+$ (1).

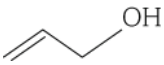
Peak at 29 in spectrum B is $CH_3CH_2^+$ and peak at 57 is $CH_3CH_2CO^+$ (1).

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4 (a) (i)

propenal  (1)

prop-2-enoic acid  (1)

prop-2-en-1-ol  (1)

(ii) Alkene (1).

(b) Potassium dichromate(VI) (1) and dilute sulfuric acid (1).

(c) Product is prop-2-enoic acid.
Absorption between 3300 and 2500 indicates O–H stretching in a carboxylic acid (1).
Absorption between 1725 and 1700 indicates C=O stretching in an alkyl carboxylic acid (1).

5 (a) C (62.07 ÷ 12.0) = 5.17; H (10.34÷ 1.0) = 10.34; O (27.59 ÷ 16.0) = 1.72 (1).
5.17 : 10.34 : 1.72 = 3 : 6 : 1 (1).
Empirical formula = C_3H_6O (1).

(b) Relative molecular mass of compound **X** = 58 (*m/z* of parent peak is 58) (1)
Empirical formula mass = 58 (1)
Molecular formula is C_3H_6O (1).

(c) (i) Compound **X** is propanone (CH_3COCH_3) (1)
[It is not an aldehyde because of the negative result with Fehling's solution]

(ii) 15 – CH_3^+ (1) 43 – CH_3CO^+ (1).

(iii) C=O (1).

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8.1 Heat energy and enthalpy

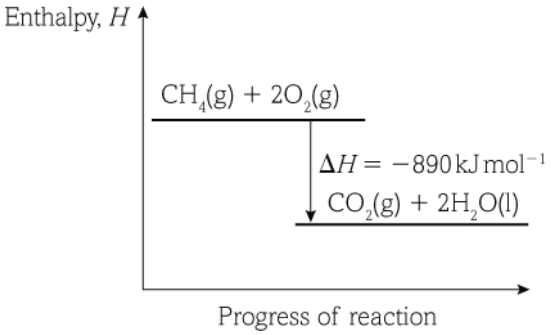
8.1.1 Introducing enthalpy and enthalpy change

1 (a) endothermic
(b) exothermic
(c) exothermic
(d) endothermic
(e) endothermic

2 The citric acid dissolves in the water of the saliva and then reacts with the sodium hydrogencarbonate. The reaction is endothermic and so the reaction mixture cools as the reaction takes place.

8.1.2 Enthalpy level diagrams

1

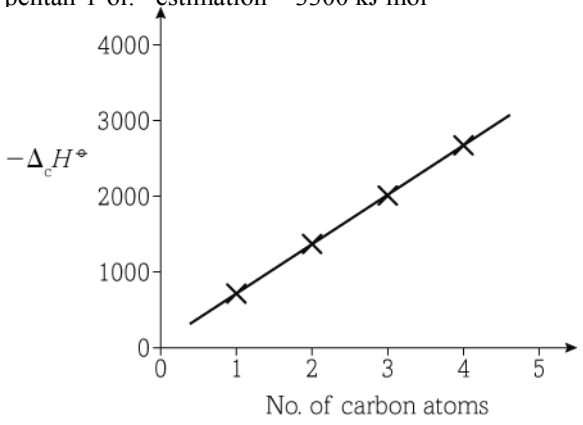


2 (a) The reaction is endothermic, absorbing 26.5 kJ when one mole of HI(g) is formed.
(b) + 53 kJ mol^{-1}.

8.1.3 Standard enthalpy change of combustion

1 (a) (i) $CH_3CH_2OH(l) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H = -1367$ kJ mol^{-1}
(ii) $CH_3OCH_3(l) + 3\frac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H = -1460$ kJ mol^{-1}
(b) Ethanol has an O—H bond and methoxymethane does not. Methoxymethane has two C—O bonds, and ethanol has only one. The O—H and the C—O bonds will have different bond enthalpies. Also, the C—H bonds in each compound will have different bond enthalpies.

2 (a) methanol: −715 kJ mol^{-1}
ethanol: −1371 kJ mol^{-1}
propan-1-ol: −2010 kJ mol^{-1}
butan-1-ol: −2673 kJ mol^{-1}
(b) pentan-1-ol: estimation − 3300 kJ mol^{-1}

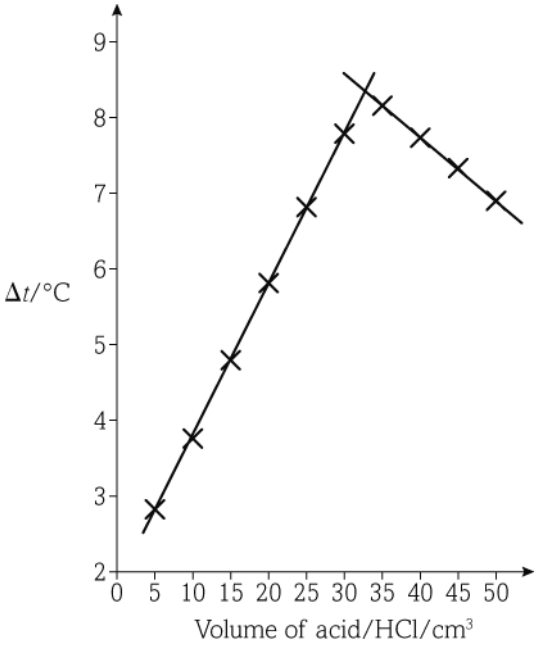


(c) The value obtained is an approximate value for the enthalpy change of combustion of hydrogen.

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8.1.4 Standard enthalpy change of neutralisation

1 (a)



End point is 32.50 cm^3, so concentration of acid is 1.54 mol dm^{-3}

(b) $\Delta T = +8.23$ K, so $\Delta H_{neut} = -57.52$ kJ mol^{-1}

(c) A polystyrene beaker with a lid, and a thermometer graduated in at least tenths of a degree.

(d) Weak acids, unlike hydrochloric acid, are only partially ionised in aqueous solution.

So, when weak acids are neutralised there will be an extra enthalpy change associated with the ionisation of the acid. This may be exothermic, as in the case of HF(aq), or endothermic, as in the case of CH_3COOH(aq).

2 (a) (i) $(\pm 0.10 \div 50.0) \times 100 = \pm 0.05\,\%$

(ii) $(\pm 0.05 \times 2) \div 32.50) \times 100 = 0.31\,\%$

(iii) $(\pm 0.05 \times 2) \div 8.23) \times 100 = 1.22\,\%$

(b) There may be a time delay between adding one sample of acid and the next. This could lead to a cooling of the solution. Ensure that the temperature is read as quickly as possible so that the addition of the next sample of acid is not delayed.

8.1.5 Standard enthalpy change of formation and Hess's Law

1 (a) $C(s) + 2H_2(g) \rightarrow CH_4(g)$

(b) $\Delta_f H^{\ominus}[CH_4(g)] = 890 - 394 - (2 \times -286) = -76\,kJ\,mol^{-1}$

2 $\Delta_r H^{\ominus} = -2692 - (-704) - (6 \times -286) = -272\,kJ\,mol^{-1}$

3 (a) The element is in its standard state as a solid.

(b) $Li(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) \rightarrow LiOH(s)$

(c) $\Delta_r H^{\ominus} = -485 - (-286) - 21 = -220\,kJ\,mol^{-1}$

8.2 Bond enthalpy

8.2.1 Bond enthalpy and mean bond enthalpy

1 (a) The enthalpy change when one mole of H—I bonds is broken to form hydrogen and iodine atoms in the gaseous state.

(b) $HI(g) \rightarrow H(g) + I(g)$

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2 (a) $(496 + 432) \div 2 = 464$ kJ mol^{-1}

(b) The data book value includes the bond enthalpies for the O—H bond in lots of different molecules.

3 The C—H bonds are in different environments and this has an effect on their strength.

4 (a) $NH_3(g) \rightarrow NH_2(g) + H(g)$
$NH_2(g) \rightarrow NH(g) + H(g)$
$NH(g) \rightarrow N(g) + H(g)$

(b) The bond enthalpies for each reaction are added together and the total is divided by three.

8.2.2 Using mean bond enthalpies

1 (a) $\Delta_r H = 436 + 158 - (2 \times 562) = -530$ kJ mol^{-1}

(b) $\Delta_r H = 612 + 193 - 612 - (2 \times 276) = -359$ kJ mol^{-1}

(c) $\Delta_r H = (6 \times 412) + 348 + (3 \times 496) - (4 \times 743) - (4 \times 463) = -516$ kJ mol^{-1}

(d) $\Delta_r H = 612 + 366 - 348 - 412 - 276 = -790$ kJ mol^{-1}

2 (a) $\frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g) \rightarrow NH_3(g)$

(b) $E(\text{N—H}) = \frac{1}{3}\{(\frac{1}{2} \times 944) + (1\frac{1}{2} \times 436) + 46) = 390.6$ kJ mol^{-1} (or 391 to 3sf)

3 $E(\text{S—F}) = 1/6\ \{1100 + 223 + (3 \times 158)\} = 299.5$ kJ mol^{-1}

8 Answers to Exam-style questions

1 (a) (i) The enthalpy change when one mole of a substance is formed from its elements in their standard states (1).

(ii) Temperature – 298 K (1) Pressure – 100 kPa (1)

(iii) $Pb(s) + \frac{1}{2}O_2(g) \rightarrow PbO(s)$

(1) correct equation as shown (i.e. must be for formation of one mole of PbO)

(1) state symbols [N.B. state symbols must always be shown in an equation for an enthalpy change, even if not asked for.]

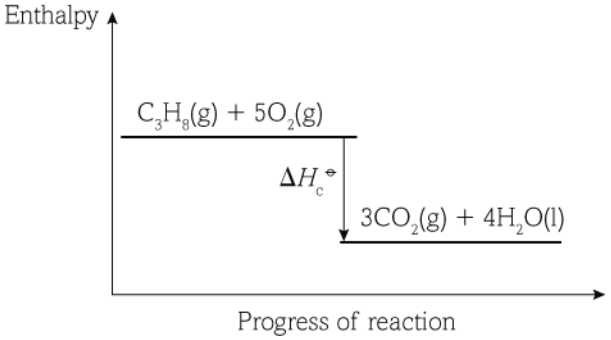
(b) $\Delta r H^{\ominus} = -735 - (3 \times -219)$ (1) $= -78$ kJ mol^{-1} (1).

(c) $\Delta f H^{\ominus} = 20 - 735 - (2 \times -219)$ (1) $= -277$ kJ mol^{-1} (1).

2 (a) Releases thermal energy when it burns (1) and ignites easily (1).

(b) (i) The enthalpy change, measured at a stated temperature (usually 298 K) and 100 kPa pressure (1), when one mole of a substance (1) is completely burned in oxygen (1).

(ii)



(1) enthalpy level of products below that of reactants.

(1) $\Delta c H^{\ominus} = -2220$ labelled with single headed arrow line, with arrow pointing downwards.

(c) (i) The enthalpy change of a reaction is independent of the path taken in converting reactants into products (1), provided the initial and final conditions are the same (1).

(ii) $\Delta c H^{\ominus} = (3 \times -394) + (4 \times -286) - (-2220) = -106$ kJ mol^{-1} (2)

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3 (a) (i) The enthalpy change when one mole of a bond (1) in the gaseous state is broken (1).

(ii) Energy is required to break bonds, so the process is endothermic (1).

(b) (½ × 436) + ½E(Cl–Cl) – 431 = –92 (1)

½ E(Cl–Cl) = 121 kJ mol−1 (1).

E(Cl–Cl) = 242 kJ mol−1 (1).

(c) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$ $\Delta_f H$= y kJ mol^{-1}

y = (½ × 436) + (½ × 158) – 562 = –265 (1).

$\Delta_f H$ [HF(g)] = –265 kJ mol^{-1} (1).

4 (a) The enthalpy change when one mole of water is formed (1) by the neutralisation of an acid with an alkali (1).

(b) Burette or volumetric pipette (1).

(c) To make sure that all of the acid is neutralised (1)

(d) (i) ΔT = +13.6 ºC = +13.6 K

n(HCl) = n(H_2O) = (0.0500 × 2.00) = 0.100 mol (1).

Q = 100.0 g × 4.18 J g^{-1} K^{-1} × 13.6 K = (+)5684.8 J = 5.68 kJ (1).

$$\Delta H = -\frac{Q}{n} = -\frac{5.68}{0.100} = -56.8 \text{ kJ mol}^{-1} \text{ (1)}$$

5 (a) $CH_3CH_2CH_2CH_2OH(l) + 6\frac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

balanced for one mole of butan-1-ol (1)

state symbols (1)

(b) n(butan-1-ol) = (0.740 ÷ 74.0) = 0.0100 mol (1).

ΔT = +10.0 ºC = +10.0 K

Q = 50.0 g × 4.18 J g^{-1} K^{-1} × 10.0 K = (+)2090 J = 2.09 kJ (1).

$$\Delta H = -\frac{Q}{n} = -\frac{2.09}{0.0100} = -209 \text{ kJ mol}^{-1} \text{ (1)}$$

(c) Any two from

- not all of the thermal energy generated from the burning is transferred to the water
- incomplete combustion of the butan-1-ol
- some butan-1-ol evaporated between the weighings

for one mark each.

6 (a) (i) $\Delta_c H$ [$CH_3OH(g)$] = (3 × 412) + 360 + 463 + (1½ × 496) – (2 × 743) – (4 × 463) (1).

= – 535 kJ mol^{-1} (1)

(ii) The standard state of methanol and water is liquid, not gaseous (1).

Mean bond enthalpies, not actual bond enthalpies, have been used (1).

(b) **B** (1).

(c) 6E(S–F) = 1100 + 223 + (3 × 158) = 1797 (1).

E(S–F) = +299.5 kJ mol^{-1} (1).

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9.1 Reaction rate

9.1.1 Reaction rate, collision theory and activation energy

1 Only a fraction of the collisions taking place each second have $E \geq E_a$. Also, many of the collisions will not have the correct orientation for reaction to occur.

2 Many reactions involving organic compounds require the breaking of covalent bonds. Since these bonds are relatively strong, the activation energies for such reactions are often high, and so heating is required. Heating under reflux is also often required, since many organic compounds are volatile. If the activation energy of the reaction is high, then the reaction may be so slow that, if refluxing were not used, the reactant would evaporate before much of it had chance to react.

3 The chlorine atoms are large enough to prevent the hydroxide ion from getting close enough to the carbon atom of the tetrachloromethane molecule in order to interact with it. (steric hindrance).

[N.B. The reason often given for the lack of hydrolysis is that the carbon atom does not contain available d orbitals to enable the required intermediate to be formed. This argument is flawed and you should not use it.]

4 The energy of a single H–Cl bond is approximately 7.2×10^{-19} J ($431\,000 \div 6.02 \times 10^{23}$).

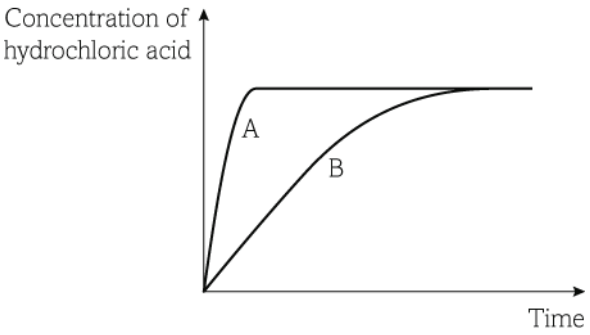
$1.0 \times 10^{-18} > 7.2 \times 10^{-19}$, so the atoms are likely to bond together, depending upon the activation energy required and the orientation of the collision.

9.1.2 Making a reaction go faster – Part 1

1 (a) The rate will increase. The molecules will be closer together, so there will be more successful collisions per second taking place.

(b) The rate will increase. There will now be more molecules in the same volume of gas, so there will be more successful collisions per second taking place.

2 (a) and (b)



Curve A represents the reaction with powdered marble.

Curve B represents the reaction with marble chips.

(c) The reaction with powdered marble will be faster than that with marble chips, since powdered marble has a larger surface area. So, the gradient of Curve A is always be greater at any given time while the reaction is taking place.

The curves level off at the same height since the same amount of marble has reacted in each case. (The acid was in excess in both reactions.)

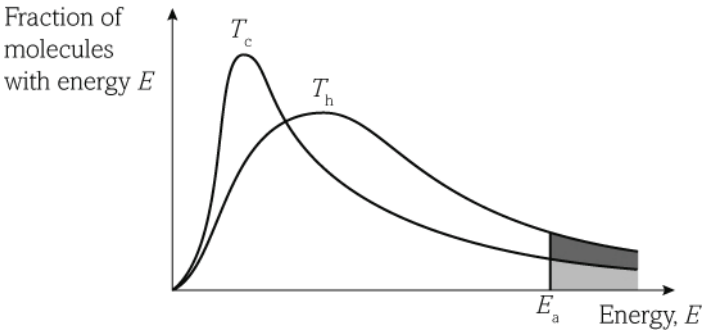
9.1.3 Making a reaction go faster – Part 2

1 (a) The rate will increase.

(b) The rate will increase.

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2 (a)

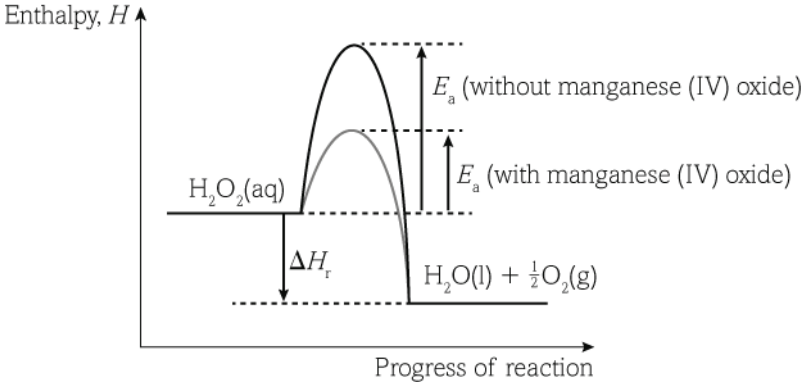


(b) The shaded areas to the right of the activation energy line represent the fraction of molecules that have $E \geq E_a$.

The fraction of molecules having $E \geq E_a$ at T_c (darker shaded area) is less than the fraction having $E \geq E_a$ at T_h (dark shaded area + light shaded area). There are less successful collisions per second at the lower temperature, so the rate of reaction will be lower.

9.1.4 Making a reaction go faster – Part 3

1 (a)



(b) When manganese(IV) oxide is added, the reaction takes place via a different route. This new route has a lower activation energy than the original route, so more molecules will have energy greater than or equal to the required activation energy for reaction. The rate of reaction increases since there will be more successful collisions per second taking place.

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9 Answers to Exam-style questions

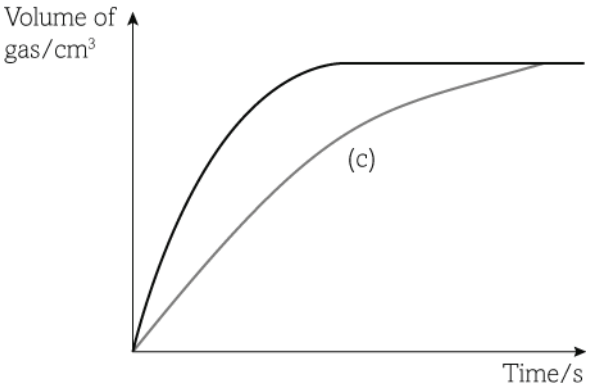
1 (a) $MgCO_3(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + CO_2(g) + H_2O(l)$

Correct equation (with no spectator ions) (1) state symbols (1).

(b) The rate of reaction decreases with time (1) and eventually becomes zero (1).

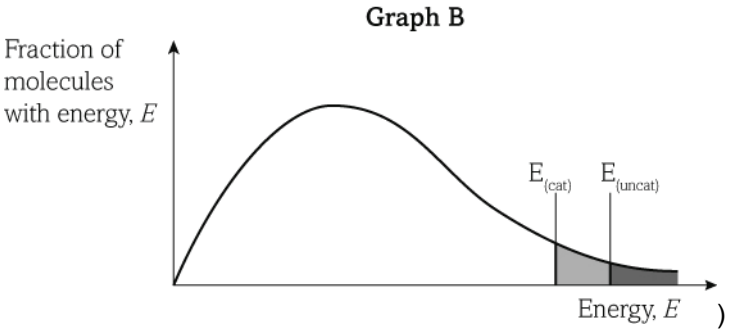
The concentration of the hydrogen ions decreases (1) and so the frequency of collisions between reacting particles decreases (1).

(c)



Slope of curve less than original (1) levels off after original curve (1).

2 (a)



)

$E_{(cat)} < E_{(uncat)}$ (1)

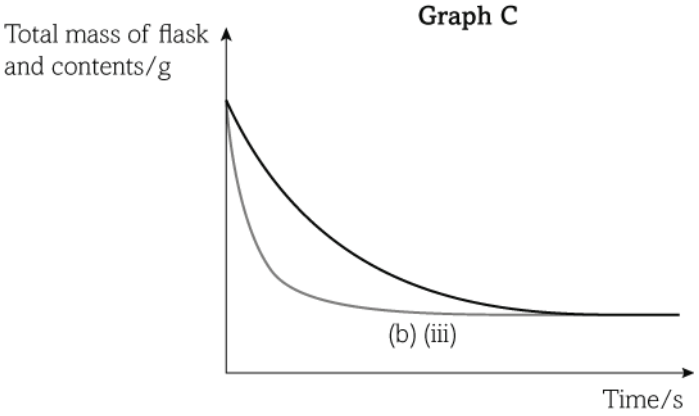
Fraction of molecules with $E \geq E_A$ is greater with catalyst (red shaded area + blue shaded area is greater than the blue shaded area) (1).

Number of successful collisions per second is greater with catalyst (1).

(b) (i) To prevent loss of acid spray (1).

(ii) Carbon dioxide gas is given off (1) and this escapes through the cotton wool (1).

(iii)



(1) slope of curve greater than original (1) curve levels off before original

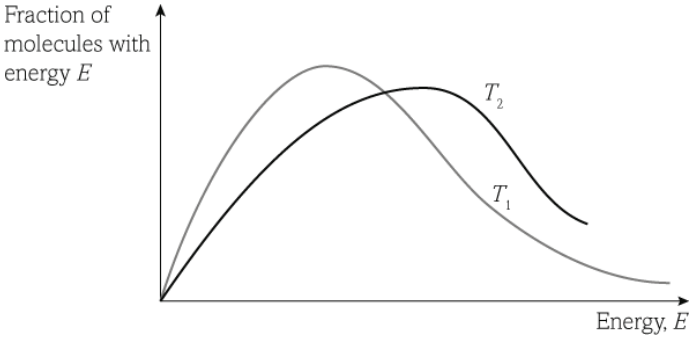
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3 (a) The statement is true, but is an oversimplification (1).

As the temperature is increased the mean kinetic energy of the particle increases as does there mean velocity (1). The particles will therefore collide more often, but the increases in collision rate does not explain the large increases in rate (1).

The fraction of molecules that energy greater than or equal to the activation energy for the reaction increase significantly (1). Therefore the number of successful collisions per second increases significantly (1).

(b)

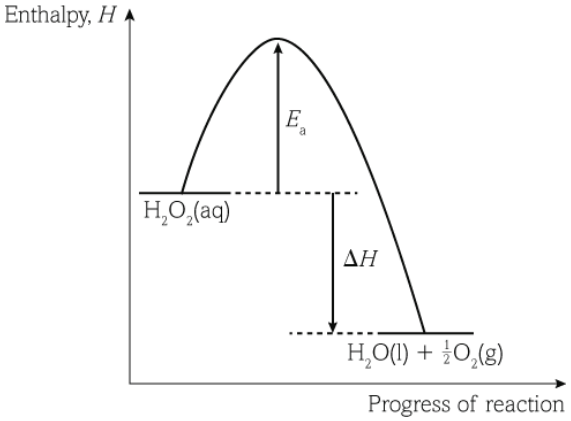


(i) Vertical axis labelled (1) Horizontal axis labelled (1).

(ii) Maximum of curve lower and to right of original (1).

Curve finishes above original (1).

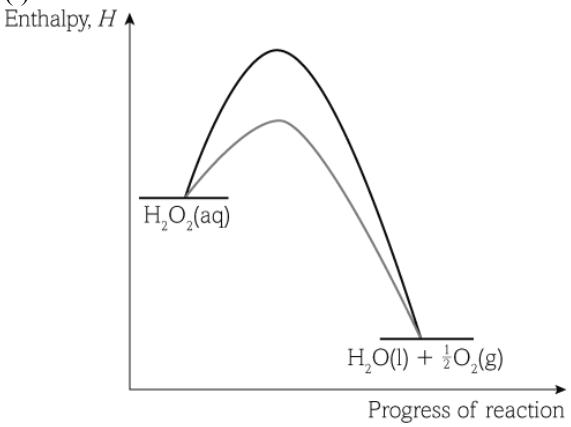
4 (a)



For E_a correctly labelled with arrow head upwards (1).

For ΔH correctly labelled with arrow head downwards (1).

(b) (i)



Curve starts and finishes at same enthalpy levels as original (1).

Maximum point on curve lower than original (1).

(ii) A catalyst provides an alternative pathway for the reaction (1) with a lower activation energy (1).

(c) Exothermic, since the enthalpy level of the products is lower than that of the reactants (1).

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5 (a) (i) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Correct equation (1) state symbols (1).

(ii) Only 44 cm^3 of hydrogen was evolved, so there was less zinc to react with the acid (1).

(b) Copper does act as a catalyst since the gas was produced more quickly (80 s with copper present as opposed to 300 s without copper) (1).

However the copper added directly was not as effective as the copper precipitated by reaction (140 s for added copper as opposed to 80 s with precipitated copper) (1)

The precipitated copper was probably more finely divided and therefore had a larger surface area (1).

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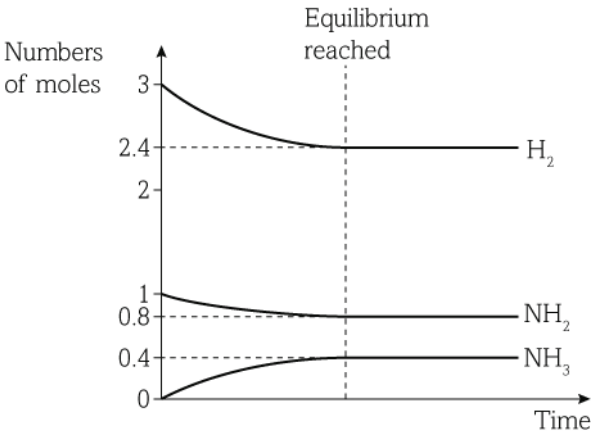
10.1 Reversible reactions and dynamic equilibrium

10.1.1 Reversible reactions and dynamic equilibrium

1 *Dynamic* – both forwards and backwards reactions are occurring at the same time. That means that hydrogen and iodine are reacting to form hydrogen iodide and, at the same time, hydrogen iodide is decomposing into hydrogen and iodine.

Equilibrium – the rate of the forwards reaction is equal to the rate of the backwards reaction. In other words, the rate at which hydrogen and iodine are reacting to form hydrogen iodide is the same as the rate at which hydrogen iodide is decomposing into hydrogen and iodine.

2



10.1.2 The effect of changes in conditions on equilibrium composition

1 (a) No effect. The reaction is neither exothermic nor endothermic.

(b) The reaction is very slow at low temperatures.

2 ΔH for the forward reaction is negative. Increasing the temperature shifts the position of equilibrium in the endothermic direction. The backward reaction (removing the CO_2 from solution) is therefore the endothermic reaction, making the forward reaction exothermic.

3 The solid lead(II) chloride would disappear. Addition of concentrated hydrochloric acid increases the concentration of chloride ions. This will shift the position of equilibrium to the right.

4 (a) Unaltered. There is the same number of moles of gas on either side of the equation.

(b) To the right. There are fewer moles of gas of the right-hand side of the equation.

(c) To the left. There are fewer moles of gas on the left-hand side of the equation.

(d) To the left. There are fewer moles of gas on the left-hand side of the equation. However, the percentage difference is very small, so the effect will be minimal.

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10.2 Equilibrium position

10.2.1 The equilibrium constant

1 (a) $\frac{[CH_3OOCH_2CH_3(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3CH_2OH(l)]}$

(b) $\frac{[NO(g)]^2}{[N_2(g)][O_2(g)]}$

(c) $\frac{[N_2(g)]^2[O_2(g)]}{[N_2O(g)]^2}$

(d) $[NH_3(g)][H_2S(g)]$

(e) $\frac{[H_2(g)]}{[H_2O(g)]}$

2 (a) $200 = \frac{[N_2O_4(g)]}{[NO_2(g)]}$

(b) $[NO_2(g)] = \frac{(0.002)^2}{200} = 3.16 \times 10^{-3}$ mol dm^{-3}

(c) (i) $\frac{1}{200} = 5 \times 10^{-3}$

(ii) $200^{½} = 14.14$

3 $K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

If the concentration of HI(g) is increased, then the magnitude of the ratio $\frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$ increases. To return this to the magnitude of K_c, the equilibrium will shift to the left in order to decrease the magnitude of the numerator and increase the magnitude of the denominator.

10.2.2 Reversible reactions in industry

1 (a) $2NH_3(g) + 2½O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$

(b) Low temperature, because the forward reaction is exothermic. Low pressure, because there are more moles of gas on the right-hand side.

(c) High temperature is used to increase the rate of reaction. Moderately high pressure may lead to an increase in rate of reaction, but the main advantage is that it reduces the size of the equipment and pipes required, thus reducing the initial capital costs.

2 High temperature, because the forward reaction is endothermic.

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10 Answers to Exam-style questions

1 (a) The rate of the forward reaction is the same as the rate of the backwards reaction (1).

The concentrations of the reactants and products remain constant over a period of time (1).

(b) As hydroxide ions are added they react with the hydrogen ions [$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$] (1).

As a result the hydrogen ion concentration decreases (1).

The equilibrium shifts to the right to produce more $CrO_4^{2-}(aq)$ ions (which are yellow) (1).

2 (a) The forward reaction is endothermic (1), so when the temperature is lowered the equilibrium shifts to the left, in the exothermic direction (1).

The concentration of iodine increases, so the colour of the mixture darkens (1).

(b) (i) More hydrogen was added (1)

(ii) The concentration of hydrogen and iodine both decrease (1), and the concentration of hydrogen iodide increases (1), until a new equilibrium is established (1).

3 (a) As the temperature increases the percentage conversion of Y_2 decreases, so the equilibrium is shifting to the left (1). The backwards reaction is therefore endothermic, making the forward reaction exothermic (1).

(b) (i) The rate will increase (1) since a new pathway of lower activation is created (1).

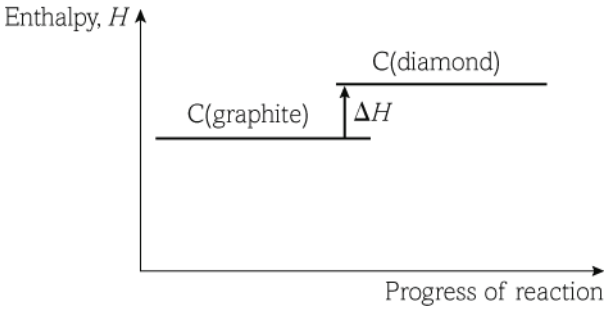
(ii) There will be no effect on the percentage conversion of Y_2 (1) since the rate of both the forward and the backward reaction are increased to the same extent (1).

4 (a) (i) The yield of methanol will decrease (1) as the equilibrium shifts to the left since the backwards reaction is endothermic (1).

(ii) The yield of methanol will increase (1) as the equilibrium shifts to the right since there are fewer moles of gas on the right hand side of the equation (1).

(b) The molecules will be closer together and so will collide more often (1). This will increase the rate of reaction (1).

5 (a)



Enthalpy level of C(diamond) above that of C(graphite) (1).

ΔH labelled with arrow in correct direction (1).

(b) Graphite is the more stable since it has a lower enthalpy (1).

(c) Diamond, as it has the higher density (1).

(d) High temperature (1) as the conversion from graphite to diamond is endothermic (1).

High pressure (1) as (the same mass of) diamond has a smaller volume (1).

6 (a) 250 atm (1). [Accept any value between 200 and 300 atm.]

(b) (i) The extra energy required to produce higher pressures will increase the cost (1).

(ii) Lower yield of ammonia (1).

(c) The catalyst is ineffective at lower temperatures (1).

(d) They are mixed with fresh nitrogen and hydrogen and sent back into the reaction chamber (1).

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7 (a) The green solution would turn yellow (1). The equilibrium moves to the left as more hydrogen ions are added (1).

(b) The yellow solution turns green (1) then blue (1).

The hydroxide ions added remove hydrogen ions and shift the equilibrium to the right (1).

The green colour is owing to a mixture of HIn(aq) and In^-(aq) (1).

8 (a) High temperature (1) as the forward reaction is endothermic (1).

Low pressure (1) as there are more moles of gas on the right hand side (1).

(b) High temperature (1). There will be more successful collisions per second as more collisions have energy greater than or equal to the activation energy (1).

High pressure (1). The molecules will be closer together and so will collide more often (1).

(c) A high temperature is used to increase both the rate of reaction and the yield of product (1).

Higher temperatures are not used since the increased rate and yield would not offset the increased energy costs (1).

A (moderately) high pressure is used to increases the rate of reaction, but higher pressures are not used since this would decrease the yield of product (1).

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