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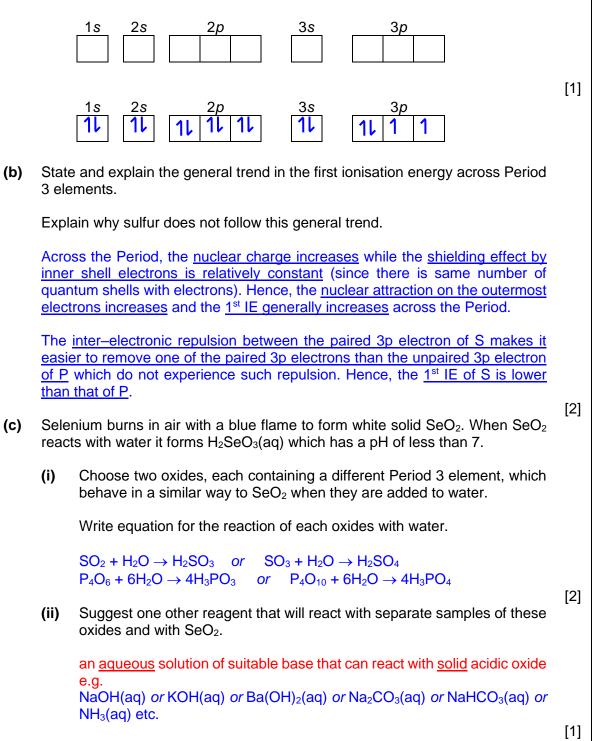
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[Turn over

Section A

Answer **all** the questions in this section, in the spaces provided.

- 1 The oxygen family is also called the chalcogens. It consists of the elements found in Group 16 of the periodic table, oxygen, sulfur, selenium, tellurium and polonium. Chalcogen can be found in nature in both free and combined states.
 - (a) Complete the diagram to show the arrangement of electrons in the orbitals of a sulfur atom.



[Total: 6]

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- 2 Nitrogen and phosphorus are elements of Group 15 in the Periodic Table.
 - (a) Nitrogen exists naturally as gaseous diatomic N≡N molecules whereas phosphorus is a solid and exists as P₄ molecules comprising of P-P single bonds.

Account for the difference in their physical states in terms of structure and bonding.

Both N₂ and P₄ have <u>simple molecular structures/ simple covalent molecules</u>. As P₄ has <u>larger number of electrons/ bigger electron cloud to be polarised</u>, <u>more energy</u> is required to overcome the <u>stronger instantaneous dipole-induced dipole interactions/attractions between</u> the <u>P₄ molecules than id-id between N₂.</u>

This results in higher melting point in P₄, hence P₄ exists as solid.

- (b) Nitrogen exhibits a range of oxidation numbers in its compounds.
 - (i) Complete the table below which refers to the various oxidation numbers of nitrogen in its compounds.

Compound	Oxidation Number of Nitrogen
NO ₂	
NO ₃ -	
N ₂ O	
NH₂OH	

Table 2.1

CompoundOxidation Number of NitrogenNO2+4NO3⁻+5N2O+1NH2OH-1

Hydroxylamine, NH₂OH is oxidised by $Fe^{3+}(aq)$, which is itself reduced to $Fe^{2+}(aq)$. In an experiment, 0.0825 g of NH₂OH required 20.00 cm³ of 0.250 mol dm⁻³ Fe³⁺ for complete reaction.

(ii) How many moles of Fe^{3+} react with one mole of NH_2OH ?

Amount of NH₂OH reacted = $0.0825/33 = 2.50 \times 10^{-3}$ mol

Amount of $Fe^{3+} = 20.00 \times 10^{-3} \times 0.250 = 5.00 \times 10^{-3} \text{ mol}$

Amount of Fe^{3+} reacted with one mole of NH₂OH = (5.00 x 10⁻³) / (2.50 x 10⁻³) = 2 mol [1]

(iii) What change in oxidation number does the nitrogen in NH₂OH undergo during the reaction with Fe³⁺?

Explain your answer.

[2]

[2]

[2]

1 Fe³⁺ \equiv 1e⁻ Amount of e⁻ gained by 2 mol of Fe³⁺ = 2 mol

<u>2 mol of e⁻</u> is lost by 1 mol of NH₂OH. Thus, <u>change in oxidation</u> number in N is +2/ from -1 to +1.

(iv) Which formula from Table 2.1 corresponds to the nitrogen-containing product of this reaction?

N₂O

(v) Construct the half equations and hence the overall balanced equation for the reaction of NH_2OH with Fe^{3+} (in acidic solution).

 $\begin{array}{ll} [R]: & Fe^{3+} + e^- \to Fe^{2+} \\ [O]: & 2NH_2OH \to N_2O + H_2O + 4H^+ + 4e^- \end{array} \end{array}$

 $2NH_2OH + 4Fe^{3+} \rightarrow N_2O + 4Fe^{2+} + H_2O + 4H^+$

[2]

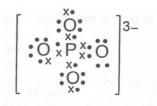
[1]

[1]

(c) Nitrate, NO_3^- , and phosphate, PO_4^{3-} , are oxoanions of nitrogen and phosphorus respectively.

Phosphoric acid, H_3PO_4 , is used in the production of Coca-Cola and other soft drinks. It serves as an acidulant, providing a tangy flavor and acting as a preservative to maintain the drink's freshness and shelf life.

Draw a dot-and-cross diagram to show the bonding PO_4^{3-} .



[1]

[1]

(d) Phosphoryl chloride is a colourless liquid with the formula $POCl_3$.

Table 2.2 shows the electronegativity values of the atoms in POCl₃.

atom	electronegativity / pauling units
phosphorus	2.2
chlorine	3.0
oxygen	3.5



(i) Explain the term *electronegativity*.

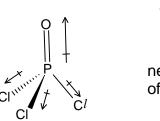
Electronegativity is a measure of the tendency / ability of an atom to <u>attract electrons</u> in a covalent <u>bond</u> towards itself.

Or Ability of an atom to pull the bonding pair of electrons towards itself.

(ii) Draw the shape of $POCl_3$.

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Indicate clearly the polarity of each bond it contains, and its overall net polarity.



net dipole moment of molecule

(iii) Predict all possible intermolecular forces which could exist between $POCl_3$ molecules.

Explain how these forces arise.

There are **instantaneous dipole-induced dipole attractions** (id-id) and **permanent dipole-permanent dipole attraction** (pd-pd) between $POCl_3$ molecules.

id-id attraction arises due to the <u>constant motion of electrons</u>, a <u>molecule develops an instantaneous dipole within itself when its</u> <u>electrons are distributed unevenly instantaneously</u>. This instantaneous dipole then <u>induces a temporary dipole on another</u> <u>molecule close to it</u>, giving rise to id-id

pd-pd attraction arises due to the <u>electrostatic attraction between</u> <u>polar molecules which have permanent dipoles</u> (or <u>has net dipole</u> <u>moment within each molecule</u>).

[3]

[2]

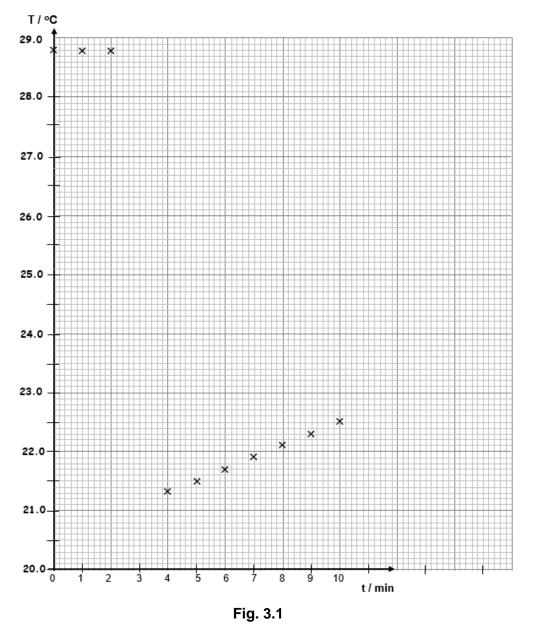
[Total: 17]

3 An experiment was conducted to determine the molar enthalpy change of a reaction, ΔH_1 .

reaction 1 NaHCO₃(s) + HC*l*(aq) \rightarrow NaC*l*(aq) + H₂O(*l*) + CO₂(g), ΔH_1

In this experiment, 5.00 g of sodium hydrogen carbonate was added 50.0 cm³ of hydrochloric acid in a polystyrene cup at time, $t_{r} = 3.0$ min. The temperature of hydrochloric acid was measured at regular time intervals, before and after sodium hydrogencarbonate is added.

A graph of temperature, *T*, against time, *t*, was obtained as shown in Fig **3.1**.



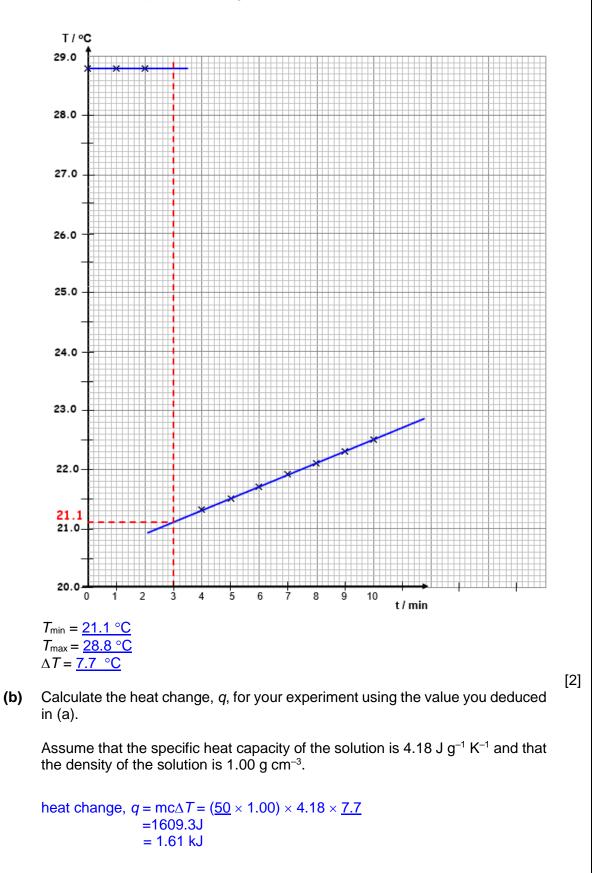
(a) Draw a best-fit straight line taking into account all of the points before = 3.0 min.

t

Draw another best-fit straight line taking into account all of the points after the temperature of the mixture has started to rise steadily.

Extrapolate (extend) both lines to t = 3.0 min.

Deduce the temperature change, ΔT , at t = 3.0 min.



(c) Determine the molar enthalpy change, ΔH_1 , for *reaction 1*. The hydrochloric acid is in excess.

reaction 1 NaHCO₃(s) + HCI(aq) \rightarrow NaCI(aq) + H₂O(I) + CO₂(g), ΔH_1

HC/(FA1) is added in excess. NaHCO3 is the limiting reagent.

Amount of NaHCO₃ added = $\frac{5.00}{84.0}$ = 0.05952 mol $\Delta H_1 = + \left(\frac{1.609}{0.05952}\right) \times 1 = +27.0 \text{ kJ mol}^{-1}$

(d) An energy cycle is shown is the diagram below.

$$2NaHCO_{3}(s) \xrightarrow{\Delta H_{3}} Na_{2}CO_{3}(s) + H_{2}O(l) + CO_{2}(g)$$

$$+ 2HCl(aq) \qquad 2\Delta H_{1} \qquad \Delta H_{2} + 2HCl(aq)$$

$$2NaCl(aq) + 2H_{2}O(l) + 2CO_{2}(g)$$

(i) Write an equation to show the relationship between ΔH_1 , ΔH_2 and ΔH_3 .

$$\Delta H_3 = 2\Delta H_1 - \Delta H_2 \tag{1}$$

(ii) Use your answers in (c) and (d)(i), calculate a value, in kJ mol⁻¹, for ΔH_3 .

Given that $\Delta H_2 = -31.6 \text{ kJ mol}^{-1}$

$$\Delta H_3 = 2(+27.0) - (-31.6)$$

= +85.7 kJ mol⁻¹ [1]

[Total: 6]

[1]

4 In the late 19th century, the two pioneers of the study of reaction kinetics, Vernon Harcourt and William Esson, studied the rate of the reaction between hydrogen peroxide and iodide ions in acidic solution.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$$

9

A student carried out a study on the kinetics of the above reaction. In Experiment 1, both $[H_2O_2]$ and $[H^+]$ were kept constant at 0.05 mol dm⁻³ and $[I^-]$ was plotted against time. The following curve in Fig. **4.1** was obtained.

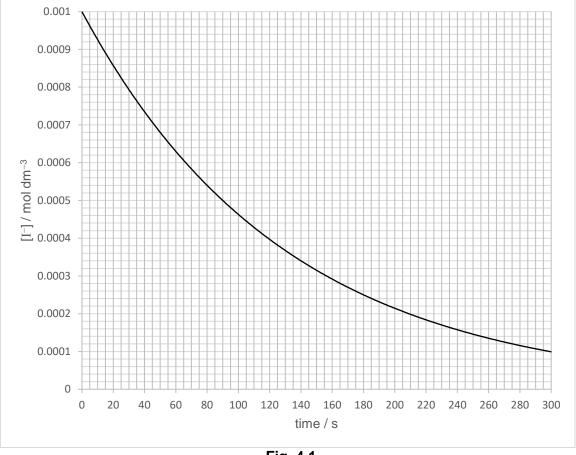
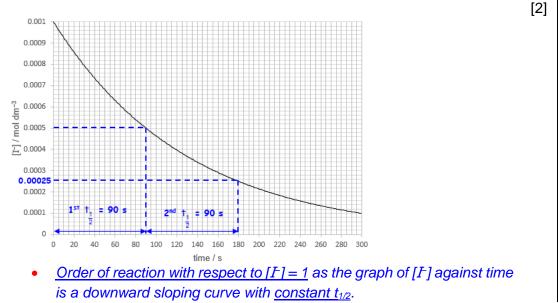


Fig. 4.1

(a) Use the graph to determine the order of reaction with respect to [I-]. Show all your workings, and draw relevant construction lines on the Fig. 4.1.



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(b) The study was repeated with the same initial $[I^-]$ but varying $[H_2O_2]$ and $[H^+]$.

Experiment no.	[H ₂ O ₂] / mol dm ⁻³	[H⁺] / mol dm ⁻³	relative rate
1	0.050	0.05	0.476
2	0.025	0.05	0.238
3	0.100	0.10	0.952

(i) Use the above data to deduce the orders with respect to $[H_2O_2]$ and $[H^+]$, explaining your reasoning.

Comparing experiment no. 1 & 2, keeping $[H^+]$ & $[I^-]$ constant. Halved $[H_2O_2]$ halved the relative rate. Order of reaction w.r.t $[H_2O_2]$ is first order.

Comparing experiment no. 1 & 3, keeping [I⁻] constant. Since order of reaction w.r.t $[H_2O_2]$ is first order, doubles $[H_2O_2]$, doubles the rate from 0.476 to 0.952. Double [H⁺] does not affects the rate. Order of reaction w.r.t [H⁺] is zero order.

[2]

[2]

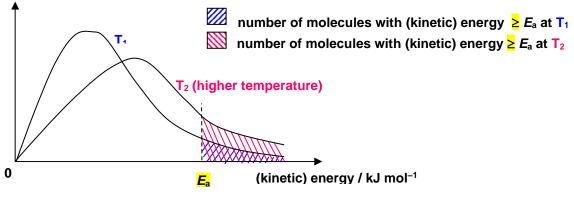
Or Substitution method

(ii) Write the rate equation and the units for rate constant for the reaction between hydrogen peroxide and iodide ions in acidic solution.

rate = $k[H_2O_2][I^-]$

unit for k: mol⁻¹ dm³ s⁻¹

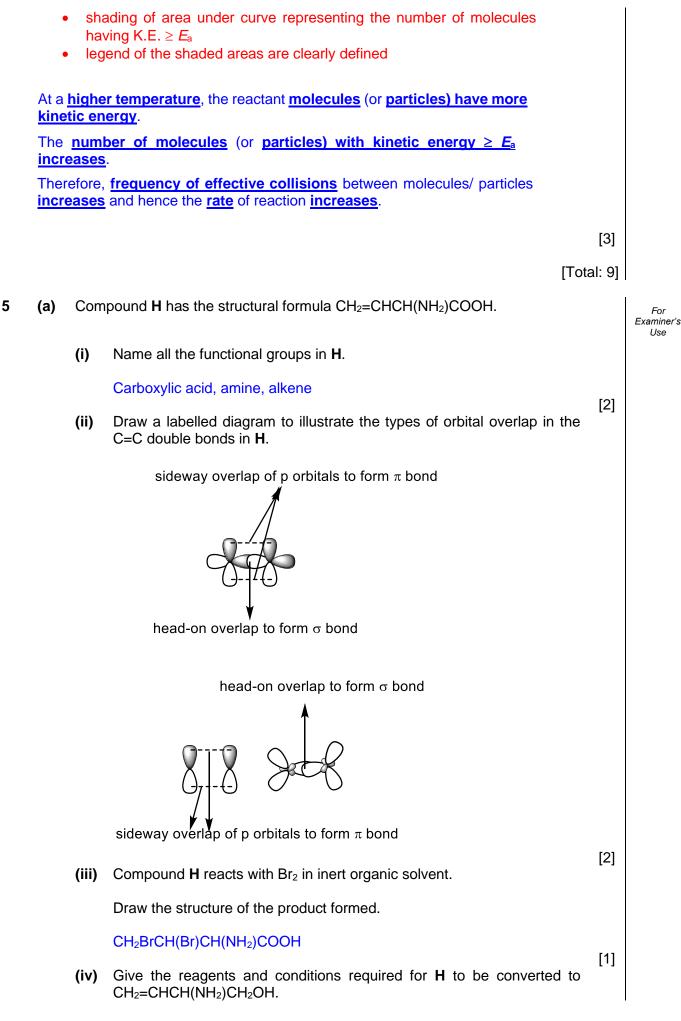
- (c) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect of temperature on the rate of reaction.
 - number of molecules



[1] for diagram

For correct diagram, the following must be shown:

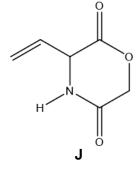
- axes are labelled with axes
- both curves start at origin and are of correct shape
- the peak of curve shifts right and is lower at higher temperature



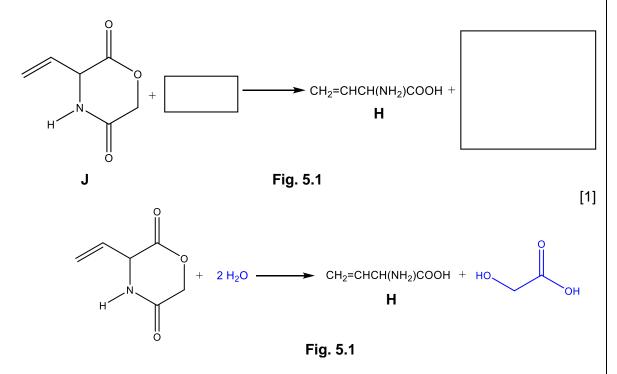
11

LiAlH₄, dry ether

(b) Compound H can be prepared from the reaction of J with an excess of hot aqueous acid.



(i) Complete Fig. 5.1 to show the equation for this reaction.



(ii) Name the type of reaction in (b)(i).

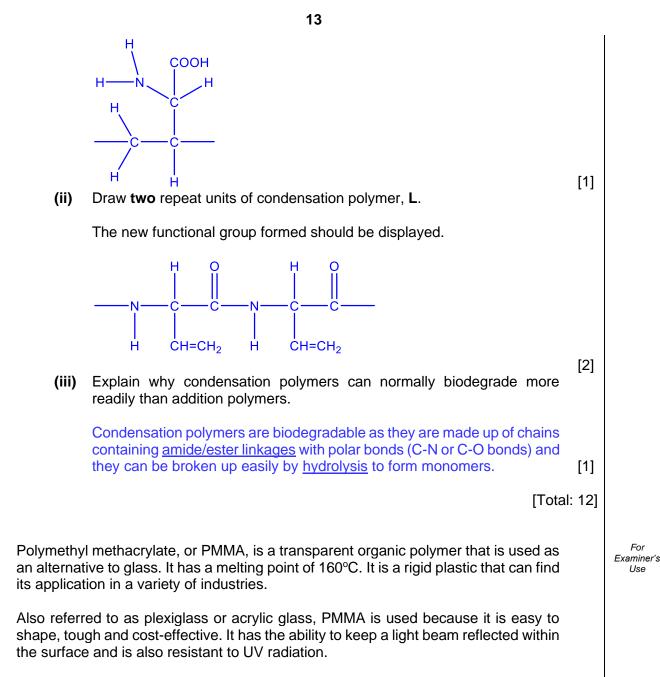
(Acid) hydrolysis

(c) Polymers consists of monomers joined together by undergoing either addition or condensation polymerisation.

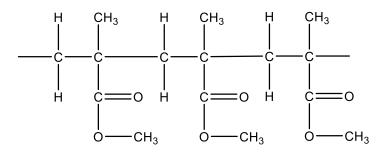
Compound **H** can react to form either an addition polymer, **K**, or a condensation polymer, **L**, depending on the conditions.

[1]

(i) Draw one repeat unit of addition polymer, K.

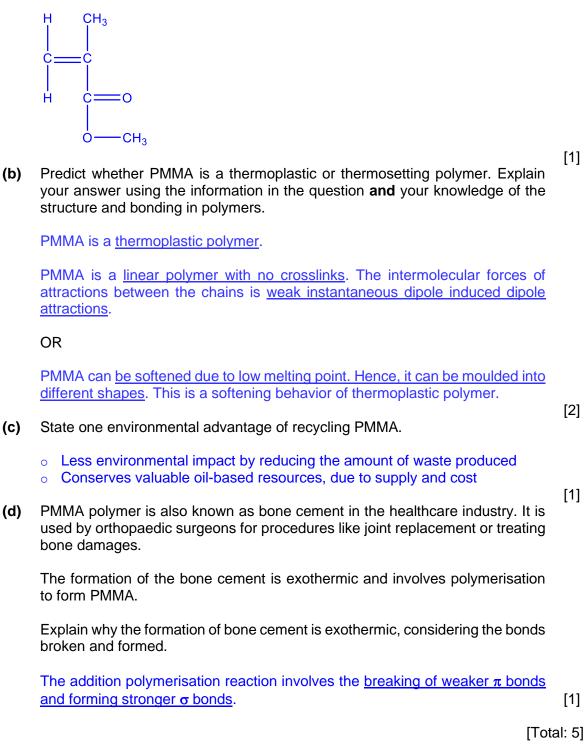


Part of the polymer chain of PMMA is shown below.



(a) Draw the monomer used to produce PMMA.

6



7 Carbon nanotubes offer a promising approach in cancer treatment through their unique physical properties. They have been shown to be effective tumor killers in those with kidney or breast cancer.

Mechanism of Action:

- 1. Injection of Multi-Walled Nanotubes (MWNTs): Multi-walled carbon nanotubes are introduced directly into the tumor.
- 2. Laser Treatment: A specialised laser that emits near-infrared radiation is used to target the tumor. The laser treatment typically lasts for about 30 seconds.
- 3. Vibration and Heat Generation: The carbon nanotubes vibrate in response to the near-infrared radiation, producing heat.
- 4. Tumor Cell Death: The generated heat raises the temperature of the tumor cells. Once the temperature reaches a certain threshold, the tumor cells begin to die, effectively shrinking the tumor.
- (a) Explain why carbon nanotubes are considered as nanomaterials rather than nanoparticles.

Carbon nanotubes have only <u>one dimension (its diameter) ranging</u> <u>from 1-100 nm.</u> (length of carbon nanotubes can go beyond the scale.) Nanoparticles, however, are substances that have <u>all dimensions</u> <u>within 1-100 nm.</u>

[2]

(b) Suggest one advantage of using carbon nanotubes in the treatment of cancer.

High Surface Area: Carbon nanotubes have a <u>large surface area to volume</u> <u>ratio</u>, allowing for the attachment of various molecules, including drugs and targeting agents.

Thermal Conductivity: They have excellent thermal conductivity, which is crucial for generating heat when exposed to certain types of radiation.

Thermal conductivity: Able to withstand high temperature without breaking down when heated to kill tumar cells.

Biocompatibility: With appropriate functionalisation, CNTs can be made biocompatible, reducing toxicity and improving safety in medical applications.

Accept other suggestions which are the properties of carbon nanotubes.

[1]

(c) Carbon nanotubes can be used as biosensors implanted in the human body due to its high electrical conductivity, high durability, low density and absence of toxic metals.

Explain why a carbon nanotube is a good conductor of electricity.

Carbon nanotube has high electrical conductivity as the <u>electron in the</u> unhybridised 2p orbital is <u>delocalised over</u> the hexagonal layer to act as mobile charge carrier.

(d) Suggest why a single carbon nanotube would have high tensile strength.

[1]

Each carbon atom forms <u>strong covalent bonds</u> with 3 adjacent C atoms via sigma bonds / head-on overlap. This forms a <u>network</u> of very strong covalent bonds between the carbon atoms, giving rise to very high tensile strength.

[1]

[Total: 5]

Section B

Answer **one** question from this section, in the spaces provided.

For 8 Use of Data Booklet is relevant to this question. (a) Examiner's Use Chlorine has two naturally occurring isotopes, ³⁵Cl and ³⁷Cl. (i) State the number of protons, neutrons and electrons in an atom of ${}^{37}Cl$. Number of protons = 17 Number of neutrons = 20 Number of electrons = 17[1] (ii) The first electron affinity is defined as the amount of energy released when one mole of gaseous atoms gains one mole electrons to form one mole of singly charged gaseous anions. $Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta H = -349 \text{ kJ mol}^{-1}$ Calculate the amount of energy released when one chlorine atom gained one electron to form chloride ion, Cl^{-} . Energy released = $349/(6.02 \times 10^{23})$ $= 5.80 \times 10^{-22} \text{ kJ}$ [1] (iii) State and explain the difference in size between the radius of the chloride ion, Cl^{-} and the radius of a chlorine atom. Cl^{-} has a bigger radius than Cl atom. $Cl: 1s^2 2s^2 2p^6 3s^2 3p^5$ Cl⁻: 1s² 2s² 2p⁶ 3s² 3p⁶ Both Cl and Cl⁻ have the same nuclear charge and same number of principal quantum shells of electrons. Compared to Cl atom, Cl^{-} ion has one more electrons in its valence shell. Due to greater inter-electronic repulsion, the electron cloud of Cl⁻ expands to give a larger Cl^{-} ion. [2] (b) The gas-phase reaction of carbon monoxide with hydrogen forming methanol is an example of an equilibrium. The value of equilibrium constant, K_{c} , is 0.0311 at 500 K. $2H_2(g) + CO(g) \Rightarrow CH_3OH(g)$ (i) Write the expression for K_c for this reaction and give its units. $K_c = \frac{[CH_3OH]}{[H_2]^2[CO]}$ units: mol⁻² dm⁶ [2] (ii) Calculate the equilibrium concentration of methanol when the equilibrium concentrations of hydrogen and carbon monoxide are 0.151 mol dm⁻³ and 0.0850 mol dm⁻³ respectively.

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• Deduce whether **X** or **Y** is at a higher pressure.

Explain your answer using references to the graph and to the equilibrium position.

Increase in pressure favours the side with lesser amount of **gas**. This means that the <u>forward reaction is favoured / equilibrium position shifts</u> to the right. which increases the % yield. Hence, higher pressure, **X** give a higher % yield.

(c) An equation involving formation of methanol is shown below.

 $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{\Delta H_1} CH_3OH(l)$

(i) The following enthalpy change of combustion can be used to calculate ΔH_1 .

ΔH_{c} methanol	= −726 kJ mol ⁻¹
$\Delta H_{\rm c}$ carbon	= -393 kJ mol ⁻¹
$\Delta H_{\rm c}$ hydrogen	= −286 kJ mol ⁻¹

Define the term standard enthalpy change of combustion.

Standard enthalpy change of combustion is the <u>heat evolved when 1</u> <u>mole of a substance is completely burnt in excess oxygen under the</u> standard conditions <u>of 298 K and 1 bar</u>.

[1]

[2]

- 19 (ii) Use the data given (c)(i) to calculate ΔH_1 . $\Delta H_1 = \Sigma m \Delta H_c$ (reactants) – $\Sigma n \Delta H_c$ (products) = -393 + 2(-286) - (-726)= -239 kJ mol⁻¹ [2] Write an equation to represent the standard enthalpy change of (iii) combustion of methanol. $CH_3OH(l) + 3/2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ Must include state symbols [1] (iv) Use the bond energies given in the Data Booklet to calculate a value for the enthalpy change of combustion of methanol. $\Delta H_c = \sum x E(reactants) - \sum y E(products)$ = [3E(C-H) + E(C-O) + E(O-H) + 2E(O=O)] - [2E(C=O) + 4E(O-H)] $= [(3x410) + 360 + 460 + (3/2 \times 496)] - [(2x805) + (4x460)]$ $= -656 \text{ kJ mol}^{-1}$ [2] (v) The value given for the standard enthalpy change of combustion of methanol in (c)(i) is different from the value calculated in (c)(iv). One reason is the bond energy values are only average values. State another reason why value given for the standard enthalpy change of combustion of methanol in (c)(i) is different from the value calculated in **(c)(iv)**. Methanol and/or H₂O is a liquid under standard conditions. The enthalpy of vapourisation of methanol and/or H₂O is not taken into consideration. [1] (vi) When 3.00 g of methanol was burned, it was found that 250 g of water was heated from 25 °C to 76 °C. Calculate the percentage efficiency of heat transfer for this experiment using relevant data from (c)(i). Assume that the specific heat capacity of the solution is 4.18 J g⁻¹ K⁻¹ and that the density of the solution is 1.00 g cm^{-3} . Heat released by burning methanol $= [3.0 / (12.0 + 1.0 \times 4 + 16.0)] \times 726$ = 68.063 kJ = 68063 J Heat absorbed by the water $= m c \Delta T$ $= 250 \times 4.18 \times (76 - 25)$ = 53295 J Percentage efficiency of heat transfer = 53295/68063 x 100% = 78.3%[2] [Total: 20]
- 9 (a) Calcium carbonate is a dietary supplement used when the amount of calcium taken in the diet is not enough.

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To meet the recommended dietary allowance of calcium, an adult would need to consume between 2.5 to 3.0 grams of calcium carbonate.

A chemist dissolve a sample of calcium carbonate tablets in 50.0 cm³ of 1.20 mol dm⁻³ hydrochloric acid, in excess. After all the bubbles were driven off, the solution was diluted with water and make up to 250 cm³ to solution.

25.0 cm³ of the resultant solution was titrated with 23.50 cm³ of 0.0200 mol dm⁻³ of sodium hydroxide for complete reaction.

(i) Write the equation for the reaction between calcium carbonate and hydrochloric acid.

 $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

(ii) Calculate the amount of hydrochloric acid remaining in 250 cm³ of resultant solution.

Amount of NaOH = Amount of HCl in 25.0cm³ = $23.50/1000 \times 0.02 = 4.70 \times 10^{-4}$

Amount of HCl in 250 cm³ = 10 x 4.70 x 10⁻⁴ = 4.70 x 10⁻³

(ii) Calculate the amount of hydrochloric acid which reacted with calcium carbonate in 250 cm³ of solution.

Initial amount of HCI = $0.050 \times 1.2 = 0.060 \text{ mol}$ Amount of HCI reacted with CaCO₃ = $0.0600 - 4.70 \times 10^{-3}$ = $5.53 \times 10^{-2} \text{ mol}$

[1]

[2]

[1]

(iii) Calculate the mass of calcium carbonate in the sample. Hence, determine if the sample of calcium carbonate tablets meets the typical recommended dietary allowance.

Amount of $CaCO_3 = (5.53 \times 10^{-2}) / 2 = 0.02765 = 0.0277 \text{ mol}$

Mass of $CaCO_3 = 0.02765 \times 100.1 = 2.77 \text{ g}$ Since mass of $CaCO_3$ calculated is between 2.5 to 3.0 g, it <u>meets</u> the dietaty allowance.

[2]

[1]

- (b) Bicarbonate, HCO₃, has a wide range of uses across various industries due to its chemical properties. One of which is the food industry which sodium bicarbonate is used as a buffering agent found in food additive.
 - (i) Define what is meant by the terms *acid* and *base* using the Brønsted-Lowry theory of acids and bases.

Brønsted–Lowry acid is a species that <u>donates a proton</u> Brønsted–Lowry base is a species that <u>accepts a proton</u>

(ii) A solution of 0.100 mol dm⁻³ of a weak base, HCO₃⁻ at 25°C was found to have pH of 9.68.

Calculate the concentration of OH⁻ in the solution.

		pOH = 14 - 9.68 = 4.32 [OH ⁻] = 10 ^{-4.32} = 4.786 x 10 ⁻⁵ mol dm ⁻³	
	(iii)	Write equation to represent the ionisation of HCO_3^- in water.	[1]
		$HCO_3^- + H_2O \Rightarrow H_2CO_3 + OH^-$	
	(iv)	Write an expression for the base dissociation constant, $K_{\rm b}$, of HCO ₃ ⁻	[1]
		$K_{\rm b} = \frac{[{\rm H}_2{\rm CO}_3][{\rm OH}^-]}{[{\rm HCO}_3^-]} \mod {\rm dm}^{-3}$	[1]
	(iv)	Calculate the K_b value of HCO ₃ ⁻ .	
		$K_{\rm b} = (10^{-4.32})^2 / 0.100 = 2.29 \times 10^{-8}$	
	(v)	Write two separate equations to show how bicarbonate, HCO ₃ ⁻ , can act as a buffering agent when small amount of acid and base are added to it.	[1]
		$HCO_3^- + H^+ \rightarrow H_2CO_3$	
		$HCO_{3}^{-} + OH^{-} \rightarrow CO_{3}^{2-} + H_{2}O$	[0]
(c)	(i)	State the formulae of the chlorides of the elements Na to P where the element is in its highest oxidation states. Explain your reason of choice.	[2]
		PCl_{5} P has <u>5 electrons in its valence</u> shell hance can from a <u>+5</u> oxidation number.	[2]
	(ii)	Magnesium and phosphorus react with chlorine to form magnesium chloride and phosphorus(V) chloride respectively.	[2]
		Write equation to show what happens when solid samples of each of these chlorides are added separately to water.	
		In each case, state the likely pH of the resultant solution.	
		MgC l_2 dissolves readily to give $[Mg(H_2O)_6]^{2+}$ which hydrolyses slightly in water, due to slightly higher charge density of Mg ²⁺ , to form a slightly acidic solution of <u>pH 6.5</u> .	
		Hydration : $\underline{MgCl_2(s) + 6H_2O(l)} \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^{-}(aq)$ Hydrolysis : $\underline{[Mg(H_2O)_6]^{2+}(aq)} \iff \underline{[Mg(H_2O)_5OH]^{+}(aq) + H^{+}(aq)}$ No need state symbols. use " \iff " for the hydrolysis equation	
		PCl_5 hydrolyses completely in water to form an acidic solution of pH 1-2 $PCl_5(s) + 4 H_2O(l) \rightarrow H_3PO_4(aq) + 5 HCl (aq)$	
	(iii)	Both magnesium chloride and magnesium oxide exist as white solids with a melting point of 714°C and 2850°C respectively. Explain the differences between the two melting points in terms of their structure and bonding.	[3]

[Turn over

Both exist as <u>giant ionic lattice</u> with strong <u>ionic bonds between oppositely</u> <u>charged ions</u>.

$$| \text{ lattice energy } | \propto | \frac{q_+ \times q_-}{r_+ + r_-} |$$

Both has the same cationic charge and radius. O^{2-} has a higher charge and smaller ionic radius than $C/^{-}$. The magnitude of lattice energy of MgO is greater than MgCl, thus stronger ionic bonds which results in higher melting point.

[Total: 20]

[2]

Additional answer space

If you use the following pages to complete the answer by any question, the question number must be clearly shown.

.....

