



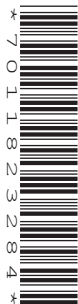
Oxford Cambridge and RSA

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Tuesday 12 June 2018 – Afternoon

Time allowed: 2 hours 15 minutes



You must have:

- the Insert (inserted)
- the Data Sheet for Chemistry B (Salters) (sent with general stationery)

You may use:

- a scientific or graphical calculator



First name										
Last name	StemUp Model Solution									
Centre number						Candidate number				

INSTRUCTIONS

- The Insert will be found inside this document.
- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above with your name, centre number and candidate number.
- Answer **all** the questions.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- Do **not** write in the barcodes.

INFORMATION

- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of **20** pages.

Answer **all** the questions.

- 1 'Morton's salt'™ contains a mixture of sodium chloride with magnesium carbonate. It is advertised using the slogan 'When it rains it pours' indicating that the table salt is free-flowing in humid weather.

Magnesium carbonate is hygroscopic (absorbs water) and forms hydrated salts, eg $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, but does not dissolve. This stops the sodium chloride absorbing water.

- (a) (i) Some data for the dissolving of NaCl is given below.

Enthalpy change	Value / kJ mol^{-1}
$\Delta_{\text{LE}}H \text{ NaCl}$	-780
$\Delta_{\text{hyd}}H \text{ Na}^+$	-402
$\Delta_{\text{hyd}}H \text{ Cl}^-$	-374

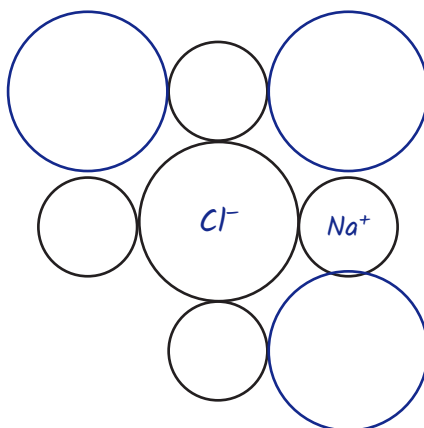
Calculate a value for the enthalpy change of solution of NaCl .

$$\begin{aligned} \Delta H_{\text{sol}} &= -\Delta_{\text{LE}}H + \Delta_{\text{hyd}}H(\text{Na}^+) + \Delta_{\text{hyd}}H(\text{Cl}^-) \\ &= +780 + (-402) + (-374) = +4 \text{ kJ mol}^{-1} \end{aligned}$$

enthalpy change of solution of NaCl = ... $+4 \text{ kJ mol}^{-1}$ [1]

- (ii) The diagram below shows the pattern of ions in **one face** of a NaCl lattice. Extend the diagram to show the repeating pattern by adding **three** more suitable ions.

Label one Na^+ ion and one Cl^- on the diagram.



[2]

- (b) Some students heat a sample of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ to try to make MgCO_3 .

Calculate the percentage loss in mass they will obtain if they succeed.

$$M_r \text{ MgCO}_3 \cdot 3\text{H}_2\text{O} = 24.3 + 12.0 + 3(16.0) + 3(18.0) = 138.3$$

$$\text{mass lost} = 3\text{H}_2\text{O} = 54.0$$

$$\% \text{ loss} = 54.0 / 138.3 \times 100 = 39.0 \%$$

$$\text{percentage loss in mass} = \dots\dots\dots 39 \dots\dots\dots \% \quad [2]$$

- (c) The students continue to heat the MgCO_3 formed and realise that the compound is decomposing, giving off CO_2 gas.

The students want to obtain $200 \text{ cm}^3 \text{ CO}_2$ at 290 K and 99 kPa.

What mass of MgCO_3 should they heat?

$$\begin{aligned} n(\text{CO}_2) &= pV / RT = (99 \times 10^3 \times 200 \times 10^{-6}) / (8.314 \times 290) \\ &= 8.21 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \quad \text{so } n(\text{MgCO}_3) = 8.21 \times 10^{-3} \text{ mol}$$

$$\text{mass} = 8.21 \times 10^{-3} \times 84.3 = 0.692 \text{ g}$$

$$\text{mass of MgCO}_3 = \dots\dots\dots 0.69 \dots\dots\dots \text{ g} \quad [3]$$

- (d) Magnesium has a higher first ionisation enthalpy than calcium.

- (i) Write an equation for the reaction for the first ionisation enthalpy of magnesium.

Include state symbols.



[1]

- (ii) Explain why magnesium has a higher first ionisation enthalpy than calcium.

The outer electron in Mg is nearer the nucleus with less shielding (fewer shells, smaller atomic radius), so the nucleus attracts the outer electron more strongly and more energy is needed to remove it. [2]

- (e) Some students are given a mixture of magnesium carbonate with another Group 2 carbonate. They dissolve the mixture in an acid. They test the solution of salts formed as shown in the table below.

Test	Result
Flame test	Green flame
Add dilute nitric acid followed by silver nitrate solution	White precipitate

- (i) Name the acid that the students used to dissolve the mixture of carbonates.

..hydrochloric acid..(HCl)..... [1]

- (ii) Name the other Group 2 carbonate that was mixed with the magnesium carbonate.

..barium carbonate..(BaCO₃)..... [1]

- 2 Propene gas, C_3H_6 , is obtained industrially from a variety of sources. Propene is mainly used as a starting material for making polymers.

(a) The mass spectrum of propene has several peaks including those at m/z 27 and 43.

- (i) Give the species responsible for these peaks

27 ... $C_2H_3^+$

43 ... $(^{13}C^{12}C_2H_6)^+$

[2]

- (ii) Propene has an isomer, cyclopropane.

Explain why high-resolution mass spectrometry would **not** distinguish between propene and cyclopropane.

Both have the same molecular formula, C_3H_6 , so they contain the same type and number of atoms.

The sum of the accurate atomic masses is the same, so both have exactly the same M_r (42.047) and give a molecular ion at the same m/z .

[2]

- (iii) Suggest, with reasons, **two** spectroscopic methods (apart from mass spectroscopy) that would distinguish between cyclopropane and propene.

Method 1 ...infrared spectroscopy.....

Reason: propene has a $C=C$ bond, so it absorbs at 1620 to 1680 cm^{-1} , and an alkene $C-H$ absorption at 3000 to 3100 cm^{-1} ; cyclopropane has neither absorption.

Method 2 ... ^{13}C NMR spectroscopy.....

Reason: propene has 3 carbon environments so gives 3 peaks, two of them at 110 to 160 ppm ($C=C$); all 3 carbons in cyclopropane are equivalent so it gives only 1 peak.

[4]

- (b) (i) How many σ and π bonds are there in a propene molecule?

Number of σ bonds 8..... Number of π bonds 1..... [1]

- (ii) Propene has a $H-C-H$ bond where the C atom forms a double bond.

What is the bond angle of this $H-C-H$ bond?

120° [1]

(c) Propene, C_3H_6 , can be made by cracking longer-chain hydrocarbons.

- (i) Write the equation for the cracking of nonane to give two molecules of propene and one other molecule.



[1]

- (ii) What mass of propene (in kg) would be obtained from 15 kg of nonane in the reaction in (i) if the percentage yield was 85%?

$$M_r C_9H_{20} = 128.0; \quad n(\text{nonane}) = 15\,000 / 128.0 = 117 \text{ mol}$$

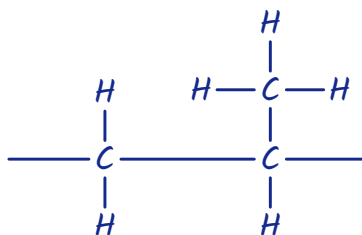
$$n(\text{propene}) = 2 \times 117 \times 0.85 = 199 \text{ mol}$$

$$\text{mass} = 199 \times 42.0 / 1000 = 8.4 \text{ kg}$$

$$\text{mass of propene} = \dots 8.4 \dots \text{ kg} \quad [2]$$

(d) Most of the propene that is manufactured is used to make the polymer poly(propene).

Draw the **full** structural formula of the repeating unit of poly(propene).



[1]

(e) Cyclohexene is another industrially important alkene.

- (i) Explain how the enthalpy change of hydrogenation of cyclohexene is used to give evidence for the bonding in the benzene molecule.

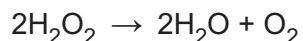
ΔH hydrogenation of cyclohexene (one C=C) is -120 kJ mol⁻¹, so benzene with three C=C bonds would give 3 × (-120) = -360 kJ mol⁻¹. The actual value for benzene is about -208 kJ mol⁻¹, much less exothermic than 3 × that of cyclohexene. So benzene does not have three C=C bonds alternating with C-C single bonds; it is more stable (by about 150 kJ mol⁻¹) as its π electrons are delocalised. [3]

- (ii)* Cyclohexene and benzene both react with bromine but in different ways.

Compare the two reactions and explain why they are different.

Cyclohexene reacts rapidly with bromine at room temperature, decolourising the orange bromine. This is electrophilic addition, $C_6H_{10} + Br_2 \rightarrow C_6H_{10}Br_2$, giving 1,2-dibromocyclohexane. The $C=C$ bond is a localised π bond with a high electron density, which polarises Br_2 and attacks the $Br^{\delta+}$ atom; a carbocation forms, then Br^- adds; both Br atoms add across the $C=C$. Benzene does not decolourise bromine at room temperature. It only reacts when heated under reflux with a halogen carrier catalyst such as Fe or $FeBr_3$. This is electrophilic substitution, $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$, giving bromobenzene and hydrogen bromide. They differ because benzene's π electrons are delocalised over the whole ring, so its electron density between two C atoms is lower than in the $C=C$ and cannot polarise Br_2 ; the halogen carrier makes a stronger electrophile, Br^+ . Benzene undergoes substitution, not addition, because substitution keeps the stable delocalised ring, whereas addition would destroy the delocalisation. [6]

- 3 Why does human hair turn grey? Studies have shown that this is caused by lower levels of the enzyme catalase in hair follicles. Catalase catalyses the breakdown of hydrogen peroxide as shown in **equation 3.1**.



Equation 3.1

When levels of hydrogen peroxide increase, the melanin (dye) in the hair is bleached.

- (a) Catalase has an active site.

Explain how this results in faster decomposition of hydrogen peroxide.

*The active site has a shape complementary to the H_2O_2 molecule, so H_2O_2 fits
and binds to the active site, forming an enzyme-substrate complex.
Bonds in H_2O_2 are then broken more easily; the reaction has an alternative
route with a lower activation enthalpy, E_a , so more molecules can react.* [3]

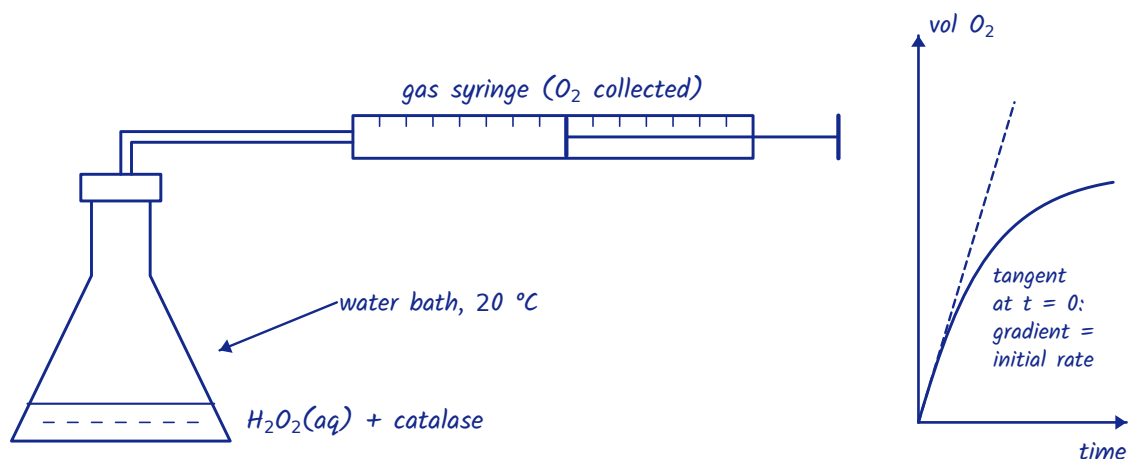
- (b) Suggest the **type** of reaction by which hydrogen peroxide bleaches melanin.

oxidation (redox): H_2O_2 oxidises the melanin [1]

- (c)* Some students are given a solution of catalase and solutions of hydrogen peroxide of different concentrations. They study the rate of reaction in **equation 3.1**.

They determine the relative initial rates of reaction at the different hydrogen peroxide concentrations, using the volume of oxygen produced.

Suggest the procedure they follow, including how the students should process their results. You may include a diagram as part of your answer.



Pipette 25.0 cm^3 of $0.05 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ into a conical flask in a water bath at 20°C .
 Add 5.0 cm^3 of catalase solution from a syringe, replace the bung at once and start a stopclock. Collect the O_2 in a gas syringe (or over water in a measuring cylinder) and record the volume every 10 s for about 2 minutes.
 Repeat for each concentration from 0.10 to 0.35 mol dm^{-3} , keeping the volume of peroxide, the volume and concentration of catalase and the temperature the same.
 Processing: plot volume of O_2 against time for each run, draw a tangent at $t = 0$ and find its gradient: this is the initial rate in $\text{cm}^3 \text{ s}^{-1}$ (or time how long it takes to make a small fixed volume of O_2 , e.g. 10 cm^3 : $\text{rate} = \text{volume} / \text{time} \propto 1/t$).
 Divide each initial rate by the smallest rate (at 0.05 mol dm^{-3}) to give the relative rates.

[6]

(d) The students record their results as shown in the box below.

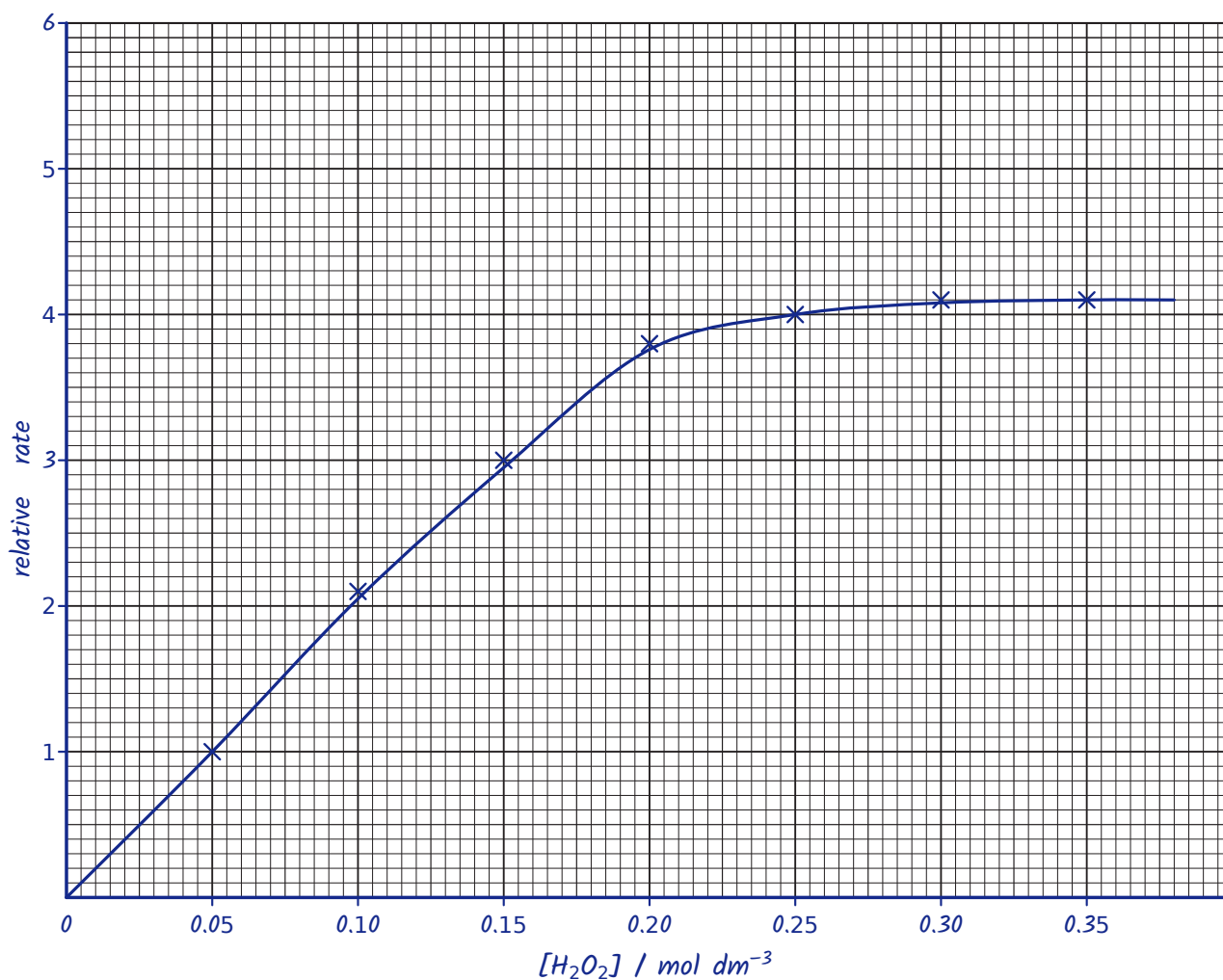
Concentrations of hydrogen peroxide: 0.05 – 0.35 in 0.05 intervals.
 Units of concentration mol dm^{-3}
 Corresponding relative rates of reaction: 1.0; 2.1; 3.0; 3.8; 4.0; 4.1; 4.1
 Temperature: 20 °C

(i) Arrange the results in a more appropriate format.

$[\text{H}_2\text{O}_2] / \text{mol dm}^{-3}$	relative rate
0.05	1.0
0.10	2.1
0.15	3.0
0.20	3.8
0.25	4.0
0.30	4.1
0.35	4.1

[2]

(ii) Use the grid below to plot a graph of the results and draw a line of best fit.



[4]

- (e) A student says that the graph shows that the decomposition of hydrogen peroxide is first order with respect to both the hydrogen peroxide concentration and the catalase concentration.

- (i) Write the rate equation that would follow from the student's statement.
Give the units of the rate constant.

Rate equation: $\text{Rate} = k[\text{H}_2\text{O}_2][\text{catalase}]$

Units of rate constant $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$

[2]

- (ii) Explain why the student is incorrect and give the correct information.

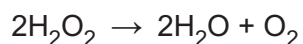
The graph is a straight line through the origin only at low concentrations, so the reaction is first order in H_2O_2 only initially (to about 0.15 mol dm^{-3}).

At higher concentrations the rate levels off at 4.1, so it becomes zero order in H_2O_2 (all active sites are occupied). Catalase concentration was kept constant, so there is no evidence for its order.

[3]

- (f) Hydrogen peroxide concentration is often measured as 'volume strength'.
 1 cm^3 of '1 volume' hydrogen peroxide produces 1 cm^3 of oxygen at RTP.

Calculate the 'volume strength' of the 0.35 mol dm^{-3} hydrogen peroxide used by the students.



Equation 3.1

Give your answer to an **appropriate** number of significant figures.

$$n(\text{O}_2) = 0.35 / 2 = 0.175 \text{ mol per dm}^3 \text{ of } \text{H}_2\text{O}_2$$

$$\text{volume of } \text{O}_2 = 0.175 \times 24.0 = 4.2 \text{ dm}^3 \text{ from } 1 \text{ dm}^3 \text{ of solution}$$

$$\text{so } 1 \text{ cm}^3 \text{ gives } 4.2 \text{ cm}^3 \text{ of } \text{O}_2 \text{ at RTP (2 s.f.)}$$

$$\text{'volume strength'} = 4.2 \text{ volume [3]}$$

- (g) The students have 20.0 cm^3 0.35 mol dm^{-3} H_2O_2 and wish to make a 0.05 mol dm^{-3} solution.

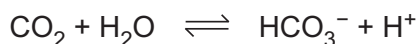
How much water should they add?

$$\text{total volume} = 20.0 \times 0.35 / 0.05 = 140 \text{ cm}^3$$

$$\text{water to add} = 140 - 20.0 = 120 \text{ cm}^3$$

$$\text{volume of water to add} = 120 \text{ cm}^3 \text{ [2]}$$

- 4 The pH of human blood needs to be held within strict limits for good health. The pH is controlled using buffer systems. One buffer system is based on the equilibrium in equation 4.1.



Equation 4.1

- (a) (i) Give the **systematic** name for HCO_3^- .

hydrogencarbonate ion [1]

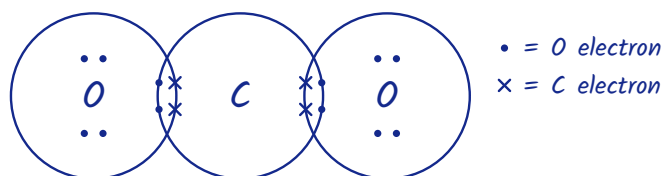
- (ii) HCO_3^- can act as either an acid or a base.

Give the **formula** of the conjugate **base** of HCO_3^- .

CO_3^{2-} [1]

- (b) (i) Draw a 'dot-and-cross' diagram for CO_2 and use it to name the shape of the molecule.

'Dot-and-cross' diagram:



Shape of molecule *linear* [2]

- (ii) A CO_2 molecule has no dipole. A student says that this is because bonds between carbon and oxygen atoms are not polar.

Discuss the student's statement.

The student is wrong; the $\text{C}=\text{O}$ bonds are polar because O is more electronegative than C ($\text{C}^{\delta+}=\text{O}^{\delta-}$). But CO_2 is linear and symmetrical, so the two bond dipoles are equal and opposite and cancel; no overall dipole. [2]

- (c) Another student says that CO_2 will form only instantaneous dipole-induced dipole bonds with water molecules.

Explain why this is incorrect.

CO_2 can also form hydrogen bonds with water molecules. A lone pair on an oxygen atom of CO_2 is attracted to a δ^+ H atom of a water molecule ($\text{O}=\text{C}=\text{O}^{\delta-} \cdots \text{H}^{\delta+}-\text{O}$). [2]

(d) For the equilibrium in **equation 4.1**:

$$K_a = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2(\text{aq})]} = 7.9 \times 10^{-7} \text{ mol dm}^{-3}$$

- (i) A saturated solution of CO_2 at 298K has a concentration of $3.3 \times 10^{-2} \text{ mol dm}^{-3}$.

Calculate the pH of this solution.

$$[\text{H}^+] = \sqrt{K_a \times [\text{CO}_2]} = \sqrt{7.9 \times 10^{-7} \times 3.3 \times 10^{-2}}$$

$$= 1.61 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(1.61 \times 10^{-4}) = 3.79$$

$$\text{pH} = \dots\dots\dots 3.79 \dots\dots\dots [2]$$

- (ii) Calculate the concentration of a solution of HCl that has the same pH as the solution in (i).

$$\text{HCl is fully dissociated, so } [\text{HCl}] = [\text{H}^+] = 1.61 \times 10^{-4}$$

$$\text{concentration} = \dots\dots\dots 1.61 \times 10^{-4} \dots\dots\dots \text{mol dm}^{-3} [1]$$

- (e) (i) The pH of healthy human blood is 7.4.

Calculate the ratio of $\frac{[\text{HCO}_3^-]}{[\text{CO}_2]}$ in healthy human blood.

$$[\text{H}^+] = 10^{-7.4} = 3.98 \times 10^{-8} \text{ mol dm}^{-3}$$

$$[\text{HCO}_3^-] / [\text{CO}_2] = K_a / [\text{H}^+] = 7.9 \times 10^{-7} / 3.98 \times 10^{-8}$$

$$= 19.8$$

$$\frac{[\text{HCO}_3^-]}{[\text{CO}_2]} = \dots\dots\dots 19.8 \dots\dots\dots [2]$$

- (ii) A patient's blood has a pH below 7.4. A student says that HCO_3^- needs to be added to the patient's blood.

Say, with reasons, whether the student is correct.

The student is correct: a pH below 7.4 means the blood contains too much H^+ (it is too acidic). Added HCO_3^- reacts with H^+ , moving the position of equilibrium 4.1 to the left, so $[\text{H}^+]$ falls and the pH increases back towards 7.4. [2]

- (f) Some students mix 20 cm^3 of $5.0 \times 10^{-3}\text{ mol dm}^{-3}$ HCl with 20 cm^3 of $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ NaOH.

Calculate the pH of the resulting solution.

$$n(\text{HCl}) = 20 \times 5.0 \times 10^{-3} / 1000 = 1.0 \times 10^{-4} \text{ mol}$$

$$n(\text{NaOH}) = 20 \times 1.0 \times 10^{-2} / 1000 = 2.0 \times 10^{-4} \text{ mol}$$

$$\text{NaOH remaining} = 1.0 \times 10^{-4} \text{ mol in } 40 \text{ cm}^3$$

$$[\text{OH}^-] = 1.0 \times 10^{-4} \times 1000 / 40 = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = K_w / [\text{OH}^-] = 1.00 \times 10^{-14} / 2.5 \times 10^{-3} = 4.0 \times 10^{-12}$$

$$\text{pH} = -\log(4.0 \times 10^{-12}) = 11.4$$

$$\text{pH} = 11.4 \quad [3]$$

- 5 This question concerns the pre-release article *The Strange Story of Napoleon's Wallpaper* that is included as an insert with this paper.

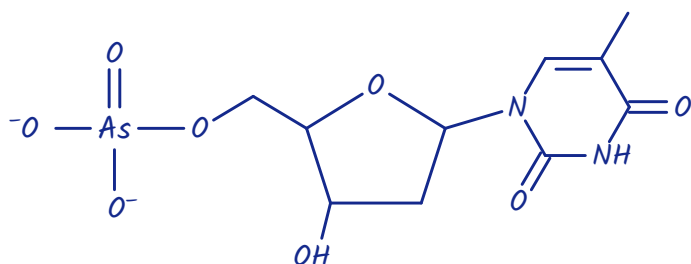
- (a) One reason arsenic is poisonous because it reacts with $-SH$ groups in amino acids.

Suggest how the removal of $-SH$ groups might interfere with the way these amino acids form proteins.

Without $-SH$ groups, cysteine residues cannot form S-S bonds (disulfide bridges), so the protein cannot fold into its correct tertiary structure. [1]

- (b) Arsenate(V) can replace phosphate(V) in nucleic acids.

Draw the skeletal formula of a DNA nucleotide containing thymine and with As instead of P.



[2]

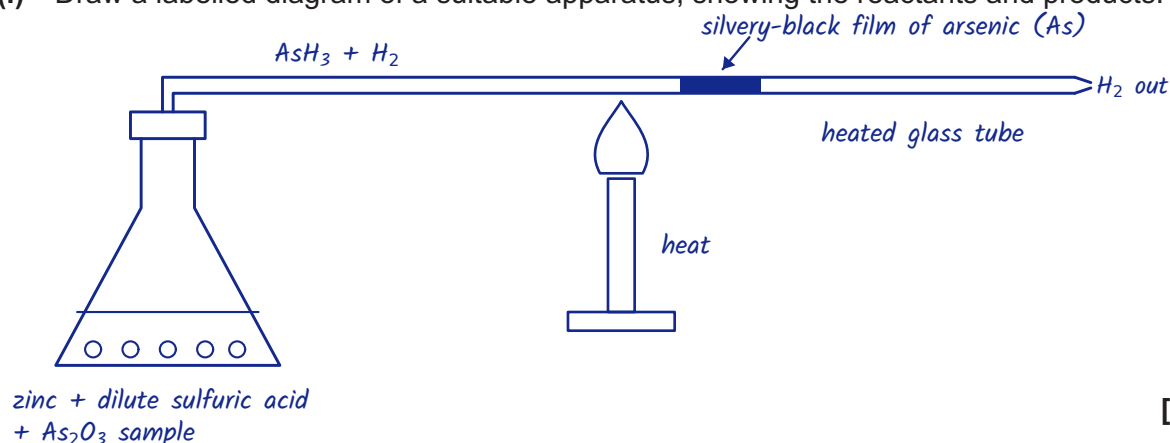
- (c) Write an equation for the reaction of a solution of As^{3+} with hydrogen sulfide. Show state symbols.



[2]

- (d) A Marsh test is carried out for arsenic in a sample of As_2O_3 .

- (i) Draw a labelled diagram of a suitable apparatus, showing the reactants and products.



[3]

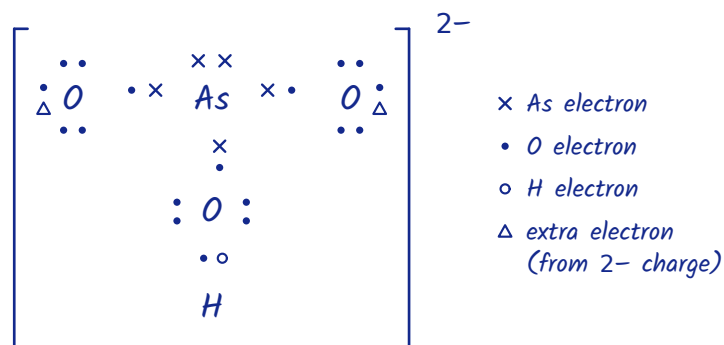
- (ii) Write equations for the formation and decomposition of arsine in the apparatus.



[2]

(e) The structure of Scheele's green can be represented as $\text{Cu}^{2+}(\text{AsO}_2\text{OH})^{2-}$.

(i) Suggest a 'dot-and-cross' diagram for the anion in Scheele's green.



[2]

(ii) State which part of Scheele's green is responsible for the green colour.

the Cu^{2+} (copper(II)) ion [1]

(f) State and explain the C–As–C bond angle in trimethylarsine.

The C–As–C bond angle is about 107.5° . As has four pairs of electrons around it: three bonding pairs (to the three C atoms) and one lone pair. The electron pairs repel each other and move as far apart as possible to minimise repulsion, giving a tetrahedral arrangement of pairs (pyramidal shape). The lone pair repels more than the bonding pairs (lone pair–bond pair repulsion > bond pair–bond pair repulsion), so the angle is reduced from 109.5° to 107.5° .

[4]

(g) Summarise the evidence that Napoleon was killed by his wallpaper.

Arsenic was found in samples of Napoleon's hair. A scrap of wallpaper from the room where he died was green and non-destructive tests showed it contained arsenic, from the pigment Scheele's Green (copper arsenite). If the wallpaper became damp and mouldy, the mould turns the copper arsenite into poisonous arsenic vapours (arsine, methyl arsines) that he breathed in. Such wallpaper had poisoned other people in the 19th century (Gosio's disease). [3]

END OF QUESTION PAPER

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