VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME .....

CT GROUP .....

CHEMISTRY 9729/03

Paper 3 Free Response **16 September 2024**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section **A**
Answer **all** questions.

Section **B**
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Section A	**1**	**/ 23**
	2	**/ 19**
	3	**/ 18**
Section B	**4**	**/ 20**
	OR 5	**/ 20**
Total		**/ 80**

This document consists of **27** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 (a) Chlorine is bubbled through 100 cm^3 of hot 4.0 mol dm^{-3} sodium hydroxide until the reaction is complete.

$$6NaOH(aq) + xCl_2(aq) \rightarrow yNaCl(aq) + zNaClO_3(aq) + 3H_2O(l)$$

(i) State the type of reaction that occurs. Explain your answer in terms of changes in oxidation numbers. [1]

(ii) Determine the values of *x*, *y* and *z*. [1]

(iii) Determine the concentration of $Na^+(aq)$, in mol dm^{-3}, after the reaction. [1]

(b) Compound **A** is an ether with molecular formula $C_4H_{10}O$. When **A** is heated in a sealed container, an equilibrium mixture is produced.

$$C_4H_{10}O(g) \rightleftharpoons C_2H_6(g) + CO(g) + CH_4(g) \qquad \Delta H = -7.00 \text{ kJ mol}^{-1}$$

Table 1.1 shows the activation energy, E_a, for the reaction in the presence and absence of I_2.

Table 1.1

E_a (with I_2) / kJ mol^{-1}	E_a (without I_2) / kJ mol^{-1}
143	224

(i) State the role of I_2 in this reaction and explain what effect it has on the value of K_c. [1]

(ii) Complete the energy profile diagram for this reaction in Fig. 1.1. Include labels to show the enthalpy change and the activation energy data in Table 1.1.

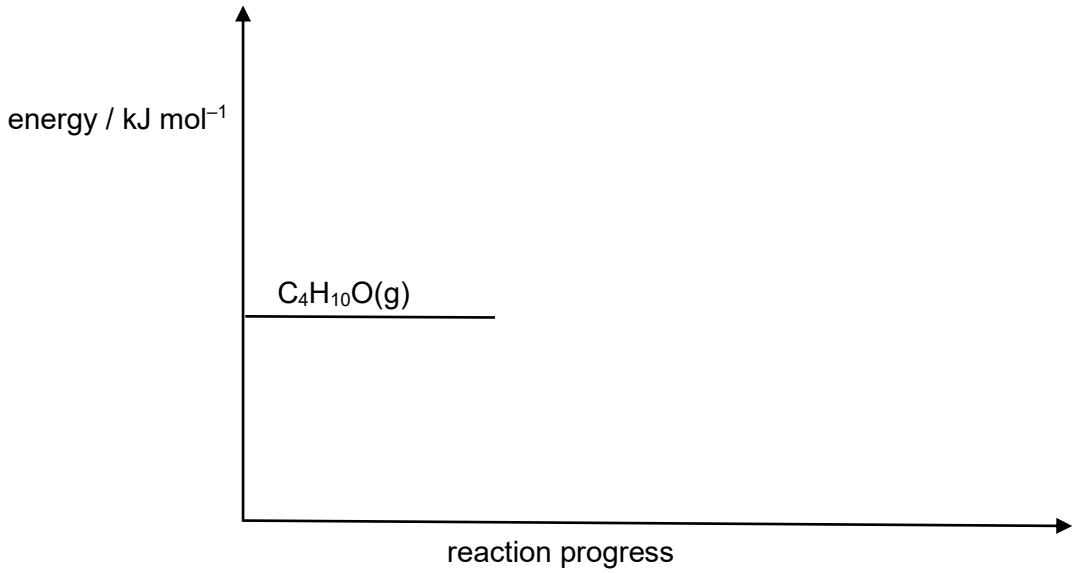

Fig. 1.1

[2]

(iii) Suggest the effect of increasing the pressure on the position of equilibrium. [1]

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(c) Potassium chloride, KC*l*, and magnesium chloride, MgCl_2, are both ionic solids.

The following data can be used to answer some parts of this question.

Table 1.2

standard enthalpy change	value / kJ mol^{-1}
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of KC*l*	+15
lattice energy, $\Delta H^{\ominus}_{latt}$, of KC*l*(s)	–701
standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of K^+	–322
standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of Cl^-	–364
standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of MgCl_2	–155
lattice energy, $\Delta H^{\ominus}_{latt}$, of MgC$l_2$(s)	–2493

(i) Define the term *entropy* and state the effect on the entropy of the chemical system for the following reaction. Explain your answer. [2]

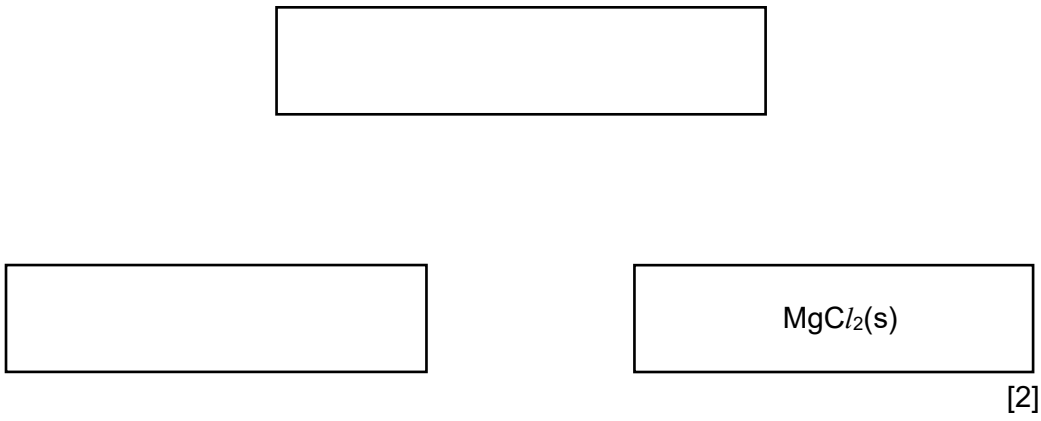
$$K^+(g) + Cl^-(g) \rightarrow KCl(s)$$

(ii) Potassium chloride dissolves readily in water at 25°C.

By considering the enthalpy change and Gibbs free energy change, state and explain the sign of the standard entropy change for the dissolution of potassium chloride. [1]

(iii) Define *enthalpy change of hydration*. [1]

(iv) Complete the energy cycle involving the enthalpy change of solution (ΔH_{sol}), lattice energy (ΔH_{latt}) of magnesium chloride, and the enthalpy changes of hydration (ΔH_{hyd}). Label the enthalpy changes in your diagram. State symbols should be used.



[2]

(v) Hence, calculate the enthalpy change of hydration of magnesium ions, Mg^{2+}. Show your working. [1]

(vi) Explain why the lattice energy of MgCl_2 is more exothermic than the lattice energy of KC*l*. [1]

(vii) Molten magnesium chloride is electrolysed for 15.0 minutes by a constant current. At the cathode, 4.75×10^{22} magnesium atoms are produced. Calculate the value of the current used. [2]

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(d) An electrochemical cell consisting of an Fe^{3+}/Fe^{2+} half-cell and a $C\mathit{l}_2/C\mathit{l}^-$ half-cell is set up. The cell reaction for the electrochemical cell is shown below.

$$C\mathit{l}_2 + 2Fe^{2+} \rightarrow 2C\mathit{l}^- + 2Fe^{3+}$$

In this experiment, the Fe^{2+} concentration is 0.15 mol dm^{-3}. Concentrations of all other species remain at their standard values.

The Nernst equation is shown below.

$$E = E^{\ominus} + \frac{0.059}{n} \lg \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where n is the number of electrons transferred

(i) A salt bridge is used in an electrochemical cell. Explain the function of the salt bridge. [1]

(ii) Use the Nernst equation to calculate the electrode potential, E, for the Fe^{3+}/Fe^{2+} half-cell in this experiment. [1]

(iii) Use your answer to **(d)(ii)** to calculate E_{cell} for this electrochemical cell. [1]

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(e) Anodisation of aluminium is widely practiced in industry.

State why aluminium objects are anodised and explain how anodising achieves this with the aid of equations. [3]

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[Total: 23]

2 (a) Deoxyhaemoglobin and oxyhaemoglobin contain iron atoms in the +2 oxidation state. Each iron atom is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand in an octahedral arrangement. The oxygen-containing ligand is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin. Each haemoglobin can bind up to four O_2 as shown below.

$$\text{deoxyhaemoglobin} + 4O_2 \rightleftharpoons \text{oxyhaemoglobin} + 4H_2O$$

(i) Explain how oxygen is transported in the body with reference to the equilibrium above. [2]

(ii) Suggest why carbon monoxide is toxic when inhaled. [1]

Buffer solutions are important in living systems. The buffer in blood mainly consists of carbonic acid, H_2CO_3, and bicarbonate, HCO_3^-. The buffer serves to maintain the pH of blood at 7.40 ± 0.05 to ensure proper functioning of biological enzymes.

(iii) Explain what is meant by a *buffer solution*. [1]

(iv) With the aid of equations, explain how the pH of blood is maintained. [2]

(v) Ringer's lactate solution is given to patients to replace fluid and electrolyte after excessive blood loss. This solution contains lactic acid, $CH_3CH(OH)CO_2H(aq)$, and lactate ions, $CH_3CH(OH)CO_2^-(aq)$, and acts as a buffer solution. The concentration of lactate ion is 0.025 mol dm^{-3} and the solution has a pH of 4.50. Calculate the concentration of lactic acid present in the solution.

The K_a of lactic acid is 1.38×10^{-4} mol dm^{-3}. [2]

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(b) The hydroxides of Group 2 are often used to neutralise acidity. For example, calcium hydroxide, $Ca(OH)_2$, is used in agriculture to neutralise acidic soil while magnesium hydroxide, $Mg(OH)_2$, is used in indigestion tablets to neutralise excess stomach acid.

(i) The solubility of calcium hydroxide, $Ca(OH)_2$, in water is 2.50×10^{-2} mol dm^{-3} at 25°C.

Calculate the pH of a saturated solution of $Ca(OH)_2$ at 25°C. [2]

(ii) An excess of solid magnesium hydroxide, $Mg(OH)_2$, was stirred with 0.500 mol dm^{-3} magnesium nitrate, $Mg(NO_3)_2$, until equilibrium was established.

The solubility product, K_{sp}, of $Mg(OH)_2$ is 1.40×10^{-11} mol^3 dm^{-9} at 25°C. Calculate the solubility of $Mg(OH)_2$ in the 0.500 mol dm^{-3} magnesium nitrate solution. [2]

(c) This question explores the chemistry of some transition metals.

(i) Explain what is meant by the term *transition element*. [1]

(ii) Explain why transition metal complexes are often coloured. [2]

(iii) Air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3. The resulting solution is then evaporated and crystals of a salt **B** is isolated. **B** has an empirical formula of $CoN_4H_{12}Cl_3$.

On adding an excess $AgNO_3$(aq) to an aqueous solution containing 0.01 mol of **B**, 1.44 g of AgCl(s) is precipitated.

The cationic complex in **B** has no net dipole moment.

Deduce the formula of the cationic complex in **B** and draw its structure. Show clearly the three-dimensional arrangement of the ligands and the overall charge of the cationic complex on the structure. [2]

(iv) Hydrogen peroxide decomposes according to the following equation.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Fe^{3+} ions can be used to catalyse the decomposition.

Use the *Data Booklet* to write two equations to explain how this reaction is catalysed by Fe^{3+} ions and calculate the $E^{\ominus}_{cell}$ values for each step. [2]

[Total: 19]

3 (a) Benzoyl chloride, C_6H_5COCl, can be synthesised by the reaction of benzoic acid with either PCl_5 or $SOCl_2$.

(i) Complete the equation for reaction 1.

reaction 1 $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl$ + …….. + ……..

reaction 2 $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl + SO_2 + HCl$

[1]

(ii) Use your answer to **(a)(i)** to suggest why it is easier to isolate the C_6H_5COCl**,** in pure form, from reaction 2 compared to reaction 1. [1]

(iii) C_6H_5COCl contains a benzene ring in its structure.

Describe and explain the shape of benzene.

In your answer, include:

- the shape and bond angle around each carbon atom
- the hybridisation of the carbon atoms
- how orbital overlap forms σ and π bonds between the carbon atoms

[3]

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(b) Phosphorus oxychloride, $POCl_3$, shows similar chemical properties to PCl_5. $POCl_3$ has a melting point of 1°C and a boiling point of 106°C. $POCl_3$ reacts vigorously with water, forming misty fumes and an acidic solution.

(i) With the aid of an equation, explain the reaction of $POCl_3$ with water. [1]

(ii) Draw a dot-and-cross diagram to show the bonding in $POCl_3$. [1]

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(c) Trioxanes are structures made up of three carbon atoms and three oxygen atoms in a six-membered ring.

Compound **C**, of molecular formula $C_3H_6O_3$, can form only **one** mono-chloro derivative when reacted with Cl_2 under light.

(i) Draw the structural formula of trioxane, **C**. [1]

There are three possible structural isomers of trioxane.

The other two trioxane structural isomers are known to be hypothetical structures and cannot be isolated.

(ii) Draw the structural formulae of the other two trioxane isomers. [1]

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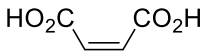
(d) Dicarboxylic acids ionise in 2 stages.

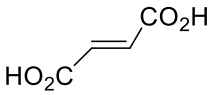
$$HO_2CRCO_2H \rightleftharpoons HO_2CRCO_2^- + H^+ \qquad K_{a1}$$

$$HO_2CRCO_2^- \rightleftharpoons {}^-O_2CRCO_2^- + H^+ \qquad K_{a2}$$

A hydrogen bond can form within a monoanion of *cis*-butenedioic acid. This intramolecular hydrogen bond stabilises the ion.



cis-butenedioic acid



trans-butenedioic acid

(i) Draw a diagram of the monoanion of *cis*-butenedioic acid showing the intramolecular hydrogen bond formed. [1]

(ii) Explain why a monoanion of *trans*-butenedioic acid is unable to form intramolecular hydrogen bonds. [2]

(iii) Suggest how the ability of these acids to form intramolecular hydrogen bonds affects the acid strength, and the value of K_{a1} for *cis*-butenedioic acid compared to *trans*-butenedioic acid. [1]

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(e) The compound **D** has the molecular formula $C_9H_8O_2$. **D** does not liberate carbon dioxide with sodium hydrogencarbonate. **D** reacts with Tollens' reagent to give an organic species **E** and a grey precipitate. Upon acidification of **E**, a white precipitate with a molecular formula of $C_9H_8O_3$ is formed.

Upon oxidation with excess hot acidified potassium manganate(VII), 1 mol of **D** gives 1 mole of carbon dioxide and 1 mol of a compound, $C_8H_6O_5$. **D** reacts with aqueous bromine to form a white precipitate **F**, $C_9H_6O_3Br_4$.

Suggest possible structures for **D, E** and **F**. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional groups present in each structure. [5]

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[Total: 18]

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Section B

Answer **one** question from this section.

4 **(a)** Describe what is meant by the term *enhanced greenhouse effect*. [1]

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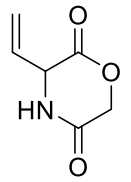
(b) Compound **K** has the structural formula CH_2=CHCH(NH_2)CO_2H and it exhibits stereoisomerism.

(i) Define the term *stereoisomerism*. [1]

(ii) Name all the functional groups in **K**. [1]

(iii) Draw three-dimensional structures for the two stereoisomers of **K** and name this type of stereoisomerism. [2]

Compound **K** can be prepared from the reaction of **L** with a controlled amount of hot aqueous acid.



compound **L**

(iv) Write the equation for the reaction between **L** and a hot aqueous acid to form **K**. [1]

(v) Suggest which compound, **K** or **L**, is a stronger base. Explain your reasoning. [2]

(vi) Compound **K** undergoes an addition reaction with hydrogen bromide. Suggest a mechanism for this reaction and use it to predict the major product. Explain your reasoning. [3]

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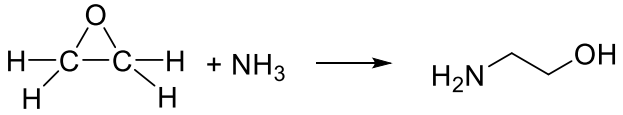
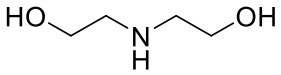
(c) 2-aminoethanol can be synthesised from oxirane as shown below.



oxirane 2-aminoethanol

(i) State the type of reaction undergone by oxirane to form 2-aminoethanol. [1]

(ii) A small amount of by-product **M** is produced during this reaction.



compound **M**

Explain how the by-product **M** is produced and hence suggest how the formation of by-product **M** can be minimised. [2]

(iii) Compound **P**, C_4H_9NO can be formed from the reaction of by-product **M**, $C_4H_{11}NO_2$, with concentrated H_2SO_4.

Compound **P** is a saturated and basic organic compound.

Suggest a structure for compound **P**. [1]

(iv) Suggest a simple chemical test to confirm that **M** has been completely removed from the reaction mixture by the concentrated H_2SO_4. [2]

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(d) In aqueous solution, iodide ions react with acidified hydrogen peroxide as shown below.

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

The initial rate of the above reaction is found to be first order with respect to I^-, first order with respect to H_2O_2 and first order with respect to H^+.

A possible four-step mechanism for this reaction is proposed below.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$
step 2 $H^+ + IO^- \rightarrow HIO$
step 3 $HIO + I^- \rightarrow I_2 + OH^-$
step 4 $OH^- + H^+ \rightarrow H_2O$

(i) Suggest which of the steps, 1, 2, 3 or 4, in this mechanism is the rate-determining step. Explain your answer. [1]

(ii) Suggest the role of HIO in this mechanism. Explain your reasoning. [1]

(iii) This reaction is repeated in two separate experiments. The experiments are carried out at the same temperature and with the same concentrations of I^- and H_2O_2.

One experiment takes place at pH 1.0 and the other experiment takes place at pH 2.0.

Suggest the value of $\frac{\text{rate at pH 1.0}}{\text{rate at pH 2.0}}$. [1]

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[Total: 20]

5 **(a)** Chlorofluorocarbons (CFCs) were commonly used as a refrigerant. In recent years, it has slowly been replaced by other organic substances.

Outline the environmental consequence of releasing CFC into the atmosphere. [1]

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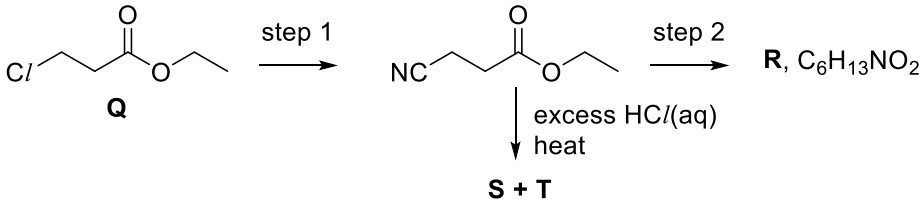
(b) A reaction scheme is shown below.



(i) Give the systematic name for **Q**. [1]

(ii) Suggest the reagents and conditions used for steps 1 and 2. [2]

(iii) Suggest the structures of compounds **R**, **S** and **T**. [2]

When compound **Q** undergoes hydrolysis under different reaction conditions, it gives $CH_2ClCH_2CO_2H$ or $CH_2(OH)CH_2CO_2H$.

(iv) Suggest which organic acid, $CH_2ClCH_2CO_2H$ or $CH_3CH_2CO_2H$ is a stronger acid. Explain your reasoning. [1]

(v) Write an equation to show how $CH_2(OH)CH_2CO_2^-$ is formed from **Q**. [1]

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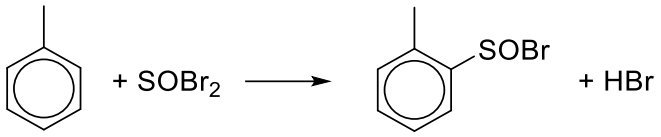
(c) The reaction of methylbenzene with thionyl bromide, $SOBr_2$, in the presence of an iron(III) bromide catalyst, $FeBr_3$, is shown below.



The mechanism of this reaction is similar to that of bromination of benzene.

(i) Suggest the mechanism for this reaction. Include relevant curly arrows and charges. [3]

(ii) This reaction produces a small amount of a by-product, **U**, $C_{14}H_{14}OS$. Suggest a structure for by-product **U**. [1]

(iii) Suggest which compound, methylbenzene or nitrobenzene, reacts with thionyl bromide at a higher rate. Explain your reasoning. [1]

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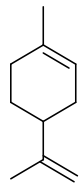
(d) Limonene, $C_{10}H_{16}$, occurs naturally in the pith oil of citrus fruits. It has been used as a biofuel in diesel engines.



limonene

(i) Use the molecular formula of limonene to write a balanced equation for its complete combustion in air. [1]

(ii) Use bond energy values from the *Data Booklet* to calculate the enthalpy change of combustion of limonene. [2]

(iii) The enthalpy change of combustion of diesel fuel is about –45 kJ g^{-1}. How does the enthalpy change of combustion of limonene per gram compare to this value? Show your working. [2]

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(e) Define the term *free radical* and explain with the aid of an equation with curly arrows how the bond in hydrogen peroxide, H_2O_2, breaks to form •OH free radical. [2]

[Total: 20]

Additional answer space

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