

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name** and **class** on this question paper, the Cover Sheet and on all the work you hand in.
- 2 Answer **ANY FOUR** questions.
- 3 Write your answers on the separate answer paper provided.
- 4 Start each question on a fresh sheet of paper.
- 5 A Data Booklet is provided.
- 6 You are reminded of the need for good English and clear presentation in your answers.
- 7 The number of marks is given in brackets [] at the end of each question or part question.
- 8 You are advised to show all workings in calculations.
- 9 You may use a calculator.
- 10 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.

Answer any four questions.

1(a) When under attack, the bombardier beetle uses 'chemical warfare'. It defends itself from attack by mixing together solutions of hydrogen peroxide and hydroquinone $(C_6H_4(OH)_2)$ in the presence of enzymes. This reaction releases free oxygen that produce enough energy to bring the mixture to boiling point. An audible explosion occurs as the beetle fires a hot spray at its attacker from its abdomen. Quinone, $C_6H_4O_2$ is one the products formed.



- (i) State Hess' Law.
- (ii) Construct an energy cycle and use the following data to calculate the enthalpy change of reaction inside the beetle.

| $C_6H_4(OH)_2 (aq) \rightarrow C_6H_4O_2 (aq) + H_2 (g)$ | ΔH^{θ} = +177 kJ mol ⁻¹ |
|---|---|
| H_2O_2 (aq) $\rightarrow H_2O$ (I) + $\frac{1}{2}O_2$ (g) | ΔH^{θ} = –95 kJ mol ⁻¹ |
| $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(I)$ | ΔH^{θ} = –286 kJ mol ⁻¹ |

(iii) Draw a labelled energy profile for the reaction above and indicate clearly the activation energy and enthalpy change of reaction.

[7]

(b) When developing exposed film from a camera, aqueous alkaline hydroquinone reacts with silver ions in a light–activated reaction in **I**.



- (i) Identify X and state the role of hydroquinone in reaction I.
- (ii) Draw the structural formula of Y and name the type(s) of reaction involved in II.
- (iii) Write a balanced equation for the reaction between quinone and each of the following reagents:
 - (1) $LiAlH_4$ in dry ether
 - (2) HBr
- (iv) State what would be observed when 2,4–dinitrophenylhydrazine is added a solution of quinone. Draw the structural formula of the organic product formed.
- (v) One student attempts to synthesise hydroquinone from 1,4-dichlorobenzene using hot aqueous sodium hydroxide. State with reasons whether the student would be successful in his attempt.

[9]

(c) Concentrated hydrogen peroxide is a dangerously reactive substance because the decomposition is very exothermic.

$$H_2O_2$$
 (I) → H_2O (I) + $\frac{1}{2}O_2$ (g) $\Delta H^{\theta} = -98.1$ kJ mol⁻¹

(i) Use ΔH^{θ} and the following data to calculate ΔG^{θ} of the reaction.

| | H_2O_2 (I) | H ₂ O (I) | O ₂ (g) |
|---|--------------|----------------------|--------------------|
| S_{f}^{θ} /J mol ⁻¹ K ⁻¹ | 109.6 | 69.9 | 205.0 |

(ii) Based on your answer in part (i), or otherwise, suggest two possible precautions to take for storing concentrated hydrogen peroxide.

[4]

2(a) Ammonium cyanate, NH₄NCO undergoes thermal decomposition to form a covalent compound urea, (NH₂)₂C=O, which is a common fertilizer.

Describe the type of bonding found in ammonium cyanate and hence suggest a dot-and-cross diagram of cyanate ion, NCO⁻, stating its shape. [3]

- (b) On heating urea above its melting point produces an organic cyclic compound N, and ammonia. N has the composition by mass of C, 28%; N, 33%; H, 2.3%; O, 37% and a relative molecular mass of 129.
 - (i) Determine the molecular formula of **N**.
 - (ii) Suggest a possible structure of **N**.

[2]

- (c) Cyanic acid (NCOH), with an acid dissociation constant of 3.5 x 10⁻⁴ mol dm⁻³, is the simplest chemical compound that contains carbon, hydrogen, nitrogen, and oxygen. A buffer solution can be prepared by mixing 500 cm³ of 0.200 mol dm⁻³ of ammonium cyanate and 500 cm³ of 0.100 mol dm⁻³ of cyanic acid solution.
 - (i) With the help of an equation, explain how the mixture can act as a buffer on addition of H⁺.
 - (ii) Calculate the pH of the prepared buffer solution.
 - (iii) A 20.0 cm³ sample of 0.100 mol dm⁻³ of cyanic acid is titrated with 0.100 mol dm⁻³ aqueous barium hydroxide, Ba(OH)₂. Use the data to sketch the pH changes that occur during the titration when a total of 30 cm³ of Ba(OH)₂ is added. Label the following points on your sketch:
 - (1) Initial pH
 - (2) End-point
 - (3) Point of maximum buffer capacity
 - (iv) At certain temperature, cyanic acid is able to form an isomer which is also an acid, via the migration of a proton. Suggest the structural formula of this isomer.

[8]

(d) Another ammonium salt, ammonium nitrate, sublimes reversibly with heat to produce ammonia and nitric acid until dynamic equilibrium is reached:

$$NH_4NO_3$$
 (s) \rightleftharpoons NH_3 (g) + HNO_3 (g)

- (i) Explain what is meant by the term *dynamic equilibrium*.
- (ii) Write an expression for the equilibrium constant, K_p for the above reaction.
- (iii) 9.00 g of ammonium nitrate is heated in a sealed container and the equilibrium constant is found to be 15.7 atm². Calculate the partial pressure of ammonia present at equilibrium.
- (iv) Hence, determine the percentage of ammonium nitrate which has dissociated, given that one mole of gas under these conditions exerts a pressure of 50 atm.

(v) At a higher temperature, the equilibrium constant is 16.8 atm². Compare this with the value given in part (iii). Deduce with reasons, whether the sublimation reaction is endothermic or exothermic.

[7] [Total: 20] **3(a)** The electrolysis of aqueous potassium chloride containing methyl orange indicator is carried out in the following apparatus using platinum electrodes. The volume of gases liberated at the electrodes is shown below:



- (i) It is found that 12 cm³ of gas is collected at the cathode after passing the current for two minutes under room conditions. Calculate the size of current used.
- (ii) Determine the volume ratio of gases collected at the anode and cathode.
- (iii) State and explain the colour of the methyl orange indicator around the electrodes.
- (iv) The electrolysis is continued over a long time and a greenish–yellow gas is liberated at the anode. Explain this observation.

[7]

- (b) (i) When potassium chloride and potassium bromide are separately added to concentrated sulfuric acid, different observations are noted. Explain the difference in behaviour of both salts towards concentrated sulfuric acid using relevant data from the *Data Booklet*. Write balanced equations for the reactions that occur.
 - (ii) Potassium bromide in concentrated sulfuric acid is used as a reagent in the following reaction scheme. It is found that organic compound **Q** produces white fumes when subjected to PCl_5 , and has no reaction with alkaline aqueous iodine. Deduce with reasons, the structures for compounds **P T**.



(c) Give a reagent, other than concentrated sulfuric acid, that can be used to distinguish between separate solutions of potassium chloride and potassium bromide. State what would be observed and write an equation for **one** of the reactions.

Identify another reagent that could be added to the mixtures from the first test to confirm the identity of the halide ions. State what would be observed in each case.

[3]

4(a) Methanoic acid decomposes in the gas phase at high temperatures as follows:

HCOOH (g) \rightarrow CO₂ (g) + H₂ (g)

The decomposition reaction is studied and following results are obtained.

| Time /s | 0 | 250 | 500 | 750 | 1000 | 1250 | 1500 |
|--------------------------------|-----|-----|-----|-----|------|------|------|
| Partial pressure of HCOOH /atm | 300 | 230 | 170 | 128 | 95 | 70 | 53 |

- (i) What is meant by the term *order of reaction*?
- (ii) Plot a suitable graph and determine the order of reaction. Show necessary working on your graph.
- (iii) Write the rate equation and calculate the rate constant, specifying its units.
- (iv) If the rate of reaction is followed by measuring concentration of methanoic acid, what effect would this have on the calculated value of rate constant in part (iii)?

[8]

- (b) Addition of some TiO_2 speeds up the decomposition reaction in part (a).
 - (i) What enables transition metals such as titanium, to act as a catalyst? State what type of catalyst TiO₂ is acting as in this reaction.
 - (ii) Briefly explain how the catalyst increases the rate of reaction.

[4]

- (c) When 0.90 g of liquid methanoic acid is completely vapourised in a gas syringe at 120 °C and 101 kPa, 316 cm³ of gaseous acid is produced.
 - (i) Calculate the relative molecular mass of the gas produced.
 - (ii) With a suitable diagram, suggest why there is a difference between the theoretical value and the value calculated in part (i).

[3]

(d) An experiment is conducted to determine the enthalpy change of neutralisation between methanoic acid and aqueous sodium hydroxide. Some solid methanoic acid is added to sodium hydroxide solution. The changes in temperature and amount of reagents mixed are recorded as follows:

| initial temperature | /°C | 24.0 |
|---|------------------|------|
| final temperature | /°C | 34.5 |
| mass of HCOOH added | /g | 1.84 |
| volume of 1 mol dm ⁻³ NaOH (aq) used | /cm ³ | 50.0 |

- (i) Define standard enthalpy change of neutralisation.
- (ii) Use the above data to calculate the enthalpy change of neutralisation, assuming that 4.2 J is required to raise the temperature of 1 cm³ solution by 1 °C.
- (iii) The magnitude of enthalpy change of neutralisation between aqueous nitric acid and aqueous sodium hydroxide is found to be larger than the value calculated in part (ii). Explain why this is so.

[5]

- **5(a)** The name, copper, comes from the Latin word "*cuprum*" meaning the island of "*Cyprus*". The discovery of copper dates from prehistoric times. Today, copper finds use in many ways, as decorative metal art and as reagents in numerous inorganic and organic reactions.
 - (i) In what way is copper *metal* different from a typical s–block metal such as calcium? Describe one difference in physical property.
 - (ii) Hot copper is a weak oxidising agent. It oxidises primary alcohols to aldehydes and is incapable of oxidising them further:

$$RCH_2OH \rightarrow RCHO + H_2$$

Write the structure of the organic product obtained when 2–phenylethanol, \bigcirc $-CH_2CH_2OH$ is allowed to react with hot copper.

- (iii) Suggest how the product in part (ii) can be distinguished from benzaldehyde,
- (iv) Outline a method to perform the following synthesis. Include in your answers, essential reagents and conditions for each step and write the structural formula of any intermediate(s) formed.

$$\bigcirc -CHO \longrightarrow \bigcirc -CONH(CH_3)$$
Br [8]

- (b) (i) When aqueous ammonia is gradually added to an aqueous solution containing Cu²⁺ (aq), several observations are noted. Describe these observations and write equations where appropriate.
 - (ii) State what will be seen when a few drops of dilute sulfuric acid are added to the resultant solution in part (i).

[4]

- (c) Copper (I) sulfate is a white powder which reacts with water to give a blue solution and a pink-coloured solid.
 - (i) By reference to the relevant E^{θ} data from the *Data Booklet*, identify the two coloured products.
 - (ii) Describe the type of reaction undergone, and write a balanced equation.
 - (iii) What is the electronic configuration of copper in copper (I) sulfate? Explain why copper (I) sulfate solution is not coloured whereas aqueous copper (II) sulfate is.

[8]