HWA CHONG INSTITUTION

C2 PRELIMINARY EXAMINATION

9746 H2 CHEMISTRY

Paper 3 Free Response

10 September 2008 **2 hours**

Do not open this booklet until you are told to do so.

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

You may use a soft pencil for any diagrams, graphs or rough working.

Answer any **four** questions.

Begin each question on a **new piece of paper**.

A *Data Booklet* is provided.

You may use a calculator.

You are reminded of the need for good English and clear presentation in your answers.

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

At the end of the examination, fasten all your work securely together.

Circle the question number that you have answered on the cover page provided.

Answer any **four** questions.

1 (a) **(i)** What do you understand by the term *dynamic equilibrium*?

The ester, ethyl ethanoate, can be formed in the following reaction:

$$CH_3CO_2H(l) + C_2H_5OH(l) = CH_3CO_2C_2H_5(l) + H_2O(l)$$

In an experiment, 0.5 mol of ethanoic acid and 1.0 mol of ethanol were shaken for a long time and allowed to reach dynamic equilibrium at room temperature. 0.42 mol of ethyl ethanoate was found to be present in the equilibrium mixture.

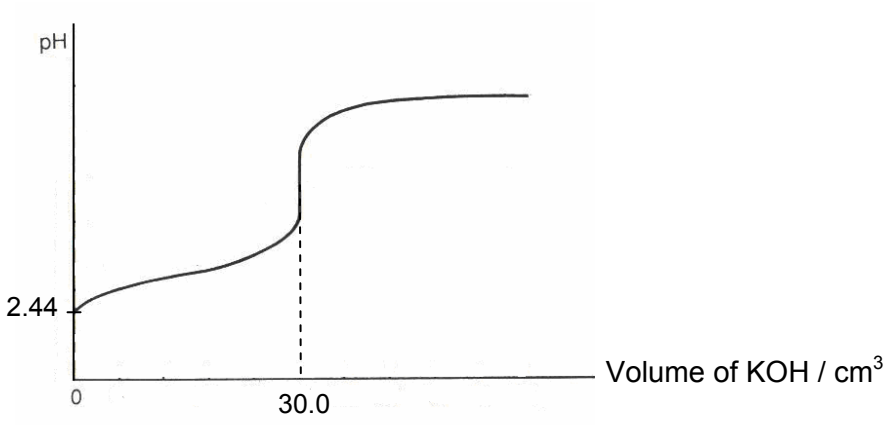
(ii) Write an expression for the equilibrium constant, K_c, and calculate its value.

(iii) Predict, with reasoning, the effect on the equilibrium when some aqueous sodium hydroxide is added to the equilibrium mixture.

(iv) Give one other compound that can be used in place of CH_3CO_2H to produce the same ester.

[6]

(b) Ethanoic acid is the main component in vinegar. When a 25.0 cm^3 sample of vinegar was titrated against 0.6 mol dm^{-3} aqueous potassium hydroxide using a pH meter, the following graph was obtained.



(i) Using the information provided, show by calculations that the acid dissociation constant, K_a, of ethanoic acid has a numerical value of 1.84×10^{-5}.

Solution **A** was prepared by adding 10.0 cm^3 of the KOH solution to the 25.0 cm^3 vinegar sample.

(ii) When a small amount of acid or base was added to solution **A**, its pH remained relatively constant. Explain qualitatively, with the aid of equations, why this is so.

(iii) Calculate the pH of solution **A**.

[8]

(c) Succinic acid, historically known as spirit of amber, plays an important biochemical role in the citric acid cycle. Its structure is shown below:

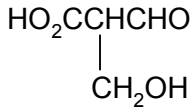
$HO_2CCH_2CH_2CO_2H$

succinic acid

In no more than four steps, propose a reaction scheme to obtain succinic acid from ethanol. State the reagents and conditions required, and draw the structure of the compound obtained in each step of your reaction scheme.

[4]

(d) Compound **P** is a structural isomer of succinic acid:



Compound **P**

Suggest a simple chemical test that could be used to distinguish compound **P** from succinic acid. State the reagents and conditions used and the expected observation for each compound.

[2]

[Total: 20]

2 (a) (i) State the full electronic configuration of the Mn^{2+} ion.

(ii) When acidified potassium manganate(VII) is added to a solution of ethanedioic acid, $H_2C_2O_4$, the reaction proceeds at a very slow rate. When a few crystals of manganese(II) sulphate are added to the mixture, the reaction speeds up and the colour changes from purple to red then finally to colourless. The red colouration is found to be due to the formation of an intermediate, $Mn^{3+}(aq)$.

The reaction may be represented as:

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(aq) + 8H_2O(l)$$

By considering relevant $E^\ominus$ values from the *Data Booklet* and from the data below, show by means of balanced equations, how $Mn^{2+}(aq)$ ions can act as a homogenous catalyst in the reaction.

$$2CO_2 + 2e^- = C_2O_4^{2-} \qquad E^\ominus = -0.49\ V$$

[5]

(b) The red colouration described in **(a)** is due to an octahedral complex ion formed between Mn^{3+} and $C_2O_4^{2-}$.

(i) Explain what you understand by the term *complex ion*.

(ii) $C_2O_4^{2-}$ is a bidentate ligand. Suggest the formula of the complex formed with Mn^{3+}.

(iii) Explain why many transition metal complexes are coloured whereas compounds of Group II metals are colourless.

[7]

(c) Potassium manganate(VII) is a useful oxidising agent, acidified solutions of which can be used to titrate reducing agents.

(i) Describe in outline the practical details you would need to follow in order to use a standard solution of potassium manganate(VII) to measure the percentage purity of a given sample of solid iron(II) ethanedioate, FeC_2O_4. In your answer, you should include:

- an equation for the titration reaction,
- an outline of the sequence of steps to carry out the titration,
- names of any other chemicals you would use.

Do not include any details of the calculation.

[3 mol of MnO_4^- reacts with 5 mol of FeC_2O_4]

(ii) When a 0.600 g sample of an impure iron(II) ethanedioate solid is dissolved in acid and titrated with 0.100 mol dm^{-3} $KMnO_4$, 20.50 cm^3 of oxidant solution is required to reach the end point. Calculate the percentage purity of the sample.

[8]

[Total: 20]

3 The elements, fluorine, chlorine, bromine and iodine are members of the halogen family.

(a) The exceptional chemical reactivity of fluorine long defeated efforts to isolate it from its compounds. Henry Moisson, a French chemist, was the first to obtain fluorine by electrolysing KHF_2 dissolved in liquid HF using platinum-iridium alloy electrodes in a platinum vessel.

(i) With reference to relevant data from the *Data Booklet*, explain why fluorine cannot be obtained by electrolysing aqueous sodium fluoride even if concentrated sodium fluoride is used.

On the other hand, chlorine is made commercially by the electrolysis of concentrated sodium chloride (brine). The overall electrolytic process may be represented by the following equation:

$$2NaCl(\text{concentrated}) + 2H_2O(l) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + Cl_2(g) + H_2(g)$$

(ii) Write the ion-electron half-equation for each of the electrode reactions in the electrolysis of brine using inert electrodes.

(iii) Using the relevant half-equation in **(a)(ii)**, calculate the current needed to produce 1 tonne of Cl_2 per day.
[1 tonne = 1×10^6 g]

[8]

(b) Chlorine and fluorine react exothermically to form an interhalogen compound, ClF_3.

(i) With the help of a diagram, describe and explain the shape of the ClF_3 molecule.

(ii) The interhalogen compounds are very strong oxidising agents.

When gaseous ClF_3 is added to water, a vigorous reaction occurs, giving three gases as the only products. The gaseous product mixture appears as white fumes. It not only turns moist blue litmus paper red but also bleaches it. In addition, it relights a glowing splint.
Construct a balanced equation, including state symbols, for the reaction.

[4]

(c) Explain each of the following, writing balanced equations, including state symbols, for any chemical reaction that occur.

(i) The boiling point of HF (19.5 °C) is higher than that of HI (–35.4 °C).

(ii) HCl can be prepared by adding concentrated H_2SO_4 to solid $NaCl$. However, the yield of HI is very low if concentrated H_2SO_4 is added to solid NaI.

(iii) When a hot glass rod is plunged into a jar of gaseous HI, some violet vapour is obtained. When the experiment is repeated with HBr, the gas remains colourless.

[8]

[Total: 20]

4 (a) With the aid of a suitable diagram, explain why an increase in temperature can cause an increase in the rate of a chemical reaction. [4]

(b) Iodine reacts with propanone in acid solution as follows.

$$I_2 + CH_3COCH_3 \xrightarrow{H^+} CH_3COCH_2I + HI$$

Kinetics studies have shown that the reaction is second order overall, and it has been suggested that the mechanism involves the following three steps.

$$CH_3COCH_3 + H^+ \rightleftharpoons CH_3\overset{+}{C}(OH)CH_3 \quad \text{(fast)}$$

$$CH_3\overset{+}{C}(OH)CH_3 \rightleftharpoons H_2C{=}C(OH)CH_3 + H^+ \quad \text{(slow)}$$

$$H_2C{=}C(OH)CH_3 + I_2 \longrightarrow CH_3COCH_2I + HI \quad \text{(fast)}$$

(i) Explain the meaning of the following terms.

- order of reaction
- rate constant

(ii) Give the rate equation for this reaction.

(iii) An experiment was carried out at 50 °C using the following concentrations of the reagents.

Initial concentration / mol dm^{-3}		
$[I_2]$	$[CH_3COCH_3]$	$[H^+]$
0.002	0.050	0.050

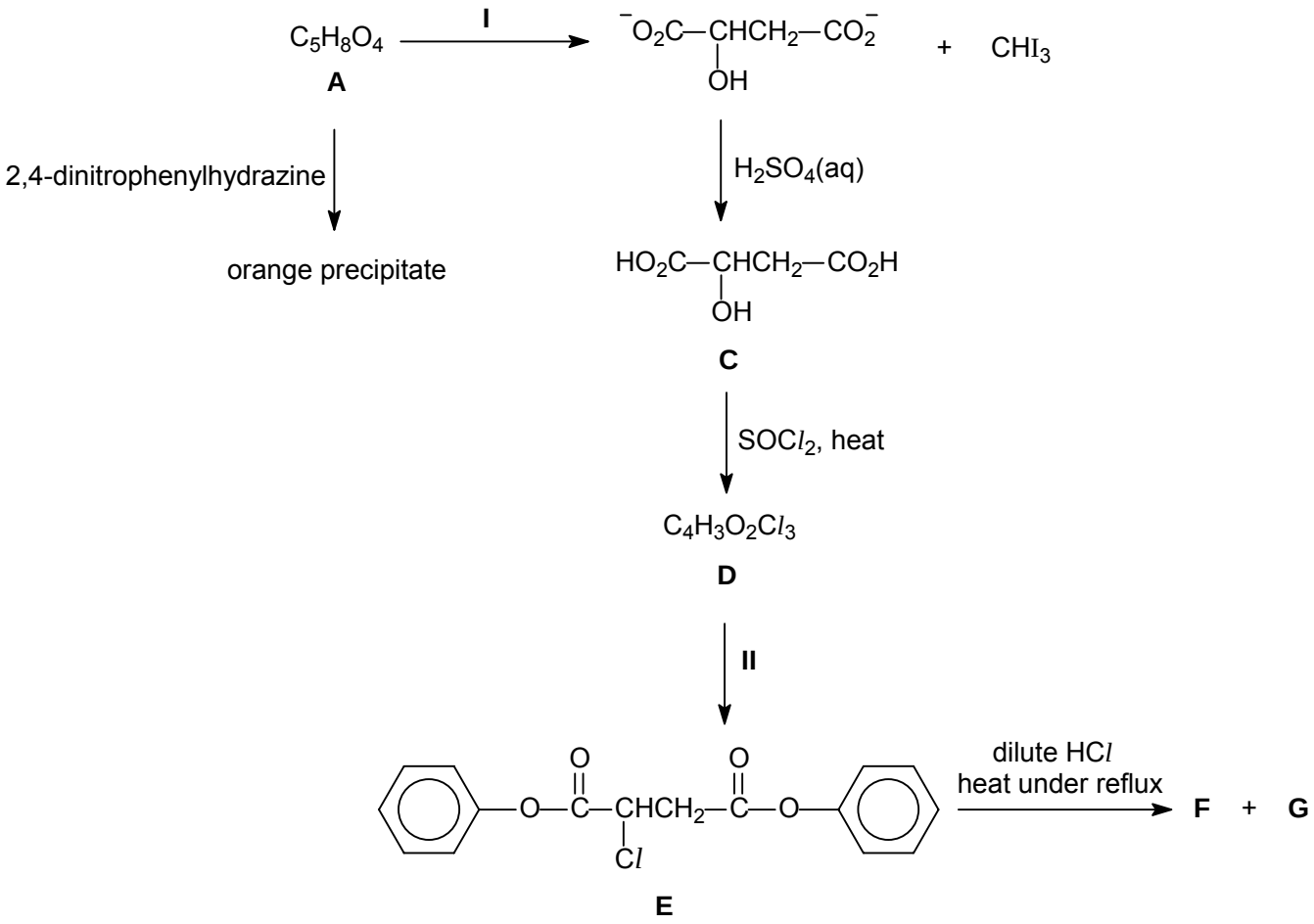
The initial rate of reaction was found to be 1.25×10^{-6} mol dm^{-3} s^{-1} under these conditions. Calculate the rate constant for this reaction, stating its units.

(iv) Suggest the role of H^+ ions in this reaction.

(v) Sketch a graph to show how the concentration of I_2 changes with time during the reaction. Justify the shape of your graph by considering the relative concentrations of the reagents used.

[8]

(c) Consider the following reaction scheme:



(i) Suggest reagents and conditions for reaction **I**, and give the structure for compound **A**.

(ii) Give the structure for compound **D** and state what you would observe when **C** is converted to **D**.

(iii) What *type of reaction* is reaction **II**? State the necessary reagents and conditions for this reaction.

(iv) Suggest structures for the organic compounds **F** and **G**.

[8]

[Total: 20]

5 (a) **(i)** Propylamine, $CH_3CH_2CH_2NH_2$, is a *Bronsted-Lowry base*.

What is understood by the terms in *italics*?

(ii) Write an expression for the base dissociation constant, K_b, for propylamine.

(iii) For propylamine, $K_b = 4.7 \times 10^{-4}$ mol dm^{-3}. Use this value to calculate the pH of a 0.100 mol dm^{-3} solution of propylamine, and hence calculate the percentage of $CH_3CH_2CH_2NH_2$ molecules ionised.

(iv) Suggest, with a reason, an indicator that you would use to determine the end-point in the titration of aqueous propylamine with dilute hydrochloric acid.

[6]

(b) Phenyalmine, $C_6H_5NH_2$, and N-methylpropylamine, $CH_3CH_2CH_2NHCH_3$, are also Bronsted-Lowry bases.

Describe and explain why the basicity of propylamine differs from those of phenylamine and N-methylpropylamine. [3]

(c) Amines are often synthesised from halogenoalkanes. Propose reaction synthesis pathways for the conversion of chloroethane into:

(i) ethylamine

(ii) propylamine

State the reagents and conditions required, and draw the structure of the intermediate compound obtained in each stage of the synthesis (where applicable).

. [3]

(d) Compound **P** has the molecular formula $C_5H_{12}O$. When **P** is heated with acidified potassium dichromate(VI), the solution remains orange. When **P** is reacted with excess concentrated sulphuric acid at 180 °C, a mixture of two isomers, **Q** and **R**, is produced. When reacted with hot concentrated potassium manganate(VII), **Q** produces effervescence, while **R** gives no effervescence. When *either* **Q** or **R** is reacted with dry hydrogen chloride gas at room temperature, compound **S** is produced as the major product.

- Identify the type of isomerism shown by compounds **Q** and **R**.
- What type of reaction is taking place in the production of compound **S** from the isomers **Q** and **R**? By choosing either **Q** or **R**, clearly describe the mechanism involved.

You should clearly include the displayed formulae of all compounds **P** – **S** in your answer. [8]

[Total: 20]

End of Paper