

SERANGOON JUNIOR COLLEGE General Certificate of Education Advanced Level Higher 2

## **CHEMISTRY**

9746/03

Preliminary Examination Paper 3 Free Response

19<sup>th</sup> August 2008 2 hours

Candidates answer on the separate paper.

Additional Materials: Answer Paper Data Booklet

## **READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work you hand in.Write in dark blue or black pen on both sides of the paper.You may use a soft pencil for any diagrams, graphs or rough work.Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any four questions.

A Data Booklet is provided.

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

The number of marks is given in the brackets [ ] at the end of each question or part question. At the end of the examination, fasten all your work securely together.

This document consists of 11 printed pages and 1 blank page

## Answer any four questions.

1. The Haber Process is the nitrogen fixation reaction of nitrogen and hydrogen over magnetite, iron oxide, to produce ammonia. This process is important because ammonia is difficult to be produced on an industrial scale, and ammonia is the precursor for many nitrogen-containing products such as nitrate fertilizers and munitions.

$$N_2(g) + 3H_2(g) = 2 NH_3(g)$$
  $\Delta H^{\circ} = -92.4 \text{ kJ mol}^{-1}$ 

(a) Write an expression for  $K_p$  for the above reaction, stating its units.

[2]

(b) When a 1:3 mixture by volume of N<sub>2</sub> and H<sub>2</sub> at an initial pressure of 200 atm is allowed to reach equilibrium at 500 °C, it was found that the percentage yield of NH<sub>3</sub> is 30 %.

$$\left(\% \text{ yield} = \frac{actual \, amount}{theoretical \, amount} \times 100\%\right)$$

- (i) Calculate the equilibrium partial pressures of  $N_2$  and  $H_2$ .
- (ii) Hence calculate a value of  $K_p$  at 500 °C.
- (iii) Suggest, with a reason, whether or not a higher temperature would favour the formation of ammonia.
- (iv) When some  $H_2$  is added to the existing equilibrium mixture, the partial pressure of ammonia is increased to 50 atm. Calculate the new equilibrium partial pressure of  $H_2$ .
- (v) The value of  $\Delta G$  is 0 kJ mol<sup>-1</sup> at 196 °C. Use this information, and any other information to calculate the value of  $\Delta S$ .
- (vi) Calculate  $\Delta G$  for the forward reaction at 500 °C.
- (vii) Based on the answer in (vi), comment on the feasibility and relate it with the reaction conditions of 200 atm and 500 °C.

[8]

- (c) Ammonia can be used as a reagent to make nitrogen-containing products.
  - (i) State the reagents and conditions that is needed for the conversion of ammonia into
    - I propanamine
    - II propanamide
  - (ii) It is noted that in the formation of propanamine, a by-product is formed which has a melting point of 270 °C and gives an immediate precipitate with aqueous silver nitrate. Suggest a structure for this by-product.

[3]

- (d) The compound propanamide, which is a product of ammonia, can be used to make other organic compounds.
  - (i) Propanamide can undergo hydrolysis to form propanoic acid.

How would you expect the rate of this reaction to compare to that of the hydrolysis of propanoyl chloride? Explain your answer using their respective reaction conditions.

(ii) State the intermediates and suggest the reagents and conditions needed for the conversion of propanoic acid into butanoic acid.

[5]

- (e) When propanamide, propanoyl chloride and propanoic acid are added into separate portions of water, solutions of pH 1.0, 2.8 and 7.0 are formed.
  - (i) Suggest which pH value is associated with each compound.
  - (ii) Give a reason for your choice of pH of propanamide.

[2] [Total: 20]

- 2 Trichloroethanoic acid (TCA), CC*l*<sub>3</sub>COOH, widely used in biochemistry for the precipitation of macromolecules such as proteins. Solutions containing trichloroethanoic acid are also used in tattoo removal.
  - (a) Trichloroethanoic acid is prepared by the reaction of chlorine with ethanoic acid.

$$CH_3COOH + 3Cl_2 \rightarrow CCl_3COOH + 3HCl$$

- (i) State the type of reaction for the preparation of trichloroethanoic acid.
- (ii) Suggest a suitable condition for this reaction.
- (iii) A by-product of this synthesis has a molecular formula of  $C_4H_4O_4Cl_2$ . Draw a suitable structure for this compound.

[3]

(b) In a laboratory experiment, the decomposition of CC*I*<sub>3</sub>COOH was conducted at 70 °C and the volume of carbon dioxide produced was monitored using 0.100 mol dm<sup>-3</sup> and 0.200 mol dm<sup>-3</sup> of trichloroethanoic acid separately.



$$CCl_3COOH \rightarrow CO_2 + CHCl_3$$

- (i) From the graph, determine the order of reaction and the rate constant, **k**.
- (ii) Determine the half life of reaction using rate constant that you have calculated in (i).
- (iii) Explain, using Maxwell Boltzmann distribution curve, the effect of lowering temperature to 60 °C.

[7]

(c) A student collected the CO<sub>2</sub> produced by delivering the gas into a measuring cylinder originally filled with water.

Some of the carbon dioxide dissolved in water to form carbonic acid,  $H_2CO_3$ . The following equilibria were established.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$
  
 $H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$   $K_a = 4.27 \times 10^{-7} \text{ mol dm}^{-3}$ 

A 20.0 cm<sup>3</sup> of 0.20 mol dm<sup>-3</sup> H<sub>2</sub>CO<sub>3</sub> was titrated with 0.20 mol dm<sup>-3</sup> of aqueous sodium hydroxide, NaOH. 20.00 cm<sup>3</sup> of NaOH was required for complete neutralisation of the following reaction.

$$H_2CO_3(aq) + NaOH(aq) \rightarrow NaHCO_3(aq) + H_2O(l)$$

- (i) What do you understand by the term weak acid?
- (ii) Calculate the initial pH of the solution.
- (iii) Calculate the pH of the solution after adding 10.00 cm<sup>3</sup> of NaOH.
- (iv) The pH at equivalence point is 8.35. Using an appropriate equation, account for this observation.
- (v) An acid-base indicator (HIn) has a  $K_a$  value of 3.00 x 10<sup>-5</sup> mol dm<sup>-3</sup>.

HIn(aq)  $\rightarrow$  H<sup>+</sup>(aq) + In<sup>-</sup>(aq)

The acidic form of the indicator (HIn) is red and the basic form (In<sup>-</sup>) is blue. Given that the indicator appears red when it contains at least 75% of HIn, and appears blue when it contains at least 75% of In<sup>-</sup>. What is the pH range for colour change of indicator? Based on your answer, suggest if this indicator is suitable for the  $H_2CO_3$  titration.

(vi) Suggest a better method of collecting the CO<sub>2</sub> gas.

[10]

[Total: 20]

- 3 This question is about physical and chemical properties of Group II compounds.
  - (a) 400 cm<sup>3</sup> of 0.015 mol dm<sup>-3</sup> of magnesium nitrate was mixed with 600 cm<sup>3</sup> of 0.2 mol dm<sup>-3</sup> of aqueous ammonia [K<sub>b</sub> of NH<sub>3</sub> =  $1.74 \times 10^{-5}$  mol dm<sup>-3</sup>].
    - (i) Write an expression for the solubility product,  $K_{sp}$ , of magnesium hydroxide.
    - (ii) Calculate the amount of  $Mg^{2^+}$  and  $NH_3$  added.
    - (iii) Given that the  $K_{sp}$  of Mg(OH)<sub>2</sub> is 1.65 x 10<sup>-10</sup> mol<sup>3</sup>dm<sup>-9</sup>, prove that there is precipitate of Mg(OH)<sub>2</sub> formed in the above resulting mixture.
    - (iv) The pH of this resulting solution is measured at 11.1. Calculate the concentration of  $Mg^{2^+}$  ions in the solution.

[5]

- (b) Magnesium nitrate decomposes at 330°C.
  - (i) Write a balanced chemical equation, with state symbols, for the decomposition of magnesium nitrate.
  - (ii) How would you expect the decomposition temperature of barium nitrate to differ from that of magnesium nitrate? Explain your answer.

[3]

- (c) Solubility of Group II sulphates vary down the group.
  - (i) With an appropriate equation, define the *enthalpy change of solution of calcium sulphate.*

| (ii) | Given: | $\Delta H^{\Theta}_{lattice}$ (CaSO <sub>4</sub> ) | = | -2704 kJmol <sup>-1</sup> |
|------|--------|--|---|---------------------------|
|      |        | $\Delta H^{e}_{hydration}$ (Ca <sup>2+</sup> )     | = | -1562 kJmol <sup>⁻1</sup> |
|      |        | $\Delta H^{e}_{hydration} (SO_4^{2})$              | = | -1160 kJmol <sup>⁻1</sup> |

Using *Hess' Law*, calculate the enthalpy change of solution of calcium sulphate. Based on the value that you have calculated, comment on the solubility of calcium sulphate.

(iii) Using relevant data from the *Data Booklet*, predict the relative solubility of calcium sulphate, barium sulphate and lead(II) sulphate.

[5]

- CompoundsUsesMgOAs refractory lining in furnacesCaCO3Used in the furnace for removal of<br/>SO2 in exhaustMgSO4<br/>(anhydrous)As an anti-inflammatory agent
- (d) The table below shows the uses of some Group II compounds.

- (i) Explain, in terms of bonding and structure, the use of magnesium oxide as a refractory lining in furnace.
- (ii) Calcium carbonate removes sulphur dioxide, forming calcium sulphite, via this reaction:

$$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g)$$

A stream of furnace exhaust containing sulphur dioxide gas was passed through 100 g of solid  $CaCO_3$ . The mass of solid was found to be 110 g after the experiment. Assuming all sulphur dioxide was removed from the stream of exhaust and converted to calcium sulphite, calculate the amount of sulphur dioxide present in the exhaust gas. [Taking A<sub>r</sub> of Ca = 40.0, S = 32.0, C = 12.0 and O = 16.0]

(iii) Anhydrous magnesium sulphate paste is sold by pharmacists as a treatment for boils (infected areas of the skin). The paste is applied to a boil to draw out water and the infected matter. Suggest why anhydrous magnesium sulphate is able to draw water out of the treated boil.

> [7] [Total: 20]

4 The reaction scheme below shows the synthesis of 4,4-dichlorodiphenyltrichloroethane (DDT).



- (a) In a school science project to study the synthesis of DDT, a student prepares some of the intermediate, chlorobenzene, by dissolving small amount of anhydrous aluminium chloride in some benzene and followed by bubbling chlorine gas into the mixture.
  - (i) Explain why aluminium chloride is soluble in benzene.
  - (ii) Will the reaction between benzene and chlorine in Step I take place if aluminium chloride is not added? Explain your answer with reference to the structure of benzene.
  - (iii) What is the role of aluminium chloride in Step I? Write a chemical equation to show how aluminium chloride takes part in the reaction.
  - (iv) During the preparation, the student was told to ensure that all equipment is dry before he put in the reactants. This is because the reaction will cease if water is present in the reacting mixture. With appropriate equation(s), explain how water stops the reaction.

[8]

(b) Name and outline the reaction mechanism in Step I.

[3]

During the research of the project, the student found that DDT was used to control insect-borne diseases in the military and in agricultural purposes. It was suggested that DDT is a carcinogen and a pollutant as well in 1962. DDT was eventually banned world-wide in 1972, except in some third-world countries to control the spread of malaria.

(c) DDT is a chlorine-based compound, thus it is inert to biological degradation over time. The student decides to remove all the chlorine by refluxing DDT with aqueous NaOH so that DDT becomes bio-degradable. Briefly discuss the feasibility of this experiment. [Equations are not necessary.]

[3]

When the student went to take some aluminium chloride from the chemical store, he realized that <u>six</u> chemical bottles in another shelf were missing their labels. The labels are "Sodium Chloride", "Magnesium Chloride", "Magnesium Oxide", "Silicon Dioxide", "Phosphorous(V) Oxide" and "Phosphorous Pentachloride". He decided to perform some tests to deduce the identities of the chemicals in the unlabeled bottles, so that they can be re-labeled correctly.

The student named the six bottles **A to F**. The following solubility tests were conducted and the observations were as follow:

- Samples from bottles **A** and **B** are insoluble in water. However, sample **A** dissolves readily in hydrochloric acid, while sample **B** dissolves readily in aqueous sodium hydroxide.
- Samples from bottle **C** and **D** are soluble in water, but sample **C** gives a solution of pH 7, whereas sample **D** gives a solution of pH 5.
- Samples from bottles E and F melt at relatively low temperature as compared to A to D.
  Both of them reacted vigorously with water to form solutions containing strong acids.
  Furthermore, sample F gave off a thick white fume when reacted with water.
- (d) Suggest identities of A to F, writing the relevant balanced equations where necessary.

[6]

[Total: 20]

(a) Myglobin is a compact protein with a single polypeptide chain of 153 amino acid residues, including the following residues: leucine, threonine, tyrosine and tryptophan.

| Leucine (leu)   | Threonine (thr)          | Tyrosine (tyr)        | Tryptophan (trp)          |
|---|--------------------------|-----------------------|---------------------------|
| CH <sub>2</sub><br>H <sub>3</sub> C—CH<br>CH <sub>3</sub> | HO—CH<br>CH <sub>3</sub> | CH <sub>2</sub><br>OH | CH <sub>2</sub><br>N<br>H |

The R groups of the amino acids are given below:

- (i) In an aqueous external environment, which of the above four amino acid residues are orientated inward and outward of the compact structure? State your reasoning.
- (ii) Draw the structures of the predominant species of tyrosine and tryptophan when they are placed in solutions of
  - I pH 2
  - **II** pH 12
- (iii) Draw the displayed formula of —leu—thr—, which is part of the polypeptide chain in myoglobin.
- (iv) Write a general equation to show how a peptide bond in the primary structure is hydrolysed by aqueous sodium hydroxide.
- (v) Tyrosine exists as a white crystalline solid while phenol exists as a liquid at room temperature. Account for this observation in terms of bonding and structure.

[13]

- (b) Myoglobin consists of only 1 polypeptide chain arranged in a tertiary structure.
  - (i) Describe the tertiary structure of myoglobin.
  - (ii) Explain, in term of bonding and structure, why myoglobin tends to coagulate and precipitate when
    - I heated,
    - II subjected to changes in pH, and
    - **III**  $Hg^+(aq)$  is added.

[7]

[Total: 20]

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12