

## Preliminary Examinations 2008

Pre-university 3

## H2 CHEMISTRY

9746 / 03

Thursday

11 Sep 2008

2h

Additional materials: Foolscap Paper Data Booklet

## READ THESE INSTRUCTIONS FIRST

- 1. Do not turn over this question paper until you are told to do so.
- 2. Write your name, class and index number in the spaces provided at the top of this page and on all the work you hand in.
- 3. Write in *dark blue* or *black pen* on both sides of the paper.
- 4. You may use a soft pencil for any diagrams or graphs.
- 5. **DO NOT** use staples, paper clips, highlighters, glue or correction fluid or tape.
- 6. Answer **FOUR** out of five questions.
- 7. Give non-exact numerical answers correct to <u>3 significant figures</u>, or <u>1 decimal</u> <u>place</u> in the case of  $M_r$  and  $A_r$ , unless a different level of accuracy is specified in the question.
- 8. The number of marks is given in brackets [] at the end of each question or part question.
- 9. You are reminded of the need for *good English* and *clear presentation* in your answers and to *show all working* in calculations.
- 10. The use of a calculator is expected, where appropriate.

- 1. This question explores the physical and chemical properties of various types of halogen-containing compounds.
  - (a) (i) By considering the structure and bonding in each compound, explain why potassium chloride and silicon (IV) chloride shows a marked difference in their melting points.
    - (ii) State what is observed when separate samples of potassium chloride and silicon (IV) chloride are added to water.

Write equation(s) for the reaction(s) which occur and, in each case, state the approximate pH of the solution formed. [4]

(a) Potassium chloride and potassium bromide are white solids which dissolve in water to form colourless solutions.

To distinguish the above compounds, often silver nitrate solution is used, leading to the formation of white silver chloride and cream silver bromide precipitates.

Suggest an alternative chemical test to distinguish the two compounds. State clearly what will be observed for both compounds and write balanced equations for any reactions that occur. [4]

(c) A solution containing  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> of Ag<sup>+</sup> ions is slowly stirred into an equal volume of solution which contains KCl and KBr, each with the same concentration of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>.

The numerical values of the solubility products are:  $K_{sp} (AgCl) = 1.8 \times 10^{-10}$  $K_{sp} (AgBr) = 3.3 \times 10^{-13}$ 

Show with clear workings, what will be observed from above. [3]

- (b)  $CH_3CI$  can form  $(CH_3)_2NH$  when reacted with an excess of  $CH_3NH_2$ .
  - (i) Outline a mechanism to show the production of  $(CH_3)_2NH$ .
  - (ii) Draw the structural formula of two other possible compounds produced in the reaction.
- (c) CH<sub>3</sub>Cl can also react with phenol under various conditions, producing different compounds.

State the two different conditions possible for reaction with phenol and draw the products formed respectively. [4]

- 2. (a) Explain the underlying chemistry for the following observations.
  - (i) Barium oxide in water produces a solution which reacts with dilute hydrochloric acid to give a solution with a pH of about 7.
  - (ii) Formation of oxides of Group II metals from their respectively carbonates becomes increasingly endothermic down the group. [4]
  - (b) Describe the reaction, if any, of the oxides of sodium, aluminium and silicon with:
    - (i) NaOH(aq) and
    - (ii) HCl(aq).

Write balanced equations for all the reactions involved, if any. [4]

(c) Using the following data, draw an energy level diagram to show the stability of benzene relative to the hypothetical cyclohexa-1,3,5-triene.





(d) Consider the following reaction sequence which starts from phenylamine.



- (i) State and explain the difference in base strength between phenylamine and ammonia.
- (ii) Suggest a chemical test to distinguish phenylamine and ammonia, stating clearly the observations for both compounds.
- (iii) 4-nitrophenylamine can be directly synthesized from phenylamine. Give the reagent(s) and condition required for the conversion.
- (iv) Name and outline a mechanism for the reaction in (iii).
- (v) Name the type of linkage which is broken in Step 3 and hence suggest a suitable reagent and condition required for this step.

(a) Industrially, methanol, a useful fuel, can be manufactured from a 2:1
 hydrogen:carbon monoxide mixture at high pressure and a temperature of 300°C
 in the presence of a finely divided solid catalyst, e.g. Cu-Zn oxide.

Under these conditions, the equilibrium yield of methanol is only of the order of 1%, yet these are the conditions chosen for a continuous commercial process in which an overall conversion of 95% can be achieved.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$
  $\Delta H_{rxn} = -91 \text{ kJ mol}^{-1}$ 

- (i) Explain why the relatively low temperature of 300°C is chosen.
- (ii) Why is a catalyst necessary for this reaction?
- (iii) What type of catalysis does this illustrate? Explain, in detail, how the catalyst works in the reaction.
- (iv) Explain how a 95% conversion can be achieved in a reaction which has an equilibrium yield of only 1%.
- (v) Explain what is meant by the term *feasible reaction* and determine the temperature conditions at which the synthesis of methanol is no longer feasible.
- (b) There is a need to ensure that there is no leakage in the industrial setup for the production of methanol. This is because carbon monoxide is toxic and can cause brain damage or even death when breathe in.
  - (i) Explain, with reference made to haemoglobin, the toxicity of carbon monoxide.
  - (ii) Suggest a method to reverse the effect of CO poisoning. [3]

(c) Using an energy cycle, calculate a value for the standard enthalpy of combustion of methanol with reference to the data provided below. [2]

Enthalpy change of combustion of CO	–283 kJ mol <sup>-1</sup>
Enthalpy change of combustion of H <sub>2</sub>	–286 kJ mol <sup>–1</sup>
Enthalpy change of vaporization of CH <sub>3</sub> OH	35.3 kJ mol <sup>-1</sup>

(d) In a steam generator, the heat released from the combustion of methanol is used for boiling of water to produce steam. The steam produced is then used to generate electricity.

About 2.10 x  $10^4$  kg of methanol is burnt everyday.

(i) Given that only 85% of heat released from the combustion process will be effectively used in the steam generator, calculate the initial temperature of water that is used in the steam generator.

(Given: Volume of water in steam generator =  $1.40 \times 10^9 \text{ cm}^3$  and density of water = 1 g cm<sup>-3</sup>)

(ii) Sometimes gasoline (C<sub>8</sub>H<sub>8</sub>) can also be used in steam generator. Suggest one environmental problem caused by the burning of gasoline. [4]

4. (a) A biochemist must prepare a solution for use as a medium in an experiment involving acid-producing bacteria.

The acid is produced when the bacteria makes use of the enzymes, e.g. *Co–Zy*, it synthesises, to break down complex molecules into simpler substances.

The pH of the medium must not change with the addition of acid produced by the bacteria.

The solution for use as the medium is made by dissolving 43.0 g of a weak base -  $(HOCH_2)_3CNH_2$ , also known as TRIS, in 1 dm<sup>3</sup> of 0.095 mol dm<sup>-3</sup> HCl.

- (i) Illustrate, using an equation, how the solution can assist in maintaining the pH in an experiment involving acid-producing bacteria.
- (ii) Given that  $pK_b$  of TRIS is 5.91, calculate the pH of the solution.
- (iii) The bacteria produce 0.01 mol of H<sup>+</sup> in presence of 1 dm<sup>3</sup> of the solution.
  Calculate the change of pH in the solution. [5]
- (b) Discuss the validity of the following statements about water.
  - (i) Dilution with a small volume of water does not affect the pH of a buffer solution.
  - (ii) At 318 K, the value of  $K_w$  is  $4.02 \times 10^{-14}$  mol<sup>2</sup> dm<sup>-6</sup>. The pH of pure water was found to be 6.70. Hence pure water becomes acidic at 318 K. [3]

(c) Lysine and proline are some of the amino acids components found in the enzyme, *Co–Zy*, produced by the bacteria.



- (i) Draw a dipeptide using the amino acids above.
- (ii) Suggest and illustrate the type(s) of interaction(s) present in the tertiary structure of a chain made up of proline and lysine peptides.
- (ii) State and explain two factors which will cause the mentioned enzyme to lose its function.
- (d) Two different experiments are done by a student.

Experiment 1: To the following compound,



Step 1: Add aqueous NaOD, reflux Step 2: KMnO<sub>4</sub> in dilute H<sub>2</sub>SO<sub>4</sub>, reflux

Experiment 2: To the following compound,



Step 1: D<sub>2</sub>O, r.t.p. Step 2: Aqueous NaOD, r.t.p. Step 3: Cold DCN, NaOD

Draw the product(s) yielded in each step of the two experiments. [5]

2SO <sub>4</sub> <sup>2-</sup> (aq) +2.01
$Mn^{2+}(aq) + 4H_2O(l) + 1.51$
2Cl <sup>-</sup> (aq) +1.36
$2Cr^{3+}(aq) + 7H_2O(l) + 1.33$
$HNO_2(aq) + H_2O(l) + 0.94$
Fe <sup>2+</sup> (aq) +0.77

The concentration of iron (II) ions in aqueous solution can be determined by titrating the solution, after acidification, with a standard solution of potassium manganate(VII).

Explain why both hydrochloric acid and nitric acid are not suitable for use in the acidification of the solution in the above titration. [4]

- (b) The aqueous Mn<sup>3+</sup> ion is as powerful an oxidizing agent as manganate(VII), but it is rarely used because it readily disproportionates into solid MnO<sub>2</sub> and Mn<sup>2+</sup> ions.
  - (i) What is meant by 'disproportionates'?
  - (ii) Write a balanced equation to illustrate the above reaction.
  - (iii) State and explain how the tendency of the Mn<sup>3+</sup> ion to disproportionate would be affected by changes in the pH of the reaction mixture. [4]
- (c) As a strong oxidizing agent, potassium manganate(VII) plays a significant role in the elucidation of organic compounds as it is able to detect the presence of certain functional groups or features of the organic compounds.

Give examples of all possible functional groups which can be oxidized by acidified KMnO<sub>4</sub>. [2]

(d) Compound J, C<sub>7</sub>H<sub>11</sub>O<sub>2</sub>Cl, is a neutral organic extract. Chemical analysis of compound J shows the following results.

Upon refluxing with NaOH(aq) followed by acidification, **J** gives two compounds - compound **K**,  $C_3H_6O_3$ , and compound **L**,  $C_4H_8O$ .

Both K and L are optically active

L decolourised bromine water.

Treatment of **J** with acidified KMnO<sub>4</sub> produced compound **M**,  $C_3H_5O_2CI$ , and **N**. Effervescence is also observed. Gas evolved forms white precipitate with  $Ca(OH)_2$ .

N contains 40.91% carbon, 4.55% hydrogen and 54.54% oxygen by mass.

One mole of **N** requires one mole of  $NaHCO_3$  for complete neutralization.

Compound N reacted with alkaline  $I_2$  to give a pale yellow solid.

Orange crystalline precipitate is observed when 2, 4 - dinitrophenylhydrazine is added to **N**.

Explain the chemistry of the reactions described and hence deduce the structures of compounds J, K, L, M and N. [10]