

INNOVA JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION 2 in preparation for General Certificate of Education Advanced Level **Higher 2** 

CANDIDATE NAME			
CLASS		INDEX NUMBER	
CHEMISTRY			9746/03

## Paper 3 Free Response

09 September 2008 2 hours

Candidates answer on separate paper. Additional Materials: Writing Papers Graph Paper

**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 working. Do not use staples, paper clips, highlighters, glue or correction fluid.

Data booklet

Answer 4 out of 5 questions.

You are advised to show all working in calculations. You are reminded of the need for good English and clear presentation in your answers. You are reminded of the need for good handwriting. Your final answers should be in 3 significant figures.

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

This document consists of 10 printed pages and 0 blank page.



## Answer <u>4 out of 5</u> questions

1 The colours of various vanadium ions are given in the table below.

Oxidation Number of vanadiuim ions	V	IV	III	II
Colour	Yellow	Blue	Green	Violet

(a) Use  $E^{\theta}$  values from the *Data Booklet*, predict what colour changes will be observed when copper is added separately and in excess to ammonium vanadate(V), NH<sub>4</sub>VO<sub>3</sub>(aq), acidified with dilute sulfuric(VI) acid. Write balanced equation(s) for the reaction(s) you predict will occur.

[3]

- (b) Anhydrous copper sulfate, CuSO<sub>4</sub>(s), is a white powder that readily dissolves in water.
  - (i) Describe and explain using balanced equations, what is seen when  $CuSO_4(s)$  is stirred with water.
  - (ii) Describe and explain the final colour change seen when an excess of  $NH_3(aq)$  is added to  $CuSO_4(aq)$ .

[4]



- (i) Suggest an identity for compound **G**.
- (ii) The hydroxide ion and ethanol can take part in an acid-base reaction. Write an equation to represent this.
- (iii) Compound **F** undergo nucleophilic substitution reactions with different nucleophiles to form compound **G** and **H** respectively. Identify the two nucleophiles in the reactions.
- (iv) Suggest a simple chemical test by which compound **F** and bromobenzene can be distinguished from each other.

[5]



- (i) State the reagents and conditions needed for step I.
- (ii) Identify the compounds **K** and **L** in the above reactions.

[3]

- (e) A simple rechargeable battery may be constructed by dipping two lead electrodes into aqueous lead(II) nitrate and passing a current for a few minutes. During the process, lead(IV) oxide is deposited on one of the electrodes. When the power source is disconnected and a bulb is connected across the two electrodes, the bulb lights for a time as the cell discharges.
  - (i) Use the electrode reactions in the *Data Booklet* to predict the **two** halfequations during the discharge. Hence, construct the overall equation for the reaction that occurs.

Calculate the  $E^{\theta}_{\text{cell}}$  for this reaction.

(ii) In a lead-acid car battery, similar reactions take place but the electrolyte of dilute sulfuric acid causes the lead(II) ions to be precipitated as  $PbSO_4(s)$ , which coats the electrode. The  $E^{\theta}_{cell}$  of this cell is +2.0 V.

Explain the difference between this  $E^{\theta}_{cell}$  and the one calculated in (i) by reference to the concentrations the relevant aqueous ions.

[5]

2 lodine is poorly soluble in water. However, it dissolves in solutions containing iodide ions as the soluble  $I_3^-$  is formed.

4

The iodide ions and iodine molecules are in equilibrium with  $I_3^-$  (aq) ions as follows:  $I_2$  (aq) +  $I^-$  (aq)  $rac{1}{=} I_3^-$  (aq)

0.080 mol of iodine and 0.058 mol of potassium iodide were dissolved in 500 cm<sup>3</sup> of water until equilibrium is reached.

(a) Write the  $K_c$  expression for the equilibrium above, stating its units.

[1]

(b) If 0.0425 mol of iodine is present at equilibrium, find the equilibrium constant of the equilibrium obtained.

[3]

(c) The aqueous solution in (b) is then shaken with 800 cm<sup>3</sup> of toluene (methylbenzene), and some of the iodine molecules present at equilibrium dissolves in the toluene layer.

A special type of equilibrium constant known as partition coefficient describes the way a solute is distributed between two immiscible solvents A and B. It is the proportion of the concentration of solute in the two immiscible solvents.

Partition coefficient =  $\frac{[\text{solute in solvent A}]_{organic}}{[\text{solute in solvent B}]_{aqueous}}$ 

After some time, it is found that the concentration of iodine in the toluene layer is  $0.0525 \text{ mol dm}^{-3}$ .

- (i) Find the amount of iodine in the aqueous layer.
- (ii) Hence, calculate the partition coefficient for iodine distributed between a layer of toluene and a layer of water at this temperature.
- (iii) Comment on your answer in part (ii) based on the interactions between molecules of iodine with each other, and also with the solvent.

[6]

(d) Methanol can be synthesized from carbon monoxide and hydrogen as follows:

Step 1: 
$$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$$
  $\Delta H > 0$ 

Step 2: CO (g) + 
$$2H_2$$
 (g) CH<sub>3</sub>OH (l)  $\Delta H < 0$ 

- (i) Suggest, with reasons, what conditions of temperature and pressure should be used to obtain a high equilibrium yield of the methanol based on Step 2.
- (ii) Suggest an economic advantage of operating these two steps in reaction vessels close to each other in an industrial plant.

[5]

- (e) An inorganic iodine compound, phosphorous tri-iodide, PI<sub>3</sub>, is unstable to be stored. Hence, it is often generated in situ from red phosphorous and iodine for its use in organic synthesis of products.
  - (i) Draw the structural formula of the organic product formed when methanol reacts with red phosphorous and iodine in situ.
  - (ii) In order to obtain the clean organic product in the reaction in (i), the products are often washed with sodium carbonate instead of sodium hydroxide.
    - Suggest one reason for the use of sodium carbonate in this step.
    - Explain why sodium hydroxide is not the preferred washing reagent.
  - (iii)  $PI_3$  and  $BI_3$  can react in a mole ratio of 1:1 to form an addition product.
    - Draw the structural formula of the addition product.
    - State the shape of the product about phosphorus atom.
    - Suggest the type of bond formed.

[5]

**3** One of the methods of preparing esters is to react together an alcohol with a carboxylic acid. This process is reversible by the reaction called ester hydrolysis. An ester, RCOOR' is hydrolysed by dilute hydrochloric acid according to the equation:

$$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$$

The table below lists the variation of the concentration of the ester with time for the two different experiments using different concentrations of hydrochloric acid at constant temperature.

Time/minute	[RCOOR'] / mol dm <sup>-3</sup>	[RCOOR'] / mol dm <sup>-3</sup>
	when [HC <i>l</i> ] = 0.20 mol dm <sup>-3</sup>	when [HC <i>l</i> ] = 0.40 mol dm <sup>-3</sup>
0	0.160	0.160
10	0.144	0.130
20	0.128	0.100
30	0.114	0.080
40	0.100	0.066
50	0.090	0.054

- (a) Plot these data on suitable axes.
- (b) Use your graph to determine the order of reaction with respect to
  - (i) ester, RCOOR' and
  - (ii) hydrochloric acid, HCl
  - (iii) Hence, write the rate equation for the reaction and calculate the rate constant of the reaction.
- (c) At the end of the experiment, only about 20% of the carboxylic acid was formed. Explain why this is so.
- (d) Explain how a catalyst increases the rate of a chemical reaction and its effect on rate constant.

[10]



- (i) Identify the electrophile in step I.
- (ii) State the reagents and conditions of steps II to IV.
- (iii) Draw the displayed formula of Compound R.
- (iv) Name the type of reaction in step II and briefly describe why this is not a good method to obtain Compound **Q**.
- (v) Describe a simple chemical test to distinguish Compound **P** from Compound **Q**.
- (vi) State which type of isomerism would be shown by Compound S. Draw the structural formulae to illustrate the isomers of Compound S.

[10]

4 TNT (2, 4, 6 – trinitromethylbenzene) was first prepared in 1863 by German chemist Joseph Wilbrand and originally used as a yellow dye. Its potential as an explosive was not appreciated for several years mainly because it was so difficult to detonate and because it was less powerful than alternatives. TNT is quite an explosive material. It can quickly destroy anything within its blast radius when detonated.

In the process of detonation, TNT is oxidized in the presence of excess oxygen into the stable products of CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub>. The energy produced during the formation of these products from 1 mole of TNT is known as enthalpy of detonation,  $\Delta H_d$ , in kJ mol<sup>-1</sup>.

- (a) State Hess's Law.
- (b) (i) Write down a balanced equation showing the detonation of 1 mole of TNT. Given the data below, construct an energy cycle to calculate the standard enthalpy change of detonation of TNT. Standard enthalpy change of formation,  $\Delta H^{\theta}_{f}$  of TNT = -54 kJmol<sup>-1</sup> Standard enthalpy change of formation,  $\Delta H^{\theta}_{f}$  of H<sub>2</sub>O, = -242 kJmol<sup>-1</sup> and Standard enthalpy change of combustion,  $\Delta H^{\theta}_{c}$  of carbon = -394 kJmol<sup>-1</sup>
  - (ii) The energy obtained from experimentally detonating TNT was 2545 kJ mol<sup>-1</sup>. Suggest a reason for the discrepancy from the value that was obtained in b(i).
  - (iii) Determine the sign of  $\Delta S$  of the detonation of TNT. Hence, or otherwise, explain why the detonation is always spontaneous.
  - (iv) Explain, in energy terms, why is TNT so explosive.

[9]

- (c) TNT can be synthesized in the laboratory in a three-step nitration of methylbenzene.
  - (i) Name the type of reaction and write the equation to show the *first* step of the synthesis of TNT from methylbenzene.
  - (ii) "Subsequent nitrations after the first one of the ring become more difficult". Comment on this sentence.
  - (iii) TNT can be converted into a non toxic form by reducing it to an amine,



State the reagent(s) and conditions required for this conversion.

[5]

- (d) Explain each of the following observations. Write balanced equations where appropriate.
  - (i) MgCO<sub>3</sub> undergoes thermal decomposition at a much lower temperature  $(353 \text{ }^{\circ}\text{C})$  than BaCO<sub>3</sub> does (1430  $^{\circ}\text{C})$ .
  - (ii) Mg and Ca metal react differently with water and give different pH values.

[6]

[Total:20]

[Turn over

- **5** Isobutylene, also known as 2-methylpropene, has significant industrial importance. It is the starting material for Methacrolein, which is a chemical used in the production of polymers.
  - (a) (i) Give the structural formulae of the two products that may be formed when hydrogen bromide is added to isobutylene.
    - (ii) State the type of reaction and show the mechanism using relevant equations.
    - (iii) Draw the two possible carbocations formed in the reaction and explain why one is formed in greater proportion to the other.

[7]

(b) Methacrolein is a clear colourless flammable liquid that has the following structure.



Suggest a 3-steps synthesis to show how Methacrolein can be converted to compound **W**.



Compound **W** 

Suggest reagents and conditions for each step and identify the intermediates.

[3]

- (c) (i) Solid sodium bromide and concentrated sulfuric acid react to give orange brown fumes.
  Construct balanced equations to explain the observations.
  - (ii) Suggest why aqueous solution of hydrogen fluoride is a much weaker acid compared to that of hydrogen bromide.

[4]

(d) The table below relates to oxides of Period 3 in the Periodic Table.

Oxide	Silicon Oxide SiO <sub>2</sub>	Sulphur Trioxide $SO_3$	
Melting Point /°C	1830	33	

- (i) With reference to the melting point of sulphur trioxide in the above table. Explain why the melting point of sulphur dioxide is less than 33°C.
- (ii) Given that the melting point of silicon chloride is -70°C. Explain the large difference in melting point between silicon chloride and silicon oxide.

[6]