



# UNIVERSITY OF TECHNOLOGY, JAMAICA

## DEPARTMENT OF SCIENCE AND MATHEMATICS

### SEMESTER II EXAMINATION

GROUP: Sci. Ed. 2

DATE: APRIL/MAY 2009

SUBJECT: PHYSICAL CHEMISTRY (CHY2007)

DURATION: 2 HRS

INSTRUCTION: ANSWER ANY FOUR (4) QUESTIONS

$$R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \text{ kPa mol}^{-1} \text{ K}^{-1};$$
$$760 \text{ mmHg} = 1 \text{ atm} = 101.3 \text{ kPa} = 760 \text{ Torr}; 1 \text{ F} = 96,500 \text{ C}$$

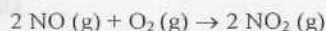
#### QUESTION NO. 1

- (a) The data shown below were collected for a second order reaction. Use an Arrhenius plot to determine the activation energy barrier and frequency factor for the reaction.

Temperature (K)	Rate Constant (L/mol.s)
90	0.00370
100	0.0773
110	0.956
120	7.781

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- [8]
- (b) The half-life for the first order reaction:  $2 \text{ N}_2\text{O}_5 (\text{g}) \rightarrow 4 \text{ NO}_2 (\text{g}) + \text{ O}_2 (\text{g})$  is 2.20 h at 30.0°C.
- (i) Calculate the rate constant for this reaction at 30.0°C. [2]
- (ii) Starting with 3.00 g of  $\text{N}_2\text{O}_5$ , how much of it remains after 8.8 h? [2]
- (iii) What length of time will be required for 0.0280 M  $\text{N}_2\text{O}_5$  to decrease to 0.0160 M? [2]
- (c) The reaction of nitrogen monoxide with oxygen is shown by the equation:



The rate of reaction can be found by measuring the concentration of  $\text{NO}_2$  at different times.

- (i) Define the term *rate of reaction*. [2]
- (ii) Sketch a graph to show how the concentration of  $\text{NO}_2$  changes with time. Indicate how the initial rate of reaction could be obtained from your graph. [4]

**Total = 20 marks**

**QUESTION NO. 2**

(a) Define the terms:

- (i) standard enthalpy of combustion [3]
- (ii) bond energy [3]

(b) Explain why enthalpy is classified as a state function. [2]

(c) Using the standard enthalpies of formation given in the table below calculate a value for the enthalpy of combustion,  $\Delta H_c^\theta$ , of propan-1-ol,  $C_3H_7OH$ . You will need to write a balanced equation for the combustion of propan-1-ol. [3]

	$C_3H_7OH(l)$	$O_2(g)$	$CO_2(g)$	$H_2O(l)$
$\Delta H_f^\theta$ (kJ mol <sup>-1</sup> )	-315	0	-394	-286

(d) In an experiment, 0.92 g of propan-1-ol, was burned and the heat given off used to raise the temperature of 250 g of water. The temperature rise was 16 °C. Given that the specific heat capacity of water is 4.2 J K<sup>-1</sup> g<sup>-1</sup>, calculate the molar enthalpy of combustion of propan-1-ol. [4]

(e) The equation for the formation of nitrogen trifluoride is given below:

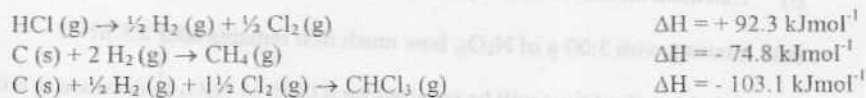


(i) Using the mean bond enthalpy values in the following table, calculate a value for the enthalpy of formation of nitrogen trifluoride. [3]

<b>Bond</b>	N-F	N≡N	F-F
<b>Mean bond enthalpy (kJ mol<sup>-1</sup>)</b>	278	945	159

(ii) A data book value for the enthalpy of formation of nitrogen trifluoride is -114 kJ mol<sup>-1</sup>. Give one reason the answer you have calculated in part (e) (i) is different from this data book value. [1]

(f) Using Hess's Law and the following reaction equations:



Calculate the standard enthalpy of reaction for the process:



**Total = 20 marks**

### QUESTION NO. 3

The acid dissociation constant,  $K_a$ , for propanoic acid has the value  $1.35 \times 10^{-5} \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ .

- (a) Calculate the pH of a  $0.169 \text{ mol dm}^{-3}$  solution of propanoic acid. [3]
- (b) A buffer solution contains  $0.250 \text{ mol}$  of propanoic acid and  $0.190 \text{ mol}$  of sodium propanoate in  $1 \text{ dm}^3$  of solution. A  $0.015 \text{ mol}$  sample of solid sodium hydroxide is then added to this buffer solution.
- (i) Using the buffer solution above explain how a buffer works. [3]
- (ii) Write an equation for the reaction of propanoic acid with sodium hydroxide. [1]
- (iii) Calculate the number of moles of propanoic acid and of propanoate ions present in the buffer solution, after the addition of the sodium hydroxide. [2]
- (iv) Calculate the pH of the buffer solution after the addition of the sodium hydroxide. [2]
- (c) In an experiment to determine the solubility product constant,  $K_{sp}$ , of calcium hydroxide, a saturated solution of calcium hydroxide at  $25^\circ\text{C}$  is carefully filtered into a clean dry flask.  $25.00 \text{ cm}^3$  of this solution are pipetted into a conical flask and three drops of phenolphthalein indicator added. The solution needs  $11.50 \text{ cm}^3$  of  $0.10 \text{ mol dm}^{-3}$  hydrochloric acid for neutralization.
- (i) Explain how the results of the above experiment can be used to obtain a value for the solubility product constant of calcium hydroxide at  $25^\circ\text{C}$ . [4]
- (ii) Calculate the solubility product constant,  $K_{sp}$ , of calcium hydroxide at  $25^\circ\text{C}$ . [5]

**Total = 20 marks**

### QUESTION NO. 4

- (a) Pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) is a weak base with  $K_b = 2 \times 10^{-9}$  at  $25^\circ\text{C}$ . What is the pH of a solution prepared by diluting  $5.00 \text{ g}$  of pyridine in water to a total volume of  $155 \text{ cm}^3$  at  $25^\circ\text{C}$ ? [5]
- (b) State Bronsted-Lowry's definitions of acids and bases. [2]
- (c) Calculate the concentration of  $\text{Ag}^+$  in a saturated solution of silver carbonate when the concentration of  $\text{CO}_3^{2-}$  ion is  $0.025 \text{ M}$  ( $K_{sp} = 8.1 \times 10^{-12}$ ). [3]
- (d) Briefly describe **face centered** and **hexagonal close packing** of solids. Use diagrams and/or suitable examples to clearly illustrate your answer. [3]
- (e) (i) State Graham's Law of molecular effusion. [2]
- (ii) If the density of hydrogen is  $0.09 \text{ g/L}$  and its rate of effusion is 6 times that of chlorine, what is the density of chlorine? [2]
- (iii) If  $9.006 \text{ g}$  of a gas are enclosed in a  $50.0 \text{ L}$  vessel at  $273.15 \text{ K}$  and  $2.000 \text{ atm}$ . What is the molar mass of the gas? Based on your answer, suggest an identity for the gas. [3]

**Total = 20 marks**

**QUESTION NO. 5**

The table below shows some standard electrode potentials.

	$E^{\theta}/V$
$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$	+ 0.77
$Cr^{3+}(aq) + e^{-} \rightarrow Cr^{2+}(aq)$	-0.41
$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$	-0.76
$Cr^{2+}(aq) + 2e^{-} \rightarrow Cr(s)$	-0.91

(a) Predict the products, if any, when the following substances are mixed. In each case use  $E^{\theta}$  values from the table to explain your answer.

- (i) iron metal with aqueous zinc (II) ions
- (ii) aqueous iron (III) ions with aqueous chromium (II) ions. [5]

(b) Calculate the e.m.f. of the following standard cell and deduce an equation for the overall cell reaction.

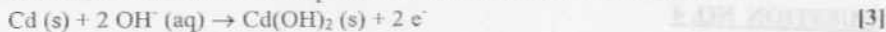


(c) (i) Using the reaction in 5 (b) above construct a well labeled galvanic cell. [3]

(ii) Briefly explain the function of the salt bridge in this galvanic cell. [2]

(d) (i) State Faraday's law. [2]

(ii) How many grams of Cadmium are consumed in a nickel-cadmium battery if it operates at a constant current of 1.0-amp for 90 s? The half reaction of interest is:



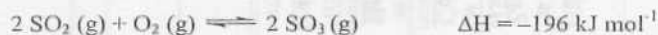
(e)  $CaCl_2(s)$  has a standard lattice dissociation enthalpy of  $+2237 \text{ kJ mol}^{-1}$ . The standard enthalpy of hydration values for  $Ca^{2+}(g)$  and  $Cl^{-}(g)$  are  $-1650 \text{ kJ mol}^{-1}$  and  $-364 \text{ kJ mol}^{-1}$ , respectively. Calculate the standard enthalpy of solution of  $CaCl_2(s)$ . [3]

**Total = 20 marks**

### QUESTION NO. 6

Colourless  $\text{N}_2\text{O}_4$  (g) decomposes on warming to give brown  $\text{NO}_2$  (g). 0.10 mol of  $\text{N}_2\text{O}_4$  (g) is placed in a  $1.0 \text{ dm}^3$  bulb and sealed and the bulb is heated to  $100^\circ\text{C}$ . When the equilibrium is established, 0.035 mol of  $\text{N}_2\text{O}_4$  (g) is found to be present.

- (a) (i) State TWO (2) characteristics of a system in dynamic equilibrium. [2]
- (ii) Write an equation for the equilibrium that exists between  $\text{N}_2\text{O}_4$  (g) and  $\text{NO}_2$  (g). [1]
- (iii) Predict what may be observed when the bulb is heated to  $200^\circ\text{C}$ . [1]
- (iv) Explain how you arrived at the prediction made in (iii). [3]
- (v) 0.40 mol  $\text{N}_2\text{O}_4$  is introduced into the system at  $100^\circ\text{C}$ . What is the effect on the equilibrium constant,  $K_c$ ? [1]
- (vi) Briefly explain your answer in a (v). [2]
- (vii) Calculate the value of  $K_c$  at  $100^\circ\text{C}$ . [3]
- (b) When sulphur dioxide and oxygen are mixed in a closed container and heated in the presence of a catalyst, the following equilibrium is established.



- (i) In an equilibrium mixture established at temperature  $T_1$ , the partial pressure of sulphur dioxide is 10.6 kPa and the partial pressure of sulphur trioxide is 90.8 kPa. Calculate the partial pressure of oxygen in this mixture, given that the value of  $K_p$  for the equilibrium at temperature  $T_1$  is 1.42. [2]
- (ii) A mixture of sulphur dioxide, oxygen and sulphur trioxide has reached equilibrium in a closed container at temperature  $T_1$ . State and explain the effect on the mole fraction of sulphur trioxide in the equilibrium mixture if the volume of the container is decreased at constant temperature. [2]
- (iii) When the temperature of the equilibrium mixture is changed from  $T_1$  to  $T_2$  at constant volume, the partial pressure of sulphur trioxide decreases. Deduce which temperature,  $T_1$  or  $T_2$ , is the higher. Explain your answer. [3]

**Total = 20 marks**

\*\*\*\*\*END OF PAPER\*\*\*\*\*

