



# NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

FACULTY OF APPLIED SCIENCES

DEPARTMENT OF APPLIED CHEMISTRY

PHYSICAL CHEMISTRY 1 FOR TCE STUDENTS

SCH1120

First Semester Examination Paper

December 2014

This examination paper consists of 6 pages

**Time Allowed: 3 hours**

**Total Marks: 100**

**Examiner's Name: Dr. Stephen Majoni**

**Useful information:**  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $1 \text{ atm} = 101\,325 \text{ Pa}$ ;  $1 \text{ bar} = 1 \times 10^5 \text{ Pa}$

## INSTRUCTIONS

1. Answer ALL questions in section A and any three (3) questions in section B
2. Each question in section A carries 10 marks and in section B carries 20 marks

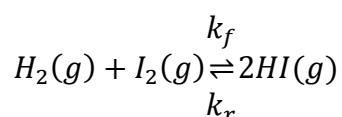
## MARK ALLOCATION

QUESTION	MARKS
A1.	10
A2.	10
A3.	10
A4.	10
B1	20
B2	20
B3	20
B4	20
<b>TOTAL</b>	<b>100</b>

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## SECTION A

1. (a) A 237 g piece of molybdenum, initially at 100.0 °C, was dropped into 244g of water at 10.0 °C. When the system came to thermal equilibrium, the temperature was 15.3°C. What is the specific heat capacity of molybdenum? [6 marks]
- (b) Molar heat capacity of a substance for a process occurring at constant pressure is greater than at constant volume, discuss. [4 marks]
2. The equilibrium constant for the reaction of hydrogen with iodine is 57.0 at 700 K.



- a) Is the rate constant  $k_f$  for the formation of HI larger or smaller than the rate constant  $k_r$  for the decomposition of HI?
- b) The value of  $k_f$  at 700 K is  $1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ . What is the value of  $k_r$  at the same temperature? [10marks]
3. (a) Write the equilibrium expression and calculate the equilibrium constant of the reaction  $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ , given that  $\Delta_R G^\theta = 32.90 \text{ kJ mol}^{-1}$  at 25°C. [5 marks]
- (b) A compound X undergoes two simultaneous first order reactions as follows:  $X \rightarrow Y$  with rate constant  $k_1$  and  $X \rightarrow Z$  with rate constant  $k_2$ . The ratio of  $k_1/k_2$  at 40°C is 8.0. What is the ratio at 300°C? The frequency factors of the two reactions are the same. [5 marks]

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4. (a) You are running the reaction  $2A + B \rightarrow 2C + 3D$ . Your lab partner has conducted the first two experiments to determine the rate law for the reaction by the method of initial rates.

Experiment #	[A] (M)	[B] (M)
1	0.0250	0.0330
2	0.0500	0.0330

Presuming that you can measure the initial rate of each experiment, which of the following concentrations for Experiment 3 would help you to determine the rate law easily?

- a)  $[A] = 0.0330 M$ ;  $[B] = 0.0330 M$
- b)  $[A] = 0.0125 M$ ;  $[B] = 0.0500 M$
- c)  $[A] = 0.0250 M$ ;  $[B] = 0.0400 M$
- d)  $[A] = 0.0250 M$ ;  $[B] = 0.0330 M$
- e)  $[A] = 0.0500 M$ ;  $[B] = 0.0330 M$

[4 marks]

- (b) At 298.15 K and a particular pressure, a real gas has a fugacity coefficient  $\Theta$  of 2.00. At this pressure, what is the difference in the chemical potential of this real gas and an ideal gas?

[6 marks]

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## SECTION B

1. Ammonia decomposes when heated according to the following equation



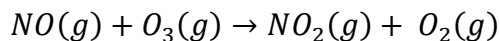
The data below was obtained from an experiment.

Time (hours)	$[NH_3]$ (mol L <sup>-1</sup> )
0	$8.00 \times 10^{-7}$
25	$6.75 \times 10^{-7}$
50	$5.84 \times 10^{-7}$
75	$5.15 \times 10^{-7}$

Evaluate the order of the reaction and the rate constant [20 marks]

2. (a) Pure iodine (105 g) is dissolved in 325 g of CCl<sub>4</sub> at 65 °C. Given that the vapour pressure of CCl<sub>4</sub> at this temperature is 531 mm Hg, what is the vapour pressure of the CCl<sub>4</sub>-I<sub>2</sub> solution at 65°C (assume I<sub>2</sub> does not contribute to the vapour pressure) [8 marks]

- (b) The reaction between nitrous oxide and ozone occur as follows



Given that the activation energy for the forward reaction is 10 kJ and the  $\Delta_r H^\circ$  is -200 kJ.

- (i) Sketch a potential-energy diagram for the reaction of nitric oxide with ozone.
- (ii) What is the activation energy for the reverse reaction? Label your diagram appropriately. [12 marks]

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3. (a) Using the following data, calculate  $\Delta_R G^0$  and K at 298.15 K for the reaction

$\text{CO(g)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ ; Based on the value of K, do you expect the mixture to consist mainly of  $\text{CO(g)}$  and  $\text{H}_2\text{O(l)}$  or  $\text{CO}_2\text{(g)}$  and  $\text{H}_2\text{(g)}$ ;

	$\Delta_f G^0$
$\text{CO(g)}$	-137.2 kJ/mol
$\text{H}_2\text{O(l)}$	-237.1 kJ/mol
$\text{CO}_2\text{(g)}$	-394.4 kJ/mol
$\text{H}_2\text{(g)}$	0

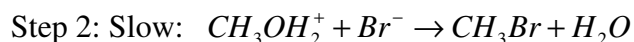
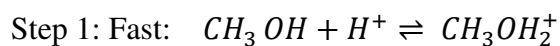
[8 marks]

(b)  $K_c$  for the reaction  $\text{I}_2\text{(g)} \rightleftharpoons 2\text{I(g)}$  is  $5.6 \times 10^{-12}$  at 500K; A mixture has  $[\text{I}_2] = 0.020 \text{ M}$  and  $[\text{I}] = 5.6 \times 10^{-12} \text{ M}$ . Is the reaction at equilibrium (at 500K)? If not, which way must the reaction proceed to attain equilibrium? [6 marks]

(c) The equilibrium constant for the reaction  $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$  at 25°C is 170. If 0.170 M  $\text{N}_2\text{O}_4$  is placed in a flask at 25°C, what is the percentage of the original  $\text{N}_2\text{O}_4$  that has reacted? [6 marks]

4. (a) Given that the reaction of  $\text{CH}_3\text{OH}$  and  $\text{HBr}$  is believed to occur via the following mechanism with a rate law given by:

$$\text{rate} = k[\text{CH}_3\text{OH}][\text{H}^+][\text{Br}^-]$$



Is the above mechanism valid, and what is the order of reaction with respect to the reacting species and the overall order of the reaction? [8 marks]

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(b) The temperature of 0.5 moles of a solid is raised from 300 to 900 K at a fixed pressure. Given that the molar heat capacity of the solid is given by the following expression.

$$C_{p,m} / (JK^{-1}mol^{-1}) = 16.88 + 4.77 \times 10^{-3}T - 8.54 \times 10^{-5}T^2$$

- i) Calculate  $\Delta H$ , and  $\Delta S$
- ii) Would it be safe to assume that the heat capacity is constant over the entire temperature range and maintains its value at 300 K. [12 marks]

***END OF QUESTION PAPER!!!***