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 = $8.314 JK^{-1} mol^{-1}$; 1 atm = 101 325 Pa; $1\ bar = 1\times10^{5}\ Pa$

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**
TOTAL	**100**

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.

$$H_2(g) + I_2(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2HI(g)$$

   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 $1 \times 10^{-5} \mathrm{M}^{-1}\mathrm{s}^{-1}$. 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 $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$, given that $\Delta_R G^{\theta} = 32.90$ kJ mol^{-1} at 25°C. [5 marks]

   (b) A compound X undergoes two simultaneous first order reactions as follows: X → Y with rate constant k_1 and X → 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]

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 Θ of 2.00. At this pressure, what is the difference in the chemical potential of this real gas and an ideal gas? [6 marks]

SECTION B

1. Ammonia decomposes when heated according to the following equation

$$NH_3(g) \rightarrow NH_2(g) + H(g)$$

The data below was obtained from an experiment.

Time (hours)	$[NH_3]$ (mol L^{-1})
0	8.00×10^{-7}
25	6.75×10^{-7}
50	5.84×10^{-7}
75	5.15×10^{-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_4 at 65 °C. Given that the vapour pressure of CCl_4 at this temperature is 531 mm Hg, what is the vapour pressure of the CCl_4-I_2 solution at 65°C (assume I_2 does not contribute to the vapour pressure) [8 marks]

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

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

Given that the activation energy for the forward reaction is 10 kJ and the $\Delta_r H^0$ 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]

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

$CO(g) + H_2O(l) \rightleftharpoons CO_2(g) + H_2(g)$; Based on the value of K, do you expect the mixture to consist mainly of $CO(g)$ and $H_2O(l)$ or $CO_2(g)$ and $H_2(g)$;

	$\Delta_f G^o$
$CO(g)$	-137.2 kJ/mol
$H_2O(l)$	-237.1 kJ/mol
$CO_2(g)$	-394.4 kJ/mol
$H_2(g)$	0

[8 marks]

(b) K_c for the reaction $I_2(g) \rightleftarrows 2I(g)$ is 5.6×10^{-12} at 500K; A mixture has $[I_2] = 0.020$ M and $[I] = 5.6 \times 10^{-12}$ 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 $N_2O_4(g) \rightleftarrows 2NO_2(g)$ at 25°C is 170. If 0.170 M N_2O_4 is placed in a flask at 25°C, what is the percentage of the original N_2O_4 that has reacted? [6 marks]

4. (a) Given that the reaction of CH_3OH and HBr is believed to occur via the following mechanism with a rate law given by:

$$rate = k[CH_3OH][H^+][Br^-]$$

Step 1: Fast: $CH_3OH + H^+ \rightleftharpoons CH_3OH_2^+$

Step 2: Slow: $CH_3OH_2^+ + Br^- \rightarrow CH_3Br + H_2O$

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]

(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 ΔH, and ΔS

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!!!