# NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

**FACULTY OF APPLIED SCIENCES**

**DEPARTMENT OF APPLIED CHEMISTRY**

**PHYSICAL CHEMISTRY FOR ENGINEERS**

**SCH1120**

**END OF SEMESTER EXAMINATION PAPER**

**December 2015**

This examination paper consists of 5 pages

**Time Allowed:** **3 hours**

**Total Marks:** **100**

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

**Useful information:** R = 8.314J $K^{-1}$ $mol^{-1}$; 1 *atm* = 101 325 Pa; 1 *bar* $= 1 \times 10^5$ *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 POSSIBLE** | **100** |

## SECTION A

1. a) Using water as an example, explain the terms triple point and critical point as applied to phase equilibrium. [4 marks]

   b) Discuss the concept of a slow cooker. [2 marks]

   c) With the aid of diagrams, discuss what happens to a solid when it is heated at a pressure which is:

      i) Lower than its triple point

      ii) Higher than its triple point [4 marks]

2) a) Colligative properties concept has found numerous applications in science and everyday life. Explain what you understand by the term 'colligative property'. [2 marks]

   b) Using appropriate diagram(s) discuss the origin and common applications of any two colligative properties. [8 marks]

3. a) Hydrogen and iodine react according to the following equation with equilibrium constant($K_C$) of 49.7 at 458 °C

   $$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

   Suppose 1.00 mol $H_2$ (g) and 2.00 mol $I_2$ (g) are placed in a vessel. Determine the equilibrium composition at this temperature. [5 marks]

   b) Calculate the emf at 25°C of the cell: Pt| $H_2$ (1 bar)|$H_2SO_4$ (0.001 M)|$CrSO_4$ (s)|Cr

   The standard electrode potentials are given below:

   $CrSO_4(s) + 2e^- \rightarrow Cr(s) + SO_4^{2-} \quad E^0 = -0.400$ [5 marks]

4. a) At 170K, the molar enthalpy of fusion of solid ammonia is 5.65 kJ $mol^{-1}$, and the molar entropy of fusion is 28.9 J $K^{-1}$ $mol^{-1}$. Is the transition shown in the equation below at equilibrium or not? if not, in which direction is the reaction proceeding in and at what temperature is the reaction going to be at equilibrium? [6 marks]

$$NH_3\,(s) \rightleftharpoons NH_3(l)$$

4. b) Ammonia is formed according to the reaction below. Under certain conditions the rate at which ammonia is formed was found to be 0.75 M $s^{-1}$.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

What are the rates of consumption of $N_2$ and $H_2$? What is the rate of reaction?

[4 marks]

## SECTION B

1. a) The following data were collected for the reaction of NO and $O_2$ as shown below

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

| Exp. No | initial [NO] M | initial [$O_2$] M | Initial rate (M $s^{-1}$) |
|---|---|---|---|
| 1 | 0.0126 | 0.125 | $1.41 \times 10^{-2}$ |
| 2 | 0.0252 | 0.250 | $1.13 \times 10^{-1}$ |
| 3 | 0.0252 | 0.125 | $5.64 \times 10^{-2}$ |

i) Write down the equations for the first order, and the second order reactions.

ii) Determine the rate law for the reaction.

iii) From the rate law, what is the overall order of reaction? [12 marks]

b) Given that two phases (α and β) are at equilibrium and

$d\mu_\alpha = -S_{m,\alpha}dT + V_{m,\alpha}dP$; derive the Clapeyron equation shown below

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

[8 marks]

2. a) 2.5 moles of a solid is heated from 200 to 900 K at normal pressure, the molar heat capacity of the solid is given by the following expression.

$$C_{p,m}/(JK^{-1}mol^{-1}) = 16.88 + 4.77\times10^{-3}T - 8.54\times10^{-5}T^{2}$$

When calculating ΔH and ΔS, what is the error associated with assuming that the heat capacity is constant over the entire temperature range maintaining its value at:

i) 300 K.

ii) 350 K

iii) 400K [15 marks]

b) Show that the accurate solubility product of a 2:1 electrolyte such as $BaCl_2$ is represented as

$$K_{sp} = \gamma_{\pm}^{3}[Ba^{2+}][Cl^{-}]^{2}$$

Where $\gamma_{\pm}$ is the mean ionic activity coefficient [5 marks]

3. The Haber-Bosch process for the production of ammonia, shown below, is one of the key industrial processes in developed countries.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

a) Using the data below, calculate $\Delta_r G^o$ for the reaction at 298 K, 800 K, and 1300K

| Temperature (K) | $\Delta_r H^o\ (kJmol^{-1})$ | $\Delta_r S^o\ (JK^{-1}mol^{-1})$ |
|---|---|---|
| 298 | -91.8 | -198.12 |
| 800 | -107.4 | -225.4 |
| 1300 | -112.4 | -228.0 |

How does the free energy change for the reaction change with temperature?

b) Calculate the equilibrium constant at each of the three temperatures.

c) Starting with one mole each of $N_2$ and $H_2$, derive a function that can be used to determine the mole fraction of ammonia in the equilibrium mixture at each of the three temperatures. [20 marks]

4. a) The following reaction mechanism has been proposed for a chemical reaction:

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + A \qquad \text{(fast equilibrium)}$$

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} AB \qquad \text{(fast equilibrium)}$$

$$AB + CD \xrightarrow{k_3} AC + BD \qquad \text{(Slow)}$$

i) Write a balanced equation for the overall reaction

ii) Deduce the rate expression that corresponds to the preceding mechanism and express the rate in terms of the reactants only [7 marks]

b) The catalytic decomposition of ozone can be represented as follows

$$step\ 1: \quad NO + O_3 \xrightarrow{k_1} NO_2 + O_2$$

$$step\ 2: \quad NO_2 + O \xrightarrow{k_2} NO + O_2$$

Identify the catalyst and, using the steady state approximation, show that the overall rate of the reaction $(\upsilon) = \frac{1}{2}\frac{d[O_2]}{dt} = -\frac{d[O]}{dt}$ [13 marks]

***End of Question Paper!!!***