NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

FACULTY OF APPLIED SCIENCE

DEPARTMENT OF APPLIED CHEMISTRY

PHYSICAL CHEMISTRY I – SCH 2104

First Semester Examination Paper

December 2016

This examination paper consists of 6 pages

Time Allowed: **3 hours**

Total Marks: **100**

Special Requirements: **Graph Paper (on request)**
R = 8.314 JK^{-1} mol^{-1}= 0.08206 dm^3 atm K^{-1} mol^{-1}
F = eNA = 9.6500x10^4 C mol^{-1}
1 atm = 760 torr = 760 mmHg = 101325 Pa

Examiner's Name: **DR B N YALALA**

INSTRUCTIONS

1. **Answer all questions from Section A and any three from Section B. Section A carries 40 marks and each question in Section B carries 20 marks.**

MARK ALLOCATION

QUESTION	MARKS
1.	**40**
2.	**20**
3.	**20**
4.	**20**
5.	**20**
TOTAL POSSIBLE MARKS	**100**

SECTION A:

1. (a) Evaluate $\Delta G°$ for the reaction in which diatomic hydrogen and oxygen gases react to form water vapor at 298K, using values of $\Delta H_f°$ and S°. Is the reaction spontaneous at 298K?

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g).$$

	ΔH_f^o kJ/mol	S^o J/mol K
$H_2(g)$	0	130.6
$O_2(g)$	0	205
$H_2O(g)$	-241.8	188.7

(5 Marks)

(b) Write both K_c and K_p expressions for the following reversible reactions:

(i) $2SO_2(g) + O_2(g) \leftrightharpoons 2SO_3(g)$

(ii) $CaCO_3(s) \leftrightharpoons CaO(s) + CO_2(g)$

(iii) $S(s) + H_2SO_3(aq) \leftrightharpoons H_2S_2O_3(aq)$

(6 marks)

(c) What is a phase diagram, and what information can be obtained from it?

(5 Marks)

(d) The standard enthalpy of decomposition of the yellow complex NH_3SO_2 into NH_3 and SO_2 is +40 kJ mol^{-1}. Calculate the standard enthalpy of formation of NH_3SO_2 given $\Delta_f H^O(NH_3, (g)) = -46.11$ kJ mol^{-1} and $\Delta_f H^O(SO_2, (g)) = -296.83$ kJ mol^{-1}.

(5 marks)

(e) State Kelvin's and Clausius' statements of the Second Law of Thermodynamics.

(4 Marks)

(f) A solution containing 0.80 grams of a protein in 100 mL of a solution has an osmotic pressure of 2.06 torr at 25.0°C.

What is the molecular mass of the protein?

(5 Marks)

(g) K_c for the reaction

$$I_2\ (g) \leftrightharpoons 2I\ (g)$$

is 5.6×10^{-12} at 500K. A mixture has $[I_2] = 0.0020$ M and [I] = 3.7 × 10-7 M. Is the reaction at equilibrium (at 500K)? If not, which way must the reaction proceed to attain equilibrium?

(4 Marks)

(h) A sample of 1.00 mol $H_2O(g)$ is condensed isothermally and reversibly to liquid water at 100°C. The standard enthalpy of vaporization of water at 100°C is 40.656 kJ mol^{-1}. Find w, q, ΔU, and ΔH for this process.

(6 Marks)

SECTION B:

2. (a) Consider an ideal gas that occupies 2.25 L at 1.33 bar. Calculate the work required to compress the gas isothermally to a volume of 1.5 L at a constant pressure of 2.0 bar followed by another isothermal compression to 0.8 L at a constant pressure of 2.5 bar.

(6 Marks)

(b) What is the work for compressing the gas isothermally and reversibly from 2.25 L to 0.8 L?

(4 Marks)

(c) Consider the following reaction:

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

At 1000 Kelvin, $\Delta H^\circ_{rxn} = -123.77$ kJ mol^{-1}. What is the enthalpy of formation for NH_3 (gas) at 300 Kelvin? Consider the following molar heat capacities: $C_{p,m}$ = 3.502R, 3.466R, and 4.217R for $N_2(g)$, $H_2(g)$, and $NH_3(g)$, respectively. State any approximations you invoke.

(5 Marks)

(d) Sulphur transforms from the rhombic form to the monoclinic form under a pressure of 1 bar at 95.4°C. Its reported enthalpy of transition is 0.38 kJ mol^{-1}. What is the entropy of transition?

(5 Marks)

3. (a) The following cell is useful for the determination of the solubility of silver bromide.

$$Ag(s) \mid AgBr(s) \mid Br\ (aq, a_{Br^-}) \parallel Ag\ (aq, a_{Ag+}) \mid Ag(s)$$

(i) What is the overall reaction for this cell, as written, given the following electrode potential

$$AgBr\ (s) + e^- \longrightarrow Ag(s) + Br\text{-}(aq, a_{Br^-})\ E° = +0.07133V$$
$$Ag^+(aq, a_{Ag^+}) + e\text{-} \longrightarrow Ag(s)\ E° = +0.7996V$$

(ii) What is the standard voltage of this cell at 298.15 K, assuming no junction potential?

(iii) What is the standard Gibbs energy change for the cell reaction, as written, at 298.15 K?

(iv) What is K_{sp} for the AgBr at 298.15 K?

(10 Marks)

(b) Determine the amount of heat required to raise the temperature of 1.768 moles of liquid Ni from 2000 K to 2500 K, as accurately as you can. Use the heat capacity of nickel (C^{Θ}_{pm}) 38.91103 $J\ K^{-1}mol^{-1}$.
[Assume that the pressure remains constant at 1 bar during the process].

(5 points)

(c) Calculate the standard molar Gibbs energy of vaporization of methanol at 298.15 K using the following values:

$\Delta_f G^{\theta}_m$ (liquid) $= -\mathbf{166.6\ KJ}$
$\Delta_f G^{\theta}_m$ (gas) $= -\mathbf{162.3\ KJ}$

$$CH_3OH(liquid) \rightarrow CH_3OH(gas)$$

(5 Marks)

4. (a) Benzene ($P\bullet$ = 96.4 $torr$) and toluene ($P\bullet$ = 28.9 $torr$) form a nearly ideal solution over a wide range. For purposes of this question, you may assume that a solution of the two is ideal.

(i) What is the total vapour pressure of the above solution containing 5.00 moles of benzene and 3.25 moles of toluene?

(ii) What is mole fraction of benzene in the vapour of the above solution?

(5 Marks)

(b) The vapor pressure over ice has been measured at several different temperatures. At 220 K it is 2.732 torr and at 230 K it is 9.195 torr. Determine the enthalpy of sublimation of ice in this region of temperature.
One must use the Clausius-Clapeyron equation to solve this problem. Assuming the enthalpy of sublimation is temperature independent, one has the equation:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{sub}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(5 Marks)

(c) Calculate ΔH and ΔU at 298 K and ΔH at 378 K for the reaction

$$C(graphite) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

Assume all heat capacities to be constant over the temperature range involved.

Given: $\Delta_f H$: C(graphite) = 0 kJ mol^{-1}, $H_2O(g)$ = -241.82 kJ mol^{-1}, CO(g) = -110.53 kJ mol^{-1}, and $H_2(g)$ = 0 kJ mol^{-1}.

Cp,m : C(graphite) = 8.53 J K^{-1} mol^{-1}, $H_2O(g)$ = 33.58 J K^{-1} mol^{-1}, CO(g) = 29.14 J K^{-1} mol^{-1} and $H_2(g)$ = 28.83 J K^{-1} mol^{-1}.

All values are at 298 K.

(10 Marks)

5. (a) Calculate the lattice enthalpy of $MgBr_2$ from the following data:

	ΔH(KJ mol^{-1})
Sublimation of Mg(s)	+148
Ionization of Mg(g) to Mg^{2+}(g)	+2187
Vaporization of Br_2(l)	+31
Dissociation of Br_2(g)	+193
Electron attachment to Br(g)	-331
Formation of $MgBr_2$(s) from Mg(s) and Br_2(l)	-524

(10 Marks)

(b) Antimony (m.p 630°C) and lead (m.p 326°C) form one eutectic mixture at 246^0C which is 81 mole percent lead, but do not form any solid solutions. Draw a temperature – composition diagram, assuming that the liquidus lines are linear, and label each region indicating which phases are in equilibrium under the conditions that the regions represent. For a mixture containing 50 mole percent lead determine,

(a) the temperature at which solid first crystallizes out,

(b) the nature and proportion of solid in the mixture at 300°C

(10 Marks)

END OF QUESTION PAPER