Birla Institute of Technology & Science, Pilani, Rajasthan – 333031

First Semester 2023-2024, Comprehensive Examination (**Closed Book**)

Subject: Physical Chemistry -I (PC-1) **Course Code**: CHEM F211

Time: 180 minutes **Date:** 18/12/2023 **Max. Marks**: 80

Instructions to the students:

1. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. **In a derivation write all the in between steps. In case of missing steps, marks will be deducted.**
4. Write brief answers to the point with proper justifications.
5. Do not exchange your calculator.

Useful Data: C_P-C_V = R, R = 8.314 J mole^{-1} K^{-1} (2 cal mole^{-1} K^{-1}, 0.082 Lit atm mole^{-1} K^{-1}), 1 cal = 4.18 J, 1 litre = 1 dm^3, 1 atm = 760 torr = 1.01325 × 10^5 Pa, 1 Pa = 1 Nm^{-2}, Latent heat of freezing of water: -80 cal/gm, Latent heat of vaporization of water: 540 cal/gm, Boltzmann constant K = 1.38×10^{-23} J/K, 1 Faraday (F) = 96500 Coulomb, 1 J = 1 kgm^{2}s^{-2}, 1 erg = 1 gm cm^{2}s^{-2}, 1J = 10^7 erg

Q1. (a) For the reaction $Br_2(g) + Cl_2(g) \leftrightharpoons 2BrCl(g)$, ΔG^0 and ΔH^0 is determined to be -1440 Cal and -320 Cal respectively at 25^{0}C. Calculate the value of K_P of this reaction at 500^{0}C. Assume $\Delta C_P = 0$ upon temperature variation. **[5M]**

(b) The internal energy change, ΔU for the following reactions at constant volume and 600^{0}C is given below

$$2C_6H_6(g) + 15O_2(g) \leftrightharpoons 12CO_2(g) + 6H_2O(g) \quad \Delta U = -1600\ kCal$$

$$2C_2H_2(g) + 5O_2(g) \leftrightharpoons 4CO_2(g) + 2H_2O(g) \quad \Delta U = -620\ kCal$$

Determine the heat of polymerization of acetylene (C_2H_2) to 1-mole benzene (C_6H_6) at constant pressure. [**4M**]

(c) Starting from $H = U + PV$, show that $\left(\frac{\partial H}{\partial V}\right)_T = \frac{\alpha T}{\kappa} - \frac{1}{\kappa}$, where α is thermal expansivity and κ is isothermal compressibility. [**6M**]

(d) One mole of an ideal gas undergoes expansion reversibly from a volume V_1 to a final volume V_2, obeying the relationship $PV^\gamma = constant$. If T_1 = 400 K and T_2 = 200 K, calculate w, q, ΔU and ΔH for this process. Given $C_P = \frac{5}{2}R$ and assume C_P and C_V values are invariant of temperature change. [**5M**]

Q2. (a) The degree of dissociation of a 0.001 M weak acid HA is found to be 10% in an aqueous solution. Calculate the expected degree of dissociation of HA if 0.1 M NaCl is added into this aqueous solution. The Debye Hückel constant, A = 0.51 at 25^{0}C. **[5M]**

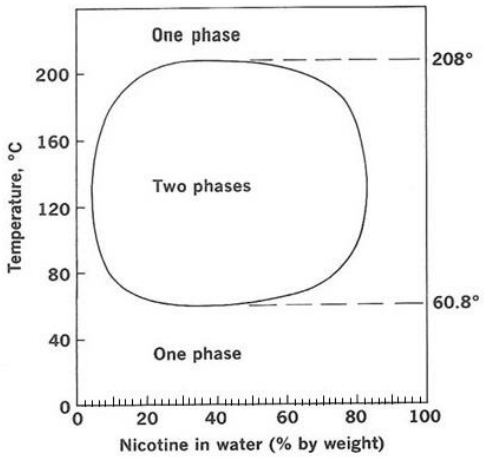
(b) Activity solubility product of a sparingly soluble salt AgCl is 10^{-10} M^2. Applying Debye-Hückel limiting law calculate its solubility in (a) water, (b) 0.1 M NaCl, and (d) 0.1 M $Ca(NO_3)_2$. Given Debye Hückel constant, A = 0.51 at 25^{0}C. **[5M]**

(c) Suppose a liquid mixture of C_6H_5Br and C_6H_5Cl forms an ideal solution. The vapor pressure of C_6H_5Br and C_6H_5Cl in their pure state is 0.7 atm and 1.2 atm respectively at 140^{0}C. Determine the composition of this mixture in liquid phase which boils at 140^{0}C under 1 atm. What will be composition of this mixture in the vapor phase at this temperature? **[6M]**

(d) Water and an organic liquid form a totally immiscible liquid pair. This liquid system boils at 90^{0}C when the barometer reads 734 mm of Hg. Upon steam distillation of this liquid system, it has been

found that the distillate contains 73 wt% of the organic liquid. Determine the vapor pressure and molecular weight of the organic liquid at 90^0C. Vapor pressure of water at 90^0C is 526 mm of Hg. **[4M]**

Q3. (a) Nicotine phase diagram is shown below at 1 atm pressure. Find the masses of water and nicotine present in each phase if 10 gm of Nicotine is mixed with 10 gm of water at 120^0C and 1 atm pressure. **[5M]**



(b) A 50 gm of phenol is mixed with a 50 gm of water to obtain the phenol-water mixture at 40^0C and 1 atm. This mixture forms two layer, a phenol layer in the bottom and a water layer in the top. The water layer is consisting of 9.2 wt% phenol and the phenol layer is consisting of 35 wt% water. Determine the amount of the water and phenol layer present in this mixture. Sketch temperature vs phenol wt% phase diagram for the above three phenol wt%. (*The critical solution temperature for phenol water system is 66^0C and the critical solution composition is 33 wt% phenol.*) **[5M]**

(c) A solution containing 5 gm of an organic solute per 25 gm of CCl_4 boils at 81.5^0C at 1 atm. If normal boiling point of CCl_4 is 76.8^0C and elevation constant, K_b = 5 ^{0}C/molal, calculate the molecular weight of the solute. **[4M]**

(d) The normal boiling point of heavy water, D_2O is 101.42^0C. The molal elevation constant K_b of D_2O is 10% higher than that of pure water, H_2O. Determine the latent heat of vaporization of D_2O in comparison to H_2O. The normal boiling point of H_2O is 100^0C. Suppose that the latent heat of vaporization of D_2O is 9960 Cal/mol and its boiling point increases from 101.42^0C to 103.2^0C. What will be the vapor pressure of D_2O in such scenario? **[6M]**

Q4. (a) The average kinetic energy of the oxygen molecules kept in a container is found to be 2 Kcal/mol. What would be the temperature of the oxygen gas? Determine also the root mean square velocity of the oxygen molecules at this temperature. [**5M**]

(b) The mean free path for the collision of O_2 is 10^{-5} cm at 27^0C and 1 atm. What will be the mean free path of O_2 at a high-altitude region where pressure is 0.13 atm and temperature is 7^0C? **[5M]**

(c) The electromotive force of the cell $Ag(s)|AgCl(s), KCl\ (m = 0.05\ molal)||AgNO_3(m = 0.1\ molal)|Ag(s)$ is 0.43 V at 25^0C. The activity coefficient of Ag^+ and Cl^- at these concentrations are estimated to be 0.85 and 0.90 respectively. Write the cell reaction and determine the solubility product of AgCl? **[5M]**

(d) The standard electromotive force of the cell $Pt, H_2(g)|HCl(aq)|Hg_2Cl_2(s)|Hg(l), Pt$ is found to be 0.2690 V at 20^0C and 0.2650 V at 30^0C. Write down the oxidation, reduction, and the overall cell reaction for this cell. Determine the values of $\Delta G^0, \Delta H^0, and\ \Delta S^0$ at 25^0C for this cell reaction. **[5M]**