**Birla Institute of Technology and Science Pilani –333031, Rajasthan**
**1$^{st}$ semester 2016-2017, Comprehensive Examination, PART-I (Closed Book)**
**Course Title: Physical Chemistry I, Course No. CHEM F211**
**Max Marks: 40, Time: 1hr 30 mins, Date: 08.12.16**

**Answer all questions with proper units. Rough work can be done alongside your answer.**

**Useful Data: 1 bar = 0.986842 atm, R = 8.314 J K$^{-1}$ mol$^{-1}$ = 82.06 cm$^3$ atm K$^{-1}$ mol$^{-1}$, F = 96485 C mol$^{-1}$, Enthalpy of fusion of ice at 0$^o$C and 1 atm = 6.03 kJ mol$^{-1}$.**

**Q1.** Calculate $\Delta H$ for heating 2.0 mol of ice at $-$ 5 $^o$C and 1 atm to liquid water at 40 $^o$C and 50 atm. Given that, the average $C_{P,m}$ of ice and liquid water are 37.8 J K$^{-1}$mol$^{-1}$ and 1.36 kJ K$^{-1}$ mol$^{-1}$, respectively; Assume that, $\alpha$ and $V_m$ are independent of T and P and their values are 3.04$\times$10$^{-4}$K$^{-1}$ and 18.1 cm$^3$mol$^{-1}$, respectively. **5.0M**

**Q2.** (i) Using virial equation as power series in P, show that for a non-ideal gas, $ln\phi = B^+P +(1/2) C^+P^2 + (1/3) D^+P^3 + ........$, where $\phi$ = fugacity coefficient of the gas. **2.5M**
(ii) Given that the second virial coefficient of H$_2$(g) at 25 $^o$C is $B$ = 14.0 cm$^3$mol$^{-1}$, calculate the fugacity coefficient and fugacity of H$_2$(g) at 25 $^o$C and 1 bar neglecting the terms after $B^+P$. **2.0M+1.0M**
(iii) Using the fugacity value of H$_2$(g) calculated in part (ii) and the mean activity coefficient of HCl in a 0.12 mol kg$^{-1}$ aqueous HCl solution at 25 $^o$C and 1 bar as $\gamma_\pm$ = 0.172, find (a) E$_{cell}$ at 25 $^o$C and 1 bar for the cell, Pt(s)|H$_2$(g, 1bar)|HCl(*aq*, 0.12 mol kg$^{-1}$)|Hg$_2$Cl$_2$(s)|Hg(*l*)|Pt(s) writing (b) reactions at both electrodes and (c) Nernst equation for overall cell reaction. Given that the standard reduction potential of cathodic reaction is 0.2680 vol. **4.0M+1.0M+1.5M**

**Q3.** The vapor pressure of a liquid mixture of acetone (ac) and chloroform (chl) at 35.2 $^o$C with $x^l_{ac}$ = 0.3365 is 249 Torr and the vapor phase composition, $x^v_{ac}$ = 0.3171. Using Lewis-Randall rule and virial equation of $ln\phi$ in terms of only $B^+P$ calculate the activity coefficients $\gamma_{I, ac}$ and $\gamma_{I, chl}$ in the liquid mixture considering that the vapor mixture above the liquid mixture behaves like non-ideal gas. Given that the second virial coefficients of pure gases are $B_{ac}$ = - 1523 cm$^3$ mol$^{-1}$ and $B_{chl}$ = - 1092 cm$^3$ mol$^{-1}$ and the vapor pressures of pure gases, $P^*_{ac}$= 344.5 Torr and $P^*_{chl}$ = 293 Torr at 35.2 $^o$C. **4.0M+4.0M**

**Q4.** For a saturated aqueous solution of NaCl with some excess of NaCl(s) present in the system, calculate the (i) number of dependent components mentioning all the components, (ii) number of independent components mentioning components and writing all relations corresponding to the values of $r$ and $a$ and (iii) degrees of freedom. Do not consider the dissociation of water. **1.5M+3.5M+1.0M**

**Q5.** Show that osmotic pressure for a solution of non-volatile solute, $\Pi = - (RT/V^*_{m,A})\ ln\gamma_A.x_A$ where $V^*_{m,A}$, $\gamma_A$, and $x_A$ are molar volume of pure solvent, activity coefficient of solvent and mole fraction of solvent in the solution. **3.0M**

**Q6.** The cell potential of the cell, Pt(s)|H$_2$(g, 1bar)|HCl(*aq*)|AgCl(s)|Ag(s) is found to be 0.33 volt at 25 $^o$C and 1 bar. (i) Write reactions at anode and cathode and overall cell reaction, (ii) Write Nernst equation for cell reaction, and (iii) Estimate the pH of the electrolyte solution assuming that activity of the cation is equal to that of anion in the electrolyte solution. Given that the standard reduction potential of the cathodic reaction in this cell = 0.22 volt. **1.5M+2.0M+2.5M**

**Answer all questions with proper units. Rough work can be done alongside your answer.**

**Useful Data: R = 8.314 J K$^{-1}$ mol$^{-1}$ = 82.06 cm$^3$ atm K$^{-1}$ mol$^{-1}$, Densities of ice and water at 0$^o$ C are 0.917 g cm$^{-3}$ and 0.999 g cm$^{-3}$, respectively, Molar mass of water is 18.015 g mol$^{-1}$.**

**Q1.** Calculate (i) $q$, (ii) $\Delta H$, (iii) $\Delta U$, (iv) $\Delta S$ and (v) $\Delta G$ for increasing pressure on 10.0 moles of water from 1 atm to 1000 atm at 25 $^o$C isothermally and reversibly. Assume that, $\alpha$ and $V_m$ are independent of temperature and pressure and their values are $3.04\times10^{-4}$K$^{-1}$ and 18.1 cm$^3$mol$^{-1}$, respectively. Express values in J/kJ units. **2.5M+1.5M+1.0M+1.5M+1.0M**

**Q2.** Using the thermodynamic data given below, formulate relation between $\Delta_rG^o$ and only temperature as a variable for the reaction, Ca(s) + (1/2)O$_2$(g) $\rightleftharpoons$ CaO(s), so that the relation can be used to estimate $\Delta_rG^o$ at any given temperature.
Given that, $\Delta_fH^o_{298}$(CaO, s) = -635.09 kJ mol$^{-1}$, $\Delta_fG^o_{298}$(CaO, s) = - 604.03 kJ mol$^{-1}$, $C^o_{p,m,298}$ (Ca, s) = 25.31 J K$^{-1}$ mol$^{-1}$, $C^o_{p,m,298}$ (CaO, s) = 42.80 J K$^{-1}$ mol$^{-1}$ and $C^o_{p,m,298}$ (O$_2$, g) = 29.36 J K$^{-1}$mol$^{-1}$. (Assume that, $\Delta_rC^o_{p,m}$ is independent of temperature). **7.0M**

**Q3.** (i) Calculate the change in the chemical potentials on increasing the pressure from 1 atm to 2 atm for ice and water at 0$^o$ C (any data required can be taken from useful data given above) and (ii) Comment on the tendency of phase transition after increasing the pressure drawing a phase diagram of water. **3.0M+2.0M**

**Q4.** Using virial equation expressed as power series in $P$ show that the Joule-Thomson coefficient, $\mu_{JT} = (RT^2/C_{P,m})[(dB^+/dT) + (dC^+/dT)P + (dD^+/dT)P^2 + ......]$. **4.0M**

**Q5.** (i) Assuming that Ca$_3$(PO$_4$)$_2$ is a strong electrolyte calculate (a) $\gamma_+$ , (b) $\gamma_-$ and (c) $\gamma_\pm$ of Ca$_3$(PO$_4$)$_2$ in a 0.005 mol kg$^{-1}$ aqueous Ca$_3$(PO$_4$)$_2$ solution at 25 $^o$C and 1 atm using Davies equation. (ii) A 2.0 mol kg$^{-1}$ aqueous solution of Ca$_3$(PO$_4$)$_2$ has a vapor pressure of 18.51 Torr at 25 $^o$C. Find the activity and activity coefficient of the water in this solution. Given that the vapor pressure of pure water at 25 $^o$C is 23.76 Torr. **2.0M+1.0M+2.0M**

**Q6.** For a solid A, $C^o_{p,m} = cT^3 + dT^4$ for 10 K$\leq$ T $\leq$30 K and $C^o_{p,m} = e + fT + gT^2 + hT^3$ for 30 K$\leq$ T $\leq$ 250 K. The solid melts at 250 K and 1 atm with $\Delta_{fus}H_m$ = 786 J mol$^{-1}$. Express $H^o_{m, 100}$ - $H^o_{m, 0}$ of A in terms of constants c d, e, f, g and h. Neglect the difference between 1-atm and 1-bar properties of the solid and liquid. **4.5M**

**Q7.** For a binary ideal solution of two liquids A and B, the phase diagram at 35 $^o$C is given below: If 2.24 mol of A and 4.76 mol of B are mixed together at 35 $^o$C then find (i) the mole fraction of B in liquid phase and vapor those are at equilibrium with each other and (ii) the number of moles of B present in both the phases at a pressure of P$'$ applying Lever rule. Given that the width of the figure is 10 cm. **2.0M+5.0M**
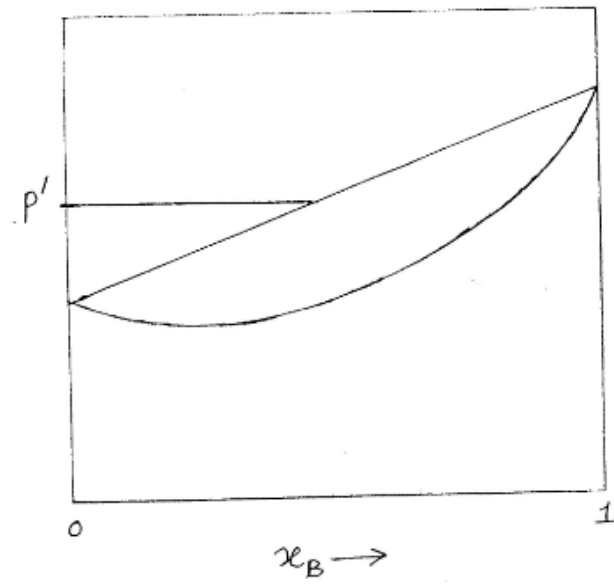
**P.T.O**

Figure for Q. No. 7.