

Birla Institute of Technology and Science Pilani –333031, Rajasthan
1st semester 2017-2018, Comprehensive Examination, PART-I (Closed Book)
Course Title: Physical Chemistry I, Course No. CHEM F211
Max Marks: 40, Time: 1hr 30 mins, Date: 13.12.17

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

Useful Data: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 82.06 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$.

Q1. (i) Show that at a low pressure, the second virial coefficient (B) is the correction to the ideal-gas molar volume. **(ii)** At 273 K measurement on argon gave $B = -21.7 \text{ cm}^3 \text{ mol}^{-1}$ and $C = 1200 \text{ cm}^6 \text{ mol}^{-2}$, where B and C are the second and third virial coefficients in the expansion of compression factor, Z in powers of $(1/V_m)$. Assuming that the perfect gas law holds sufficiently well for the estimation of the second and third terms of the expansion, calculate the compression factor of argon at 100 atm and 273 K. Neglect the terms beyond square term. **(iii)** From this result, estimate the molar volume of argon under these conditions. **2M+3M+1M**

Q2. A gas obeys equation of state, $P(V_m - b) = RT$ where $b = 0.0167 \text{ L mol}^{-1}$. Estimate the values of fugacity coefficient at 100 atm and 1000 atm at 298.15 K. Using these fugacity coefficient values calculate molar Gibbs free energy change for increasing pressure from 100 atm to 1000 atm at 298.15 K. **4M**

Q3. (i) Show depression in freezing point and **(ii)** elevation in boiling point by clearly drawing figures for change in chemical potential of solvent with temperature. **(iii)** Mention assumptions made for this discussion. **1.5M+1.5M+1M**

(iv) Show that $\ln(\gamma_A x_A) = \int_{T_f^*}^{T_f} (\Delta_{\text{fus}} H_{m,A} / RT_f^2) dT_f$ (here all terms have their usual meanings). **6M**

(v) Show that for an ideally-dilute solution, the depression in freezing point is proportional to the molality of the non-volatile solutes where proportionality constant depends on the properties of solvents. **3M**

Q4. The vapor pressure for a liquid mixture of acetone (ac) and chloroform (chl) at 35.2 °C with liquid composition, $x_{\text{ac}}^l = 0.4188$ is 248 torr and has composition of vapor above this liquid, $x_{\text{ac}}^v = 0.4368$. **(i)** Estimate activity coefficients, $\gamma_{l,\text{ac}}$ and $\gamma_{l,\text{chl}}$ assuming the vapor mixture and the pure vapor are ideal. **(ii)** Estimate activity coefficients, $\gamma_{l,\text{ac}}$ and $\gamma_{l,\text{chl}}$ assuming the vapor mixture and the pure vapor are non-ideal. Given that, $P_{\text{ac}}^* = 344.5 \text{ torr}$ and $P_{\text{chl}}^* = 293 \text{ torr}$ at 35.2 °C; $\phi_{\text{ac}} = 0.9781$ and $\phi_{\text{chl}} = 0.9838$ at 35.2 °C and 248 torr; $\phi_{\text{ac}}^* = 0.9841$ and $\phi_{\text{chl}}^* = 0.9820$ at 35.2 °C and at their respective vapor pressures. **3M+5M**

Q5. (i) 150 gm of Ni metal is added with 330 gm of Cu metal and these metals are then heated to 1200°C at 1 atm pressure. Using the phase diagram given below estimate amount (in gm) of Ni and Cu present in the phases those are at equilibrium with each other at 1200°C and 1 atm pressure using Lever rule. Given that, atomic weights of Ni and Cu are 58.693 and 63.546 g mol⁻¹, respectively. **7M**

P.T.O.

(ii) Calculate the degrees of freedom for multiphase region of this phase diagram writing the values of all quantities in Gibbs phase rule. Give a reasonable choice of the independent intensive variable(s). 1M+1M

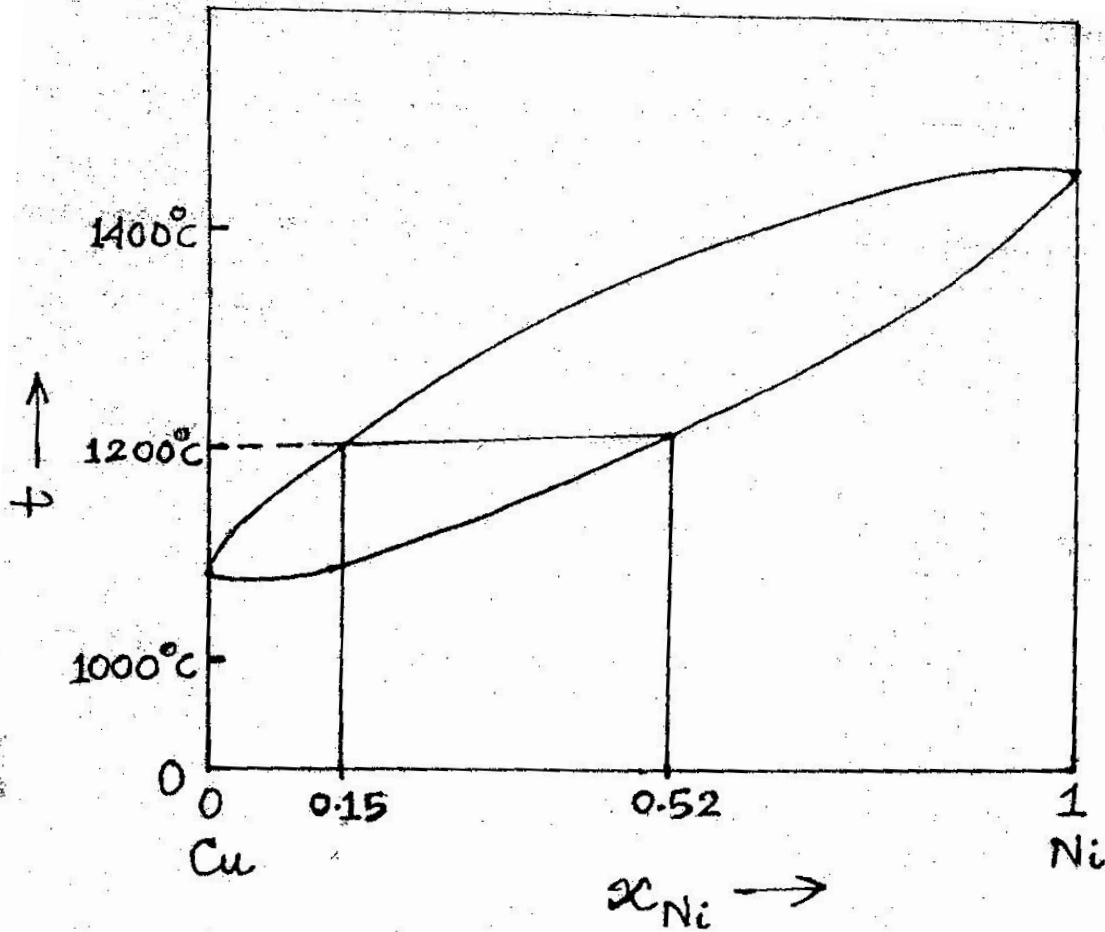


Fig for Q 5 (i) and (ii)

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Q1. 1.5 moles of an ideal gas initially at 15°C and 9.0 atm pressure is confined to a cylinder of cross-section 100 cm^2 . The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm . Calculate (i) w , (ii) ΔH , (iii) ΔG , (v) ΔS_{sys} and (vi) ΔS_{sur} . Given $C_{v,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$. **1.0M+1.5M+1M+2.5M+0.5M**

Q2. Calculate (i) q , (ii) ΔS and (iii) ΔG of 25 gm of methanol (mass density is 0.791 gm cm^{-3}) when the pressure is increased isothermally and reversibly from 100 kPa to 100 MPa at 25°C . Given that $\kappa_T = 1.26 \times 10^{-9} \text{ Pa}^{-1}$ and $\alpha = 3.12 \times 10^{-4} \text{ K}^{-1}$ (both are independent of pressure). **5M+1M+2M**

Q3. The equilibrium constant of a reaction is found to fit the expression $\ln K = A + (B/T) + (C/T^3)$ between 400 K and 500 K with $A = -2.04$, $B = -1176 \text{ K}$, and $C = 2.1 \times 10^7 \text{ K}^3$. Calculate the standard reaction enthalpy at 450 K . **2.5M**

Q4. The enthalpy of fusion of mercury is $2.292 \text{ kJ mol}^{-1}$, and its normal freezing point is 234.3 K with a change in molar volume of $+0.517 \text{ cm}^3 \text{ mol}^{-1}$ on melting. At what temperature will the bottom of a column of mercury (density 13.6 gm cm^{-3}) of height 10 m be expected to freeze? Assume that enthalpy of fusion and volume of fusion are constant. **4M**

Q5. (i) The vapor pressure of a 0.1 mol kg^{-1} aqueous solution of ZnSO_4 is 20.13 torr at 25°C . Calculate activity and activity coefficient of water in this solution considering complete dissociation of ZnSO_4 . Given that the vapor pressure of pure water at 25°C is 23.76 torr . **2M**

(ii) Estimate γ_{\pm} of ZnSO_4 in its 0.1 mol kg^{-1} aqueous solution at 25°C by constructing a galvanic cell using a zinc rod and $\text{Hg}(l)\text{-Hg}_2\text{SO}_4(s)$ for the purpose of making two electrodes and $0.1 \text{ mol kg}^{-1} \text{ ZnSO}_4(aq)$ solution as a common electrolyte. Write cell, reactions at anode and cathode and overall cell reaction. Given that the *e.m.f.* of this cell is 1.473 V at 25°C . **(iii)** Calculate the activity of ZnSO_4 in this solution. **1M+0.5M \times 3=1.5M+4M+1M**

Q6. Estimate the pH of the unknown aqueous solution of HCl used as an electrolyte in the following cell at 25°C and 1 atm .

$\text{Pt}(s)|\text{H}_2(g, 1 \text{ bar})|\text{HCl}(aq)|\text{Salt bridge KCl}(0.1 \text{ mol kg}^{-1})|\text{KCl}(0.1 \text{ mol kg}^{-1})|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}(l)|\text{Pt}(s)$
Given that, the $E_{\text{cell}} = 0.45 \text{ V}$, liquid-junction potential, $E_j = 0.027 \text{ V}$, neglect the difference between bar and atm. **6.0M**

Q7. For a just saturated (no excess of solid) aqueous solution of ZnSO_4 , calculate C , C_{ind} and f writing all components, all independent components and all relations corresponding to the values of r and a . Consider the ionization of water. **1M+2M+0.5M**

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