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

First Semester 2022-2023, Comprehensive Examination (**Closed Book**)

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

Duration: 180 minutes **Date**: December 27, 2022 **Max. Marks**: 80

Note: *Please check that the question paper is printed on both sides. Attempt all the questions.* ***Start answering each question on a fresh page and answer all parts of the question together****. Pencil should not be used*. *Symbols have usual meaning*.

Do not scribble on the question paper.

Useful Data: Universal gas constant, R = 2 cal mol^{-1} K^{-1} or 8.314 J mol^{-1} K^{-1} or 0.082 L-atm mol^{-1} K^{-1}, 1 L-atm = 24.4 cal, Faraday constant (F) = 96500 Coulomb/mole, 1 calorie = 4.2 Joule, 1 Joule = 10^7 erg, Avogadro number (N_A) = 6.023×10^{23}, Boltzmann constant (k) = 1.38×10^{-23} J/K, Planck constant (h) = 6.625×10^{-34} J-s, elementary charge (e) = 1.6×10^{-19} Coulomb, 1 atomic mass unit = 1.6603×10^{-27} kg, 1 atmospheric pressure unit = 760 mm of Hg (101.325 kPa)

Q1. (i) The vapor pressure of NH_4HS is 50 cm of Hg at 25^0C. Calculate the total pressure when NH_4HS dissociates at 25^0C in a vessel, which already contains NH_3 at a pressure of 32 cm of Hg. Given NH_4HS dissociates as $NH_4HS\ (s) \leftrightharpoons NH_3(g) + H_2S(g)$. **[4 M]**

(ii) The equilibrium constant for the gaseous reaction $H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$ at 427^0C is K = 55.3.

(a) What amount of HI (**in gms unit**) will be formed at equilibrium if 1 mole of H_2 and 1 mole of I_2 is placed in a one litre vessel at 427^0C? (Given molecular weight of HI is 128 gm/mole.)

(b) Will there be any reaction at 427^0C in a mixture consisting of 0.70 atm of HI and 0.02 atm of H_2 and I_2 (**these are the partial pressure of the respective chemicals**)?

If so, in which direction the reaction will occur? **[6 M]**

(iii) The vapor pressure of H_2O at 373.6 K and 372.6 K is 1.018 atm. and 0.982 atm. respectively. Calculate molar entropy of vaporization and change in volume per mole when water vaporizes at 373 K. Assume that the water vapor behaves ideally **[5 M]**

(iv) A mixture of benzene and toluene contains 30 % by weight of toluene. The vapor pressure of pure toluene and pure benzene is 36.7 mm of Hg and 118.2 mg of Hg respectively at 30^0C. If the mixture of benzene and toluene form an ideal solution, calculate the total pressure and partial pressure of each constituent above the solution at 30^0C. (Given molecular weight of toluene and benzene is 92 gm/mol and 78 gm/mol respectively.) **[3 M]**

(v) Calculate the entropy of mixing if two moles of N_2 gas are mixed with one mole of O_2 gas at the same temperature and pressure. Assume ideal behavior for the gas. **[2 M]**

Q2. (i) 1 gm of urea when dissolved in 100 gm of a certain solvent decreases its freezing point by 0.2^0C. 1.6 gm of unknown substance when dissolved in 80 gm of same solvent decreases the freezing point by 0.36^0C. Calculate the molecular weight of the unknown compound. (Given molar mass of urea is 60 gm mol^{-1}) [**3 M**]

(ii) Blood is said to be isotonic (**having same osmotic pressure**) with 0.85% NaCl solution (weight/volume) at 40^0C. Assuming complete dissociation of NaCl, calculate total concentration of various solutes in blood. What will be approximate freezing point of blood? (**Given freezing point constant, K_f = 1.86 ^{0}C/molal**) [**5 M**]

(iii) Given vapor pressure of pure water at 25^0C is 23.8 mm of Hg, calculate the vapor pressure of 20 % (weight/weight) glucose solution. (**Molecular weight of glucose and water is 180 gm/mole and 18 gm/mole respectively**) [**3 M**]

(iv) If boiling point of an aqueous solution is 100.1 ^{0}C, what is its freezing point? Given latent heat of fusion (l_f) and vaporization (l_v) is 80 calorie/gm and 540 calorie/gm respectively. Given normal boiling point and freezing point of water is 100^0C and 0^0C respectively at 1 atm pressure. Consider the pressure is 1 atm pressure. **[4 M]**

(v) A totally immiscible liquid system composed of H_2O and an organic liquid boil at 90^0C when barometer reads 734 mm of Hg. The distillate contains 73% by weight of the organic liquid. What is the molecular weight and vapor pressure at 90^0C of the organic liquid? (Given vapor pressure of water at 90^0C is 526 mm of Hg) [**3 M**]

(vi) A solution composed of 10 gm of a non-volatile solute in 100 gm diethyl ether, has vapor pressure 426 mm of Hg at 20^0C. If vapor pressure of pure ether is 442.2 mm of Hg at the same temperature, what is the molecular weight of the solute? (Given molecular weight of diethyl ether is 74 gm/mol) [**2 M**]

Q3. (i) The thermodynamic dissociation constant for acetic acid, CH_3COOH is 1.75×10^{-5} at 25^0C. Calculate using Debye-Huckel theory, the degree of dissociation of 0.001 M acetic acid in 0.05 M $Ca(NO_3)_2$. [**5 M**]

(ii) An aqueous solution contains 0.01 M propionic acid and 0.02 M sodium propionate at 25^0C. Find pH, hydrogen ion concentration and degree of dissociation of propionic acid in this solution. (Given dissociation constant of propionic acid is $K_a = 1.34 \times 10^{-5}$) [**5 M**]

(iii) Solubility of a sparingly soluble salt AgCl at 25^0C is 10^{-4} M. Calculate its solubility in 0.1 M $AgNO_3$ solution. (Consider the effect of ionic strength. The Debye-Huckel constant A at 25^0C is 0.51) [**4 M**]

(iv) The degree of dissociation of a weak acid CH_3COOH is found to be 10% when the concentration of CH_3COOH in an aqueous solution is 0.001 M. Calculate the expected degree of dissociation of the 0.001 M CH_3COOH in a solution containing 0.1 M NaCl. (Given the Debye-Huckel constant, A of the solution is 0.51) [**6 M**]

Q4. (i) The electromotive force for the cell, $Zn(s)|ZnCl_2(m)|AgCl(s), Ag(s)$ is E = 1.240 V at 25^0C and 1.260 V at 35^0C if $m_{ZnCl2} = 1 \times 10^{-3}$ molal. Write down the cell reaction and calculate ΔG, ΔH and ΔS at 25^0C. **[5 M]**

(ii) For the cell (Pt) $H_2|HCl|AgCl(s), Ag(s)$, E^0=0.222 V. If the measured electromotive force of the cell is 0.385 V, what is the pH of the solution? (Given $P_{H_2} = 1\ atm$, and the temperature is 25^0C) **[4 M]**

(iii) The electromotive force of the cell $Zn\ (s)|Zn^{2+}(a = 0.01)||Fe^{3+}(a = 0.01), Fe^{2+}(a = 0.001)|Pt$ is E = 1.71 V (volt). Calculate the equilibrium constant of the cell reaction of this cell. (Consider the temperature of the reaction is 25^0C.) [**5 M**]

(iv) The potential of the cell Cd(s)|CdI_2(*a*) AgI(s)|Ag(s) is found to be E = 0.2860 at 25^0C. Calculate the mean ionic activity of the ions in the solution and the activity of the electrolyte. (Given $E^0_{Cd^{2+}/Cd} = -0.403\ V$ and $E^0_{AgI/I^-} = -0.1522\ V$) [**4 M**]

(V) Calculate the root mean square velocity of oxygen molecule having kinetic energy of 2 Kcal/mole. What would be the temperature of the oxygen molecule? **[2 M]**

******* The End *******