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FIRST SEMESTER 2019-2020 | **COMPREHENSIVE EXAM (CLOSED BOOK)**

PHYSICAL CHEMISTRY I (CHEM F211) | **DURATION: 3 HOURS (FN)**

MARKS : 100 | **DATE : 09/12/2019**

Write answers of Q.1 and Q.2 in first two pages of answer sheet. All parts of the question should be answered together. Start a new question from a fresh page. Make an index . Report all answers in Boxes.

Useful data: R = 8.314 $JK^{-1}mol^{-1}$=1.987 Cal/mol-K= 82.06 cm^3atm/mol-K=0.08206 dm^3 atm/mol-K, Atomic masses of H, O, C, N, Ar = 1.0, 16.0,12.0,14,39.95 g mol^{-1}respectively, 1 bar = 0.9869 atm= 750 torr , Avogadro constant = 6.022 x 10^{23} mol^{-1} ; F = 96485 C/mol

Q.1 Choose the correct alternative: [**2 x 5 = 10**]

(i) What is the $(\nu_\pm)^\nu$ of 0.001*m* $BaCl_2$ aqueous solution ?

[a] 0.004 **[b]** 1.59 **[c]** 4 **[d]** 0.002

(ii) The combustion of solid glucose in an adiabatic bomb calorimeter give -2801 kJ/mol as the $\Delta_c U^\circ_{298}$. What will be the $\Delta_c H^\circ_{298}$ of glucose (in kJ/mol)?

[a] -2808.5 **[b]** -2801 **[c]** -2796 **[d]** -2803.5

(iii) Given the standard Gibbs energy for a chemical reaction as $\Delta G^o = 12RT$, the standard equilibrium constant (K_p^o) for the reaction is close to

[a] 6×10^{-12} **[b]** 6×10^{-6} **[c]** 6×10^{12} **[d]** $6 \times 10^{\mathbf{6}}$

(iv) When Clapeyron equation is used to study the effect of pressure on the solid to liquid transition of water, the ΔT is obtained as -7.5 K cm^3atm J^{-1}. The ΔT in K is approximately equal to

[a] -7.5 **[b]** 7.5 **[c]** 0.76 **[d]** -0.76

(v) For N_2 (g), the Van der Waal's constant $a = 1.35 \times 10^6$ cm^6 atm mol^{-2} and b = 38.6 cm^3 mol^{-1}. The critical temperature of N_2 (g) is close to

[a] 126 K **[b]** 77 K **[c]** 252 K **[d]** 151 K

Q.2 STATE TRUE OR FALSE (Give justifications for your answers) **[2 x 3 = 6]**

(i) For the acid dissociation constant (K_a) in aqueous solution of a weak acid HA of the order of 1×10^{-7} mol^2/kg^2, the molality of H_3O^+ is approximately equal to 0.000316mol/kg.

(ii) The osmotic pressure at 25°C and 1 atm of a 0.0250mol/dm^3 solution of glucose ($C_6H_{12}O_6$) in water is close to 0.61 atm.

(iii) The work done by a closed system can exceed the decrease in the system's internal energy.

Q.3(a) For the Daniel cell at 25 ºC and 1 bar**: Cu′|Zn |$ZnSO_4(m_1)$ | | $CuSO_4(m_2)$ | Cu ,** with m_1=0.00200 mol/kg and m_2 = 0.00100 mol/kg**,** ξ^o values for the right and left half cells are 0.339 and -0.762 V respectively.

(i) Calculate the ionic strength (I_m/m_0) of $ZnSO_4$ and $CuSO_4$ solutions.

(ii) Estimate ξ at 25 ºC of this cell using the Davies equation to estimate the activity coefficients and assuming that the salt bridge makes ξ_J negligible.

(iii) When the cell is connected to a load, into which terminal (left or right) do electrons flow from load. [**4+8+2 = 14**]

Q.3(b) An ideal solution of liquids B and C with x_B^l= 0.400 at 25°C has a vapour pressures of 139 torr and a vapour composition of x_B^v= 0.650. Find the vapour pressure of pure B and the partial pressure of C at 25°C. Assume ideal solution. [**4**]

Q.4 (a) For the acetone – chloroform solution at 35.2°C, the vapour pressures P and acetone vapour-phase mole fractions, $\mathbf{x^v_{ac}}$, are given as functions of the liquid – phase acetone mole fraction, $\mathbf{x^l_{ac}}$.

(i) Find the Convention I activity coefficients with x^l_{ac} = 0.3365.

(ii) Find $\Delta_{mix}G$ of the solution containing 0.3365 mole of acetone and 0.6635 mole of chloroform at 35.2°C and 1 bar. Given

x^l_{ac}	x^v_{ac}	P/torr
0.0000	**0.0000**	**293**
0.3365	**0.3171**	**249**
1.0000	**1.0000**	**344.5**

[4 +3]

Q.4 (b) A certain perfect gas has $C_{V,m} = a + bT$, where a = 25.0 J/(mol K) and b = 0.0300 J/(mol K^2). Let 4.00 mol of the gas go from 300 K and 2.00 atm to 500 K and 3.00 atm . Calculate ΔU, ΔH and ΔS for this change of state. [**3**+**2+4**]

ΔU (kJ)	ΔH(kJ)	ΔS (J/K)

Q.5(a) The ideal gas reaction $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ at 600 K has ΔH^o = 217.9 kJ/mol, and ΔG^o = 72.4 kJ/mol. Calculate the temperature at which K_p^o is 30 for this reaction. Assume ΔH^o is constant in the temperature range of interest. [**5**]

Q.5(b) A certain ideal gas mixture is held at constant volume at 410°C and has the following initial partial pressures for $Cl_2(g)$ as 352 torr, CO(g) as 345 torr, for $COCl_2(g)$ as 0 torr. At equilibrium, total pressure is 450 torr. Find partial pressure (in torr) of $COCl_2$ at equilibrium and calculate K_P^o at 410°C for the reaction $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$. ($P^o$ = 750torr). **[5]**

Q.6(a) State Trouton-Hildebrand-Everette (THE) rule and what is the molar entropy of vaporization ($\Delta_{vap}S_{m,nbp}$) of a liquid that boils at 380 K at 1 atm in terms of R? Estimate using THE, enthalpy of vaporization ($\Delta_{vap}H_m$ in kJ/mol) of pure Zn, given the normal boiling point of Zn is 911°C. (Assume reversibility during vaporization). **[5]**

Q.6(b) The molar enthalpy of vaporization of $Br_2(l)$ is 30.7 kJ/mol at its normal boiling point of 58.8°C. Using differential form of Clapeyron equation, calculate the differential $\left(\frac{dT}{dP}\right)$ in K/Pa. (Assume ideal gas for vapor phase). **[5]**

Q.7(a) Estimate the virial coefficient B (in m^3mol^{-1}) of 17 g of NH_3 in 1000 cm^3 at 35 bar pressure and at 450 K. (Consider the virial equation involving virial coefficient up to B only). **[5]**

Q.7(b) Using reduced van der Waals equation, calculate the pressure (in atm) of 40 g of $C_3H_8(g)$ in a container of volume 500 cm^3 at 50°C.
(Critical constants of $C_3H_8(g)$: T_c = 369.8 K, P_c = 41.9 atm, $V_{m,c}$ = 58 cm^3/mol). **[5]**

8 (a) For 15 g of $CH_4(g)$ at 25°C and 1 atm, calculate the number of molecules whose speed lies in the range 200.000 m/s to 200.002 m/s.[Assume perfect gas behavior for $CH_4(g)$]. **[5]**

8(b) For $N_2(g)$ at 400 K and 1.5 atm, estimate the average speed (in m s^{-1}) and number of molecular collisions (in $cm^{-2}s^{-1}$) with a container wall of area 1.00 cm^2 that occur in 1s [Assume perfect gas behavior for $N_2(g)$]. [**5**]

9(a) The solubility product for AgBr in water is 7.7 ×10^{-13} mol^2/kg^2 at 25°C. Find the solubility of AgBr (in mol/kg) in **(i)** pure water, and **(ii)** 0.050 mol/kg of KNO_3 added aqueous solution. **[5]**

9(b) The normal freezing point of D_2O (where D ≡^{2}H) is 3.82°C and $\Delta_{fus}H_m$ is 6305 J/mol.
(i) Calculate the cryoscopic constant (K_f) of D_2O.**(ii)** Find the freezing point of a solution of 1 g of CH_3COCH_3 in 60 g of D_2O. **[5]**

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