RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FIFTH SEMESTER EXAMINATION, FEBRUARY 2022

THIRD YEAR [BATCH 2019-22]

Date : 26/02/2022 **CHEMISTRY (HONOURS)**

Time : 11 am – 1 pm **Paper : XI [CC11]** Full Marks : 50

[Attempt **one question** from **each unit**]

Unit –I

[10 Marks]

1. a) The standard Gibbs energy of reaction for the decomposition $H_2O(g) = H_2(g) + ½\ O_2(g)$ is 118.08 kJ mol^{-1} at 2300K. What is the degree of dissociation of $H_2O(g)$ at 2257K and 1 bar? [2]

   b) N_2O_4 in its gaseous state, remains in equilibrium with NO_2 (g). At P, the degree of dissociation, α, being proportional to ξ (extent of reaction) and K_P being the equilibrium constant, show that

   $$\alpha = \left(\frac{K_P}{K_P+4P}\right)^{\frac{1}{2}}$$ [3]

   c) i) Justify that for the reaction – $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ K_P is independent to P, but K_X is not.

   ii) P Independence to K_P does not mean that the amounts of reactants and products at equilibrium do not change with the change in pressure. True or false, explain. [3+2]

2. a) Consider a reaction 2A + 3B = C + 2D

   i) Find out the expression for the reaction Gibbs energy, Δ_rG, in terms of μ's of respective species.

   ii) How does the plot of G vs ξ look like for Δ_rG as large (–)ve? [Using graphical plot]

   iii) Explain the equilibrium composition with respect to reactants and products. [2+1+1]

   b) i) Thermodynamically prove that the concentration ratio of I_2 is two phases at equilibrium is constant, when I_2 is added to H_2O-CCl_4 system.

   ii) What will happen in the equilibrium, if KI is added? [2+1]

   c) A well-known industrial reaction is the water gas reaction CO_2 (g) + H_2 (g) = CO (g) + H_2O (g), whose $\ln K_P$ vs T curve gives a value of $\ln K_P$ = 350 at 1200K. Calculate ΔG^0 and ΔS^0 at 1200K. [Slope = 3.81]. [3]

Unit –II

[16 Marks]

3. a) i) Show graphically how melting point of a solution changes with composition, for a liquid mixture A and B, at a fixed pressure. (A and B form a compound at a stoichiometric ratio 2:1, the melting ponts are in the order $A_2B > A > B$).

ii) In the diagram locate the melting points of the pure species A, A_2B and B, their melting point curves in the mixture and the eutectic points. [2+4]

b) i) Draw the typical cooling curves for water (in the range -10 C to 110 C) for two different pressures P_h and P_l (take $P_h > P_l$) .

ii) In the diagram mark the melting point, boiling point along with the latent heats of fusion and evaporation. [2+4]

c) Could the freezing point be ever elevated upon addition of solute? Explain deriving relevant expressions. [4]

4. a) Calculate the number of phases, number of components and degrees of freedom in the following systems: [3+3]

i) $AlCl_3 + 3H_2O \rightarrow Al(OH)_3$ (partially insoluble)

ii) A sugar solution at the boiling point of solvent water.

b) Draw a chemical potential vs T diagram for a species in the three states (solid, liquid and gas) at two different pressures (P_h and P_l with $P_h > P_l$). [3]

c) A solution of A in B deviates positively from the Raoult's law. In a T-composition diagram show qualitatively how the boiling point of the solution changes with mole fraction of any of the two components in the diagram label clearly.

i) the phases present in the various regions of the phase space,

ii) the azeotropic point,

iii) boiling point curves for pure A and B. [3]

d) i) "pickle preserves fruits or vegetables for years" . Explain the underlying mechanism.

ii) Predict whether a solution of water and alcohol would show positive or negative deviation from the Raoult's law. [2+2]

Unit –III

[12 Marks]

5. a) Consider the following sets of populations for 4 equally spaced energy levels

ε/K_B	Set A	Set B	Set C
300	5	3	4
200	7	9	8
100	15	17	16
0	33	31	32

i) Demonstrate that the sets have same energy.

ii)Which of the sets is the most probable? Justify. [2+2]

b) For an ensemble consisting of a mole of particles having 2 energy levels separated by hν = 1.0×10^{-20} J. At what temperature will internal energy of system equal 1.00 kJ. [3]

c) Use thermodynamic relation and the definition of partition function for an ideal gas (consisting N no of indistinguishable particles) to show that

$$A = -RT\left(ln\frac{z}{N} + 1\right)$$

with $z = \sum e^{\frac{-\epsilon_i}{k_B T}}$. [3]

d) What are the criteria for a system to be microcanonical ensemble? What type of ensemble is the system – '1 mol of He atoms'? [2]

6. a) Consider a system consisting two different types degrees of freedom, vibrational and rotational, which are assumed to be of weakly coupled in nature. Show that the overall partition function of the system can be written as the product of vibrational and rotational partition functions. [3]

b) For a harmonic oscillator, g_i being the degeneracy of ith level and $\varepsilon_0 = 0$, show that all the particles will reside in ground level and partition function is expressed by g_0 at low temperature. [3]

c) Use Stirling's approximation to simplify the term $\frac{n!}{\left(\frac{n}{2}!\right)^2}$. [2]

d) In NMR spectra, energy separation, between spin states is created by placing nuclei in a magnetic field. Protons have two possible spin states +1/2 and -1/2. If NMR spectrometers employ magnetic field strength ~1.45T. What is the ratio of population between two spin states at 298K? [$\Delta E = 2.82 \times 10^{-26}$ JT^{-1} B] [2]

e) Assume the 1D gas molecular velocity distribution function as

$$f(u_x) = Ae^{\left(\frac{-mu_x^2}{2K_B T}\right)}$$

What is the value of A? [2]

Unit –IV

[12 Marks]

7. a) Find out the expression of pH of a buffer solution made up of weak acid and salt of its conjugate base. [3]

b) Calculate pH of 1×10^{-7} M solution of HCl at 25°C. Consider, $K_w = 10^{-14}$ mol^2 dm^{-6}. [2]

c) It is found that 0.1 M solution of three sodium salts NaX, NaY and NaZ at 25 °C have pHs 7.0, 9.0 and 11.0, respectively. Arrange the acids HX, HY and HZ in order of increasing strength. Where possible, calculate the ionization constants of the acids. [2]

d) Calculate the hydrolytic constant, degree of hydrolysis and pH of 0.25 M NaCN solution at 25°C (K_a(HCN) = 4.8×10^{-10} M). [3]

e) Briefly discuss on useful range of acid-base indicator. [2]

8. a) Calculate pH of a solution prepared by mixing 50.0 mL of 0.20 M CH_3COOH and 50.0 mL of 0.10 M NaOH solution. [Given K_a of acetic acid is 1.80×10^{-5}.] [2]

b) Derive the expression of pH of a solution of a salt of weak base and strong acid. [3]

c) Explain the term buffer index and buffer capacity. [2]

d) The dissociation constant of aniline as a base at 25°C is 5.93×10^{-10}. The ionic product of water at 25°C is 1.008×10^{-14}. Calculate the percentage hydrolysis of aniline hydrochloride in 0.1 M solution at 25°C. [2]

e) How do you apply the concept of solubility product in purification of common salt. [1]

f) For propanoic acid $K_a = 1.34 \times 10^{-5}$ M at 25 °C. Find for a 0.01 M solution of the acid:

i) the degree of dissociation.

ii) Hydrogen-ion concentration. [2]

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