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14 (CHM-I) CH 103

2017

CHEMISTRY

Paper : CH-103

(Physical Chemistry)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

[Symbols here signify their usual meanings.]

1. Answer ***any five*** from the following :

4×5=20

- a) Evaluate the partition function for a molecule with an infinite numbers of equally spaced non-degenerate energy levels.
- b) Find the expression for partition function, ground state population and excited state population for a system of one state at zero energy and another state at the energy ϵ .

Contd.

- c) What is characteristic vibrational temperature ? What is its significance ?
- d) Find the characteristic vibrational and characteristic rotational temperature for CO for its ground electronic state using following data :
- $\tilde{\nu}_e$ and $\tilde{\nu}_e x_2$ for CO are 2170cm^{-1} and 13.3cm^{-1} respectively.
- e) Derive the relations between molecular partition function q and canonical partition function Q for distinguishable independent and indistinguishable independent molecules.
- f) For an ensemble consisting of 1 mole of particles having two energy levels separated by $h\nu = 1.00 \times 10^{-20}\text{J}$, at what temperature will the internal energy of this system equal 1 kJ?
- g) Derive the electronic partition function for NO molecule.

2. Answer **any two** from the following :

$$4 \times 2 = 8$$

- a) Discuss the kinetics of anionic polymerization.

- b) (i) List the *three* mechanistic steps involved in controlled chain-growth polymerizations.
- (ii) List the *three* mechanistic steps involved in uncontrolled chain-growth polymerizations.
- (iii) Explain the last step involved in uncontrolled chain-growth polymerizations with an example.
- (iv) For an uncontrolled chain-growth polymerization, in general, describe the relative proportions of polymer : monomer that would be present at 10, 50 and 90% monomer conversions.
- c) Discuss the principle of Gel Permeation Chromatography (GPC).
- d) An anionic polymerization is initiated with a solution containing 0.1 *mole* of *n*-butyllithium in 100 *mL* of *n*-hexane. Initiator (1 *mL*) is added to a litre of hexane solution containing 1 mole of styrene monomer. At the end of the reaction, another mole of styrene is added and the reaction is terminated with water. What is the molecular mass of the polystyrene extracted from the solution ?

3. Answer **any six** from the following :

4×6=24

- a) For $T > T_B$ the equation of state $P(V_m - b) = RT$ is an improvement over the ideal gas law because it takes the ideal volume of the molecules into account. Derive an expression for the fugacity coefficient for a gas that obeys this equation of the state. Prove that $f = P^2/P_{ideal}$ if $V(\text{real}) \sim V(\text{ideal})$ is constant.
- b) Calculate the volume occupied by 1.0 kg of CH_4 gas at $T = 230\text{K}$ and $P = 68 \text{ bar}$ to find $V(\text{real}) - V(\text{ideal})$, if $z = 0.95$. Calculate fugacity of the gas under this condition.
- c) What can be known from activity coefficient value? One of the ways of determining the activity coefficients is from data on vapour pressure measurement. For solutions of acetone and chloroform, the vapor pressures and mole fractions are given below at

35°C. Find the activity coefficients of acetone and chloroform for the composition of serial number 2 below.

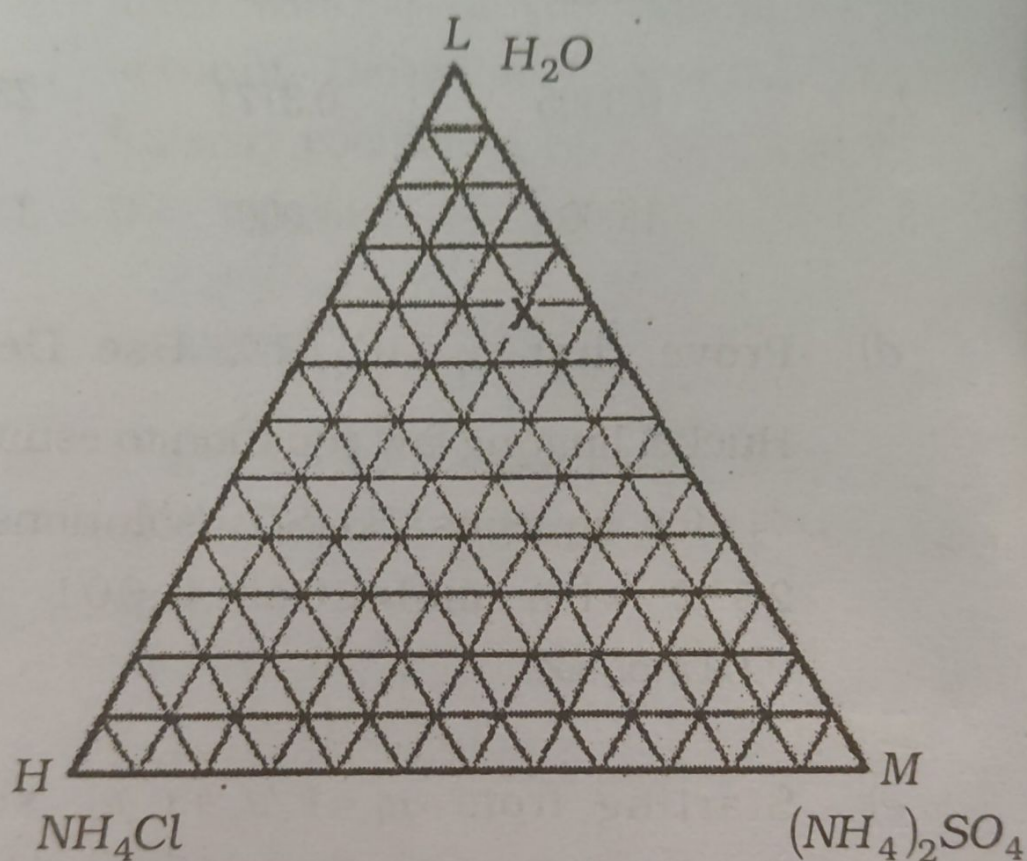
Serial no.	X_{acetone} (liquid)	X_{acetone} (vapour)	P (atm)
1.	0.000	0.000	293
2.	0.3365	0.3171	250
3.	1.000	1.000	344

d) Prove that $\gamma_i = W_{el}/RT$. Use Debye Hückel limiting law equation to estimate $\gamma_{\pm}$ for aqueous Na_2SO_4 solutions at 25°C with molalities 0.001 and 0.01 mol/kg.

e) Starting from $\mu_i = \nu_+ \mu_+ + \nu_- \mu_-$ show that electrolyte's chemical potential in solution can be found as

$\mu_i = \mu_i^0 + \nu RT \ln \nu_{\pm} \gamma_{\pm} \nu m_i / m_0$. How will you define μ_i^0 ?

- f) In the following phase diagram of a three component system of L (water), H (ammonium chloride), and M (ammonium sulphate) locate a point which represents a composition $X_L = 0.6$, and $X_M = 0.1$



Draw a phase diagram for this system at constant temperature and pressure and draw a line to show the change in composition of an unsaturated solution at point X if the solution is evaporated isothermally and isobarically.

g) Two pairs of liquids (A and C) and (B and C) are completely miscible and one pair (A and B) is partially miscible at room temperature and under atmospheric pressure. Draw a phase diagram for this system and explain. While drawing the diagram consider that C is more soluble in B than in A.

h) Define the term flux used in irreversible thermodynamics. What is the significance of L_{11} in the equation $J_1 = L_{11}X_1 + L_{12}X_2$?

Write the name of the phenomena for the following coupled forces operating on the system —

(A) ΔT , ΔP (B) ΔC , $\Delta \phi$

i) Consider a system in a stationary mode having two fluxes and two corresponding forces. Show that absolute value of cross coefficients must be smaller than or equal to the geometric mean of corresponding primary coefficients.

4. Answer **any two** from the following :

4×2=8

- a) What is meant by coefficient of variation? Calculate mean, standard deviation and coefficient of variation of the following percentage values :

2.08, 2.21, 2.09, 2.16, 2.14, 2.07, 2.14, 2.18, 2.11

- b) What is correlation coefficient? For the values $x_1, x_2, x_3 \dots \dots x_n$ and $y_1, y_2, y_3 \dots \dots y_n$ deduce the regression line.

- c) Interpolate $f(x)$ in a linear line at $x = 10$. The values for f_o and f_i are 15 and 35 at $x_o = 7$ and $x_j = 19$.

Is there any difference between Correlation Coefficient and Simple Linear Regression? Explain.

Following relations and data may be useful for you.

- (a) Vapour partial pressure,

$$p_i = a_i (\text{liquid}) \times P_i^*$$

$$\text{and } p_i = x_i (\text{vapour}) P$$

- (b) Debye-Hückel Limiting Law at 25°C for water as solvent is

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

- (c) Boltzmann constant (k_B or k)

$$= 1.38064 \times 10^{-23} \text{JK}^{-1}$$