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14 (CHM-1) 103

2022

CHEMISTRY

Paper : CH-103

(Physical Chemistry)

Full Marks : 60

Time : Three hours

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

(The Symbols signify their usual meaning)

1. Answer **any four** questions : $3 \times 4 = 12$

(a) For an ideal gas we can write the relation

$\mu = \mu(T, P) = \mu^0 + RT \ln P/P_0$. For a real gas which has pressure P , how would you like to define a term fugacity so that the chemical potential would come out right ?

Contd.

(b) Express fugacity for a Van der Waals gas for $a > 0$ and $b > 0$.

(c) Calculate the fugacity of a gas at 1000 K under 1000 atm, when $b = 0.04 \text{ dm}^3 \text{ mol}^{-1}$.

(d) Prove that fugacity coefficient $= \exp [f_0(Z-1)/P.dP]$, where Z is the compressibility factor.

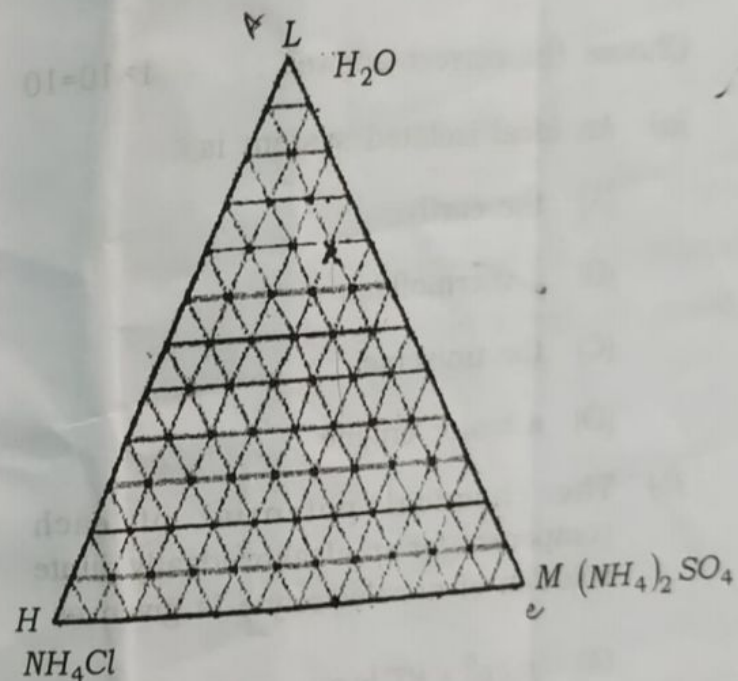
(e) Starting with relation $\mu_i = \nu_+ \mu_+ + \nu_- \mu_-$, prove that

$$\mu_i = \mu_i^0 + RT \ln \left[(\gamma_{\pm})^{\nu} (m_+/m^0)^{\nu_+} (m_-/m^0)^{\nu_-} \right]$$

for strong electrolytes when there is ion pairing.

(f) Find a relation to relate chemical potential of an electrolyte with the chemical potentials of its ions.

2. Draw a phase diagram for a system consisting of acetic acid, water and chloroform and explain it. What are the mole fractions of different components at X in the following diagram ? 4



3. Answer **any two** questions : 2×2=4

(a) What is the difference between an equilibrium state and a steady state ?

(b) What is the physical significance of Onsager's reciprocal relation?

(c) Prove that cross phenomenological coefficients may be positive or negative in a steady state situation.

4. Choose the correct answer : $1 \times 10 = 10$

(a) An ideal isolated system is

(A) the earth

(B) a thermoflask

(C) the universe

(D) a motor engine

(b) The chemical potential of each component for an ideal or ideally dilute solution of nonelectrolyte is given as

(A) $\mu_i = \mu_i^0 + RT \ln a_i$

(B) $\mu_i = \mu_i^0 + RT \ln x_i$

(C) $\mu_i = \mu_i^0 + RT \ln P_i$

(D) $\mu_i = \mu_i^0 + RT \ln f_i$

(c) For $Ca_{v+}(PO_4)_{v-}$, the values for v_+ , v_- , z_+ and z_- respectively are

(A) 3, 2, +3, and -2

(B) 3, -2, +3, and -2

(C) 3, 2, +2, and -3

(D) 3, 2, -3, and -2

(d) When temperature is very high ($T \gg \theta_v$, θ_v is characteristic vibrational temperature), the value of mean vibrational energy will be

(A) kT

(B) $\frac{1}{2} kT$

(C) $\frac{3}{2} kT$

(D) $\frac{3}{2} R$

(e) Consider N particles at temperature T , pressure P , volume V and chemical potential μ having energy E . The parameters that are kept constant for a canonical ensemble are

(A) N, V, T

(B) N, V, E

(C) N, P, T

(D) μ, V, T

(f) In a three-level system, all levels are nondegenerated having energies $0, \epsilon$ and 2ϵ respectively. At temperature, $T = 0$ and $T = \infty$, the partition function will be

(A) 0 and 3 respectively

(B) 1 and 3 respectively

(C) 0 and ∞ respectively

(D) 1 and ∞ respectively

(g) NO molecule has doubly degenerate ground electronic level and low lying doubly degenerate 1st electronic excited level. At room temperature the 1st electronic excited level is thermally accessible. If the ground and 1st excited levels have energies 0 and ϵ respectively, the electronic partition function of the molecule will be

(A) 2

(B) $2 - 2e^{-\beta\epsilon}$

(C) $2 + 2e^{-\beta\epsilon}$

(D) $1 + 2e^{-\beta\epsilon}$

(h) In a polymer which of the following statements is correct?

(A) Number average molar mass is always greater than weight average molar mass.

(B) Weight average molar mass is always greater than number average molar mass.

- (C) Polydispersity Index (PDI) is always less than one.
- (D) Viscosity average molar mass is always less than number average molar mass.

(i) A colorimetric titration yielded three non-concordant readings. To obtain a better reading, the titration was repeated three more times. Yet, concordant reading wasn't obtained among all the six readings. So, increasing the number of readings we had

- (A) increased accuracy
- (B) increased precision
- (C) decreased the standard error of the mean
- (D) increased the standard deviation

(j) Among 100 students in an M.Sc class, the favorite chemistry courses were, Quantum Chemistry (42), Statistical Thermodynamics (25), Retrosynthesis (8), Natural Products (13), Metallurgy (13). The variance-mean ratio will be

- (A) >1

- (B) <1

- (C) 1

- (D) indeterminate

5. Answer **any four** of the following :

4×4=16

(a) Find the partition function of a system one state at zero energy and another state at energy ϵ . Give the plot showing the variation of partition function with temperature.

(b) It is possible to derive any thermodynamic function from the partition function. Derive a relation between internal energy (U) and partition function (q).

(c) For a monatomic perfect gas, show that the entropy

$$S = nR \ln \frac{e^{5/2} kT}{p \Lambda^3}$$

where Λ is the thermal wavelength.

(d) What is residual entropy? Calculate the residual molar entropy for FCIO_4 molecule.

- (e) Derive an expression of translational partition function for a molecule of mass m in a container of volume V .

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

$$4 \times 2 = 8$$

(a) Why is gel permeation chromatography (GPC) also called the size exclusion chromatography? Discuss briefly the advantages of GPC over other polymer molecular weight determination methods.

(b) Define degree of polymerization and polydispersity index (PDI) of a polymer sample. Under what ideal conditions, will the PDI of a polymer sample become equal to 1?

(c) Discuss briefly the kinetics of cationic polymerization.

7. The following four points on the graph depict the change in the equilibrium constant (K_{eq}) of a unimolecular reaction as a function of absolute temperature. The points represent experimental data and the straight line represents a linear regression. Given that the straight line has a slope of 0.1 and an intercept of 0, find out if the straight line represents a linear regression obtained from least squares method.

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