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14 (CHM - 1) 103

2021

(Held in 2022)

CHEMISTRY

Paper : CH-103

(Physical Chemistry)

Full Marks : 60

Time : Three hours

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

1. Answer question number (a) and **any four**
from the rest : $4+(5\times 4)=24$

(a) Choose the correct answer :

- (i) For oxygen at 273 K following table
is given for pressures on
corresponding fugacities :

P (atm.)	50	100	200	400
f (atm.)	48	92.5	174	338

Contd.

ΔG_{real} and ΔG_{ideal} for compression of 1 mole of the gas from 50 to 200 atm, at 273 K respectively are —

- (A) 2875 J and 3146 J
- (B) 3146 J and 2875 J
- (C) 2785 J and 3416 J
- (D) 2275 J and 3346 J

(ii) Which is not correct ?

- (A) The compositions of the two conjugate solutions are given by the two ends of tie lines in a phase diagram of three liquids (say A, B and C) where one pair of liquids (say B and C) is partially miscible while other liquid (A) is soluble in both B and C.
- (B) Fugacity of a gas may be equal to, greater than or less than the pressure.
- (C) Phase rule for a system of three components at constant temperature or at constant pressure is $F = 5 - P$.

(D) The phenomenon of steady state obtained by pressure difference and temperature difference in a system is known as thermo-osmosis.

(iii) Which is Fick's law ?

- (A) $J_Q = -k dt / dx$
- (B) $J_m = -D dC / dx$
- (C) $J_Q = -D dC / dx$
- (D) $J_m = -k dt / dx$

(iv) For $Al(NO_3)_3$ which is true ?

- (A) $\mu(Al(NO_3)_3, aq) = 3\mu(Al^{3+}, aq) + \mu(NO_3^-, aq)$
- (B) $\mu(Al(NO_3)_3, aq) = 3\mu(Al^{3+}, aq) + 3\mu(NO_3^-, aq)$
- (C) $\mu(Al(NO_3)_3, aq) = \mu(Al^{3+}, aq) + 3\mu(NO_3^-, aq)$
- (D) $\mu(Al(NO_3)_3, aq) = \mu(Al^{3+}, aq) + \mu(NO_3^-, aq)$

(b) Draw the phase diagram of $NH_4Cl(s)$, $(NH_4)_2SO_4(s)$, and water system.

Explain indicating in the diagram the fate of the solution when you go on adding water to a mixture of the two solids initially taken in the mole fraction ratio of $NH_4Cl(s) : (NH_4)_2SO_4(s) = 2 : 8$ at constant temperature and pressure.

(c) Starting with expression, $G = H + TS$ prove that for an ideal gas $\mu = \mu^0 + RT \ln P/P^0$. Why μ is not equal to $\mu^0 + RT \ln P/P^0$ for a real gas? Define fugacity coefficient and state its significance.

(d) Find an expression for fugacity coefficient for a real gas. Define standard state for real gases.

(e) Find an expression for molality scale chemical potential for an electrolyte dissolved in a solvent, considering ion pair formation.

(f) The partial molar entropy and partial molar volume of a species can be calculated from measurements of chemical potential of the species as a function of temperature and pressure by use of two Maxwell relations for fundamental equation for G . State the two relations.

Calculate the fugacity of nitrogen gas under 50 bar and at 298 K.
 $(a = 1.5 L^2 \text{ bar mol}^{-2} \text{ and } b = 0.04 L \text{ mol}^{-1})$

(g) Find the general form of phenomenological relations. What is ORR and why it is important?

(h) What are fluxes and coupled forces? Define entropy production in a system where several forces are acting to keep the system under a steady state. How do you prove that $L_{ii} > 0$, but L_{ij} may be positive or negative.

2. Answer **any four** from the following questions : 5×4=20

(a) Evaluate the partition function for a molecule with an infinite number of equally spaced non-degenerate energy levels. From the derived expression, show the plot partition function as a function of temperature.

(b) Consider a three-level system where the energy levels are equally spaced and non-degenerate. The ground state energy is zero. Find an expression of the partition function for the system. Show the plot of the population of states P_0, P_1 and P_2 against temperature.

- (c) Define canonical, micro-canonical and grand canonical ensembles. Derive a relation between canonical partition function and molecular partition function for distinguishable independent molecules.
- (d) Derive the Sackur-Tetrode equation for the entropy of a monatomic gas. Calculate the entropy change for one mole of a monatomic ideal gas when it is transferred from 300 K at 20 atm. to 600 K at 4 atm pressure.
- (e) Define characteristic rotational temperature (θ_R) and characteristic vibrational temperature (θ_V). Show that $\langle \epsilon^T \rangle : \langle \epsilon^R \rangle : \langle \epsilon^V \rangle = 3/2 : 1 : 1$, where $\langle \epsilon^T \rangle, \langle \epsilon^R \rangle, \langle \epsilon^V \rangle$ are translational, rotational and vibrational mean energies respectively. (Given, $T \gg \theta_R, T \gg \theta_V$)
- (f) Derive an expression for equilibrium constant in terms of partition function.

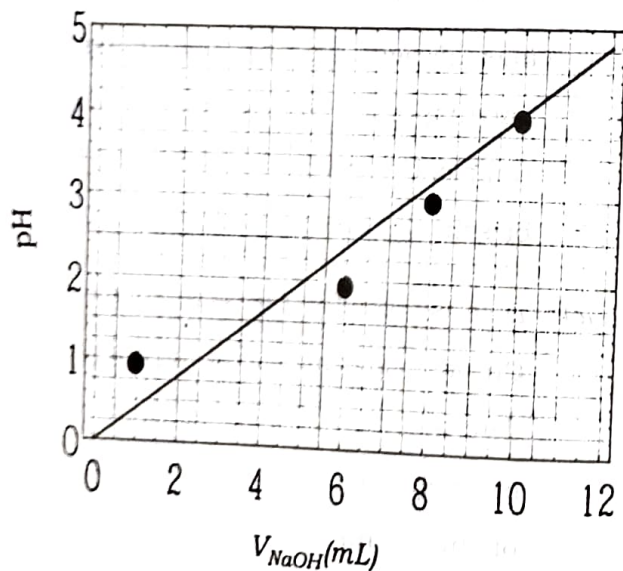
3. Answer **any two** of the following questions : 4×2=8

- (a) Discuss the kinetics of free radical chain polymerization. Define kinetic chain length and degree of polymerization.
- (b) Equal numbers of molecules with $M_1 = 10,000$ and $M_2 = 1,00,000$ are mixed. Calculate number average molar mass, weight average molar mass and polydispersity index (P.D.I.) of the sample. Under what condition the P.D.I. of sample becomes 1 ?
- (c) Discuss briefly the Gel Permeation Chromatographic (GPC) technique for determination of the molecular weight of a polymer ? What are the advantages of this technique ?

4. Answer the following question :

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The following four points on the graph depicts the change in pH of an acidic solution upon titration with an NaOH solution. The points represent experimental data and the straight line represents a linear regression. Given that the straight line has a slope of 0.4 and an intercept of 0, find out if the straight line represents a linear regression obtained from least squares method.



5. Select the correct answer from the given options :
1+1=2

(a) An acid base titration yielded three non-concordant readings. To obtain a better neutralization volume, the titration was repeated three more times. Yet, concordant reading wasn't obtained among all the six readings. So, increasing the number of readings —

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

(b) Among 100 students in an M.Sc class, the least favorite chemistry courses were Quantum Chemistry (25), Statistical Thermodynamics (42), Retrosynthesis (13), Natural Products (8), Metallurgy (13). What is the Index of Dispersion ?

- (A) > 1
- (B) < 1
- (C) 1
- (D) Indeterminate.