SC

SEAT No._____

[84]

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SARDAR PATEL UNIVERSITY

M. Sc. SEMESTER-I Examination

Saturday 27th October, 2018

10.00 A.M. To 01.00 P.M.

Physical Chemistry-I: PS01CCHE03 [Total Marks: 70]

N.B. Figures to the right of each of the question indicate marks

1. Choose appropriate answer of the following **[08]**

(i) The actual behavior of real gases can be studied by considering

(a) Free energy function (b) Pressure

(c) Volume (d) Temperature

(ii) Under the given set of conditions the process is regarded to be non-spontaneous if the value of ΔF is

(a) Negative (b) Positive (c) Zero (d) All

(iii) At freezing point the solution will always be in equilibrium with

(a) pure solute (b) pure solid solvent

(c) pure solvent (d) all of these

(iv) Fugacity integration constant depends on

(a) Temperature & nature of gas (b) Nature of gas & pressure

(c) Temperature & pressure (d) All of these

(v) The vapor pressure curve for solution exhibiting negative deviations which one is true

(a) CCl_4 + Benzene (b) Benzene + Cyclohexane

(c) $CHCl_3$ + Acetone (d) CCl_4 + Toluene

(vi) Which of the following is not an example of extensive property?

(a) Heat capacity (b) Mass

(c) Volume (d) Density

(vii) The rotational partition function (Q_{rot}^{0}) is given by

(a) $\frac{b\,I}{\sigma}$ (b) $\frac{b\sigma}{I}$ (c) $\frac{\sigma\,I}{b}$ (d) $\frac{b\,I}{m}$

(viii) If the solution is dilute, that is no. of moles of solvent is in excess of the total no. of moles of reacting substance then, $\Sigma nM =$ _____

(a) n_0M_o (b) Σn (c) ΣM_0 (d) All of these

2. Attempt any SEVEN of the following **[14]**

1. Discuss the thermodynamic significance of partial molar properties.
2. The nature of standard state is of no thermodynamic significance for activity and activity coefficient. Justify
3. Derive the equation for relative fugacity of an infinitesimal isothermal process.
4. Derive the equation for variation of fugacity of a gas with temperature.
5. Derive the expression of Direct method for partial molar property.
6. Give the confirmation of 3rd law of thermodynamics.
7. Give the criteria for the reaction to occur spontaneously.
8. Explain vapor pressure curves for ideal solutions.
9. Obtain the relation $f = P^2V/RT$

3. [A] Discuss Lewis-Randall rule for the determination of fugacity value in a gas mixture. **[6]**

[B] Derive the relation : $\ln f = \frac{b}{(v-b)} - \frac{2a}{RTV} - \ln\frac{(V-b)}{RT}$ **[6]**

OR

[B] Calculate the fugacity of ethane at T = 104.4 ^{0}C and P = 60 atm. on the basis of $\ln f = \ln P + \int_0^P \frac{K-1}{P}\,dP$ **[6]**

P (atm.)	13.61	27.22	40.82	54.43	68.04
κ	0.9509	0.8999	0.8476	0.7931	0.7349

4. [A] Derive the general form of reaction isotherm. What is the significance of reaction isotherm from chemical point of view? **[6]**

[B] What is Metathesis? Derive the equation for equilibrium constant for such reaction. [6]

OR

[B] (i) The EMF of the cell: [3]
$Tl_{amalgam}$ (N_2' = 0.00326) / $Th_{solution}$ / $Tl_{amalgam}$ (N_2 = 0.0986) is (-0.111118 volt) at 20 ^{0}C. Calculate the a_2/N_2 and a_2 for the Thallium in right hand amalgam.

(ii) Explain free energy function and also state it's applications [3]

5. [A] Define ideal solution. State the difference between the solution exhibiting positive and negative deviation from ideal behavior. [6]

[B] Obtain the relation for activity of solvent freezing point measurements. [6]

OR

[B] (i) The radiator of an automobile can hold 10 kg of water. It is proposed to prevent the freezing point of water at atmospheric temperature of 263.15 K by adding glycol. How much glycol is needed? If we use methanol in place of glycol then, what weight of methanol will be required under similar circumstances? [3]
[Given: Mol. Wt. Glycol = 62 gm/mol and that of methanol is 32 gm/mol, ΔH_f = 6008 J/mol., R = 8.314 J $K^{-1}mol^{-1}$]

(ii) Deduce the precise form of Duhem-Margules equation. [3]

6. [A] Derive the relation of partial molar volumes from density measurements. [6]

[B] At concentration exceeding 0.25 m the volume of NaCl solution per 1000 gm of water at 25 ^{0}C is given by, V = 1002.9 + 16.40m + 2.5m^2 – 1.2m^3 ml. The molar volume of pure water at 20 ^{0}C is 18.069 ml mol^{-1}. Derive the general expression for the partial molar volume and apparent molar volume of NaCl in aqueous solution and compare the values for a 1 molal solution. [6]

OR

[B] Derive the fundamental equation for partial molar properties. [6]

—X—