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[44 / A-24]

No of printed pages: 03

SARDAR PATEL UNIVERSITY

M.Sc. – Chemistry (First Semester) (CBCS)

Physical Chemistry-I

Course No: PS01CCHE03

Saturday, 09th April, 2016

Time: 10:30 A.M. to 01:30 P.M.

Total Marks: 70

Que.1 **Select correct answer of the followings** **(08)**

1 A gas described by van der Waal equation

(A) Behaves similar to an ideal gas in the limit of large molar volumes

(B) Behaves similar to an ideal gas in the limit of large pressures

(C) Is characterized by van der Waals coefficients that are independent on identity of the gas

(D) None of the above is correct

2 For the following reaction occurring in an automobile, $2C_8H_{18(g)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$; the sign of ΔH, ΔS and ΔG would be

(A) -, +, + (B) -, +, - (C) +, -, + (D) +, +, -

3 When a graph is drawn from partial pressure of a gas in vapour phase versus mole fraction of the gas in solution, it represents

(A) Avogadro's law (B) Boyle's law

(C) Charles's law (D) Henry's law

4 Which of the following statement is true? The entropy of the universe

(A) Increases and tends towards maximum value

(B) Decreases and tends to be zero

(C) Remains constant

(D) Decreases and increases with a periodic rate

5 The entropy of crystalline substance at absolute zero going by the third law of thermodynamics should be taken as

(A) 100 (B) 0

(C) 50 (D) Different for different substances

6 The signs for ΔH, ΔS and ΔG for the freezing of liquid water at -10^0C respectively are

(A) +, -, + (B) -, -, 0 (C) -, +, - (D) -, -, -

7 During depression of freezing point in a solution the following are in equilibrium

(A) Liquid solvent, solid solvent (B) Liquid solvent, solid solute

(C) Liquid solute, solid solute (D) Liquid solute, solid solvent

8 A binary liquid solution is prepared by mixing of n-heptane and ethanol. Which one of the following statements is correct regarding the behavior of the solution

(A) The solution formed is an ideal solution

(B) The solution is non-ideal, showing positive deviation from Raoult's Law.

(C) The solution is non-ideal, showing negative deviation from Raoult's Law

(D) n-heptane shows positive deviation while ethanol shows negative deviation from Raoult's Law.

Que.2 **Attempt any SEVEN of the followings** **(14)**

1 Derive an expression: F_2-$F_1 = RTln\frac{f_2}{f_1}$

2 For ideal gaseous mixture, derive $\mu_i = \mu_c^* + RTlnC_i$ from $\mu_i = \mu^* + RTlnP_i$

3 How can we distinguish molar properties and partial molar properties?

4 How can we distinguish partial molar properties and apparent molar properties?

5 It is required to pass CO at 10 atmospheres and water(g) at 5 atmosphere pressure into a reaction chamber at 700^0C and to withdraw carbon monoxide and hydrogen at partial pressure at 1.5 atm. is this possible thermodynamically? The equilibrium constant for the reaction is 0.71.

6 Derive an expression for mean ionic activity coefficient.

7 State applications of free energy function.

8 Show that mixing of two liquids which yield a system exhibiting positive deviation from Raoult's law there is an absorption heat?

9 Calculate the free energy change in (cal) for the composition of N_2 gas from 1 to 200 atmospheres at 25^0C.

Que.3 **A** What is the difference between pressure and fugacity? Derive an expression $lnf = lnp - \int_0^p \frac{\alpha}{RT}\,dp$ **(06)**

B The compressibility of a gas may be represented by $\frac{PV}{RT} = A + BP + CP^2 + DP^3$ .Where A,B,C,D are functions of the temperature. Hence derive an equation for the fugacity as a function of the pressure at a given temperature. For nitrogen at 0^0C, A is 1.000, B is -5.314×10^{-4}, C is 4.276×10^{-6} and D is -3.292×10^{-9} with P in atm. Upto 400 atm. Evaluate the fugacity of the gas at 300 atm. Pressure. **(06)**

OR

B The fugacity of $Hg_{(l)}$ at 100^0C and 1.0 atm. is 0.272 mm. having density 13.35 gm cm^{-3} and its molecular weight 200.6 gm $mole^{-1}$. Find its fugacity at the same temperature under a pressure of 100 atm. assuming it to be incompressible. **(06)**

Que.4 **A** Consider a general reaction at a constant temperature and derive an expression for law of equilibrium to provide a relationship between the activities of reactants and products. **(06)**

B Derive an equation for the partition function for a chemical reaction and also derive $K_f = \frac{\left(\frac{Q^0}{N}\right)_L^l \times \left(\frac{Q^0}{N}\right)_M^{m\times---}}{\left(\frac{Q^0}{N}\right)_A^a \times \left(\frac{Q^0}{N}\right)_B^{b\times---}} \times e^{\frac{-\Delta H_Q^0}{RT}}$ by using partition function. **(06)**

OR

B Taking the equilibrium constant (K_f) for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \leftrightarrow NH_3$ is to be 0.00655 at 450^0C and utilizing the heat of reaction and heat capacity data, derive general expression for the variation of equilibrium constant with temperature. Determine the value of K_f at 327^0C. **(06)**

(ΔH^0 = -9.13, $\Delta\alpha = -7.46$, $\frac{1}{2}\Delta\beta = 3.69 \times 10^{-3}$, $\frac{1}{3}\Delta\gamma = -0.47 \times 10^{-6} cal$)

Que.5 **A** Discuss the freezing point method for determining activity of solvent in solution. **(06)**

B **(i)** Show that in a dilute solution, the depression of the freezing point is proportional to the mole fraction of the solute. **(03)**

B **(ii)** How one can use the freezing point method for determination the molecular weight of the solute in the dilute solution? **(03)**

OR

B Mixtures of benzene and toluene behave almost ideally at 30^0C, the vapour pressure of pure benzene is 118.2 mm. and that of pure toluene is 36.7 mm. Determine the partial pressures and weight composition of the vapour in equilibrium with a liquid mixture consisting of equal weights of the two constituents. **(06)**

Que.6 **A** What is isotonic solution? Derive an expression **(06)**

$$ln\gamma_{\pm} = ln\gamma_R + \ln r + 2\int_0^{a_R^{1/2}} \frac{r-1}{a_R^{1/2}} .da_R^{1/2}$$

B Write note on method of intercept. **(06)**

OR

B A solute is dissolved in 1kg of water. The volume at 25^0C and 1 atm. can be expressed as V= 1000.38 + 20.56m + 2.02 m^2 – 0.24 m^3. Calculate the volume of solute and apparent molar volume for 0.5 molal solutions. **(06)**

BEST OF LUCK