2018
CHEMISTRY
CHM 101
PHYSICAL CHEMISTRY – I

Full Marks : 80

Time: 3 Hours

The figures in the margin indicates full marks for the questions

1   For a diatomic molecule, if the temperature is increased by two fold how its rotational partition function will change?   1

2   Discuss the vibrational contribution of partition function to the chemical potential.   5

3   What is thermal wavelength? How it varies with volume?   2

4   For a monoatomic ideal gas with no internal degree of freedom, show that $G_t = -NKT \ln\left[\dfrac{KT}{\rho\Lambda^3}\right]$ 4

5   Define residual entropy and the weight of configuration.   2

6   Establish the Onsager relation.   4

7   What is Flux? How it is related to the force?   3

8   Deduce Integrated Kirchhoff equation.   4

9   State the physical significance of fugacity. Show that at low pressure fugacity is equal to pressure. Calculate the free energy accompanying the compression of 1 mole of a gas at 57°C from 25 to 200 atm. The

1   .   **P.T.O.**

fugacities of the gas at 57°C may be taken as 23 and 91 atm respectively, at pressures of 25 and 200 atm. $\quad$ 1+2+2

10 Define activity of a substance. The activity of 2.5 moles of a substance changes from 0.05 to 0.35. What would be the change in its free energy at 27° C. $\quad$ 1+1

11 Discuss briefly three component system of water-acetic acid and chloroform. The following equations give the vapour pressures of ice and water:

$\ln P_{vapour}$ (ice) = -(6140.1/T) + 24.00

$\ln P_{vapour}$ (water) = -(5432.8/T) + 21.41

where P is in mm Hg. Calculate the temperature at the triple point.

3+2

12 State the significance of Mark-Kuhn-Houwink-Sakurada equation. What are the factors on which constants 'a' and 'k' of the equation depends? The intrinsic viscosity of a polystyrene sample in toluene at 25° C is 0.0504 dm^3g^{-1}. Calculate the molar mass of the sample. Given that k = 3.8 × 10^{-5} dm^3g^{-1} and a = 0.63. $\quad$ 2+1+2

13 Derive van't Hoff equation for a polymer sample relating osmotic pressure and molar mass of the sample. Insulin, a hormone that regulates carbohydrates metabolism in the blood, was isolated from a pig. Osmotic pressure of the sample of 8.0 gL^{-1} at 30° C was found to be 26.1 torr. Calculate the molecular weight of the insulin sample. (Given R =0.08206 atm $mol^{-1}K^{-1}$) $\quad$ 3+2

14 Write the difference between

a) LDPE and HDPE

b) The Sedimentation velocity method and the Sedimentation equilibrium method $\quad$ 3+3

15 Deduce an expression for Born's free energy change when the ion is introduced from vacuum into a medium of dielectric constant ϵ. How dielectric constants determine the spontaneity of this process? $\quad$ 5+1

16 Name the methods use to determine solvation number of electrolytes.

2

17 Discuss the structure of water in presence of a cation $\quad$ 5

18 Using the random-walking model of ions, establish a relation between the mean square distance and the coefficient of macroscopic Fick's law. $\quad$ 7

19 Discuss about the approximation laid down to establish the Debye-Huckel equation for ion-solvent interaction. Comment on the applicability & validity of this form of equation w.r.t. electrolytic solution. $\quad$ 5+2

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