

MAY 2015

P/ID 40123/PCHC

Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

1. Define differential heat of solution.
2. Write the expression for the variation of chemical potential with temperature at constant pressure.
3. Write the expression for the fugacity of a Van der Waal's gas.
4. What is meant by probability factor?
5. Express the rate constant of a bimolecular reaction in terms of partition functions.
6. Define volume of activation.
7. How is Arrhenius energy of activation determined?
8. What is meant by secondary kinetic isotope effect?
9. Show that C_2 operation changes R_x .
10. Mention the point groups of SF_6 and phenanthrene.

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

11. (a) (i) Define partial molar volume. Explain the determination of partial molar volume of solvent in a solution of nonvolatile solute using density measurements. (14)
- (ii) How partial molar volumes are useful in understanding the behaviour of a mixture of two liquids. (6)

Or

- (b) (i) Obtain the expression for the activity of a solvent in a dilute solution of nonvolatile solute in terms of the depression in freezing point. (15)
- (ii) The variation of the activity of water in dilute KCl solution is given by

$\ln a_1 = -9.702 \times 10^{-3} \theta - 5.2 \times 10^{-6} \theta^2$
where θ is the depression in freezing point. Calculate the activity of water in a KCl solution which has a freezing point of -0.345°C .

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12. (a) Draw the potential energy surfaces for any two chemical reactions and explain.

Or

- (b) Explain the determination of free energy of activation, enthalpy of activation and entropy of activation. Explain the significance of each.

13. (a) Derive an expression for the variation of rate constant of a reaction between ions with the dielectric constant of the solvent using single sphere models. How can it be verified experimentally?

Or

- (b) Explain the determination of the catalytic coefficients for a general acid-base catalysis.

14. (a) (i) What symmetry elements make D_{3h} point group. Give two examples for D_{3h} point group. (5)
(ii) Explain the construction of character table for C_{3v} point group. (15)

Or

(b) Show using group theory that $\pi-\pi^*$ transition results in a strong uv band whereas $n-\pi^*$ transition leads to a weak band taking HCHO as example. The character table of C_{2v} point group is given below :

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	Z, x^2 , y^2 , z^2
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x