

2007

CHEMISTRY

PAPER-I

Full Marks : 75

Time : 3 hours

The Figures in the right hand margin indicate marks

Candidates are required to give their answers in their own- words as far as practicable

Illustrate the answers wherever necessary

GROUP-A

Answer any *one* question

- 1** (a) Define precise values and expectation values in quantum mechanics.
- (b). State and prove 'Turn Over' rule.
- (c) Find the

$$\{\tilde{H}, r_{\pm}^n\}.$$

(2 + 2) + 6 + 5

(Turn Over)

Or

(a) Find the commutator

(i) $[L_z, L_x]$

(ii) $[L_x, L_y]$

where L_+ and L_- are raising and lowering operators respectively.

(b) What is tunneling? Explain this with the help of uncertainty principle.

(c) Prove that if A and B are Hermitian operators then $[A, B]$ is anti-Hermitian.(d) If $AV = aV$, what is the value of 'b' in the eigen-equation $e^{iA} V = bV$ (3 + 3) + 3 + 4 + 2

2. (a) Show that

$$(\hat{L}_x, \hat{L}_y) = 2A(\hat{L}_z, -\hat{L}_y z)$$

(b) What is meant by phase velocity and group velocity? How can it be shown that the energy of subatomic material particles is transported by wave packet? 5+(4+6)

GROUP - B

Answer *any two* questions

(a) Obtain the expression for the thermodynamic probability of the distribution of n . particles in i -different energy states , the i state being g . -fold degenerate and hence obtain the Boltzmann distribution formula in term of the energy multiplier θ and the molecular partition function.

(b) Using Boltzmann distribution formula calculate the ratio of population of particles in two nondegenerate levels with energies $.10$ and 20 K cal/mole at 27° C. 11+4

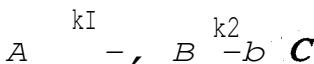
4. (a) Find out the expression for molecular partition function due to rotational motion and hence show that the molar rotational. energy is RT .

(b) What is fugacity co-efficient ? What is its utility ?

(c) Define a grand-canonical ensemble.

- (d) 2 gm-moles of water initially at 27°C are converted to a final state of vapour at 227°C at 1 atmospheric pressure. Given that heat capacity of water and water vapour are 1 cal/gm and 0.40 cal/gm respectively, latent heat of vaporisation of water is 540 cal/gm, compute the total change in entropy. (Assume ideal behaviour of vapour). (5+2)+(1+1)+3+3

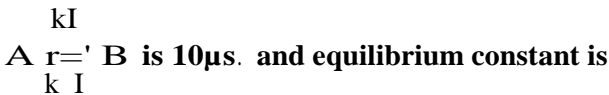
5. (a) Considering the following consecutive reaction,



obtain expressions for the maximum concentration of B and also for the time when concentration of B will be maximum.

- (b) What is flow method? What are its limitations?

- (c) Relaxation time for the fast reaction



1.0×10^{-3} . Calculate k_1 and k_{-1} . 7+4+4

6. (a) How does the electron transfer reactions by inner sphere mechanism occur? Show with a suitable example. Illustrate with an example.

(b) Write down the salient features of transition state theory.

(c) The protein catalase catalyzes the reaction



and has a Michaelis constant $K_m = 25 \times 10^{-3} \text{ mol dm}^{-3}$ and a turnover number of $4.0 \times 10^7 \text{ s}^{-1}$. Calculate the initial rate of this reaction if the total enzyme concentration is $0.16 \times 10^{-6} \text{ mol dm}^{-3}$ and the initial substrate concentration is $4.32 \times 10^{-6} \text{ mol dm}^{-3}$. Calculate $v_{m, \infty}$ for this enzyme. Catalase has a single active site. 6+4+5

GROUP -C

Answer any *two* questions

7. (a) Solve linearised Poisson-Boltzmann equation for dilute ionic solution (given below) and find its approximate solution

$$\nabla^2 \psi = -\frac{\rho_f}{\epsilon_0} - \sum_i z_i e n_i \exp\left(-\frac{z_i e \psi}{k_B T}\right) \quad (r)$$

(symbols have their usual meaning).

- (b) Define Debye-Huckel reciprocal. length (rnH) and show that

$$\text{rnH} = \frac{500 \text{ DEO KB T }^{1/2}}{NA^2 \epsilon I}$$

(symbols have their **usual meaning**).

- (c) Calculate Debye-Huckel reciprocal length of **ionic atmosphere** for 5×10^{-3} (N) K₂S₀₄ solution **in a solvent of dielectric constant 60** at 27°C. 5+5+5

8. (a) Writedown the Butler-Volmer equation for one-step single electron transfer electrodic reaction and explain the terms involved. Show that V) near equilibrium it reduces to Ohm's law for interfaces and (ii) far away from equilibrium it becomes an exponential Tafel's law.
- (b) Describe the basic principle for determination of dissociation constant of a weak electrolyte precisely by a conductometric method.
- (c) Describe the basic principle of cyclic voltametry briefly. 8+4+3

(a) Write down the selection rule and hence deduce the expression of frequency for the P and R branch of line in vibration-rotation combined spectrum.

(b) Partial infra-red spectral data of $^{12}\text{C}^{16}\text{O}$ molecule under high resolution are as follows :

Line	w, cm ⁻¹	Line	w, cm ⁻¹
P ₁	2139.43	R ₁	2147.08
P ₂	2135.55	R ₂	2150.86
P ₃	2131.63	R ₃	2154.59
P ₄	2127.68	R ₄	2158.31

Calculate the bond length of $^{12}\text{C}^{16}\text{O}$.

(c) Energy expression of a diatomic molecule exhibiting Morse potential is given by,

$$E = (v + \frac{1}{2}) h\nu - \frac{h^2 x^2}{4\mu r_0^2} \quad (+!)$$

For what value of vibrational quantum number, the molecule will dissociate. Deduce an expression for the dissociation energy of the molecule.

(1+2+2)+5+(3+2)

10. (a) What is Raman Scattering? How does classical mechanics account for the existence of Rayleigh as well as Raman lines

(b) What do you mean by London dispersion energy? **F₂ and Cl₂ are gases at room temperature, Br₂ is liquid and I₂ is solid. Explain.**

(c) Explain, why only molecules **having permanent dipole moment are rotationally active.**

$$1(Z+J)+(S+Z)\pm 3$$

11. (a) Define rotational constant of a molecule. The **rotational** constant for H³⁵Cl is observed to be 10.5909 cm⁻¹. What is the value of the **rotational constant** for ²D₃₅₀₁

(b) On what factors does the intensity of a spectral line depend? Show that the intensity of a spectral line in the rotation spectra will be maximum when

$$j = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

[The symbols have their usual significance].

(c) Show that in the spectrum of a non-rigid rotator, the separation between successive lines decreases steadily with increasing J value.

5+5+5