PG/I/CHEM/I/07

2007

CHENIISTRY

PAPER-I

Full Marks :7 5

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

Or

(a) Find the **commutator**

(i) $[L_Z \; L_+]$

(ii) $[L_- \; L_+]$

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 $\hat{A}$ and $\hat{B}$ **are Hermitian operators** then $[A, B]$ **is anti-Hermitian.**

(d) If $A\psi = a\psi$, **what is the value of** 'b' **in the eigen-equation** $e^{A}.\psi = b\psi$ (3 + 3) + 3 + 4 + 2

2. (a) Show that

$$(L_L, z) = 2A(9\hat{L}, -\hat{L}yz)$$

(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 0 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,

$$A \xrightarrow{kI} B \xrightarrow{k2} C$$

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

$$A \underset{k\_I}{\overset{kI}{r='}} B$$

is 10μs. **and equilibrium constant is** 1.0x 10-3 . **Calculate kl andk _r .** 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

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

and has a Michaelis constant $K_m = 25 \times 10^{-3}$ mol dm^{-3} and a turnover number of 4.0×10^7 S^{-1}. Calculate the initial rate of this reaction if the total enzyme concentration is 0.016×10^{-6} mol dm^{-3} and the initial substrate concentration is 4.32×10^{-6} mol dm^{-3}. Calculate v_{max} 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

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\phi}{dr}\right) = \frac{\sum_i z_i e^2 f_i(r)}{KBT}$$

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

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

$$\text{rnH} - \frac{500\ DEO\ KB\ T\ 1/2}{NA^2eI}$$

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

(c) Calculate Debye-**Huckel reciprocal length of ionic atmosphere** for 5 x 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 week electrolyte precisely by a conductometric method.

(c) Describe the basic principle of cyclic voltametry briefly. 8+4+3

(a) Writedown 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 12C 160 **molecule under high resolution are as follows :**

Line	w, cm-	Line	w, cm-
P,	2139.43	RI	2147 08
P2	2135.55	**R2**	**2150.86**
P3	2131.63	R3	2154.59
P4	2127.**68**	**R4**	**2158.31**

Calculate the bond length of 12C 160 .

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

$$E = (v+21 \text{ by} - \boldsymbol{hvxe\ (+!)}$$
$$\boldsymbol{2}$$

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 existance of Rayleigh as **well as Raman fines**

(b) What do you mean by London dispersion energy? **F2 and Cl2 are gases at room temperature**, **Br2 is liquid ' and 12 is solid. Explain.**

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

1Z+J)+(S+Z)±3

11. (a) Define rotational constant of a molecule. The **rotational** constant for H35 Cl is observed to be 10.5909 cm" . What - is the value of the **rotational constant** for 2 D 3501

(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 ! value.

5+5+5