PG/IS/CH - 1101/09

M.Sc 1st Semester Examination, 2009

CHEMISTRY

PAPER—CH-1101

Full Marks : 40

Time : 2 hours

Answer **five** questions
taking **one** from each Group

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* of the following

1. (*a*) Describe one Gedanken experiment to derive an expression for the approximate uncertainty relation.

(*b*) If two hermitian operators commute, they must have common eigenfunction. Show this with examples. 4 + 4

2. (*a*) Show with derivation and explanation that the process for classical wave equation is not same for quantum mechanical wave equation.

(*b*) If $\hat{A}u = u^*$, will $\hat{A}$ be linear? 6 + 2

Or

(*a*) Derive the exact uncertainty relation and hence using that relation get the uncertainty relation in the precise form for the pairs of canonically conjugate variables (x, P_x).

(*b*) Show that the non-degenerate eigenfunctions of a hermitian operator are orthogonal to each other. 5 + 3

GROUP—B

Answer any *one* of the following

3. Deduce the expression for "Bjerrum critical distance" and thereby obtain the condition for ion-pair formation. Deduce also the related expression for the ion-pair formation constant.

3 + 2 + 3

4. (*a*) What is ion association ? Show that the interionic distance, r_{min} for which the probability of finding two oppositely charged ions together is $\frac{z_+ z_- \epsilon^2}{2DKT}$.

(*b*) Define charge density. Write down Poisson's equation for electrical potential (ψ).

Show that,

$$\psi = \frac{Z_i \epsilon}{Dr} - \frac{Z_i \epsilon K}{D}.$$

4 + 4

Or

(*a*) Derive an expression for the association constant of an electrolyte solution using Fuoss model.

(*b*) How would you determine the association constant of the ions forming a weak acid of HA-type by EMF measurements? 5 + 3

GROUP—C

Answer any *one* of the following

5. (*a*) What do you understand by "principle of detailed balancing"?

(*b*) Write short note on reversible or opposing reaction.

(*c*) Write down the working principle of flash photolysis. 3 + 4 + 1

6. (*a*) Find out the relaxation time of the reaction.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C.$$

(*b*) The constant pressure molar heat capacity of $O_2(g)$ from 300 K to 1000 K is given by

$$C_p(T)/JK^{-1}mol^{-1} = 25 \cdot 42 + (12 \cdot 92 \times 10^{-3} K^{-1}) T - (38 \cdot 52 \times 10^{-7} K^{-2}) T^2$$

where T is in Kelvins. Calculate the values of ΔS when 1 mole of $O_2(g)$ is heated at constant pressure from 300 K to 1000 K. 6 + 2

Or

(*a*) Considering the following consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

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? 5 + 3

GROUP—D

Answer any *one* of the following

7. (*a*) Define ensemble and thermodynamic probability.

(*b*) Derive Fermi-Dirac distribution law. (1 + 1) + 6

8. (*a*) State and explain 'partition function'. Derive an expression for 'vibrational partition function' (Q_v).

(*b*) If $Q_t = \frac{(2\pi mkT)^{3/2} v}{h^3}$, show that molar translational heat capacity, $C_v = \frac{3}{2}R$. 4 + 4

Or

(*a*) Derive Sackur-Tetrode equation for an ideal gas.

(*b*) Distinguish between bosons and fermions. 5 + 3

GROUP—E

Answer any *one* of the following

9. (*a*) What do you mean by prolate and oblate symmetric top? Give one example of each. Write down the energy expression for prolate and oblate symmetric top.

(*b*) Show that, for a rigid diatomic molecule, the transition moment integral given non-zero value only when $\Delta M = 0$ and $\Delta J = \pm 1$. (where symbols have their usual significance) Given below the Recursion formula for Associated Legendre function.

$$(2J+1)x\ P_J^{|M|}(x) = (J-|M|+1)P_{J+1}^{|M|}(x) + (J+|M|)\,P_{J-1}^{|M|}(x).$$

(1 + 1 + 1) + 5

10. (*a*) Write down the expression and also give a schematic plot of Morse potential for Anharmonic oscillator.

(*b*) Show that the spacing between two consecutive vibrational level, for Anharmonic Oscillator decreases with the increase in vibrational quantum number.

(*c*) What do you mean by Raman Scattering ? How do you account for the appearence of Stokes and Anti-Stokes Raman lines using the principles of Quantum Mechanics.

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

Or

(*a*) The intensity of lines in the microwave spectra of a rigid diatom has been found to maximise in the intermediate j values— comment.

(*b*) What do you mean by fundamentals, overtones and hot bands in vibrational spectra ? Obtain the expression of frequency for these bands. 4 + (2 + 2)
