

**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

$$\text{is } \frac{z_+ z_- \epsilon^2}{2DKT}.$$

- (b) Define charge density. Write down Poisson's equation for electrical potential ( $\psi$ ).

Show that,

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

4 + 4

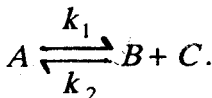
Or

- (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.



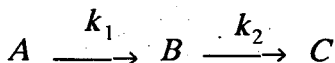
(b) The constant pressure molar heat capacity of  $O_2(g)$  from 300 K to 1000 K is given by

$$C_p(T)/JK^{-1}mol^{-1} = 25.42 + (12.92 \times 10^{-3} K^{-1}) T - (38.52 \times 10^{-7} K^{-2}) T^2$$

where  $T$  is in Kelvins. Calculate the values of  $\Delta S$  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



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 appearance 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.

$$4 + (2 + 2)$$