

M.Sc. 1st Semester Examination, 2012**CHEMISTRY**

PAPER – CEM- 101

*Full Marks : 40**Time : 2 hours*

Answer any **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*

GROUP – A

Answer any *one* of the following

1. Show that $\psi^* \psi$ satisfies the Uncertainty equation. 8
2. If the functions ψ_1, ψ_2 etc. are given, which are normalised but not orthogonal, derive the general formula for orthonormal ϕ_n using the given functions. 8

GROUP – B

Answer any *one* of the following

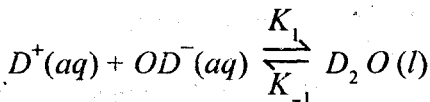
3. (a) Distinguish between identical distinguishable and indistinguishable particle.
- (b) Derive the expression for molecular translational partition function of a perfect monoatomic gas. 3 + 5
4. (a) Define grand canonical ensemble.
- (b) Obtain the expression for the thermodynamic probability for the distribution of a system of particles which can be described by antisymmetric wave function and hence derive the appropriate distribution. 2 + 6

GROUP – C

Answer any *one* of the following

5. (a) What do you understand by "principle of detailed balancing"?
- (b) Derive the rate expression of flow method of a kinetic reaction. 2 + 6

6. (a) "Transition state theory is better than collision theory" – Justify the statement.
- (b) The equilibrium constant for the reaction



at 25°C is $K_c = 4.08 \times 10^{16} \text{ mol}^{-1} \text{ dm}^3$. The rate constant K_{-1} is independently found to be $2.52 \times 10^{-6} \text{ s}^{-1}$. What do you predict for the observed relaxation time for a temperature jump experiment to a final temperature of 25°C? The density of D_2O is $\rho = 1.104 \text{ g cm}^{-3}$ at 25°C. 2 + 6

GROUP – D

Answer any *one* of the following

7. (a) How do you obtain the electrical potential as a function of its distance from a central ion in a dilute electrolyte solution?
- (b) "The ion atmosphere around an ion can be considered to possess certain effective thickness" – explain.

(c) Calculate optimum separation distance between Zn^{2+} and SO_4^{2-} in aqueous ZnSO_4 solution at 25°C to form Bjerrum's ion pair. (Given, dielectric constant of water = 80, $e = 4.8 \times 10^{-10}$ esu, $k = 1.34 \times 10^{-16}$ ergs k^{-1} molecule $^{-1}$.) 4 + 2 + 2

8. (a) Obtain an expression for association constant of an ion pair following Fuoss model.
- (b) What do you mean by mean ionic activity co-efficient? Calculate the mean ionic activity co-efficient of 0.02 M Na_3PO_4 solution at 298 K using DH limiting equation [Given $A = 0.51 \text{ M}^{-1/2}$]. 5 + 1 + 2

GROUP – E

Answer any *one* of the following

9. (a) Use Harmonic oscillator model to explain that there must be some fluctuation in dipole moment during molecular vibration to show vibrational transition. And also deduce the selection rule ($\Delta v = \pm 1$) for vibrational transition. Identity relation for Hermite polynomial is give below :

$$\xi H_v(\xi) = v \cdot H_{v-1}(\xi) + \frac{1}{2} H_{v+1}(\xi).$$

- (b) How do you obtain the fundamental vibrational frequency of a non-rigid diatomic molecule from its rotational spectra ? (2 + 3) + 3

10. (a) Schematically show the orientations of angular momentum vector of a rigid diatomic molecule in its $J = 0, 1, 2$ state ($J =$ rotational quantum number). What inference can you draw from your above schematic diagram ?

- (b) Find out the fundamental vibrational frequency and rotational constant (\bar{B}) of HCl molecule from some lines of P and R branches given in the following table. (Use rigid rotator-Harmonic oscillator model).

Line	$\bar{\nu} (\text{cm}^{-1})$	Line	$\bar{\nu} (\text{cm}^{-1})$
P_1	2865.10	R_0	2906.24
P_2	2843.62	R_1	2925.90
P_3	2821.56	R_2	2944.90
P_4	2798.94	R_3	2963.29

- (c) "Amplitude of vibration of a quantum Harmonic Oscillator increases with the increase in vibrational quantum number." – Justify or criticize the statement.

3 + 3 + 2

