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

$$D^{+}(aq) + OD^{-}(aq) \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} D_2O\,(l)$$

at 25° C is $K_C = 4{\cdot}08 \times 10^{16}\ \text{mol}^{-1}\ \text{dm}^3$. The rate constant K_{-1} is independently found to be $2{\cdot}52 \times 10^{-6}\ \text{s}^{-1}$. 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 $\rho = 1{\cdot}104\ \text{g cm}^{-3}$ 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, $e = 4{\cdot}8 \times 10^{-10}$ esu, $k = 1{\cdot}34 \times 10^{-16}$ 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 $A = 0{\cdot}51\ M^{-1/2}$]. 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 Harmite polynomial is give below :

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

(*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	$\bar{\nu}\,(cm^{-1})$	Line	$\bar{\nu}\,(cm^{-1})$
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
