M.Sc. 1st Semester Examination, 2011

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

Canditates 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. Discuss critically :

(*a*) The conventional statement of the uncertainty principle is not correct.

(*b*) Starting from classical wave function the corresponding differential equation is derived, but in a similar way from wave function of a subatomic matter particle, the respective differential equation is not derived. 4 + 4

2. (*a*) What is meant by time localisation of a wave packet ? Using it derive the uncertainty product.

(*b*) If the potential energy operator of the Schrödinger equation contains $\hat{V}(t)$ only, show that its solution represents a stationary state. 4 + 4

GROUP – B

Answer any *one* of the following

3. (*a*) What is an ensemble ?

(*b*) Obtain an expression for the thermodynamic probability of distribution of particles describable by symmetric wave function. Under what conditions does such a distribution reduce to Boltzmann distribution ? 2 + (4 + 2)

4. (*a*) Obtain the expression for the rotational contribution to the molar entropy of a homonuclear diatomic gaseous molecule.

(*b*) Calculate the translational molecular partition function for H_2 in a volume of $1 cm^3$ at $T = 300$ K. ($h = 6{\cdot}62 \times 10^{-34}$ Js, $K = 1{\cdot}38 \times 10^{-23}$ JK^{-1} 4 + 4

GROUP – C

Answer any *one* of the following

5. (*a*) Define consecutive reaction with a suitable example.

(*b*) Is unimolecular reaction possible according to collission theory ?

(*c*) The gas-phase rearrangement reaction. Vinyl allyl ether→ allyl acetone has a rate constant of $6{\cdot}015 \times 10^{-5}$ s^{-1} at 420 K and a rate constant of $2{\cdot}971 \times 10^{-3} s^{-1}$ at 470 K. Calculate the values of the Arrhenius parameters A and E_a. Calculate the values of $\Delta^{\neq}H^{\circ}$ and $\Delta^{\neq}S^{\circ}$ at 420 K (Assume ideal-gas behavior). 3 + 1 + 4

6. (*a*) Write down the principle of flow method to study a kinetic reaction.

(*b*) Find out the expression for the relaxation time of the reaction

$$H_2O\ (aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H^+\ (aq) + OH^-(aq)$$

where, k_1 and k_{-1} are the forward and backward reaction rate constant respectively.

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. 6 + 2

8. (*a*) Deduce the expression for 'Bjerrum critical distance' of ion-pair formation and thereby obtain the condition for ion pair formation.

(*b*) How would you determine experimentally very accurate value of association constant of an electrolyte by any suitable method ? 4 + 4

GROUP – E

Answer any *one* of the following

9. (*a*) Justify or criticize the following (any *two*) : 2 x 2

(*i*) A molecule can not be at rest (no vibration) even in its lowest vibrational level ($v = 0$).

(*ii*) For a rigid diatomic molecule, energy gap between the consecutive energy levels decreases with the increase in rotational quantum number.

(*iii*) For a diatomic molecule obeying Harmonic Oscillator principle, the amplitude of vibration decreases with the increase in vibrational quantum number.

(*b*) Starting from the energy expression of Anharmonic Oscillator, deduce the expression of its dissociation energy. 4

10. (*a*) Write down the energy expression of a diatomic vibrator using rigid rotor and Harmonic oscillator model. (Assume there is no interaction between rotational and vibrational motion). Deduce the frequencies (at least three) of *P* and *R* branch lines. Comment on your results.

(*b*) Rotational Raman shifts are twice the frequency of Rotation of the molecule. Explain. (2 + 3) + 3