

**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  
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. 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)

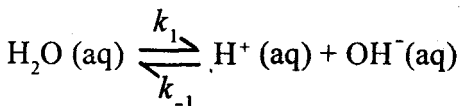
4. (a) Obtain the expression for the rotational contribution to the molar entropy of a homonuclear diatomic gaseous molecule.
- (b) Calculate the translational molecular partition function for  $H_2$  in a volume of  $1\text{ cm}^3$  at  $T = 300\text{ K}$ .  
 ( $h = 6.62 \times 10^{-34}\text{ Js}$ ,  $K = 1.38 \times 10^{-23}\text{ JK}^{-1}$ ) 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 collision theory?
- (c) The gas-phase rearrangement reaction. Vinyl allyl ether  $\rightarrow$  allyl acetone has a rate constant of  $6.015 \times 10^{-5}\text{ s}^{-1}$  at  $420\text{ K}$  and a rate constant of  $2.971 \times 10^{-3}\text{ s}^{-1}$  at  $470\text{ K}$ . Calculate the values of the Arrhenius parameters  $A$  and  $E_a$ . Calculate the values of  $\Delta^\ddagger H^\circ$  and  $\Delta^\ddagger S^\circ$  at  $420\text{ K}$  (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



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. :S  
ir

(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.  $(2 + 3) + 3$
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