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PG/IIS/CEM-201/14

M.Sc. 2nd Semester Examination, 2014

CHEMISTRY

PAPER – CEM - 201

*Full Marks : 40*

*Time : 2 hours*

Answer **five** questions taking **one** from each Group.

*The figures in the right-hand margin indicate marks*

GROUP – A

Answer any **one** of the following :

1. Find out the eigenfunction and  $\hat{L}_z$  and show that its eigenvalues are integral for orbital motion. 4 + 4
2. Derive the lowest eigenvalue and lowest eigenfunction of linear Harmonic Oscillator by operator technique. 4 + 4

( Turn Over )

( 2 )

GROUP – B

Answer any **one** of the following :

3. (a) Define 'phase space' and 'thermodynamic probability'.

(b) What are 'Fermions' ?

(c) Calculate the rotational partition function for CO at 25°C having characteristic rotational temperature 2.77 K.

$$\left\{ \left( 1\frac{1}{2} + 1\frac{1}{2} \right) + 2 + 3 \right\}$$

*Or*

Assuming the expression for the thermodynamic probability of distribution of  $n$  distinguishable particles in  $i$ -different states, the  $i$ th state being  $g_i$ -fold degenerate, obtain the Boltzmann distribution Law in terms of the energy multiplier  $\beta$  and the molecular partition function.

8

4. (a) Obtain an expression for the translational contribution to the molar energy of a perfect monoatomic gas molecule.

( 3 )

- (b) What is the significance of molecular partition function ? 6 + 2

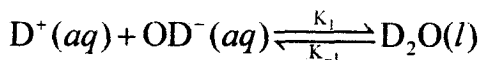
GROUP – C

Answer any one of the following :

5. (a) Define Oscillating reaction with a suitable example.
- (b) The presence of  $4.8 \times 10^{-6} \text{ mol dm}^{-3}$  of a competitive inhibitor decreases the initial rate of  $1.11 \times 10^{-4} \text{ mol dm}^{-3}\text{s}^{-1}$  by a factor of 3.6. If the maximum velocity of the reaction and the substrate concentration are  $0.64 \text{ mol dm}^{-3}\text{s}^{-1}$  and  $4.32 \times 10^{-6} \text{ mol dm}^{-3}$  respectively, find out the equilibrium constant for the binding reaction between the enzyme and the inhibitor. Given  $K_m = 25 \times 10^{-3} \text{ mol dm}^{-3}$ . 4 + 4
6. (a) What is redox reaction ?
- (b) How does a redox reaction occur by inner sphere mechanism ?

( 4 )

(c) 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  $\rho = 1.104 \text{ gcm}^{-3}$  at 25°C. 1 + 3 + 4

#### GROUP – D

Answer any **one** of the following :

7. (a) How do you obtain the unit of diffusion co-efficient from Fick's first law ?
- (b) Derive Einstein's relation  $\bar{x}^2 = 2Dt$ , where the terms have their usual significances.
- (c) Derive the electrophoretic component of drift velocity of ion. 2 + 4 + 2

( 5 )

8. (a) Derive an expression of concentration over-potential involving limiting current density.

(b) Prove Heynovsky's equation,

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i},$$

where the terms bear usual significances.

4 + 4

### GROUP – E

Answer any **one** of the following :

9. (a) State and explain the selection rule for pure rotational Raman transition of diatomic molecule.

(b) What is stimulated Raman Scattering ? Use energy level diagram to explain the appearance of stimulated stokes and Anti-stokes vibrational Raman Scattering.

5 + 3

10. (a) Write down the MO configuration of  $N_2$  and  $O_2^-$  and also deduce their MO term symbols.

( 6 )

- (b) State the selection rule for electric dipole transitions between the electronic states of linear molecule.
- (c) Write down vector the diagrams of spin and spin wave functions for molecular triplet electronic state.  $4 + 2 + 2$

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