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

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 ith state being g_i-fold degenerate, obtain the Boltzmann distribution Law in terms of the energy multiplier β 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.

(*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 $4{\cdot}8 \times 10^{-6}$ mol dm^{-3} of a competitive inhibitor decreases the initial rate of $1{\cdot}11 \times 10^{-4}$ mol $dm^{-3}s^{-1}$ by a factor of 3·6. If the maximum velocity of the reaction and the substrate concentration are 0·64 mol $dm^{-3}s^{-1}$ and $4{\cdot}32 \times 10^{-6}$ mol dm^{-3} respectively, find out the equilibrium constant for the binding reaction between the enzyme and the inhibitor. Given $K_m = 25 \times 10^{-3}$ mol dm^{-3}. 4 + 4

6. (*a*) What is redox reaction ?

(*b*) How does a redox reaction occur by inner sphere mechanism ?

(*c*) The equilibrium constant for the reaction

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

at 25°C is $K_c = 4{\cdot}08 \times 10^{16}$ mol^{-1}dm^3. The rate constant K_{-1} is independently found to be $2{\cdot}52 \times 10^{-6}$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 $\rho = 1{\cdot}104$ 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

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.

(*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
