2013

DDE

M.Sc. Part-I Examination

CHEMISTRY

PAPER—I

Full Marks : 75

Time : 3 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Answer any *five* questions taking at least *two* from each group.

Group—A

1. (a) Constructing a wave packet from two sine (or cosine) wave show that for a particle (i.e. wave packet) $\Delta x \, op_x \geq h$, where Δx and op_x are the position & momentum uncertainty in x direction.   5

   (b) Considering a thought experiment show that we can not determine position and momentum at the same time of a particle. In that case also $\Delta x \, op_x \approx h$. 5

   (c) What do you mean by Hermition operator ? Show that $\hat{p}_x$ operator in quantum mechanics in a Hermitian operator.   5

(Turn Over)

2. (a) Write down the equation for Schwarz inequality. From it derive the following general uncertainty principle regarding the measurements of two dynamical variable :

$$\Delta A \ \Delta B \geq \frac{1}{2}\left\{i\left[\hat{A} \ \hat{B}\right]\right\}$$

[where A & B are two dynamical variable and $\hat{A}$ and $\hat{B}$ are their corresponding two quantum mechanical operators and ΔA & ΔB are their uncertainty in measurement.] 2+8

(b) Using the above general uncertainty principle find out the uncertainty product of position and momentum. Explain the above result. 5

3. (a) State and explain Nernst Heat Theorem and show how this leads to Planck's formulation of the Third Law of Thermodynamics. 7

(b) Show how the absolute entropy of a gas at a temperature T can be measured with the help of the Third Law. 8

4. Assuming the expression for the thermodynamic probability of distribution of n distinguishable particles in i-different energy states, the ith state being g_i-fold degenerate, derive the approximate distribution law in terms of the partition function and the energy multiplier β.

Consider three states with energies E_1, E_2 and E_3, $(E_3 > E_2 > E_1)$ with populations 1000, 100, 10 respectively. Using the Boltzmann distribution, show that the energy levels are equispaced. 11+4

5. (a) What do you mean by the term, thermodynamic probability of a distribution ? Establish the relation between entropy and thermodynamic probability. 2+6

(b) Explain the meaning of the term partition function, obtain the expression relating partition function and internal energy of a system. 2+5

Group—B

6. (a) For a parallel reaction $A \underset{K_2}{\overset{K_1}{\lessgtr}} \begin{smallmatrix} B \\ C \end{smallmatrix}$, find out the concentration of B and C at time t and show that $\frac{C_B}{C_C} = \frac{K_1}{K_2}$. 6

(b) Derive the expression for relaxation time for 2nd order reaction of this type $A+B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} P$. 6

(c) Determine the time at which concentration of intermediate is maximum for the reaction $K_a = 2K_I = 0.1 \ sec^{-1}$. 3

7. (a) State and explain Lindemann's Hypothesis. 4

(b) Derive Michaelis Constant for enzyme catalysed (monogenous) reaction. 6

(c) Considering the following sequential reaction $A \xrightarrow{K_A} J \xrightarrow{K_P} P$, and assuming that only reactant in present at t = 0 and using steady state approximation for intermediate. What is the expected time dependence of P ? 6

8. (a) Derive Gibbs Adsorption equation.   7

  (b) Derive Kelvin equation.   5

  (c) What are Micelles and reverse Micelles?   3

9. (a) 'Rotational energy levels of a non-rigid diatomic molecule are equispaced' — Justify or criticize the statement.

How do you obtain $\vec{B}$ and $\vec{D}$ from the rotational spectra of a non-rigid diatomic molecule?   3+3

  (b) Amplitude of vibration of a Harmonic oscillator increases with the increase of vibrational quantum number. — Explain.   4

  (c) What do you understand by Raman Scattering? Explain classically the appearance of stock and anti-stock Raman lines of a molecule.   1+4

10. (a) State Franck-Condon Principle. How does it explain the relative intensities of vibronic transitions when the position of minimum of the excited state (r_e'') is greater than the minimum of the ground state (r_e').   5

  (b) Write down the expression of Morse potential surface. Give a comparison of Morse potential with the Harmonic potential.   2+3

  (c) There must be some fluctuation of dipole moment for a molecule during vibration to show 1R activity — Explain.   5