NEW / OLD

2015

M.Sc. Part–I Examination

CHEMISTRY

PAPER—I

(Physical Chemistry)

The figures in the right-hand margin indicate full marks.

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

Illustrate the answers wherever necessary.

New Syllabus

Answer questions of Group—A and B and C.

Answer *five* questions taking at least *two* from Group—A and B.

Full Marks : 100 *Time* : 4 Hours

Old Syllabus

Answer questions of Group—A and B.

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

Full Marks : 75 *Time* : 3 Hours

Group—A

(*New & Old Syllabus*)

1. (a) Find out the value of $\left[x^n, \hat{p}_x\right]$. 3

(b) What do you mean by the term expectation value in quantum mechanics? Calculate the average value of operator $\hat{A}$ for a mixed state defined by : $\Psi_{mix} = C_1\Psi_1 + C_2\Psi_2$, where Ψ_1 & Ψ_2 are two non-degenerate orthonormal eigenfunction of $\hat{A}$.

1+4

(c) What do you mean by the term quantum mechanical tunnelling? Deduce a mathematical relation co-relating among the several parameters of particle and energy barrier, on which the tunneling probability of sub-atomic particle depends.

1+6

2. (a) Define the quantum mechanical angular momentum operator, and also its $x_1 - y_1 - z$ components. 3

(b) Show that $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}z$. 5

(c) If in polar co-ordinate the $\hat{L}_z$ operator is defined as $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$, then find out the normalized eigen function of $\hat{L}_z$ operator. Also show that the eigenvalue of $\hat{L}_z$ operator is integral multiple of $\hbar$.

$3\frac{1}{2} + 3\frac{1}{2}$

3. (a) State and explain the Nernst Heat Theorem.

(b) Show how the standard entropy of a substance above its boiling point can be determined with the help of the Third Law of thermodynamics.

(c) Explain why the concept of activity is essential in thermodynamics.

4+7+4

4. Obtain the expression for thermodynamic probability of distribution of *n* indistinguishable particles in i-different energy states, the ith state being g_i-fold degenerate and there is no restriction on the occupation number of the particles. Starting from this expression, obtain the appropriate distribution law.

7+8

5. (a) Consider energy levels separated by (i) 10 kt (ii) 5 kt and (iii) kt and calculate the partition functions in each case. Explain the significance of the result.

(b) Derive the expression for entropy of n molecules of a substance in terms of molecular partition function.

(c) Calculate two energy states E_1 and E_2, $(E_2 > E_1)$ of a molecule separated by 10 Kcal mol^{-1} at 27°C, occupied by 1000 and 100 molecules respectively. Calculate the temperature at which the population is reversed. 4+6+5

Group—B

(New & Old Syllabus)

6. (a) What do you mean by 'relaxation time'? Derive an expression for 'relaxation time' for 1st order opposing reaction of this type :

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

2+5

(b) As per Linderman theory there should be an observable transition from first order kinetics to second order kinetics — Explain this statement with rate expression. 5

(c) The gas phase decomposition of NOBr is second order in [NOBr], with K = 0·810 $M^{-1}s^1$ at 10°C. One starts with $4{\cdot}00\times10^{-3}$ M NOBr in a flask at 10°C. How many seconds does it take to use up $1{\cdot}5\times10^{-3}$ M NOBr? 3

7. (a) For a homogeneous enzyme catalysic reaction derive Michaelis Menten Equation and show how Km is determined from this? 9

(b) For auto catalyic reaction of this type A → P prove that $\frac{1}{[A]_0+[P]_0}\ln\frac{([P]_0+x)[A]_0}{([A]_0-x)[P]_0} = Kt$ where x = rate of change of either species (in time t) A and P. 3

(c) Give two examples of complementary and non-complementary electron-Transfer reaction. 3

8. (a) Establish the relation for adsorption of solid on liquid : $\Gamma_{2,1} = -\frac{C_2}{RT}\left(\frac{\partial\gamma}{\partial C_2}\right)_T$

where the terms indicate the usual meaning. 8

(b) What are reverse micelles? 3

(c) 1 gm of charcoal absorbs 100 ml of 0.5 (M) acetic acid to from a monolayer and there by the molarity of acetic acid reduced to 0·49 . Calculate the surface area of charcoal adsorbed by each molecule of acetic acid. Total surface area of charcoal is $3{\cdot}01\times10^{2}m^{2}g^{-1}$. 4

9. (a) Classify these molecules on the basis of moment of inertia for microwave spectroscopy :

HCN, CCl_4, C_2H_4, CH_3Cl. 4

(b) Explain effect of isotropic substitution for rotational spectra. 4

(c) How the relative population of rotational level depends on degeneracy ? 3

(d) 'Spacing between consecutive vibrational level decreases with the increase in vibrational quantum number for anharmonic oscillator'. — Explain. 4

10. (a) What is meant by Raman Scattering ? How do you explain classically the appearance of stokes and anti-stokes Raman lines ? 2+5

(b) Show that for non-rigid rotator the frequency of transition from J → J+1 is given by,

$$\bar{\nu} = \bar{B}\,J(J+1) - \frac{4\bar{B}^3}{\bar{\omega}^3}J^2(J+1)^2$$

where symbols have their usual significances. 8

Group—C
(*New Syllabus*)

11. Answer any *five* of the followings : 5×5

(i) Find the Fourier transform of the following —

$$f(x) = \begin{cases} 1-x^2, & |x| \le 1 \\ 0 & |x| > 1 . \end{cases}$$

(ii) Find the dimension of a rectangle whose areas is maximum and circumference is minimum.

(iii) Show that, $\left[\hat{L}_z, \hat{L}_+\right] = \hbar L_+$

where symbols have their usual significances.

(iv) State Franck-Condon Principle. Sketch and explain the relative intensities of vibronic transitions when the minima of the excited state potential surface are just above the ground state minima.

(v) What is meant by homogeneous and inhomogeneous boarding of spectral lines. Write a short note on Uncertainty broadening.

(vi) Considering a suitable example, show that the slowest step is the rate determining step.

(vii) Explain the significance of the Lagrangian Multipliers α and β and express α in terms of molecular partition function.
