2018

M.Sc.

Part–I Examination

CHEMISTRY

PAPER—I

Full Marks : 100

Time : 4 Hours

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

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

Illustrate the answers wherever necessary.

(Physical Chemistry)

Answer questions from Group–A, B and C

Answer any *five* questions,

taking at least *two* from Group–A and B

Group–A

1. Obtain the expression for the thermodynamic probability of distribution of n-indistinguishable particles describable by symmetric wave function and derive the appropriate distribution law.   7+8

2. (a) Obtain the expression for entropy in terms of molecular partition function.

   (b) State the Nernst Heat Theorem. Explain the principle of determination of the absolute entropy of a substance by using Plank's law. 7+4+4

3. Show that for a simple harmonic oscillator $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ (symbols have their usual meaning). Also define raising and lowering operators (Use ladder operator technique) 9+3+3

4. (a) Define a vector space V over field F. Give an example of a real vector space. 3

   (b) What do you mean by everywhere convergent power series. Show that if a power series $a_0 + a_1x + a_2x^2 + \dots$ converges for $x = x_1$, then the series converges absolutely for all real x satisfying $|x| < |x_1|$. 3

   (c) Write the general form of a Fourier Series. Write down the Dirichlet's conditions on the interval $[-\pi, \pi]$ for the real valued function $y = f(x)$. 3

   (d) Check whether the subset S of $\mathbb{R}^3$ defined by $S = \left\{(x,y,z) \in \mathbb{R}^3 : x^2 + y^2 = z^2\right\}$ is a subspace of R^3 or not. 3
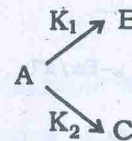
   (e) Find the radius of convergence of the power series $\sum_{n=0}^{\infty} a_n x^n$ where $a_n = \left(\frac{1}{3}\right)^n$ if n be odd and $\left(\frac{1}{2}\right)^n$ if n be even. 3

Group–B

5. (a) For parallel reaction

   Prove that $C_B / C_C = \dfrac{K_1}{K_2}$. 3

(b) In plug flow system derive an expression for final concentration of reactant. From this expression define contract time. 5

(c) What is the advantage of relaxation method over flow method ? 4

(d) The isomerization of cyclopropane follows the Lindeman mechanism and is found to be unimolecular. The rate constant at high pressure is $1.5 \times 10^{-4} torr^{-1} sec^{-1}$ and that at low pressure is $6 \times 10^{-6} torr^{-1} sec^{-1}$. Find out the pressure of cyclopropane at which the reaction changes its order. 3

6. (a) Using collision theory, for a bimolecular reaction derive the relation —

$$K_2 = A.e^{-Ea/RT}$$

Where $A = \sqrt{2} \ \pi \sigma^2 \ Ca \dfrac{N}{103}$.

Each symbol indicates the usual meaning. 5

(b) In redox reaction for one electron transfer explain inner-sphere mechanism with example. 3

(c) Derive an expression for the rate constant (K_2) for a bi-molecular reaction using transition state theory. 4

(d) Calculate ΔH^*, $\Delta G^\#$ and $\Delta S^\#$ for the second order reaction.

$$2NO_2 \ (g) \longrightarrow 3NO(g) + O_2 \ (g)$$

at 500K, Given $A = 2.0 \times 10^9 \ sec^{-1}$

$Ea = 111 \ KJ \ mole^{-1}$. 3

7. (a) Derive BFT adsorption equation for multilayer formation process. 10

(b) Derive the expression for the Vapour pressure of a droplet. 3

(c) A certain solid sample absorbs 0.52 mg of hydrogen when the pressure of gas is 34KPa and temperature is 35°C and 0.32 mg when the pressure is 5 KPa at the same temperature. The Langmuir isotherm describe the above process. Calculate the fraction of surface covered for each case. 2

8. (a) Explain the observation of isotopic substitution of diatomic molecule in rotational spectroscopy— 3

(b) How relative population varies with rotational levels ? Calculate vale of J max for rotational spectroscopy. 2+3

(c) What is the necessary condition for a molecule to be 1R active ? Explain with reason. 4

(d) Use the anharmonic oscillator model to obtain the dissociation energy of a diatomic molecule. 3

Group–C

9. Answer any *five* :

(a) What is flash photolysis ?

(b) What are fermions ? Give an example.

(c) Write short note on microoven.

(d) Write the expression for the entropy of liquid at a temperature T above the boiling point of the liquid.

(e) Define — (i) Skeletal vibration and (ii) Group vibration.

(f) State and explain Franck-Condon principle.

(g) Evaluate the commutator, $\left[\hat{L}^2, \hat{L}_z\right]$.

(h) Obtain the Fourier expansion of f(x) in $\left[-\pi, \pi\right]$ where,

$$f(x) = \begin{cases} 0 & -\pi \leq x < 0 \\ \dfrac{\pi x}{4} & 0 \leq x \leq \pi \end{cases}$$

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