NEW & OLD

2017

M.Sc. Part-I Examination

CHEMISTRY

PAPER—I

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.

(Physical Chemistry)

For New Syllabus

Full Marks : 100

Time : 4 Hours

Answer questions for Group–A, Group–B and Group–C.

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

For Old Syllabus

Full Marks : 75

Time : 3 Hours

Answer questions for Group–A and Group–B.

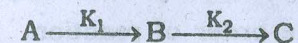Answer *five* questions taking at least *two* from each group.

(Turn Over)

Group–A

1. (a) Deduce the expression of wave function and eigen value for $\hat{L}_z$ operator. Explain the relative orientations of angular momentum vector w.r.t z-axis for $l = 2$. 5+3

   (b) Derive the exact uncertainty relation. 8

2. (a) Consider a particle of mass 'm' confined in a one dimensional box. Use the appropriate boundary condition to obtain the expresion for the wave function. 9

   (b) What is meant by a hermitian operator ? Show that if ψ_1 and ψ_2 are non-degenerate wave functions of a hermitian operator, then these are orthogonal. 6

3. What is meant by activity of a substance. Discuss the principle of its measurement by osmotic coefficient method. 3+12

4. Obtain the expression for the thermodynamic probability of the distribution of n distinguishable particles in i-different energy levels, the ith state being g-fold degenerats and derive the Boltzmann distribution law in terms of the energy multiplier β and the molecular partition function. 6+9

Group–B

5. (a) Write down the principle of Detailed Balancing for any chemical reaction. 3

   (b) For a consecutive reaction of the type —
   $$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$
   determine the maximum concentration of B. 4

   (c) A reversible reaction is 2nd order for forward reaction and 1st order for backward reaction, show that the relaxation time t^* is —
   $$t^* = \frac{1}{K_1(a_e + b_e) + K_2}$$
   where a_e = equilibrium concentration of Reactant A
   b_e = equilibrium concentration of Reactant B
   K_1 and K_2 are the specific rate consts of forward and backward reactions respectively. 5

   (d) For the action of Br_2 on fumaric acid, following data were obtained

   First Experiment :

(t) (min)	concentration
0	8.87 moles lit^{-1}
95	7.89 moles lit^{-1}

   Mean concentration = 8.37 and $-\dfrac{dc_1}{dt} = 0.0106$

2nd Experiment :

(t) (min)	concentration
0	3.81 moles lit^{-1}
1.32	3.51 moles lit^{-1}

Mean concentration = 3.66 and $-\dfrac{dc_2}{dt} = 0.00227$

(in appropriate unit)

Find out the order of reaction.   3

6. (a) Describe the Linderman hypothesis to show that the unimolecular reaction is possible according to collision theory.   4

(b) Calculate the Arrhenins factor, A and rate constant for the reaction, $CH_3 + H_2 \rightarrow CH_4 + H$ at 200°C if the collision diameter is 3.0×10^{-10} m and it is assumed that activation energy is zero for the reaction.   4

(c) Discuss the mechanism of enzyme catalysed reaction given by Michaelis and Menten.   7

7. (a) Derive Gibbs Adsorption equation.   7

(b) A long chain fatty acid of molecular weight 256 has a density of 0.82 g/cm^3. If 0.102 mg of the acid is required to form a closed packed monolayer film over 500 cm of water surface, estimate the cross-section of the molecule. If measurement is done at 25°C what is the surface tension of the solution? Surface tension of water is 0.071 Nm^{-1}.   5

(c) Discuss Thermodynamics of Micellisation.   3

8. (a) The spacing between the consecutive vibrational level decreases with the increase in vibrational quantum for anharmonic oscillator. — Explain.   3

(b) Give classical and quantum mechanical explanation of Raman Spectroscopy.   4

(c) With the help of Jablonsky diagram explain the terms—
(i) vibrational relaxation, (ii) internal conversion, (iii) intersystem crossing.   2×3

(d) Calculate the relative populations of the fifth rotational level with respect to ground rotational level of the ground vibrational state of HCl^{35} at 300K.
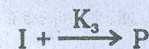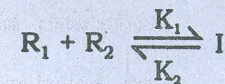
Given that $B_v = 10.5934$ cm$^{-1} - \left(0.3072 \text{ cm}^{-1}\right)^{\frac{1}{2}}$

$= 10.4398$ cm^{-1} for $v = 0$

Group–C

(For New Syllabus)

Answer any five questions from the followings.   5×5

9. (a) Write down the expression for the rate of formation of P for the following reaction mechanism :

$$R_1 + R_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} I$$

$$I + \overset{K_3}{\longrightarrow} P$$

I is the reactive intermediate.

(b) In what conditions kinetic measurements in flow systems are useful and what are the types of flow systems?

(c) Derive an expression for the concentration of the product in an autocatalytic reaction.

(d) Write a short note on reverse micelles.

(e) Rotational lines of rigid diatomic molecules are equispaced. — Justify or criticized.

(f) Amplitude of vibration of a diatomic molecule increased with the increase in vibrational quantum no. — Explain.

(g) Evaluate the commutator, $\left[L^2, L_z \right]$.

(h) State, under what conditions, Bose-Einstein distribution is reduced to Boltzmann distribution? What are fermions? Give an example.

(i) State and explain the Nernst Heat Theorem.

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