NEW

Part–III   3-Tier

2019

CHEMISTRY

(Honours)

PAPER—VII

Full Marks : 45

Time : 2 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.

Group—A

Answer any *one* question.   1×15

1. (a) What do you understand by partition function.   2

   (b) Find the ratio of population of two states such that $E_2 - E_1 = KT$. Degeneracy of corresponding energy levels are ں and 1.   2

   (c) Show that a *diatomic molecule* dissociates into atoms if it is present in the vibration state of a vibrational quantum number.

$$v = \frac{1}{2x_e} - \frac{1}{2}$$

x_e = anharmonicity constant of the anharmonic oscillator. 2

(d) Ag is known to crystallise in fcc form and the distance between the nearest neighbour atoms is 2.87 Å. Calculate the density of Ag. (Atomic weight of Ag = 108). 3

(e) "Zero point energy of a harmonic oscillator is a consequence of uncertainty principle."—Explain. 2

(f) The reaction $2A \rightleftharpoons A_2$ occurs both thermally and photo chemically. The photo chemical reaction takes place with the following steps. 4

(i) $A \xrightarrow{hv(I_a)} A\star$ (ii) $A\star + A \xrightarrow{K_2} A_2$

(iii) $A_2 \xrightarrow{K_3} 2A$ (iv) $A\star \xrightarrow{K_4} A + hv'$
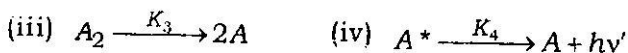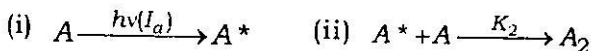
Applying the steady state approximation to A*, show

that $[A_2] = \dfrac{I_a}{K_3\{1 + \frac{K_4}{(K_2[A])}\}}$ at photostationary

equilibrium. Also show that $[A_2]$ in independent of $[A]$,

when A is present in large excess. Compare the result

with that in the thermal equilibrium case.

    (Continued)

2. (a) The wave function for a 1 s orbited for a hydrogen atom is $\psi_{1s} = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$ (where a_0 = Bohr radius).

Depict graphically the plots of (i) ψ_{1s} against r and (ii) $4\pi r^2 \psi_{1s}^2$ again r. Explain the graph. Find the most probable value of r in the 1s state. $\qquad$ 1+1+2

(b) Define 'consolute temperature'. Explain its existance with the help of a labelled diagram for water triethyl amine system. $\qquad$ 1+2

(b) State the third law of thermodynamics relating entropy of a perfectly crystalline solid at zero Kelvin. Show that the statement is consistent with the statistical definition of entropy(s). Comment on the value of s at $T = 0$ for CO. $\qquad$ 1+2+2

(d) Define quantum yield. 'The quantum-yield of a photochemical reaction may different from unity'— comment. $\qquad$ 1+2

Group—B

Answer any *two* questions. $\qquad$ 2×10

3. (a) The distance between two successive parallel planes in a *cubic crystal* can not be $\dfrac{a}{\sqrt{7}}$. comment (a = length of the edge of the cube). $\qquad$ 2

(b) Heat capacity of a solid is given by Einstein's equation as follows :

$$C_V = 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{\left(e^{h\nu/kT} - 1 \right)^2}$$

Hence,

(i) Obtain Dulong Petit's law

(ii) Give definition and significance of Einstein characteristic temperature.

(iii) Explain why Einstein's theory of heat capacity of solid fails to explain the experimental temperature variation of heat capacity. 2+2+2

(c) Sodium crystallizes in b.c.c. structure with $a = 4.24\text{Å}$. Calculate (i) theoretical density and (ii) radius of 'Na' atom.

2

4. (a) Point out the characteristics of a first order phase transition. Plot 'G' versus 'T' and $\left(\frac{dG}{dT} \right)_P$ versus 'T' for such a transition, with proper reasoning.

2+1½+1½

(Continued)

(b) State Raoult's law and Henry's law. Show that in a non-ideal solution, if one component obeys Raoult's law over a certain range of composition, the other components obeys Henray's law over the same range.

1+1+3

5. (a) The rotational spectrum of $^{79}Br^{19}F$ shows a series of euqidistant lines spaces 0.714333 cm^{-1} apart. Calculate the rotational constant B, the moment of inertia and bond length of the molecule. 4

(b) How does 'molar polarization' vary with temperature ? Explain using proper equation. 2

(c) Draw Schematically the energy levels of an anharmonic oscillator and hence explain the following for a diatomic molecule

(i) Existence of overtones and hot bands in the IR spectrum and

(ii) Dissociation. 4

6. (a) Show that the functions of simple harmonic oscillator

$\psi_0(x) = \frac{1}{\pi^{1/4}} e^{-x^2/2}$ and $\psi_1(x) = \left(\frac{1}{4\pi}\right)^{1/4} 2x e^{-x^2/2}$ are

orthogonal. 2

(b) Write down time independent Schrödinger equation of a one-dimensional harmomic oscillator. 2

(c) Draw the sketches of ψ and $|\psi|^2$ for a particle in one-dimensional box for the first three energy levels. 3

(d) Define thermodynamic probability. Derive the relation : $S = k \ln w$. 3

Group—C

Answer any *five* questions : 2×5

7. (a) Calculate the number of components, number of phases and degrees of freedom of a binary azeotrope system.

(b) Draw planes with Millar indices $(1\,1\,\bar{1})$ and $(2\,1\,0)$).

(c) The wave number of vibration of $H^{35}Cl$ molecule is $2991\ cm^{-1}$. Calculate the force constant of H-Cl bond.

(d) Express mathematically the potential energy of Morse oscillator and state the significance of the terms.

(e) For the ground state of the one dimensional harmonic oscillator, find the average value of the kinetic energy and of the potential energy.

(Continued)

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

(g) What is meant by singlet excited state and triplet excited state ?

(h) What are the assumptions made for deriving Maxwell-Boltzmann distribution law ?

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