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(6th Semester)

CHEMISTRY

ELEVENTH PAPER (CHEM–363)

(Physical Chemistry—III)

Full Marks : 55

Time : 2½ hours

(PART : A—OBJECTIVE)

(*Marks* : 20)

The figures in the margin indicate full marks for the questions

SECTION—A

(*Marks* : 5)

Tick (✓) the correct answer in the brackets provided : 1×5=5

1. The unit of molar absorption coefficient ( ) is

(a) mol ^{1} dm^{3} cm ^{1} ( ) *(b)* mol dm^{3} cm ^{1} ( )

(c) mol dm ^{3} cm ( ) *(d)* mol ^{1} dm^{3} cm ( )

2. When $\overset{*}{n}\ m$ 1, the eigenfunctions are

(a) diagonal ( ) *(b)* orthogonal ( )

(c) arbitrary ( ) *(d)* normalized ( )

3. The relationship between entropy and thermodynamic probability is given by

(a) $k\ S \ln W$ ( ) *(b)* $S\ W \ln k$ ( )

(c) $S\ k \ln W$ ( ) *(d)* $W\ k \ln S$ ( )

4. The molecule which is IR inactive but Raman active is

(a) protein ( ) *(b)* N_2 ( )

(c) HCl ( ) *(d)* SO_2 ( )

5. The relationship between free energy change and e.m.f. of a cell is given by

(a) $G \quad nFE$ ( ) *(b)* $G \quad nFE$ ( )

(c) $G \quad nFE$ ( ) *(d)* $G \quad nFE$ ( )

SECTION—B

(*Marks* : 15)

Answer the following questions : 3×5=15

1. What is photosensitization? Write all the steps involved in photosensitized reaction between $H_2(g)$ and $O_2(g)$.

2. State and explain photoelectric effect.

3. Derive the multiplication theorem of partition function.

4. Calculate J_{max} for a rigid diatomic molecule at 27 °C for which rotational constant is 1·566 cm ^{1}.

5. Set up calomel electrode and give electrode reactions and e.m.f. of such an electrode.

(PART : B—DESCRIPTIVE)

(*Marks* : 35)

The figures in the margin indicate full marks for the questions

1. *(a)* Define quantum yield. 1

(b) State and explain Stark-Einstein law of photochemical equivalence. 3½

(c) A monochromatic radiation is incident on a solution of 0·05 *M* concentration of an absorbing substance. The intensity of radiation is reduced to $\frac{1}{4}$th of its initial value after passing through 100 mm length of the solution. Calculate the molar extinction coefficient of the substance. 2½

OR

2. *(a)* Discuss the photochemical reaction involving decomposition of acetaldehyde. 3

(b) Complete the following photochemical reaction : 2

$$UO_2^2 \quad H_2C_2O_4 \xrightarrow[250 \quad 440\,nm]{h} UO_2^2 \quad \ldots$$

(c) A certain system absorbs 3 10^{18} quanta of light per second. On irradiation of 20 minutes, 0·003 mole of reactant was found to have reacted. Calculate the quantum yield of the process. 2

3. *(a)* Discuss in detail the Einstein's theory of heat capacity of monoatomic solids. 3½

(b) Give expression for zero point energy. 1

(c) A photon of wavelength 3000 Å strikes a metal surface, the work function of the metal being 2·13 eV. Calculate—

(i) the energy of the photon in electron volt (eV);

(ii) kinetic energy of the emitted photon. 2½

OR

4. *(a)* Derive Schrödinger wave equation and extend it up to Hamiltonian operator. 4

(b) A particle with a mass 6·65×10 ^{27} kg is confined in an infinite square well of width a. The energy of 3rd level is 2×10 ^{24} J. Calculate a. 3

5. *(a)* Derive an expression for the molecular translational partition function of an ideal gas. 3½

(b) Calculate the characteristic vibrational temperature and the vibrational partition function for H_2(g) molecule at 2727 °C, the fundamental vibrational frequency of H_2(g) is given to be 4405·3 cm ^{1}. 3½

OR

6. *(a)* On the basis of molecular partition function, derive expression for entropy of a monoatomic ideal gas. 3

(b) Write expression only for molar heat capacity at constant volume in terms of molecular partition function. 1

(c) Calculate the translational entropy of I_2(g) molecule in calories at 27 °C and 1 atm. (Molecular mass of I_2 254) 3

7. *(a)* Using the energy level expression and the appropriate selection rule, discuss the energy level diagram and the spectral transitions for a pure rotational (microwave) spectrum of a rigid diatomic rotor. 4

(b) Calculate the vibrational frequency in cm ^{1} and the spacings between the vibrational energy levels in eV in case of CO whose force constant is 1840 N m ^{1}. (C 19·9×10 ^{27} kg, O 26·6×10 ^{27} kg and 1 eV = 8066 cm ^{1}.) 3

OR

8. *(a)* Discuss the classical theory of Raman spectroscopy and show how Stokes and anti-Stokes lines appear in the Raman spectrum of a molecule. 3

(b) Spacing between lines in a microwave spectra of HI is 13·2 cm ^{1}. Calculate the bond length of HI. (H 1 10 ^{3} kg mol ^{1} and I 127 10 ^{3} kg mol ^{1}) 2

(c) What are overtones and hot bands? 2

9. *(a)* Establish relationship between the e.m.f. and equilibrium constant (k) for a general reversible cell reaction. 3

(b) Give only expression for enthalpy and e.m.f. of a cell reaction. 1

(c) Write the cell reaction and calculate e.m.f. of the cell

$$Fe,\ Fe^{2}\ (0{\cdot}1\ M)/Cd^{2}\ (0{\cdot}001\ M),\ Cd$$

[Given : $E^{\circ}(Cd^{2}\ /Cd)$ 0·40 V and $E^{\circ}(Fe^{2}\ /Fe) = -0{\cdot}44$ V] 3

OR

10. *(a)* What are concentration cells? Derive an expression for e.m.f. of a concentration cell with transference. 1+3½=4½

(b) Calculate G° and S° for the cell

$$Cd\,(Hg),\ CdSO_4\ \frac{8}{3}H_2O\,(s)\ //\ CdSO_{4\,(satd)},\ Hg_2SO_4\,(s),\ Hg$$

if $\left(\frac{E^{\circ}}{T}\right)_p$ for the cell is 5 10 ^{5} V K ^{1}. (Given E° 1·0183 V).

[Physical constants : H = 6·626×10 ^{34} J-s; N_A 6·022×10^{23} mol ^{1}] 2½

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