**2025**

( CBCS )

( 6th Semester )

**CHEMISTRY**

ELEVENTH PAPER

**( Physical Chemistry—III )**

*Full Marks* : 75

*Time* : 3 hours

*The figures in the margin indicate full marks for the questions*

**( SECTION : A—OBJECTIVE )**

( *Marks* : 10 )

Tick (✓) the correct answer in the brackets provided : 1×10=10

1. A photochemical reaction takes place by the absorption of
   (a) infrared radiation ( )
   (b) γ-rays ( )
   (c) visible and ultraviolet radiations ( )
   (d) X-rays ( )
2. If a photochemical reaction obeys Einstein law, then the quantum yield is
   (a) 0 ( )
   (b) >1 ( )
   (c) <1 ( )
   (d) 1 ( )

3. When $\int \Psi n^* \Psi m \, d\tau = 1$, the eigenfunctions are

(a) arbitrary ( )

(b) diagonal ( )

(c) orthogonal ( )

(d) normalized ( )

4. As the wavelength of the radiation decreases, the intensity of the black-body radiations

(a) decreases ( )

(b) increases ( )

(c) first decreases then increases ( )

(d) first increases then decreases ( )

5. The electronic partition function of H atom in the ground electronic state is

(a) 2 ( )

(b) 1 ( )

(c) 0 ( )

(d) 4 ( )

6. The canonical partition function of a system of independent indistinguishable particles is

(a) $q^N N!$ ( )

(b) $N!/q^N$ ( )

(c) $q^N / N!$ ( )

(d) None of the above ( )

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

(a) HCl ( )

(b) $SO_2$ ( )

(c) $N_2$ ( )

(d) KCl ( )

8. Which of the following cannot show a vibrational absorption spectrum?

(a) OCS ( )

(b) $CH_2=CH_2$ ( )

(c) $H_2O$ ( )

(d) $CO_2$ ( )

9. The electrode potential of hydrogen electrode in neutral solution and 298 K is

(a) zero ( )

(b) −0·41 V ( )

(c) −0·49 V ( )

(d) +0·41 V ( )

10. When equilibrium is reached inside the two half-cells of the electrochemical cells, what is the net voltage across the electrodes?

(a) >1 ( )

(b) <1 ( )

(c) =0 ( )

(d) Not defined ( )

## ( SECTION : B—SHORT ANSWERS )

( *Marks* : 15 )

Answer the following questions : 3×5=15

### UNIT—I

1. State and explain chemiluminescence by giving suitable example.

**OR**

2. Distinguish between photochemical and thermal reactions.

## UNIT—II

**3.** Describe Planck's quantum theory of radiation.

**OR**

**4.** State and explain photoelectric effect.

## UNIT—III

**5.** Derive the multiplication theorem of partition function.

**OR**

**6.** Derive the relationship between pressure ($P$) and molecular partition function ($q$).

## UNIT—IV

**7.** Describe briefly the Born-Oppenheimer approximation of molecular energies.

**OR**

**8.** Discuss the selection rule in Raman spectroscopy and also discuss Raman and IR activity in case of $H_2O$ and $CO_2$ molecules.

## UNIT—V

**9.** Differentiate between electrolytic and electrochemical cells.

**OR**

**10.** Write the cell reaction and also calculate the standard cell e.m.f. for the cells $Zn,\ Zn^{2+}\ (1\ M) \| Fe^{2+}\ (1\ M),\ Fe^{3+}\ (1\ M);$ Pt. Given $E^{\circ}(Fe^{3+}, Fe^{2+}) = +0{\cdot}77$ V and $E^{\circ}(Zn^{2+}, Zn) = -0{\cdot}76$ V.

## ( SECTION : C—DESCRIPTIVE )

( *Marks* : 50 )

Answer the following questions : 10×5=50

### UNIT—I

1. *(a)* State and explain Beer-Lambert law of light absorption by solution. In the process, also obtain expressions for absorbance and transmittance of the solution. 5

   *(b)* Calculate the number of moles of HCl(g) produced by the absorption of 1 J of radiant energy of $\lambda = 480$ nm in the reaction $H_2(g) + Cl_2(g) = 2HCl$, if quantum yield ($\Phi$) for the photochemical reaction is $1 \times 10^6$. 3

   *(c)* What do you mean by quenching? Explain. 2

**OR**

2. *(a)* Discuss, in detail, the photolysis of hydrogen iodide. 4

   *(b)* A 0·003 *M* solution of a coloured substance transmits 75% of incident light of 500 nm when placed in a cell of length 1 cm. Calculate molar extinction coefficient and hence the optical density of 0·001 *M* of the solution in the same cell at the same wavelength. 3

   *(c)* What are photosensitizers? Discuss in detail the mechanism of photosensitizers by giving suitable examples. 3

### UNIT—II

3. *(a)* Describe the black-body radiation. 3

   *(b)* What are the postulates of quantum mechanics? 3

   *(c)* Derive Schrödinger wave equation. 4

**OR**

**4.** *(a)* Discuss, in detail, Debye theory of heat capacity of monatomic solids. 3

*(b)* Discuss zero-point energy. 3

*(c)* Derive an expression for free particles in one-dimensional box. 4

## UNIT—III

**5.** *(a)* Derive relationship between entropy ($S$) and molecular partition function ($q$) of an ideal gas. 3

*(b)* Calculate the characteristic rotational temperature and the rotational partition function for $H_2$ gas molecule at 3000 K, given that the moment of inertia of $H_2$ (g) molecule at this temperature is $4 \cdot 6033 \times 10^{-48}$. 3

*(c)* Derive an expression for Maxwell distribution law which gives most probable distribution for a microstate. 4

**OR**

**6.** *(a)* What are the limitations of classical thermodynamics? 3

*(b)* Derive Sackur-Tetrode equation in case of an ideal monatomic gas. 3

*(c)* Derive an expression for the molecular translational partition function of an ideal gas. 4

## UNIT—IV

**7.** *(a)* Discuss, in detail, quantum theory of Raman spectroscopy. 3

*(b)* Discuss the rule of mutual exclusion principle, taking $CO_2$ as an example. 3

*(c)* State and explain Franck-Condon principle. 4

**OR**

8. *(a)* Explain anharmonicity with the help of Morse potential curve. 3

*(b)* What are radiative and non-radiative transitions? 3

*(c)* Derive an expression for the rotational energy of a rigid diatomic rotor. 4

## UNIT—V

9. *(a)* Describe the determination of pH of a solution using glass electrode. 3

*(b)* Define liquid junction potential (LJP) and also derive the expression for its potential. 3

*(c)* Derive an expression for e.m.f. of a concentration cell with transference number. 4

**OR**

10. *(a)* For the Daniel cell involving the cell reaction

$$Zn\,(s) + Cu^{2+}\,(aq) \leftrightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

the standard free energies of formation of Zn (s), Cu (s), $Cu^{2+}$ (aq) and $Zn^{2+}$ (aq) are 0, 0, 64·4 and −154·0 kJ $mol^{-1}$ respectively. Calculate the standard e.m.f. of the cell. 3

*(b)* Establish the relationship of e.m.f. with *(i)* enthalpy and *(ii)* entropy of the cell. 3

*(c)* Explain the term 'electrode potential'. Derive Nernst equation for describing the effect of concentration of electrolyte on electrode potential. 1+3=4

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