2022

(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. Opacity of the absorbing medium is given by

(a) $\frac{I_0}{I_t}$ ( )

(b) $\frac{I_t}{I_0}$ ( )

(c) $\log \frac{I_0}{I_t}$ ( )

(d) $\log \frac{I_t}{I_0}$ ( )

2. Which of the following are the reactions in which the molecules absorbing light do not themselves react but induced other molecules to react?

(a) Free radical reactions ( )

(b) Photosynthesis reactions ( )

(c) Photosensitized reactions ( )

(d) Dark reactions ( )

3. In Schrödinger's wave equation, the symbol represents the

(a) wavelength of the spherical wave ( )

(b) amplitude of the spherical wave ( )

(c) frequency of the spherical wave ( )

(d) velocity of the spherical wave ( )

4. When $_{n\ m}$ 0, the eigenfunctions are

(a) normalized ( )

(b) arbitrary ( )

(c) diagonal ( )

(d) orthogonal ( )

5. The relationship between molar partition function and work function is given by

(a) $A \quad kT \ln Q$ ( )

(b) $A \quad (kT) \ 1 \ln Q$ ( )

(c) $A \quad kT (\ln Q) \ 1$ ( )

(d) $A \quad kT \ln Q$ ( )

6. In terms of molecular partition function q, the internal energy of a molecule is given by

(a) $U \quad nRT \left(\frac{\ln q}{V}\right)_T$ ( )

(b) $U \quad nRT \left(\frac{\ln q}{T}\right)_V$ ( )

(c) $U \quad nRT^2 \left(\frac{\ln q}{V}\right)_T$ ( )

(d) $U \quad nRT^2 \left(\frac{\ln q}{T}\right)_V$ ( )

7. The rotational energy of a diatomic molecule in terms of wave number is

(a) $_J \quad \frac{h^2}{8\ ^2 I} J(J \quad 1)$ ( )

(b) $_J \quad \frac{h^2}{8\ ^2 Ic} J(J \quad 1)$ ( )

(c) $_J \quad \frac{h}{8\ ^2 Ic} J(J \quad 1)$ ( )

(d) $_J \quad \frac{h^2}{8\ Ic} J(J \quad 1)$ ( )

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

(a) HCl ( )

(b) SO_2 ( )

(c) N_2 ( )

(d) protein ( )

9. The relationship between equilibrium constant and standard e.m.f. of a cell is given by

(a) $\ln k \quad \frac{RT}{nFE}$ ( )

(b) $\ln k \quad \frac{nRT}{FE^{\circ}}$ ( )

(c) $\ln k \quad \frac{nFE^{\circ}}{RT}$ ( )

(d) $\ln k \quad \frac{FE^{\circ}}{nRT}$ ( )

10. For the half-cell reaction $2H_2O(l) \quad O_2(g) \quad 4e \quad 4OH \ (aq), \quad G^{\circ}/FE^{\circ}$

(a) 1 ( )

(b) 2 ( )

(c) 3 ( )

(d) 4 ( )

(SECTION : B—SHORT ANSWER)

(*Marks* : 15)

Answer the following questions : 3×5=15

UNIT—I

1. What are photosensitizers? Explain photosensitization by taking suitable examples.

OR

2. State and explain Grotthuss-Draper law of photochemical reaction.

UNIT—II

3. Describe Planck's quantum theory of radiation.

OR

4. State and explain photoelectric effect.

UNIT—III

5. Derive the relationship between partition function and heat capacity of an ideal gas at constant volume (C_v).

OR

6. What is the physical significance of partition function?

UNIT—IV

7. Show that for a rigid diatomic rotor, the moment of inertia is given by $I \quad r^2$.

OR

8. The force constant of CO is 1840 N m ^{1}. Calculate the vibrational frequency in cm ^{1}, given that ^{12}C 19 9 10 ^{27} kg and ^{16}O 26 6 10 ^{27} kg.

UNIT—V

9. Write a short note on reference electrode (SHE).

OR

10. For the cell Al/Al^{3} (a) $\|$ Sn^{4} (a) / Sn^{2} / Pt, the standard electrode potentials (EP) at 298 K are $E^{\circ}_{Al^{3}\ /Al}$ 1 66 V and $E^{\circ}_{Sn^{4}\ ,\ Sn^{2}\ /Pt}$ 0 15 V. Write the cell reaction. Calculate *(a)* cell e.m.f. when the activities are all 0·1 and *(b)* G° for the cell reaction.

(SECTION : C—DESCRIPTIVE)

(*Marks* : 50)

UNIT—I

1. *(a)* What is chemiluminiscence? Discuss the mechanism of chemiluminiscence in an organic anion-cation reaction. 3

(b) Discuss in detail the photolysis of hydrogen iodide. Why does quantum yield fall below 2 in this case? 4

(c) For the photolysis of gaseous HI by light of wavelength 253·7 nm, the quantum yield was found to be 2. Calculate the number of moles of HI decomposed if 300 J of light of this wavelength is absorbed. 3

OR

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

(b) State and derive Beer-Lambert law for light absorption by solution. 4

(c) When a substance *A* was exposed to light, 0·002 mol of it reacted in 20 minutes and 4 seconds. At the same time *A* absorbed 2 0 10^6 photons of light per second. Calculate the quantum yield of the reaction. 3

UNIT—II

3. *(a)* Discuss in detail Einstein's theory of heat capacity of monatomic solids. 4

(b) Describe the blackbody radiation. 4

(c) Discuss zero-point energy. 2

OR

4. *(a)* Derive time-independent Schrödinger wave equation and extend the equation up to Hamiltonian form. 5

(b) Derive the expression for free particle in one-dimensional box and also calculate the energy for the same. 2

(c) Light of wavelength 5500 Å falls on a sensitive metal plate having work function 1·7 eV. Find *(i)* energy of the photon, *(ii)* kinetic energy of the photoelectron and *(iii)* stopping potential. (Mass of *e* 9 11 10^{31} kg) 3

UNIT—III

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

(b) Compute the rotational temperature and the rotational partition function for H_2(g) at 27 °C, given that the moment of inertia of H_2(g) molecule at this temperature is 4 6033 10^{48} kg m^2. 3

(c) Write only the expression relating to pressure and molecular partition function of an ideal gas. 2

OR

6. (a) Derive an expression for the molecular vibrational partition function of an ideal diatomic gas. How does it vary at low and high temperatures? 4

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

(c) Calculate the translational partition function of benzene in a volume of 1 m^3 at 25 °C. (Molar mass of benzene 78 g mol^{-1}) 3

UNIT—IV

7. (a) Derive an expression for the vibrational energy of a diatomic molecule and write the selection rule. 4

(b) State and explain Franck-Condon principle. 4

(c) State mutual exclusion rule for vibrational transitions. 2

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. 4

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

(c) What are overtones and hot bands? 2

UNIT—V

9. (a) What are concentration cells? Derive an expression for e.m.f. of a concentration cell without transference. 5

(b) Calculate the equilibrium constant of the cell reaction 2Ag Zn 2Ag Zn^2 occurring in the zinc-silver cell at 25 °C, when [Zn^2] 0 10 *M* and [Ag] 10 *M*. The e.m.f. of the cell is found to be 1·62 V. 3

(c) What is liquid junction potential? 2

OR

10. *(a)* What are concentration cells? Derive an expression for the e.m.f. of a concentration cell without transference. 1+3=4

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

(c) What are the cell reactions? Calculate the cell e.m.f. at 25 °C of the cell

$$Zn / Zn^{2} \ (a \ 1) \| Pb^{2} \ (a \ 1) / Pb$$

Given $E^{\circ}(Pb^{2}$, Pb) 0 126 V and $E^{\circ}(Zn^{2}$, Zn) 0 763 V. 3

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