2024

(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. The energy E absorbed per mole of the reacting substance is given by

(a) $E = hc$ ( )

(b) $E = hc / \lambda$ ( )

(c) $E = hc / \lambda^2$ ( )

(d) $E = N_A hc / \lambda$ ( )

2. Absorbance (A) of the absorbing medium (solution) is given by

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

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

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

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

3. When $\int \psi_n^* \psi_m d\tau = 0$, the eigenfunctions are

(a) arbitrary ( )

(b) diagonal ( )

(c) orthogonal ( )

(d) normalized ( )

4. The emissive power (E) of a blackbody at any temperature is equal to

(a) σT^3 ( )

(b) σT^{-3} ( )

(c) σT^4 ( )

(d) σT^{-4} ( )

5. As temperature increases, partition function

(a) increases ( )

(b) decreases ( )

(c) remains the same ( )

(d) increases or decreases ( )

6. The relation between molar partition function and work function is given by

(a) $A = -kT \ln Q$ ( )

(b) $A = kT \ln Q$ ( )

(c) $A = (kT)^{-1} \ln Q$ ( )

(d) $A = kT (\ln Q)^{-1}$ ( )

7. The wave number range of IR radiation is

(a) $4000\ cm^{-1} - 8000\ cm^{-1}$ ( )

(b) $100\ cm^{-1} - 1000\ cm^{-1}$ ( )

(c) $500\ cm^{-1} - 4000\ cm^{-1}$ ( )

(d) $500\ cm^{-1} - 1000\ cm^{-1}$ ( )

8. Which of the following molecule will not show pure rotational spectroscopy?
   (a) CO ( )
   (b) HCl ( )
   (c) H_2O ( )
   (d) CO_2 ( )

9. Which of the following can be used to measure pH?
   (a) A concentration cell ( )
   (b) A hydrogen electrode ( )
   (c) A glass electrode ( )
   (d) All of the above ( )

10. What is the EMF of a galvanic cell if $E^{\circ}_{(anode)}$ is –0·76 volt and $E^{\circ}_{(cathode)}$ is 0·80 volt?
   (a) 1·56 volts ( )
   (b) –1·56 volts ( )
   (c) 0·04 volt ( )
   (d) –0·04 volt ( )

(SECTION : B—SHORT ANSWERS)

(*Marks* : 15)

Answer the following questions : 3×5=15

UNIT—I

1. Distinguish between thermal and photochemical reactions.

OR

2. What are photosensitizers? Explain the mechanism of photosensitization by taking suitable example.

UNIT—II

3. Describe Planck's quantum theory of radiation.

OR

4. Explain the zero-point energy of a simple harmonic oscillator.

UNIT—III

5. Discuss the multiplication theorem of partition function.

OR

6. What is the physical significance for partition function?

UNIT—IV

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

OR

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

UNIT—V

9. Establish the relationship between EMF of the cell and equilibrium constant (K) for a general cell reaction.

OR

10. What is liquid junction potential (LJP)? Derive the expression for liquid junction potential.

(SECTION : C—DESCRIPTIVE)

(*Marks* : 50)

Answer the following questions : 10×5=50

UNIT—I

1. *(a)* State and explain Beer-Lambert law and its limitation. 3

(b) Describe the Jablonski diagram in relation with non-radiative and radiative transition. 4

(c) A monochromatic radiation falls on an absorbing substance solution of concentration 0·05 *M*. The intensity of radiation is reduced to $\frac{1}{4}$th of the initial value after passing through 10 cm length of the solution. Calculate the molar extinction coefficient of the absorbing substance solution. 3

OR

2. *(a)* Discuss in detail the photolysis of acetaldehyde. 4

(b) What is meant by chemiluminiscence? Discuss the mechanism of chemiluminiscence in an organic anion-cation reaction. 3

(c) A sample of gaseous HI was irradiated by light of wavelength 253·7 nm when 307 J of energy was found to decomposed $1{\cdot}30\times10^{-3}$ mole of HI. Calculate the quantum yield of HI. 3

UNIT—II

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

(b) Derive the Schrödinger wave equation. 4

(c) Calculate the vibrational partition function for Br_2 at 300 K, if the vibrational frequency is $151{\cdot}2\ cm^{-1}$. 3

OR

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

(b) Derive the expression for free particles in one-dimensional box and also calculate the energy for the same. 4

(c) An electron in 1 D (dimensional) box of width 10 Å (angstrom) undergoes a transition from the ground state to the 1st excited state. Calculate the wavelength of the promoted electron. 3

UNIT—III

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

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

(c) The force constant of CO is $1840\ N\ m^{-1}$. Calculate the vibrational frequency in cm^{-1}. Given that $^{12}C = 19{\cdot}9\times10^{-27}$ kg and $^{16}O = 26{\cdot}6\times10^{-27}$ kg. 3

OR

6. *(a)* Derive an expression for the molecular rotational partition function of an ideal gas. 3

(b) Derive Boltzmann distribution law for a system containing n molecules having a total energy (E). 4

(c) Derive the relationship between partition function and internal energy (U) of an ideal gas. 3

UNIT—IV

7. *(a)* Derive an expression for simple harmonic oscillator and its selection rule. 3

(b) Discuss in detail the application of microwave spectroscopy in the determination of bond distances in polyatomic molecules. 4

(c) Given that the spacing between the vibrational levels of CO is $8{\cdot}45\times10^{-2}$ eV. Calculate the force constant K of the bond in CO molecule. 3

OR

8. *(a)* Explain Raman effect.Write a short note on "why Stokes lines are more intense than anti-Stokes lines". 3

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

(c) The inter-nuclear distance of CO is 1·13 Å. Calculate the moment of inertia. Given that $^{12}C = 1{\cdot}99\times10^{-26}$ kg and $^{16}O = 2{\cdot}66\times10^{-26}$ kg. 3

UNIT—V

9. *(a)* Write a note on quinhydrone electrodes. 3

(b) What are galvanic cells? Derive Nernst equation for the variation of electrolyte concentration on electrode potential. 4

(c) The EMF of the cell, Cd (s), $CdCl_2 \cdot 2{\cdot}5\,H_2O$ (saturated)//AgCl (s), Ag, in which the cell reaction is

$$Cd\ (s) + AgCl\ (s) + aq \rightarrow CdCl_2 \cdot 2{\cdot}5\,H_2O\ (saturated) + 2\ Ag\ (s)$$

is 0·0653 V at 25 °C and 0·6915 V at 0 °C. Calculate the free energy change (ΔG) and the entropy change (ΔS) for the cell reaction. 3

OR

10. *(a)* Write the expression for the relation between electrical energy and enthalpy of cell reaction. 3

(b) What are concentration cells? Derive an expression for the EMF of a concentration cell without transference. 4

(c) Determine the standard equilibrium constant for the following reaction, when EMF of the cell is 0·21 V at 298 K : 3

$$Cd^{+2} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+}$$

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