

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)  $\sigma T^3$  ( )
  - (b)  $\sigma T^{-3}$  ( )
  - (c)  $\sigma T^4$  ( )
  - (d)  $\sigma T^{-4}$  ( )
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)  $4000 \text{ cm}^{-1} - 8000 \text{ cm}^{-1}$  ( )
  - (b)  $100 \text{ cm}^{-1} - 1000 \text{ cm}^{-1}$  ( )
  - (c)  $500 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$  ( )
  - (d)  $500 \text{ cm}^{-1} - 1000 \text{ cm}^{-1}$  ( )

8. Which of the following molecule will not show pure rotational spectroscopy?
- CO ( )
  - HCl ( )
  - H<sub>2</sub>O ( )
  - CO<sub>2</sub> ( )
9. Which of the following can be used to measure pH?
- A concentration cell ( )
  - A hydrogen electrode ( )
  - A glass electrode ( )
  - All of the above ( )
10. What is the EMF of a galvanic cell if  $E_{(\text{anode})}^{\circ}$  is -0.76 volt and  $E_{(\text{cathode})}^{\circ}$  is 0.80 volt?
- 1.56 volts ( )
  - 1.56 volts ( )
  - 0.04 volt ( )
  - 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 chemiluminescence? Discuss the mechanism of chemiluminescence 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  $1.30 \times 10^{-3}$  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  $\text{Br}_2$  at 300 K, if the vibrational frequency is  $151.2 \text{ cm}^{-1}$ . 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  $10 \text{ \AA}$  (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  $1840 \text{ N m}^{-1}$ . Calculate the vibrational frequency in  $\text{cm}^{-1}$ . Given that  $^{12}\text{C} = 19.9 \times 10^{-27} \text{ kg}$  and  $^{16}\text{O} = 26.6 \times 10^{-27} \text{ kg}$ . 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**

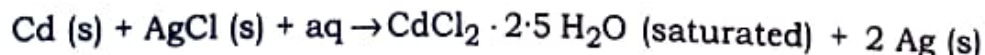
7. (a) Derive an expression for simple harmonic oscillator and its selection rule. 3
- (b) Discuss in detail the application of microwave spectroscopy in the determination of bond distances in polyatomic molecules. 4
- (c) Given that the spacing between the vibrational levels of CO is  $8.45 \times 10^{-2}$  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  $1.13 \text{ \AA}$ . Calculate the moment of inertia. Given that  $^{12}\text{C} = 1.99 \times 10^{-26} \text{ kg}$  and  $^{16}\text{O} = 2.66 \times 10^{-26} \text{ kg}$ . 3

**UNIT—V**

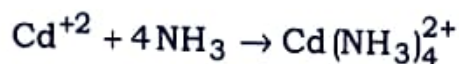
9. (a) Write a note on quinhydrone electrodes. 3
- (b) What are galvanic cells? Derive Nernst equation for the variation of electrolyte concentration on electrode potential. 4
- (c) The EMF of the cell,  $\text{Cd (s), CdCl}_2 \cdot 2.5 \text{ H}_2\text{O (saturated)} // \text{AgCl (s), Ag}$ , in which the cell reaction is



is  $0.0653 \text{ V}$  at  $25^\circ\text{C}$  and  $0.6915 \text{ V}$  at  $0^\circ\text{C}$ . Calculate the free energy change ( $\Delta G$ ) and the entropy change ( $\Delta S$ ) 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



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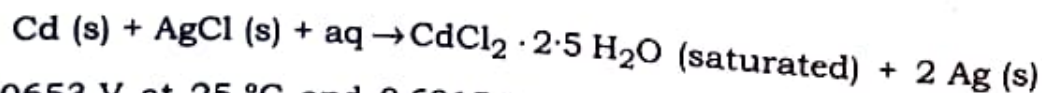
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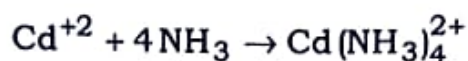
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