2023

(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

Use of calculator may be permitted.

Values of constants are provided at the end of the question paper.

(SECTION : A—OBJECTIVE)

(*Marks* : 10)

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

1. Absorbance (A) of a solution and transmittance (T) are related as

(a) $A = \log T$ ( )

(b) $A = -\log T$ ( )

(c) $\log A = T$ ( )

(d) $\log A = -T$ ( )

2. One einstein is the energy associated with

(a) 1 photon ( )

(b) 1×10^{21} photons ( )

(c) 1×10^{23} photons ( )

(d) 1 mole of photons ( )

3. The system for which energy (E) increases quadratically with the quantum number (n) is

(a) particles in a one-dimensional box ( )

(b) hydrogen atom ( )

(c) one-dimensional harmonic oscillator ( )

(d) rigid rotor ( )

4. Rayleigh-Jeans formula for energy density between wavelength λ and $\lambda + d\lambda$ in case of blackbody radiation is given by

(a) $E_\lambda d\lambda = 8\pi kT / \lambda^4$ ( )

(b) $E_\lambda d\lambda = 8\pi kT / \lambda^5$ ( )

(c) $E_\lambda d\lambda = 8\pi kT / \lambda^3$ ( )

(d) $E_\lambda d\lambda = 8\pi kT / \lambda^2$ ( )

5. The relation between the entropy (S) of a system and the thermodynamic probability (W) is given by

(a) $S = K \ln W$ ( )

(b) $W = K \ln S$ ( )

(c) $K = S \ln W$ ( )

(d) $S = W \ln K$ ( )

6. The unit of molecular partition function is

(a) S^{-1} ( )

(b) JK^{-1} ( )

(c) cm^{-1} ( )

(d) dimensionless ( )

7. Which of the following molecules will show pure rotational spectrum?

(a) H_2 ( )

(b) O_2 ( )

(c) NH_3 ( )

(d) $NH_4Cl(s)$ ( )

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

(a) HCl ( )

(b) SO_2 ( )

(c) N_2 ( )

(d) protein ( )

9. At 0 K, the cell potential is

(a) $= 0$ ( )

(b) $= E^\circ$ ( )

(c) $< E^\circ$ ( )

(d) $> E^\circ$ ( )

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

(a) $\Delta G = nFE$ ( )

(b) $\Delta G = \pm nFE$ ( )

(c) $-\Delta G = nFE$ ( )

(d) $\Delta G = \Delta nFE$ ( )

(SECTION : B—SHORT ANSWER)

(*Marks* : 15)

Answer the following : 3×5=15

UNIT—I

1. State and explain chemiluminescence by taking a suitable example.

OR

2. Distinguish between photochemical and thermal reactions.

UNIT—II

3. What is photoelectric effect? Explain Einstein's photoelectric equation.

OR

4. Discuss in detail, Planck's theory of blackbody radiation.

UNIT—III

5. Derive the expression for work function and molar partition function.

OR

6. Derive the multiplication theorem of partition function.

UNIT—IV

7. State and explain Franck-Condon principle.

OR

8. Discuss the basis of Raman spectroscopy. What are Rayleigh, Stokes and anti-Stokes lines? Explain with diagram.

UNIT—V

9. Write a short note on quinone-hydroquinone electrode.

OR

10. 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 : $E^{o}\ (Cd^{2+}/\ Cd) = -0{\cdot}40$ V and $E^{o}\ (Fe^{2+}/\ Fe) = -0{\cdot}44$ V]

(SECTION : C—DESCRIPTIVE)

(*Marks* : 50)

Answer the following : 10×5=50

UNIT—I

1. *(a)* State and explain Beer-Lambert law for light absorption by solution. 3

(b) Discuss the photochemical reaction involving dissociation of hydrogen iodide molecule. 3

(c) State and explain Stark-Einstein law of photochemical equivalence. 4

OR

2. *(a)* A sample of gaseous HI was irradiated by light of wavelength 253·7 nm when 307 J of energy was found to decompose $1{\cdot}30 \times 10^{-3}$ mole of HI. Calculate the quantum yield of HI. 3

(b) State and explain Grotthus-Draper law. 3

(c) Explain the terms 'photosensitization' and 'quenching'. Give two examples of photosensitized reaction. 4

UNIT—II

3. *(a)* A photon of wavelength 4000 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;

(iii) the velocity of the photoelectron (mass of electron = $9{\cdot}109 \times 10^{-31}$ kg). 3

(b) Set up and solve Schrödinger wave equation for a particle in an infinite one-dimensional (1-D) box. 3

(c) What are the postulates of quantum mechanics? 4

OR

4. *(a)* An electron is confined in 1-D box of length 1 Å. Calculate its ground state energy in electron volts. Is quantization of energy levels observable? Comment. 3

(b) Discuss in detail Debye theory of heat capacity of monoatomic solids. 3

(c) Derive Schrödinger wave equation. 4

UNIT—III

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

(b) Calculate the characteristic vibrational temperature and the vibrational partition function of H_2 (g) molecule at 2727 °C, the fundamental vibrational frequency of H_2 (g) is given as $4405{\cdot}3\ cm^{-1}$. 3

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

OR

6. *(a)* The rotational constant of HCl (g) is $10{\cdot}59\ cm^{-1}$. Calculate the rotational partition function of HCl (g) at 500 K. 3

(b) What are the limitations of classical thermodynamics? 2

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

UNIT—IV

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

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

(c) How does interaction of electromagnetic radiation with a molecule lead to different types of spectra? Explain. 3

OR

8. *(a)* Explain anharmonicity with the help of Morse potential curve. 2

(b) What are overtones and hot bands? 2

(c) The pure rotational spectrum of gaseous HCl consists of a series of equally-spaced lines separated by $20{\cdot}80\ cm^{-1}$. Calculate the *(i)* moment of inertia and *(ii)* inter-nuclear distance. The atomic masses are $^{1}H = 1{\cdot}673\times10^{-27}$ kg, $^{35}Cl = 58{\cdot}06\times10^{-27}$ kg. 3

(d) What are radiative and non-radiative transitions? 3

UNIT—V

9. *(a)* What are concentration cells? Derive an expression for e.m.f. of a concentration cell with transference. 1+3=4

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

(c) Differentiate between electrolytic and electrochemical (galvanic) cells. 3

OR

10. *(a)* Calculate the e.m.f. of the cell

$$Cr / Cr^{3+} (0{\cdot}1\ M) \,\|\, Fe^{2+} (0{\cdot}01\ M) / Fe$$

Given

$$E^{\circ}_{(Cr^{3+}/Cr)} = -0{\cdot}75 \text{ V}$$

$$E^{\circ}_{(Fe^{2+}/Fe)} = -0{\cdot}45 \text{ V} \qquad 3$$

(b) Define liquid junction potential (LJP) and also derive the expression for its potential. 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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Value of the constants are given below :

Planck's constant $(h) = 6{\cdot}626 \times 10^{-24}$ J-s

Boltzmann constant $(k) = 1{\cdot}38 \times 10^{-23}$ J/K

Velocity of light $(c) = 3 \times 10^{8}$ m/s

1 eV = $1{\cdot}602 \times 10^{-19}$ J