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(CBCS)

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

(Physical Chemistry—III)

Full Marks : 75

Time : 3 hours

(PART : A—OBJECTIVE)

(*Marks* : 25)

The figures in the margin indicate full marks for the questions

SECTION—A

(*Marks* : 10)

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

1. A photochemical reaction takes place by the absorption of

(a) visible and ultraviolet radiation ( )

(b) infrared radiation ( )

(c) heat energy ( )

(d) -rays ( )

2. One einstein is the energy associated with

(a) one molecule ( )

(b) one photon ( )

(c) Avogadro number of photons ( )

(d) Faraday number of photons ( )

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

(a) arbitrary ( )

(b) diagonal ( )

(c) normalized ( )

(d) orthogonal ( )

4. The zero point energy for a particle in a one-dimensional box is given by

(a) $\frac{n^2h^2}{8ma^2}$ ( )

(b) $\frac{n^2}{8ma^2}$ ( )

(c) $\frac{2h^2}{8ma^2}$ ( )

(d) $\frac{4h^2}{8ma^2}$ ( )

5. As temperature increases, partition function

(a) increases ( )

(b) decreases ( )

(c) remains the same ( )

(d) increases or decreases ( )

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

(a) 4 ( )

(b) 2 ( )

(c) 1 ( )

(d) 0 ( )

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

(a) H_2 ( )

(b) CO_2 ( )

(c) HCl ( )

(d) N_2 ( )

8. The wave number range of IR radiation is

(a) 500 cm ^{1}– 4000 cm ^{1} ( )

(b) 4000 cm ^{1}– 8000 cm ^{1} ( )

(c) 100 cm ^{1}– 1000 cm ^{1} ( )

(d) 500 cm ^{1}– 1000 cm ^{1} ( )

9. The activity coefficient and molality of an electrolyte are related by the expression

(a) $a \quad m/$ ( )

(b) $a \quad m$ ( )

(c) $a \quad ^{m}$ ( )

(d) $a \quad m$ ( )

10. A voltaic cell has an E° value of –1·00 V. The reaction

(a) is spontaneous ( )

(b) has a positive G° ( )

(c) has a negative G° ( )

(d) has $K \quad 1$ ( )

SECTION—B

(*Marks* : 15)

Answer the following questions : 3×5=15

1. Distinguish between thermal and photochemical reactions.

OR

2. Write a short note on chemiluminescence.

3. Describe Planck's quantum theory of radiation.

OR

4. A photon of wavelength 4000 Å strikes a metal surface, the work function of the metal being 2·13 eV. Calculate the energy of the photon in eV. (Mass of electron 9 109 10 ^{31} kg)

5. What is the physical significance of partition function?

OR

6. Discuss the multiplication theorem of partition function.

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

OR

8. What are the conditions of getting IR spectra of a diatomic molecule?

9. Differentiate between reversible and irreversible electrochemical cells.

OR

10. What is meant by activity coefficient of an electrolyte? Write the expression to calculate the activity coefficient of Na_2SO_4.

(PART : B—DESCRIPTIVE)

(*Marks* : 50)

The figures in the margin indicate full marks for the questions

1. *(a)* What are photosensitized reactions? Give one example. 3

(b) What are meant by quantum energy and Einstein energy? State Einstein's law of photochemical equivalence. 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

OR

2. *(a)* What are the causes of low- and high-quantum yields? 4

(b) State and derive Beer-Lambert law for light absorption by solution. 3

(c) Describe the photochemical decomposition of acetaldehyde. 3

3. *(a)* Derive Schrödinger wave equation. 5

(b) An electron is confined in a one-dimensional box of length 1 Å. Calculate the ground-state energy in electron-volt. 2

(c) Describe the black-body radiation. 3

OR

4. *(a)* Derive an expression for the energy of a particle in a one-dimensional box. 5

(b) Write Schrödinger wave equation for hydrogen atom in polar coordinates. Separate the resultant equation into three equations using the techniques of separation of variables. 4

(c) What is photoelectric effect? 1

5. *(a)* Derive Boltzmann distribution law for a system containing n molecules having a total energy E. 5

(b) Calculate the vibrational partition function for Br_2 at 300 K, if the vibrational frequency is 151·2 cm^{-1}. 2

(c) Write the expressions for Helmholtz free energy and entropy in terms of partition function. 3

OR

6. *(a)* Derive an expression for the molecular rotational partition function of an ideal diatomic gas. 4

(b) Show that the internal energy of a system of N independent particles is given by $U \quad nRT^2 \left(\frac{\ln q}{T}\right)_V$. 4

(c) Calculate the translational partition function of a molecule of oxygen gas at 1 atm and 298 K moving in a vessel of volume 24·4 dm^3. 2

7. *(a)* What do you mean by zero-point energy? What is the difference between zero-point energy of a harmonic oscillator and an anharmonic oscillator? 3

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

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

OR

8. *(a)* State Raman effect. What are Stokes and anti-Stokes lines? 2

(b) Explain the following terms : 1+1=2

(i) Fundamental vibrational frequency

(ii) Hot bands

(c) The pure rotational spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20·08 cm ^{1}. Calculate the internuclear distance of the molecule. The atomic masses are ^{1}H 1 673 10 ^{27} kg and ^{35}Cl 58 06 10 ^{27} kg. 3

(d) Write notes on the following : 1½+1½=3

(i) Fluorescence

(ii) Phosphorescence

9. (a) Derive Nernst equation for describing the effect of concentration of electrolyte on electrode potential. 5

(b) What is liquid junction potential? 2

(c) Calculate 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

OR

10. (a) What are concentration cells? Derive an expression for the e.m.f. of a concentration cell with transference. 4

(b) What are redox titrations? Illustrate giving a suitable example how the titrations are carried out potentiometrically. 3

(c) Find the pH of a solution placed in a hydroquinone half-cell which was coupled with standard Calomel electrode. The e.m.f. of the combined cell is 0·123 V at 25 °C. (Given : E°_{Q} 0 6996 V and $E_{Calomel}$ 0 2415 V) 3

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