2014

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

Course No. : Chem–363

(Physical Chemistry—III)

Full Marks : 55

Time : 2 hours

(PART : B—DESCRIPTIVE)

(*Marks* : 35)

The figures in the margin indicate full marks for the questions

1. *(a)* State and explain Stark-Einstein law of photochemical equivalence. 1+2=3

(b) When a substance *A* was exposed to light 0·002 mole of it reacted in 20 minutes and 4 seconds. At the same time *A* absorbed $2{\cdot}0\times10^{6}$ photons of light per second. Calculate the quantum yield of the reaction. 2

(c) Write a short note on chemi-luminescence. 2

OR

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

(b) Discuss the photochemical reaction involving the decomposition of acetaldehyde. 3

3. *(a)* Derive Schrödinger wave equation. 4

(b) An electron in a one-dimensional box of width 10 Å undergoes a transition from the ground state to the first excited state. Calculate the wavelength of the photon absorbed. 3

OR

4. *(a)* What are the postulates of quantum mechanics? 4

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

5. *(a)* Show that the expression relating internal energy of a system to the molecular partition function is given by

$$U = NkT^2 \left[\frac{\partial \ln q}{\partial T}\right]_V$$ 3

(b) Calculate using statistical mechanics the values of S°, H° and G° for $H_2(g)$ at 3000 K. 4

OR

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

(b) Evaluate the translational partition function for oxygen atom at 300 K contained in a volume of 22·414 dm^3. 2

7. (a) Write the expression for the quantised rotational energy levels of a linear molecule. 1

(b) The pure rotational spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20·80 cm^{-1}. Calculate the internuclear distance of the molecule. The atomic masses are

$$^{1}H = 1{\cdot}673 \times 10^{-27} \text{ kg and}$$

$$^{35}Cl = 58{\cdot}06 \times 10^{-27} \text{ kg}$$ 3

(c) Describe briefly Franck Condon principle. 3

OR

8. *(a)* What are Rayleigh, Stokes and anti-Stokes lines? 1

(b) A sample was excited by the 4358 Å line of mercury. A Raman line was observed at 4447 Å, calculate the Raman shift in cm^{-1}. 2

(c) Explain anharmonicity with the help of Morse potential curve. 2

(d) Write short notes on the following : 1+1=2

(i) Fundamental frequency

(ii) Overtones

9. *(a)* Explain the term 'electrode potential'. Derive Nernst equation for describing the effect of concentration of electrolyte on electrode potential. 1+3=4

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

OR

10. *(a)* What are concentration cells? Derive an expression for the EMF of concentration cell with transference. 1+3=4

(b) The EMF of the cell

$Cd, CdCl_2 \cdot \frac{5}{2}H_2O$ (saturated) || AgCl (s), Ag

in which the cell reaction is

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

is 0·0654 V at 25 °C and 0·6915 V at 0°C. Calculate the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of the cell reaction at 25 °C. 3

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Physical constants :

Boltzmann constant $k = 1{\cdot}380 \times 10^{-23}$ JK^{-1}

Planck constant $h = 6{\cdot}626 \times 10^{-34}$ J-s

Speed of light $c = 2{\cdot}998 \times 10^{8}$ ms^{-1}

Avogadro number $N_A = 6{\cdot}022 \times 10^{23}$ mol^{-1}

2014

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

Course No. : Chem 10.1

(Physical Chemistry - III)

(PART - A OBJECTIVE)

(Marks : 30)

The figures in the margin indicate full marks for the questions

SECTION - A

(Marks : 5)

Put a Tick (✓) mark against the correct answer in the brackets provided for it. 1×5=5

2. One einstein is the energy associated with

(a) one molecule ( )

(b) one photon ( )

(c) Avogadro number of photons ( )

(d) Faraday number of photons ( )

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

(a) orthogonal ( )

(b) diagonal ( )

(c) normalized ( )

(d) arbitrary ( )

3. 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) $S = W \ln k$ ( )

4. Which of the following radiations has the highest frequency?

(a) Microwave ( )

(b) Radio wave ( )

(c) Infrared ( )

(d) X-ray ( )

5. The electrode potential of hydrogen electrode in neutral solution and 298 K is

(a) zero ( )

(b) –0·41 V ( )

(c) –0·49 V ( )

(d) +0·41 V ( )

SECTION—B

(Marks 15)

Answer the following questions : 3×5=15

1. Distinguish between photochemical and thermal reactions.

2. Define molecular partition function. What is the physical significance of this quantity?

3. Describe Planck's quantum theory of radiation

4. Explain the terms 'activity coefficient' and 'mean ionic activity coefficient'

8. Describe the effect of solvents on electronic transitions energies

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