2015

(6th Semester)

CHEMISTRY

ELEVENTH PAPER

Course No. : Chem–363

(Physical Chemistry—III)

Full Marks : 55

Time : 2½ hours

(PART : B—DESCRIPTIVE)

(*Marks* : 35)

The figures in the margin indicate full marks for the questions

1. *(a)* State and explain Lambert-Beer law for light absorption by solution. What is meant by molar absorption coefficient? How are transmittance and absorbance related to each other? 4

(b) A 10^{-3} *M* aqueous solution of a certain substance absorbs 10% of the incident radiation in a path length of 1 cm. Calculate the concentration required for 90% absorption of the incident radiation. 3

OR

2. *(a)* Discuss the photochemical reaction involving the dissociation of hydrogen iodide molecule. 4

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

3. *(a)* Discuss Einstein's theory of heat capacity of monatomic crystal and also comment on the results obtained on a plot. 4

(b) 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 eV (electron volt), *(ii)* the kinetic energy of the emitted photon, and *(iii)* the velocity of the photoelectron (mass of electron $=9{\cdot}109\times10^{-31}$ kg). 3

OR

4. *(a)* Set up and solve Schrödinger wave equation for a particle in an infinite one-dimensional (1-D) box. What is zero point energy for the same particle? 4

(b) 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

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

(b) Calculate the rotational temperature and the rotational partition function for H_2 gas at 2727 °C given that the moment of inertia of H_2 gas molecule at this temperature is $4 \cdot 6033 \times 10^{-48}$ kg m^2. 3

OR

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

(b) For H_2 gas at 3000 K, calculate the characteristic vibrational temperature and the vibrational partition function given that the fundamental vibrational frequency of H_2 molecule is 4405·3 cm^{-1}. 3

7. *(a)* 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

(b) The fundamental vibrational frequency of HCl is 2890 cm^{-1}. Calculate the force constant of this molecule.

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

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

OR

8. *(a)* Discuss the following giving examples : 2+2=4

(i) Franck-Condon principle

(ii) Mutual exclusion rule

(b) The internuclear distance of CO molecule is 1·13 Å. Calculate energy (in joules and in eV) and the angular velocity of this molecule in the first excited rotational level.

[$C = 1 \cdot 99 \times 10^{-26}$ kg and

$O = 2 \cdot 66 \times 10^{-26}$ kg] 3

9. *(a)* Define galvanic cell with a suitable example. 1

(b) Establish the relationship between e.m.f. and equilibrium constant for a cell reaction involving reversible cell. 3½

(c) A Zn rod is placed in 0·1 *M* solution of $ZnSO_4$ at 25 °C. Assuming dissociation of the salt up to 95%, calculate the potential of the electrode at this temperature $E^\circ(Zn^{2+}/Zn) = -0 \cdot 76$ V. 2½

OR

10. *(a)* Set up calomel electrode and through appropriate electrode reactions. Find the electrode potential of such an electrode. 4

(b) For the Daniell cells

$$Zn(s)\,|Zn^{2+}(aq), C_1||Cu^{2+}(aq), C_2|Cu(s)$$

write the half-cell reaction and the overall cell reaction and also find e.m.f. of the cell if the standard free energies of Zn(s), Cu(s), Cu^{2+}(aq) and Zn^{2+}(aq) are 0, 0, 64·4 kJ mol^{-1} and −1·54 kJ mol^{-1} respectively. 3

Physical Constants :

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

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

Speed of light, $c = 3 \times 10^{8}$ ms^{-1}

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

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Course No. : Chem–363

(Physical Chemistry—III)

(PART : A—OBJECTIVE)

(*Marks* : 20)

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SECTION—A

(*Marks* : 5)

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

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. Rayleigh-Jeans formulae for energy density between wavelengths λ and $\lambda + d\lambda$ in case of black-body 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) $E_\lambda d\lambda = 8\pi kT / \lambda^2$ ( )

3. In terms of molecular partition function q, the internal energy of a molecule is given by

(a) $U = nRT[\partial \ln q / \partial V]_T$ ( )

(b) $U = nRT[\partial \ln q / \partial T]_V$ ( )

(c) $U = nRT^2[\partial \ln q / \partial v]_T$ ( )

(d) $U = nRT^2[\partial \ln q / \partial T]_V$ ( )

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

(a) HCl ( )

(b) SO_2 ( )

(c) N_2 ( )

(d) protein ( )

5. At 0 K, the cell potential is equal to

(a) 0 ( )

(b) E° ( )

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

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

SECTION—B

(*Marks* : 15)

Answer the following questions : 3×5=15

1. Write the mechanisms of photosynthetic dissociation of *(a)* hydrogen molecule and *(b)* ethylene molecule.

2. What are the boundary conditions applied on a wave function? What is meant by normalized wave function?

3. Establish the relationship between molar and molecular partition functions.

4. Calculate J_{max} for a rigid diatomic molecule at 300 K for which the rotational constant is 1 566 cm^{-1}

8. Define liquid junction potential (LJP) and also derive expression for its potential

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