West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2015

PART-II

CHEMISTRY– Honours

Paper– IV

Duration : 2 Hours

Full Marks : 50

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

Use separate answer scripts for [**CEMAT-24-PA & CEMAT-24-PB**]

CEMAT-24-PA

Answer any *two* questions, taking *one* from each Unit.

UNIT - I

1. a) State the postulates of Planck's quantum theory. Planck distribution law for black body radiation in the frequency range ν to $\nu + d\nu$ is

$u_\nu d_\nu = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT}-1} d\nu$. Show that the wavelength corresponding to the maximum energy density is inversely proportional to the absolute temperature. [Terms have their usual significance] 1 + 3

b) Define a Hermitian operator. Confirm whether the operator, $\frac{h}{2\pi i}\frac{d}{dx}$ is Hermitian or not. 3

c) What does the term degenerate levels mean ? Determine the degree of degeneracy of the level $\frac{38h^2}{8ma^2}$ of a particle in a cubical box. 1 + 2

d) In the Compton experiment, a beam of X-rays with wavelength 0·0588 nm is scattered through an angle of 45°. What is the wavelength of the scattered beam ? 3

2. a) Calculate the uncertainty in position assuming uncertainty in momentum within 0·1% for (i) a tennis ball weighing 200 gm and moving with a velocity of 10 metre/sec (ii) an electron moving in an atom with a velocity of 2×10^8 cm/sec. Comment on the result. 3

b) Which of the following functions are acceptable in quantum mechanics ?

(i) $\cos x + \sin x$ for $0 \leq x \leq \frac{\pi}{2}$

(ii) e^{-ax} for $x \leq 0$. 2

c) Show that the length of the one dimensional box is an integral multiple of $\lambda/2$, where λ is the wavelength associated with the particle wave. 3

d) If $\hat{A}$ and $\hat{B}$ are Hermitian operators, show that $\hat{A}\hat{B}$ is a Hermitian operator if $\hat{A}\hat{B} = \hat{B}\hat{A}$. $2\frac{1}{2}$

e) Determine the value of x at which the first excited wave function of the simple harmonic oscillator exhibits maximum or minimum.

[Given : $\psi_1(x) = \left(\frac{a}{4\pi}\right)^{\frac{1}{4}} (2\alpha^{\frac{1}{2}} x) e^{-\alpha x^2/2}$, $\alpha = (k\mu)^{\frac{1}{2}}/\hbar$, k = force constant, μ = reduced mass] $2\frac{1}{2}$

Unit - II

3. a) How much more likely is a 1s electron in a hydrogen atom to be at a distance a_0 from the nucleus than at the distance $a_0/2$? Given : Radial wave function of 1s electron : $R = \frac{2}{a_0^{3/2}} e^{-r/a_0}$. 3

b) "In the photostationary state of dimerization of anthracene at its large concentration, the concentration of dimer is independent of the concentration of monomers." Justify. 4

c) An uranyl oxalate actinometer is irradiated for 20 mins with light of λ = 4350 Å and oxalic acid equivalent to 15 ml of 0·001 (M) $KMnO_4$ is found to have been decomposed. The intensity of the incident beam is $3{\cdot}245 \times 10^{16} S^{-1}$. Find the quantum yield. 3

d) Explain photosensitized reactions and give an example of photosensitized reaction which is useful to mankind. 2

4. a) Hydrogen wave function is given by $\psi_{1S} = \left(1/\pi a_0^3\right)^{1/2} e^{-r/a_0}$. Determine the most probable value of r in this state. 4

b) Briefly explain the phenomena of fluorescence and phosphorescence. 3

c) The reaction ($2A \rightleftharpoons A_2$) occurs both thermally and photochemically.

The photochemical reaction takes place with the following steps :

(i) $A \xrightarrow{h\nu(I_{abs})} A^*$

(ii) $A^* + A \xrightarrow{K_2} A_2$

(iii) $A_2 \xrightarrow{K_3} 2A$

(iv) $A^* \xrightarrow{K_4} A + h\nu'$.

Applying the steady state approximation to A^*,

Show that $[A_2] = \dfrac{I_{abs}}{K_3\left[1+K_4/K_2(A)\right]}$ at photostationary equilibrium.

Also, show that $[A_2]$ is independent of $[A]$, when $[A]$ is present in large excess. 3 + 2

CEMAT-24-PB

Answer any *two* questions taking *one* from each unit.

Unit - I

5. a) What do you mean by fugacity of a gas ? Express fugacity in terms of measurable properties (such as P, V) of the gas and state how it can be determined. 3

b) Show that

(i) $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j \neq n_i}$

(ii) $\frac{d \ln k_p}{dT} = \frac{\Delta H^\circ}{RT^2}$. 2×2

c) At 25°C for the reaction : $Br_2(g) = 2Br(g)$, we have $\Delta G^\circ = 161{\cdot}67$ KJ/mol and $\Delta H^\circ = 192{\cdot}81$ KJ/mol. At what temperature will the system contain 10 mol per cent bromine atoms in equilibrium with bromine vapour at $P = 1$ atm. 4

d) 'If $\Delta G^\circ = 0$ for a reaction, the reaction is thermodynamically impossible.' Comment. 2

6. a) For the equilibrium $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$.

$K_p = 8 \times 10^{-9}$ at 127°C. Calculate the degree of dissociation of phosgene and ΔH° for the reaction at that temperature.

[Given : total pressure is 2 atm and $\Delta S^\circ_{400K} = 30$ cal $deg^{-1} mole^{-1}$] 4

b) Derive the relation $\sum_i n_i d\mu_i = 0$. 3

c) A solute goes into solution with evolution of heat. How will the solubility change with temperature ? Assume van't Hoff equation to apply in case of solubility. 3

d) What is meant by chemical potential (μ) of a substance ? Is it an extensive property ? Explain the significance of μ with regard to equilibrium state of a system. 3

UNIT-II

7. a) Define conductance, specific conductance and equivalent conductivity of an electrolyte solution. Write down the SI units of each quantity. $3 + 1\frac{1}{2}$

b) While ionic mobility increases with temperature, both the transport numbers of H^+ and Cl^- ions in aqueous solution of HCl approach 0·5 as the temperature is increased. Justify or criticize. $2\frac{1}{2}$

c) The standard reduction potentials for Fe^{+3}, Fe^{+2} : Pt and Sn^{+4}, Sn^{+2} :Pt at 25°C are 0·77V and 0·15 V. Set up the cell, write down the cell reactions and calculate the equilibrium constant of the reaction occurring in the cell. 5

8. a) Discuss the principle of determination of pH of a solution using a glass electrode. 3

b) Given that E° is 0·152 for $Ag + I' = AgI + e^-$ at 25°C and E° for $Ag = Ag^+ + e^-$ is – 0·800 V at 25°C. Calculate K_{sp} for AgI. 2

c) A conductivity cell has a resistance of 250 Ω when filled with 0·02 M KCl at 298 K and one of 10^5 Ω when filled with 6×10^{-5} M NH_4OH solution. The specific conductance of 0·02 M KCl is 0·277 $\Omega^{-1}m^{-1}$ and the equivalent conductances of NH_4^+ and OH^- are $7{\cdot}34 \times 10^{-3}$ and 0·0198 m^2 equiv$^{-1}\Omega^{-1}$ respectively. Calculate the cell constant and the degree of dissociation of NH_4OH solution in 6×10^{-5} M solution. 3

d) Define buffer capacity. Find the condition when it has maximum value. 2 + 2