



CHE(H) - II
P-IV

CEMA(HN)-04

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

$$u_{\nu} d\nu = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} d\nu. \text{ Show that the wavelength corresponding to}$$

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

SUB.-B.Sc.(HN)-CEMA-6044

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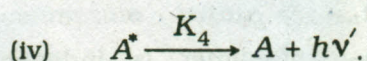
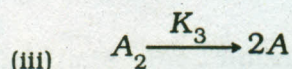
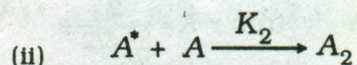
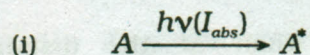
- c) What does the term degenerate levels mean? Determine the degree of degeneracy of the level $\frac{38h^2}{8ma^2}$ of a particle in a cubical box. 1 + 2
- d) In the Compton experiment, a beam of X-rays with wavelength 0.0588 nm is scattered through an angle of 45° . What is the wavelength of the scattered 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, $\mu =$ 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 $\lambda = 4350 \text{ \AA}$ 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 $3.245 \times 10^{16} \text{ S}^{-1}$. 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 :



Applying the steady state approximation to A^* ,

Show that $[A_2] = \frac{I_{abs}}{K_3 [1 + K_4/K_2(A)]}$ 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

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

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

c) At 25°C for the reaction : $\text{Br}_2(g) = 2\text{Br}(g)$, we have $\Delta G^\circ = 161.67 \text{ KJ/mol}$ and $\Delta H^\circ = 192.81 \text{ KJ/mol}$. At what temperature will the system contain 10 mol per cent bromine atoms in equilibrium with bromine vapour at $P = 1 \text{ atm}$. 4

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

6. a) For the equilibrium $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$.

$K_p = 8 \times 10^{-9}$ 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 $\Delta S^\circ_{400K} = 30 \text{ cal deg}^{-1} \text{ mole}^{-1}$] 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 $25^\circ C$ 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 $25^\circ C$ and E° for $Ag = Ag^+ + e^-$ is -0.800 V at $25^\circ C$. Calculate K_{sp} for AgI. 2

- c) A conductivity cell has a resistance of 250Ω when filled with 0.02 M KCl at 298 K and one of $10^5 \Omega$ when filled with $6 \times 10^{-5} \text{ M NH}_4\text{OH}$ solution. The specific conductance of 0.02 M KCl is $0.277 \Omega^{-1}\text{m}^{-1}$ and the equivalent conductances of NH_4^+ and OH^- are 7.34×10^{-3} and $0.0198 \text{ m}^2 \text{ equiv}^{-1}\Omega^{-1}$ respectively. Calculate the cell constant and the degree of dissociation of NH_4OH solution in $6 \times 10^{-5} \text{ M}$ solution. 3
- d) Define buffer capacity. Find the condition when it has maximum value. 2 + 2