

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  $\nu$  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.

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[ Turn over

- 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  $45^\circ$ . 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  $2 \times 10^8$  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  $\lambda$  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 :  $\psi_1(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha^{1/2}x)e^{-\alpha x^2/2}$ ,  $\alpha = (k\mu)^{1/2}/\hbar$ ,  $k =$  force constant,  $\mu =$  reduced mass }
- $2 \frac{1}{2}$

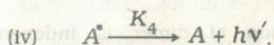
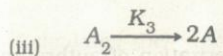
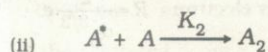
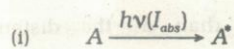
## Unit - II

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)  $\text{KMnO}_4$  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

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- 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  $A^*$ ,

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

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.

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nically.

b) Show that

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

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

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

large

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

3 + 2

$K_p = 8 \times 10^{-9}$  at 127°C. Calculate the degree of dissociation of phosgene and  $\Delta H^\circ$  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

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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 ( $\mu$ ) of a substance ? Is it an extensive property ? Explain the significance of  $\mu$  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  $E^\circ$  is 0.152 for  $Ag + I^- = AgI + e^-$  at  $25^\circ C$  and  $E^\circ$  for  $Ag = Ag^+ + e^-$  is -0.800 V at  $25^\circ C$ . Calculate  $K_{sp}$  for AgI. 2

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