लक्ष्यं विद्धमानम्

WEST BENGAL STATE UNIVERSITY

B.Sc. Honours PART-II Examinations, 2017

CHEMISTRY-HONOURS

PAPER-CEMA-IV

Time Allotted: 2 Hours | Full Marks: 50

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All Symbols are of usual significance.

CEMAT-24-PA

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

Unit-I

1. (a) Find the eigenvalue of the operator p_x^2 for the function $\psi(x) = A\sin kx$. 3

Given that, $\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = \frac{k^2\hbar^2}{2m}\psi(x)$, A and k are constants.

(b) If two Hermitian operators $\hat{A}$ and $\hat{B}$ have all the eigenfunctions common, then show that $[\hat{A}, \hat{B}] = 0$. Assume that all the eigenstates of $\hat{A}$ and $\hat{B}$ are non-degenerate and show that all the eigenvalues of $\hat{A}$ are real. 5

(c) "A particle confined in a one dimensional box cannot have zero energy." Justify or contradict on the basis of Heisenberg's uncertainty principle. 2

(d) Determine whether the following functions are well behaved or not in the indicated intervals. 3

(i) $\frac{1}{x}$ $(0, \infty)$ (ii) $\tan x$ $(0, \pi)$

2. (a) Test whether the function $f(x) = \sin x \cos x$ is eigenfunction of the operator $\frac{d^2}{dx^2}$ or not. 2

(b) Find $< x >$ and $< p_x >$ of a one dimensional harmonic oscillator in its first excited state $\psi_1(x)$. Given that $\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2}$, where α is a constant. 2+2

(c) What is meant by Hermitian operator? Verify whether the operator $\frac{d}{dx}$ is a Hermitian operator or not. 3

(d) Explain why $\frac{\partial \psi}{\partial x}$ should be continuous for $\psi(x)$ to be a well-behaved eigenfunction of the Hamiltonian operator. Why is normalization of ψ necessary? 2+2

Unit-II

3. (a) Justify Einstein's law of photochemical equivalence, from the photon picture of light. 2

(b) State the basis of Franck Condon principle. 2

(c) An uranyl oxalate actinometer is irradiated for 15 minutes with light of wavelength 4350Å and oxalic acid equivalent to 12.0 cc of 0.001 (M) $KMnO_4$ is found to have been decomposed. The quantum efficiency of the actinometer at this wavelength being 0.58. Find out the average intensity of light used in (i) ergs per sec and (ii) quanta per sec. 4

(d) Find the radial distribution function for the following hydrogenic orbital. 4
$\psi = C\, re^{-Zr/2a} \sin\theta \cos\phi$, C is constant.

4. (a) Evaluate $|\psi|^2 \, d\tau$ for a 1s-electron of H-atom at the nucleus. 2

$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$, a_0 = constant.

(b) Explain why quantum yield of a photochemical reaction can be less than 1. 2

(c) Explain the differences between photostationary state and the state of chemical equilibrium. 3

(d) Acetaldehyde decomposition proceeds through the following mechanism. 3

(i) $CH_3COOH + h\nu \longrightarrow CH_3 + CHO$

(ii) $CH_3 + CH_3CHO \xrightarrow{K_2} CH_4 + CH_3CO$

(iii) $CH_3CO \xrightarrow{K_3} CH_3 + CO$

(iv) $CH_3 + CH_3 \xrightarrow{K_4} C_2H_6$

Find out the expression of $-\frac{d}{dt}[CH_3CHO]$.

(e) Find the positions of the radial nodes of the following orbital. 2

$$\psi = K(c - br + ar^2)e^{-\alpha r}$$

Where a, b, c, K and α are constants.

CEMAT-24-PB

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

Unit-I

5. (a) Starting from Clausius inequality obtain the criteria for spontaneity when the entropy and volume remain constant. 3

(b) Define chemical potential in terms of internal energy. Comment on the relative slope of μ versus T plot at constant pressure for liquid phase and gaseous phase. 2+2

(c) State the universal criteria of material equilibrium in terms of chemical potential. Derive from it the condition for chemical equilibrium. 1+2

(d) 20.85 g of PCl_5 is taken in a 4-litre closed vessel at 250°C. The equilibrium pressure of the mixture is found to be 1.825 atm. Find out the partial pressure of Cl_2 and the value of K_p. 3

6. (a) Derive an expression for fugacity of a Van der Waal's gas neglecting the intermolecular attraction and hence find out the value of fugacity at 10 atm and at 300 K assuming that $b = 0.043$ L mol^{-1}. 4

(b) Define $\Delta_r G$. Point out the differences between $\Delta_r G$ and ΔG^0 for a chemical reaction. 2+2

(c) "K_p is independent of pressure at constant temperature for all gaseous reaction." – Justify or contradict. 2

(d) n_1 moles of an ideal gas and n_2 moles of the same ideal gas are mixed together under constant temperature and pressure. Derive an expression for ΔS_{mix} and hence find out ΔS_{mix} for the process. 3

Unit-II

7. (a) Justify the use of alternating current and platinised platinum electrodes in conductance measurements in aqueous medium. 2+2

(b) Obtain the condition for maximum buffer capacity of an acid-base buffer. 3

(c) The equilibrium constant for the reaction 2+2+1

$$Sn^{2+} + 2Fe^{3+} = Sn^{+4} + 2Fe^{2+} \text{ at } 25°C \text{ is } 1.0 \times 10^{21}$$

(i) Construct a cell in which the reaction may occur.

(ii) Calculate the standard E.M.F. of the cell and ΔG^0 for the process.

8. (a) Explain which of the following solution will have greater value for (i) specific conductance and (ii) equivalent conductance. 2+2

0.1 M KCl and 0.01 M KCl

(b) It is desired to prepare a buffer solution of pH 4.5 using aqueous solution of acetic acid (HOAc) and sodium acetate (NaOAc). Given that K_a for HOAc = 1.8×10^{-5}. Calculate the weight of sodium acetate that must be added to 1 litre of 1(N) HOAc (Ignore any volume change due to mixing). 3

(c) Derive the relation $\frac{\partial(E^0/T)}{\partial(1/T)} = -\frac{\Delta H^0}{nF}$, where the terms have their usual significance. 3

(d) Equal volumes of aqueous solution of 0.1 M $Pb(NO_3)_2$ and 0.1 M K_2SO_4 are mixed together. Calculate the ionic strength of the resulting solution. 2