WEST BENGAL STATE UNIVERSITY

B.Sc. Honours Part-II Examination, 2022

CHEMISTRY

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) State Heisenberg's position-momentum uncertainty principle. How is position uncertainty is defined here?   3

   (b) 2.14 eV is required to remove an electron from Cs. (i) What is the cut off λ for photo electric emission from Cs (ii) Will a light of 6000Å liberate an electron from Cs?   3

   (c) Find the zero point energy of particle of mass 1×10^{-28} kg confined in a rectangular box of sides $L_x = L$ and $L_y = 2L$, where L is 10 nm.   3

   (d) Evaluate the commutators $[x, y]$ and $\left[\dfrac{1}{x}, p_x\right]$.   4

2. (a) Calculate the probability of finding a particle of mass m confined in a 1-D box of length L within the length $x = \dfrac{L}{4}$ to $x = \dfrac{3L}{4}$.   3

   (b) Justify or contradict the following statement.   3

   "The energy values of a particle of mass m, which is confined in a 1-D box of length L is given as, $E_n = \dfrac{n^2 h^2}{8mL^2}$, where $n = \pm 1, \pm 2, \pm 3, \cdots\cdots$".

   (c) Draw the ψ^2 versus x curve for a harmonic oscillator at its zero point energy level. How does the profile satisfy Bohr correspondence principle at high quantum numbers? — Explain.   4

   (d) Show that if $\hat{A}$ and $\hat{B}$ are Hermitian then $\hat{A}\hat{B}$ is also Hermitian only if $\hat{A}$ and $\hat{B}$ commute.   3

Unit-II

3. (a) What is an atomic orbital? What significance does it have?   2+2

   (b) If light absorbed by a 1M solution is 90% of the incident light, find the molar extinction coefficient of the sample in terms of path length. Hence find the unit of molar extinction coefficient. On what factors does it depend?   4

   (c) An electronic transition gives rise to line spectra interspersed by continuum. Draw the relevant potential energy diagram. State and explain the principle required for such vertical transitions.   4

4. (a) Define radial distribution function. Find the probability of finding the electron around the nucleus in the ground state of a hydrogen atom in a spherical volume of width dr.   2+2

   (b) Draw the $\frac{1}{\Phi}$ vs. $[M]$ plot for the reaction $A \rightarrow B + C$ having the following mechanism and indicate the value of slope and intercept. [Φ = quantum yield]   4

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

   (ii) $A^* + M \xrightarrow{k_1} M + A$

   (iii) $A^* \xrightarrow{k_2} B + C$

   (c) By the help of Jablonskii diagram explain that phosphorescence occurs at longer wavelength than fluorescence.   4

CEMAT-24-PB

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

Unit-I

5. (a) Explain the variation of G as a function of ξ (advancement) for a chemical reaction of the type $A(g) \rightleftharpoons B(g)$ at constant T and P. What will be the nature of the plot of G vs ξ at fixed T and P if B is removed as soon as it is formed from A? — Explain.   4+2

   (b) Given $\ln K = 3 + \left(\frac{2 \times 10^4}{T} \right)$, Find ΔH^0 and ΔS^0 for the reaction.   4

   (c) A gas obeys the equation $z = 1 + \frac{\alpha P}{1 + \alpha P}$. Calculate the fugacity (f) for the gas.   3

6. (a) Define chemical potential of a component in a mixture in terms of the internal energy of the mixture.   2

   (b) Find out the minimum work to be done to separate the components of a mixture containing equal moles of two ideal gases. The temperature and pressure remain constant throughout the process.   3

(c) Gaseous iodine at 1 atm is 1% dissociated into atoms at 600°C and 25% dissociated at 800°C. Calculate ΔH^0 for the dissociation. Assume ideal behaviour. 4

(d) Staring from the van't Hoff equation $\left(\dfrac{d \ln K_P}{dT} = \dfrac{\Delta H}{RT^2} \right)$, show that for a liquid $\rightleftharpoons$ vapor equilibrium, Clausius Clapeyron equation $\left[\ln\left(\dfrac{P_1}{P_2} \right) = \dfrac{\Delta H_{vap}}{R} \left(\dfrac{1}{T_1} - \dfrac{1}{T_2} \right) \right]$ is obtained, where T_1 and T_2 are the boiling points of the liquid at pressure P_1 and P_2 respectively. 4

Unit-II

7. (a) For an weak electrolyte HA, variation of $\dfrac{1}{\Lambda_{eq}}$ with $\Lambda_{eq} C$ gives a straight line with unit slope and positive intercept. Derive the expression of Λ_{eq} in terms of dissociation constant and degree of dissociation of HA. [Terms have their usual significance] 4

(b) What do you mean by buffer capacity? 2 ml of 0.1(N) NaOH is added to 10 ml of 0.1(N) CH_3COOH solution. Find the buffer capacity. 2+3

(c) Of the following cells 3

   (i) $Cd(Hg)/CdSO_4(satd.)/Hg_2SO_4(s)/Hg(l)$ and

   (ii) $Cd(s)/CdCl_2(aq)/HNO_3(aq)/H_2(g)/Pt$.

Which cell will require a salt bridge and why?

8. (a) Calculate the emf of the following cell at 25°C: 5

$$Pt/H_2(g)(1\,bar)/H^+(0.3\,m)//H^+(0.7\,m)/H_2(g)(1\,bar)/Pt$$

Will the cell reaction be spontaneous? What will be the equilibrium constant of the cell? Will the equilibrium constant change on changing the concentration of H^+ in the LHS side?

(b) A conductivity cell at 25°C has a resistance of 650 ohms when filled with KCl solution and 2500 ohms when filled with 0.1(M) NH_4OH solution. Specific conductance of the KCl solution at 25°C is 1.4×10^{-3} S cm^{-1}. Equivalent ionic conductivities of NH_4^+ and OH^- at infinite dilution are 73.4 and 198 S cm^2 $equiv^{-1}$ respectively. Calculate the cell constant and dissociation constant of NH_4OH solution at 25°C. 4

(c) The solubility product of $CaCO_3$ is 4.8×10^{-9}. Find out the solubility of $CaCO_3$ in presence of a solution containing NaCl, KCl and $MgCl_2$ each having concentration 0.1 M in the solution. 3

N.B. : *Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.*

————×————