3 Yr. Degree/4 Yr. Honours 4th Semester Examination, 2025 (CCFUP)

Subject : Chemistry

Course: CHEM4012 (Major)

(Physical Chemistry)

Time: 3 Hours **Full Marks: 60**

The figures in the right hand margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any ten* questions from the following: 2×10=20

(a) Show that $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T, V, n_{j\neq i}}$.

(b) State the thermodynamic criteria for the formation of an ideal solution.

(c) State whether the transport number of Cl^- in NaCl and KCl of same concentration are same or different. Give reason.

(d) From equipartition principle, show that $\overline{C}_v = 3R$ for a monatomic solid.

(e) For the reaction at equilibrium $2A(g) + 3B(g) \rightleftharpoons C(g) + 2D(g)$, what will be the effect on equilibrium due to introduction of inert gas at constant pressure?

(f) For an operator, $\hat{A} = \frac{\hat{d}}{dx} + \hat{x}$. Find $\hat{A}^2$

(g) Define autocatalytic reaction. Give an example.

(h) Define 'ionic mobility'. Find its unit.

(i) How does the equivalent conductance of acetic acid vary with dilution? Explain with depiction.

(j) State Nernst's heat theorem. Hence show that the heat capacity would remain unaltered in the vicinity of absolute zero temperature.

(k) Show the plot of logk vs pH for a (i) specific H^+ ion and (ii) specific OH^- ion catalyzed reactions.

(l) Name two experiments for each where light behaves as (i) particle and (ii) wave.

(m) Prove that $\hat{p}_x$ is hermitian.

(n) Interpreted a chemical equilibrium in terms of $dG_{P,T}$ & $G_{P,T}$. Depict graphically.

(o) Show that the temperature coefficient of a homogeneous thermal chemical reaction will be between 1·00 –1·02 if all collisions are effective.

2. Answer *any four* questions from the following: 5×4=20

(a) (i) Write down the expression of ΔG_{mix} when two ideal gases are mixed up at constant T & P. Hence show that $|\Delta G_{mix}|$ is the largest when the gases are mixed up in equimolar proportions.

(ii) Suggest a linear plot for determination of Michaelis–Menten constant experimentally. 3+2

(b) (i) For the reaction at equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Find an expression of K_p in terms of the extent of reaction (x) at equilibrium when N_2 and H_2 are mixed up in 1 : 3 mole ratio.

Also show that at low pressure, $K_p \approx \frac{64}{27}\frac{x^2}{p^2}$.

(ii) "An equilibrium constant is dimensionless." — Comment. 3+2

(c) (i) State, wtih proper reason, whether the following functions behave well within the given range of variables a) $\psi_1 = \cos^{-1}\left(\frac{x}{8}\right), -8 \le x \le 8$, b) $\psi_2 = \sin\left(\frac{5\pi y}{2}\right), -\alpha \le y \le \alpha$, c) $\psi_3 = \ln|7|, -10 \le 7 \le 10$.

(ii) Calculate the de Broglie wavelength of an electron accelerated from rest by a potential of 1000 volt. 3+2

(d) (i) The equivalent conductance at infinite dilution for $AgNO_3$, KNO_3 and KCl are 133, 145 and 150 Scm^2 g-equiv^{-1} at 25°C.

Calculate I. λ_0 (AgCl)

II. λ_0 (NaCl) – λ_0 ($NaNO_3$)

(ii) The equivalent conductance of a 0.01(N) $La(NO_3)_3$ solution is 140.5 Ohm^{-1} cm^2 g-equiv^{-1}. Find its molar conductance in SI unit. 3+2

(e) (i) Prove that the Hermitian operators have real eigenvalues.

(ii) Find the commutation: $\left[\hat{x}, \hat{p}_x\right] = ?$ 3+2

(f) (i) Briefly outline the Lindemann scheme of gas phase unimolecular reactions. Also show that the reaction obeys a first order kinetics at high pressure.

(ii) A catalyst does not affect the equilibrium of a reaction. — Comment. 4+1

3. Answer *any two* of the following: 10×2=20

(a) (i) Derive a suitable expression that can explain the change of rate constant of an ionic reaction with the change in ionic strength of the medium. Hence predict the effect of increasing ionic strength on the rate constant for each of the following reactions:

(I) $S_2O_8^{=} + I^- \longrightarrow I_2 + 2\,SO_4^{=}$

(II) Inversion of cane sugar

(ii) K_p for a reaction $2A(g) + B(g) \rightleftharpoons 2C(g) + 3D(g)$ is $1{\cdot}5 \times 10^{-2}$ at 27°C. Find K_e at the same temperature.

(iii) CO have a residual entropy of 4·76 J mol^{-1} K^{-1}. — Comment. (4+2)+2+2

(b) (i) Starting from Ostwald's dilution law, obtain a relation showing the linear variation of $1/\lambda$ with $\lambda.c$ for a weak acid.

(ii) The resistance of a conductivity cell filled with 0·02 N KCl solution at 18°C is 17·6 Ohm and when filled with 0·1N acetic acid is 92 Ohm. The specific conductance of 0·02 N KCl solution is 0·0024 Ohm^{-1} cm^{-1} and $l_{H^+} = 315$, $l_{Ac^-} = 35$ Ohm^{-1} cm^2. Find the dissociation constant of the acetic acid.

(iii) Find y in terms of x if y be an eigenfunction of the operator $\left(\hat{x}\cdot\frac{\hat{d}}{dx}\right)$ with eigenvalue m. 3+5+2

(c) (i) Given, vibrational partition function $(f_{vib}) = \frac{1}{1-e^{-h\gamma/KT}}$ and energy

$$U_{vib} = \left(\frac{\partial \ln f_{vib}}{\partial T}\right)_V \cdot NKT^2$$

N = Number of oscillators

K = Boltzmann Constant

h = Planck's Constant

Hence find an expression of $\bar{C}_V$ for monatomic solids. Show that $\bar{C}_V << 3R$ at low temperature. How far the results obtained from this theory satisfies the experimental results?

(ii) $\hat{A} = \frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}$ and $\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$ defined in (0, L) for quantum number n.

Find the average value, $\langle \hat{A} \rangle$.

(iii) Show the conductometric titration curve when $AgNO_3$ is titrated by KCl. Give reason. (3+1+1)+3+2

(d) (i) The work function of K is 2·2 eV and that of Ni is 5·0 eV. Will violet light of $\lambda = 4000$ Å cause the photoelectric emission in K? What will happen in case of Ni? Give reason. Also calculate the maximum kinetic energy of the electrons emitted.

(ii) Starting from the Gibbs-Helmholtz relation arrive at the van't Hoff reaction isobar. Show a plot of $\ln(K_p)$ vs $1/T$. Comment on the slope.

(iii) The effect of temperature on chemical equilibrium from van't Hoff equation and Le Chatelier's principle have no difference. —Explain. (2×1+2)+(3+1)+2