2015

CHEMISTRY — HONOURS

Third Paper

(Group – B)

Full Marks – 50

The figures in the margin indicate full marks

Candidates are required to give their answers in their own words as far as practicable

CHT 23a

Unit – I

Answer ***any three*** questions

1. (a) Derive the relationship $\frac{d \ln K_p}{dT} = -\frac{\Delta H^\circ}{RT^2}$. 3

(b) In the above relationship, ΔH° is assumed to be a constant. If this is not so and ΔH° can be expressed as a power series in T, such as

$$\Delta H^\circ = \Delta H_o^\circ + A'T + B'T^2 + C'T^3 + ...$$

Obtain an expression for $\ell_n K_p$ using this value of ΔH°. 2

2. (a) Consider the phase transition $H_2O(\ell) \rightleftharpoons H_2O(v)$ and depict with a graphical representation, the variation of chemical potential of H_2O against temperature at constant pressure in the vicinity of its boiling point. 2

(b) A mixture is composed of A and B in the molar ratio of 1 : 0.3. For a change of -10 Jmol^{-1} in the chemical potential of A, what would be the corresponding change in the chemical potential of B ? 3

3. (a) What are the factors on which the Debye-Hückel constant (A) depends ? 2

(b) The mean ionic activity coefficient of a 1-2 type electrolyte in 0.005 M solution is 0.75. Calculate Debye-Hückel constant using the limiting law. 3

4. (a) "The relation $K_p = K_c.(RT)$ for the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ implies that K_p/K_c has the S.I. unit Joule mol^{-1}" — Justify or criticize the statement. 2

(b) Show that $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{s,p,n_j(j\neq i)}$. 3

5. (a) The ionic strength of 0.1 N CH_3COOH solution is 0.001 at 20°C. Calculate the pH of the solution. 2

(b) Show that the degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of the solution. 3

Unit – II

Answer ***any two*** questions

6. (a) Why are free-fall raindrops assumed to be spherical in shape ? 2

(b) The viscosity coefficient of N_2 gas is 1.78×10^{-4} poise at 25°C and 1 atm. pressure. Using hard sphere model theory, calculate the collision diameter at the given condition. 3

7. (a) Temperature has different effects on variation of viscosities of liquids and gases. Explain. 2

(b) Calculate the change in surface energy when 125 tiny spherical air bubbles of same size merge together to form a large bubble of volume $\left(\frac{\pi}{6}\right)$ cm^3 in water at 25°C. ($\gamma_{H_2O} = 72$ dynes-cm^{-1} at 25°C) 3

8. (a) Derive Laplace's equation of excess pressure inside a spherical bubble, suspended in air. 3

(b) Mercury has a convex surface in a glass tube. Hence, comment on the relative values of mercury-glass and air-glass surface tensions. 2

CHT 23b

Unit – I

Answer ***any three*** questions

9. (a) Determine, citing reasons, whether the following function is acceptable as well behaved wave function or not within the indicated interval :

$$e^{-x}\cos x (0,\infty).$$ 2

(b) Write down an expression for 'Compton Shift' and indicate therein the parameter 'Compton wavelength'. What is the value of scattering angle for which the Compton shift becomes maximum ? 3

10. (a) Heisenberg's uncertainty principle demands that the zero-point energy of a harmonic oscillator be non-zero. Explain. 2

(b) Evaluate the commutator : $\left(\hat{x}^n, \hat{p}_x\right)$. 3

11. (a) Photoelectric effect gives a strong evidence in favour of particle nature of light. Account for the statement. 2

(b) Find the de Broglie wavelength of electrons that have been accelerated from rest through a potential difference of 1 kV. 3

12. (a) Show that the wavefunctions corresponding to different eigenvalues of a Hermitian operator are orthogonal. 3

(b) If $c \sin(ax)$ is an eigenfunction of $\frac{d^2}{dx^2}$, calculate the eigenvalue. 2

13. (a) Explain whether the function $e^{-\frac{iEt}{\hbar}}\Psi(x)$ represents a stationary state or not. 3

(b) Calculate the degeneracy of the level having an energy of $\frac{14h^2}{8ma^2}$ for a particle of mass m confined in a cubic box of edge length a. 2

Unit – II

Answer ***any two*** questions

14. (a) Show that $\frac{\partial(E^\circ/T)}{\partial(1/T)} = \frac{\Delta H^\circ}{nF}$, where the terms have their usual significance. 3

(b) A potentiometer equipped with glass-saturated calomel electrode gave a reading of 0.0232 V at 25°C for a pH 2.5 buffer. What is the pH of another buffer for which the same potentiometer reads 0.111 V ? 2

15. (a) 200 ml of 0.002 M $BaCl_2$ solution is added to 300 ml of 0.003 M Na_2SO_4 solution. Calculate the specific conductance of the resulting mixture.

[Given : $\lambda_\pm$ values at 25°C of $\frac{1}{2}Ba^{++}$, Cl^-, Na^+ and $\frac{1}{2}SO_4^{=}$ are 80, 76, 50 and 80 S cm^2 $equiv^{-1}$ respectively.] 3

(b) Why the equivalent conductance at infinite dilution values cannot be obtained by plotting equivalent conductance vs. $\sqrt{c}$ for weak electrolytes ? 2

16. (a) Will the conductometric titration curves for titration of sulphuric acid and oxalic acid (both dibasic) with NaOH be same ? Give reasons. 2

(b) Set up a reversible cell without transference for the process

$$CuSO_4(a_1) \longrightarrow CuSO_4(a_2),\ a_2 < a_1$$

and find out the emf of the cell. 3