2021

CHEMISTRY — HONOURS

Seventh Paper

(Group-A)

Full Marks : 75

The figures in the margin indicate full marks.

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

CHT–33a

Unit-I

Answer ***any three*** questions.

1. (a) The density of Lithium metal is 0·53 g cm^{-3} and the separation of the (100) planes of the metal is 350 pm. Determine whether the lattice is *fcc* or *bcc*. [At. Wt of Li = 6·3941]

   (b) Why do electrolytes increases the surface tension of a liquid? Explain with the help of Gibbs adsorption isotherm. 3+2

2. (a) Show that the distance of separation between the successive *hk* planes in two dimensional square lattice is $a/(h^2+k^2)^{1/2}$, where a is the unit distance along x and y axes.

   (b) Temperature variation of polarization can predict the polar or non-polar nature of a substance.— Comment. 3+2

3. (a) Describe the characteristic of Stern double layer model.

   (b) Distinguish between physisorption and chemisorptions using appropriate examples. 3+2

4. (a) Define, with an example, lyophilic colloid. Explain what do you mean by the term 'gold number'.

   (b) What is 'Tyndall effect'? What type of information does one gather from the quantitative data of such experiments? 3+2

5. (a) A liquid of molecular weight 18 g mol^{-1} and density $0{\cdot}995\times10^3$ kg m^{-3} has a dielectric constant 78·5 and refractive index 1·383. Calculate the values of its molar polarization, molar refraction and dipole moment neglecting atomic polarization.

   (b) Although KCl is actually isomorphous with NaCl, yet from x-ray studies, it appears that KCl has a simple cubic lattice. —Justify. 3+2

Unit-II

Answer ***any two*** questions.

6. (a) Verify that the wave function A $\exp(-Bx^2/2)$ is an eigenfunction of the simple harmonic oscillator (in one dimension) Hamiltonian. Here $B=2\pi(\mu k/h)^{1/2}$ (terms have their usual significance). Find the eigenvalue.

(b) Normalize the wave function of a harmonic oscillator in the v=1 level, $\psi_1=A.x.\exp(-\alpha x^2/2)$

Given: $\int_0^{\alpha} x^2 \exp\left(-ax^2\right)dx=\dfrac{1}{4a\left(\pi/a\right)^{1/2}}$ 3+2

7. (a) Find the most probable value of r for 1s electron in a hydrogen atom.

(b) Justify the existence of the zero point energy in the case of a quantum harmonic oscillator in the light of Heisenberg's uncertainty principle. 3+2

8. (a) How can you construct the real wave function for $2P_x$ orbital using the following expression for $\psi_{(2,\,1,\,+1)}$ and $\psi_{(2,\,1,\,-1)}$?

Given, $\psi_{(2,\,1,\,\pm1)} = 1/(64\pi)^{1/2}.(1/a_0)^{5/2}.r.\exp(-r/2a_0).\sin\theta.\exp(\pm\, i\phi)$

where the terms have their usual significance.

(b) Explain why $2s$ and $2p$ orbitals of hydrogen atom are degenerate. 3+2

CHT–33b

Unit-I

Answer ***any three*** questions.

9. (a) The vapour pressure of A is 939·4 mm. Hg and that of B is 495·8 mm Hg at 140ºC. Assuming that they form an ideal solution, what will be the composition of a mixture that boils at 140ºC under 1 atm? What will be the composition of the vapour at this temperature?

(b) Starting from Clapeyron equation, deduce the Clausius-Clapeyron equation, mentioning the necessary assumptions. 3+2

10. (a) Using the concept of chemical potential (μ), derive thermodynamically a relation between the osmotic pressure of a binary solution and its molar concentration. Mention the assumptions and approximations you use.

(b) A 0·1 molal solution of an organic acid in benzene depressed the freezing point of benzene by 0·26K. If the organic acid dimerises in benzene, then what is the degree of dimerization of the acids?

Given: K_f for benzene = 5·1 K kg mol^{-1} 3+2

11. (a) The slope of the solid-gas coexistence curve must be greater than that of the liquid-gas coexistence curve near the triple point of pressure vs. temperature phase diagram of water. Justify using necessary equation.

(b) Derive Nernst distribution law using the concept of chemical potential. 3+2

12. (a) For CCl_4, K_b=5·03, K kg mol^{-1} and K_f=31·8 K kg mol^{-1}. If 3·0 gm of a substance in 100 gm of CCl_4 raises the boiling point by 0·6K, calculate the depression of freezing point, the relative lowering of vapour pressure and the molar mass of the substance (given density of CCl_4=1·59 g cm^{-3} and molar mass is 153·823 g mol^{-1}).

(b) The lowering of chemical potential of a solvent in presence of a solute is an entropy effect.–Comment. 3+2

13. (a) Draw the phase diagram (T vs. mole % of B) of a system consisting of solids A and B forming a stable compound A_2B with congruent melting point. Show the different phases present in different regions of the diagram. State the degrees of freedom at eutectic point. [Given: m.p of A_2B > m.p of A > m.p of B.]

(b) Explain Konowaloff's rule. 3+2

Unit-II

Answer ***any two*** questions.

14. (a) Explain with S-T diagram, the principle of cooling by adiabatic demagnetisation of a paramagnetic substance.

(b) Assume the Debye Heat Capacity equation to be applicable, show that the entropy of a perfect solid at very low temperature should be equal to 1/3 C_P,where C_P is the heat capacity of solid at the given temperature. 3+2

15. The Boltzmann distribution may be represented by expressing the number of molecules (N_i) in the level ε_i (under isothermal condition) as N_i=A exp ($-b\varepsilon_i$), where A and b are constants.

Answer the following questions taking b=1/kT.

(a) Obtain an expression for A in terms of b and show that it is related to the partition function.

(b) Show that $N_{i+1} < N_i$ for any finite temperature with $\varepsilon_i < \varepsilon_{i+1}$. 3+2

16. (a) Derive Barometric distribution formula from Boltzmann energy distribution relation.

(b) In the neighbourhood of absolute zero, all processes should occur without any change in entropy. —Justify or criticized. 3+2

CHT–33c

Unit-I

Answer ***any three*** questions.

17. (a) What is primary kinetic salt effect? How will the rate constant of the reaction

$$S_2O_8^{2-}+I^- \rightarrow \text{product}$$

be influenced by the addition of KCl in the reaction mixture?

(b) Draw potential energy diagrams showing the various possibilities of photodissociation of a diatomic molecule. 3+2

Please Turn Over

18. (a) Radiation of wavelength 2540 Å was passed through a cell containing 10 ml of a solution of 0·0495(M) oxalic acid and 0·01(M) uranyl sulphate; after the absorption of $8{\cdot}81\times10^8$ ergs radiation, the concentration of oxalic acid was reduced to 0·0383(M). Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.

(b) State Frank-Condon principle. State its significance. 3+2

19. (a) "Unimolecular reactions are not always first order."— Justify the statement using Lindemann's mechanism.

(b) What do you mean by 'photostationary state'? State with reason whether it is a steady state or an equilibrium state. 3+2

20. (a) At 460 nm, a blue filter transmits 72·2% of the light and a yellow filter 40·7% of the light. What is the transmittance, at the same wavelength, of two filters in combination?

(b) State and explain the Stark-Einstein law of photochemical equivalance. 3+2

21. (a) What is entropy of activation? State under what condition it can be negative.

(b) Why was the 'Steric factor' introduced in the collision theory of reaction rate? 3+2

Unit-II

Answer ***any two*** questions.

22. (a) Discuss the effect of anharmonicity on the vibrational spectra of a heteronuclear diatomic molecule.

(b) The rotational specturm of $^{79}Br^{19}F$ shows a series of equidistant lines 0·71433 cm^{-1} apart. Calculate the bond length of the molecule. 3+2

23. (a) The total relative population at an rotational energy, E_j of a rigid diatomic molecule is:

Populaton $\propto$ (2J+1) exp $(-E_j/kT)$

Show that the population is a maximum at the nearest integral J value to

$$J=\sqrt{kT/2hcB}-\tfrac{1}{2}$$

(Terms have their usual meaning.)

(b) A linear molecule has the formula AB_2. Discuss how would you ascertain whether the molecule has the structure BAB as ABB, using Raman and IR spectra together. 3+2

24. (a) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centered at 1876·6 cm^{-1} and 3724·20 cm^{-1} respectively. Calculate the zero point energy of the molecule.

(b) A microwave spectrophotometer capable of operating only between 60 and 90 cm^{-1}, was used to observe the rotational spectra of HI. Absorptions were measured as follows for three successive lines: 64·276, 77·130 and 89·985 cm^{-1} respectively. Determine the J values between which transitions occur between 60 and 90 cm^{-1}. 3+2