

# Semester-I Model Question

## Model Questions For Semester-III B.Sc Chemistry Honours

### (Physical Chemistry)

- 1) What is meant by ionic mobility? State (without derivation) its relationship with the ion conductance.
- 2) If the resistance of a 0.1N aqueous solution of KCl is measured in different conductivity cells, will the values of the conductances, specific conductance, and equivalent conductance be different? Give reasons for your answer.
- 3) Depict with explanation the nature of the conductometric curves i) sodium hydroxide with  $\text{H}_2\text{SO}_4$  as titrant and ii)  $\text{H}_2\text{SO}_4$  with  $\text{BaCl}_2$  as titrant.
- 4) The specific conductance of a saturated solution of AgBr after subtracting that of the water is  $1.174 \times 10^{-7}$  mho/cm at  $25^\circ\text{C}$ . The ionic mobilities of  $\text{Ag}^+$  and  $\text{Br}^-$  ions at infinite dilution are  $6.4 \times 10^{-4}$  and  $8.1 \times 10^{-4}$   $\text{cm}^2/\text{volt}/\text{cm}$  respectively. Calculate the solubility product of AgBr at  $25^\circ\text{C}$ .
- 5)  $\Lambda^0$  values decrease in the order  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$  — Explain.
- 6) Define transport number of an ion. Discuss the moving boundary method for the determination of transport number of an ion.
- 7) The mobility of  $\text{NH}_4^+$  ion is  $7.623 \times 10^{-3}$   $\text{m}^2/\text{VS}$ .  
Calculate i) the velocity of the ion if 15.0 volts are applied across electrodes 25 cms apart.  
ii) the transport number of the ion in  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solution if the mobility of the  $\text{C}_2\text{H}_3\text{O}_2^-$  ion is  $4.239 \times 10^{-3}$   $\text{m}^2/\text{VS}$ .
- 8) You are supplied with a solution containing HCl and  $\text{H}_2\text{SO}_4$ . How would you estimate each using conductometric titrations. (Give the curves)
- 9) How does the activity coefficient of an ion vary with its concentration? Discuss in the light of Debye-Huckel limiting law.
- 10) What is meant by ionic mobility? State its relationship with ion conductance.
- 11) If the resistance of 0.1N aqueous KCl solution is measured in different conductivity cells with different cell constant, will the values of conductance, specific conductance and equivalent conductance differ? Give reasons for your answer.
- 12) Depict with brief explanation the nature of the conductometric titration curve of i) sodium hydroxide with sulphuric acid as titrant and ii) Sulphuric acid with barium chloride as titrant.
- 13) Explain the statement 'the degree of dissociation' of a weak electrolyte increases with a decrease in concentration and approaches 1 as  $c \rightarrow 0$ .

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- 14) Calculate the ionic strength of a solution containing 50 ml of 0.2 N BaCl<sub>2</sub>, 25 ml of 0.4 N K<sub>4</sub>[Fe(CN)<sub>6</sub>] and 25 ml of 0.4 N NaCl assuming no interaction between the ions and complete dissociation of the electrolytes.
- 15) Define transference number of an ion. Discuss the principle of its determination by moving boundary method.
- 16) Justify or otherwise the following statement:  
Although the size of lithium, sodium, and potassium ions in the order  $r_{Li^+} < r_{Na^+} < r_{K^+}$ , their transference numbers in their chlorides of same concentration follow the order  $t_{Li^+} < t_{Na^+} < t_{K^+}$  at a definite temperature. Ion conductance increases with temperature.
- 17) Define specific conductance of an electrolyte solution. How does it vary with dilution and temperature? 3
- d) What factors can influence the speed of an ion in solution? What is ionic-mobility? Find its unit in SI system.
- 18) The molar conductance of 0.01(M) CH<sub>3</sub>COOH (aq) at 298 K was measured as  $\Lambda_m = 1.65 \text{ mSm}^2/\text{mol}$ . Determine the degree of ionization and  $P_{K_a}$  of the acid at 298 K. Given limiting molar conductance of CH<sub>3</sub>COOH (aq) at 298 K is  $39.05 \text{ mS m}^2/\text{mol}$ .
- 19) Sketch the graph of the conductometric titration of AgNO<sub>3</sub> solution with KCl solution. Explain the nature of the graph.
- 20) In a conductometric titration, what precaution will you adopt? State with reason.
- 21) Define transference number. Obtain a relation between the transference and ion conductance of an electrolyte.
- 22) Describe the Hittorf's method of determination of transference number of AgNO<sub>3</sub>.
- 23) Explain: i) H<sup>+</sup> and OH<sup>-</sup> ions have very large ion conductance in water ii) the ion conductance of lithium ion is less than that of potassium ion.
- 24) Calculate the ionic strength of a solution obtained by mixing aqueous solutions of 20 ml of 0.01 (M) NaCl and 20ml of 0.02(M) Na<sub>2</sub>SO<sub>4</sub> solution.
- 25) Explain the variation of solubility and concentration solubility product of AgCl at a given temperature in i) 0.1(N) AgNO<sub>3</sub> and ii) 0.1(N) KNO<sub>3</sub> solution
- 26) Depict with brief explanation, the conductometric titration curve of acetic acid by NaOH as titrant. 3
- 27) Define equivalent conductance and molar conductance. Establish the relation between specific conductance and equivalent conductance.
- 28) The resistance of a conductivity cell when filled with 0.02M KCl solution is 164 ohm at 298K. however, when filled with 0.05 M AgNO<sub>3</sub> solution the resistance is found to be 78.5 ohm. Its specific conductance of 0.02 M KCl solution is  $2.76 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$   
Calculate —
- i) The conductance of 0.05M Ag NO<sub>3</sub> solution.

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- ii) The molar Conductance of  $\text{AgNO}_3$  solution.
- 29) Discuss the effect of concentration on transference number.
- 30) The molar ionic conductance at infinite dilution for  $\text{H}^+$  and  $\text{OH}^-$  are 349.8 and 196.7  $\text{ohm}^{-1} \text{cm}^2$ . Assuming that molar conductance differ very slightly from conductance at infinite dilution; calculate the ionic product of water at  $25^\circ\text{C}$ .
- 31) The equivalent conductances of 0.001 N, *KCl*, *NaCl* and  $\text{Na}_2\text{SO}_4$  are 149.9, 126.5 and 153.3 respectively. Calculate an approximate value for the equivalent conductance of  $\text{Na}_2\text{SO}_4$  of the same concentration. 3
- 32) What is the effect of dilution on equivalent conductance of electrolytes?
33. (a) Distinguish between a metallic and an electrolytic conductor.
- 34) Give the experimental observation which led Kohlrausch to propose the law of independent migration of ions.
- 35) 'Equivalent conductances of both strong and weak electrolytes increase with dilution, but the reasons are different: Explain.
- 36) Write down the form of the Debye-Huckel limiting law explaining the terms involved. Calculate the mean ionic activity coefficient of a 0.015(A) aqueous solution of magnesium chloride at 300 K using Debye-Huckel limiting law. [ $A = 0.51$  for water at 300 K]. 4
- 37) At 290 K the mobility at infinite dilution of the ammonium ion is  $7.6 \times 10^{-4}$  while that of the chloride ion is  $7.9 \times 10^{-4} \text{cm}^2 \text{volt}^{-1} \text{sec}^{-1}$ . Calculate  $\Lambda^0$  of ammonium chloride and transport number of the two ions. 4
- 38) Calculate the ionic strength of 0.01M  $\text{MgCl}_2$  in water. 1
- 39) State the Kohlrausch's Law of Independent migration of ions. What is its utility? 2
- 40) Define equivalent conductance. Discuss how the equivalent conductance ( $\lambda$ ) of a strong electrolyte varies with its concentrations. 1+ 3
- 41) Define the mean ionic activity coefficient of an electrolyte. Calculate the mean ionic activity coefficient of a 2:1 electrolyte at a molarity of 0.002M in aqueous solution at  $25^\circ\text{C}$ . ( $A = 0.509$ )
- 42) Show schematically the variation of equivalent conductance of a weak electrolyte with concentration. Briefly discuss the principle of determination of equivalent conductance at infinite dilution of a weak electrolyte. 4
- 43) A moving boundary experiment is done to measure the transference number ( $t_+$ ) of  $\text{Li}^+$  in 0.01 mol/L  $\text{LiCl}$  in a tube having a cross-sectional area of  $0.125 \text{cm}^2$ , the boundary moves 7.3 cm in 1490s using a current of  $1.8 \times 10^{-3}\text{A}$ . Calculate  $t_+$ .
- 44) What is 'Ultraviolet' Catastrophe' associated with black-body radiation? What is the conceptual breakthrough associated with successful formulation for explaining spectral energy distribution curve for black body radiation?

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- 45) What is photoelectric effect? How did Einstein explain the effect on the basis of quantum theory. Find out the longest wavelength of light just able to eject a least bound photoelectron from a metal with work function 4.3 eV [  $1\text{eV} = 1.602 \times 10^{-19}\text{J}$  ]
- 46) What do you understand by eigen-functions and eigenvalues in quantum mechanics? Show that  $\psi = A \exp \{-x^2/2\}$  is an eigen function of the operator  $H = -d^2/dx^2 + x^2$  and find its eigenvalue.
- 47) What information do you get from the statement that operators  $\hat{A}$  and  $\hat{B}$  commute?
- 48) Evaluate the commutator  $[\hat{x}, \hat{p}_x^2]$
- 49) What are the degeneracies of the first two energy levels for a free particle confined in a 3-dimensional box with  $a = b = 1.5c$ ? ( $a$ ,  $b$ , &  $c$  are dimensions of the box).
50. (a) Draw a plot of KE of photo electron vs frequency of the incident radiation in a photoelectric experiment. What inference regarding physical quantities may be drawn from the equation of such plot?
- (b) State and explain Wien displacement law. At what wavelength does the maximum in the energy density distribution function for a black -body occurs if (i)  $T = 300\text{ K}$ ? and (ii)  $T = 500\text{ K}$ .
- (c) What is the essential condition for a function to be eigen function ? Show that linear combination of any two eigen functions is an eigen function.
- (d) Is linear momentum operator a linear one? Answer with reason(s).
51. (a) Calculate the wavelength of an electron ( $m_e = 9.1 \times 10^{-31}\text{ kg}$ ) having energy equal to 100 eV. ( $1\text{eV} = 1.602 \times 10^{-19}\text{J}$ ).
- (b) Calculate the average linear momentum,  $\langle p_x \rangle$  for a free particle in the  $n$ th quantum state of a one- dimensional box.
- 52) The energy eigen function for a particle confined to move in one dimensional box of length  $L$  is given by.  $\Psi_n = A \sin(n\pi x/L)$  (symbols have usual significance)
- (i) Find  $A$  (ii) Calculate  $\langle x \rangle$ , the average value of  $x$ ; (iii) Draw schematically the curves showing the variation of  $\Psi_n$  and  $|\Psi_n|^2$  for  $n = 1$  and  $n = 2$ , Where is the particle most likely to be found when  $n = 1$ ?
- (53) Draw plots of kinetic energy for the ejected photoelectrons versus frequency of 'the incident radiation in a photoelectric experiment with three different metals. What inference regarding physical quantities may be drawn from the equation of such plot?
- (54) Show that  $e^{ikx}$  and  $e^{-ikx}$  are the eigen functions of the x-directional linear momentum operator. What are the corresponding eigen values?
- 55) Write down Hamiltonian operator for the H-atom in 3-dimensions.