

B.SC. CHEMISTRY  
SIXTH SEMESTER  
PHYSICAL CHEMISTRY IV  
BSC – 601  
[USE OMR FOR OBJECTIVE PART]

2025/05

**SET  
A**

Duration: 3 hrs.

Full Marks: 70

Time: 30 min.

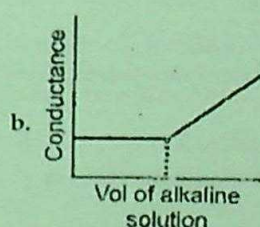
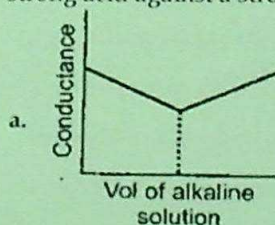
( Objective )

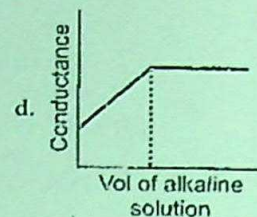
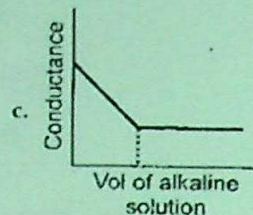
Marks: 20

1×20=20

*Choose the correct answer from the following:*

- For a first-order reaction, the plot of  $\log [A]$  vs. time is:
  - Linear with negative slope
  - Linear with positive slope
  - Parabolic
  - Exponential
- The Arrhenius equation relates the rate constant to:
  - Pressure
  - Activation energy
  - Volume
  - Molecular weight
- In the reaction  $A + B \rightarrow C$ , doubling the concentration of A doubles the rate, but doubling B quadruples the rate. The overall order is:
  - 1
  - 2
  - 3
  - 0
- In a pseudo-first-order reaction:
  - All reactants are in equal concentration
  - Product decomposes
  - Catalyst is used
  - One reactant is in large excess
- The graphical representation of a second-order reaction is linear for:
  - $[A]$  vs. time
  - $\log [A]$  vs. time
  - $1/[A]$  vs. time
  - $t^{1/2}$  vs.  $[A]$
- Which of the following plots will be obtained from a conductometric titration of a strong acid against a strong base?





7. Which of the following equality holds for Debye-Huckel-Onsagar equation?
- $\Lambda_m = \Lambda_m^0$  as  $c = 0$
  - $\Lambda_m = \Lambda_m^0$  as  $c = \infty$
  - $\Lambda_m = \Lambda_m^0$  as  $c = 1$
  - $\Lambda_m = \Lambda_m^0$  as  $c = \Lambda$
8. What is the ionic strength of an 1M solution of  $\text{Na}_3\text{PO}_4$ ?
- 1
  - 3
  - 6
  - 12
9.  $\Lambda_m^0(\text{NH}_4\text{OH})$  is equal to
- $\Lambda_m^0(\text{NH}_4\text{OH}) + \Lambda_m^0(\text{NH}_4\text{Cl}) - \Lambda_m^0(\text{HCl})$
  - $\Lambda_m^0(\text{NH}_4\text{Cl}) + \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaOH})$
  - $\Lambda_m^0(\text{NH}_4\text{Cl}) + \Lambda_m^0(\text{NaOH}) - \Lambda_m^0(\text{NaCl})$
  - $\Lambda_m^0(\text{NaOH}) + \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NH}_4\text{Cl})$
10. The degree of freedom at triple point in the phase diagram of single component water system is
- 0
  - 1
  - 2
  - 3
11. The decomposition of  $\text{CaCO}_3$  in a closed vessel is represented by the following equation  
 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$   
 The number of phases, component and degree of freedom respectively are
- 2, 2, 2
  - 2, 3, 1
  - 2, 2, 1
  - 3, 2, 1
12. The degrees of freedom (F) for the eutectic point is
- 0
  - 1
  - 2
  - 3
13. Gibbs phase rule is, when no chemical reaction occurs
- $F - C + P = 2$
  - $F + C + P = 2$
  - $F + C - P = 2$
  - $F - C - P = 2$
14. The reduced phase rule equation for a two component system is
- $F = 4 - P$
  - $F = 3 - P$
  - $F = 5 - P$
  - $F = 2 - P$
15. The unit of specific conductance is
- $\text{Sm}$
  - $\text{Sm}^{-1}$
  - $\text{S}^{-1}\text{m}$
  - $\Omega^{-1}$
16. The electrochemical cell potential (E) after reactant and product reach equilibrium is (EO is standard cell potential and n is number of electron involved)
- $E = E^0 + nF/RT$
  - $E = E^0 - RT/nF$
  - $E = E^0$
  - $E = 0$

17. The negative sign in the expression  $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$  means
- Zn is more reactive than hydrogen
  - Zn is less reactive than hydrogen
  - Zn will get reduced and  $\text{H}^+$  will get oxidised
  - No information can be obtained as mentioned above
18. EMF is measured in
- Volt
  - Volt. Coulomb
  - Coulomb
  - Joule
19. Consider an electrolyte  $\text{M}_x\text{A}_y$  ionising as  $\text{M}_x\text{A}_y \rightleftharpoons x\text{M}^+ + y\text{A}^-$  the activity,  $a$  of the electrolyte is
- $a = (a_i)^{x+y}$
  - $a = (a_i)^{x \cdot y}$
  - $a = (a_i)^{x/y}$
  - None of the above
20. A fuel cells convert
- It converts electrical energy to chemical energy
  - It converts chemical energy to Electrical energy
  - (a) & (b) are true
  - None of the above

### **Descriptive**

Time : 2 hrs. 30 min.

Marks : 50

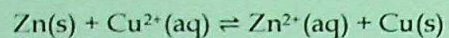
*[ Answer question no.1 & any four (4) from the rest ]*

- A 1<sup>st</sup> order reaction is 50% completed in 20 mins at 27 °C and in 5 mins at 47 °C. The energy of activation of the reaction is? 3+3+2+2=10
  - For the strong electrolytes, NaOH, NaCl and  $\text{BaCl}_2$ , the molar ionic conductances at infinite dilution are  $248.1 \times 10^{-4}$ ,  $126.5 \times 10^{-4}$  and  $280.0 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$  respectively. Calculate  $\Lambda_m^0$  for  $\text{Ba(OH)}_2$ .
  - Explain why KCl-NaCl- $\text{H}_2\text{O}$  system should be regarded as a 3-component system whereas KCl-NaBr- $\text{H}_2\text{O}$  system should be regarded as a 4-component system?
  - What is a galvanic cell? Write its applications.

2. a. Show how the half-life of a 1st order reaction varies with temperature. 2+3+2+  
3=10
- b. For the opposing reaction  $B+C \rightleftharpoons D+E$  ( $k_1$  and  $k_2$  is the rate constants for the forward and backward reaction). The forward reaction has  $E_a = 100 \text{ KJmol}^{-1}$  and  $A = 1.0 \times 10^{10} \text{ M}^{-1}\text{S}^{-1}$ . The equilibrium concentration of A, B, C & D are 1.0, 2.0, 5.0, 4.0 M respectively at 700 K. find  $k_1$  and  $k_2$  at this temperature.
- c. In a 1<sup>st</sup> order reaction, if time taken for completion of 50% of reaction in 't' second, find the time required for the completion of 99.9% of the reaction.
- d. For a reaction with  $E_a$  of  $49.8 \text{ KJmol}^{-1}$ , find the ratio of rate constants at 600 K and 300 K.
3. a. For the reaction scheme  $A+B \rightleftharpoons C$  ( $k_1$  and  $k_2$  is the rate constants for the forward and backward reaction), and  $B+C \rightarrow D$  ( $k_3$  is the rate constant). Find the rate of formation. 2+3+2+  
3=10
- b. The specific rate constant of decomposition of a compound is represented by  $\ln k = 5.0 - 12000/T$ . The  $E_a$  of decomposition for this compound at 300 K is?
- c. For a parallel 1<sup>st</sup> order reaction where, X gives Y and Z simultaneously. The ratio of the concentration of  $[Y]/[Z] = 1/4$ . Find  $k_2$ , if  $k_1 = 1 \times 10^{-4} \text{ S}^{-1}$ .
- d. Write three postulates of Lindeman's theory. Write the rate expression and draw the graph when the pressure is very high.
4. a. Explain the application of conductance measurement for the determination of solubility and solubility product of a sparingly soluble salt. 3+2+3+  
2=10
- b. Calculate mean ionic activity coefficient  $\gamma_{\pm}$  of  $\text{Na}_2\text{SO}_4$  at a molality of 0.001 in aqueous solution at 25 °C.
- c. A potential of 12.0 volts was applied to two electrodes placed 20 cm apart. A dilute solution of ammonium chloride was placed between the electrodes when  $\text{NH}_4^+$  ion was found to cover a distance of 1.60 cm in one hour. What is the mobility of  $\text{NH}_4^+$  ion?
- d. The resistance of a 0.5 M solution of an electrolyte in a cell was found to be  $45 \Omega$ . Calculate the specific conductance of the solution if the electrodes in the cell are 2.2 cm apart and have an area of  $3.8 \text{ cm}^2$ .

5. a. Sketch the general phase diagram for a two component system that are not miscible in the solid state and form a eutectic mixture. Explain it. 3+3+4  
=10
- b. The vapor pressure of water at 95 °C is found to be 634 mm. what would be the vapor pressure at a temperature of 100 °C ? The molar heat of vaporization in this range of temperature is 40593 J mol<sup>-1</sup>.
- c. Draw the triangular plot for the three component system consisting water-chloroform-acetic acid. Explain briefly.
6. a. What do you mean by congruent and incongruent melting point? 2+2+2+  
4=10
- b. What do you mean by phase and component of a system?
- c. Explain the variation of molar conductivity with dilution for strong electrolyte.
- d. Calculate the solubility product of the sparingly soluble salt CaF<sub>2</sub> from the following data:  
The molar ionic conductances (at infinite dilution) of Ca<sup>2+</sup> and F<sup>-</sup> ions are  $104 \times 10^{-4}$  and  $48 \times 10^{-4}$  Sm<sup>2</sup>mol<sup>-1</sup> respectively. The specific conductance of the saturated solution of CaF<sub>2</sub> at room temperature is  $4.25 \times 10^{-3}$  Sm<sup>-1</sup> and for water it is  $2 \times 10^{-4}$  Sm<sup>-1</sup>.
7. a. Write the half reactions and redox reactions for the Daniell cell where Zinc and Copper are used. 2+3+3+  
2=10
- b. Derive the Nernst Equation in the following form  
$$E = \frac{2.303RT}{nF} (\log K - \log Q)$$
- c. Derive the following equation which gives the effect of concentration of reactants and products involved in the cell reaction on the EMF of the cell  
$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{(C)^x (D)^d}{(A)^a (B)^b}$$

d. The standard cell potential for the reaction is



is +1.10 volt. Calculate the Gibbs free energy change during the reaction.

( $F = 96500 \text{ coulomb.mol}^{-1}$ )

8. a. Write the Faraday's laws of electrolysis?

1+2+2+  
2+3=10

b. What is a concentration cell? Write the applications.

c. Write about the Concentration cells with transference and without transference?

d. What is Conductometric Titration? Write the importance of this method?

e. What is the basis of Electrochemical Series? Explain its importance in electrochemistry.

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