B. Sc. CHEMISTRY
FOURTH SEMESTER
PHYSICAL CHEMISTRY IV
BSC – 403
(Use Separate Answer Scripts for Objective & Descriptive)

Duration: 3 hrs.   Full Marks: 70

(PART-A: Objective)

Time: 30 min.   Marks: 20

Choose the correct answer from the following: **1X20=20**

1. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called _____.
   - a. Cell potential
   - b. Cell emf
   - c. Potential difference
   - d. Cell voltage

2. Which of the following statement is not correct about an inert electrode in a cell?
   - a. It does not participate in the cell reaction
   - b. It provides surface either for oxidation or for reduction reaction.
   - c. It provides surface for conduction of electrons
   - d. It provides surface for redox reaction.

3. For the given cell, $Mg\,|\,Mg^{2+}\,||\,Cu^{2+}\,|\,Cu$ (i) (ii)
   - a. Mg is cathode
   - b. Cu is cathode
   - c. Cu is the oxidising agent
   - d. None of the above

4. EMF is measured in
   - a. Volt
   - b. Volt. Coulomb
   - c. Coulomb
   - d. Joule

5. In an **electrolytic** cell the electrode at which the electrons enter the solution is called the _____; the chemical change that occurs at this electrode is called _____.
   - a. Anode, oxidation
   - b. Anode, reduction
   - c. Cathode, oxidation
   - d. Cathode, reduction

6. Which of the following is a weak electrolyte?
   - a. CH_3COOH
   - b. NaOH
   - c. KCl
   - d. H_2SO_4

7. The unit of specific conductance is
   - a. ohm cm
   - b. $ohm^{-1}\,cm^{-1}$
   - c. $ohm\,cm^{-1}$
   - d. $ohm^{-1}\,cm$

8. The degree of dissociation of an electrolyte is
   - a. Λ^0_m/Λ_m
   - b. $\Lambda_m - \Lambda^0_m$
   - c. Λ_m/Λ^0_m
   - d. $\Lambda^0_m - \Lambda_m$

9. If v_+ and v_- respectively be the speed of cation and anion then the transport numbers of cation is
   a. $v_-/(v_+ - v_-)$
   b. $v_-/(v_+ + v_-)$
   c. $v_+/(v_+ - v_-)$
   d. $v_+/(v_+ + v_-)$

10. The unit of cell constant is
    a. m^{-1}
    b. m
    c. S m
    d. S m^{-1}

11. Which one is not part of distortion polarizability?
    a. Atomic polarizability
    b. Electronic polarizability
    c. Orrientational polarizability
    d. All of them

12. Unit of polarizability is
    a. $J^{-1} C^{-1} m^2$
    b. $J^{-1} C^2 m^2$
    c. $J^{-1} C m^2$
    d. $J^{-1} C m^{-2}$

13. For which of the following molecules Maxwell relation will hold?
    a. Benzene
    b. Water
    c. Carbon tetrachloride
    d. Carbon dioxide

14. Quantum theory of diamagnetism and paramagnetism was formulated by
    a. Langevin
    b. Debye
    c. Maxwell
    d. van Vleck

15. Neel temperature is related to
    a. Ferromagnetism
    b. Anti-ferromagnetism
    c. Diamagnetism
    d. Paramagnetism

16. The activity 'a' is related to the activity coefficient 'γ' by the equation
    a. $a=m/\gamma$
    b. $\gamma=a-m$
    c. $a=m+\gamma$
    d. $a=m\gamma$

17. In quinhydron electrode there is equimolar mixture of
    a. Quinone and quinoline
    b. Quinone and quinoid
    c. Quinone and hydroquinone
    d. Hydroquinone and sodium hydroxide

18. Which of the following electrodes is not used to measure pH of a solution?
    a. Glass electrode
    b. Quinhydrone electrode
    c. Hydrogen gas electrode
    d. Standard Hydrogen electrode

19. pH of the acid solution using quinhydrone electrode is calculated using the formula, pH =
    a. $pH = \dfrac{(0.457 - E_{quin})}{0.05916}$
    b. $pH = \dfrac{(0.457 - E_{cell})}{0.05916}$
    c. $pH = \dfrac{(0.457 - E_{ref})}{0.05916}$
    d. None of the above

20. The standard electrode potential of calomel electrode is
    a. 0.242 V
    b. 0.771 V
    c. 0.699 V
    d. 0.457 V

Time : 2 hrs. 40 min.   Marks : 50

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

1. a. What do you mean by liquid junction potential? How EMF measurement is   5+5=10
       useful in the determination of activity coefficient of electrolyte?

    b. What are concentration cells? Derive expressions for the EMFs of
       concentration cell without transference.

2. a. What are the different types of electrochemical cells?   2+5+3
                                                                                  =10
    b. Derive the equation

$$E = \frac{0.0591}{n} \left(\log K - \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

    c. A zinc rod is placed in 0.1M solution of Zinc sulphate at 25°C. Assuming that
       the salt is dissociated to the extent of 95 percent at this dilution, calculate the
       potential of the electrode at this temperature? E^o (Zn^{2+}, Zn) = - 0.76V.

3. a. What is electrode potential? Write the conditions of Standard electrode   4+2+4
       potential?   =10

    b. Write the relation of electrical energy and free energy change of a cell
       reaction.

    c. For the Daniel cell involving the cell reaction
       Zn(s) + Cu^{2+}(aq) $\rightleftharpoons$ Zn^{2+}(aq) + Cu(s)
       The standard free energies of formation of Zn(s), Cu(s), Cu^{2+}(aq) and Zn^{2+}(aq)
       are 0, 0, 64.4 kJ mole⁻¹ and   -154.0 kJ/ mole⁻¹ respectively.
       Calculate the standard EMF of the cell?

4. a. Discuss Arrhenius theory of electrolytic dissociation. What are the   5+3+2
       limitations of the said theory?   =10

    b. Define specific conductivity and equivalent conductivity. Deduce the
       relation between them.

    c. Find the expression for molar ionic conductance at infinite dilution in terms
       of limiting ionic mobility.

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5. a. Explain the mechanism of high mobility H^+ ions. Mention the factors on which conductance of an ion depend.   5+2+3 =10

    b. Explain what do you mean by Debye-Fakenhagen effect.

    c. State and explain Walden's rule.

6. a. Why Clausius-Mosotti equation is not obeyed by polar molecules. How Debye improved upon that?   4+2+4 =10

    b. Using Maxwell's relation and Clausius-Mosotti equation derive Lorentz-Lorenz equation.

    c. If μ is dipole moment of mono substituted benzene then derive expressions for 1,2- and 1,3- disubstituted benzene. Use these expressions to find dipole moments of ortho, meta and para dichloro benzene given dipole moment of chloro benzene is 1.69 D.

7. a. Discuss molecular interpretation of paramagnetism.   3+4+3 =10

    b. At 25^0C, a coordinate compound (M = 200 g/mol) has density equal to 3.24 g cm^{-3}. If it contains three unpaired electrons, calculate the molar magnetic susceptibility and the magnetic susceptibility.

    c. Describe ferromagnetism and anti-ferromagnetism.

8. a. Describe briefly various types of electrodes which can be used for determining pH of a solution.   6+4=10

    b. Discuss the potentiometric titration of acid-base and precipitation.

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