

**B.Sc. CHEMISTRY
FOURTH SEMESTER
PHYSICAL CHEMISTRY IV
BSC – 403
[USE OMR FOR OBJECTIVE PART]**

**SET
A**

Duration: 3 hrs.

Full Marks: 70

Time: 30 min.

Marks: 20

(Objective)

1X20=20

Choose the correct answer from the following:

- Which of the following is correct for the electrolyte KCl?
 - $t_+ = t_-$
 - $t_+ > t_-$
 - $t_+ < t_-$
 - None of these
- For an electrolyte solution, the ratio a/m is called _____
 - Activity
 - Activity coefficient
 - Ionic strength
 - Molality
- The standard electrode potential of hydrogen electrode is
 - 0.242 V
 - 0.0 V
 - 0.771 V
 - 0.699 V
- The EMF of the concentration cell with transference is given by
 - $E = \frac{RT}{F} \ln \frac{a_2}{a_1}$
 - $E = t_- \frac{RT}{F} \ln \frac{a_2}{a_1}$
 - $E = \frac{RT}{F} \ln a_1 a_2$
 - $E = t_+ \frac{RT}{F} \ln a_1 a_2$
- If $t_+ = t_-$ then the liquid junction potential will be
 - $\frac{RT}{F}$
 - $\frac{a_2}{a_1}$
 - 0.0
 - $\ln \left(\frac{a_2}{a_1} \right)$
- Among benzene derivatives, which di-substituted benzene derivative has maximum dipole moment if both the substituted groups are same?
 - o- Isomer
 - p- isomer
 - m- isomer
 - Benzene
- C.G.S unit of dipole moment is
 - $\text{e.s.u} \times \text{cm}^{-1}$
 - $\text{e.s.u}^{-1} \times \text{cm}^{-1}$
 - $\text{e.s.u} \times \text{cm}$
 - $\text{e.s.u}^{-1} \times \text{cm}$
- Which of the following is a property of a diamagnetic material
 - It gets weakly magnetized in the direction opposite to an applied magnetic field
 - It can retain magnetism when the external field is removed
 - It exhibits an attractive effect when placed in a magnetic field
 - It shows strong attraction to magnets

9. Which of the following is not a property of a paramagnetic material
- It gets weakly magnetized in the direction opposite to an applied magnetic field
 - It does not retain magnetism when the external field is removed
 - It exhibits an attractive effect when placed in a magnetic field
 - It shows strong attraction to magnets
10. For a diamagnetic substance, the value of magnetic susceptibility is----
- Positive
 - Zero
 - Negative
 - All of these
11. The unit of cell constant is
- m^{-1}
 - m
 - S m
 - $S m^{-1}$
12. If v_+ and v_- respectively be the speed of cation and anion, the transport number of the anion is
- $v_+ / (v_+ + v_-)$
 - $v_- / (v_+ + v_-)$
 - $v_- / (v_+ - v_-)$
 - $v_+ / (v_+ - v_-)$
13. Kohlrausch law can be expressed as
- $\Lambda_m^\circ = \lambda_+^\circ - \lambda_-^\circ$
 - $\Lambda_m^\circ = \lambda_-^\circ - \lambda_+^\circ$
 - $\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$
 - $\Lambda_m^\circ = \lambda_+^\circ \lambda_-^\circ$
14. The unit of specific conductance is
- $M S^{-1} V^{-1}$
 - $M^{-1} S^{-1} V$
 - $M^2 S^{-2} V^{-1}$
 - $M^2 S^{-1} V^{-1}$
15. The degree of dissociation (α) is equal to
- $\Lambda_m / \Lambda_m^\circ$
 - $\Lambda_m^\circ / \Lambda_m$
 - $\Lambda_m - \Lambda_m^\circ$
 - $\Lambda_m + \Lambda_m^\circ$
16. The standard cell potential for the reaction is
- $$\text{Zn (s)} + \text{Cu}^{2+} (\text{aq}) \rightleftharpoons \text{Zn}^{2+} (\text{aq}) + \text{Cu (s)}$$
- is +1.10 volt. The Gibbs free energy change during the reaction is
($F = 96500 \text{ coulomb.mol}^{-1}$)
- $-21.2 \text{ k j mol}^{-1}$
 - $+ 212 \text{ k j mol}^{-1}$
 - $-212 \text{ k j mol}^{-1}$
 - -212 j mol^{-1}
17. The electrochemical cell potential (E) after reactant and product reach equilibrium is
(E° is standard cell potential and n is number of electron involved)
- $E = E^\circ + nF/RT$
 - $E = E^\circ - RT/nF$
 - $E = E^\circ$
 - $E = 0$

18. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that

- (i) This redox couple is a stronger reducing agent than the H^+/H_2 couple.
- (ii) This redox couple is a stronger oxidising agent than H^+/H_2 .
- (iii) Cu can displace H_2 from acid.
- (iv) Cu cannot displace H_2 from acid.

- a. (ii) and (iv) are correct option
- b. (ii) and (iii) are correct option
- c. (iii) and (iv) are correct option
- d. All are correct

19. In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

Assertion: Current stops flowing when $E_{\text{cell}} = 0$.

Reason: Equilibrium of the cell reaction is attained.

- a. Both assertion and reason are true and the reason is the correct explanation of assertion
- b. Both assertion and reason are true and the reason is not the correct explanation of assertion
- c. Assertion is true but the reason is false.
- d. Both assertion and reason are false

20. Find the incorrect relations

- a. $E = \frac{0.0591}{n} (\log K - \log \frac{[\text{C}][\text{D}]^d}{[\text{A}]^a [\text{B}]^b})$
- b. $E = E^\circ - (2.303 nF/RT) \log Q$
- c. $E = E^\circ - (RT/nF) \ln Q$
- d. None of the above

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(Descriptive)

Time : 2 hrs. 30 mins.

Marks : 50

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

- a. Calculate the liquid junction potential associated with the following cell 3+3+1+
1+2=10
- $\text{Ag(s), AgCl(s), HCl}(m_1 = 1.0, \gamma_1 = 0.809) : \text{HCl}(m_2 = 0.05, \gamma_2 = 0.830), \text{AgCl(s), Ag(s)}$
- If the transference number of H^+ is 0.83.
- b. What is the Clausius-Mossotti equation, and what is its significance in describing the polarization behavior of a material?
- c. Under what condition is $E_{\text{cell}} = 0$ and $\Delta G = 0$?
- d. What does the negative sign in the expression $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$ mean?
- e. What are the conditions of standard electrode potential?
1. a. 20 ml of 0.1M HCl solution is being titrated against 0.1M solution of NaOH using a hydrogen electrode as the indicator electrode and a saturated calomel electrode as the reference electrode. What would be the EMF of the cell initially and after the addition of 5.0, 10.0, 19.9, 20.0 and 25 ml of NaOH solution. 5+5=10
- b. Discuss the potentiometric titration of redox reaction using suitable example.
2. a. Write two advantages of potentiometric titration. Explain determination of pH of a solution using glass electrode. How EMF measurement is useful in the determination of transport number? 7+3=10
- b. The index of refraction of a gas $\text{C}_n\text{H}_{2n+2}$ is found to be 1.00139 when the gas is at STP. Given the molar refraction as 1.1 and 0.90 $\text{cm}^3 \text{ mol}^{-1}$ for H and C, determine the formula for hydrocarbon?

- 1
- a. Estimate the dipole moment of CHCl_3 molecule. Given, $\mu_{\text{C-Cl}} = 1.47 \text{ D}$ with Cl as the negative end and $\mu_{\text{C-H}} = 0.4 \text{ D}$ with C as the negative end. ($\theta = 108.48^\circ$). 3+2.5+
2.5+2=
10
- b. The bond length between Na and Cl in NaCl molecule is given by 2.36 \AA and its dipole moment is 8.5 D , Calculate its % ionic character?
- c. Determine the shape of BF_3 and NH_3 with the help of dipole moment.
- d. Find the dipole moment of OH- bond in H_2O ? Given, dipole moment and bond angle in H_2O are 1.85 D and 105° respectively)
5. a. What is the Lorentz-Lorentz equation, and what role does it play in describing the refractive index of a material? 2+2+3+
3=10
- b. What is Curie temperature and Neil's temperature?
- c. Derive the relation: $E = -\Delta H/nF + T \left(\frac{\partial E}{\partial T}\right)_P$
- d. For the Daniel cell involving the cell reaction
- $$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$$
- The standard free energies of formation of Zn(s) , Cu(s) , $\text{Cu}^{2+}(\text{aq})$ and $\text{Zn}^{2+}(\text{aq})$ are 0 , 0 , $64.4 \text{ kJ mole}^{-1}$ and $-154.0 \text{ kJ/ mole}^{-1}$ respectively. Calculate the standard EMF of the cell?
6. a. Define equivalent conductance. How is it related with specific conductance? Discuss the variation of molar conductivity with concentration for (i) KCl and (ii) CH_3COOH in aqueous solution. 5+5=10
- b. Explain the mechanism of high mobility of H^+ ion. Mention the factors on which conductance of an ion depend.

7. a. Define degree of ionization. How can you measure the degree of ionization and ionization constant for acetic acid from conductance measurement? 5+5=10
- b. Resistance of a conductivity cell filled with 0.1 mol L⁻¹ KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.2 mol L⁻¹ KCl solution is 520 Ω, find the conductivity and molar conductivity of 0.02 mol L⁻¹ KCl solution. The conductivity of 0.1 mol L⁻¹ solution is 1.29 S m⁻¹

8. a. What is EMF of a cell? Write its unit? 2+4+2+
2=10
- b. Derive the Nernst Equation

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

- c. What is an Electrochemical Series? Write the importance of the electrochemical series.
- d. 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° (Zn²⁺, Zn) = - 0.76V.

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