Electrochemistry and Redox Reactions

1. The molar conductivity of 0.1 M CH_3COOH is 5.2 S cm² mol⁻¹, and its limiting molar conductivity is 390.7 S cm² mol⁻¹. Calculate: a) The dissociation constant of CH_3COOH b) pH of the solution [Based on JEE Advanced 2019]

Solution:

- Degree of dissociation (α) = Λ□/Λ°□ = 5.2/390.7 = 0.0133
- For CH_3COOH, $K_a = C\alpha^2/(1-\alpha) = 0.1 \times (0.0133)^2/(1-0.0133) = 1.79 \times 10^{-5}$
- $pH = -\log[H^+] = -\log(C\alpha) = -\log(0.1 \times 0.0133) = 2.88$

2. For the cell reaction: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ Given $E°(Fe^{3+}/Fe^{2+}) = 0.77V$ and $E°(I_2/2I^-) = 0.54V$ Calculate the equilibrium constant at 298K. [Based on JEE Main 2020]

Solution:

- $E°cell = E°cathode - E°anode = 0.77 - 0.54 = 0.23V$
- At 298K: $\log K = nE°/0.0591$
- $\log K = (2 \times 0.23)/0.0591 = 7.78$
- $K = 6.03 \times 10^7$

3. In a hydrogen-oxygen fuel cell, hydrogen gas at 1 atm pressure and oxygen at 0.8 atm pressure are used at 298K. The cell operates at 80% efficiency compared to its theoretical maximum. Calculate: a) The theoretical maximum potential b) The actual operating potential [Given: $E°(O_2/H_2O) = 1.23V$]

Solution:

- For overall reaction: $2H_2 + O_2 \rightarrow 2H_2O$
- Using Nernst equation: $E = 1.23 - (0.0591/4)\log(1/P_{O_2})$
- $E = 1.23 - (0.0591/4)\log(1/0.8) = 1.22V$ (theoretical)
- Actual potential = $1.22 \times 0.8 = 0.976V$

4. For the Galvanic cell: $Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu$ After passing current for time t: $[Zn^{2+}] = 1.2M$ and $[Cu^{2+}] = 0.8M$ Calculate the cell potential at this instant if $E°cell = 1.1V$ [Based on JEE Advanced 2018]

5. A current of 0.5 ampere was passed through $CuSO_4$ solution for 2 hours using platinum electrodes. Calculate: a) Mass of copper deposited at cathode b) Volume of oxygen liberated at anode at STP [Based on JEE Main 2017]

6. In the electrolysis of $CuSO_4$ solution using copper electrodes, the solution turns blue at the anode because:

Options: (a) SO_4^{2-} ions are oxidized to form blue SO_3 (b) Cu^{2+} ions are reduced to form blue $Cu(OH)_2$ (c) Cu atoms from anode are oxidized to form Cu^{2+} ions (d) O_2 gas formed at anode reacts with water to form blue ozone

Correct Answer: (c)

Explanation:

- At anode: $Cu \rightarrow Cu^{2+} + 2e^-$ (oxidation)
- Cu^{2+} ions are hydrated, giving blue color
- Mass of Cu^{2+} increases near anode
- No SO_4^{2-} oxidation or Cu^{2+} reduction occurs at anode

7. For the cell reaction: $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$ If $E°(Cu^{2+}/Cu) = 0.34V$ and $E°cell = 2.0V$, the value of $E°(Al^{3+}/Al)$ is:

Options: (a) -1.66V (b) +1.66V (c) -2.34V (d) +2.34V

Correct Answer: (a)

Solution:

- $E°cell = E°cathode - E°anode$
- $2.0 = 0.34 - E°(Al^{3+}/Al)$
- $E°(Al^{3+}/Al) = -1.66V$

8. The transport number of Na^+ in NaCl solution is 0.4. The fraction of current carried by Cl^- ions is:

Options: (a) 0.4 (b) 0.6 (c) 1.4 (d) 1.0

Correct Answer: (b)

Explanation:

- $t_+ + t_- = 1$
- If $t_+ = 0.4$, then $t_- = 0.6$
- Cl^- carries 60% of the current

9. Calculate the EMF of the cell: $Pt|H_2(g, 1\ atm)|HCl(0.01M)||AgCl(s)|Ag$ Given: $E°(AgCl/Ag) = 0.22V$

Solution:

- Anode (H_2): $H_2 \rightarrow 2H^+ + 2e^-$
- Cathode (AgCl): $AgCl + e^- \rightarrow Ag + Cl^-$
- Using Nernst equation: $E = E° - (0.0591/n)\log([Cl^-][H^+]^2/PH_2)$
- $E = 0.22 - 0.0591\log(0.01)$
- $E = 0.22 + 0.118 = 0.338V$

10. In a concentration cell: $Zn|ZnSO_4(0.01M)||ZnSO_4(0.1M)|Zn$ Calculate: a) Cell potential at 298K b) Direction of electron flow c) Changes in concentration after passing 96,500C

Solution: a) E = (0.0591/2)log(0.1/0.01) = 0.0296V b) Electrons flow from dilute to concentrated solution c) Using Faraday's law:

- Moles of Zn^{2+} transferred = 1
- Concentration changes by 1M in each compartment

11. Given the standard reduction potentials: Cr^{3+}/Cr = -0.74V Fe^{2+}/Fe = -0.44V Cd^{2+}/Cd = -0.40V Ni^{2+}/Ni = -0.25V

Which of the following reactions will occur spontaneously?

Options: (a) $Cr + Fe^{2+} \rightarrow Cr^{3+} + Fe$ (b) $Fe + Cd^{2+} \rightarrow Fe^{2+} + Cd$ (c) $Ni + Cd^{2+} \rightarrow Ni^{2+} + Cd$ (d) $Cd + Ni^{2+} \rightarrow Cd^{2+} + Ni$

Correct Answer: (d)

Explanation:

- Calculate E°cell for each reaction
- Reaction is spontaneous if E°cell > 0
- For option (d): E°cell = -0.25 - (-0.40) = +0.15V
- Therefore, only option (d) is spontaneous

12. Three electrolytic cells containing solutions of $AgNO_3$, $CuSO_4$, and $CrCl_3$ are connected in series. If 0.108g of silver is deposited, calculate: a) The mass of copper deposited b) The mass of chromium deposited [Atomic masses: Ag=108, Cu=63.5, Cr=52]

Solution: Using Faraday's second law:

- For Ag: m_1 = 0.108g, n_1 = 1, M_1 = 108
- For Cu: n_2 = 2, M_2 = 63.5
- For Cr: n_3 = 3, M_3 = 52

m_2 = (0.108 × 63.5 × 1)/(108 × 2) = 0.0317g Cu m_3 = (0.108 × 52 × 1)/(108 × 3) = 0.0173g Cr

13. For the reaction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ Calculate the volume of 0.02M $KMnO_4$ required to oxidize 50mL of 0.05M Fe^{2+} solution.

Options: (a) 25mL (b) 50mL (c) 75mL (d) 100mL

Correct Answer: (a)

Solution:

- Balanced equation: $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
- Moles of Fe^{2+} = 0.05 × 0.050 = 0.0025 moles

- $MnO_4^-:Fe^{2+}$ = 1:5
- Moles of MnO_4^- required = 0.0025/5 = 0.0005 moles
- Volume of $KMnO_4$ = 0.0005/0.02 = 0.025L = 25mL

14. A voltaic cell consists of copper and aluminum electrodes: $Cu|Cu^{2+}(1.0M)||Al^{3+}(1.0M)|Al$
    Given: $E°(Cu^{2+}/Cu)$ = 0.34V, $E°(Al^{3+}/Al)$ = -1.66V

Which statement is incorrect?

Options: (a) Aluminum electrode is anode (b) Copper ions are reduced (c) Cell potential is 2.00V (d) Electrons flow from copper to aluminum

Correct Answer: (d)

Solution:

- E°cell = E°cathode - E°anode = 0.34 - (-1.66) = 2.00V
- Al is oxidized (anode): $Al \rightarrow Al^{3+} + 3e^-$
- Cu^{2+} is reduced (cathode): $Cu^{2+} + 2e^- \rightarrow Cu$
- Electrons flow from Al to Cu

15. For an electrochemical cell at 298K: $2Ag^+ + Zn \rightarrow 2Ag + Zn^{2+}$ The cell potential is 1.56V. After some time, $[Zn^{2+}]$ = 0.01M and $[Ag^+]$ = 0.1M. Calculate the cell potential.

Solution:

- $E = E° - (0.0591/n)\log([Zn^{2+}]/[Ag^+]^2)$
- $E = 1.56 - (0.0591/2)\log(0.01/0.1^2)$
- $E = 1.56 - 0.0295\log(1)$
- E = 1.56V

16. The molar conductivity of NH_4OH decreases on dilution from 0.1M to 0.01M by 10 units. Calculate the percent dissociation at both concentrations if $\Lambda°m$ = 238 S cm² mol⁻¹.

Options: (a) 1.2% and 3.8% (b) 2.1% and 6.7% (c) 3.4% and 10.8% (d) 4.2% and 13.3%

Correct Answer: (b)

Solution:

- Let Λm at 0.1M = x
- Then Λm at 0.01M = x + 10
- $\alpha_1 = x/238 \times 100\%$ (for 0.1M)
- $\alpha_2 = (x + 10)/238 \times 100\%$ (for 0.01M)
- Using Ostwald's dilution law and solving:
- x = 5 S cm² mol⁻¹
- α_1 = 2.1% and α_2 = 6.7%

17. In the electrolysis of Na_2SO_4 solution using platinum electrodes:

Which statement is correct?

Options: (a) Na^+ is reduced at cathode (b) SO_4^{2-} is oxidized at anode (c) H_2 gas is evolved at cathode (d) O_2 gas is reduced at anode

Correct Answer: (c)

Explanation:

- At cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
- At anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
- Na^+ and SO_4^{2-} are spectator ions
- H_2O is preferentially reduced/oxidized

18. Calculate the pH at which the electrode potential of hydrogen electrode equals its standard electrode potential.

Solution:

- $E = E° - (0.0591)pH$
- When $E = E°$
- $0 = 0 - 0.0591pH$
- $pH = 0$

19. For a fuel cell: $2H_2 + O_2 \rightarrow 2H_2O$ $\Delta H = -571.6$ kJ/mol and $\Delta G = -457.2$ kJ/mol Calculate: a) Maximum potential b) Efficiency of the fuel cell

Solution: a) $E° = -\Delta G/nF = 457200/(4 \times 96500) = 1.18V$ b) Efficiency = $(\Delta G/\Delta H) \times 100 = (457.2/571.6) \times 100 = 80\%$

20. The conductivity of 0.1M acetic acid is 4.95×10^{-4} S/cm. If $\Lambda°m$ for acetic acid is 390.7 S $cm^2\ mol^{-1}$, calculate: a) Molar conductivity b) Degree of dissociation c) Dissociation constant

Solution: a) $\Lambda m = \kappa \times 1000/c = 4.95 \times 10^{-4} \times 1000/0.1 = 4.95$ S $cm^2\ mol^{-1}$ b) $\alpha = 4.95/390.7 = 0.0127$ c) $Ka = c\alpha^2/(1-\alpha) = 0.1 \times (0.0127)^2/(1-0.0127) = 1.63 \times 10^{-5}$