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UNIT 9

Electro Chemistry

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1. Define anode and cathode

The anode of a device is the terminal where current flows in from outside. The cathode of a device is the terminal where current flows out. By current we mean the positive conventional current. Since electrons are negatively charged, positive current flowing in is the same as electrons flowing out.

2. Why does conductivity of a solution decrease on dilution of the solution

The conductivity of a solution is directly proportional to number of ions present in a unit volume of the solution because current is carried forward by the ions. With dilution number of ions in unit volume decreases so that conductivity also decreases. Hence with dilution conductivity decreases.

3. State Kohlrausch Law. How is it useful to determine the molar conductivity of weak electrolyte at infinite dilution.

At infinite dilution, the limiting molar conductivity of an electrolyte is equal to the sum of the limiting molar conductivities of its constituent ions. i.e., the molar conductivity is due to the independent migration of cations in one direction and anions in the opposite direction.

Determination of for weak electrolytes: The molar conductivity of a weak electrolyte at infinite dilution cannot be determined by extrapolation method. However, values for weak electrolytes can be determined by using the Kohlrausch's equation.

$$\alpha = \frac{\Lambda_m}{\Lambda_m^o}$$

Λ_m - Molar conductivity

Λ_m^o - Molar conductivity at infinite dilution

4. Describe the electrolysis of molten NaCl using inert electrodes

Electrolysis of Molten NaCl. If sodium chloride is melted (above 801 °C), two electrodes are inserted into the melt, and an electric current is passed through the molten salt, then chemical reactions take place at the electrodes. Chlorine gas bubbles out of the melt above the anode.

5. State Faraday's Laws of electrolysis

Faraday's first law

The mass of the substance (m) liberated at an electrode during electrolysis is directly proportional to the quantity of charge (Q) passed through the cell.

$$m \propto Q$$

$$m = Z It$$

Faraday's second law

When the same quantity of charge is passed through the solutions of different electrolytes, the amount of substances liberated at the respective electrodes are directly proportional to their electrochemical equivalents.

6. Describe the construction of Daniel cell. Write the cell reaction.

Anodic oxidation

The electrode at which the oxidation occurs is called the anode. In Daniel cell, the oxidation takes place at zinc electrode, i.e., Electrons are liberated at zinc electrode and hence it is negative (-ve).



Cathodic reduction

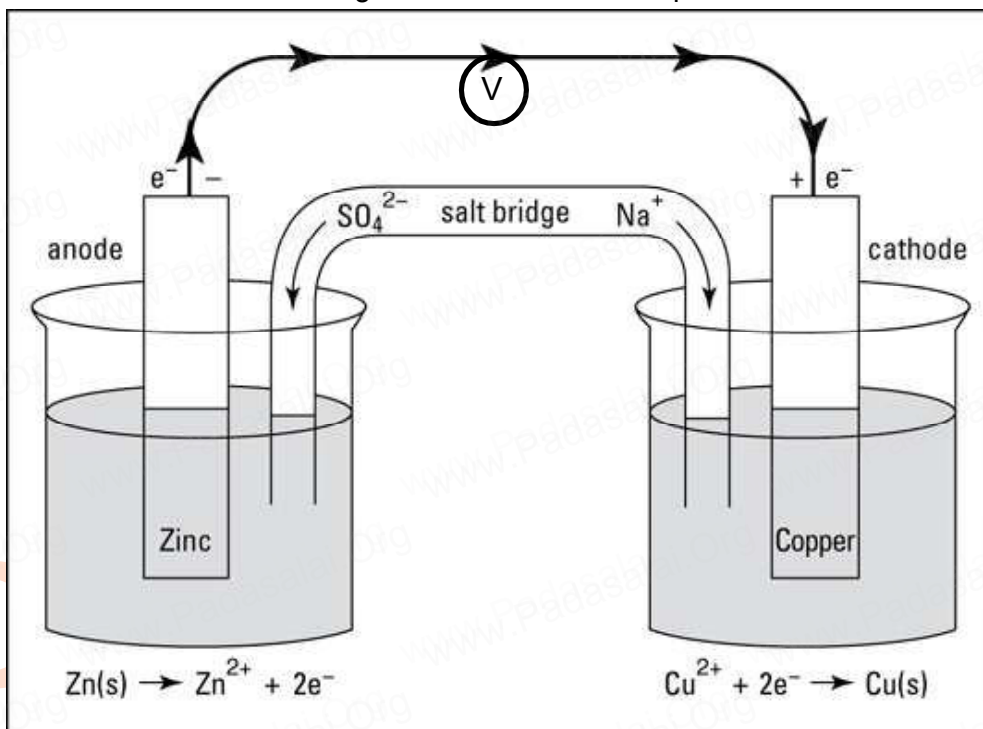
As discussed earlier, the electrons flow through the circuit from zinc to copper, where the Cu^{2+} ions in the solution accept the electrons, get reduced to copper and the same get deposited on the electrode. Here, the electrons are consumed and hence it is positive (+ve).



The total reaction is: $\text{Zn}_{(\text{s})} + \text{Cu}^{2+}_{(\text{aq})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + \text{Cu}_{(\text{s})}$

Salt bridge

The electrolytes present in two half cells are connected using a salt bridge To maintain the electrical neutrality in both the compartments, the non reactive anions SO_4^{2-} (from Na_2SO_4 taken in the salt bridge) move from the salt bridge and enter into the anodic compartment, at the same time some of the 2Na^+ ions move from the salt bridge into the cathodic compartment.



7. Why is anode in galvanic cell considered to be negative and cathode positive electrode?

The anode is the electrode where oxidation (loss of electrons) takes place; in a galvanic cell, it is the negative electrode, as when oxidation occurs, electrons are left behind on the electrode. This is why the cathode is a positive electrode; because positive ions are reduced to metal atoms there

8. The conductivity of a 0.01M solution of a 1 :1 weak electrolyte at 298K is $1.5 \times 10^{-4} \text{ S cm}^{-1}$.

i) molar conductivity of the solution

ii) degree of dissociation and the dissociation constant of the weak electrolyte

Given that : $\lambda_{\text{cation}}^{\circ} = 248.2 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda_{\text{anion}}^{\circ} = 51.8 \text{ S cm}^2 \text{ mol}^{-1}$

i) Molar conductivity $\Lambda_m = \frac{\kappa \times 10^{-3}}{C}$ $\Lambda_m = \frac{1.5 \times 10^{-2} \times 10^{-3}}{0.01} = 1.5 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$

ii) degree of dissociation $\Lambda_m^{\circ} = \Lambda_{\text{cation}}^{\circ} + \Lambda_{\text{anion}}^{\circ}$, $\Lambda_m^{\circ} = (248.2 + 51.8) = 300 \text{ cm}^2 \text{ mol}^{-1}$

(or) $\Lambda_m^{\circ} = 300 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ $\alpha = \frac{1.5 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}}{300 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}} = 0.05$

dissociation constant of the weak electrolyte $K_a = \frac{C\alpha^2}{1-\alpha}$,

$$K_a = \frac{0.01 \times (0.05)^2}{1 - 0.05} = \frac{0.01 \times 0.025}{0.95} = \frac{0.00025}{0.95} = 2.63 \times 10^{-5}$$

9. Which of 0.1M HCl and 0.1 M KCl do you expect to have greater Λ°_m and why?

0.1 M HCl will have greater Λ°_m because, H^+ (aq) being smaller in size than Na^+ (aq) and have greater mobility.

10. Arrange the following solutions in the decreasing order of specific conductance.

i) 0.01M KCl ii) 0.005M KCl iii) 0.1M KCl iv) 0.25 M KCl v) 0.5 M KCl

$$0.5 \text{ M KCl} > 0.25 \text{ M KCl} > 0.1 \text{ M KCl} > 0.01 \text{ M KCl} > 0.005 \text{ M KCl}$$

Conductivity changes with the concentration of the electrolyte. The number of ions per unit volume carrying the current decreases on dilution, so conductivity always decreases with decrease in concentration. Hence the number of ions per unit volume that carry charge in a solution decreases

11. Why is AC current used instead of DC in measuring the electrolytic conductance?

Using DC causes polarisation of the electrodes and electrolyte which leads to error in measured conductance values over a period of time. In AC there is no polarisation due to non-continuous flow of current, hence, AC is used

12. 0.1M NaCl solution is placed in two different cells having cell constant 0.5 and 0.25cm⁻¹ respectively. Which of the two will have greater value of specific conductance.

So the cell with higher cell constant has greater value of specific conductance i. e 0.5 cm⁻¹ .

$\frac{1}{\rho}$ is called specific conductance which is directly proportional to the cell constant .

13. A current of 1.608A is passed through 250 mL of 0.5M solution of copper sulphate for 50 minutes. Calculate the strength of Cu²⁺ after electrolysis assuming volume to be constant and the current efficiency is 100%.

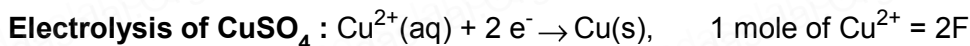
$$V = 250 \text{ mL} ,$$

$$(\eta) \text{ efficiency is } 100\%$$

$$Q = I \times t$$

$$Q = 1.608 \times 50 \times 60 = 4824 \text{ C}$$

$$\text{Number of faraday's of electricity} = \frac{4824}{96500} = 0.5F$$



$$\text{At } 0.5 \text{ F electricity will deposit} = \frac{1 \text{ mol}}{2F} \times 0.5 = 0.025 \text{ mol}$$

$$\text{before number of molar of } Cu^{2+} \text{ in } 250 \text{ ml of solution} = \frac{0.5}{1000} \times 250 = 0.125 \text{ mol}$$

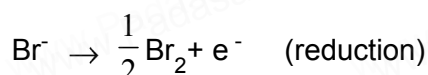
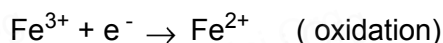
$$\text{Number of molar of } Cu^{2+} \text{ after electrolysis} = 0.125 - 0.025 = 0.1 \text{ mol}$$

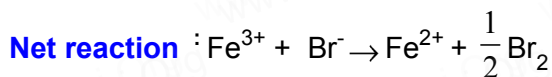
$$\text{Conc of } Cu^{2+} = \frac{0.1 \text{ mol}}{250 \text{ mL}} \times 1000 = 0.4 \text{ M}$$

14. Can Fe³⁺ oxidises bromide to bromine under standard conditions?

$$\text{Given: } E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$$

$$E^\circ_{Br_2/Br^-} = -1.09 \text{ V}$$





$$E^\circ_{\text{cell}} = -1.09 \text{ V} + 0.771 = -0.319 \text{ V}$$

E°_{cell} value is negative the reaction is not feasible, So Fe^{3+} will not oxidize Br^- to Br_2 .

15. Is it possible to store copper sulphate in an iron vessel for a long time?

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V} \text{ and } E_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

No we can't store copper sulphate in an iron vessel. Iron is more reactive than copper and it will displace copper from its sulphate solution. No, we can't store CuSO_4 solution in an iron vessel. Because iron is more reactive than copper.

16. Two metals M_1 and M_2 have reduction potential values of $-x\text{V}$ and $+y\text{V}$ respectively. Which will liberate H_2 and H_2SO_4 .

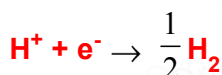


$$E^\circ = -0.76 \text{ V}$$



$$E^\circ = +0.80 \text{ V}$$

The first metal has a negative reduction potential and so more reactive than Hydrogen, whose reduction potential is given as



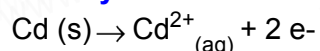
$$E^\circ = 0.00 \text{ V}$$

So the metal with negative reduction potential will liberate H_2 gas from Dil. H_2SO_4 . Here the metal with electrode potential of -0.76 V , is Zinc and with $+0.80 \text{ V}$ is Silver. Zinc will liberate Hydrogen gas from dilute H_2SO_4 and Silver will not.

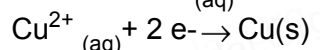
17. Reduction potential of two metals M_1 and M_2 are $E^\circ_{M_1^{2+}/M_1} = -2.3 \text{ V}$ and $E^\circ_{M_2^{2+}/M_2} = 0.2 \text{ V}$. Predict which one is better for coating the surface of iron. Given : $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$

M_1 is more positive oxidation potential than the oxidation potential of Fe which due to indicates that it will better for coating the surface of iron.

18. Calculate the standard emf of the cell: $\text{Cd} / \text{Cd}^{2+} \parallel \text{Cu}^+ / \text{Cu} (\text{s})$, and determine the cell reaction. The standard reduction potentials of $\text{Cu}^{2+} / \text{Cu}$ and $\text{Cd}^{2+} / \text{Cd}$ are 0.34 V and -0.40 V respectively. Predict the feasibility of the cell reaction.



$$\text{oxidation } E^\circ_{\text{cd} / \text{cd}^{2+}} = -0.40 \text{ V}$$



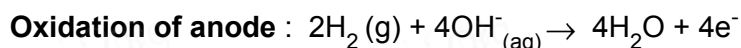
$$\text{reduction } E^\circ_{\text{Cu}^{2+} / \text{Cu}} = 0.34 \text{ V}$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+} / \text{Cu}} - E^\circ_{\text{cd} / \text{cd}^{2+}} = 0.34 - (-0.40) = 0.74 \text{ V}$$

E°_{cell} is +ve, But ΔG is -ve so the reaction is feasible

19. In fuel cell H_2 and O_2 react to produce electricity. In the process, H_2 gas is oxidised at the anode and O_2 at cathode. If 44.8 litre of H_2 at 25°C and 1 atm pressure reacts in 10 minutes , what is average current produced? If the entire current is used for electro deposition of Cu from Cu^{2+} , how many grams of Cu deposited?



1 mole of H_2 gas = 2 moles of electron at 25°C , 1 atm

1 mole of H_2 gas = 22.4 litres

$$\text{no of moles of } \text{H}_2 \text{ gas produced} = \frac{1 \text{ mole}}{22.4 \text{ litre}} \times 44.8 \text{ litre} = 2 \text{ moles of } \text{H}_2 \text{ gas}$$

2 moles of H_2 gas = 4 moles of electron at 25°C , 1 atm = $4F$

$$Q = I \times t \quad I = \frac{Q}{t} = \frac{4 \times 96500}{10 \times 60} = 643.3 \text{ A} \quad \text{Cu}^{2+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Cu(s)}, \quad 1 \text{ mole of Cu}^{2+} = 63.5 \text{ g}$$

The fuel cell entire current is used for electro deposition of Cu from Cu^{2+} is 4F is used for electrolysis = $2 \times 63.5 \text{ g} = 127 \text{ g Cu}$ deposited

20. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 2.935 g of Ni was deposited in the first cell. The amount of Cr deposited in the another cell? Give : molar mass of Nickel and chromium are 58.74 and 52 gm⁻¹ respectively.

Molar mass of Nickel = 58.74 and Molar mass of Chromium = 52 gm⁻¹

$$\frac{m_{\text{Ni}}}{m_{\text{Cr}}} = \frac{Z_{\text{Ni}}}{Z_{\text{Cr}}}$$

$$(Z) \text{ equivalent weight of Cr} = \frac{52}{3} = 17.33 \quad \text{and} \quad (Z) \text{ equivalent weight of Ni} = \frac{58.84}{2} = 29.35$$

$$\frac{2.935}{m_{\text{Cr}}} = \frac{29.35}{17.33} \quad m_{\text{Cr}} = \frac{2.935 \times 17.33}{29.35} = 1.733 \text{ g}$$

21. A copper electrode is dipped in 0.1M copper sulphate solution at 25°C. Calculate the electrode potential of copper. [Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$]

$$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \quad E^\circ_{\text{red}} = E^\circ_{\text{red}} - \frac{0.0591}{n_{\text{cell}}} \log \frac{[\text{P}]}{[\text{R}]} \quad E^\circ_{\text{red}} = 0.34 - \frac{0.0591}{2} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$$

$$E^\circ_{\text{red}} = 0.34 - \frac{0.0591}{2} \log \frac{1}{0.1} \quad E^\circ_{\text{red}} = 0.34 - 0.03 = 0.31 \text{ V}$$

22. For the cell $\text{Mg(s)} / \text{Mg}^{2+}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) / \text{Ag(s)}$, calculate the equilibrium constant at 25°C and maximum work that can be obtained during operation of cell. Given :

$$E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V} \quad \text{and} \quad E^\circ_{\text{Ag}^{2+}/\text{Ag}} = 0.80 \text{ V}$$

$$\text{Soln:} \quad E^\circ_{\text{Cell}} = +0.80 - (-2.37 \text{ V}) = 3.17 \text{ V}$$

$$\Delta_r G^\circ = -n F E^\circ \quad \Delta_r G^\circ = -2 \times 96500 \times 3.17$$

$$\Delta_r G^\circ = -611810 \text{ CV} = -611810 \text{ J}$$

Calculate the value of equilibrium constant.

$$\Delta_r G^\circ = -2.303 \times RT \times \log K_c \quad \log K_c = \frac{-\Delta_r G^\circ}{2.303 RT}$$

$$\log K_c = (-) \frac{(-611810 \text{ J})}{2.303 \times (8.314 \text{ JK}^{-1}) \times (298 \text{ K})} \quad \log K_c = 107.2250$$

$$K_c = \text{Antilog}(107.2250) = ?$$

$$K_c = 1.679 \times 10^{107}$$

23. 8. 2×10^{12} litres of water is available in a lake. A power reactor using the electrolysis of water in the lake produces electricity at the rate of $2 \times 10^6 \text{ Cs}^{-1}$ at an appropriate voltage. How many years would it take to completely electrolyse the water in the lake. Assume that there is no loss of water except due to electrolysis.

At anode : $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$

At cathode : $2 \times (2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-)$

Net reaction : $6\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 2\text{H}_2 + 4\text{OH}^- + \text{O}_2$

4 Faraday \Rightarrow 2 mole of $\text{H}_2\text{O} = 36 \text{ g} = 36 \text{ mL}$

density of water = 1000 g/lit

Volume of water in lake = 8.2×10^{12} litres

$$\text{volume of water} = \frac{36}{1000} = 3 \times 10^{-3}$$

$$1 \text{ mL of } \text{H}_2\text{O} = \frac{4 \times 96500}{36} \text{ faraday}$$

Electrolysis of water in the lake produces electricity at the rate of $2 \times 10^6 \text{ Cs}^{-1}$

$$t = \frac{4 \times 96500 \times 8.2 \times 10^{12}}{36 \times 10^{-3} \times 2 \times 10^6} = \frac{3165200 \times 10^{12}}{72 \times 10^3} = 43961 \times 10^9 \text{ sec}$$

Number of years required completely electrolyse the water in the lake

$$\text{(Number of years required)} \quad t = \frac{43961 \times 10^9 \text{ sec}}{31.5 \times 10^6} = 1.3955 \times 10^6 \text{ years}$$

24. Derive an expression for Nernst equation (refer text book)

25. Write a note on sacrificial protection.

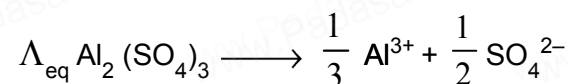
Sacrificial protection is the protection of iron or steel against corrosion by using a more reactive metal. Pieces of zinc or magnesium alloy are attached to pump bodies and pipes. The protected metal becomes the cathode and does not corrode. The anode corrodes, thereby providing the desired sacrificial protection.

26. Explain the function of $\text{H}_2 - \text{O}_2$ fuel cell.(refer text book)

27. Ionic conductances at infinite dilution of Al^{3+} and SO_4^{2-} are $189 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm.equiv.}^{-1}$ and $160 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm.equiv.}^{-1}$. Calculate equivalent and molar conductance of the electrolyte at infinite dilution.

$$\text{Al}^{3+} = 189 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm.equiv.}^{-1}$$

$$\text{SO}_4^{2-} = 160 \text{ ohm}^{-1} \text{ cm}^2 \text{ gm.equiv.}^{-1}$$



Equivalent conductance

$$\Lambda_m \text{Al}_2(\text{SO}_4)_3 = 2 \times 189 + 3 \times 160 = 63 + 80 = 858 \text{ mho cm}^2 \text{ mol}^{-1}$$

Molar conductance

$$\Lambda_{\text{eq}} \text{Al}_2(\text{SO}_4)_3 = \frac{189}{3} + \frac{160}{2} = 63 + 80 = 143 \text{ mho cm}^2 \text{ gm.equiv.}^{-1}$$

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