

Electrochemistry

Key Concepts

A cell is of two types:-

- I. Galvanic Cell
- II. Electrolytic cell.

In Galvanic cell the chemical energy of a spontaneous redox reaction is converted into electrical work. Batteries and fuel cells are very useful forms of galvanic cells

In Electrolytic cell electrical energy is used to carry out a non-spontaneous redox reaction.

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

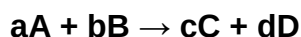
The standard potential of the cells are related of standard Gibbs energy.

$$\Delta_r G^0 = -n F E^0_{\text{cell}}$$

The standard potential of the cells is related to equilibrium constant.

$$\Delta_r G = -RT \ln k$$

Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.



Nernst equation can be written as

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The conductivity, K of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature.

Molar Conductivity, λ_m , is defined by λ_{sp} / C where C is the concentration in mol L⁻¹

$$\lambda_m \text{ or } \Lambda_M = \frac{k \times 1000}{M}$$

the unit of molar conductivity is $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Conductivity(Specific conductance) decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolyte . there is sharp

increase in molar conductivity of weak electrolyte on decreasing concentration or increasing dilution.

Kohlrausch law of independent migration of ions. The law states that limiting conductivity of an electrolyte can be represented as the sum of the individual contribution to the anion and cation of the electrolyte.

Faraday's laws of Electrolysis

- I. The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.
- II. The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.

Cells and Batteries:

Cells are of two types: (a) Primary Cell (b) Secondary cell

There are mainly two types of batteries.

(a) Primary

Corrosion of metals is an electrochemical phenomenon

In corrosion metal is oxidized by loss of electrons to oxygen and formation of oxides.

Anode (Oxidation): $2\text{Fe(s)} \rightarrow 2\text{Fe}^{2+} + 4\text{e}^-$

Cathode (Reduction): $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

Atmospheric Oxidation:

$2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)} + 1/2\text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 4\text{H}^+(\text{aq})$

QUESTION CARRYING 1 MARK

1. Name the factor on which emf of a cell depends:-

Ans. Emf of a cell depends on following factor-

- a. Nature of reactants.
- b. Concentration of solution in two half cells.
- c. Temperature
- d. Pressure of gas.

2. What are the units of molar conductivity?
(cm² ohm⁻¹ mol⁻¹ or Scm²mol⁻¹)

3. What is the EMF of the cell when the cell reaction attains equilibrium?
 Ans. Zero

4. What is the electrolyte used in a dry cell?
 Ans. A paste of NH₄Cl, MnO₂ and C

8. How is cell constant calculated from conductance values?

Ans. Cell constant= specific conductance/ observed conductance.

9. What flows in the internal circuit of a galvanic cell?

Ans. Ions

10. Define electrochemical series.

Ans. The arrangement of various electrodes in the decreasing or increasing order of their standard reduction potentials is called electrochemical series.

QUESTIONS CARRYING TWO MARKS

1. Calculate emf of the following cell at 298K
 Zn/Zn²⁺ (10⁻⁴ M) || Cu²⁺ (10⁻²M)/Cu

Given E⁰ Zn²⁺/Zn=-0.76V

E⁰Cu²⁺/Cu=+0.34V

Ans. Cell reaction is as follows.

Zn(s) + Cu²⁺(aq)→ Zn²⁺(aq) + Cu(s)

n = 2

T=298K

E_{cell}= (E⁰Cu²⁺/Cu-E⁰Zn²⁺/Zn) -0.0591V log $\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$

= 0.34V-(-0.76)-0.02955Vlog $\frac{10^{-4}}{10^{-2}}$

$$= 1.10\text{V} - 0.02955\text{V} \log 10^{-2}$$

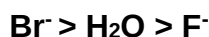
$$= 1.10\text{V} + 2 \times 0.02955\text{V}$$

$$= 1.10\text{V} + 0.0591\text{V}$$

$$= 1.1591\text{V}$$

2. Electrolysis of KBr (aq) gives Br₂ at anode but KF(aq) does not give F₂. Give reason.

Ans. Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of Br⁻, H₂O, F⁻ are in the following order.



Therefore in aq. Solution of KBr. Br⁻ ions are oxidized to Br₂ in preference to H₂O. On the other hand, in aq. Solution of KF, H₂O is oxidized in preference to F⁻. Thus in this case, oxidation of H₂O at anode gives O₂ and no F₂ is produced.

3. Define corrosion. Write chemical formula of rust.

Corrosion is a process of deterioration of metal as a result of its reaction with air and water, surrounding it. It is due to formation of sulphides, oxides, carbonates, hydroxides, etc.

Formula of rust- Fe₂O₃.xH₂O

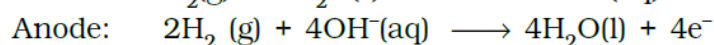
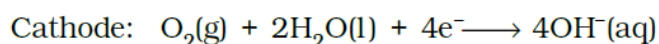
4. Why mercury cell gives the constant voltage.

Ans. Mercury cell gives a constant voltage in its life because the overall reaction does not involve any ion in solution whose concentration can change during its life time.

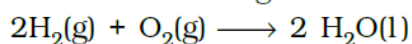
5. What is fuel cell? Write reaction involved in H₂-O₂ fuel cell.

Ans. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells.

Reactions involved in H₂ - O₂ fuel cell can be presented as follows:-



Overall reaction being:



QUESTION CARRYING THREE MARKS

1. Write any three differences between potential difference and E.M.F.
- | E.M.F | POTENTIAL DIFFERENCE |
|--|--|
| 1.It is difference between electrode potential of two electrodes when no current is flowing through circuit. | 1.It is difference of potential between electrode in a closed circuit. |
| 2. It is the maximum voltage obtained From a cell. | 2.It is less than maximum voltage Obtained from a cell. |
| 3. It is responsible for steady flow of Current. | 3.It is not responsible for steady Flow of current. |
2. For the standard cell
 $\text{Cu(s)}/\text{Cu}^{2+}(\text{aq})||\text{Ag}^{+}(\text{aq})/\text{Ag(s)}$
 $E^{\circ} \text{ Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$
 $E^{\circ} \text{ Ag}^{+}/\text{Ag} = +0.80 \text{ V}$
- Identify the cathode and the anode as the current is drawn from the cell.
 - Write the reaction taking place at the electrodes.
 - Calculate the standard cell potential.

Ans. From the cell representation

Ag/Ag^{+} electrode is cathode and Cu/Cu^{2+} electrode is anode.

Reaction at anode: $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-}$

Reaction at cathode: $2\text{Ag}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow 2\text{Ag(s)}$

$$\begin{aligned}
 E^0_{\text{cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\
 &= E^0_{\text{Ag}^+/\text{Ag}} - E^0_{\text{Cu}^{2+}/\text{Cu}} \\
 &= +0.80 \text{ V} - (+0.34\text{V}) \\
 &= +0.80\text{V} - 0.34\text{V} \\
 &= 0.46\text{V}
 \end{aligned}$$

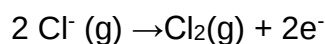
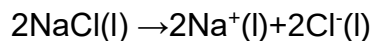
3. Can we store copper sulphate in (i) Zinc vessel (ii) Silver vessel? Give reasons.
 Given $E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$, $E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$, $E^0_{\text{Ag}^+/\text{Ag}} = +0.80\text{V}$

Ans. (i) No (ii) Yes

Explanation: A metal having lower reduction potential can displace a metal having higher reduction potential from solution of its salt.

Since standard reduction potential of Zn^{2+} ($E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$) is less than the standard reduction potential of Cu^{2+} ($E^0_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$), Zn can displace copper from copper sulphate solution. Thus, CuSO_4 solution can be stored in silver vessel.

4. How many grams of chlorine can be produced by the electrolysis of molten NaCl with a current of 1.02 A for 15 min?



2 mole 1mol

$$Q = n f$$

$$Q = 2 \times 96500 \text{ C/mol} = 1.93 \times 10^5 \text{ C}$$

$$\text{Quantity of electricity used} = I \times t$$

$$= 1.02 \text{ A} \times (15 \times 60) \text{ s}$$

$$= 900 \text{ C}$$

Molar mass of $\text{Cl}_2 = 2 \times 35.5 = 71 \text{ g mol}^{-1}$ $\times 10^5 \text{ C}$ of charge produce chlorine = 71g

$1.93 \times 10^5 \text{ C}$ of charge produce chlorine = 71g

$$900 \text{ C of charge produce chlorine } \frac{71 \times 900}{1.93 \times 10^5}$$

$$= 0.331 \text{ g}$$