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Electrolysis

"The decomposition of a compound using electricity is called electrolysis of the compound."

In electrolysis, electricity is used for carrying out a chemical change. The apparatus in which electrolysis is carried out is called **voltameter.** During electrolysis, the cations being positively charged get attracted towards the negatively charged electrode (cathode) and anions being negatively charged get attracted towards the positively charged electrode (anode). Cations and anions get discharge on respective electrode by gaining or losing electrons at respective electrode.

Discharge potential

It is minimum potential difference required to be applied across the electrodes to carry out the electrolysis and subsequent discharge of the ions on the electrode.

In general, discharge potential of an ion is equal to the electrode potential of the respective ion.

When two or more ions compete to get discharged on an electrode, then the ions having low discharge potential preferentially discharges on respective electrodes.

Here, the ions having lower electrode potential (reduction potential) gets discharged preferentially at anode while, those having higher electrode potential (reduction potential) gets discharged preferentially at cathode.

Over voltage or bubble voltage-

For discharge of a metal at cathode, the voltage required is almost equal to its standard electrode potential. However, for liberation of gases such as oxygen some extra voltage is required, which is called over voltage or bubble voltage.

Selective/Preferential Discharge of ions during Electrolysis

During electrolysis, the cations being positively charged get attracted towards the negatively charged electrode (cathode) and anions being negatively charged get attracted towards the positively charged electrode (anode). If more than one cations or anions reach to an electrode, only one of them preferentially gets discharged at one electrode. Thus, there is a choice amongst the ions that which will get discharged on an electrode.

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During electrolysis of aqueous solutions, if a cation has higher electrode potential (reduction potential) than water (-0.83 V), then it preferentially discharges at cathode (e.g. electrolysis of copper and silver salts), otherwise H_2 gas is liberated due to reduction of water at cathode (e.g. Na, K, Ca salts etc.).

Similarly, if an anion has higher oxidation potential than water (-1.23V), then it preferentially discharges at anode e.g. Br^- (-1.09V), I^-(-0.53V) etc., otherwise O_2 gas is liberated due to oxidation of water at anode e.g. F^- (-2.87 V), SO_4^{2-} (-2.01V) etc.

The order of ease of discharge (oxidation) of certain anions at anode-

$$\mathbf{F^- < SO_4^{2-} < NO_3^- < Cl^- < Br^- < I^- < OH^-}$$

Factors affecting selective discharge of ions

(1) Position of ion in Electrochemical Series

In electochemical series, different ions are arranged in increasing order of the ease to which they get discharged during electrolysis. Here, the lower the position of an ion (either cation or anion) in the electochemical series, more easily it gets liberated at the electrode.

(a) Selective Discharge of Cations

A more reactive metal has greater tendency to get oxidized (lose electrons) forming cations. Hence, its ions have very weak tendency to gain electrons i.e. have very weak tendency to get discharged at cathode. Thus, the greater the reactivity of a metal, the lesser is the tendency of its ions to get discharged at the cathode.

A metal having more negative (or less positive) value of its standard electrode potential (standard reduction potential) is preferred for discharge at cathode as compared to that having less negative (or more positive) value of its standard electrode potential (standard reduction potential).

The order of ease of discharge of some most common metal ions during electrolysis at cathode is as under-

$K^+ < Ca^{2+} < Na^+ < Mg^{2+} < Al^{3+} < Zn^{2+} < Fe^{2+} < Pb^{2+} < H^+ < Cu^{2+} < Hg^{2+} < Ag^+$

Thus, the ions of reactive metals like potassium and sodium have very weak tendency to get discharged and therefore, have a very strong tendency to remain left in the electrolyte solution.

Hydrogen ions and ions of less reactive metals like copper and silver have a very strong tendency to get discharged at cathode.

In fact, in aqueous solution, hydrogen ions get preferentially discharged over the ions of the metals above hydrogen in the reactivity series. On the other hand, a metal ion lying below hydrogen in the reactivity series such as Cu^{2+},

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Hg^{2+}, Ag^{+} etc. get preferentially discharged over H^{+} ions producing metal at cathode.

(b) Selective Discharge of Anions

An anion having less negative (or more positive) value of its standard electrode potential (standard reduction potential) is preferred for discharge at anode as compared to that having more negative (or less positive) value of its standard electrode potential (standard reduction potential).

The order of ease of discharge of some most common anions during electrolysis at anode is as under-

$$\mathbf{F^- < SO_4^{2-} < NO_3^- < Cl^- < Br^- < I^- < OH^-}$$

Here, sulphate and nitrate ions have very weak tendency to get discharged at anode and therefore they have a very strong tendency to remain left in the electrolyte solution. Thus, they are not electrolysed during electrolysis.

On the other hand, hydroxide ions release electrons most easily (i.e. get oxidized most easily) and therefore, they have the highest ease of discharge during electrolysis producing oxygen gas at anode.

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$$

(2) Concentration of ions in solution

In general, the ion having more concentration in solution is preferred in getting discharged irrespective of its position in electrochemical series. Thus, if an ion is present in higher concentration then it always preferentially get discharged regardless of its ease of discharge. For example, during electrolysis of concentrated NaCl solution, the ions present in electrolytic solution are- Na^+, Cl^- (due to dissociation of NaCl), H^+ and OH^- (due to partial dissociation of water).

Here, the concentration of Na^+ and Cl^- in the solution is more than H^+ and OH^- ions. Thus, during electrolysis of concentrated NaCl, both Na^+ and Cl^- will get discharged at respective electrode instead of H^+ and OH^- ions though they occupy higher positions in electro chemical series i.e have lesser tendency to get discharged.

Thus, the electrode reactions will be as under-

At cathode-

$$Na^+ + e^- \rightarrow Na \qquad \text{(Reduction)}$$

At anode-

$$Cl^- \rightarrow \tfrac{1}{2} Cl_2 + e^- \qquad \text{(Oxidation)}$$

Thus, during electrolysis of concentrated NaCl solution, sodium is deposited at cathode while, chlorine gas is liberated at anode.

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(3) Nature of Electrode

The material of which the electrode is made determines whether it will take part in the electrolytic reaction or not. On this basis, there are two types of electrodes –

(a) Inert electrodes- These electrodes do not take part in the reaction. The most common inert electrodes platinum, graphite, iron etc.

(b) Active electrodes- These electrodes take part in the reaction. The most common active electrodes are copper, nickel, silver etc. If anode is made up of any of these metals, then the metal atoms themselves gets oxidized (lose electrons) and there is no discharge of any anion at the anode.

$$Cu \rightarrow Cu^{2+} + 2e^-$$
$$Ni \rightarrow Ni^{2+} + 2e^-$$
$$Ag \rightarrow Ag^{+} + e^-$$

For example, during electrolysis of aqueous copper sulphahte using copper electrodes, both of SO_4^{2-} and OH^- ions migrate towards anode and try to get discharged. Here, since copper is an active electrode, it loses its electrons and gets converted into Cu^{2+} ions. Thus the electrode reaction at anode is as under,

$$Cu \rightarrow Cu^{2+} + 2e^-$$

Here, none of the anions of solution succeed to get discharged at anode.

Similarly, both of Cu^{2+} and H^+ ions of solution migrate towards cathode and compete to get discharged. Since, the position Cu^{2+} ion in electrochemical series is lower than H^+ ion, Cu^{2+} ions get preferentially discharged at cathode while, H^+ ions remain left in solution. Thus, the electrode reaction at cathode is as under-

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Here, Cu^{2+} ions generated at anode are getting discharged at cathode. Thus, the blue colour of the solution (which is due to Cu^{2+} ions) remains unchanged.

Some Common Examples of Electrolysis

(1) Electrolysis of molten NaCl

When molten NaCl is electrolyzed, sodium is obtained at cathode while, chlorine gas is released at anode.

$$2NaCl \xrightarrow{\text{Melt}} 2Na^+ + 2Cl^-$$

At anode -

$$2Cl^- \rightarrow Cl_2(g) + 2e^- \qquad \text{(oxidation)}$$

At cathode -

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$$2Na^+(aq) + 2e^- \rightarrow 2Na(s) \quad \text{(reduction)}$$

Net reaction-

$$2NaCl\,(Molten) \xrightarrow{Electricity} \underset{(at\ cathode)}{2Na(s)} + \underset{(at\ anode)}{Cl_2(g)}$$

(2) Electrolysis of Dilute aqueous NaCl

Water is capable of undergoing both oxidation and reduction

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq.) + 4e^- \quad E^0 = +1.23V$ (Oxidation)

$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad E^0 = -0.83V$ (Reduction)

Thus, if an aqueous solution of a salt or hydroxide is electrolyzed, one or both of these two reactions compete with the electrolysis of the solute. For example, in electrolysis of aqueous sodium chloride, hydrogen is produced at the cathode instead of sodium.

In fact, in aqueous NaCl, both NaCl and water undergo ionization as under-

$2NaCl\,(aq) \rightarrow 2Na^+(aq) + 2Cl^-(aq)$

$2H_2O\,(l) \rightarrow 2H^+(aq) + 2OH^-(aq)$

Thus, there are two cations i.e. Na^+ and H^+ in solution. When electric potential is applied both Na^+ and H^+ ions go to the cathode and compete to get discharged. The position of H^+ ion in electrochemical series is lower than Na^+ ion. Hence, H^+ ions have low discharge potential (higher reduction potential) and get preferentially discharged at cathode while, Na^+ ions remain left in solution. Thus, the electrode reaction at cathode is as under-

$$2H^+ + 2e^- \rightarrow H_2$$

In fact, at cathode there is competition between following two reduction reactions-

$Na^+(aq.) + e^- \rightarrow Na\,(s) \quad E^0 = -2.71V$

$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad E^0 = -0.83\ V$

Here, reduction of Na^+ ($E° = –2.71$ V) is energetically more difficult than the reduction of water (- 0.83 V). Thus, the reaction with higher value of E^0 (i.e. less negative value of E^0) is preferred i.e. $H_2(g)$ is produced at the cathode instead of sodium metal.

Similarly, there are two anions i.e. Cl^- and OH^- in the solution. Both of these two ions migrate towards the anode during electrolysis and compete to get discharged. Here, the position of OH^- in electrochemical series is lower than Cl^- ion. Hence, OH^- ions have low discharge potential (lower reduction potential or higher oxidation potential) and therefore, they should get discharged

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preferentially but in practice, due to over voltage of O_2, Cl^- ions get discharged at anode while, OH^- ions remain left in solution.

Thus, the electrode reaction occurring at anode is as under-

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

In fact, at anode there is competition between following two oxidation reactions-

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad E^0 = +1.36\ V$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq.) + 4e^- \qquad E^0 = +1.23V$$

Here, the reaction with lower value of E^0 should be preferred and therefore, water should preferentially be oxidized. However, due to overpotential of oxygen, in practice the oxidation of Cl^- ions is predominant.

Thus, the electrode reactions and overall reaction occurring during the electrolysis of dilute aqueous NaCl will be as under-

At anode –

$$2Cl^- \rightarrow Cl_2(g) + 2e^- \qquad E^0 = +1.36\ V \quad \text{(oxidation)}$$

At cathode –

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq.) \qquad E^0 = -0.41\ V \text{ (reduction)}$$

Net reaction-

$$2Cl^- + 2H_2O \rightarrow Cl_2(g) + H_2(g) + 2OH^- \qquad E = -1.77\ V$$

Here, colourless alkaline solution left in electrolytic tank after electrolysis is in fact, dilute solution of NaOH.

(3) **Electrolysis of concentrated NaCl solution-** During electrolysis of concentrated NaCl solution the ions present in electrolytic solution are- Na^+, Cl^-, H^+ (due to partial dissociation of water) and OH^- (due to partial dissociation of water).

Here, since the concentration of Na^+ and Cl^- in the solution is more than H^+ and OH^- ions both Na^+ and Cl^- ions get preferentially discharged at respective electrode instead of H^+ and OH^- ions though they occupy higher positions in electro chemical series i.e have lesser tendency to get discharged.

Thus, the electrode reactions will be as under-

At cathode-

$$Na^+ + e^- \rightarrow Na \qquad \text{(Oxidation)}$$

At anode-

$$Cl^- \rightarrow \tfrac{1}{2}\,Cl_2 + e^- \qquad \text{(Reduction)}$$

Thus, during electrolysis of concentrated NaCl solution, sodium is deposited at cathode while, chlorine gas is liberated at anode.

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(4) Electrolysis of Aqueous $CuSO_4$ using copper electrodes

When aqueous $CuSO_4$ is electrolyzed using copper electrodes, copper dissolves at anode and equivalent amount of copper ions from solution deposits at cathode.

$$CuSO_4\,(aq) \rightarrow Cu^{2+}\,(aq) + 2SO_4^{2-}\,(aq)$$

In fact, in aqueous $CuSO_4$ both $CuSO_4$ and water undergo ionization.

$$2CuSO_4\,(aq) \rightarrow 2Cu^{2+}\,(aq) + 2SO_4^{2-}\,(aq)$$
$$4H_2O\,(l) \rightarrow 4H^{+}\,(aq) + 4OH^{-}\,(aq)$$

Here, both Cu^{2+} and H^+ ions migrate towards cathode and compete to get discharged.

Since, the position Cu^{2+} ion in electrochemical series is lower than H^+ ion, they get preferentially discharged at cathode while, H^+ ions remain left in solution. Thus, the electrode reaction at cathode is as under-

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Similarly, both of SO_4^{2-} and OH^- ions migrate towards anode and try to get discharged. Here, since copper is an active electrode, it is attacked by ions of solution. Hence, it loses its electrons and gets converted into Cu^{2+} ions. Thus the electrode reaction at anode is as under,

$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

Here, none of the anions of solution succeed to get discharged at anode.

The electrode reactions occurring during electrolysis are as follows-

At anode –

$$Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2e^{-}\,(aq) \qquad \text{(oxidation)}$$

At cathode –

$$Cu^{2+}\,(aq) + 2e^{-} \rightarrow Cu(s) \qquad \text{(reduction)}$$

Here, the net reaction is the dissolution of copper at anode and its deposition on cathode. Since, Cu^{2+} ions which are getting discharged at cathode from solution, get regenerated at anode, the blue colour of the solution (which is due to Cu^{2+} ions) remains unchanged.

(5) Electrolysis of Aqueous $CuSO_4$ using Platinum electrodes

Platinum anode being inert is not attacked by Cu^{2+} ions of solution. Hence, when aqueous $CuSO_4$ is electrolyzed, using platinum anode O_2 gas is released at anode, while copper deposits at cathode.

In aqueous solution of $CuSO_4$ both $CuSO_4$ and water undergo ionisation-

$$2CuSO_4\,(aq) \rightarrow 2Cu^{2+}\,(aq) + 2SO_4^{2-}\,(aq)$$
$$4H_2O\,(l) \rightarrow 4H^{+}\,(aq) + 4OH^{-}\,(aq)$$

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Thus, there are two cations i.e. Cu^{2+} and H^+ in the aqueous solution of $CuSO_4$. Both of these two ions migrate towards cathode during electrolysis and compete to get discharged. Here, the position Cu^{2+} ion in electrochemical series is lower than H^+ ion. Hence, Cu^{2+} ions get preferentially discharged at cathode while, H^+ ion**s** remain left in solution.

Thus, the electrode reaction at cathode is as under-

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Similarly, there are two anions i.e. SO_4^{2-} and OH^- in the solution. Both of these two ions migrate towards the anode during electrolysis and compete to get discharged. Here, the position of OH^- ion in electrochemical series is lower than SO_4^{2-} ion and therefore, OH^- ions preferentially get discharged at anode while SO_4^{2-} ion**s** remain left in solution. Thus, the electrode reaction at anode is as under-

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$$

Thus, during electrolysis of dilute $CuSO_4$ solution, copper is deposited at cathode while, oxygen gas is liberated at anode. Here, blue colour of the aqueous $CuSO_4$ decolourises rapidly and a colourless solution is left in electrolytic tank The electrode reactions and overall reaction occurring during electrolysis are as follows-

At anode –

$$4OH^-(s) \rightarrow O_2(g) + 2H_2O(l) + 4e^-(aq) \quad \text{(oxidation)}$$

At cathode –

$$2Cu^{2+}(aq) + 4e^- \rightarrow 2Cu(s) \quad \text{(reduction)}$$

Net reaction-

$$2CuSO_4(aq) + 4H_2O(l) \xrightarrow{\text{Electricity}} \underset{\text{(at cathode)}}{2Cu(s)} + \underset{\text{(at anode)}}{O_2(g)} + \underset{\text{(In electrolytic tank)}}{H_2SO_4(aq)}$$

Here, blue colour of the aqueous $CuSO_4$ decolourises rapidly and a colourless solution is left in electrolytic tank after electrolysis, which is in fact, the dilute aqueous solution of H_2SO_4.

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(6) Electrolysis of water

Pure water is bad conductor of electricity and therefore, does not undergo electrolysis easily. However, when water acidified with sulphuric acid (dilute sulphuric acid) or aqueous alkalies is electrolysed, then H_2 is obtained at cathode while, O_2 is released ad anode. Here, if we have to produce hydrogen and oxygen, then the electrolyte used must be energetically more difficult to oxidize or reduce than water itself. Electrolysis of a solution of sulphuric acid or of a salt such as $NaNO_3$ results in the electrolysis of water.

$4H_2O + 4e– \rightarrow 2H_2(g) + 4OH^–$ $\quad E = -0.41\ V([OH^-] = 10^{-7}\ M)$

$2H_2O \rightarrow O_2(g) + 4H^+ + 4e–$ $\quad E^0 = +1.23\ V$

$2H_2O \rightarrow 2H_2(g) + O_2(g)$ $\quad E^0 = -1.64\ V$

Electrolytic production of hydrogen is usually carried out with a dilute solution of sulfuric acid. This process is generally too expensive for industrial production unless highly pure hydrogen is required. However, it becomes more efficient at higher temperatures, where thermal energy reduces the amount of electrical energy required, so there is now some interest in developing high-temperature electrolytic processes. Most hydrogen gas is manufactured by the steam reforming of natural gas.

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