06th Oct. 2023

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Electro-chemistry

Electrodes:-

Electrodes are the rods, plates of solid conductors through which an electric current enters and leaves the electrolytic solution.

Anode:-

The electrodes which is connected to the positive pole of the battery is called anode. It is this rod or plate through which the conventional current enters the electrolyte or the electrons leave it.

~AK~

Cathode:-

The electrode which is connected to the negative pole of the battery is called cathode. It is this rod or plate through which the conventional current leaves the electrolytic solution or the electrons enter through it.

Oxidation:-

Oxidation is the process which involves loss of electrons by an atom, ion or molecules. The loss of electron results in the increase of positive charge or decrease of negative charge of the atom or ion undergoing oxidation.

Reduction:-

Reduction in the process which involves gain of electron by an atom ion and molecule the gain of electrons results in the decrease of positive charge or increase of negative charge.

Electrode potential:-

The tendency of an electrode to lose or gain electrons when it is in contact with its one ions in the solution is called electrode potential.

Electro-chemical ~~Akies~~:-

A series obtained by arranging the various electrodes or half-cells i.e, redox equilibria on the basis of their increasing standard reduction potential with respect to standard hydrogen electrode is called electron-chemical series.

Arrhensive theary:-

Arrhenians perposed the theary of ionisation in the year 1887. The main postulates of this theory are:-

① Ionization

By the mere process of solution, the molecule of substance split up in to positively and negatively charge particle called "ions". The ions ~~charging~~ carrying positive charge are called cations and the ions carrying negative charge, are called anions.

The process of spontaneous splitting up of an electrolyte into ions when dissolved in a solvent is called electrolytic dissociation or ionisation.

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② cations are generally, mettalic radicals obtained by loss of electrons from the metallic atoms. Anions are non metallic atom or radicals obtained by gain of electron by non metallic atoms.

③ Electrically neutral:-

The total charge on cations present is equal limit opposite to that of anions present so that the solution is ~~electrically~~ electrically neutral.

4) Degree of ionization:-

The electrolyte may not be completely ionized only a fraction of the total number of molecules is ionized. This fraction is called degree of ionization.

$$\text{Degree of ionization} = \frac{\text{no. of molecules dissociated into ions}}{\text{Total of molecules taken}}$$

5) Equillibrium State:-

Molecules of the solutes are constantly spliting up into ions and the ions are constantly reuniting to give original molecules Thus a state of dynamic equilibrium exists between ionized and an ionized molecules - eg. in sodium chloride solution in water.

The following equilibrium exists-

$$NaCl \longrightarrow Na^+ + Cl^-$$

6) Coductivity of Solution:-

Conductivity of solution is due to the presence of ions in the solution. The number of ions depends on the degree of ionization, Greater the degree of ionization, larger is the number of ions.

(4) Free movement of ions:-

The ions are free to move and are in random motion. Under the influence of electric current these are directed towards oppositely charged electrodes.
Electric current does not produce ions, but it only has a directive effect.

#. primary cells:-

These are the cells in which the redox reaction occure only once and the cell becomes dead after sometimes, and cannot be used again. Such cells cannot be recharged some common example are- dry cell and mercury cell.

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Secondary cell:-

These are the cells which can be recharged by passing an electric current through them and hence can be used over and again. Some common example are- lead storage battery, nickel cadmium storage cell and lithium iodine cell.

Faraday's first law :-

The law states that the mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte solution. Thus, if W gram of the substance is deposited on Q coulombs of electricity.

$$W \propto Q$$

or, $$W = Z \cdot Q$$

where Z is a constant of ~~proportional~~ proportionality and is called electrochemical equivalent (E.C.E) of the substance deposited. If a current of C amperes in passed for t seconds, then.

$$Q = C \times t$$

So that

$$W = Z \times Q$$

or, $$W \simeq AK\alpha$$

now, when C = 1 ampere and t = 1 second a current of 1 ampere is passed through an electrolyte solution for one second, then

$$W = Z \times 1 \times 1$$

$$W = Z$$

Hence, electrochemical equivalent of substance may be define as —

define as the mass of the substance deposited when a current of one ampere is passed for one second.

i.e, a quantity of electricity equal to one coulomb is passed

#. Faraday's second law:-

The law stated that when the same quantity of electricity is passed through the solution of different electrolyte connected in series, the masses of the substance produced at the electrodes are directly proportional to their equivalent masses.

Let us consider the passage of electricity through the solution of $CuSO_4$ and $AgNO_3$ connected in series, so that same amount of electricity is passed through them, then from the second law, we get,

$$\frac{\text{mass of copper diposited}}{\text{mass of silver diposited}} = \frac{\text{Equivalent mass of copp}}{\text{Equivalent mass of silv}}$$

Verification of the second law:-

Let us consider two electrolytic cells connected in series, so that same amount of electricity is passed through them. Suppose W_1 and W_2 are the masses of the elements dipasited at their respective cathodes and E_1 and E_2 are their respective equivalent masses, then

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$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \quad \text{——— (i)}$$

Now the,

Now according to Faraday's first law -

$$W = Z = c \times t$$

putting the value of W in eq (i) we get -

$$\frac{W_1}{W_2} = \frac{Z_1 \times c \times t}{Z_2 \times c \times t} = \frac{E_1}{E_2} \quad [\text{Since } c \times t \text{ is same in cell}]$$

or, $$\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

In other words the electrochemical equivalent of an element is directly proportional to its equivalent mass i.e.

$$E \propto Z$$

or, $$E = F \times Z$$

where F is constant of proportionality and is know as faraday constant.

Electrolysis of an aqueous copper sulphate solution using copper electrode.

The electrolysis of an aqueous solution of copper sulphate using copper electrode result in transfer of copper metal from the anode to the cathode during electrolysis. The copper sulphate is ionized in a aqueous solution.

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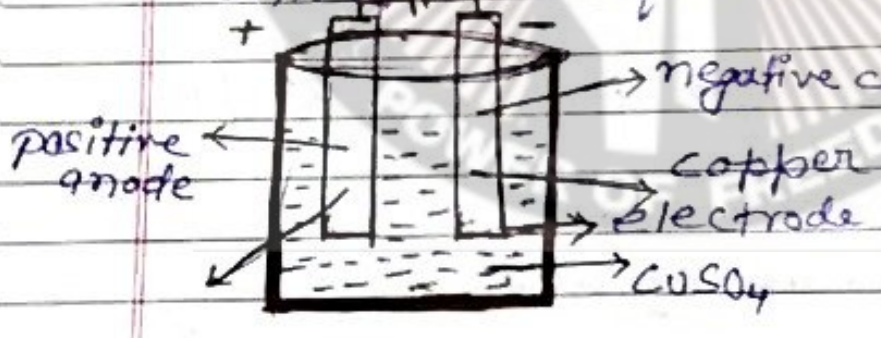

The positively charged copper ion migrate to the cathode, where each gain two electron to became copper atom that are deposited on the cathode.

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

At anode, each copper atom loses to electrons to become copper ions, which go into solution.

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

electrolysis of molten

Sodium chloride:-

Here the electrolyte is molten sodium chloride the electrodes/platinum metal are of inert nature and therefore do not undergo any chemical reaction.

#Process:-

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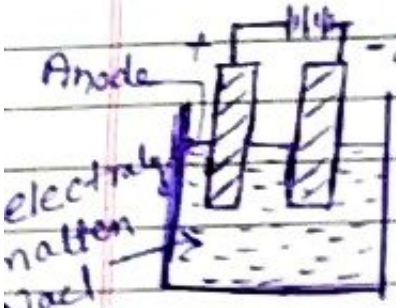
Molten sodium chloride is takes as an electrolyte in the electrolytic cell. Two platinum rods are dipped in it, which act as electrodes. They are connected to the two terminal of the battery. The electrode connected to positive terminal is "Anode and the electrode connected to negative terminal is called cathode.



On passing electricity through it Na^+ ions move towards cathode and Cl^- ions move towards Anode

Ionisation $\longrightarrow NaCl \rightleftharpoons Na^+ + Cl^-$

At anode:-

chloride ion on reaching to anode releases an electron to the electrode and a neutral atom is formed. As chlorine molecules are diatomic therefore two chlorin atom unit to give molecule of gas which evolves at anode:-

$$Cl^- \longrightarrow Cl + e^-$$
$$Cl + Cl \longrightarrow Cl_2 \uparrow$$

Anode half reaction an oxidation reaction.

At cathode :-

Na^+ ions move towards cathode accepts electron from it and get reduced (gaining of electron) and appear at the cathode in the from of sodium metal

$$Na^+ + e^- \longrightarrow Na^+$$

cathode half reaction an reduction reaction.