21.9.2020
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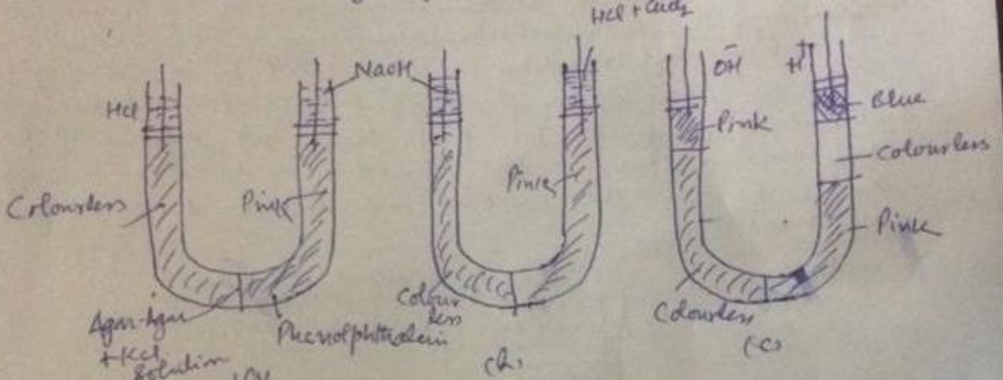
Migration of Ions

In the electrolysis, the ions present in the solution are liberated at the electrodes. This shows that ions move towards the electrodes. The movement of ions towards the oppositively charged electrodes is called migration of ions. This was demonstrated by Noyes by a simple experiment.



Migration of ions.

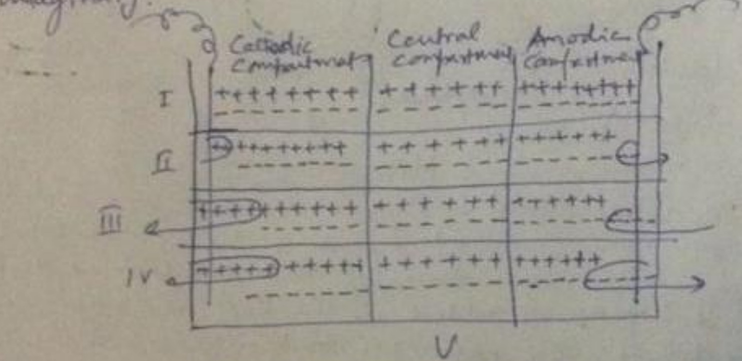
The U-tube shown in Fig.(a) is filled with a dilute solation of agar-agar containg KCl and a little phenolphthalein. KCl increases the conductance of the solution. A drop of dil HCl and dil NaOH is added in the left and right limbs, respectively. The agar-agar solution placed in the right libs becomes pink whereas the left limb remains colourless. The U-tube is cooled in ice bath for a few minutes to set the agar-agar like a jelly. The position of the boundary is marked by scattering the charcoal on each side.

Now a solution of HCl and $CuCl_2$ is poured gently on the right side limb fig(b) and a solution of NaOH on the left side. When current is allowed to flow by inserting metal electrodes in each limb, the H^+ and Cu^{++} move towards the left limb while OH^- moves towards the right limb. The movement of H^+ ions is indicated by disappearance of pink colour in the left limb and the development of blue colour in the right limb shows the movement of Cu^{++} fig(c). This experiment clearly indicates the migration of ions.

Discharge of Ions : Hittorf's Rule.

It is surprising at first look, that equivalent quantities of different ions are liberated at the two electrodes in the electrolysis of a given solution inspite of the possible differences in the speed of ions moving towards the respective electrode. This anamoly was explained by Hittorf by means of theoretical device shown in fig. V represent an electrolytic cell in which there are an equivalent number of positive and negative ions indicated by + and − signs.

The condition of the system at the commencement of electrolysis is shown in fig. There are 8 pairs of positive and negative ions in the anodic and cathodic compartment and 6 pairs in the central compartment. These compartments are imaginary.



Theoretical device of Hitrof.

Suppose that the cations only are able to move under the influence of an applied potential and that two of these ions move towards the cathode fig II. There will be two unpaired ions at the cathode and similarly two unpaired ions at the ~~respective~~ anode. These unpaired ions will get discharged at the respective electrodes. Thus the same number of cations and anions will be discharged at the cathode and anode respectively, even though only cations were able to move.

NOW let both anions and cations move and that both have the same velocity. Thus if two cations moves towards the cathode, two anions move towards the anode in the same time. Now four cations and four anions will be discharged at respective electrodes.

Suppose cations and anions move with different velocities. If while the two cations are moving in one direction, three anions are carrying electricity in the opposite direction. Five ions are to be discharged at the electrodes.

From the above discussion it is concluded:—

(a) Ions are always discharged in equivalent amounts at the electrodes irrespective of the speed of ions.

(b) The concentration of the electrolyte changes around the electrodes as a result of differances in their speed.

Transport Number

From the above discussion it is clear that the number of ions discharged at each electrode depends upon the sum of the speeds of the two ions. But according to Faradays first law of electrolysis, the number of ions discharged at an electrode is proportional to the total quantity of electricity passed through the solution. Thus.

$$\left.\begin{array}{l}\text{Total quantity of electricity}\\ \text{that passed through the solution}\end{array}\right] \propto \text{sum of speeds of the ions}$$

$$\left.\begin{array}{l}\text{The amount of electricity carried}\\ \text{by a particular ions}\end{array}\right] \propto \text{the speed of that particular ion}$$

$$\text{or}\quad \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{\cancel{\text{Fract}}\ \text{Fraction of current carried by anion}}{\text{Fraction of current carried by cation}}$$

If u_a is the speed of anion and u_c that of cation, then

$$\frac{u_a}{u_c} = \frac{\text{Fraction of current carried by anion}}{\text{fraction of current carried by cation}}.$$

$$1+\frac{u_a}{u_c} = 1+\frac{\text{fraction of current carried by anion}}{\text{fraction of current carried by cation}}$$

$$\frac{u_a+u_c}{u_c} = \frac{\text{Fraction of current carried by cation + fraction of current carried by anion}}{\text{Fraction of current carried by cation}}$$

or
$$\frac{u_c}{u_a+u_c} = \frac{\text{Fraction of current carried by a cation.}}{\text{Total current}} \quad -①$$

$$\frac{u_c}{u_a+u_c} = n_c$$

Where n_c is the transport number of cation.

The fraction of the current carried by the ions are called their transport numbers or transference numbers.

Similarly $\frac{u_a}{u_a+u_c} = n_a$.

$$n_a + n_c = \frac{u_a}{u_a+u_c} + \frac{u_c}{u_a+u_c}$$

$$\boxed{n_a + n_c = 1.} \quad — ②$$