Electrochemistry

1. Electrolyte and non-electrolyte
2. Strong electrolytes and weak electrolytes
3. Ionization and Dissociation
4. Mobility of ions
5. Transport number
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Electrolyte: An electrolyte is a compound that conducts an electric current when it is an aqueous solution or molted.

* All ionic compound are electrolytes

⇒ when ionic compounds dissolve, they break apart into ions which are then able to conduct a current.

⇒ Insolube ionic compound such as $CaCO_3$ are electrolytes.

Non-electrolyte: A non electrolyte is a compound that does not conduct an electric current in either aqueous solution or in the molten state.

Example: Many molecular compounds such as sugar or ethanol.

when these compounds dissolve in water, they do not produce ions.

Strong electrolyte: A strong electrolyte is a solution that completely or almost completely, ionizes or dissociates in a solution.

- These ions are good conductors of electric current in the solutions.

→ Strong acids, strong bases, soluble ionic salts are strong electrolytes.

Weak electrolyte: A weak electrolyte is a solution that is not completely ionizes or dissociates in a solution.

→ $HC_2H_3O_2$ (acetic acid), H_2CO_3 (carbonic acid), NH_3 (ammonia), H_3PO_4 (phosporic acid) are the examples of weak electrolytes.

Ionization: Ionization refers to the reaction in which the polar covalent compounds are converted into ions in water.

⇒ It is the process that involves the formation of ions.

⇒ It involves the creation of charges across the participating species.

Dissociation: Dissociation refers to the separation of ions which are already present in electrovalent compounds or ionic compounds.

⇒ It is the process of breaking up of a moiety into its constituent atoms, molecules and ions.

⇒ It occurs due to a weak bond between species.

Difference between ionization and dissociation:

Ionization	Dissociation
① It is the process which produces new charged particles.	① It is the separation of charged particles which already exist in a compound.
② It involves polar covalent compound or metals.	② It involves ionic compounds.
③ Irreversible	③ Reversible
④ Involve covalent bond between atoms	④ Involve ionic bonds in compound.
⑤ Always produces charged particles.	⑤ It produces either charged particles or electrically neutral particles.

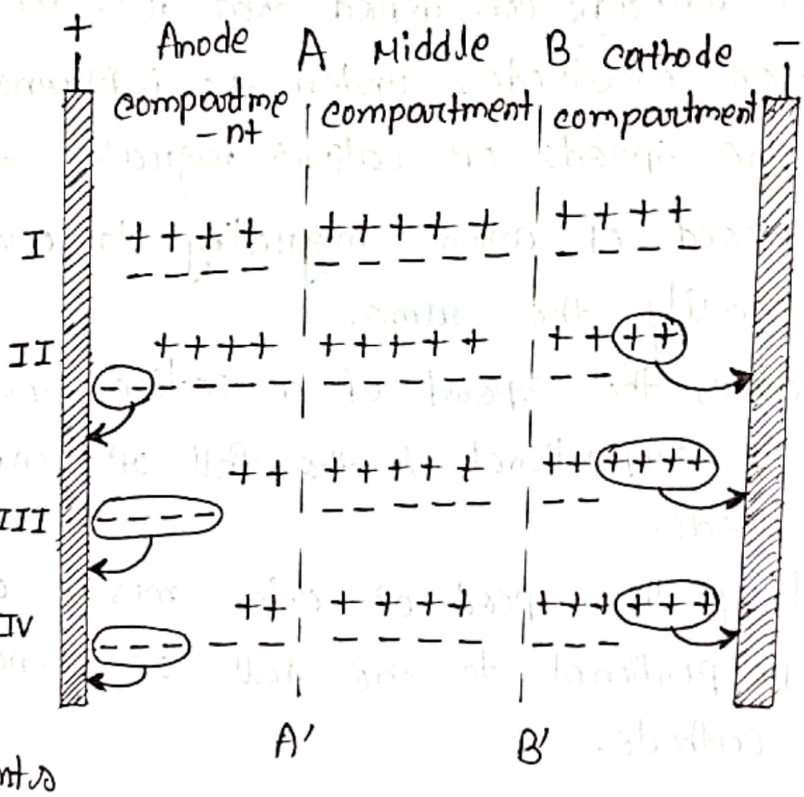
Mobility of Ions / Relative speed of ions:

It is already considered that ions move to the oppositely charged electrodes under the influence of the electric current. But the speeds of cations migrating towards the cathode and the speed of anions migrating towards the anode are not necessarily the same.
However, the speed of a cation moving away from the anode will be proportional to the fall of concentration of cations around the anode.
Similarly, the speed of anion moving away from the cathode will be proportional to the fall of concentration of anions around the cathode.

☐ Hittorf's gave a general rule is known as Hittorf's Rule.
It states that:

"The loss of concentration around any electrode is proportional to the speed of ions moving away from it."

Illustration of Hittrof's Rule:



In the figure,
A is the anode . C is the cathode.
AA' and BB' are two imaginary planes which divide the cell into three compartment.

→ Anode compartment
→ Middle compartment
→ Cathode compartment
→ The sign (+) represents a cation and ⊖ represents a anion.

Before electrolysis, let there be 13 ion-pairs in the cell. The number of ion-pairs in the two outer compartments is 4 each and there are 5 ion-pairs in the middle compartment (position I).

(i) Let the anions alone be capable of movement

When 2 anions have move towards the anode, we get the position (II). The cataions have not move at all. The number of discharged anions and cations is the same viz 2. The concentration in the anode compartment has not altered while in the cathode compartment it has fallen by two ion-pairs.

(ii) Let the anions and cations move at the same rate

When 2 ions of each type have crossed towards the opposite electrods, we get the condition shown in (III)

The number of discharged anions and cations is the same viz. 4.

Anode and cathode compartment has fallen to the same extent by 2 ion pairs.

(iii) Let the cations move at twice the speed of the anions

When cataion have moved to the cathode compartment, one anion passes into the anode compartment. This state is shown in (IV). Total number of discharged anions and cations is again same. In the concentration,

Cathode compartment has fallen by one ion-pair,

Anode compartment has fallen by two ion pairs.

Transport number: The fraction of the total electric current carried by the cation or the anion is termed its transport number or hittrof's number.

If V_+ represents the speed of migration of the cation and V_- that of the anion,

the transport number of cation $= \dfrac{V_+}{V_+ + V_-}$

the transport number of anion $= \dfrac{V_-}{V_+ + V_-}$

Transport number of the cation is represented by t_+ and that of the anion by t_-.

Thus, $t_+ = \frac{V_+}{V_+ + V_-}$

$t_- = \frac{V_-}{V_+ + V_-}$

or, $\frac{t_+}{t_-} = \frac{V_+}{V_-}$ and $t_+ + t_- = 1$

if the speed ratio V_+/V_- be denoted by r we have,

$r = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$

$\therefore t_- = \frac{1}{1+r}$

Mathematical problem

1. A solution of silver nitrate containing 12.14 g of silver in 50 ml of solution was electrolysed between platinum electrodes, After electrolytes, 50 ml of the anode solution was found to contain 11.55 g of silver, while 1.25 g of metallic silver was deposited on the cathode. Calculate the transport number of Ag^+ and NO_3^- ions.

Solution:

Weight of Ag in 50 ml of the solution before electrolysis
$= 12.14 g$

weight of Ag in 50 ml of the solution after electrolysis
$= 11.55 g$

Fall in concentration of Ag $= 12.14 - 11.55$
$= 0.59 g$
$= 0.0055 g\ eq$

weight of Ag deposited is silver coulmeter $= 1.25 g$
$= 0.0116\ geq$

Hence,
Transport number of Ag^+ (t_{Ag^+})

$$= \frac{\text{fall in conc. around anode}}{\text{No. of g. eqvt deposited in silver coulometer}}$$

$$= \frac{0.0055}{0.0116}$$

$$= 0.474$$

$\therefore$ Transport number of NO_3^- $(t_{NO_3^-}) = 1 - 0.474$
$= 0.526$

(Ans)

[2] In an electrolysis of copper sulphate between copper electrodes the total mass of copper deposited at the cathode was 0.153g and the masses of the anode liquid of copper per unit volume of the anode liquid before and after electrolysis were 0.79 and 0.91 g respectively. Calculate the transport number of Cu^{2+} and SO_4^{2-} ions.

Solutions:

Wt. of copper in the anode liquid before electrolysis = 0.79 g
Wt. of copper in the anode liquid after electrolysis = 0.91 g

$$\text{Increase in weight} = 0.91 - 0.79 = 0.12\ g$$

Increase in weight of copper cathode in coulmeter = 0.153 g

This means that if no copper had migrated from the anode, increase in weight would have been 0.153 g

$$\text{But actual increase} = 0.12$$

Fall in concentration due to migration of Cu^{2+}

$$\text{ion} = 0.153 - 0.12 = 0.033$$

$$\therefore \text{Transport number of } Cu^{2+} \text{ ion} = \frac{0.033}{0.153} = 0.215$$

$$\therefore \text{Transport number of } SO_4^{2+} \text{ ion} = (1 - 0.215) = 0.785$$

Example. The speed ratio of silver and nitrate ions in a solution of silver nitrate electrolysed between silver electrodes is 0.916. Find the transport number of the two ion.

Solution :

We know that
$$t_{-} = \frac{1}{1+r}$$

where t_{-} is the transport number of the anion and r is the speed ratio of the anion and the cation.

$$\therefore \qquad t_{NO_3^-} = \frac{1}{1+0.916} = 0.521$$

and
$$t_{Ag^+} = 1 - t_{NO_3^-} = 1 - 0.521$$
$$= 0.479$$