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1. Learning Outcomes

In this module,

- You shall learn about the information regarding the concept of transport number.
- You shall learn about migration of ions and determination of transport number using moving boundary method.

2. Introduction: Migration of ions

Arrhenius studied the conduction of current through aqueous solutions of electrolytes. According to Arrhenius, the conductivity of solutions is due to the presence of ions. Electrolyte molecules are split up into positively charged ions (cations) and negatively charged ions (anions). These charged ions are free to move through the solution to the oppositely charged electrodes. As the current is passed between the electrodes of the electrolytic cell, the ions migrate to the opposite electrodes. Usually ions move with different speeds. The migration of ions through the electrolyte solution can be demonstrated by the electrolytic conductors.

When current is passed through a solution of an electrolyte, positive ions move towards the negative electrode and negative ions move towards the positive electrode and current is carried (transported) by the migration of ions present in the solution. As cations and anions move with different speeds due to difference in size, hydration and charge, the fraction of the total current carried by each ion will not necessarily be the same. The faster moving ions will carry a greater fraction of the total current. For example, in dilute solutions of lithium chloride, the lithium ion carries 0.33 of the total current while the faster moving chloride ion carries the balance i.e. 0.67 of the total current. Similarly, in dilute solutions of hydrochloric acid, faster moving H^+ ion carries 0.82 of the total current while Cl^- ion carries only 0.18 of the total current.

3. Transport number

The quantitative relationship between the fraction of the current carried by an ion and its speed is expressed in terms of transport number.

If, u_+ = the speed of the cation and

u_- = the speed of the anion

Then, the current carried by cation $\propto u_+$

the current carried by anion $\propto u_-$.

$\therefore$ total current carried by both the ions $\propto u_+ + u_-$

The fraction of the total current carried by cation,

$$t_+ = \frac{\text{Current carried by the cation}}{\text{Total current carried}} \quad \dots (1)$$

i.e. $t_+ = \frac{u_+}{u_+ + u_-}$

and the fraction of the total current carried by the anion

$$t_- = \frac{\text{Current carried by the anion}}{\text{Total current carried}}$$

$$t_- = \frac{u_-}{u_+ + u_-} \quad \dots (2)$$

where, t_+= the transport number of the cation and

t_- = the transport number of the anion

The above equations (13 and 14) hold good for a strong binary electrolyte which yields equal number of positive and negative ions (e.g. $AgNO_3$, NaCl, $CuSO_4$ etc.) in a solution.

Definition : *Hence the transport number (or transference number or Hittorf number) of an ion is defined as the fraction of the total current carried by that ion.*

Since the two ions carry between them all the current, the sum of the two transport numbers must be unity.

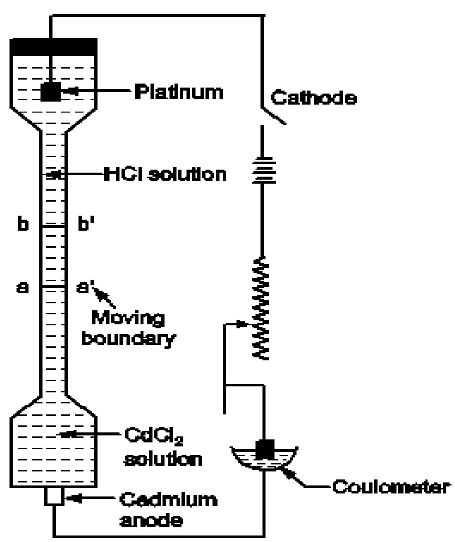
i.e. $t_+ + t_- = 1$ … (3)

If the transport number of the cation is known then by subtracting it from unity, the transport number of the corresponding anion can be determined and vice versa.

4. Determination of Transport number: Moving boundary method

Principle :

A sharp boundary between two electrolyte solutions, having different cations (+ve ions), moves towards the cathode when it is subjected to an electric field. By observing the volume swept by the moving boundary for a given quantity of electricity passed through the cell, it is possible to calculate the transport number of the cation of the solution into which the boundary moves.



Experimental Procedure : In this method, the cell consists of a long vertical tube of uniform bore. (Fig. 1.9). Suppose that we have to determine the transport number of H^+ ion. The cell is filled with cadmium chloride and hydrochloric acid solutions as shown in Fig. 1.9. Hydrochloric acid is called the principal electrolyte and cadmium chloride is called the indicator electrolyte. The concentrations of the solutions are so adjusted that HCl solution is lighter than $CdCl_2$ solution. Therefore HCl solution floats over the $CdCl_2$ solution and a sharp boundary appears between the two solutions. Here $CdCl_2$ is taken as the indicator electrolyte because its cation (Cd^{++}) does not move faster than the cation (H^+) whose transport number is to be determined and also it has the common anion (Cl^-) with hydrochloric acid.

The anode is a stick of cadimium metal. It is inserted at the bottom. The cathode is a platinum foil. It is inserted at the top. When a small current is passed through the cell, cadmium dissolves at the anode, hydrogen is evolved at the cathode, Cl^- ions move towards the anode and H^+ ions move towards the cathode. As hydrogen ions move towards the cathode, their place is taken by cadmium ions and hence the boundary between the two solutions also moves upward.

Calculations : Suppose the boundary moves through a distance *l* cm, say from aa' to bb'. Then the volume of the liquid has been moves up is *l*a cc where a is the cross-sectional area of the tube in sq. cm. If the concentration of the acid is c gram equivalents per litre then the number of gram equivalents of H^+ ions carried towards the cathode = $\frac{lac}{1000}$.

Since one gram equivalent or one equivalent material carries one Faraday electricity, the electricity carried by $\frac{lac}{1000}$ gram equivalent H^+ ions = $\frac{lac}{1000}$ Faradays = $\frac{96500\ lac}{1000}$ Coulombs

(F, 1 Faraday = 96500 Coulombs)

Suppose the total electricity that flows in the same time as measured in a coulometer included in the circuit is Q coulombs. Then the transport number of H^+ ions is given by

$$t_{H^+} = \frac{96500\ lac}{1000\ Q} \quad \ldots (4)$$

If I = current in amperes and

t = time in seconds

then, $Q = I\,t$

$$\therefore \quad t_{H^+} = \frac{96500\ lac}{1000\ I\ t} \text{ and } t_{u^-} = 1 - t_{H^+} \qquad \ldots (5)$$

5. Summary

- Migration of ions is very important concept in electrochemistry.
- Transport number denotes the fraction of total current carried by that ion.
- The summation of fraction of total current carried by the cation and anion is always unity.
- Moving boundary method is reliable method for the determination of transport number.

Video 1:
https://drive.google.com/file/d/1AVwv8NugIMezcnfeWm77fgnlKaTgwW47/view?usp=sharing

Video 2:
https://drive.google.com/file/d/1acjwSFAfSTEL0HjhlviScPIZH_oT7GKB/view?usp=sharing

Video 3:
https://drive.google.com/file/d/1H-uzDVBU1QIMxFTjMaHfrHZW2WYL6Lk4/view?usp=sharing

Assignment:
https://forms.gle/iGhRnowsZ5Gn3wiHA

Know more:

Suggested readings, web links

1. https://en.wikipedia.org/wiki/Ion_transport_number#:~:text=invalidated%20the%20results.-,Moving%20boundary%20method,influence%20of%20an%20electric%20field
2. https://www.emedicalprep.com/study-material/chemistry/electrochemistry/transport-number-transference-number/