



Electrochemistry

**(Transport Number, Hittorf's Method,
Moving Boundary Method)**

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Transport number

During electrolysis, the current carried by the anions and cations, and the amount carried by each is proportional to its speed.

If u and v represents the speed of migration of the cation and anion, then $\frac{u}{u+v}$ represents the fraction of current carried by the cation, and $\frac{v}{u+v}$ represent the fraction of current carried by the anion, and is called its transport number or Hittorf's number. It is denoted by symbols like t_+ and t_-

Hence,

$$\text{Transport number of cation } (t_+) = \frac{\text{Current carried by the cation}}{\text{Total current}}$$

$$\text{Transport number of the cation } (t_+) = \frac{u}{u+v}$$

Transport number

Transport number of cation (t_+)

$$t_+ = \frac{u}{u + v}$$

Similarly, the transport number of anion (t_-) is given by

$$t_- = \frac{v}{u + v}$$

The fraction of the total current carried by the ions is directly proportional to their velocities (Hittorf's rule).

$$t_- + t_+ = 1$$

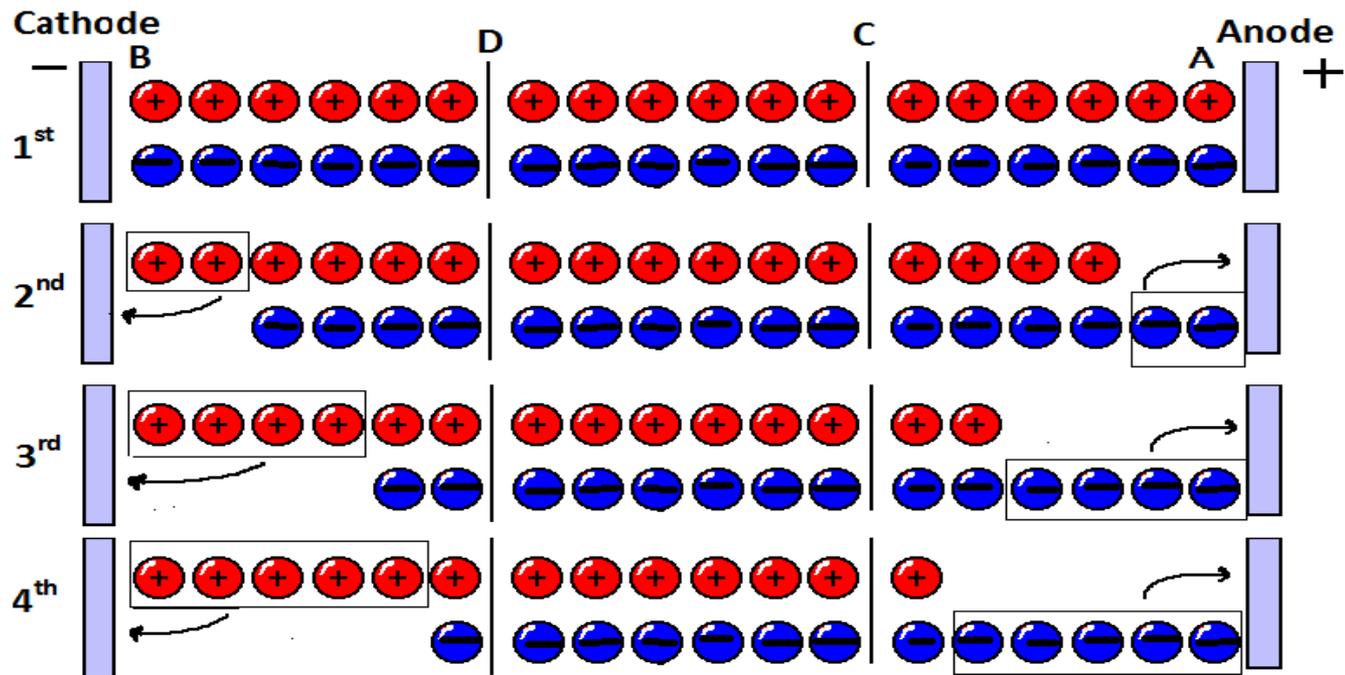
Determination of Transport Number

The are two methods for determination of transport number

1. **Hittorf's Method**
2. **Moving Boundary Method**

Relative speed of ions during electrolysis

- Let us consider a electrolytic vessel containing two metal electrodes A and B. The vessel is divided into three compartments AC, CD and DB, termed as anodic, central and cathodic compartments respectively.



Relative speed of ions during electrolysis

- Before electrolysis, the position of the solution is represented as (1st) in the diagram. Now, suppose that on applying potential, only two of the cations move towards the cathode. This condition will be as represented in the diagram in 2nd. There will be two unpaired cations in the cathodic compartment. There will also be two unpaired anions left in the anodic compartment. As unpaired ions always get discharged at the respective electrodes (by the gain or loss of electrons as the case may be), two cations will be discharged at the cathode and two anions will be discharged at the anode.

Relative speed of ions during electrolysis

- Now suppose that if two cations move towards the cathode and two anions will move towards the anode in the same time as represented by 3rd. Now four cations and four anions will be discharged at the respective electrodes.
- Finally, If cations and anions move with different velocities so that two cations move towards the cathode, and three anions move towards the anode. In this case, five unpaired cations and five unpaired anions (i.e the same number) will be discharged at the respective electrodes as shown at 4th in the diagram.
- Thus, Even if only cations are moving, the same number of cations and anions will be discharged, at the respective electrodes.

Hittorf's Rule

It is based on the fact that during electrolysis “the loss in amount of electrolyte around any electrode is proportional to the speed of the ion moving away from it”

$$\frac{\text{loss around cathode}}{\text{loss around anode}} = \frac{\text{speed of anion}}{\text{speed of cation}} = \frac{v}{u}$$

Adding 1 to both sides we get

$$1 + \frac{\text{loss around cathode}}{\text{loss around anode}} = 1 + \frac{v}{u}$$

$$\frac{\text{loss around anode} + \text{loss around cathode}}{\text{loss around anode}} = \frac{u + v}{u}$$

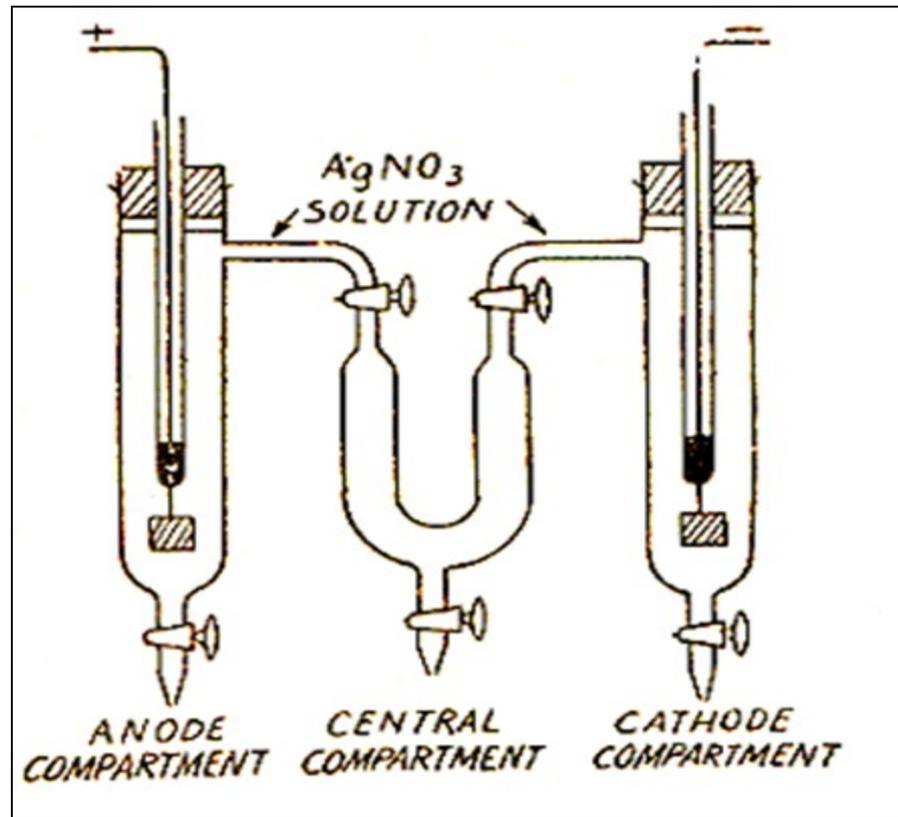
Taking the reciprocal, we get

$$\frac{\text{loss around anode}}{\text{Total loss}} = \frac{u}{u + v} = t_+$$

Hittorf's Method (Experimental procedure)

- Hittorf's apparatus consists of a two limbed vessel, connected by a narrow U-tube in the middle. Both limbs as well as the U-tube are provided with stop-cocks at the bottom for the withdrawal of the solution.
- The two limbs are provided with Pt electrodes. To determine the transport numbers of Ag^+ in AgNO_3 the electrodes are either of Pt or pure Ag.
- The apparatus is filled with a standard solution of AgNO_3 (usually 0.1N) and the cell is connected in series with a source of direct current (like battery).

Hittorf's Method

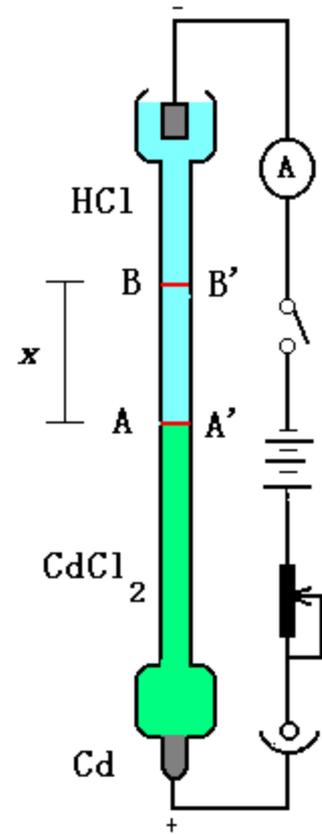


Hittorf's Method

- After the electrolysis, the solutions from anodic as well as central compartments are withdrawn separately by opening stop-cocks at the bottom and analysed by titration with standard ammonium thiocyanate (NH_4CNS) solution.
- The change in amount of electrolyte in the anode compartment is thus obtained.
- The amount of solution withdrawn from anode for analysis should include all the solution, whose composition has changed. This can be checked by withdrawing a further portion of solution from the anode limb, and finding whether it has the same composition as the original AgNO_3 solution or not.
- Thus, solution left after withdrawal from it must be of starting (or initial) concentration.

The moving boundary method

- This method is based on the direct observation of migration of ions in an electric field. The conductivity cell, in this method consists of a vertical tube filled with cadmium chloride and hydrochloric acid.
- HCl is the principal electrolyte, and CdCl_2 serves as the indicator electrolyte to enable formation of a boundary.



The moving boundary method

- The concentrations of the solutions are so adjusted that hydrochloric acid floats over cadmium chloride, since HCl is lighter than the cadmium chloride solution.
- A sharp boundary appears between the two solutions. The selection of the indicator electrolyte is done carefully, so that its cation do not move faster than the cation whose transport number is to be determined, and it should have the same anion as the principal electrolyte; cadmium chloride fulfills both the requirements.
- The mobility of cadmium ions is less than that of hydrogen ions and it has a common anion with hydrochloric acid.

The moving boundary method

- The anode is a stick of cadmium metal inserted at the bottom, while the cathode at the top is a platinum foil.
- When a small current is made to flow through the conductivity cell, the anions (chloride ions) move towards the anode while, cations (hydrogen ions followed by cadmium ions) move towards the cathode.
- The boundary separating the two solutions also moves upwards and if the boundary moves through a distance l cm (say, from AA' to BB') then the volume of the liquid that has moved up is lA cm³. Let the concentration of the acid be C gram equivalents per litre
- Then the number of gram equivalents of H⁺ ions carried towards the cathode = $\frac{lAC}{1000}$

Thank you

