TDC-2

Transport Number or Transference number :-

It has been observed that no. of ions discharge on both electrode is directly proportional to the sum of the speed of the two ions.

But a/c to faraday's law of electrolysis -

"The total no of ions discharged is directly proportional to the total quantity of electricity passed."

Hence,

Total quantity of electricity passed $\propto$ Sum of the speed of the two ions.

or Electricity carried by a particular ion $\propto$ speed of that ions.

or $$\frac{\text{speed of the cation } (U_c)}{\text{speed of the anion } (U_a)} = \frac{\text{Electricity carried by cation}}{\text{Electricity carried by anion}}$$

or $$1 + \frac{U_c}{U_a} = 1 + \frac{\text{Electricity carried by cation}}{\text{Electricity carried by anion}}$$

or $$\frac{U_a + U_c}{U_a} = \frac{\text{Electricity carried by anion} + \text{Electricity carried by cation}}{\text{Electricity carried by anion}}$$

or $$\frac{U_a}{U_a + U_c} = \frac{\text{Electricity carried by anion}}{\text{Total quantity of electricity}}$$

$$\text{or} \quad \frac{U_a}{U_a + U_c} = n_a \text{ or } t_-$$

Where, n_a or t_- is the transport no. of anion.

$$n_a = \frac{\text{Electricity Carried by anion}}{\text{Total quantity of electricity}}$$

So, Transport no. of anion or cation may be defined as the fraction of electricity carried by anion or cation respectively.

Then,

$$n_c \text{ or } t_+ = \frac{U_c}{U_a + U_c} = \frac{\text{Electricity carried by cation}}{\text{Total quantity of electricity}}$$

hence, $n_a + n_c = 1$

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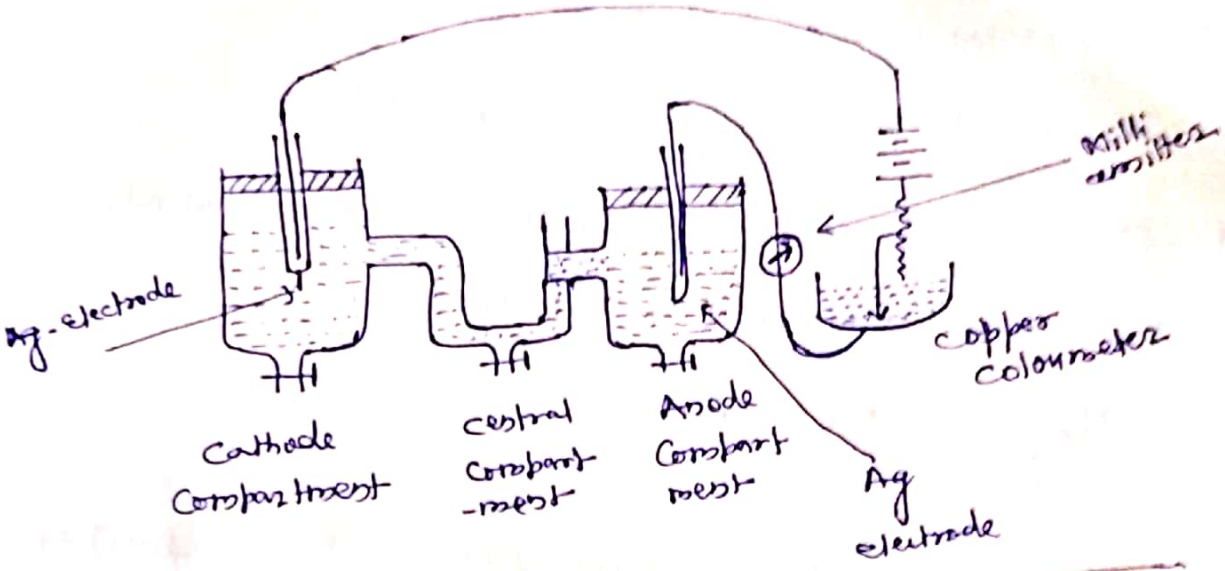
Experimental determination of transport number by Hittorf's method —

Let us suppose that the transport no of silver ion in silver nitrate ($AgNO_3$) is to be determined. The electrodes are made them either of Pt or pure Ag and the electrolyte is dilute solution of $AgNO_3$.



The Concentration of $AgNO_3$ should be maintained constant in the middle Compartment. The experiment is completed in the following steps —

(1) The $AgNO_3$ sols of known Concentration is filled in the apparatus.

(2) A Current of 10 to 20 milli amperes is passed for about 2 to 3 hours. An appreciable change in Concentration around the electrode is avoided to prevent the diffusion. The total amount of electricity passed is measured by Coulometer.

(3) Solution from cathode and anode Compartment is drained in to a beaker and the weight of the sol

Contd. —

– is noted. Solution is titrated by NH_4CNS (Ammonium thio cyanate). The amount of the electrolyte in the same weight of water before and after electrolysis, loss in the electrode compartment is obtained.

Calculation :-

Let 'No' be the no. of equivalents of the ions taken in the given compartment and 'Nf' be the no. of equivalence present after electrolysis.

(a) If the electrodes are not attacked –

If it is used as electrode, there is no electrode reaction, then the transport no. of Ag^+ –

$$n_{Ag^+} = \frac{No - Nf}{Ne}$$

where Ne is the no. of equivalent of Ag deposited in a Coulometer.

(b) If the electrodes are attacked –

If Ag electrode is used NO_3^- attacked the Ag-electrode bringing Ag^+ in to the anodic compartment & hence the concentration of Ag will be increased.

Hence, decrease in concentration will be –

$$No + Ne - Nf$$

$$n_{Ag^+} = \frac{No + Ne - Nf}{Ne}$$

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