Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Second Year)

Subject: Chemistry

Paper Code: CHC-103

Paper Title: Physical Chemistry and Organic Chemistry

Unit: Conductance

Module Name: Transference number and its experimental

determination using moving boundary methods

Module No: 19

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Notes:

<u>Transference number or transport number</u>

Number of ions discharged at each electrode depends upon the sum of speed of the cation and anions.

The quantity of electricity carried by each ion is directly proportional to the speed of the concerned ion.

So,

Amount of electricity carried by anion α speed of anion (μ_a)

Amount of electricity carried by cation α speed of cation (μ_c)

Total amount of electricity carried α speed of anion + speed of cation

 $\alpha \quad (\mu_a) \qquad \qquad + \qquad (\mu_c)$

Transport number of an ion is defined as "the fraction of the total electricity or current carried by that ion"

Designated as t

Transport number of anion, ta

 $= \frac{Amount of electricity carried by anion}{total electricity passed}$

$$=\frac{(\mu_a)}{(\mu_a)+(\mu_c)}$$

Similarly, transport number of cation , $t_{\text{\tiny c}}$

$$= \frac{Amount of electricity carried by Cation}{total electricity passed}$$

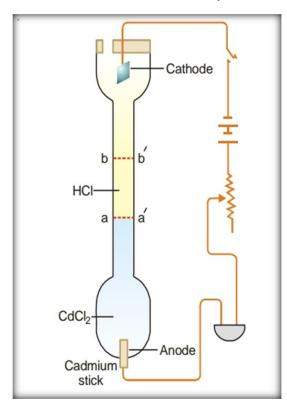
$$=\frac{(\mu_c)}{(\mu_a)+(\mu_c)}$$

$$T_a + t_c = \frac{(\mu_a)}{(\mu_a)+(\mu_c)} + \frac{(\mu_c)}{(\mu_a)+(\mu_c)} = 1$$

So if the transport number of one is known that of the other can be calculated.

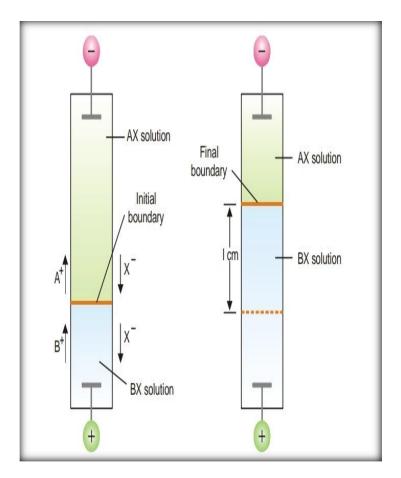
Determination of transport number using moving boundary method Experiment: To determine the transport number of H⁺ ion in solution of HCl.

- The conductivity cell in this method consists of a vertical tube of uniform bore filled with cadmium chloride and hydrochloric acid.
- Hydrochloric acid is the principal electrolyte while cadmium chloride serves as indicator electrolyte to enable the formation of boundary.



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- The concentration of the solution are so adjusted that hydrochloric acid solution is lighter than the cadmium chloride solution and therefore, floats over the cadmium chloride solution.
- A sharp boundary appears between the two solutions.
- The selection of the indicator electrolyte has to be made carefully.
- Its cation should 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 fulfils both these requirements.
- The mobility of cadmium ion is less than that of hydrogen ion and it has a common anion with hydrochloric acid.
- The anode at the bottom is of cadmium metal while the cathode at the top is of Pt foil.
- When small current passes through the conductivity cell, the chloride ions move towards the anode while hydrogen ions followed by cadmium ions move towards cathode.
- The boundary separating the two solution moves upwards.
- If boundary moves through distance I cm then the volume of the liquid that has moved up is IA cm³ where A is the cross sectional area of the tube in cm²



Let the concentration of the acid be C gram equivalent per litre,

Then the number of gram equivalent of H⁺ ions carried towards the cathode = $\frac{IAC}{1000}$

Since each gram equivalent carries one faraday of electricity, the electricity carried by H⁺ ions = $\frac{IAC}{1000}$ Faradays

$$Q = \frac{Weight of substance deposited= W}{equivalent weight} Eq wt$$

Since the total quantity of electricity that flows in the same time as measured in a coulometer is equal to Q Faradays then,

Transport number of H+ =
$$\frac{IAC}{1000 \, Q}$$

$$Q = \frac{It}{F}$$