

## Transport number

The fraction of the total current carried by one of the ionic species is known as transport number or transference number or Hittorf's number.

$$\text{Transport number of anion } (t_-) = \frac{\text{Current carried by anion}}{\text{Total current passed through the solution}}$$

$$\text{Transport number of cation } = \frac{\text{Current carried by cation}}{\text{Total current passed through the solution}}$$

But we know that the quantity of electricity carried by each ion is directly proportional to the speed of the concerned ion.

So, the amount of electricity carried by anion  $\propto$  speed of anion ( $u_a$ )  
Amount of electricity carried by cation  $\propto$  speed of cation ( $u_c$ )

$\therefore$  Total amount of electricity carried  $\propto$  speed of anion + speed of cation  
 $\propto u_a + u_c$

$$\text{Thus, transport number of anion } (t_-) = \frac{u_a}{u_a + u_c}$$

$$\text{and transport number of cation } (t_+) = \frac{u_c}{u_a + u_c}$$

$$t_- + t_+ = \frac{u_a}{u_a + u_c} + \frac{u_c}{u_a + u_c}$$

$$t_- + t_+ = \frac{\cancel{u_a + u_c}}{u_a + u_c}$$

$$\boxed{t_- + t_+ = 1} \quad \text{--- (1)}$$

From equation (1) we see that

(i) The sum of the transport numbers of all species taking part in the transport of electricity is equal to unity.

and (ii) If the transport number of the one of the ionic species is known then that of other can be easily calculated by equation

$$\boxed{t_+ + t_- = 1}$$

①

## Experimental determination of transport number

- ① Hittorf's method
- ② Moving boundary method
- ③ EMF method.
- ④ From ionic mobility.

### ① Hittorf's method.

#### Principle.

This method is based on the principle that "During electrolysis, the fall in concentration around the electrode is directly proportional to the speed of ions moving away from that electrode".

Thus, fall in concentration around cathode  $\propto$  speed of anion ( $u_a$ )  
and fall in concentration around anode  $\propto$  speed of cation ( $u_c$ )

$$\therefore \frac{\text{fall in concentration around cathode}}{\text{fall in concentration around anode}} = \frac{u_a}{u_c}$$

$$\text{or, } 1 + \frac{\text{fall in concentration around cathode}}{\text{fall in concentration around anode}} = 1 + \frac{u_a}{u_c}$$

$$\text{or, } \frac{\text{fall in concentration around anode} + \text{fall in concentration around cathode}}{\text{fall in concentration around anode}} = \frac{u_c + u_a}{u_c}$$

$$\frac{\text{Total fall of concentration}}{\text{fall in concentration around anode}} = \frac{u_c + u_a}{u_c}$$

$$\text{or, } \frac{\text{fall of concentration around anode}}{\text{Total fall of concentration}} = \frac{u_c}{u_c + u_a} \quad \text{--- (1)}$$

But we know that,

$$\text{transport number of cation } (t_+) = \frac{u_c}{u_c + u_a} \quad \text{--- (2)}$$

From eq<sup>n</sup> (1) and eq<sup>n</sup> (2) we get -

$$\frac{\text{fall of concentration around anode}}{\text{Total fall of concentration}} = t_+ \quad \text{--- (3)}$$

(2)

similarly,

Fall of concentration around cathode.

Total fall of concentration

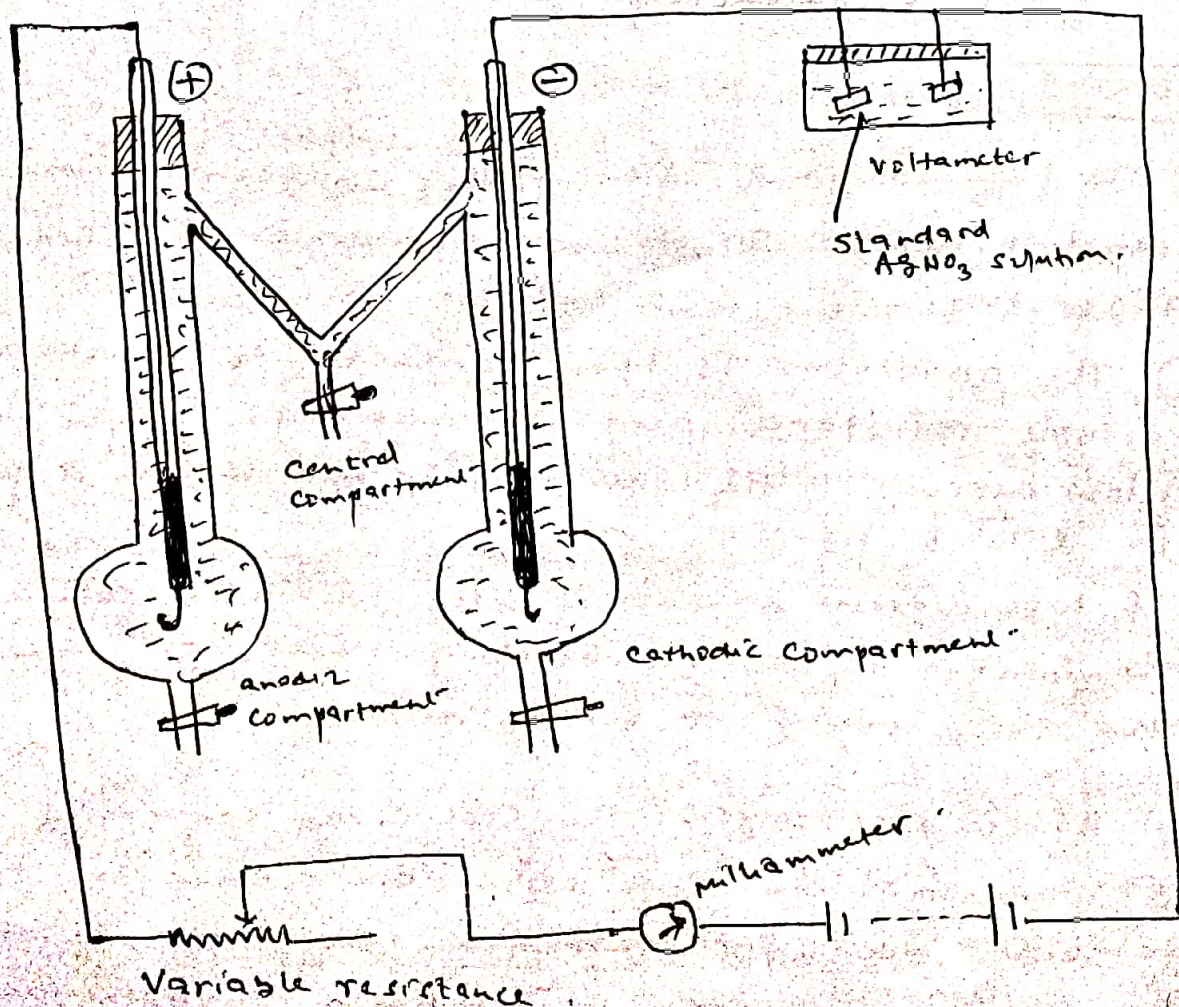
$$= t_- \quad \text{--- (4)}$$

### Important points

- (i) equations (3) and (4) are valid only if the electrodes are not attacked by ions in solution.
- (ii) if anode is attacked by anions, there will be an increase in the concentration around the anode instead of decrease. However, this increase in concentration at anode is equal to decrease in concentration that would have taken place if the anode were inert.

Suppose we have to determine transport number of  $Ag^+$  and  $NO_3^-$  ions in a solution of  $AgNO_3$

### Apparatus



(3)

- (i) Apparatus consists of two vertical glass tube connected by a V-tube in the middle. The end tubes containing the anode and cathode constitute the anodic and cathodic compartment respectively. and V-tube constitutes the central compartment.
- (ii) The tubes are provided with the stop cocks at the bottom.
- (iii) The electrodes are made of suitable metal (attackable or non-attackable) and sealed in glass tube which pass through rubber stopper. Some mercury is also placed in the glass tube to ensure proper contact.
- (iv) The apparatus is filled with a standard solution of silver nitrate.
- (v) In addition to this apparatus, the circuit also contain a silver voltmeter or an ammeter for determining the total electricity passed. The voltmeter contains standard  $\text{AgNO}_3$  and platinum electrodes.

### Working.

- (i) The  $\frac{N}{10}$  solution of salt ( $\text{AgNO}_3$ ) containing ions whose transport number are to be determined is filled in apparatus.
- (ii) The apparatus is then connected to a battery, variable resistance and Voltmeter in series. A low current of the order of 1-20 milliamperes is passed for 2 to 3 hours. If high current density is used, diffusion sets in and the solution in the various compartments are mixed and thus leading to wrong results.
- (iii) After electrolysis the stop cocks connecting the V-tube with the side tubes are opened and the solutions are withdrawn from the various compartments separately. The concentration is determined by titration against  $\text{KCN}$  solution. There

(4)

should be no change in the concentration of the solution from V-tube i.e. central compartment.

Knowing the original concentration of solution taken, the change in concentration is determined separately.

(iv) The weight of Ag deposited in voltmeter is also determined separately. This represents the total quantity of electricity passed through the electrolysis.

### Calculation.

When electrodes are unattackable.

This can be done by using platinum electrodes.

Let (i) weight of  $AgNO_3$  in 'a' gram of anode solution before electrolysis = x gram.

(ii) The weight of  $AgNO_3$  in b gram of anode solution after electrolysis = y gram.

(iii) wt. of  $AgNO_3$  in 'a' gram of anode solution after electrolysis =  $\frac{y}{b} \times a = z$  (let)

$\therefore$  fall in concentration around anode =  $(x - z)$  gram.

Let weight of Ag deposited in voltmeter = w gram.

$$\therefore \frac{\text{Total weight of } AgNO_3 \text{ electrolysed}}{\text{weight of Ag deposited in voltmeter}} = \frac{\text{Eq. wt. of } AgNO_3}{\text{Eq. wt. of Ag}}$$

$$\frac{\text{Total weight of } AgNO_3 \text{ electrolysed}}{w} = \frac{170}{108}$$

$$\text{Total weight of } AgNO_3 \text{ electrolysed} = \frac{170}{108} \times w = w' \text{ (let)}$$

Now, transport number of  $Ag^+$  is given by

$$t_{Ag^+} = \frac{\text{Loss in weight of } AgNO_3 \text{ around anode}}{\text{Total weight of } AgNO_3 \text{ electrolysed}}$$

(5)

$$t_{Ag^+} = \frac{X-Z}{W}$$

and transport number of  $NO_3^-$  ion is given by.

$$t_{NO_3^-} = 1 - t_{Ag^+} = 1 - \frac{X-Z}{W}$$

When electrodes are attackable.

This can be obtained by using Ag anode in  $AgNO_3$  solution.

In this case  $Z > X$  i.e. concentration of  $AgNO_3$  in the anodic compartment after electrolysis is more than that before electrolysis. This is due to fact that  $NO_3^-$  ions after losing charge at the anode attack the silver anode to form  $AgNO_3$ . Thus, concentration of  $AgNO_3$  in the anodic compartment increases.

The fall in concentration of  $AgNO_3$  in the anodic compartment due to migration of  $Ag^+$  ions may be calculated as -

$$\begin{aligned} \text{Amount of } AgNO_3 \text{ formed by the discharge of } NO_3^- \text{ ions} \\ \text{at anode} &= n \cdot \text{no. of } NO_3^- \text{ ions discharged} \\ &= \text{Total } AgNO_3 \text{ electrolysed} = W (\text{let}) \end{aligned}$$

$$\therefore \text{actual increase in concentration of anodic compartment} = W$$

$$\text{But observed increase in concentration of anodic compartment} = Z - X$$

$$\begin{aligned} \therefore \text{Fall in concentration due to the migration of } Ag^+ \text{ ions} \\ = \text{actual increase} - \text{observed increase.} \end{aligned}$$

$$= W - (Z - X)$$

$$\text{Hence } t_{Ag^+} = \frac{W - (Z - X)}{W}$$

$$\begin{aligned} t_{NO_3^-} &= 1 - t_{Ag^+} = 1 - \frac{W - (Z - X)}{W} \\ &= \frac{W - W + Z - X}{W} = \frac{Z - X}{W} \end{aligned}$$

## Moving Boundary Method

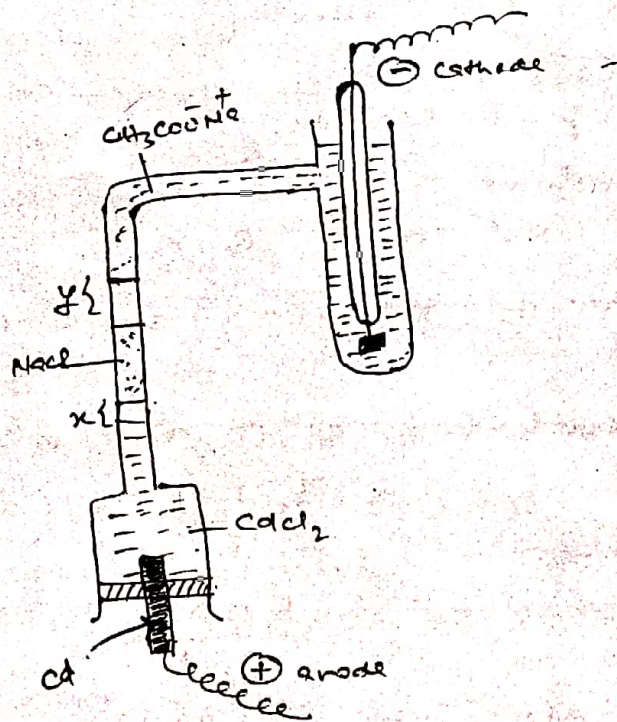
Suppose we have to determine transport number of  $\text{Na}^+$  in  $\text{NaCl}$ . To do it we have to select another suitable electrode called the indicator electrolyte which has a common ion with electrolyte under investigation. We take  $\text{CdCl}_2$  as indicator electrolyte.

The concentrations of solutions are so adjusted that  $\text{NaCl}$  solution is lighter than the  $\text{CdCl}_2$  solution.

Therefore  $\text{NaCl}$  solution floats over the  $\text{CdCl}_2$  solution.

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 same anion as the principle electrolyte.  $\text{CdCl}_2$  fulfils both these requirements. The mobility of cadmium ion is less than that of  $\text{Na}^+$  ion and it has a common anion with  $\text{NaCl}$ .

The anode at the bottom is of cadmium metal while cathode at the top is a platinum foil. Over the solution of  $\text{NaCl}$  a less dense solution of  $\text{CH}_3\text{COONa}$  is floated.



When constant current is passed for 5 to 6 hours. The  $\text{Na}^+$  ions move upwards towards cathode closely followed by the  $\text{Cd}^{2+}$  ions. The sharp boundary moves

gradually upwards. The movement of boundary between NaCl and  $\text{CdCl}_2$  can be easily followed on account of difference in the refractive indices of the two solutions.

The migration of  $\text{Cl}^-$  ions can also be observed as the acetate ions are slow moving than the chloride ions.

At the end of experiment, the distance through which the boundary has moved is noted. The time for which the current has passed is noted.

Let a current of  $I$  ampere is passed for  $t$  seconds, the quantity of electricity carried by  $\text{Na}^+$  ions is given by  $t_+ I t$  Coulombs, where  $t_+$  is transport number of cation,  $\text{Na}^+$  ion.

Let concentration of NaCl solution =  $c$  gm. equiv./c.c.  
cross sectional area of moving boundary  
=  $a$   $\text{cm}^2$

$$\therefore \text{amount of } \text{Na}^+ \text{ ion that migrated upwards} = \frac{t_+ I t}{F} \quad \text{--- (1)}$$

where  $F$  = Faraday.

Distance by which NaCl -  $\text{CdCl}_2$  boundary moving during  $t$  seconds =  $x$  gm. cm.

$\therefore$  volume of solution cleared by the migration of  $\text{Na}^+$  ion =  $a \cdot x$

$$\text{Number of gm. equiv. of } \text{Na}^+ \text{ ions transported} = a \cdot x \cdot c \quad \text{--- (2)}$$

According to eq<sup>n</sup> (1) and eq<sup>n</sup> (2) we have

$$a x c = \frac{t_+ I t}{F}$$

$$t_+ = \frac{F a x c}{I t} \quad \text{--- (3)}$$

$$\text{Similarly } t_- = \frac{F a y c}{I t} \quad \text{--- (4)}$$

where  $y$  is the distance by which NaCl -  $\text{CH}_3\text{COONa}$  boundary moves during  $t$  second and  $t_-$  is the transport number of  $\text{Cl}^-$  ion.