

TRANSPORT NUMBER

311
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TRANSPORT NUMBER: (Migration of Ions)

The fraction of current the total current carried by a charged species is known as transport No., or TRANSFERENCE NO., or HITTORF'S NO., t_+ & t_- or $t_+ & t_-$ or $\eta_+ & \eta_-$

Ex. HNO₃ - NO₃⁻ ions carry only 16% of the total current & the rest by H⁺, i.e. 84%.
62% of the current. From the above definition

$$t_- = \frac{\text{Fraction of current carried by anions}}{\text{Total current passed thro electrolyte}}$$

and

$$t_+ = \frac{\text{Fraction of current carried by cations}}{\text{Total current passed thro electrolyte}}$$

From the defn

But the amt. of current transported or carried dep. is directly proportional to the speed of the ions

Thus amt. of current carried by anion \propto speed of anion (u_a)
 " " " " cation \propto " cation (u_c)
 Total " " \propto speed of anion + speed of cation
 $\propto (u_a + u_c)$

$$t_+ = \frac{u_a}{u_a + u_c} \dots (1)$$

$$t_+ = \frac{u_c}{u_a + u_c} \dots (2)$$

Adding eqⁿs (1) & (2)

$$t_+ + t_- = \frac{u_a + u_c}{u_a + u_c} = 1$$

$$t_+ + t_- = 1 \dots (3)$$

Eqⁿ (3) is very imp^t, as it gives us the initial information

(I) The ^{sum} T.N. of all the ions taking part in transport of current is unity

(II) If the T.N. of one of the ions is known the other is automatically known.

Determination of ~~Hittorf's~~ T.N. by Hittorf's Method :-

(2)

The T.N. can be determined by various methods

- (1) Ionic Mobility
- (2) E.M.F. Measurement
- (3) Moving boundary method
- (4) Hittorf's method

Hittorf determined the T.N. on the basis of the principle — the decrease of ions around the electrode is directly proportional to the speed of the ions moving away from that electrode.

Thus

$$\text{Fall around anode (+)} = \frac{u_c}{u_a}$$

Adding 1 on both sides

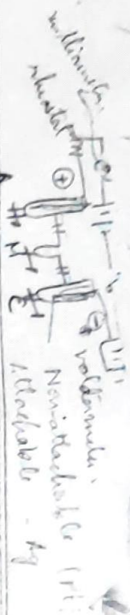
$$\text{Fall around cathode + anode} = \frac{u_a + u_c}{u_a}$$

Adding reciprocal

$$\frac{u_a}{u_a + u_c} = \frac{\text{Fall around cathode}}{\text{Total decomposition in Total volume Electrolyte}} = t_+$$

$$\text{Fall around cathode} \propto \frac{u_a}{u_c}$$

$$\text{Fall around anode} \propto \frac{u_c}{u_a}$$



Similarly

attending

fall around ~~another~~ $\Delta_e = t$

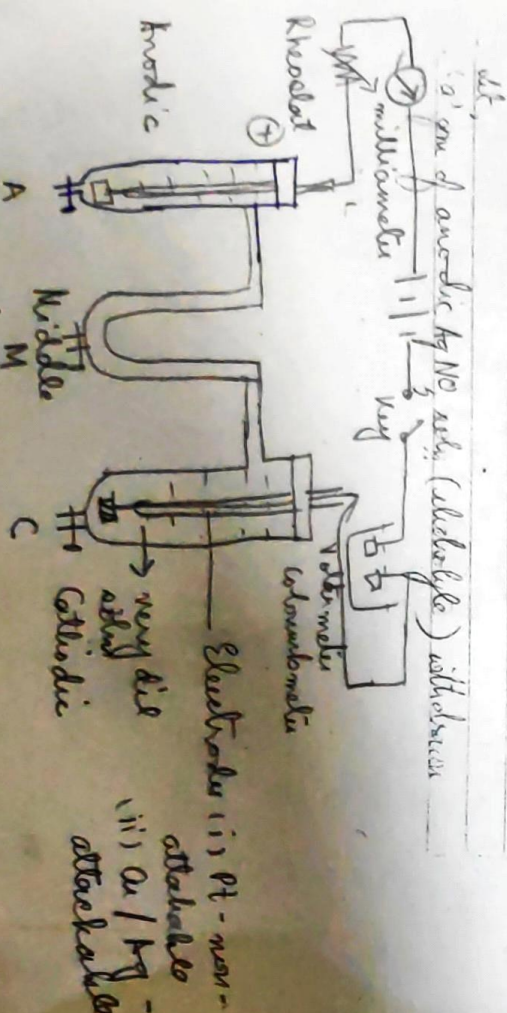
• Total decomposition hat 4

The T_N 's can only be determined if the anodic & cathodic waves are well resolved to max. The charging curve fills with Fe^{2+} , Fe^{3+} , KNO_3 & CaSO_4 (0.1N)

I have submitted a proposal to the Advisory Commission to cover a Manual of the mechanical disturbances to permit-

After electrolysis (pH 2-3, 1 hr.) the resulting neutral compound was taken out, weighed and analysed by titration (by NH_4SCN or NaCl) to chl., and, decomposed, & distillationally up to 50°C .

~~Ad. 2nd of May 1862 (1862) not a in~~
~~October~~



(3)

after electrolysis solution = $6 \text{ gm of } \text{HNO}_3$
(acidic)

$$x(a-b) \text{ gm of } H_2O (\text{absent}) = 'b' \text{ gm " "}$$

$$= 6/E \text{ gm sec}^2 = X$$
 (where $E = \text{sq. ft. of nuclei, here } E = 170$)

again if

(c) gm of anhydrous nitric acid before electrolysis
residue = d gm of HNO_3

2. $(c-d)$ gm of H_2O exsolvn = 'd' gm of $AgNO_3$

$$\begin{aligned} &= \cancel{a} \cancel{b} \cancel{c} \cancel{d} \cancel{e} \cancel{f} \cancel{g} \cancel{h} \cancel{i} \cancel{j} \cancel{k} \cancel{l} \cancel{m} \cancel{n} \cancel{o} \cancel{p} \cancel{q} \cancel{r} \cancel{s} \cancel{t} \cancel{u} \cancel{v} \cancel{w} \cancel{x} \cancel{y} \cancel{z} \\ &= \frac{d(a-b)}{(c-d)} \quad \text{gm } \sqrt{49N} \end{aligned}$$

$$= \frac{cI(a-b)}{(c-d)E} \text{ gm sqm.}$$

Wt. of Ag deposited in the voltmeter = 2.9 gm

$$\therefore \text{Total wt. of } \text{HNO}_3 \text{ absorbed} = \frac{2 \text{ gm. eqn}}{107.82 (\text{m eq wt of H})} = 2 \text{ gm eqn.}$$

~~2000~~

If the ions are very dilute then $a-b$ is a and $c-d$ is c and this actually followed in actual calculations.

Case I: when electrodes are non-attainable

$X < Y$ is less in conc. in anodic compartment \therefore less of anode around anode

$$t_+ = \frac{Y-X}{Z} \quad (\text{is. } \frac{Y-X}{Z} \text{ g. eq. of anode around anode})$$

$$t_- = \frac{Z - (Y-X)}{Z} \quad \text{Total salt displaced}$$

Case II: Attainable electrodes (\therefore Ag in AgNO_3)

$X > Y$ is, increase in conc. at anode

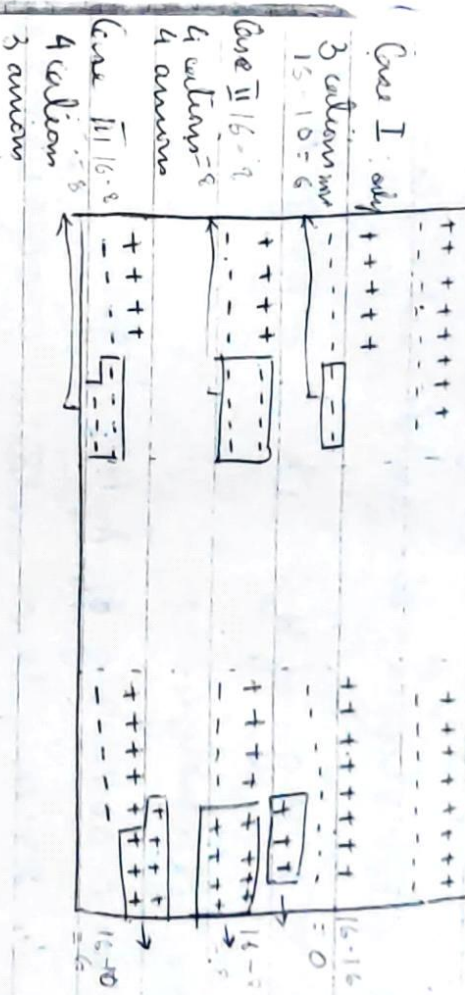
This is because during electrolysis all the NO_3^- reaching the anode is displaced by Ag as AgNO_3 the amt. of AgNO_3 added due to NO_3^- ions which has equal to Z but actually it is less because Ag ions also migrate to cathode

\therefore in case in anode = $X - Y$

$$\text{salt lost actually } t_- = \frac{Z - (X-Y)}{Z}$$

$$t_+ = \frac{X-Y}{Z}$$

$Z = \text{total displacement}$



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Case I: Speed of cation = 3 ions

$$\text{Fall in conc at anodic} = 16 - 10 = 6$$

Speed of anion = nil

$$\text{Fall in conc at cathodic} = 16 - 16 = 0$$

nil

If all in conc take place only at anodic chamber due to non-movement of anion (a) (b)

① A AgNO_3 soln containing 0.00739 gm of AgNO_3 per gram of water is electrolysed b/w Ag -electrodes.

During the expt 0.078g of Ag were deposited on the cathode. At the end of the expt anode soln contained ~~23.14~~ 23.14 g of H_2O and ~~0.236~~ 0.236 g of AgNO_3 . What is transp. no. of Ag .

Ans: After electrolysis, the anode soln has

(a) 23.14 gm of H_2O (b) 0.236g $\text{AgNO}_3 = X$

Before electrolysis:

(a) 0.00739 g of AgNO_3 / gm.

\therefore 23.14 g H_2O contains 0.00739 x 23.14 =

$$= 0.1719 = Y$$

Amt. of Ag deposited = 0.078g of Ag

$$\therefore X = \frac{\text{Amt. of Ag deposited} \times \text{eq wt of Ag}}{\text{eq. wt. of Ag}}$$

$$= \frac{0.078 \times 170.88}{107.88} = 0.1222 \text{ g}$$

\therefore Fall in conc at anode = $X - (X - Y)$

$$= 0.1222 - (0.236 - 0.171) = 0.057 \text{ g}$$

$$\therefore t_+ = \frac{X - (X - Y)}{X} = \frac{0.057}{0.122} = 0.469$$

Alternate calculation on (*)

(*) Alternate calculation:

① No. of eqwt of Ag deposited at cathodes

$$X = \frac{0.078}{107.88} = 0.000723$$

After before electrolysis:

23.14 g of water contains

$$\frac{0.236}{169.88} = 0.0013892$$

$$\text{gm eqwt of AgNO}_3 = X$$

Before electrolysis

1g of H_2O contains 0.00739 g of AgNO_3

23.14 g " " 0.00739 x 23.14 = 0.1719 g of AgNO_3

$$= \frac{6.171}{169.88} = 0.0010066 \text{ gm eqwt of AgNO}_3 = Y$$

$$\therefore t_+ = \frac{X - (X - Y)}{X} = \frac{0.000723 - (0.001389 - 0.0010066)}{0.000723}$$

$$= \frac{7.23 - 3.824}{7.23} = 0.471$$

(1) In electrolyzing a solu containing 7.39 g of AgNO_3 in 1000 g of water was found that after electrolysis 23.376 g of the anolyte contained 0.236 g of Ag^+ . In the coulometer in series, the amt of Cu deposited was 0.023 g. Calculate the transp. no. of Ag^+ and NO_3^-
($\text{Ag} = 108$, $\text{Cu} = 63.54$, $N = 14$, $O = 16$)

In coulometer, amt of Cu deposited

$$= 0.0230 \text{ g}$$

$$\therefore X = \frac{0.023}{63.54/2} = 0.000724 \text{ gm eqv.}$$

Before electrolysis:

1000 g of water contains

$$\frac{7.39}{170} = 0.0435 \text{ g eqv. of } \text{AgNO}_3$$

After electrolysis: $X =$

$$23.376 \text{ g of water contains} = \frac{0.236}{170} = 0.001389 \text{ g eqv. of Ag}$$

Before electrolysis: $Y =$

$$23.376 \text{ g of water before electrolysis} = \frac{0.0435}{1000} \times 23 = 0.00101685$$

$$t_+ = \frac{X - (X - Y)}{X}$$

$$= \frac{0.000724 - (0.001389 - 0.001017)}{0.000724}$$

$$= \frac{7.72}{7.72} = 0.486 \text{ and } t_- = 1 - 0.486 = 0.514$$

(2)

90.25 g of AgNO_3 solu containing 5.039 g of Ag^+ was electrolyzed using Pt-electrodes, till the amt of Ag deposited in the coulometer in series was 1.424 g. After electrolysis 20.893 g of the anolyte contained 0.193 g of AgNO_3 . Calculate the transp. no. of Ag ions:

No. of equivalents of Ag deposited at coulometer

$$X = \frac{1.424}{167.88} = 0.01318 \text{ gm eqv}$$

Before electrolysis:

$$90.25 - 5.039 = 85.21 \text{ g of water}$$

$$\therefore 85.21 \text{ g of H}_2\text{O contains} \frac{5.039}{169.88} = 0.0296 \text{ g eqv. of } \text{AgNO}_3 \text{ or } \text{Ag}^+$$

After electrolysis:

$$20.893 \text{ g} - 0.193 \text{ g} = 20.7 \text{ g of water}$$

$$20.7 \text{ g of H}_2\text{O contains} \frac{0.193}{169.88} = 0.001156 \text{ g eqv.} = X$$

Before electrolysis:

$$85.21 \text{ g of H}_2\text{O contains} 0.0296 \text{ g eqv. of } \text{AgNO}_3$$

$$20.7 \text{ g} \quad \frac{0.0296}{85.21} \times 20.7 = 0.007802 \text{ gm eqv. of } \text{Ag}^+$$

$$t_+ = \frac{Y - X}{Z} = \frac{0.007802 - 0.001136}{0.01318} = 0.4601$$