The factors affecting ionic conductivity :

Ionic conductivity in electrolytes depends on two main factors:

(i) the concentration of free charge carriers (ions).
(ii) the ability of the charge carriers (ions) to move in an electric field.

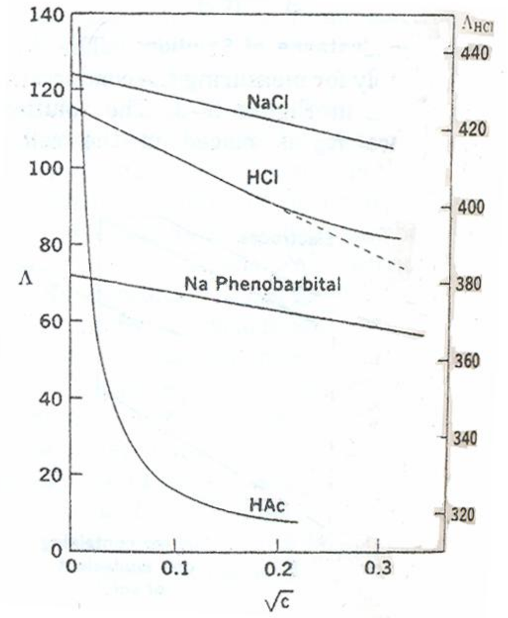
Obviously, charge carriers tend to be present at high concentration when the concentration of dissolved salt in an electrolyte phase is high, and in general more concentrated salt solutions are expected to exhibit higher conductivities.

Variation of conductance with concentration :

Both the specific and equivalent conductance's of solution vary with concentration . For strong electrolytes at concentrations up to several equivalents per liter , the specific conductance increases sharply with increase in concentration. In contrast , the specific conductance's of weak electrolytes start at lower values in dilute solutions and increase much more gradually .

in both instances the increase in conductance with concentration is due to the increase in the number of ions per unit volume of solution .

Unlike the specific conductance , the equivalent conductance Λ of both strong and weak electrolytes increase with dilution .



Equivalent conductance's of electrolytes in aqueous solution at $25^{o}C$

C/eq..liter	KCl	HCl	AgNO3	CH3COOH
0.000	149.86	426.16	133.36	390.7
0.0005	147.81	422.74	131.36	67.7
0.001	146.95	421.36	130.51	49.2
0.02	138.34	407.24	121.41	11.6
0.05	133.37	399.09	115.24	7.4
0.20	123.9	379.6	101.8	----
1.00	111.9	332.8	------	-------

The manner in which Λ varies with concentration can be judged from the table and the plot of Λ vs. $\sqrt{C}$.

On dilution of a strong electrolyte Λ rapidly approaches already in 0.001 N solution a value close to the limiting value of the conductance at zero concentration Λ_0 . On the other hand , although the equivalent conductance of weak electrolytes' increases rapidly on dilution, at the concentrations mentioned it is still very far from its limit .

Λ at 25°C for 0.001 N NaCl is 123.7 as against a Λ_0 of 126.5 . At the same concentration and temp. Λ for acetic acid is only 49.2 , while Λ_0 is 390.7 .

Because of that the behaviour of the equivalent conductance's of strong and weak electrolytes on dilution , quite diverse procedures must be used for obtaining their limiting equivalent conductance's .

● The specific conductance L for strong and weak electrolyte start at lower value then increase gradually for weak electrolyte in dilute solution, while for strong electrolyte it increase sharply due to increase the number of particles in solution increase.

● Equivalent conductance Λ as plotted vs. √C for strong electrolyte it reaches zero Λ_o while for weak electrolyte it never reaches zero Λ_o it still very far its limit,

Arrhenius ascribed the decrease in conductance to variation of degree of dissociation

$\alpha = \Lambda / \Lambda_o$ = mole of ionized/ total mole.

For strong electrolyte $\alpha \approx 1$.While for weak electrolyte due to:

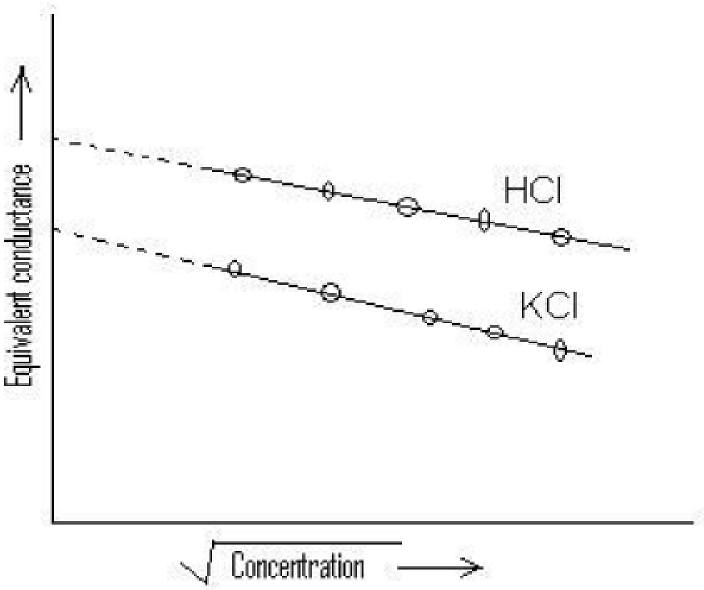
1)The partial dissociation of electrolyte.
2)The interionic attraction between ions present

Equivalent conductance's at infinite dilution:

In an extensive series of measurement during the nineteenth century , Frindrich Kohlrausch showed that at law concentrations the molar conductivities of strong electrolytes vary linearly with the square root of the concentration :

$$\Lambda = \Lambda_m^o - b\sqrt{C}$$

Where b is a constantand ,C is the concentration of the electrolyte in mol/L. &Λ^o_m is the limiting molar conductivity. The validity of this finding may be seen from the plots of HCl & KCl as shown in the fig .



To obtain Λ^o_m of such electrolytes the curve may be extrapolated to $\sqrt{C} = 0$ and the intercept read (Λ^o_m) .

Equivalent conductance's at infinite dilution for weak electrolytes are obtained by application of Kohlrauschs law of independent migration of ions.

This law states that at infinite dilution , where dissociation for all electrolytes is complete and where all inter ionic effects disappear , each ion migrates independently of its co-ion , and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature and not at all on that of the ion with which it is associated

$$\Lambda_o = \nu_+ \lambda_o^+ + \nu_- \lambda_o^-$$

λ_o is the equivalent ionic conductance at infinite dilution or limiting molar conductivity of the ions . v_+ and v_- are the numbers of cations and anions per formula unit of electrolyte .

Calculate the value of Λ^o_m(limiting molar conductivity) of $BaCl_2$ at 25°C ; if λ_+ = 12.72 & λ_- =7.63 mS.m^2.mol^{-1} respectively ?

$$\Lambda_m^o = \nu_+\lambda_+ + \nu_-\lambda_-$$

$$\Lambda_m^o = 12.72 + 2\times 7.63$$

$$\Lambda_m^o = 27.98 mS.m^2.mol^{-1}$$

Limiting ionic conductivities in water at 25°C /λ mS.m^2.mol^{-1}			
H^+	34.96	OH^-	19.91
Na^+	5.01	Cl^-	7.63
Ca^{+2}	11.90	CO_3^{-2}	13.86
Zn^{+2}	10.56	$SO4^{-2}$	16.0

“Conductivity of ions is constant at infinite dilution and it does not depend on nature of co-ions.”

Kohlrausch

Uses of Kohlrausch’s law

- Calculation of molar conductivity at infinite dilution for weak electrolytes
- Calculation of degree of dissociation.
- Calculation of dissociation constant for a weak electrolyte
- Calculation of solubility of sparingly soluble salt.

APPLICATIONS OF KOHLRAUSCH LAW

- **A) Determination of molar conductivities of weak electrolytes:**

  It is not possible to determine value of Λ^o_m for weak electrolyte like CH_3COOH, NH_4OH , etc. BY the extrapolation of the molar conductivity values to zero concentration .

  From the value of of Λ^o_m HCl, Λ^o_m CH_3COONa and Λ^o_m NaCl the value of Λ^o_m CH_3COOH can be calculated.

  $$\Lambda^o_{CH3\ COOH} = \Lambda^o_{CH3COONa} + \Lambda^o_{HCI} - \Lambda^o_{NaCI}$$

  $$= \lambda^o_{m\ (H+)} + \lambda^o_{m\ (Cl-)} + \lambda^o_{m\ (\ CH3COO-)} + \lambda^o_{m\ (\ Na+)} - \lambda^o_{m\ (\ Na+)} + \lambda^o_{m\ (Cl-)}$$

  $$= \lambda^o_{m\ (H+)} + \lambda^o_{m\ (\ CH3COO-)}$$

  $$\Lambda^o_{CH3\ COOH} = \Lambda^o_{CH3\ COOH}$$

The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are 14.99 mSm^2mol^{-1}, 14.50 $mSm^2mol^{-1}$and 13.34 mSm^2mol^{-1} respectively at 25°C. Calculated the limiting molar conductivity of AgCl at this temperature ?

$$\Lambda^o_{m(AgCl)} = \Lambda^o_{m(AgNO_3)} + \Lambda^o_{m(KCl)} - \Lambda^o_{m(KNO_3)}$$

$$\Lambda^o_{m(AgCl)} = 13.34 + 14.99 - 14.50$$

$$\Lambda^o_{m(AgCl)} = 13.83 mS.m^2.mol^{-1}$$

The limiting molar conductivities of NaI , $NaCH_3CO_2$, and $Mg(CH_3CO_2)_2$ are 12.69 , 9.10 , and 18.78 $mS.m^2.mol^{-1}$ respectively at 25^oC .what is the limiting molar conductivities of MgI_2 at the same temp..

Q1/ If the molar conductivities at infinity dilution of NaCl, HCl, and CH_3COONa are 126.4, 426.1, and 91.0 $ohm^{-1}.cm^2.\ mol^{-1}$. What will be that of acetic acid?

Q2/ At 291 K, the molar conductivity, at infinity dilution of NH_4Cl, NaOH, and NaCl are 129.8, 217.4, and 108.9 $ohm^{-1}\ cm^2\ mole^{-1}$ respectively. if the molar conductivity of a normal solution of NH_4OH is 9.33 $ohm^{-1}\ cm^2\ mole^{-1}$, what is the percentage dissociation of NH_4OH at this dilution.

Q3/ From the following molar conductivity at infinity dilution:
$\Lambda_o$for $Ba(OH)_2$ = 457.6 $ohm^{-1}\ cm^2\ mol^{-1}$ $\Lambda_o$for $BaCl_2$ = 240.6 $ohm^{-1}\ cm^2\ mol^{-1}$ $\Lambda_o$for NH_4Cl = 129.8 $ohm^{-1}\ cm^2\ mol^{-1}$
Calculate $\Lambda_o$for NH_4OH.

B-Calculate of the degree of dissociation for weak electrolyte At infinity dilution.

we have

Degree of dissociation, $(\alpha) = \Lambda/\Lambda_o$

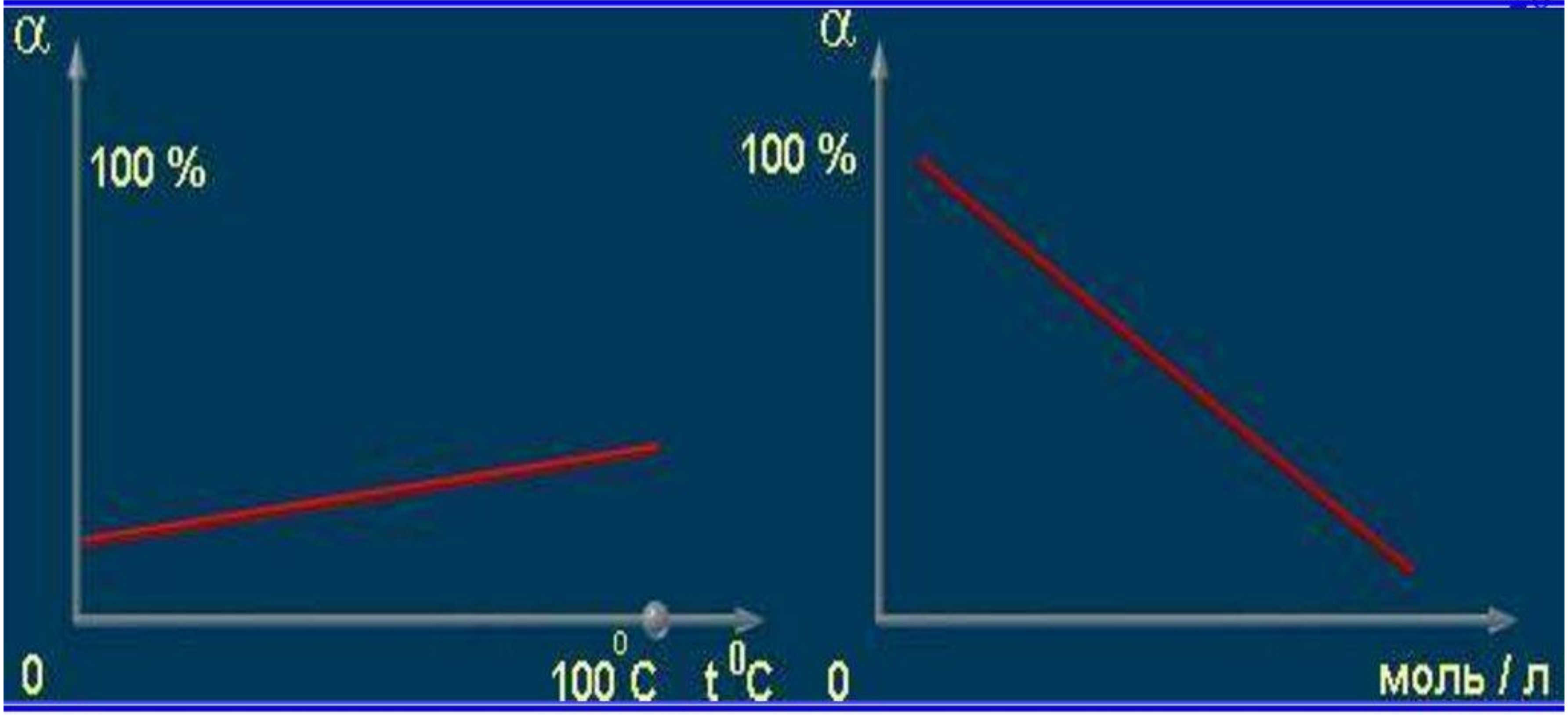
The value of Λ_o for weak electrolytes can be calculated using Kohlrausch Law.

Factors pertaining to degree of ionization

- Nature of solute.
- Nature of solvent.
- Dilution
- Temperature.

Values of the degree of dissociation (ex)depends upon the following factors

1. nature of solute
2. nature of solvent
3. concentration
4. temperature



When temperature is increased, degree of ionization increase too

When concentration is increased, degree of ionization decrease

Determination of degree of ionization :

The determination of the degree of ionization of weak electrolytes is a problem of importance in physical and analytical chemistry .

Water is a weak electrolyte and ionizes according to the equation :

$$H_2O = H^+ + OH^-$$

To find the degree of ionization α at say 25ºC , Λ is required , Since Λ = L_s *V_e , where Ve is the volume in cubic centimeters containing one equivalent of water , V_e must be molecular weight of water divided by the density of the water at 25ºC & L_s= $0.58*10^{-7}$ .therefore :

$$\Lambda = \left(0.58 \times 10^{-7}\right) \frac{18}{0.9971}$$

$$\Lambda = 1.05 \times 10^{-6}$$

Λ_0 for water is the sum of the equivalent ionic conductance's of H^+ and OH^- ions ,

$$\Lambda_o = 349.8 + 198$$

$$\Lambda_o = 547.8 \Omega^{-1} cm^2 eq^{-1}$$

Then:

$$\alpha = \frac{\Lambda}{\Lambda_o} = \frac{1.05 \times 10^{-6}}{547.8}$$

$$\alpha = 1.9 \times 10^{-9}$$

i.e, water is ionized to the extent of $1.9*10^{-9}$ per cent at 25ºC .

Calculate the degree of dissociation of water if (specific conductance L for water is 0.14x10^{-7}mho cm^{-1}) .

Calculate Λ_o for water if λ^o H^+ and for λ^o OH^- is 349.8 and 198 respectively at 0°C. If the density is 0.9971gcm^{-3}

$$H_2O \leftrightarrow H^+ + OH^-$$

C-Calculation of solubility of a sparingly soluble salt :

Such as AgCl, $BaSO_4$, $PbSO_4$ etc., which dissolve to a very small extent in water, are called sparingly soluble salt. As they dissolve very little, their solutions are considered as infinity dilute. Further as their solutions are saturated, their concentration is equal to their solubility.

Thus, by determining the specific conductivity (L) and the molar conductivity (Λ_o) of such solution, we can obtain solubility as follows:

$$\Lambda_o = \frac{1000L}{S}$$

The specific conductance at 25^oC of a saturated aqueous solution of $SrSO_4$ is $1.482*10^{-4}$, while that for water used is $1.5*10^{-6}$ mho.cm^{-1} .Determine the solubility of $SrSO_4$ in water . If ionic conductances at infinite dilution of ½ Sr & ½ SO_4 are 59.46 & 79.8 mhos cm^2 eq^{-1} .

Ostwald's Dilution Law

The weak electrolyte ionizes to a very small extent and their molar conductivity doesn't attain a limiting value at high dilution. In such solutions there is equilibrium between free ions and undissociated molecules. The equilibrium can be written in the form:

$$MA \leftrightarrow M^{+} + A^{-}$$

$t=t_{eq}$	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Where M^+ = A^- = free ions MA = undissociated portion of the electrolyte including both nonionized molecules and ion pairs. By law of equilibrium,

$$k = \frac{a_{M^{+}} . a_{A^{-}}}{a_{MA}} \ldots\ldots(1)$$

Where, a's = activities of indicated species
K = the equilibrium constant called dissociation constant of the electrolyte

$$k = \frac{c\alpha . c\alpha}{c(1-\alpha)} \ldots\ldots(2)$$

$$k = \frac{c\alpha^2}{1-\alpha} \ldots\ldots(3)$$

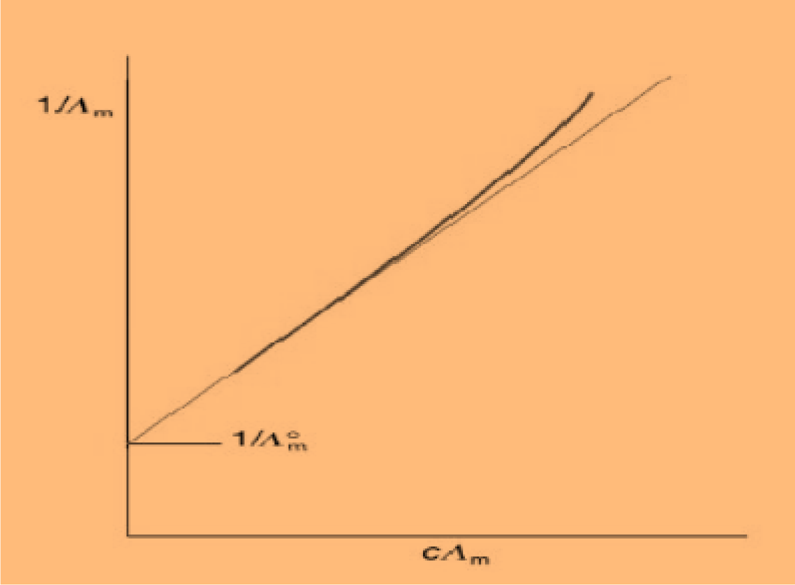
$$\alpha = \frac{\Lambda_m}{\Lambda_m^o} \ldots\ldots\ldots(4)$$

Then :

$$k = \frac{\left(\frac{\Lambda}{\Lambda_o}\right)^2 c}{1-\left(\frac{\Lambda}{\Lambda_o}\right)} \ldots\ldots(5)$$

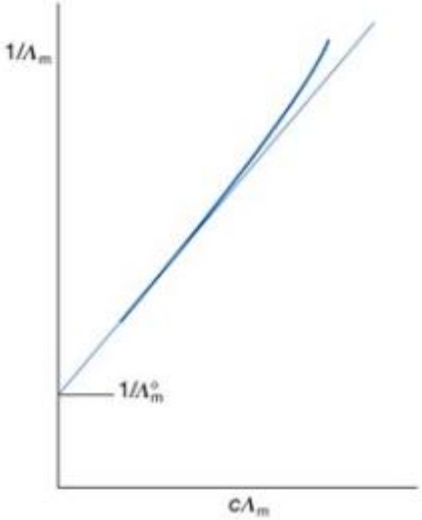
And ;

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{\Lambda c}{k\Lambda_o^2}$$



Ostwald’s dilution law

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a\left(\Lambda_m^0\right)^2}$$



The molar conductivity of 0.005M acetic acid at 25^oC is Λ_m= 2.29 mSm^2 mol^{-1} and Λ_o= 39.05 mSm^2 mol^{-1} . Calculate the degree of dissociation and dissociation constant.

$\alpha = \Lambda / \Lambda_o$, $\alpha = 2.29 / 39.05 = 0.05864$

$$k_c = \frac{\alpha^2 C}{1-\alpha} = \frac{(0.05864)^2 \times 0.005}{1-0.05864}$$

$K_c = 1.83*10^{-5}$

Determination of Hydrolysis constant :

The salt derived from a strong acid and weak base it hydrolyzed to form the strong acid and weak base .

$$C_6H_5NH_2 + HCl \leftrightarrow C_6H_5NH_3Cl$$

Weak base **strong acid** **aniline chloride**

$$C_6H_5NH_3Cl \leftrightarrow C_6H_5NH_3^+ + Cl^-$$

$$C_6H_5NH_3^+ + H_2O \leftrightarrow C_6H_5NH_2 + H_3O^+$$

C 0 0

(1-α)C αC αC

$$k_h = \frac{\left[H_3O^+\right]\left[C_6H_5NH_2\right]}{\left[C_6H_5NH_3^+\right]} = \frac{\alpha^2 C}{(1-\alpha)}$$

The equivalent conductance for the salt:

$$\underset{\text{Solution}}{\Lambda_s} = \underset{\text{unhydrolysis salt and acid}}{(1-\alpha)\Lambda_c} + \underset{\text{acid}}{\alpha\Lambda_a} + \underset{\text{base (neglected)}}{\alpha\Lambda_b}$$

Where: Λ_c, Λ_a, Λ_b equivalent conductance for the un hydrolysis salt, acid and the base, as equivalent conductance for the weak base is so small then it can be neglected:

$$\Lambda_s = (1-\alpha)\Lambda_c + \alpha\Lambda_a \quad \rightarrow \quad \Lambda_s = \Lambda_c - \alpha\Lambda_c + \alpha\Lambda_a$$

$$\Lambda_s - \Lambda_c = \alpha(\Lambda_a - \Lambda_c)$$

$$\alpha = \frac{\Lambda_s - \Lambda_c}{\Lambda_a - \Lambda_c}$$

where: Λ_c from the conductance of salt in aniline which [common ion formation] decrease the dissociation of the salt its nearly about its equivalent for un dissociation salt.

- **Hydrolysis constant K_h :**

$$K_h = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]} = \frac{\alpha^2 c}{1-\alpha}$$

$$K_a = \frac{K_w}{K_h}$$ (for salt from weak acid and strong base)

$$K_b = \frac{K_w}{K_h}$$ $(Kw = 1x10^{-14})$ (for salt from weak base and strong acid)

K_w : the Ion product constant of water

Transference and Transference numbers :

Although current is transported through a solution by migration of positive and negative ions , the fraction of the total current carried by each is not necessarily the same . Thus in dilute solution of magnesium sulfate the magnesium ion carries a bout 0.38 of the total current , while the sulfate ion carries 0.62 . Similarly in dilute nitric acid solution the nitrate ion carries only 0.16 of the total current , the hydrogen ion 0.84 .

The salfate & hydrogen ions transport the greater fraction of the total current because they move faster than the other ion present .

If both ions in a solution moved with the same speed , each would transfer past any fixed plane in the solution the same quantity of electricity in any given time .

The quantitative relation between the fraction of the current carried by an ion and its speed can be established as follow .

Let the average migration velocity of cation in the solution be v+ cm per second , the charge of this ion be z+ and the number of these ions n+ . Similarly , the velocity of the anion be v- , its change z- and the number n-.

So the current carried by the positive & negative ions must be :

$$I_+ = \frac{n_+ v_+ z_+ e}{d} \;\&\; I_- = \frac{n_- v_- z_- e}{d} \;.........(1)$$

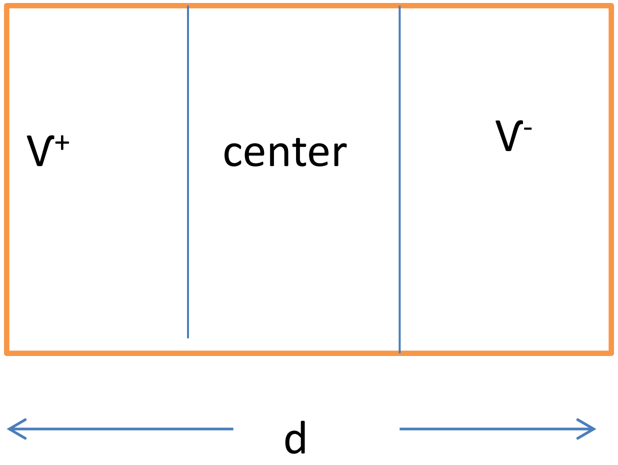
Consequently the total current carried by both ions is :

$$I = I_+ + I_- ....(2)$$

$$I = \frac{n_+ v_+ z_+ e + n_- v_- z_- e}{d}$$

But the total charge of the cations must be equal to that of the anions :

$$n_+ z_+ = n_- z_-$$



Therefore :

$$I = \frac{nze(\nu_+ + \nu_-)}{d} \text{.......}(3)$$

From eq. 1&3 the fraction of the total current carried by the cations is :

$$\tau_+ = \frac{I_+}{I} = \frac{\nu_+}{(\nu_+ + \nu_-)} \text{.......}(4)$$

And the fraction of the total current curried by the anions is :

$$\tau_- = \frac{I_-}{I} = \frac{\nu_-}{(\nu_- + \nu_+)} \text{......}(5)$$

τ_+ &τ_- are the transport or transference number of the cations and anions respectively .

On dividing eq. 4 by eq. 5 we see that :

$$\frac{\tau_+}{\tau_-} = \frac{\nu_+}{\nu_-} \text{......}(6)$$

So the transport number of the ions & the fractions of the total current they carry are directly proportional to their absolute velocities .

When ($\tau_+ = \tau_-$) the both ions contribute equally to the transport of current . However , when v_+ dose not equal to v_- , $\tau_+ \neq \tau_-$ and the ions will carry different proportions of the total current .

The sum of the two transference number must be unity , i.e :

$$\tau_+ + \tau_- = 1$$

And ;

$$\tau_+ = \frac{\lambda_+}{\Lambda}, \tau_- = \frac{\lambda_-}{\Lambda}$$

At 25^{o}C the transport number of H^+ ion in HCl & CH_3COO^- ion in CH_3COONa are 0.81 & 0.47 respectively . The equivalent conductance at infinite dilution of HCl & CH_3COONa are 426 & 91.0 Ω^{-1} cm^2 eq^{-1} respectively . Calculate the equivalent conductance of acetic acid at infinite dilution .

$$\lambda_{H^+} = \Lambda^o \times \tau_{H^+}$$

$$\lambda_{H^+} = 426 \times 0.81 = 345.06$$

$$\lambda_{CH_3COO^-} = \Lambda^o_{CH_3COONa} \times \tau_{CH_3COO^-}$$

$$\lambda_{CH_3COO^-} = 91 \times 0.47 = 42.77$$

$$\Lambda^o_{CH_3COOH} = \lambda_{H^+} + \lambda_{CH_3COO^-}$$

$$\Lambda^o_{CH_3COOH} = 387.83 \Omega^{-1} cm^2 eq^{-1}$$

Determination of Transport Number

The are two methods for determination of transport number

1. Hittorf's Method
2. Moving Boundary Method

Hittorf's Rule :

As a result of passage of current through a solution concentration changes directly related to the velocities of the ions occur in the vicinity of the electrodes . to understand the nature of these changes and their dependence on the ionic speeds , consider the cell illustrated under I in fig (1) , let the cell be divided by the imaginary planes AA' and BB' into three compartments , anode , center or bulk , and cathode and let each compartment contain five equivalents of positive ions and the same number of equivalents of negative ions .

If the speeds of the tow ions are equal and if 4 faradays of electricity are passed through the cell , four equivalents of positive ions in the cathode compartment will accept electrons from the electrode and deposit . Again four equivalents of negative ions in the anode compartment will give up their electrons to the anode and will also deposit . The result of these changes is summarized under II . While these changes at the electrodes are taking place , the ions migrate through the solution .

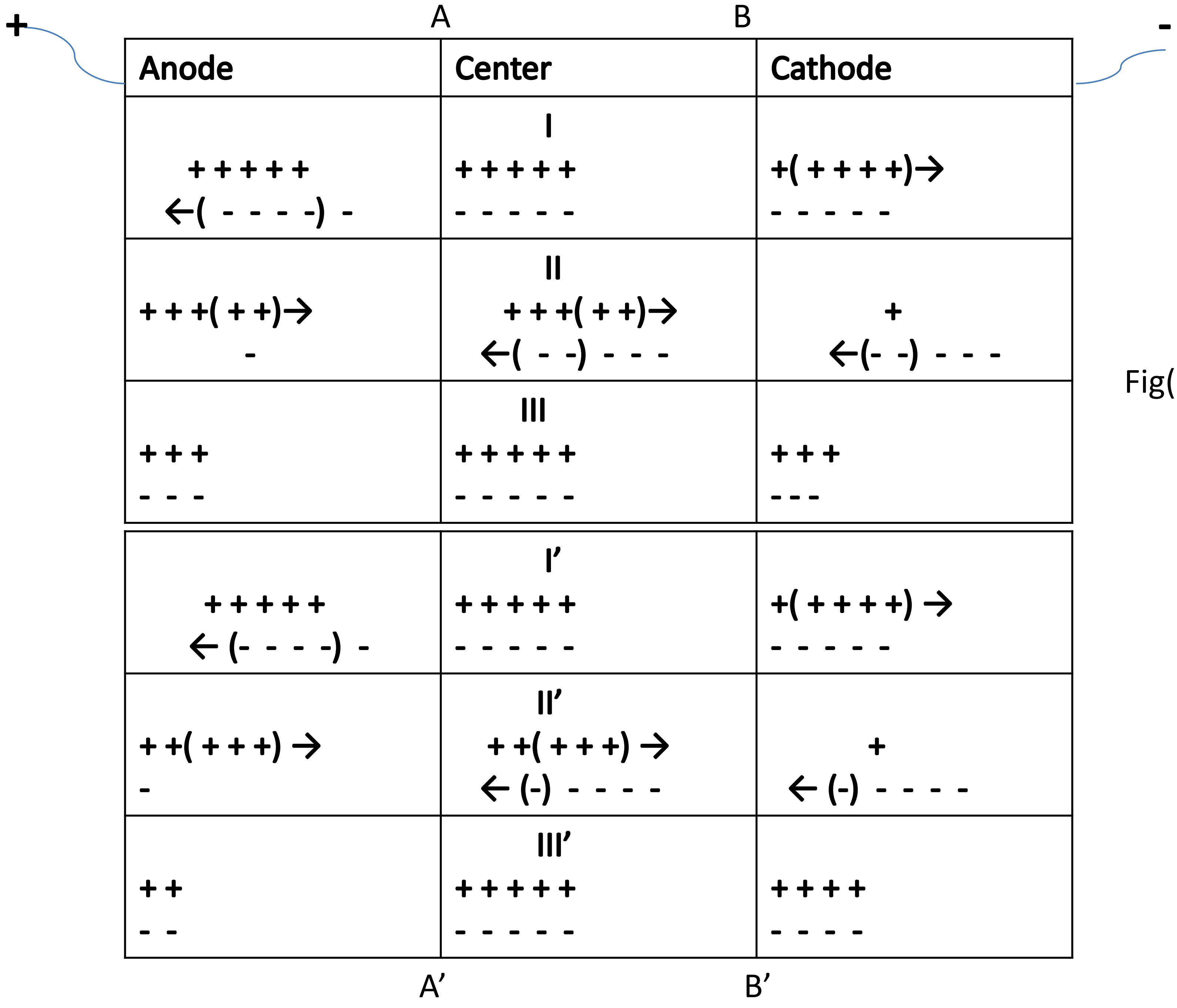
Since both ions move with the same speed , each must carry one-half the current the cations must transport 2 faraday of electricity from left to right , the anions 2 faradays of electricity from right to left .

..

So two equivalents of positive ions must move from the anode compartment into the center and the same number of equivalents from center into the cathode compartment .simultaneously , two equivalents of negative ions must move from the cathode to the center then from the center to the anode . The result is III .

From III it is evident that the concentration in the central has not change by passage of current , but the concentration in the cathode & anode have both decreased and have the same cons. .

However , the situation is different when the speeds of the ions are not the same , when the speed of cation is three times that of the anion , the quantity of electricity being again 4 faraday s .as before , four equivalents of each ion are deposited at the electrodes . But , since the cation carries here three times as much current as the anion



Anode	Center	Cathode
+ + + + + ←(- - - -) -	I + + + + + - - - - -	+(+ + + +)→ - - - - -
+ + +(+ +)→ -	II + + +(+ +)→ ←(- -) - - -	+ ←(- -) - - -
+ + + - - -	III + + + + + - - - - -	+ + + - - -
+ + + + + ← (- - - -) -	I’ + + + + + - - - - -	+(+ + + +) → - - - - -
+ +(+ + +) → -	II’ + +(+ + +) → ← (-) - - - -	+ ← (-) - - - -
+ + - -	III’ + + + + + - - - - -	+ + + + - - - -

Fig(1)

Concentration changes due to transference

However , the situation is different when the speeds of the ions are not the same , when the speed of cation is three times that of the anion , the quantity of electricity being again 4 faraday s .as before , four equivalents of each ion are deposited at the electrodes . But , since the cation carries here three times as much current as the anion , three equivalents of positive ion must migrate from anode to center and then from center to cathode compartment.

At the same time only one equivalent of anions leaves the cathode section to center then to anode compartment .

From III', where the final state of the cell is given , it is seen that there is no change in concentration in the center compartment .Moreover , as before there are concentration changes at the two electrodes , but this time the two are not the same

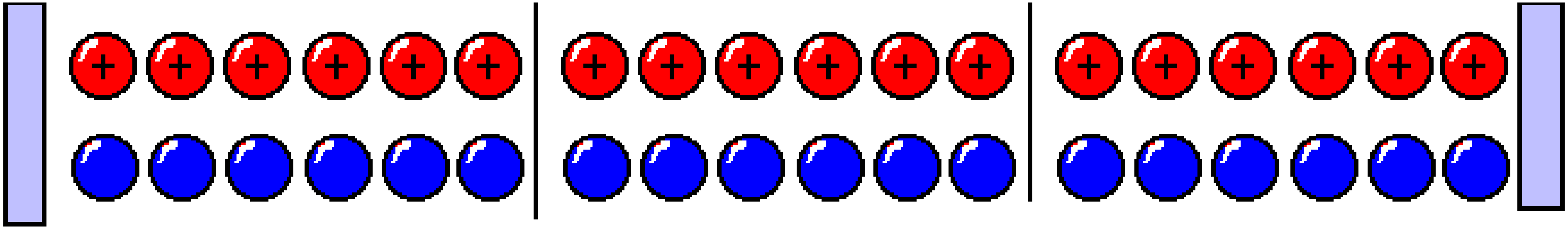
So when $v_+:v_- = 3 : 1$, the the loss in concentration of cations from the anode compartment due to migration is three times that of anions from the cathode section .

This parallelism between concentration loss due to migration and the velocity of the ion responsible for it leads to Hittorf's rule :

Measurement of transference numbers

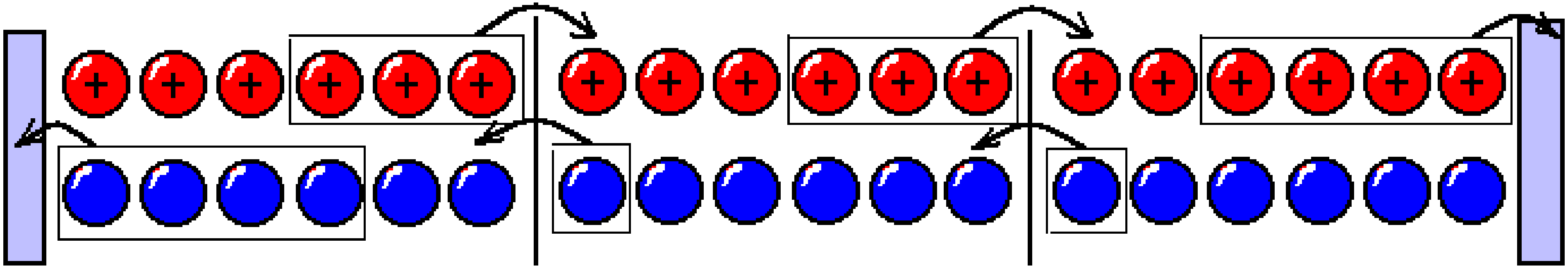
1) Hittorf method (1853)

Electrolysis of HCl solution



Anodic region **Bulk solution** **cathodic region**

When 4 Faraday pass through the electrolytic cell

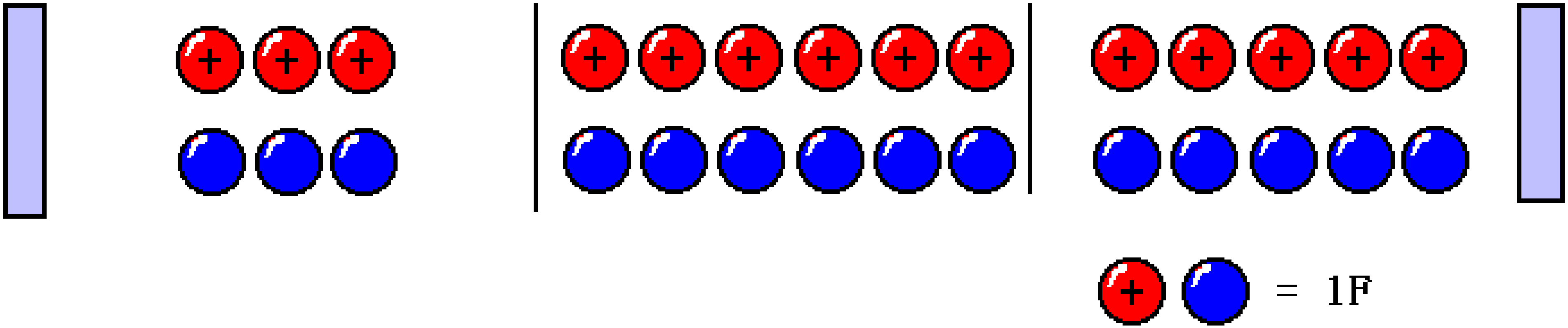


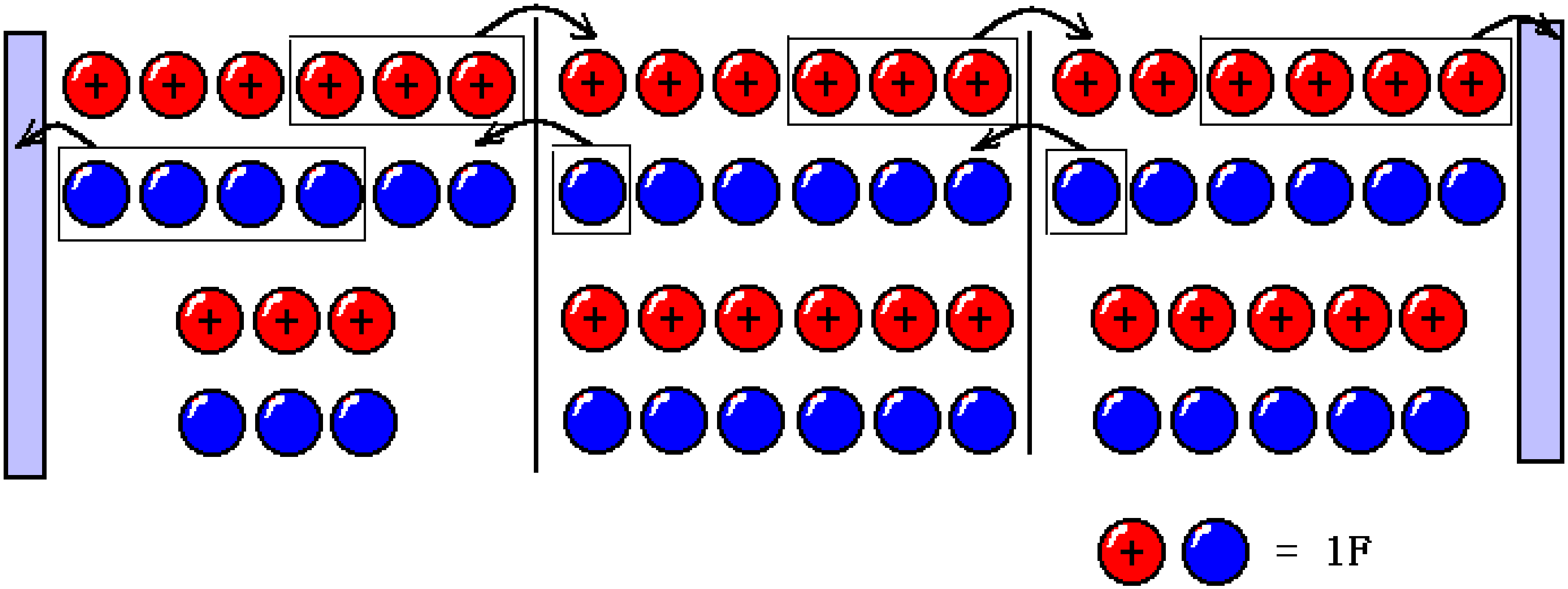
$4\ Cl^- -4e^- \rightarrow 2\ Cl_2\uparrow$

$4\ H^+ +4e^- \rightarrow 2\ H_2\uparrow$

3 mol $H^+ \rightarrow$ 1
mol $Cl^- \leftarrow$

3 mol $H^+ \rightarrow$ 1
mol $Cl^- \leftarrow$





For anodic region:

$$C_{residual} = C_{initial} - C_{react} + C_{transfer}$$

$$3 = 6 - 4 + C_{transfer}$$

$$t_- = 1 / 4 = 0.25$$

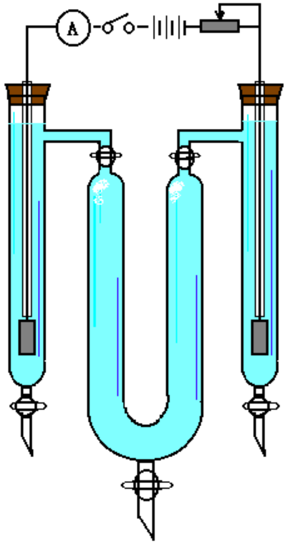
$$t_+ = 3 / 4 = 0.75$$

$$\frac{\text{Loss in cation eq. at anode due to migration}}{\text{Loss in anion eq. at cathode due to migration}} = \frac{\nu_+}{\nu_-} = \frac{\tau_+}{\tau_-}$$

Since the total current passed through the cell is proportional to $[(\tau_+ + \tau_-) = 1]$ then :

$$\frac{\text{Loss in cation eq. at anode due to migration}}{\text{Equivalents of current passed}} = \frac{\tau_+}{1} = \tau_+$$

$$\frac{\text{Loss in anion eq. at cathode due to migration}}{\text{Equivalents of current passed}} = \frac{\tau_-}{1} = \tau_-$$



Hittorf's transference cell