Definition

It is a branch in chemistry which deals with the qualitative and quantitative studies of chemical changes brought about by the passage of electricity. It is also deals with the conversion of chemical energy to electrical energy.

Cathode:

An electrode at which reduction occurs (i.e gain of electrons) is called cathode

Anode:

An electrode at which oxidation occurs(i.e loss of electrons) is called anode.

Cell:

A device formed by the combination of anode and cathode which helps to bring about a chemical change brought about by the passage of electricity.

Electrolyte:

A substance which splits up into ion in aqueous solutions and conducts the electricity.

Electrolysis:

The process of decomposition of an electrolyte by the passage of an electric current is called electrolysis.

Conductors:

A substance which conducts the electricity in all state is called a conductor.

The conductors are classified into two types:

1) **Electronic conductors**: In these conductors, the flow of electric current in solid or fused state is due to electrons. No transfer of material takes place after the passage of the current. Eg. Solid molten metals and few solid salts (Cus , CdS)

2) **Electrolyte conductors**: Conductors in which the electric current is carried by the ions present in the solution are called electrolytic conductors. These are generally solutions of electrolytes or molten salts. Eg. NaCl, AgNO$_3$

Distinguish between : Electronic conductors and Electrolytic conductors

Electronic conductors	Electrolytic conductors
1)The electric current is due to flow of electrons	1) The electric current is carried by the ions in the solution
2) Transfer of material takes place	2)Transfer of material is associated with the passage of electric current
3)The flow of – ve charge takes place in on direction.	3) Both +e and - ve charge move in opposite direction
4)Resistance offered by an electronic conductor increases with increase in temperature	4)Resistance offered by an electrolytic conductor decreases with increase in temperature

Specific resistance (ρ) : Resistance offered by a conductor is directly proportional to length and inversely proportional to the area of cross-section

$$R \propto \frac{l}{a} \ \therefore R = \rho \frac{l}{a}$$

Here ρ is called specific resistance of a conductor. On rearrangement we get,

$$\rho = \frac{Ra}{l}$$

When a = 1 sq.cm and l = 1 cm, the R = ρ

Hence specific resistance is defined as the resistance in Ohms offered by a conductor of 1 sq.cm in cross-sectional area and of length one cm or is the resistance of 1 cm³ of conductivity material

Specific conductance or Conductivity : As conductance is inversely proportional to resistance , the conductance of the conductor will be directly proportional to area of the cross-section 'a' of the conductor and is inversely proportional to the length of the conductor.

$$L \propto \frac{a}{l} \ \therefore L = k \frac{a}{l}$$

Where k (kappa) is a constant for a given conductor and is called specific

conductance.

On rearrangement of the above equation, we get

$$k = L\frac{l}{a}$$

When a = 1 sq.cm or 1 cm^2, l = 1 cm, then

$$k = L$$

Thus the **specific conductance or conductivity** is defined as the conductance in Siemens offered by a conductor of **1 m^2** in cross-sectional area and of **1m length** or it is the conductance in Siemens of a cubic material of edge **1 m.**

Relation between the specific conductance and specific resistance:

Specific conductance is given by $k = L\frac{l}{a}$, but conductance $L = \frac{1}{R}$

Therefore , $k = \frac{1}{R}\frac{l}{a} - - - - - 1$

Specific resistance is given by $\rho = \frac{Ra}{l}$, rearranging equation (1) we get,

$$\frac{1}{k} = R \cdot \frac{a}{l} \ ie. \frac{1}{k} = \rho$$

N.B.:- Specific conductance cannot be used for comparison of conducting power of two different electrolytes as it depends upon the concentration of the electrolytes.

Equivalent conductance: It is defined as the conductance produced by a certain volume of a solution containing 1 gm equivalent of an electrolyte when the solution is placed between two parallel electrodes 1cm apart and large enough to contain the whole solution between them.

Let us assume that **1 gm equivalent** of a substance is dissolved in **V ml** of the solution and let this solution be placed between the two || electrodes 1 cm apart. Therefore the area occupied by the solution will be Vsq.cm. Hence conductance of the solution is given as $L = k\frac{a}{l}$

When a = V sq.cm and l = 1 cm, then L = k.V

This conductance will be equal to equivalent conductance as the conductance is offered by 1 g, equivalent of the substance,

$$Therefore, \Lambda = k.V - - - - (I)$$

For **V** ml of solution , the amount of substance dissolved is **1gm eq**.

Therefore 1000ml of solution,the amount of substance will be **1000/V**

i.e . Concentration of the solution,

$$c = \frac{1000}{V} \qquad \therefore V = \frac{1000}{c}$$

Substituting the value of V in equation (I) above we get,

$$\Lambda = k.\frac{1000}{c} = \frac{1000k}{c}$$

Therefore to determine eqv. conductance, the specific conductance (k) should be known as eqv. conductance cannot be measured directly.

SI unit of eqv. conductance : S m^{2}g.eqv.$^{-1}$

Molar conductance: It is defined as the conductance of all the ions produced by dissolving 1 mole or 1 gm-mol wt of a substance (electrolyte) in a certain volume and of the solution, placed between two || electrodes 1 cm apart and large enough to contain all the ions in the solution.

Molar conductance is given by the expression,

$$\mu = \frac{1000k}{M}$$, where k is specific conductance, M is concentration in moles/lit

SI unit of molar conductance: S m^{2}mol^{-1}

1)**Electrolyte:** A substance which forms a conducting solution when dissolved in water is called an electrolyte.

2) Strong electrolyte: An electrolyte which ionises to a maximum extent in dilute aqueous solutions is called a strong electrolyte.e.g HCl, NaOH, NaCl etc

3)Weak electrolyte: An electrolyte which ionizes to a less extent in dilute aqueous solutions is called a weak electrolyte.eg.CH$_3$COOH, NH$_4$OH etc.

Distinguish between strong electrolyte and weak electrolyte

Sr.No.	Strong electrolyte	Weak electrolyte
1	It dissociates to a maximum extent in dilute aqueous solution.	It dissociates to a less extent in dilute aqueous solution.
2	The degree of dissociation is one.	The degree of dissociation is always less than one.
3	Law of mass action is not applicable	Law of mass action is applicable.
4	Their solutions have high conducting power.	Their aqueous solutions have less conducting power.

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Degree of dissociation: The fraction of the total number of moles of the electrolyte that dissociates into its ions at equilibrium is called degree of dissociation.

Factors affecting degree of dissociation:

a)Nature of solute or electrolyte: The degree of dissociation for strong electrolytes is considered as unity while for weak electrolytes, it is always less than one.

b)Nature of the solvent: The degree of dissociation is directly proportional to the polarity of solvent.Higher the polarity of the solvent, more is the degree of dissociation.

c)Concentration of the solution: The degree of dissociation increases with the decrease in concentration of the solution.

d)Temperature of the solution: The degree of dissociation increases with the increase in temperature of the solution.

Ostwald's dilution law:

Consider the dissociation of a weak electrolyte BA as shown below. Let α be its degree of dissociation and let one mole of the weak electrolyte be dissolved in V dm^3 of the solution.

$$BA \longleftrightarrow B^+ + A^-$$

Moles at start   **1**   **0**   **0**

Moles at equilibrium   **1--α** α α

Moles at equilibrium/dm^3 $\dfrac{\mathbf{1--\alpha}}{\mathbf{V}}$ $\dfrac{\alpha}{\mathbf{V}}$ $\dfrac{\alpha}{\mathbf{V}}$

By law of mass action

$$K = \frac{[B^+][A^-]}{[BA]}$$

where **K** = equilibrium constant

$$K = \frac{\dfrac{\alpha}{V} \cdot \dfrac{\alpha}{V}}{\dfrac{1-\alpha}{V}}$$

$$K = \frac{\alpha^2}{1-\alpha} \cdot \frac{1}{V}$$

For a weak electrolyte, α is very small compared to 1 and hence $1 - \alpha \approx 1$

$$\therefore \quad K = \frac{\alpha^2}{V}.$$

$$= \alpha^2 .c \text{ (because } c = 1/V \text{ where c is the initial}$$
concentration of the solution

$$\therefore \alpha = \sqrt{K/c}$$

$$or \quad \alpha = \sqrt{K.V}$$

Thus the degree of dissociation of a weak electrolyte is **inversely proportional** to **square root of its concentration** or **directly proportional** to **square root of its dilution**.

Application of Kohlrausch law**:**

1) Determine the degree of dissociation of weak electrolyte:

If Λ_0 is the molar conductivity of the weak electrolyte at zero concentration and Λ is its conductivity at any other concentration, then the degree of dissociation of the weak electrolyte is given by

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

According to Ostwald's dilution law, the dissociation constant of a weak electrolyte is given by

$$K = \frac{\alpha^2.C}{1-\alpha}$$

Substituting the value of α in the above equation, we get

$$K = \frac{(\Lambda/\Lambda_0)^2.C}{1-\Lambda/\Lambda_0}$$

$$= \frac{\Lambda^2.C \times \Lambda_0}{\Lambda^2_0(\Lambda_0 - \Lambda)}$$

$$= \frac{\Lambda^2.C}{\Lambda_0(\Lambda_0 - \Lambda)}$$

2) **Determination of solubility of a sparingly soluble salt**.

Solubility is defined as the conc. of the salt in its saturated solution at a definite temperature. Sparingly soluble salts. Such as $AgCl$, $BaSO_4$, have a very low solubility . for eg. Solubility of $SrSO_4$ is 5.260×10^{-4} mole/lit. Conductance measurement helps to determine accurately such low solubility values.

Procedure:

a) Determine the cell constant of the cell by dipping it in 0.1M KCl solution whose specific conductance at a given temperature is known.

b) Prepare a saturated solution of sparingly salt in conductivity water at a given temperature. Take this solution in a clean beaker and immerse a conductivity cell in it. Connect the cell to a conductometer and note the conductance value of the solution.

c) Wash the electrode with conductivity water, dry it and now dipped in a beaker contaiining conductivity water. Note its conductance value from the conductometer.

Calculation of solubility product of a sparingly soluble salt.

1) Determine the cell constant by using the following relation

Cell constant = Specific conductance of KCl solution
                ─────────────────────────────────────
                        Conductance of KCl

2) Determination of specific conductance of water and salt solution by using the relation

$$k = \text{cell constant} \times \text{conductance}$$

i.e $k_{water} = \text{cell constant} \times \text{Conductance}_{water}$

The sp. cond. of the saturated solution of the sparingly soluble salt is then given by,

$k_{sat.\ soln.} = \text{cell constant} \times \text{Conductance}_{satd.solution}$

3) Determination of specific conductance of the salt

This specific conductance is due to salt water and hence specific conductance of the salt is given by,

$k_{salt} = k_{soln.} - k_{water}\ \Lambda$

4) Determination of Λ_∞ from Kohlrausch law:

As the saturated solution of the salt is very dilute, therefore

$$\Lambda = \Lambda_\infty = \lambda_0^+ + \lambda_0^-$$

5) Determine the solubility of the salt

The eqv. conductance of the salt is then given by,

$$\Lambda = \frac{1000 k_{salt}}{c}, \text{ where c is conc. in gm eqv/lit}$$

If a solubility of a salt is expressed in gms eqv./lit or mole/lit, then if S is the solubility of the sparingly soluble salt in gm-eqv/lit then c in the above equation may be expressed by S.

$$\Lambda = \frac{1000 k_{salt}}{S}$$

But $\Lambda = \Lambda_\infty = \lambda_0^+ + \lambda_0^-$

$$\lambda_+^0 + \lambda_-^0 = \frac{1000 k_{salt}}{S} \text{ hence,}$$

$$S = \frac{1000 k_{salt}}{\lambda_+^0 + \lambda_-^0}$$

3) Determination of ionic product of water

Pure water is a poor conductor of electricity. Conductivity of water (ie. Redistilled water obtained by distilling water with KMnO₄) considered to be purest form of water, show conductance and its specific conductivity at 25⁰C is **5.54 x 10⁻⁸** Siemens. Water , being a weak electrolyte , ionizes to a very small extent, as follows,

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

By applying law of mass action to the above equilibrium, we get

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

As water is in large excess its concentration of water remains practically const.

$$K[H_2O] = [H^+][OH^-]$$
$$K[constant] = [H^+][OH^-]$$
$$K_w = [H^+][OH^-]$$

Where **Kw** is called the ionic product of water.

To determine the ionic product, conc. of H⁺ and OH⁻ ions must be known. This is determined by placing pure distilled water in the conductance cell and finding out the resistance of it. The specific conductance is then obtained by the equation,

$$k_{water} = \frac{cell\ const.}{R}$$

The accurately measured value of sp. conductance of water at 25⁰C is **5.8 x 10⁻⁸** moles cm⁻¹ . As water ionizes to a very less extent, its eqv. conductance value (λ_v) and eqv. conductance value at infinite dilution are almost equal.

$$\Lambda = \Lambda\infty$$

To determine **Λ∞** , we use the Kohlrausch law,

$$\Lambda_\infty = \lambda_0^+ + \lambda_0^-$$
$$= 349.8 + 198.0$$
$$= 537.8\ mhocm^2$$

Since **Λ** $= \lambda_\infty$

$$\Lambda\infty = \frac{1000k}{c}$$ where **c** is conc. in gm eqv./lit of water

Therefore $$c = \frac{1000 \times 5.8 \times 10^{-8}}{537.8}$$

= 1.059 x 10 $^{-7}$ gm-eqv./lit

Since water gives rise to one H$^+$ and one OH$^-$ ions, therefore,

$$[H^+] = [OH^-] = 1.059 \times 10^{-7} \text{gm-eqv./lit}$$

$$K_w = [H^+][OH^-] = 1.059 \times 10^{-7} \times 1.059 \times 10^{-7}$$

$$= 1.1 \times 10^{-14} \text{ at } 25^0C$$

Transport number:I

It is defined as the fraction of the total current carried by an ion in an electrolytic solution.

Factors affecting the transport number of an ion :

1) **Temperature** : The transport number increases with the temperature and approaches a certain limiting value of 0.5. This is because velocity of an ion increases with increase in temperature and therefore ion will carry large fraction of a current. However once elevated temperature is reached, both the cations and anions migrate with equal speed and therefore posses equal transport number. Hence transport number of ions ions greater than 0.5 decreases with increase in temperature, while those less than 0.5 increases.

Eg. HCl	0^{0}C	0.846	KCl	25^{0}C	0.490
	18^{0}C	0.832	KCl	30^{0}C	0.498

2) **Nature of co-ion**: The transport number of an ion in a given solution of its salt is affected by the velocity of the co-ions present in the solution. At a given temperature, an ion move with same velocity in all of its salt solution. However fraction of the current carried by the same ion in its salt solutions will depend upon velocity of the co-ion. Co-ion moving with greater velocity will decrease the transport number of the ion and vice versa. Thus ion will have different transport in different salts. Eg. t$_+$ of Cl$^-$ in NaCl is 0.61 , while in HCl it is only 0.17.

3) **Size of an ion**: The velocity of an ion is inversely proportional to the size of an ion. Ions with large size move with less velocity and hence transport number of such ions are less. In short, the transport number

of an ion increases with the decrease in size of the ion.

4) **Formation of an complex ion**: It has been found that the transport number of cadmium in 0.005N CdI$_2$ is 0.445 and it changes to 0.003 in 0.5N solution at 18^{0}C. This is due to the formation of the complex ion in the solution at higher concentration. The complex ion may be represented as ,

$$2CdI_2 \leftrightharpoons Cd_2I_4 \leftrightharpoons Cd^{++} + [CdI_4]^{--}$$
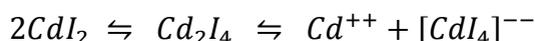
As the Cd^{+2} ion forms a part of the complex ion, it move towards anode during electrolysis. This decreases the number of Cd^{+2} ions reaching towards cathode. Besides as the mobility of complex ion is greater than Cd^{+2} ion , therefore number of Cd^{+2} ions is less in 0.5N solution than 0.005N CdI solution.

5) **Concentration:** The transport number of an ion increase with decrease in the concentration of the electrolyte. However at infinite dilution, it reaches a limiting value. The variation of transport number with concentration is represented by the relation,

$$t = t_0 - A\sqrt{C}$$

Here t and t$_0$ are the transport number of a given ion in the solution of concentration C and that to at infinite dilution resp. and A is a constant. A plot of   t v/s $\sqrt{C}$ gives a straight line with a – ve slope , which corresponds to constant A and intercept on Y axis corresponds to t$_0$.

HCl	0.1	0.05	0.01
t$_+$	0.835	0.834	0.833

6) **Hydration of ions**: When an electrolyte is dissolved in water, water molecule gets attached to the ions of the electrolyte. This increases the size of the ion, which retards its speed and hence the transport number. Eg. It is found that among the three ion Li$^+$, Na $^+$, K$^+$, the transport number of ions decreases in the order   Li $^+$ < Na $^+$< K$^+$. This is because Li$^+$ ion even though smaller in size, exert a strong filed around it and thus large number of water molecules are attracted towards it. This increase its size and thereby decreases the transport number [t (Li$^+$)= 0.33 m ,
t(Na $^+$) = 0.38, t(K$^+$)= 0.48]

Determination of transport number of an ion by moving boundary method

It is the most accurate method used to determine transport number of ions in recent years. It is based on the direct observation of migration of ions under the influence of an applied potential.

Diagram:
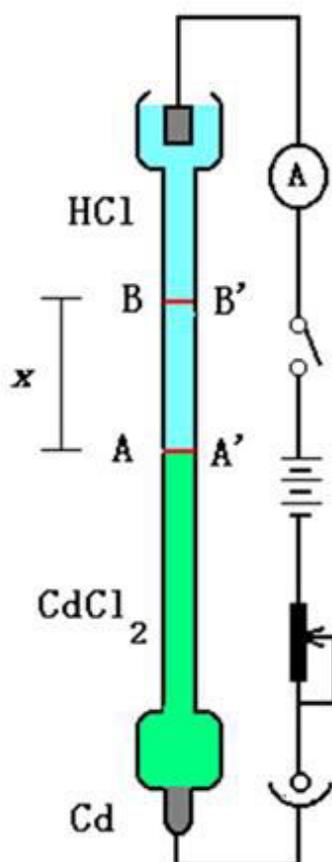
Construction:

The apparatus used for this method consist of a long gas tube which is graduated in c.c. and having two electrodes, one at the base and other at the top. The glass tube is mounted vertically and is connected in series with a milliammeter, variable resistance, a coulometer and a key. The electrode at the top is a **platinum wire** which acts as **cathode** while the **base electrode** is **metal rod** acting as anode.

Working: Consider the determination of transport number of H^+ ions in HCl solution by moving boundary method. For this purpose, the lower part of the cell is filled with an electrolyte of $CdCl_2$ while HCl solution of known concentration is slowly added from the top so that a clear boundary is visible at the junction of the two solutions. A Pt. wire in HCl solution acts as cathode while Cd stick in $CdCl_2$ solution acts as an anode.

On passing a current between two electrodes, hydrogen gas is evolved at the cathode and the hydrogen ions migrate upward through the cell. As these ions move towards the cathode, their position is taken by Cd^{+2} ions and hence the boundaries between the two solutions also move upwards. The boundary between these two electrolytes is visible because of a difference in refractive index of the solutions. Since Cd^{+2} ions have a lower velocity than H^+ ions, they never overtake the later and a sharp boundary is always maintained between the two solutions. The total current passed through the solution is determined by using Ag-coulometer. It is determined by the initial and final position of the boundary and volume swept by the boundary is noted.. The transport number of H^+ ions is then calculated as follows.

Let the conc. of H^+ ions in HCl solution be **C** gmeqv/lit. Let **A** be the area of the cross-section of the glass tube and **d** be the displacement of the boundary from initial to final position.

The volume swept by the boundary = **A x d**

The no. of gm-eqv of H^+ ions migrated towards cathode $= \dfrac{V}{1000} \times C = \dfrac{A \times d \times C}{1000}$

Now 1 gm-eqv = 1 Faraday

$\dfrac{A \times d \times C}{1000}$ gm-eqv = $\dfrac{A \times d \times C}{1000}$ Faraday

Hence the quantity of charge carried by H^+ ions in V cc of solution ie.

$$I_+ = \frac{A \times d \times C}{1000}$$

Therefore transport number of H^+ ions $= \dfrac{I_+}{Q}$

$$= \frac{A \times d \times C}{1000 \times Q} = \frac{A \times d \times C}{1000 \times It}$$

Where, Q is quantity of electricity passed, I is the current in amperes and t

	is the time in seconds.
	Problems
1	In a moving boundary experiment with 0.1N KCl using 0.005N LiCl, as indicator solution, a constant current of 0.005893 amp was passed for 2130 seconds and the boundary was observed to move through 5.6cm in a tube of 0.1142 sq.cm. cross-section. Calculate the transport number of K$^+$ and Cl$^-$ ions.
Ans	A = 0.1142 sq.cm. $Q = \frac{0.005893 \times 2130}{96500}$ $C = 0.1N$ $d = 5.6\,cm$ $$t_{K^+} = \frac{C \times A \times d}{1000 \times Q} = \frac{0.005893 \times 2130 \times 96500}{1000 \times 0.05983 \times 2130} = 0.492$$ $$\therefore\ \ t_{Cl^-} = 1 - t_{K^+} = 0.508$$

2	Calculate the transport number of H$^+$ and Cl$^-$ ions from the following data obtained by moving boundary method using CdCl$_2$ as an indicator electrolyte.
	     i) Concentration of HCl solution = 0.1N
	     ii) Wt of Ag deposited = 0.1209 gm
	     iii) Distance moved by the boundary = 7.5cm
	     iv) Cross-section of the tube = 1.24sq.cm.

Ans	$$t_{H^+} = \frac{C \times A \times d}{1000 \times Q}$$ $Q = 0.1209\ faraday$ (108 gm are deposited by 1 faraday therefore 0.1209) A=1.24 sq.cm., d= 7.5cm, C=0.1N $$t_{H^+} = \frac{0.1 \times 1.24 \times 7.5 \times 108}{1000 \times 0.1209} = 0.8308$$ $$\therefore\ \ t_{Cl^-} = 1 - t_{H^+} = 1 - 0.8308 = 0.1692$$
3	In a moving boundary method, with 0.0198N solution of NaCl, it was observed that, the boundary moved through a distance of 5.98 cm in a tube with a cross-sectional area of 0.112 sq.cm. A constant current of 0.0017 amp was passed for 1954 seconds. Find the transport number of Na$^+$ and Cl$^-$ ions.

Ans	C = 0.0198 , d = 5.98 cm , A = 0.112 sq.cm $$Q = \frac{0.0017 \times 1954}{96500}$$ $$t_{Na^+} = \frac{C \times A \times d}{1000 \times Q} = \frac{0.0198 \times 0.112 \times 5.98 \times 96500}{1000 \times 0.0017 \times 1954} = 0.3835$$ $$\therefore \quad t_{Cl^-} = 1 - t_{Na^+} = 1 - 0.3835 = 0.6145$$
	6) 0.48]

Characteristic of indicator electrolyte

The electrolyte selected and placed at the basal portion should satisfy the following conditions:

i) The anion should be common to both electrolytes (Here Cl⁻ is common to $CdCl_2$ and HCl)

ii) The speed of Cd^{+2} should be less than H^+ ions

iii) The solution of $CdCl_2$ should be more denser than HCl solution. The electrolyte $CdCl_2$ is also called an indicator electrolyte.

iv) A sharp boundary must be established at the starting of the experiment.

v) Concentration of two solutions must be in correct ratio.

Abnormal transport number:

Transport number of ions are usually + ve fractions. And the sum of transport number of cation and anion is unity. But in certain solution of higher concentration , the transport number values of cations/ anions are – ve / exceed greater than unity. Such transport numbers are called abnormal transport number. This can be explained as follows:

Consider a dilute solution of CdI_2

$$CdI_2 \leftrightharpoons Cd^{2+} + 2I^-$$

It gives Cd^{+2} ions and Iodide ions. When an electric current is passed, the ions move towards opposite charge electrodes and they show normal values of the transport number.

Now if the concentration of CdI_2 is increased, then the free iodide ions combines with undissociated molecules of cadmium iodide to form a complex ion, $CdI_2 + 2I^- \leftrightharpoons [CdI_4]^{2-}$

This decreases the number of Cd^{+2} ions in the solution and the complex anion containing Cd ion move towards anode. Thus the transport number

of Cd^{+2} ion decreases due to their migration towards anode instead of cathode. Cd^{+2} and $[CdI_4]^{2-}$

As concentration of the solution increase, more number of complex ions are formed and as a result the Cd^{2+} ions in the solution carry less electric current. Therefore their transport number becomes – ve. Since the sum of transport number of cadmium and complex ion should be unity, the

$t_{complex\ ion}$ >1. Such a behaviour of transport number is called abnormal transport number.

Conc. of CdI_2	0.01	0.1	0.2	0.5	1N
$t_{Cd^{+2}}$	0.44	0.3	0.13	-0.002	-0.42

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