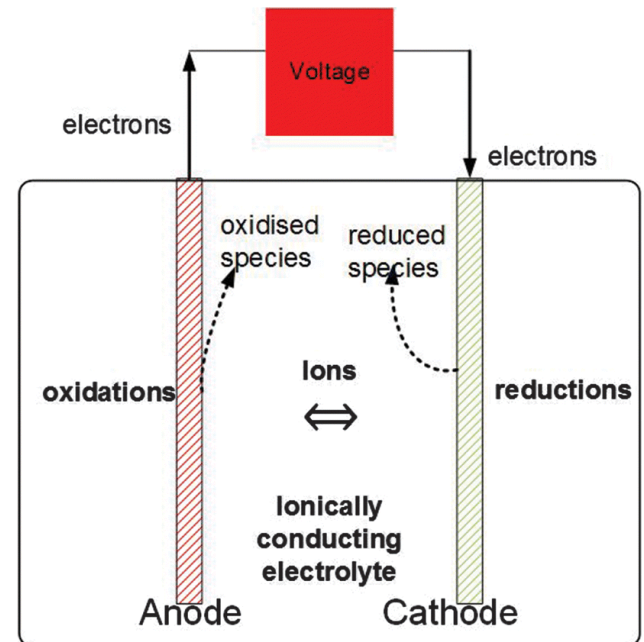


Electrolytic conductance :

Current flow between electrodes in electrochemical cells occurs through the electrolyte phase and is described in terms of a solution resistance for the electrolyte between the electrodes.

The magnitude of this resistance depends on the ionic conductivity of the electrolyte .



Conductance & Specific conductance :

Resistance and specific resistance are commonly used for metallic conductors, where the atoms are static. In case of electrolytic solutions the electricity is virtually conducted by constantly moving ions. So it was thought more meaningful to define another quantity called **conductance**

The conductance of an electrolytic solution is defined as the reciprocal of its resistance

Conductance C is given by :

$$C \equiv \bar{C} = \frac{1}{R} \quad \text{Ohm}^{-1} \text{ or mho or } \Omega^{-1} \text{ or Siemens (S)}$$

The conductance of a sample decreases with its length (l) and increases with its cross-sectional area (A)

For metals:

Ohm's Law

$$R = \frac{E}{I}$$

R : **resistance**,

Unit: Ohm, Ω

$$R = \rho \frac{l}{A}$$

resistivity

Unit: $\Omega \cdot \text{m}$

For electrolyte solution:

electric conductance (C) or \bar{C} :

Definition: $C = 1/R$

Unit: Ω^{-1} , mho, Siemens, S

Reciprocal of resistance

Conductivity or Specific conductance (L) :

Definition: $L = 1/\rho$

Unit: $\text{S} \cdot \text{m}^{-1}$

$$C \equiv \bar{C} = L \frac{A}{l}$$

Specific conductance : reciprocal of specific resistance , also known as **Conductivity**.

$$L = \frac{1}{\rho} \quad \text{Mho.cm}^{-1} \equiv \text{S} \cdot \text{Cm}^{-1}$$

Specific conductivity is defined as the conductance of a one centimeter cube of substance or solution .

$$L = \left(\frac{l}{A} \right) \bar{C}$$

$$L(\text{ohm}^{-1} \cdot \text{cm}^{-1}) = k_{\text{cell}} (\text{cm}^{-1}) \cdot \bar{C} (\text{ohm}^{-1})$$

Where: (l) is the length of the electrode.(A) is the area of the electrode. (K_{cell}) cell constant

Equivalent conductance Λ (Lambda) :

Equivalent conductance is defined as the conductance of all ions present in one gram equivalent of the substance or electrolyte in the solution at the given concentration

$$\Lambda = \frac{1000.L}{C}$$

Units of Equivalent conductivity:

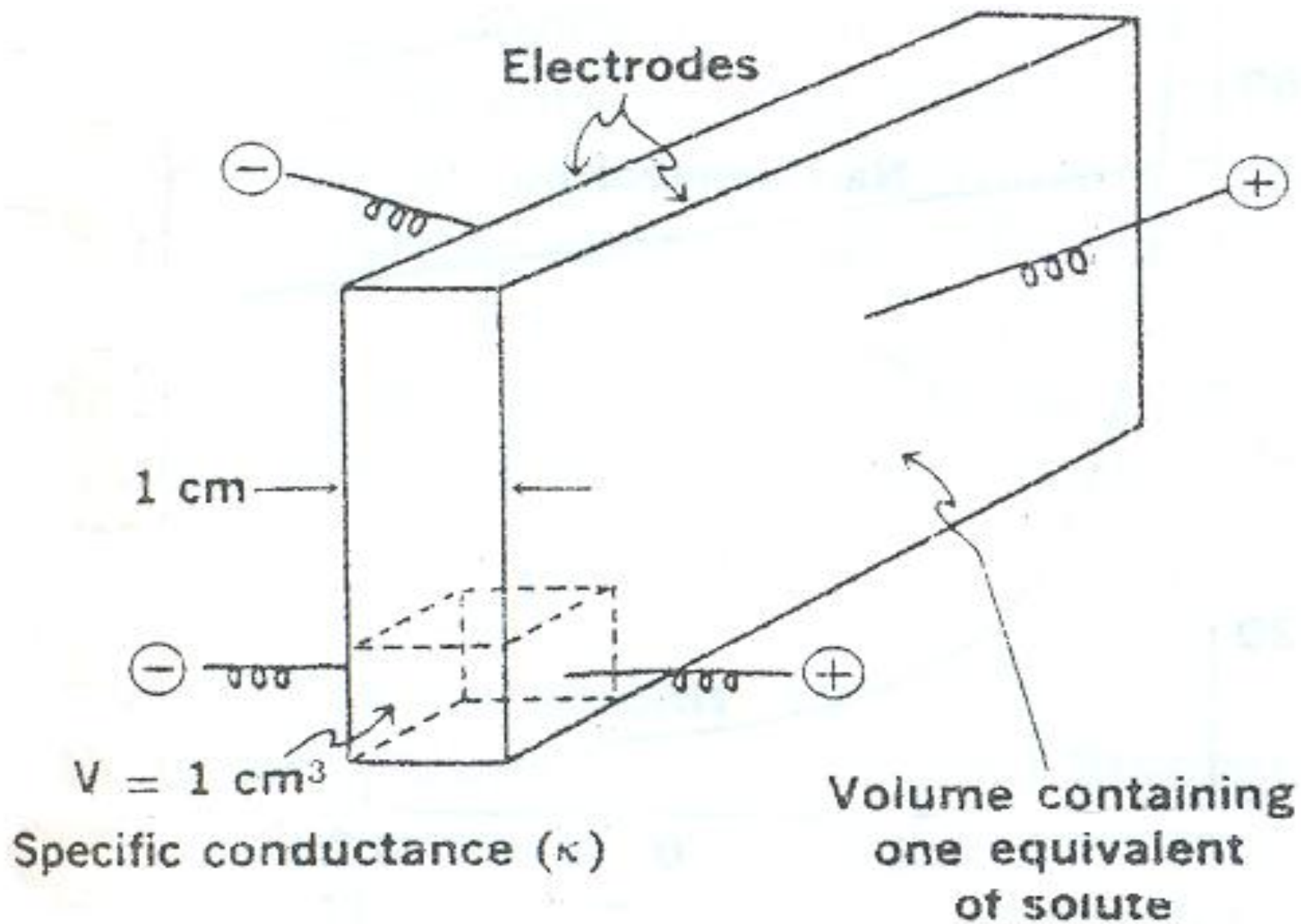
$$\text{Ohm}^{-1} \text{ Cm}^2 \text{ eq}^{-1}$$

If a sparingly soluble electrolyte ionizes in a simple manner, it is possible to calculate its solubility from specific conductance and the equivalent conductance

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

S in equi.g.cm^{-3}

Λ is never determined directly, but is calculated from the specific conductance



For a saturated solution of AgCl at 25°C, the specific conductance for water & AgCl solution was found to be $1.6 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ & $3.41 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ respectively. Determine the solubility of AgCl in water in moles per liter & the solubility constant K_{sp} , at 25°C. If the Λ_o is $138.3 \text{ equiv}^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$.

$$L_{AgCl} = L_{solution} - L_{H_2O}$$

$$L_{AgCl} = 1.81 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$$

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

$$S = \frac{1000 \times 1.81 \times 10^{-6}}{138.3}$$

$$S = 1.31 \times 10^{-5} \text{ g.eq}^{-1}$$

$$k_{sp} = [Ag^+][Cl^-]$$

$$k_{sp} = (1.31 \times 10^{-5})^2$$

Electrolytic conductance

- If the solution is 0.1 N in concentration, then the volume containing 1 gram equivalent of the solute will be 10 liters ($10,000 \text{ cm}^3$) and the equivalent conductance will be 10,000 times more than the specific conductance.
- The specific conductance of a strong electrolytic solution (κ) steadily decreases on dilution, while the equivalent conductance Λ of a strong electrolyte solution steadily increases on dilution (why?).

Molar Conductivity:

Molar conductivity is defined as the conductance of all the ions present in mole of the electrolyte in the solution

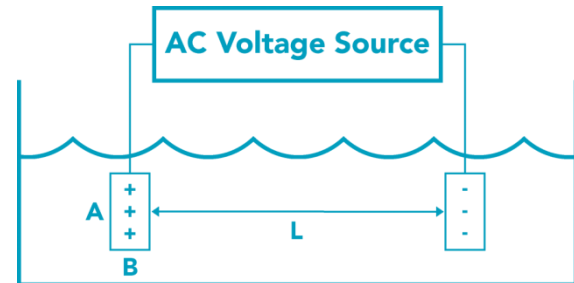
$$\Lambda_m = \frac{1000 \cdot L}{M} \quad \text{Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Equivalent conductance = (Molar conductance)/n

Cell constant:

It is the ratio of distance between two electrodes to the area of cross-section of the electrode.

$$\left(\frac{l}{A} = k \right)$$



Cell constant

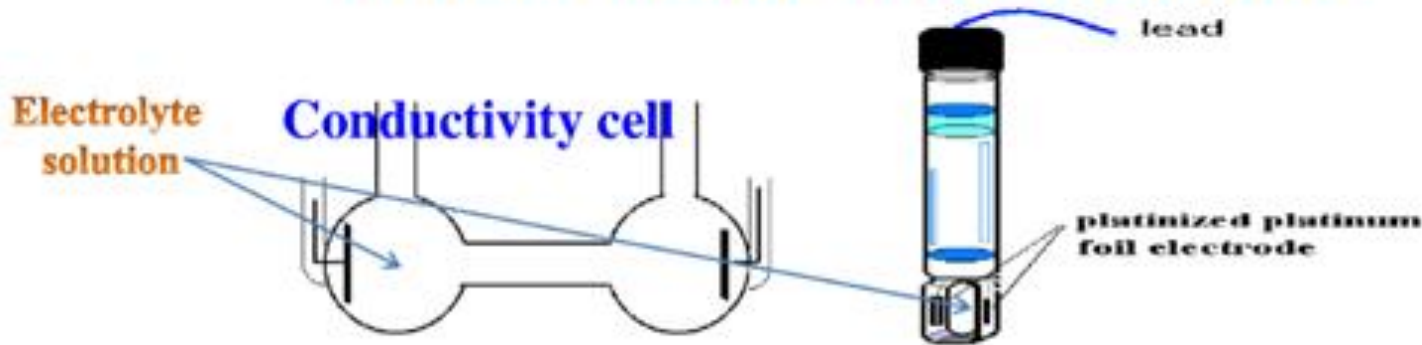
$$L = \bar{C} \left(\frac{l}{A} \right) = K_{cell} \bar{C}$$

$$K_{cell} = LR$$

EXAMPLE

The conductance of a solution is $0.689 \Omega^{-1}$. If the **cell constant** is 0.255 cm^{-1} , calculate the specific conductance of the solution.

Measurement of conductance

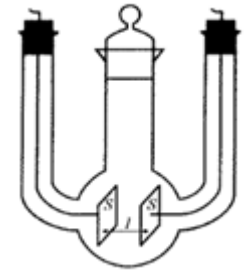


The solution are placed between two platinied platinum plates having area of cross section $A \text{ cm}^2$ & separated by distance 1.0 cm the cell constant (l/A) of the conductivity cell is determined by using 0.1M KCl solution .

The specific conductance L can be measured .

$$L = (l/A) \bar{C}$$

Also , molar conductance or equivalent conductance of solution can be calculate .



Example: The measured resistance of a cell containing 0.1g.equiv. of KCl in 1000ml at 25°C was found to be 3468.9 ohms, the specific conductance of this solution is 0.012856 ohm⁻¹ cm⁻¹ at 25°C. An exactly 0.1N solution of another substance in the same cell had a resistance of 4573.4ohms; calculate the equivalent conductance of this electrolyte at the given concentration the (conductance of the water is so small that it may be neglected).

$$K_{\text{cell}} = L.R \rightarrow K_{\text{cell}} = 0.012856 \times 3468.9 \rightarrow K_{\text{cell}} = 44.597 \text{ cm}^{-1} .$$

$$L = K_{\text{cell}} / R \rightarrow L = 44.597 / 4573.4 = 0.009751 \text{ ohm}^{-1}$$

$$\Lambda = \frac{1000L}{C} \rightarrow \Lambda = \frac{1000 \times 0.009751}{0.1}$$

$$\Lambda = 97.51 \text{ equ}^{-1} . \text{ohm}^{-1} . \text{cm}^2$$

-The resistance of a conductivity cell when filled with 0.02M KCl solution is 164 ohm at 298K. However, when filled with 0.05M AgNO₃ solution, its resistance is found it be 78.5 ohm. If the specific conductivity of 0.02M KCl is $2.768 \times 10^{-3} \text{ ohm}^{-1}.\text{cm}^{-1}$.

Calculate:

- A- The specific conductivity (κ) of 0.05M AgNO₃
- B- The molar conductivity of AgNO₃ Solution

-Calculate resistance for 0.01N KCl solution if that equivalent conductance (Λ) is equal $141.3 \text{ cm}^2.\text{ohm}^{-1}.\text{eq}^{-1}$, the cell constant is 1.48cm^{-1} , conductivity of distilled water is $10^{-6} \text{ ohm}^{-1}.\text{cm}^{-1}$.

Pure water or conductance water: Which should be used in preparing as a solvent for conductance studies solution.

- distilled water : shows poorly conductivity (weak electrolytes) but it increased by absorbing gases such as $\text{CO}_{2(g)}$, $\text{NH}_{3(g)}$ from laboratory atmosphere, alkali and other electrolytes from the glass vessels impurity. Pure distilled water resistivity is about 18 million Ω per cm ,But drop to 12 million $\Omega \text{ cm}^{-1}$ due to impurity .
- conductance water: which its conductivity $=0.8 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ this can be made by:
 - i) Using Ion exchanger (resins). That change with H^+ , OH^- (ions) and finally transferred the cations to the resin .
 - ii) by redistilling of distilled water in special apparatuses in the presence of potassium permanganate KMnO_4 and sodium hydroxide NaOH .

$$L_{\text{solution}} - L_{\text{water}} = L_{\text{solute}}$$

Determination of conductance:

For measuring resistances of electrolytic solutions the Wheatstone bridge method is employed, shown in fig 1, R_x the unknown resistance whose value is to be determined, is placed in one arm of the bridge, a variable known resistance R_s in the other. AB is a uniform slide wire across which moves a contact point C. To balance the bridge the contact is moved along this resistance until no current from the battery E flows through the galvanometer G.

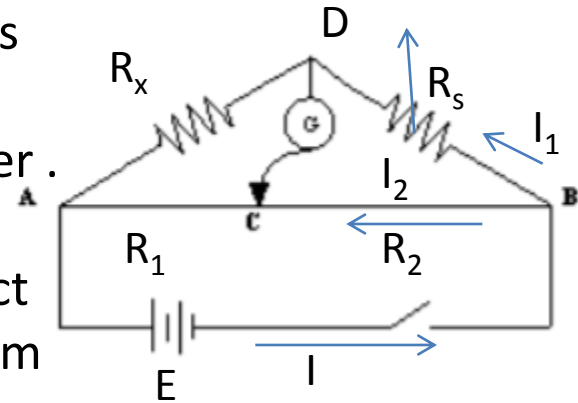


Fig 1

When this condition is reached R_s , the resistance from A to C R_1 , and that from C to B R_2 , are read, R_x is then calculated from these according to the following consideration.

When the current I from the battery reaches point B it divides into two parallel paths and into the two currents I_1 and I_2 . These currents lead to potential drops across the resistances they traverse.

The purpose of balancing the bridge is to find a point along AB, namely C, such that the potential drop from B to C is equal to that from B to D. When this point is found, D and C are at the same potential and no current flows through the branch containing the galvanometer.

The condition for bridge balance is , then :

$$R_s I_1 = R_2 I_2$$

But , when these IR drops are equal , those from D to A and from C to A must also be equal . Hence :

$$R_x I_1 = R_1 I_2$$

Dividing now the second equalities by the first , we obtain :

$$\frac{R_x}{R_s} = \frac{R_1}{R_2}$$

And , therefore :

$$R_x = R_s \left(\frac{R_1}{R_2} \right)$$

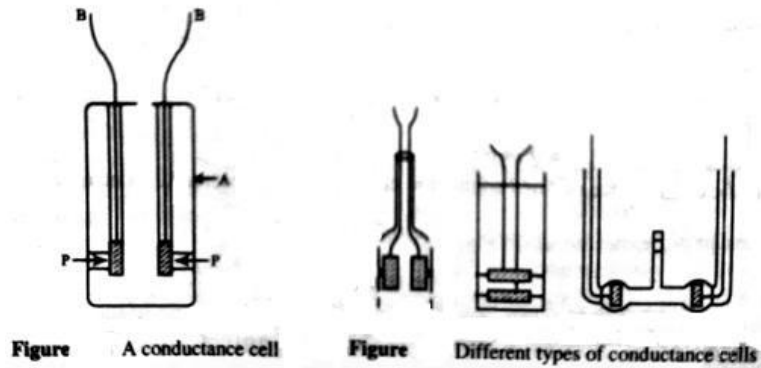
Although the principle of the Wheatone bridge as just given remains the same , several modification in technique are necessary before calculating the resistance of electrolytic solution by this method .

1-Direct current cannot be used , as it would cause electrolysis and concentration changes at the electrodes . To avoid these , alternating current is employed . Usually at a frequency of 500 – 2000 cycles per second , and supplied by either a vibrating tuning fork or a vacuum tube oscillator .

2-The electrodes in the cell are of stout platinum and they are coated with a layer of finely platinum black this tends to decrease the effect of “polarization”. This coating of finely platinum black, produced by electrolytic deposition, adsorbs gases and catalyzes their reaction. In this way the formation of non conducting gas film is prevented

The cells employed for conductance work are of various types and shapes , depending on the purpose and on the accuracy required . They are constructed of glass , with electrodes of either platinum or gold .

The distance apart the electrodes are placed in a cell is determined by the conductance of the solution to be measured , for solution of high conductance the electrodes are widely spaced , while for poorly conducting solutions the electrodes are mounted near each other . The figure below shown several cell .



- what is the purpose of using alternating current instead of direct current?

sol/ Alternating current use in order to avoid the polarization effects which causes electrolysis of the solution and these results will change the resistance of the solution.

The conductance cell is usually calibrated using standard aqueous KCl (potassium chloride) solution.

$c/ \text{mol} \cdot \text{dm}^{-3}$	0	0.001	0.0100	0.100	1.00
$L/S \text{ m}^{-1}$	0	0.0147	0.1411	1.289	11.2

Relative standards are often used in scientific measurement.

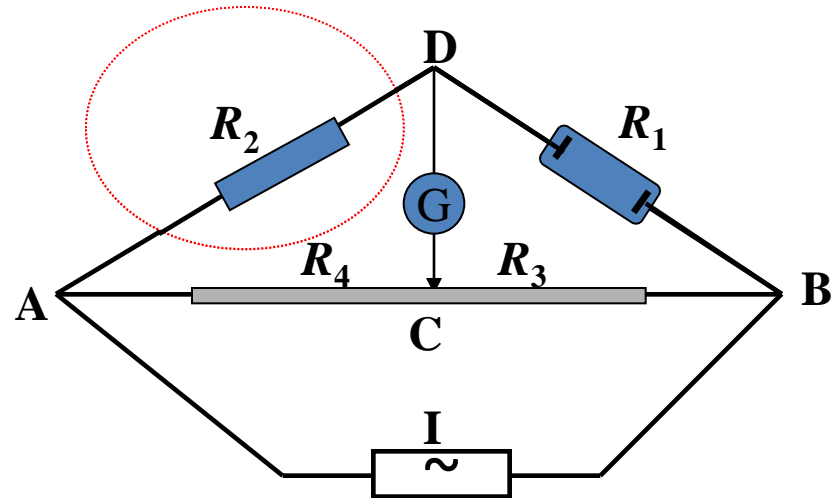
Measurement of conductance:

Wheatstone Bridge Circuit

High-frequency alternative current, ca. 1000 Hertz



Conductometer



$$R_3 \times R_2 = R_4 \times R_1$$

$$R_1 = \frac{R_2 R_3}{R_4}$$

$$\bar{C} = \frac{1}{R_1}$$

$$\bar{C} = L \frac{A}{l}$$

EXAMPLE

The conductance of a cell containing an aqueous $0.0560 \text{ mol}\cdot\text{dm}^{-3}$ KCl solution whose conductivity is $0.753 \text{ }\Omega^{-1}\cdot\text{m}^{-1}$ is $0.0239 \text{ }\Omega^{-1}$. When the same cell is filled with an aqueous $0.0836 \text{ mol}\cdot\text{dm}^{-3}$ NaCl solution, its conductance is $0.0285 \text{ }\Omega^{-1}$. Calculate the conductivity of the NaCl solution.

To determine cell constants either 1.0 , 0.1 ,or 0.01 demal solutions of potassium chloride are used .

A demal solution is a solution containing 1.0 g mole of salt per cubic decimeter of solution at 0°C , or 76.6276 g of KCl in 1000g of water .

- 0.1 demal 7.478g of potassium chloride KCl in 1000g of water
- 0.01 demal 0.7462 g of potassium chloride KCl in 1000g of water

Why KCl solution use when we measured conductivity?

KCl solution has the following physical properties :

- 1. It is easily dissolve**
- 2. It is stable at high temperature**
- 3. It has high molecular weight**
- 4. It is non-hygroscopic**

In a particular cell a 0.01 demal solution of KCl gave a resistance of 150 ohm at 25°C, while a 0.01N solution of hydrochloric acid gave a resistance of 51.4 ohm at the same temperature. The specific conductance of demal solution is 0.0014 ohm⁻¹cm⁻¹. Calculate the equivalent conductance ?

$$k_{cell} = L.R$$

$$k_{cell} = 0.0014 \times 150$$

$$k_{cell} = 0.21132 \text{ cm}^{-1}$$

$$L = \frac{k_{cell}}{R} = \frac{0.21132}{51.4}$$

$$L = 0.004111 \Omega^{-1} . \text{cm}^{-1}$$

$$\Lambda = \frac{1000L}{C} = \frac{0.00411 \times 1000}{0.01}$$

$$\Lambda = 411.1 \Omega^{-1} . \text{cm}^2 . \text{eq}^{-1}$$