

Electrochemistry

Electrochemistry is the branch of chemistry that deals with the relation between chemical changes and electricity. It deals with the study of electrical properties of electrolytes and also the chemical changes brought about by passage of electricity.

Electrolysis and Electrical Conductance

Electrolytes are electrovalent substances that form ions in solution which **conduct an electric current**. Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes.

Nonelectrolytes, on the other hand, are covalent substances which furnish neutral molecules in solution. Their water-solutions **do not conduct an electric current**. Sugar, alcohol and glycerol are typical nonelectrolytes.

An electrolyte invariably undergoes chemical decomposition as a result of the passage of electric current through its solution.

The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed **Electrolysis** (lyo=breaking).

The process of electrolysis is carried in an apparatus called the **Electrolytic cell**.

The cell contains water-solution of an electrolyte in which two metallic rods (electrodes) are dipped. These rods are connected to the two terminals of a battery (source of electricity). The electrode connected to the positive terminal of the battery attracts the negative ions (anions) and is called **anode**. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called **cathode**.

ELECTRICAL CONDUCTANCE

Substances that allow the passage of current through them are called **conductors** and the phenomenon is called **electrical conductance**.

Conductors are further divided into two categories, namely, **metallic** and **electrolytic conductors**.

Metallic Conductors

In metallic conductors, the conductance is only due to the presence of free mobile electrons. Hence, these are also referred to as electronic conductors. This electronic conductance is not accompanied by any

chemical change. The passage of current only causes physical changes, and there is no transfer of matter.

The factors that affect metallic conductance are as follows:

1. Temperature: Metallic conductance is inversely proportional to temperature. As the temperature increases, metallic conduction decreases.
2. Structure: The ease of flow of electrons depends on the structure of the metal.
3. Density: The denser the metal, lesser will be the metallic conductivity.
4. Number of valence electrons per atom: As the number of valence electrons increases, the charge on the metal cation increases; this increases the conductivity.

Electrolytic Conductors

The substances which conduct electricity both in the fused state and in the aqueous solution are called electrolytic conductors or electrolytes. These substances dissociate in molten state or aqueous solution to furnish ions. The conduction is due to the presence of these mobile ions. For example, molten or aqueous solution of sodium chloride.

Based on the extent of dissociation, electrolytes are classified into two types:

1. Strong electrolytes: These electrolytes are almost completely dissociated in their aqueous solutions and have a large value of conductance. For example, HCl, HNO₃, NaOH, KOH, NaCl and KCl.

2. Weak electrolytes: These electrolytes which do not undergo complete dissociation even in their dilute aqueous solutions and have low value of conductance. In the solution of a weak electrolyte, there exists an equilibrium between the undissociated molecules and their ions. For example, CH₃COOH, HCOOH and NH₄OH.

The dissociation of acetic acid is shown as follows:



Factors Affecting Electrolytic Conductance

Among the various factors, the following greatly influence the conductance of a solution:

1. Temperature: In case of strong electrolytes, increase in temperature increases the speed of the ions. This results in increased conductivity. In case of weak electrolytes, increase in temperature increases the degree of dissociation.

There is increase in both the number of ions as well as their speed. Hence, the conductivity increases.

2. Concentration: Generally, the conductance of a solution depends on the number of ions present in the solution and the speed of the ions. At higher concentration, the force of attraction between the ions increases, which decreases the speed of the ions. Hence, conductance decreases with increase in concentration.

3. Nature of electrolyte: In case the solution is dilute, the ions are farther apart, and their interionic interactions can be neglected; However, in a concentrated solution, the interionic interactions are higher, which restricts their free motion, and reduces the conductivity.

4. Ionic size and their extent of solvation: In solution state, the solvent–solute interactions are higher, which restricts the free motion of ions, thus decreasing the conductivity. On dilution, these interactions decrease, and ionic mobility, and hence conductance increases.

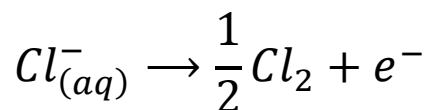
5. Viscosity: In a more viscous solvent, the ionic mobility is low, and thus conductivity of ions is decreased.

CONDUCTANCE IN SOLUTIONS OF ELECTROLYTES

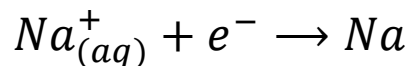
In a solution that contains ions, electrical charge is carried through the liquid by the movement of ions, not electrons. The transport of electrical charge by ions is called **electrolytic conduction**. This conduction is also called **solution conductance**. The passage of current causes physical as well as chemical changes, and the matter gets transferred in form of ions.

Consider the process of conductance of electrolyte NaCl in an aqueous solution (Fig. 1). The aqueous solution consists of Na^+, Cl^-, H^+, OH^- ions.

When electricity is provided by a battery or a DC source, the electrodes acquire electrical charges. They attract ions of opposite charge redox reactions take place at the electrodes. At the anode, the oxidation reaction occurs.



The electrons from the anode are pumped through the external circuit. These electrons are delivered to the cathode where reduction occurs:



The overall effect is that there is a flow of electrons through the external wire resulting from the flow of ions in the solution. The resulting conductance is the electrolytic conductance.

Names, symbols and units for electrical quantities

By Ohm's law, the current I , flowing through a solution of resistance R , is related to potential difference, V by

$$V = IR$$

Here, R is the resistance, offered by solution to the flow of current.

Greater is the resistance offered by the solution, lesser will be the flow of current through the solution.

Resistivity

If a solution is placed between two parallel electrodes having cross-sectional area (A) and distance (l) apart, the resistance R is directly proportional to its length and inversely proportional to its area,

$$R \propto l \quad \Rightarrow \quad R \propto \frac{l}{A} \quad \therefore \quad R = \rho \frac{l}{A}$$

where, (ρ) is called **specific resistance** or **resistivity**, Its SI unit is ($\Omega \cdot m$).

It is defined as the resistance of unit cube of a material, i.e.

$$l = 1\text{cm}, A = 1\text{cm}^2, \text{ then } R = \rho$$

Specific conductance

The reciprocal of resistivity (specific resistance) is called conductivity (specific conductance) and is represented by (κ) (kappa).

$$\kappa = \frac{1}{\rho}$$

$$\frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} \Rightarrow \kappa = \frac{1}{R} \times \frac{l}{A}$$

Electrical Conductance

The reciprocal of resistance R is called electrical conductance. It is the ease with which the electricity flows through a

solution. It is represented by G.

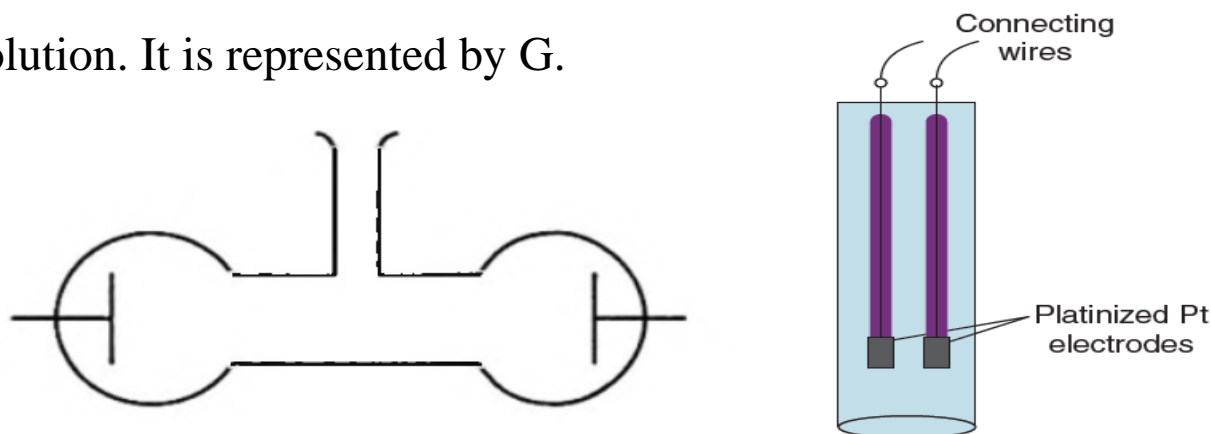


Figure (1): A simple conductivity cell

Thus

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \times \frac{A}{l}$$

Specific conductance

$$\kappa = (\text{conductance})G \times \frac{l}{A}$$

If $l = 1\text{cm}$ and $A = 1\text{cm}^2$, then:

$$\kappa = (\text{conductance})G$$

Thus, conductivity of a solution is defined as the conductance of a solution of 1cm length and its area of cross-section of 1cm². In other words, specific conductance is the conductance of one centimeter cube of a material. The SI unit of conductance is Ω^{-1} , i.e. Siemens(S) Thus specific conductance is expressed as S.cm⁻¹ or ohm⁻¹.cm⁻¹.

Cell constant

The ratio of length to the cross-sectional area is called the **cell constant** and it is a characteristic parameter of conductivity of cell used for the experiment.

$$\text{Cell constant } (G^*) = \frac{l}{A} = R \cdot \kappa$$

If (l) is in (m) and (A) is (m^2), then cell constant is expressed in (m^{-1}) and specific conductance in ($S.m^{-1}$).

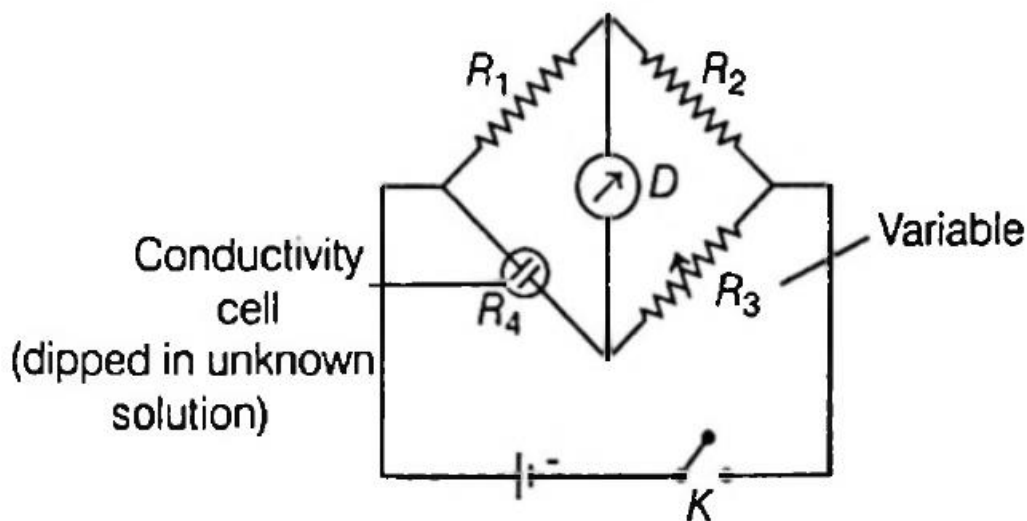
$$1 S.cm^{-1} = 100S.m^{-1}$$

$$1S.m^{-1} = 0.01 S.cm^{-1}$$

Name	Symbol	SI unit	Abbreviations for SI unit
Current	I	ampere	A
Electrical potential	ϕ	volt	V
Resistance	R	ohm (volt per ampere)	$\Omega = \frac{V}{A}$
Conductance or G	$L = R^{-1}$	siemens or ohm ⁻¹	$S = \Omega^{-1}$
Specific resistance (resistivity)	$\rho = \frac{RA}{l}$	ohm metre	Ωm
Specific conductance (conductivity)	$\kappa = \rho^{-1}$	ohm ⁻¹ metre ⁻¹ or siemens per metre	S / m
Molar conductivity	$\Lambda_m = \frac{\kappa}{C_m}$	siemens square metre mol ⁻¹	$S m^2 / mol$ $1 S m^2 mol^{-1} = 10^4 S cm^2 mol^{-1}$ $1 S cm^2 mol^{-1} = 10^{-4} S m^2 mol^{-1}$
Equivalent conductivity	$\Lambda_{eq} = \frac{\kappa}{C_{eq}}$	siemens square metre equivalent ⁻¹	$S m^2 / equivalent$

The cell constant of the conductivity cell is determined by measuring the resistance of a solution of an electrolyte of known conductivity at a given temperature. Generally, a solution of KCl at 298 K is used, for which the conductivity values are reported in literature at different concentrations and temperatures.

Measurement of R is done using **Wheatstone Bridge** principle as shown in the circuit. R_1 and R_2 are known resistances, R_3 is a variable resistance and R_4 is the unknown resistance (under study) of a conductivity cell.



Example 1: (Measurement of cell constant)

The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3} S \cdot cm^{-1}$.

Solution:

$$G^* = \frac{l}{A} = R \cdot \kappa = 1500 \text{ ohm} \times 0.146 \times 10^{-3} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$$

$$G^* = 0.219 \text{ cm}^{-1}$$

$$G^* = 21.9 \text{ m}^{-1}$$

Example 2 (Measurement of cell constant)

When a certain conductivity cell was filled with 0.1 M KCl, which has a specific conductivity of $1.12 \Omega^{-1} \cdot \text{m}^{-1}$ (it had a resistance of 55Ω at 25°C). Calculate the cell constant.

Solution:

$$G^* = R \cdot \kappa$$

$$G^* = 1.12 \times 55 = 61.6 \text{ m}^{-1}$$

Equivalent conductance and molar conductance

Molar conductance is defined as the conductance of an electrolytic solution due to all the ions obtained from 1 mol of electrolyte at a given concentration. Mathematically:

$$\Lambda_m = \frac{1000\kappa(S.cm^{-1})}{C(\frac{mol}{L})}$$

where κ is the specific conductance of the solution and C is the molar concentration of the solution. The units of molar conductance in S.I. system are $S.m^2.mol^{-1}$.

Another physical quantity called the equivalent conductance is also used. It is the conductance of an electrolytic solution due to all the ions obtained from 1 gram-equivalent (1 g-equiv.) mass of the electrolyte at a given concentration. Therefore,

$$\Lambda_{eq} = \frac{1000\kappa(S.cm^{-1})}{N(\frac{eq}{L})}$$

In S.I. system, equivalent conductance has $S m^2 g\text{-equiv}^{-1}$ as the unit.

The molar conductance of the solution reaches the maximum value. This value is called molar conductance at infinite dilution [Λ_m^o].

✓ **Problem:** For which of the following aqueous solution of a specific concentration the molar conductance (Λ_m) and equivalent conductance (Λ_{eq}) will be same:

- (a) CaCl_2 solution (b) NaCl solution (c) MgSO_4 solution (d) $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution

Soln. (b) For NaCl solution concentration in terms of both normality (i.e., no. of eq/litre) and molarity (i.e., no. of mole / litre) is same, $\therefore \Lambda_m = \Lambda_{eq}$

Effect of Dilution on Molar Conductance

Conductance of a solution depends on the number of ions. It is observed that molar conductance increases upon dilution. This may be due to the increase in the degree of dissociation of the electrolyte or due to decreased ion-ion force of attraction.

With dilution, the influence by other ions on the movement of an ion decreases. At a particular dilution, the ion becomes totally independent of other ions. At this point, it contributes maximum towards the conductance of the solution. The part of the conductance of the solution due to movement of an ion is referred to as ionic conductance.

Under the conditions, the molar conductance of the solution reaches the maximum value. This value is called molar conductance at infinite dilution (Λ_m^o).

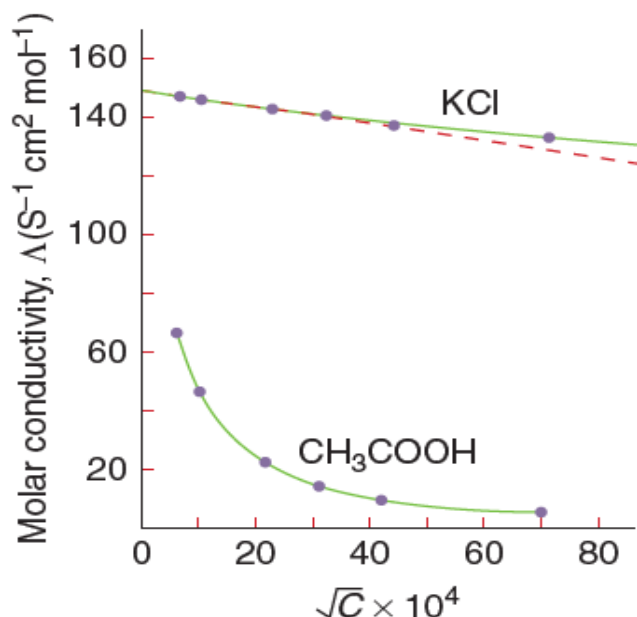
The molar conductance at infinite dilution of an electrolyte is the maximum value that an electrolyte can offer.

Kohlrausch's Law

The variation in molar conductivity with concentration for strong electrolytes is given by an empirical relation proposed by Kohlrausch based on a number of experimental observations. At low concentrations, the relation is represented by the equation

$$\Lambda_m = \Lambda_m^o - k\sqrt{C}$$

where k is a constant that is specific for a given solvent at a given temperature, but varies with the type of electrolyte, that is, the number of charges on the ions produced by dissociation of the electrolyte.



Electrolytes	Λ_m^0 ($S\ m^2\ mol^{-1}$)	Difference	Remarks
KCl NaCl	14.99×10^{-3} 12.65×10^{-3}	2.34×10^{-3}	Difference in conductance is due to difference in conductance of K^+ and Na^+ ions
KNO_3 $NaNO_3$	14.5×10^{-3} 12.16×10^{-3}	2.34×10^{-3}	
KCl KNO_3	14.99×10^{-3} 14.5×10^{-3}	0.49×10^{-3}	Difference in conductance is due to difference in conductance of Cl^- and NO_3^- ions
NaCl $NaNO_3$	12.65×10^{-3} 12.16×10^{-3}	0.49×10^{-3}	
HCl HNO_3	42.62×10^{-3} 42.13×10^{-3}	0.49×10^{-3}	

Example 14.3 [Measurement of equivalent and molar conductance)

When a certain conductivity cell was filled with 0.020 M KCl which has a specific conductivity of ($0.2768\ ohm^{-1} \cdot m^{-1}$), it had a resistance of $82.40\ \Omega$ at $25^\circ C$. With 0.0025 M K_2SO_4 , it has a resistance of $326\ \Omega$.

Calculate:

- the cell constant
- conductivity of K_2SO_4 solution
- equivalent conductance and molar conductance of K_2SO_4 .

Solution:

a- $G^* = \kappa \times R = 0.2768 \times 82.4 = 22.81 \text{ m}^{-1}$

b- specific conductance of K_2SO_4 solution

$$\kappa = \frac{G^*}{R} = \frac{22.81 \text{ m}^{-1}}{326 \Omega} = 0.07 \text{ S} \cdot \text{m}^{-1}$$

c- $\Lambda_m = \frac{1000 \times 0.0007 \text{ S} \cdot \text{cm}^{-1}}{0.0025 \left(\frac{\text{mol}}{\text{L}}\right)} = 280 \text{ S} \cdot \text{cm}^2 / \text{mol}$

$$\Lambda_{eq} = \frac{1000 \times 0.0007 \text{ S} \cdot \text{cm}^{-1}}{0.005 \left(\frac{\text{eq}}{\text{L}}\right)} = 140 \text{ S} \cdot \text{cm}^2 / \text{equ}$$