

Conductivity

Arrhenius theory of electrolytic dissociation

The main points of the theory are:

1. Arrhenius proposed that when an electrolyte is dissolved in water, it dissociates into electrically charged particles called ions. The positively charged ions are called cations, and the negatively charged ions are called anions. In solution, a dynamic equilibrium exists between the undissociated molecules and the ions formed. This can be represented as:



2. The ions present in the solution are free to move independently when an electric field is applied. Cations move towards the negative electrode (cathode), while anions move towards the positive electrode (anode).
3. The number of cations and anions may not be equal, but the total positive charge is always equal to the total negative charge. Therefore, the solution as a whole remains electrically neutral.
4. The extent of dissociation is not the same for all electrolytes. It depends on the concentration of the electrolyte, the temperature, and the nature of the electrolyte.

Conductivity of electrolyte solutions:

Solutions, like metallic conductors, obey Ohm's law. The law states that the current strength (I) is directly proportional to the applied potential difference (V) and inversely proportional to the resistance (R) of the conductor.

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

The *conductance* (C) of a solution is the inverse of resistance (R); the lower the resistance of a solution, the greater its conductance.

Unit of C : ohm^{-1} or mho. Its official designation is Siemens (S).

The resistance of a sample increases with its length (l) and decreases with its cross-sectional area (A). Therefore,

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

The constant of proportionality (ρ) is called the *specific resistance or resistivity* of the conductor.

If $l = 1\text{m}$ and $A = 1\text{m}^2$, then $\rho = R$. Hence, specific resistance (ρ) is the resistance of a conductor of unit length and of a unit area of cross-section. On other words, specific resistance (ρ) is the resistance of a unit cube of the material.

Specific conductance or conductivity (κ): The specific conductance or conductivity of any conductor is defined as the reciprocal of specific resistance(ρ).

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

or

$$\kappa = \frac{l}{RA}$$

Unit of κ : $\text{Ohm}^{-1}\text{m}^{-1}$ or moh m^{-1} or S m^{-1} .

Now, if $l = 1\text{m}$, $A = 1\text{m}^2$, then

$$\kappa = \frac{1}{R} = C$$

Specific conductance or conductivity (κ) is the conductance of a material of a unit length and unit area of cross-section. Alternatively, *specific conductance* is the conductance of a one-meter cube of the material.

Molar Conductivity (Λ_m)

The *molar conductivity* is the conductivity the solution would have if there were one mole of the electrolyte in one meter cube of the solution. Thus, *molar conductivity is the conducting power of all the ions produced by 1 mole of electrolyte in a given solution.*

Molar conductivity (Λ_m) is related to the specific conductance (κ) by the relation:

$$\Lambda_m = \frac{\kappa}{c}$$

where c is the molar concentration of the added electrolyte.

Unit:

$$\Lambda_m = \frac{\kappa}{c} = \frac{\text{Sm}^{-1}}{\text{mol m}^{-3}} = \text{Sm}^2\text{mol}^{-1}$$

Prob 1: The molar conductivity of 0.100 M KCl (m) at 298 K is $129 \text{ S cm}^2\text{mol}^{-1}$. The measured resistance in a conductivity cell was 28.44Ω . The resistance was 31.60Ω when the same cell contained 0.0500 M NaOH (aq). Calculate the molar conductivity of NaOH (aq) at that concentration.

Solution:

Conductivity of 0.100M KCl(aq)

$$\Lambda_m = \frac{\kappa}{c}$$

or

$$\begin{aligned}\kappa &= \Lambda_m c = 1.29 \times 10^{-2} \text{Scm}^2 \text{mol}^{-1} \times 0.10 \text{molL}^{-1} \\ &= 1.29 \times 10^{-2} \text{Scm}^2 \text{mol}^{-1} \times 10^{-4} \text{mol cm}^{-3} = 1.29 \times 10^{-2} \text{S cm}^{-1}\end{aligned}$$

Cell constant

$$K = \kappa R = 1.29 \times 10^{-2} \text{S cm}^{-1} \times 28.44 \text{ Ohm} = 0.367 \text{ cm}^{-1} [\because \text{S} = \text{Ohm}^{-1}]$$

For NaOH(aq),

$$\kappa = \frac{K}{R} = \frac{0.367 \text{ cm}^{-1}}{31.60 \text{ Ohm}} = 1.16 \times 10^{-2} \text{S cm}^{-1}$$

$$\therefore \text{molar conductivity, } \Lambda_m = \frac{\kappa}{c} = \frac{1.16 \times 10^{-2} \text{S cm}^{-1}}{0.0500 \text{ molL}^{-1}} = \frac{1.16 \times 10^{-2} \text{S cm}^{-1}}{5 \times 10^{-5} \text{ molcm}^{-3}} = 232 \text{ Scm}^2 \text{mol}^{-1}$$

Problem 2: Specific resistance and resistance of 0.01 M KCl solution at 298 K are 0.1413 Sm⁻¹ and 94.3 Ohm. Using the same conductivity cell resistance of 0.02M AgNO₃ solution was found to be 50.3 Ohm. Calculate (a) cell constant of the conductivity cell, (b) specific conductance and molar conductivity of AgNO₃ solution.

Solution:

For KCL solution,

$$\kappa = 0.1413 \text{ Sm}^{-1}$$

$$R = 94.3 \text{ Ohm}$$

Cell constant

$$K = \kappa R = 0.1413 \text{ S m}^{-1} \times 94.3 \text{ Ohm} = 13.32 \text{ m}^{-1} [\because \text{S} = \text{Ohm}^{-1}]$$

For AgNO₃ solution:

$$R = 50.3 \text{ Ohm}$$

Specific conductance,

$$\kappa = \frac{K}{R} = \frac{13.32 \text{ m}^{-1}}{50.3 \text{ Ohm}} = 0.2648 \text{ S m}^{-1}$$

\therefore Molar conductivity,

$$\Lambda_m = \frac{\kappa}{c} = \frac{0.2648 \text{ S cm}^{-1}}{0.02 \text{ mol dm}^{-3}} = \frac{0.2648 \text{ S cm}^{-1}}{0.02 \times 10^3 \text{ mol m}^{-3}} = 1.324 \times 10^{-2} \text{ Scm}^2 \text{mol}^{-1}$$

variation of specific conductance with dilution

Conductivity decreases with dilution. This is due to the fact that although the total number of ions increases with dilution, owing to increased dissociation, the number of ions per unit volume decreases resulting in a decrease in conductivity.

For strong electrolytes, the increase in specific conductance with increase of concentration is sharp; but for weak electrolytes, the increase in specific conductance is more gradual. Therefore, for strong electrolytes κ is almost proportional to the concentration. But, in case of weak electrolytes, concentration dependence of increase in specific conductance is not large with increase in concentration.

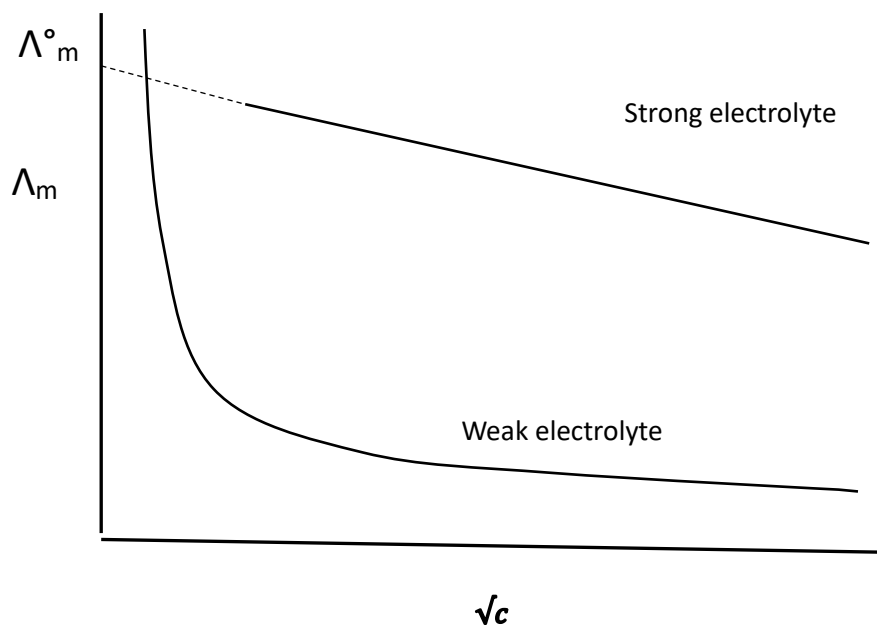
Variation of molar conductivity with concentration

Variation of molar conductivity with concentration depends on the type of electrolyte:

(i) Strong electrolyte: For strong electrolyte molar conductivity decreases only slightly as its concentration is increased. Almost all inorganic salt (ionic solids) and strong acids fall in this category. Strong electrolytes are fully ionized in solution.

ii) Weak electrolytes: For weak electrolyte molar conductivity is normal at concentrations close to zero, but falls sharply to low values as the concentration increases. Weak electrolytes are substances that are not fully ionized in solution. e.g. weak Bronsted acid and bases such as CH_3COOH and NH_3 .

Variation of molar conductance with concentration is shown below for both strong and weak electrolytes:



The conductance of a solution depends on the number of ions and ionic mobility. The sharp increase in Λ_m of a weak electrolyte as $c \rightarrow 0$ is due mainly to the rapid increase in the degree of ionization. Increase

in the degree of dissociation indicates an increase in the number of ions. Also, at higher dilutions interionic attractions are smaller, therefore ionic mobility is greater.

In case of strong electrolytes, Kohlrausch showed that at low concentrations the molar conductivities of strong electrolytes vary as the square root of the concentration:

$$\Lambda_m = \Lambda_m^0 - k\sqrt{c}$$

The constant Λ_m^0 is the limiting molar conductivity or molar conductivity at infinite dilution:

$$\Lambda_m^0 = \lim_{c \rightarrow 0} \Lambda_m$$

When $c \rightarrow 0$, all interionic effects are absent. This can be obtained by extrapolating the Λ_m vs \sqrt{c} curve for strong electrolytes to zero concentration. k is a coefficient which is found to depend on stoichiometry of the electrolyte (whether MA type or M_2A type, etc.).

In case of strong electrolytes (since strong electrolytes are completely ionized), the number of ions is the same at all dilutions and the variation of Λ_m with dilution is due to the change in the speed of the ions with dilution. In concentrated solutions of such electrolytes, interionic attractions among the oppositely charged ions would be quite appreciable. Electrolytes other than 1 : 1 type form ion-pairs, which reduces the ionic concentrations. In case of 1:1 electrolyte, interionic forces considerably lower the speed of the ions and hence conductivity of the solution. As the dilution is increased, the interionic attractions decrease with the result that the ions will move more freely.

Kohlrausch Law of Independent Migration of Ions

At infinite dilution where all interionic effects are absent, each ion of an electrolyte migrates independently of its co-ion, and contributes a definite share to the total molar conductivity of the electrolyte. This is called Kohlrausch law of independent migration of ion.

If 1 mol of an electrolyte ionizes to give ν_+ mole of cation and ν_- mole of anion then molar conductivity of the electrolyte at infinite dilution is given by

$$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$$

where λ_+^0 is the molar conductivity of cation at infinite dilution and λ_-^0 is that of the anion.

For strong electrolytes, Λ_m^0 can be estimated directly by extrapolating the Λ_m vs \sqrt{c} curve to zero concentration. But in case of weak electrolytes, Λ_m^0 can't be obtained directly by extrapolating the Λ_m vs \sqrt{c} curve to zero concentration. By applying Kohlrausch law, Λ_m^0 for weak electrolyte can be obtained.

e.g. Applying Kohlrausch's law Λ_m^0 for acetic acid can be expressed as:

$$\begin{aligned}
\Lambda_m^0(\text{CH}_3\text{COOH}) &= \lambda^0(\text{H}^+) + \lambda^0(\text{CH}_3\text{COO}^-) \\
&= [\lambda^0(\text{H}^+) + \lambda^0(\text{Cl}^-)] + [\lambda^0(\text{Na}^+) + \lambda^0(\text{CH}_3\text{COO}^-)] - [\lambda^0(\text{Na}^+) + \lambda^0(\text{Cl}^-)] \\
&= \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl})
\end{aligned}$$

Since the quantities on the right-hand side are experimentally determined and are known, hence $\Lambda_m^0(\text{CH}_3\text{COOH})$ can be calculated.

Problem 3: The molar conductivities at infinite dilution of KCl, KNO_3 and AgNO_3 at 298 K are $0.01499 \text{ Sm}^2\text{mol}^{-1}$, $0.01450 \text{ Sm}^2\text{mol}^{-1}$ and $0.01334 \text{ Sm}^2\text{mol}^{-1}$ respectively. What is the molar conductivity of AgCl at infinite dilution at 298 K?

Solution: Applying Kohlrausch's law Λ_m^0 for AgCl can be expressed as:

$$\begin{aligned}
\Lambda_m^0(\text{AgCl}) &= \lambda^0(\text{Ag}^+) + \lambda^0(\text{Cl}^-) \\
&= [\lambda^0(\text{Ag}^+) + \lambda^0(\text{NO}_3^-)] + [\lambda^0(\text{K}^+) + \lambda^0(\text{Cl}^-)] - [\lambda^0(\text{K}^+) + \lambda^0(\text{NO}_3^-)] \\
&= \Lambda_m^0(\text{AgNO}_3) + \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KNO}_3) \\
&= (0.01334 + 0.01499 - 0.01450) \text{ Sm}^2\text{mol}^{-1} \\
&= 0.01383 \text{ Sm}^2\text{mol}^{-1}
\end{aligned}$$

Problem 4 Calculate limiting molar conductivity of BaCl_2 in water at 298 K. Given that limiting ionic conductivities of Ba^{2+} and Cl^- at 298 K are $12.72 \text{ mS m}^2 \text{ mol}^{-1}$ and $7.63 \text{ mS m}^2 \text{ mol}^{-1}$ respectively.

Degree of dissociation or Degree of ionization

Degree of dissociation is the fraction of the total number of molecules dissociated. This is given by

$$\alpha_c = \frac{\text{number of molecules dissociated}}{\text{total number of molecules}}$$

where c indicates the concentration dependence of α .

For all strong electrolytes at all concentrations $\alpha = 1$. For weak electrolytes $\alpha < 1$ at a given concentration, and only at infinite dilution $\alpha = 1$.

Arrhenius showed that for an electrolyte at a given concentration, the ratio of molar conductivity of the electrolyte to its molar conductivity at infinite dilution is the degree of dissociation at that concentration.

$$\alpha_c = \frac{\Lambda_m}{\Lambda_m^0}$$

where Λ_m molar conductivity of the electrolyte at concentration c, Λ_m^0 molar conductivity at infinite dilution.

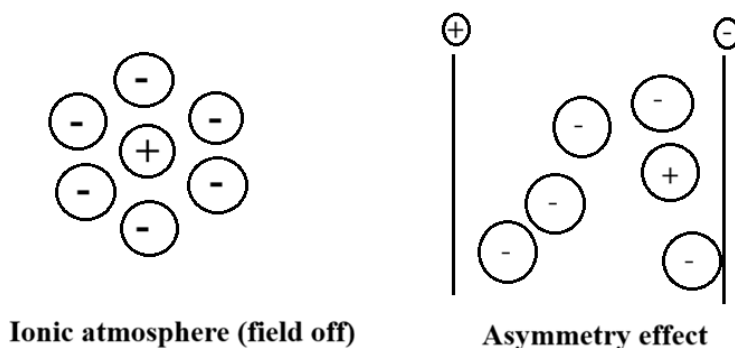
The above equation can't be applied to strong electrolytes, because strong electrolytes are completely ionized at all concentrations i.e., at all concentrations $\alpha = 1$ which implies $\Lambda_m = \Lambda_m^0$.

Debye-Huckel-Onsager Theory

To account for the variation of molar conductance of strong electrolytes with concentration, Debye and Huckel proposed this theory in 1923. The main postulates are:

i) *Formation of ionic atmosphere*

As a result of electrostatic attraction between oppositely charged ions, each ion in solution is surrounded by the oppositely charged ions i.e. each ion is surrounded by an ionic atmosphere of oppositely charged ions. On the absence of an electric field, the ionic atmosphere is spherically symmetrical with respect to a central ion as shown in figure below:



ii) *Asymmetry Effect or Relaxation Effect*

When a potential is applied across the solution, ions move towards oppositely charged electrodes. In the first place, the ions forming the ionic atmosphere do not have time to adjust itself to remain spherically symmetrical around the central ion. The atmosphere thus lags behind. Because the two charges are opposite, the resultant is a retardation of the moving ion. This reduction of the ions' mobility is called relaxation effect or asymmetry effect.

iii) *Electrophoretic effect*

The moving ions experiences a viscous drag due to the presence of solvent molecules associated with it. When the ionic atmosphere is present, this drag is enhanced because the ionic atmosphere moves in an opposite direction to the central ion. This enhanced viscous drag is called electrophoretic effect and it reduces ionic mobility of the ions, and hence also reduces their conductivities.

Debye and Huckel showed that these retarding effects on an ion produce a decrease in molar conductivities of ions when concentration (c) is increased. When dilution is increased, both the effects begin to decay and at infinite dilution, interionic attraction is absent since the separation between the ions is maximum. Hence, molar conductivity becomes maximum at infinite dilution.

For a 1:1 electrolyte (like KCl), Debye-Huckel derived the following relation:

$$\Lambda_m = \Lambda_m^0 - \left[\frac{82.4}{(\epsilon T)^{\frac{1}{2}} \eta} + \frac{8.90 \times 10^5 \Lambda_m^0}{(\epsilon T)^{\frac{3}{2}}} \right] \sqrt{c}$$

Here, ϵ is dielectric constant of the solvent.

T = temperature of solution (K).

η = velocity coefficient of solution.

This is known as the Debye-Huckel-Onsager equation. This equation explains how molar conductivity varies with concentration. The limiting molar conductivity is always greater than the molar conductivity at finite concentrations. The decrease in molar conductivity arises due to two main effects: the electrophoretic effect and the asymmetry (relaxation) effect. The first term inside the bracket represents the contribution of the electrophoretic effect, while the second term represents the contribution of the asymmetry effect. The sum of these two terms, when multiplied by \sqrt{c} , gives the total decrease in molar conductivity from its limiting value. In other words, as the concentration increases, these effects become more significant, leading to a reduction in Λ_m from Λ_m^0 .

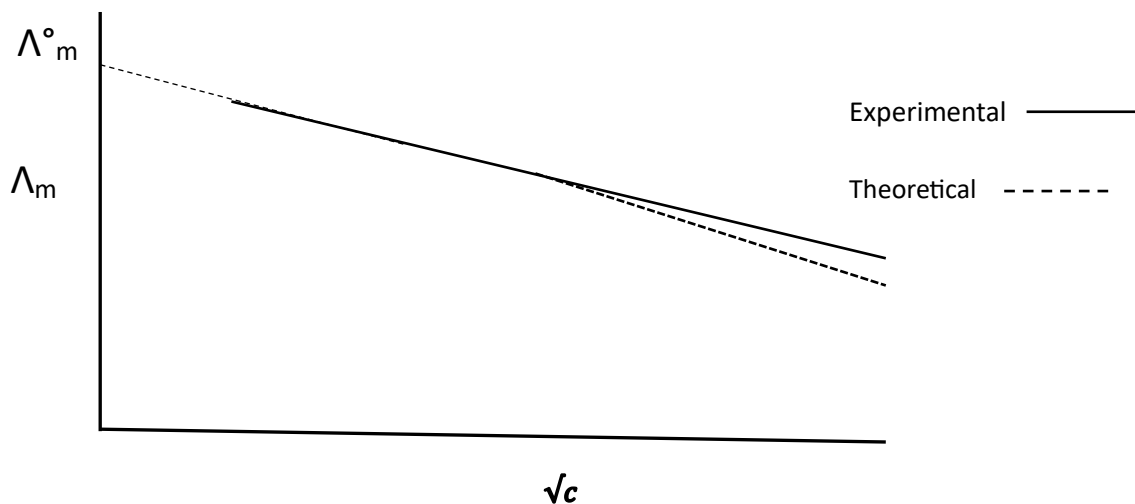
The equation can be simplified as

$$\Lambda_m = \Lambda_m^0 - [A + B \Lambda_m^0] \sqrt{c}$$

Here

$$A = \frac{82.4}{(\epsilon T)^{\frac{1}{2}} \eta} \quad ; \quad B = \frac{8.90 \times 10^5}{(\epsilon T)^{\frac{3}{2}}}$$

Limitation: At higher concentration Debye-Huckel-Onsager theory shows lower value of molar conductivity than the experimentally observed values.



Debye–Falkenhagen Effect

The Debye–Falkenhagen effect refers to the increase in conductance of an electrolyte solution when subjected to a high-frequency alternating electric field.

When the frequency of the alternating current is high, the time of oscillation becomes very small compared to the relaxation time of the ionic atmosphere. Under these conditions, the ionic atmosphere does not get distorted and remains symmetric around the central ion. As a result, the asymmetry (relaxation) effect is greatly reduced or completely absent, leading to an increase in conductance. Therefore, conductance becomes dependent on the frequency of the applied field—the higher the frequency, the higher the conductance.

Experimentally, the conductance remains nearly constant up to low frequencies (around 10 cycles per second), but at higher frequencies, it increases and approaches a limiting value corresponding to the complete disappearance of the asymmetry effect. This phenomenon is also referred to as the dispersion of conductance.

Wien Effect

The increase in conductance of an electrolyte solution under a high potential gradient (strong electric field) is called Wien effect.

At very high field strengths (e.g., $\sim 20,000 \text{ V cm}^{-1}$), ions move so rapidly that they traverse distances comparable to several times the thickness of their ionic atmosphere within its relaxation time. As a result, the ionic atmosphere does not have sufficient time to form properly around the moving ion.

Consequently, the ion becomes nearly free from the influence of its oppositely charged ionic atmosphere. Both the electrophoretic and asymmetry (relaxation) effects become negligibly small or may even disappear. Due to this, the conductance of the solution increases with increasing field strength and approaches a limiting value. This phenomenon is known as the Wien effect.

Walden Rule

The Walden rule relates the molar conductivity of an electrolyte to the viscosity of the solvent. It states that the product of limiting molar conductivity (Λ_m^0) and the viscosity of the solvent (η) remains approximately constant at a given temperature:

$$\Lambda_m^0 \eta = \text{constant}$$

This implies that ions move more easily (higher conductivity) in solvents of lower viscosity, and vice versa. Thus, ionic mobility is inversely proportional to the viscosity of the medium.