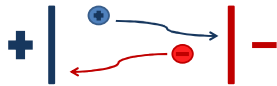


Ionic conductivity

Electric field

- Ions in electrolyte can move (if not stirred on purpose and without any current passed through it) due to self-diffusion or convection only.
- In an electric field this movement has an established direction: cations (+) are moving towards negative electrode (-) and anions (-) are moving towards positive electrode (+). This phenomenon is called **migration**.



Ionic mobility

- Mobility of an ion translates into maximum velocity of an ion, that defines maximum current that can flow through the given electrolyte.
- For the electrolyte solution such as NaCl (that fully dissociates, anions to cations ratio is 1:1 and both are singly charged ions) current is defined as:

$$I = e \cdot A \cdot E \cdot (N_+ \cdot u_+ + N_- \cdot u_-)$$

$$[A \cdot s \cdot m^2 \cdot V \cdot m^{-1} \cdot m^{-3} \cdot m^2 \cdot s^{-1} \cdot V^{-1} = A \cdot m^{2-1-3+2} = A]$$

current = elementary charge · field cross-section area ·
 · electric field intensity · (number of ions · ionic mobility)
 elementary charge is $1.602 \cdot 10^{-19} \text{ C}$ [C=A·s]

Electrolyte-electrode

- Phases on interface of which electrolyte transfer electrons (by oxidizing/reducing ions/into ions) are called **electrodes** (usually they are solid).
- Conducting electricity is a result of ion movement – electron transfer on the **electrode-electrolyte interphase**, ionic movement in electrolyte to the other electrode and a second electron transfer at the other electrode-electrolyte interphase.

Migration

Movement in the electric field theoretically should be an uniformly accelerated motion, although acceleration is limited at one point due to friction force (it exists at the molecular level as well). It is that force that defines maximum ionic velocity (in the given solvent, at the given electric potential, at the given temperature), that is called **ionic mobility (u)**, and it is measured in $m^2/(s \cdot V)$ [(m/s)/(V/m)].

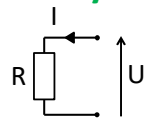
Current intensity vs conductivity

- I Ohm's law: $I = U/R$ ($I = E \cdot L/R$)
- II Ohm's law: $R = L/(\kappa \cdot A)$

If R in 1. is substituted with 2. then: $I = \kappa \cdot E \cdot A$
 where κ is **electrolyte conductivity**.

If one substitutes I in the previous equation:
 $I = e \cdot A \cdot E \cdot (N_+ \cdot u_+ + N_- \cdot u_-)$ with one above, then:
 $\kappa = e \cdot (N_+ \cdot u_+ + N_- \cdot u_-)$ (e – constant – elementary charge)

Conclusion: ionic conductivity depends on mobility and number of ions.



Conductivity

- **Specific conductivity** is a parameter of the material (e.g. metal, solution), measured in Siemens per centimeter (S/cm). Conductivity is a parameter of a specific sample with a fixed dimensions. Conductivity is the inverse of resistivity.
- In order to convert measured conductivity (or resistance) of a sample to specific conductivity of the material, one have to take into account dimensions of a conductivity cell that are calculated in the form of so-called **cell constant**. Due to the complicated (at least, usually) shape of the conductivity cell, cell constant is calibrated with the solution of a known conductivity, such as KCl solution with 0.01 M concentration.

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Conductivity

Calculate specific conductivity of the X solution, where resistance is $R = 50 \text{ Ohm}$ and the cell constant is

$$k = 0.5 \text{ cm}^{-1}$$

$$\kappa = k/R = 0.5 / 50 = 0.01 \text{ S}\cdot\text{cm}^{-1} = 10 \text{ mS}\cdot\text{cm}^{-1} \quad [\text{Ohm} = \text{S}^{-1}]$$

Calculate specific conductivity of the Y solutions, where resistance is $R = 20 \text{ Ohm}$ and the cell constant is

$$k = 0.1 \text{ cm}^{-1}$$

$$\kappa = k/R = 0.1 / 20 = 0.005 \text{ S}\cdot\text{cm}^{-1} = 5 \text{ mS}\cdot\text{cm}^{-1}$$

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Theory vs practice - purity

One ion surrounded by solvent molecules only is a theoretical situation. In practice it is impossible to obtain such a pure solution – other ions or other impurities will be always present at least at the 1 ppm concentration level. That still means billions of millions of atoms/compounds/ions.

Extremely pure substances for medical or ultra-pure for specialty applications have their purity at the 99.9999% level, which means exactly 1 ppm level of impurities. Most of the “pure” substances in our environment is not even 99% pure (water, fuels), although their purity is enough for “normal” applications.

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Purity/precision cont'd

The manufacturing cost of the compound/material unit with a given purity, regardless of the base cost (raw material), is increasing by more-less order of magnitude for every order of magnitude of the required purity.

It is a similar case with measuring apparatuses or manufacturing equipment – for every order of magnitude of precision or purity of production the cost increases more-less by order of magnitude. For balances it is:

Bathroom/kitchen scale ($d=100\text{-}10\text{g}$) – tens of \$

General laboratory balance ($d=0.1\text{g}\text{-}0.01\text{g}$) – \$100-\$300

Analytical balance ($d=1\text{mg}$) – \$1,000-\$2,000

Analytical balance, high precision ($d=0.1\text{mg}\text{-}0.01\text{mg}$) – \$5,000-\$15,000

Microbalance ($d=1\mu\text{g}\text{-}0.1\mu\text{g}$) – \$30,000+

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Molar conductivity – again

- If one ion shows up in the volume of pure solvent, it would interact with solvent only, thus having the freedom of movement in any direction;
- When the counter-ion shows up, ions have a chance to form ionic pair, thus slowing the movement of ions (they stop for the time of ionic pair existence). Subsequently, they go into separate ways, and upon the next meeting they would form pair again. Ionic pair does not have a charge (“0”) and does not move in an electric field. Formation of an ionic pair even for a tick, statistically slows down mean value of ionic velocity.
- The more ions in the solution, the higher chance for them to meet each other and to be slower, statistically.

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Molar conductivity

- Conductivity (and mobility) of an ion per concentration is called **molar conductivity**:

$$\Lambda = \kappa / c$$

$$\Lambda = 1000 \cdot \kappa / c \quad (1000 \text{ is from } \text{dm}^3 \text{ conversion to } \text{cm}^3)$$

- It is the highest for the infinitesimal concentration (Λ_0 – **limiting molar conductivity**). When the ion does not have any “obstacles”, it is moving the fastest – along with the addition of further ions the mobility relatively drops (and so the molar conductivity, as the concentration is increasing). It is not changing the fact, that the higher concentration, the highest ionic conductivity is (molar conductivity is not decreasing linearly with the concentration).

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Molar conductivity

Calculate the molar conductivity of the solution with 0.01 mol/dm^3 concentration, that has specific conductivity of 1 mS/cm :

$$\Lambda = 0.001 \cdot 1000 / 0.01 = 100 \text{ S}\cdot\text{cm}^2/\text{mol}$$

$[\text{S}\cdot\text{cm}^{-1} \cdot \text{cm}^3\cdot\text{dm}^{-3} / \text{mol}\cdot\text{dm}^{-3} = \text{S}\cdot\text{cm}^2/\text{mol}]$

Calculate the molar conductivity of the solution with 0.1 mol/dm^3 concentration, that has specific conductivity of 5 mS/cm :

$$\Lambda = 0.005 \cdot 1000 / 0.1 = 50 \text{ S}\cdot\text{cm}^2/\text{mol}$$

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Molar conductivity

- If anions to cations ratio is 1:1 (given that both are singly charged ions) then in the given volume, the number of ions is equal (or number of their charges has to be equal):
 $N_+ = N_- = c \cdot N_A$ (concentration \cdot Avogadro number)
number of ions in the dm^3 : $[\text{dm}^3 = \text{mol}\cdot\text{dm}^{-3} \cdot \text{mol}^{-1}]$
- Faraday constant is equal to a charge in one mole of ions (singly charged):
 $F = e \cdot N_A \approx 96500 \text{ C/mol}$ ($N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$, $e = 1.602 \cdot 10^{-19} \text{ C}$)
- From the equation $\kappa = e \cdot (N_+ u_+ + N_- u_-)$ one can derive:
 $\kappa = e \cdot (c \cdot N_A \cdot u_+ + c \cdot N_A \cdot u_-) = e \cdot c \cdot N_A \cdot (u_+ + u_-)$
 $\kappa = F \cdot c \cdot (u_+ + u_-)$
- After substituting above in $\Lambda = \kappa / c$ one gets:
 $\Lambda = F \cdot (u_+ + u_-)$

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Ionic molar conductivity

- As it was shown before, ionic conductivity consists of conductivities of all ions:
 $\Lambda = F \cdot u_+ + F \cdot u_-$ $\lambda_i = z_i \cdot F \cdot u_i$ (z – ionic charge)
 $\Lambda = \lambda_+ + \lambda_-$

Thanks to that equation one can determine ionic mobility that would not be possible to obtain in any other way. *E.g.* by measuring conductivity of NaCl, KBr and KCl one can determine **molar ionic conductivity** of Cl^- , Br^- , Na^+ and K^+ , but also determine without direct measurement the ionic conductivity of NaBr (although only for the given temperature, solvent and concentration; unfortunately, it works properly for the infinitesimal concentrations only).

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Molar conductivity

Molar conductivity dependence of the concentration for strong electrolytes is linear (for low concentrations) and is described by (empirical) Kohlrausch equation:

$$\Lambda = \Lambda_0 - a \cdot c^{1/2}$$

where a is an experimental constant determines for the given electrolyte in a given temperature;
 c is a concentration;
 Λ_0 is a limiting molar conductivity.

Molar conductivity dependence of the concentration for strong electrolytes is non-linear (including electrolytes for new battery generations).

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Molar conductivity

In reality, the molar conductivity is described by very complicated and multi-parameter equations, usually determined experimentally due to complexity of effects connected to the conductivity phenomenon. They are based on Debye-Hückel theory, that was the first to take ionic solvation layer into consideration. Conductivity calculations also require to take into account that ion in the electric field is moving against the solvent. Solvent molecules that do not solvate ions and surround the solvated ion are not moving in the electric field.

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Molar conductivity

Moreover, there are other ions in the vicinity of the ion migrating towards electrode. They are moving in the same or opposite direction. According to Debye-Hückel theory, other ions have share in “slowing down” the ion. That effect can be calculated if other parameters are known, such as the average sphere radius in which the given ion is capable of attracting its counter-ions (so-called ionic atmosphere).

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Molar conductivity

Indirect result of existence of such a sphere of interactions is ionic strength and A parameter (for activity coefficient equation). Of course, radius of that sphere is dependent of concentration. Apart from that, equations use also viscosity and solvent dielectric constant.

Equation that best reflects conductivity dependence of the concentration, that has its base in theory (not empirical one) and is not overly complex is the Fuoss-Onsager equation.

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Molar conductivity

Fuoss-Onsager equation:

$$\Lambda = \Lambda_0 - S \cdot c^{1/2} + E \cdot c \cdot \log(c) + J \cdot c$$

where: Λ – molar conductivity;

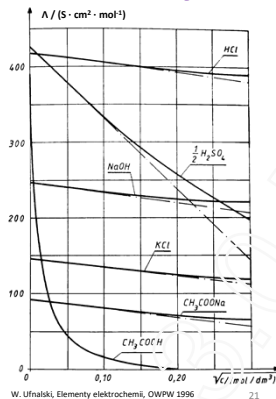
Λ_0 – limiting molar conductivity;

S, E and J – constant derived from dielectric constant, viscosity, temperature, limiting molar conductivity, ionic radii, etc.

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Limiting molar conductivity

Molar conductivity at infinitesimal dilution (limiting molar conductivity) can be determined through the extrapolation of linear regression of low concentration range conductivity data to zero (for weak electrolytes it would be a non-linear regression, from the Fuoss-Onsager equation, for instance):



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Ionic molar conductivity

Calculate molar conductivity of HCl in the infinitesimal dilution (Λ_0), knowing that:

$$\Lambda_0(\frac{1}{2}H_2SO_4) = 860 \text{ S cm}^2/\text{mol}$$

$$\Lambda_0(Na_2SO_4) = 260 \text{ S cm}^2/\text{mol}$$

$$\Lambda_0(NaCl) = 126 \text{ S cm}^2/\text{mol}$$

$$\Lambda_0(HCl) = \lambda_0(H^+) + \lambda_0(Cl^-)$$

$$\Lambda_0(HCl) = \lambda_0(Na^+) + \lambda_0(Cl^-) - \lambda_0(Na^+) - 0.5 \lambda_0(SO_4^{2-}) + \lambda_0(H^+) + 0.5 \lambda_0(SO_4^{2-})$$

$$\Lambda_0(HCl) = \Lambda_0(NaCl) - 0.5 \Lambda_0(Na_2SO_4) + 0.5 \Lambda_0(H_2SO_4)$$

$$\Lambda_0(HCl) = 126 - 260/2 + 860/2 = 426 \text{ S} \cdot \text{cm}^2/\text{mol}$$

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Ionic molar conductivity

Ionic molar conductivity can be used for instance to confirm the value of water ions concentrations product (result of autodissociation) ($[H_3O^+][OH^-] = 10^{-14}$) (all data at 25°C):

$$\Lambda_0(H^+OH^-) = \lambda_0(H^+) + \lambda_0(OH^-) = 548 \text{ S} \cdot \text{cm}^2/\text{mol}$$

Conductivity of water: $5.8 \cdot 10^{-8} \text{ S/cm}$

Concentration of water in water(!): 55.3 mol/dm^3

$$\Lambda = \kappa/c = 1.048 \cdot 10^{-6} \text{ S} \cdot \text{cm}^2/\text{mol}$$

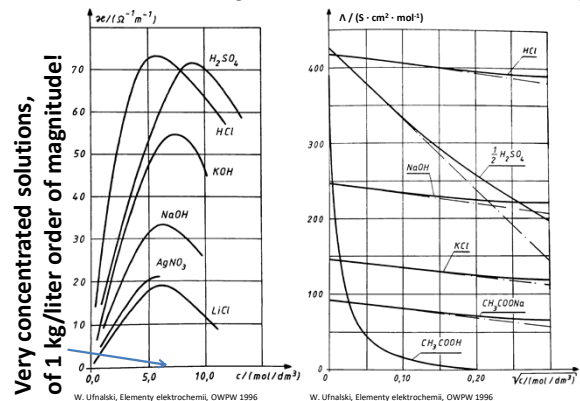
$$\text{Water dissociation degree: } \alpha = \Lambda/\Lambda_0 = 1.91 \cdot 10^{-9}$$

$$\text{Ionic concentration (H}^+ \text{ and OH}^- \text{) to: } \alpha \cdot c_{H_2O} = 1.056 \cdot 10^{-7}$$

$$\text{The concentration product: } [H_3O^+][OH^-] = 1.11 \cdot 10^{-14}$$

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Conductivity vs ionic conductivity



Very concentrated solutions, of 1 kg/liter order of magnitude!

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Ionic associations

To explain, why there are drops in conductivity and then (for weak electrolytes) slight increases with the concentration growth, theory of association formation has been formed, so-called Fuoss-Kraus formalism. In modern times, a model has been made, that uses that theory and enables possibility of calculating/estimating fractions of ions, ionic pairs and triplets in the electrolyte (in % of all ionic forms).

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Fuoss-Kraus formalism

$$K_I = \frac{1-\alpha_I}{\alpha_I^2 c} \quad K_T = \frac{\alpha_T}{\alpha_I c (1-\alpha_I-3\alpha_T)}$$

After transformation it yields:

$$\alpha_I = \frac{-1 + \sqrt{1 + 4K_I c}}{2K_I c} \quad \alpha_T = \frac{K_T \alpha_I (1 - \alpha_I) c}{1 + 3K_T \alpha_I c}$$

$$\alpha_P = 1 - \alpha_I - 3\alpha_T$$

where α is share of the component in question in the sum of all ionic forms.

Overall molar conductivity is:

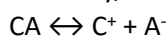
$$\Lambda = \alpha_I \Lambda_0^I + \alpha_T \Lambda_0^T$$

And for small enough values of α_I i α_T (infinitesimal dilution) this equation can be substituted with equations for α_I and α_T which gives:

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Fuoss-Kraus formalism

Normally, dissociation is (C – cation, A – anion):



Formally, in order for triplets to form, they need more electrolyte molecules. Formal notation of such process can look in the following way:



Constants of those equilibria are K_I and K_T , respectively.

(I – “free” ions, P – ionic pairs, T – triplets)

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Fuoss-Kraus formalism

$$\Lambda \sqrt{c} = \frac{\Lambda_0^I}{\sqrt{K_I}} + \frac{\Lambda_0^T K_T c}{\sqrt{K_I}}$$

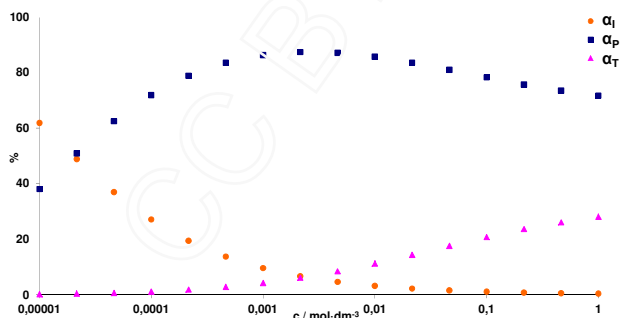
This equation for very low concentrations should give a straight line in $\Lambda c^{1/2} = f(c)$ coordinates

$$(y = ax + b, \text{ thus } \Lambda \sqrt{c} = \frac{\Lambda_0^I}{\sqrt{K_I}} + \frac{\Lambda_0^T K_T c}{\sqrt{K_I}})$$

From the linear regression one can obtain a and b coefficients. Limiting molar conductivity can be obtained for instance from Fuoss-Onsager equation. Λ_0^T is 2/3 of the Λ_0^I value. Thus, one can calculate K_I and K_T , from which one can yield fractions of ions, ionic pairs and triplets (α_I , α_P and α_T).

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Ionic associations



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