

Chemistry course
ACME Faculty, EHVE course
B.Sc. Studies, I year, I semester
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Electrochemistry, part 1 Basics and ionics

Electrolyte - repetition

Liquid or solid substance that conducts electricity by means of ions. Mobility of ions is possible when they have freedom of movement. Freedom can be provided with molten salt (ionic liquid), adequate solid state structure or (most common case) solvation of ions in a solution by solvent molecules (separation of ions and thus their dissociation).

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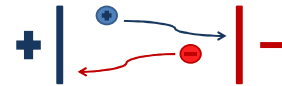
Electrolyte-electrode

- Phases, at interface of which electrolyte transfer charge (by oxidizing or reducing ions), are called **electrodes** (most commonly solid).
- Current conductivity is a result of ionic mobility – specifically charge transfer at the **electrode interface** with **electrolyte**. Next step is the movement of ion through electrolyte to the other “coast” (second electrode). Then the second charge transfer happens (opposite to that at first electrode) at the electrode-electrolyte interface.

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Electric field

- Ions in electrolyte can move due to (when they are not stirred or under the influence of electric field) self-diffusion or convection.
- In electric field that movement has specified direction – cations (+) move towards negative electrode (-) and anions move towards positive electrode (+). That is called **migration**.



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Migration

Motion of charge in electric field should be uniformly accelerated. However, acceleration above certain velocity is reduced due to frictional force (which exists also on a molecular level). That force defines maximum ionic velocity (in a given solvent, given electric field and given temperature), which is called **ionic mobility (u)**, measured in $\text{m}^2/(\text{s}\cdot\text{V})$ [(m/s)/(V/m)].

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Ionic mobility

- Ionic mobility is defining maximum ionic velocity, which is defining maximum current possible to flow through a given electrolyte.
- For electrolyte solution such as NaCl (fully dissociating, 1:1 anion to cation ratio, both ions have single charge):

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

[A·s · m² · V·m⁻¹ · m⁻³ · m²·s⁻¹·V⁻¹ = A·m²⁻¹⁻³⁺² = A]

current = elementary charge · cross-sectional area of field ·
 · electric field intensity · (number of ions · ionic mobility)
 elementary charge is 1.602·10⁻¹⁹ C [C=A·s]

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Current vs conductivity

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

Substituting II eq. to I eq. gives: $I = \kappa \cdot E \cdot A$

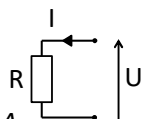
where κ is **electrolyte conductivity**.

Substituting the last equation to

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

$\kappa = e \cdot (N_+ u_+ + N_- u_-)$ (e – constant – elementary charge)

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



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Molar conductivity

- When in a given volume of pure solvent exists only one ion, then it is interacting exclusively with a solvent and has a freedom of movement in each direction;
- When a counter-ion shows up in this volume, there is a chance for them to meet and form an ion pair. That is slowing down statistical movement of an ion (it is stopping for a time of ion pair existence). After they split up, they can form ion pair again later. Ion pair has neutral charge and is not moving in electric field. Forming it is decreasing ionic mobility of both ions statistically.
- The more ions are in a given volume, the bigger chance for them to meet and interact, slowing down that way.

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Molar conductivity

- Conductivity (indirectly mobility) of an ion based on a concentration is called **molar conductivity**:

$$\Lambda = \kappa / c$$

- Usually it is biggest for the infinitesimal concentration (Λ_0 – **limiting molar conductivity**). When ion does not have any “obstacles” on its way, it is moving the fastest. With addition of other ions its mobility relatively decreases (and so is molar conductivity due to concentration increase). However, with increase of a concentration usually ionic conductivity increases (molar conductivity is decreasing in non-linear way).

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Molar conductivity

- When anions to cations ratio is 1:1 (charges are -1 and +1), in a given volume the number of ions is:

$$N_+ = N_- = c \cdot N_A \quad (\text{concentration} \cdot \text{Avogadro number})$$

- Faraday constant is an electric charge of one mole of ions:

$$F = e \cdot N_A \approx 96\,500 \text{ C/mol}$$

$$(N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1} \quad e = 1.602 \cdot 10^{-19} \text{ C})$$

- From $\kappa = e \cdot (N_+ u_+ + N_- u_-)$ equation we can derive:

$$\kappa = F \cdot c \cdot (u_+ + u_-)$$
- After substituting the above into $\Lambda = \kappa/c$ we obtain:

$$\Lambda = F \cdot (u_+ + u_-)$$

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Molar ionic conductivity

As it can be seen, molar conductivity is an additive quantity. It consists of conductivities of individual IONS (it works the same way with more than two ions in one solution):

$$\Lambda = F \cdot u_+ + F \cdot u_- \quad \lambda_i = z_i \cdot F \cdot u_i \quad (z - \text{ion's charge})$$

$$\Lambda = \lambda_+ + \lambda_-$$

Thanks to that equation we can derive molar ionic conductivity of ions that otherwise could not be determined, e.g. by measuring NaCl, KBr and KCl conductivities one can determine **molar ionic conductivity** of Cl⁻, Br⁻, Na⁺ and K⁺, but also NaBr molar conductivity without measuring it (of course just for the given temperature, solvent and concentration; the last one unfortunately has to be very small – infinitesimal, because only for such concentrations this method has no big error).

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Molar ionic conductivity

Determine limiting molar conductivity (Λ_0) of HCl, knowing that:

$$\Lambda_0(\text{H}_2\text{SO}_4) = 860 \text{ S} \cdot \text{cm}^2/\text{mol}$$

$$\Lambda_0(\text{Na}_2\text{SO}_4) = 260 \text{ S} \cdot \text{cm}^2/\text{mol}$$

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

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

$$\Lambda_0(\text{HCl}) = \lambda_0(\text{Na}^+) + \lambda_0(\text{Cl}^-) - \lambda_0(\text{Na}^+) - 0.5 \lambda_0(\text{SO}_4^{2-}) + \lambda_0(\text{H}^+) + 0.5 \lambda_0(\text{SO}_4^{2-})$$

$$\Lambda_0(\text{HCl}) = \Lambda_0(\text{NaCl}) - 0.5 \Lambda_0(\text{Na}_2\text{SO}_4) + 0.5 \Lambda_0(\text{H}_2\text{SO}_4)$$

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

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Molar ionic conductivity

Molar ionic conductivity can be applied to confirm the product of water ions concentration (originating from water autodissociation) ($[H_3O^+][OH^-] = 10^{-14}$)

(all data at 25°C):

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

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

$$\text{Concentration of water in water(!): } 55.3 \text{ mol/dm}^3$$

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

$$\text{Dissociation degree of water: } \alpha = \Lambda/\Lambda_0 = 1.91 \cdot 10^{-9}$$

Ion concentration (both H^+ and OH^-) is:

$$\alpha \cdot c_{H_2O} = 1.056 \cdot 10^{-7}$$

Thus, product of concentrations is: $[H_3O^+][OH^-] = 1.11 \cdot 10^{-14}$

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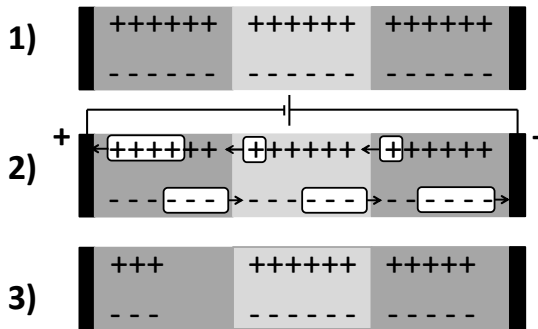
Transference numbers

- In real measurements one cannot determine ions' share of conductivity in a previously shown way (mostly because infinitesimal concentrations are impractical). To obtain molar ionic conductivity of an ion i , one has to measure the **transference number** (t_i) of this ion.
- If the charge Q was transferred through an electrolyte, then the transference number of ion i is equal to $t_i = Q_i/Q$, i.e. the ion's i share of the whole transferred charge: $t_+ = \lambda_+/\Lambda$

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Transference numbers

- If we only have + and -, and $t_+ = 0.25$ and $t_- = 0.75$:



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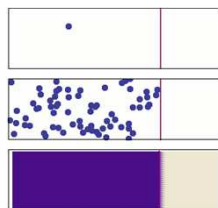
Diffusion

- As one can see, after certain charge is transferred, a shortage of ions can happen on one side of a cell (or even both sides). Even if new ions appear on one side (because they come out of an electrode), it can happen anyway. What then?
- Current passing will decrease to a maximum rate equal to ions production at electrode (which can be smaller than amount needed by powered device).
- Shortage of both types of ions on one side will be continuously supplemented by produced ions on other side of a cell, so a concentration gradient will form.
- When increase of potential is not causing current increase, it means that the limiting diffusion current has been reached. It has a lot of consequences.

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Diffusion

- Diffusion is a phenomenon in which particles are spreading in a given phase as long as they will obtain uniform concentration in a whole available space.
- Diffusion is „driven“ with a differences of given particle concentrations - the bigger they are, the faster diffusion is.



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Diffusion

- The speed rate of ions in an electric field ($u_i \cdot E$) results from ionic mobility. In the same way diffusion rate results from diffusion coefficient ($D_i/(R \cdot T)$). In case of ions' depletion at the electrode and upon forming stable concentration gradient, those rates will be equal to each other

$$u_i \cdot E = D_i/(R \cdot T), \text{ thus } D_i \text{ can be calculated:}$$

$$D_i = u_i \cdot k \cdot T / (z_i \cdot e) \quad (\text{Boltzmann constant } k = R/N_A)$$

Because k and e are constants, diffusion depends only on particle/ion mobility and temperature.

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Viscosity

From the formula for viscous friction force one can derive, how strongly the **viscosity** „restrains” particle: $6 \cdot \pi \cdot \eta \cdot r_i$. It is balanced by movement in an electric field (maximum velocity value is a friction result).

Thus a mobility formula can be derived as well as diffusion formula containing viscosity (η):

$$u_i = e \cdot z_i / (6 \cdot \pi \cdot \eta \cdot r_i) \quad (r_i - \text{particle radius})$$

$$D_i = k \cdot T / (6 \cdot \pi \cdot \eta \cdot r_i)$$

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Viscosity

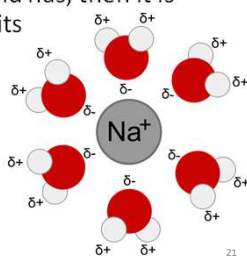
- Because mobility is inversely proportional to viscosity, so is the conductivity (molar as well), for instance: $\Lambda_0 \cdot \eta = \text{const}$
- Viscosity is inversely proportional to temperature (temperature increases, viscosity drops). Conductivity is directly proportional to temperature (conductivity increases with temperature).

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Ion solvation

Presence of a particle radius in formula *e.g.* for diffusion coefficient (at known viscosity) can be used for calculating hydration (solvation) degree. Ions radii are known. When measurements suggest bigger radius than the ion should have, then it is bigger by solvent molecules in its solvation layer.

As solvent molecules dimensions are also known, thus it is possible to estimate number of molecules surrounding the ion in a solvation layer.



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Why do ions move toward electrodes?

Movement of ions toward electrodes (and why do electrodes have opposite charges) results from one of two possibilities:

- Voltage can be applied from the external source;
- Electrodes can be built from different materials (of a different electrochemical potential). If on every electrode immersed in electrolyte spontaneous reactions take place, then on every electrode-electrolyte interphase potentials form (non-measurable parameter). Their difference is called **electromotive force (emf)** (which is measurable). Emf is defining maximum current which is possible to obtain from a given set (pair) of electrodes.

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Electromotive force

Electrons between electrodes are moving through an external circuit (if they are connected through it). Then an oxidation can occur at one electrode (and giving electrons to a circuit) and reduction at other electrode (receiving electron from a circuit). In summary, there is a redox reaction going on, but with separated half-reactions (without the necessity of direct contact between atoms to pass an electron between them, as it was described on inorganic chemistry lecture).

The **anode** is electrode where oxidation occurs.

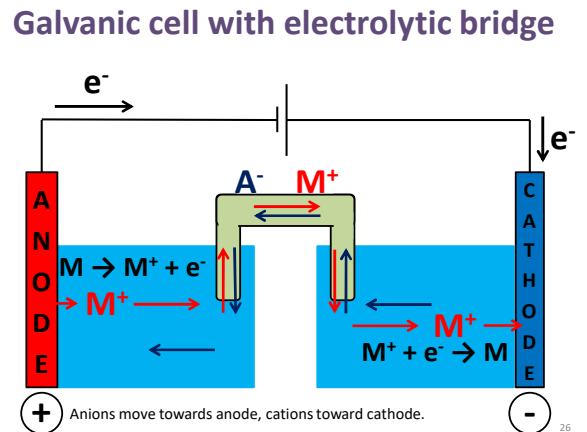
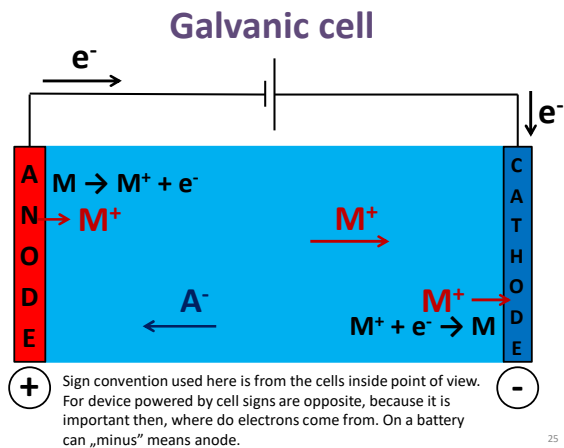
The **cathode** is electrode where reduction occurs.

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Galvanic cell

- System of anode, electrolyte and cathode is called **galvanic cell**.
- Current (electrons) flowing through a circuit between electrodes can power a receiver (engine, bulb, *etc.*).
- System of one electrode and electrolyte surrounding it is called **half-cell**.
- Half-cells can share electrolyte or be connected by electrolytic bridge (pipe with liquid electrolyte - ionic conductor with membranes on its ends not allowing for solutions to mix, but able to pass ions).

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Interfacial boundary

- Boundary between phases is very important. It is on contact of electrode and electrolyte where all electron charge transfer process occur. Only at the interface ions can receive or give away their electron(s). Electrode conducts electrons, electrolyte – ions exclusively.

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Electrochemical series

- Electrodes (reactions that occur at them) do not possess any potential individually. Only upon a contact between any two electrodes one can determine their relative potential (between them).
- Electrode potentials are measured in standard conditions (e.g. 25°C, 1013hPa).
- Measured redox reactions are compiled in **electrochemical series**.
- Reference point for series is **standard hydrogen electrode (SHE)** ($\text{H}_3\text{O}^+ + \text{e}^- \rightarrow 1/2\text{H}_2 + \text{H}_2\text{O}$) (half-cell notation: $\text{Pt}, \text{H}_2 | \text{H}^+$).
- Above the standard potential of a given half-cell oxidation occurs (below its value reduction occurs).

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Electrochemical series

Li^+/Li	-3.045 V	AgCl/Ag	+0.222 V
Ca^{2+}/Ca	-2.864 V	$\text{Hg}_2\text{Cl}_2/2\text{Hg}$	+0.268 V
Na^+/Na	-2.711 V	Cu^{2+}/Cu	+0.338 V
Mg^{2+}/Mg	-2.370 V	$\text{I}_2/2\text{I}^-$	+0.536 V
Al^{3+}/Al	-1.700 V	$\text{MnO}_4^-/\text{MnO}_4^{2-}$	+0.558 V
$\text{SO}_4^{2-}/\text{SO}_3^{2-}$	-0.932 V	$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.771 V
Zn^{2+}/Zn	-0.763 V	Ag^+/Ag	+0.799 V
Cr^{3+}/Cr	-0.744 V	Pt^{2+}/Pt	+0.963 V
Fe^{2+}/Fe	-0.441 V	Cl_2/Cl^-	+1.358 V
Ni^{2+}/Ni	-0.234 V	Au^{3+}/Au	+1.498 V
Pb^{2+}/Pb	-0.126 V	$\text{MnO}_4^-/\text{Mn}^{2+}$	+1.531 V
$\text{H}_3\text{O}^+/\text{H}_2$	0.000 V	F_2/F^-	+2.866 V

(SO₄²⁻ + H₂O + 2e⁻ → SO₃²⁻ + 2OH⁻) (2H₃O⁺ + 2e⁻ → H₂ + 2H₂O)

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