

Diffusion in solutions

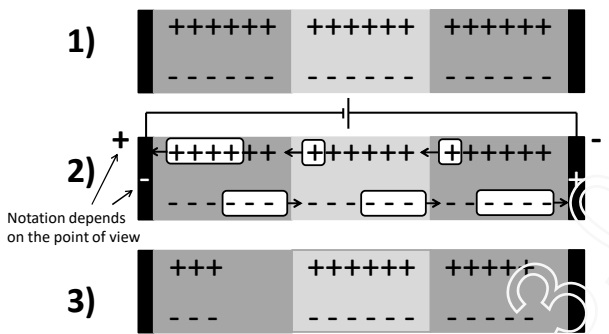
Transference numbers

- In real conductivity measurements (unlike the infinitesimal concentration considerations) it is impossible to determine ions' shares in conductivity (different ions have a different conductivity-concentration relations). In order to determine the (molar) conductivity of ion i , one have to measure the **transference number** (t_i) of that ion.
- If the charge Q was transferred through the electrolyte, then transference number of ion i is: $t_i = Q_i/Q$, so the share of the charge transferred by the given ion in the whole charge transferred is: $t_+ = \lambda_+/\Lambda$

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Transference numbers

- If we have only + and - ions, e.g. $t_+ = 0.25$ and $t_- = 0.75$



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Transference numbers

The above scheme is used to determine transference numbers with Hittorf method. In this method one use cell composed of three glass bulbs with valves between them, that can shut off bulbs from each other and separate them. Upon transferring known charge through the electrolyte bulbs are closed, separated and weighed. Difference in mass can be used to estimate transference number.

Unfortunately, Hittorf method and its modifications are not sufficient to investigate electrolyte for Li-ion cells, because working electrode required for it is lithium that is susceptible to moisture and air.

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Transference numbers

Bruce-Vincent method bases on transference number definition: $t_i = Q_i/Q$, where $Q = I \cdot T$ (current·time), so in the given moment $t_i = I_i/I$, assuming, that one can measure current for only one ion at the time.

Such situation can take place, if sample is polarized long enough. If electrodes are not accepting and are not producing one of the ions (are blocking against anions), but if they are accepting/producing another ion (reversible against lithium cation), then upon formation of stable concentration gradient the whole current flowing through the cell is the result of lithium cation movement. Transference number can be calculated then from the steady-state current to initial current ratio: $t_+ = I_s/I_0$

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Transference numbers

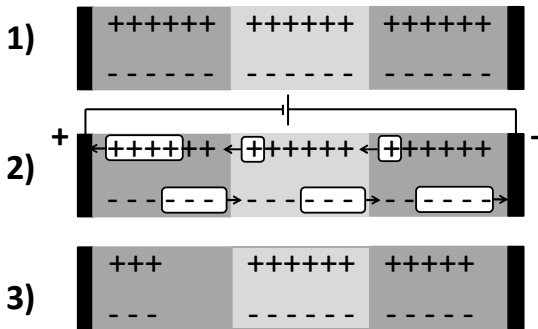
It was observed, that during the operation of such tested cell electrodes (especially such reactive like metallic lithium) change their properties (particularly resistance at their surface, which changes current). Thus, in order to calculate real transference number, it is necessary to take into account changes in current that result from electrode resistance changes, apart from anion movement

fade. Thus, the corrected formula is: $t_+ = \frac{I_s(\Delta V - R_0 I_0)}{I_0(\Delta V - R_s I_s)}$

where: I – current; R – interphase layer resistance; ΔV – polarization voltage; s – steady-state (after polarization); 0 – initial (before polarization).

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Transference numbers



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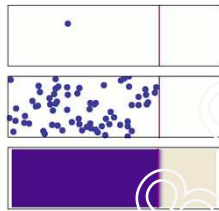
Diffusion

- As shown, in certain moment one side can run short of ions. Even if ions are appearing on one side (electrode „produces” new ones), then it still can come to that. What happens then?
- Current intensity drops.
- Both types of ion at the electrode are in shortage. On the other side of the cell new ions are still produced. Concentration will be willing to compensate. Thus, concentration gradient will form.
- When voltage increase between electrodes is not causing further current increase, then it means the limiting diffusion current has been achieved. It has a lot of consequences and applications.

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Diffusion

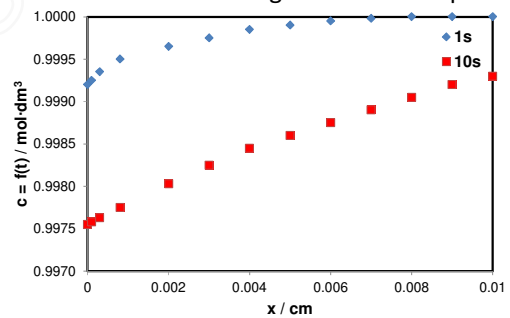
- Diffusion is the phenomenon of particles spreading in the given phase until they achieve uniform distribution (concentration) in the whole available volume of the phase.
- Diffusion is driven by the difference of the given particle type – the higher difference, the faster diffusion (result of entropy laws).



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Diffusion

Electrolyte concentration plot change over time due to diffusion near the working electrode interphase:



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Diffusion

- The flow (J [mol/(cm²·s)]) of ions i is equal to the product of their velocity and concentration:
 $J_i = v_i \cdot c_i$
- Velocity of the ion is proportional to the gradient of the chemical potential (μ_i), as well as its distance (x) derivative:
 $v_i = -K_i \cdot (d\mu_i/dx)$
- As the chemical potential is
 $\mu_i = \mu_i^0 + R \cdot T \cdot \ln a_i$ ($a_i \approx c_i$)
thus $v_i = -K_i \cdot R \cdot T \cdot (1/c_i \cdot dc_i/dx)$
- So: $J_i = -K_i \cdot R \cdot T \cdot (dc_i/dx)$
where $D_i = K_i \cdot R \cdot T$ [cm²/s]
thus $J_i = -D_i \cdot (dc_i/dx)$ (1 Fick's law)

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Diffusion

Diffusion is driven by the chemical potential gradient and as such, by the concentration gradient (for instance):

$$-f_{\text{diff}} = -RT/c_i \cdot (dc_i/dx)$$

thus: $(dc_i/dx) = -f_{\text{diff}} \cdot c_i / (R \cdot T)$, which substituted to the Fick's equation yields:

$$v_i \cdot c_i = -D_i \cdot (dc_i/dx) \rightarrow v_i = -f_{\text{diff}} \cdot D_i / (R \cdot T)$$

Electrical force is $f_{\text{el}} = z \cdot F \cdot E$,

Thus the velocity in the electric field is

$$v_i = u_i \cdot E = f_{\text{el}} \cdot u_i / (z \cdot F)$$

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Diffusion

Just like velocity of ions in the electric field ($u_i/(z_i \cdot F)$) is the result of the ionic mobility, the same way the diffusion rate is the result of the diffusion coefficient ($D_i/(R \cdot T)$).

In case of the ions depletion and stable concentration gradient formation, rates will be the same and so will be both the diffusion and the electrical force:

$u_i/(z_i \cdot F) = D_i/(R \cdot T)$, from which one can yield D_i :

$$D_i = u_i \cdot k \cdot T / (z_i \cdot e) \quad (\text{Boltzmann constant: } k = R/N_A, e = F/N_A) \\ (\text{Einstein's equation})$$

As k and e are constants, diffusion depends on the particle (type) mobility and the temperature.

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Diffusion

Diffusion can be related to the molar conductivity as well. Molar conductivity is a result of ionic mobility (ν – salt stoichiometry – how many ions of the given type are present in the single molecule):

$$\Lambda = \lambda_- + \lambda_+ = F \cdot (\nu_+ \cdot z_+ \cdot u_+ + \nu_- \cdot |z_-| \cdot u_-)$$

Upon substitution with Einstein's equation one yields:

$$D_i = u_i \cdot k \cdot T / (z_i \cdot e) = u_i \cdot R \cdot T / (z_i \cdot F)$$

$$u_i = D_i \cdot z_i \cdot F / (R \cdot T)$$

$$\Lambda = (\nu_+ \cdot z_+^2 \cdot D_+ + \nu_- \cdot |z_-|^2 \cdot D_-) \cdot F^2 / (R \cdot T) \\ (\text{Nernst-Einstein equation})$$

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Viscosity

From the formula for the viscous friction (against the ball in liquid) one can get information on how strongly the particle is "decelerated" by the viscosity:

$f_{\text{visc}} = 6 \cdot \pi \cdot \eta \cdot r_i \cdot v_i$ (Stokes' equation). It is counterbalanced by the electrical force (maximum velocity is the result of the friction): $f_{\text{el}} = v_i \cdot z_i \cdot F / u_i$

From this, one can yield the formula for the mobility and formula showing relation between diffusion and viscosity (η):

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

$$D_i = k \cdot T / (6 \cdot \pi \cdot \eta \cdot r_i) \quad (\text{Stokes-Einstein equation}) \\ (\text{upon combining with Einstein equation})$$

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Viscosity

As $u_i = e \cdot z_i / (6 \cdot \pi \cdot \eta \cdot r_i)$

and $\lambda_i = z_i \cdot F \cdot u_i \rightarrow u_i = \lambda_i / (z_i \cdot F)$

then $\Lambda_0 \cdot \eta = e \cdot F \cdot (z_+ + |z_-|) / (6 \cdot \pi \cdot (r_+ + r_-)) = \text{const}$

For the given salt. Product $\Lambda_0 \cdot \eta = \text{const}$ is called the **Walden product**. It is fulfilled only for the very low concentrations (close to infinitesimal concentrations) and weakly solvated ions. However, it determines general rule that with the increase of viscosity the conductivity drops. This general trend (not necessarily linear as suggested by the Walden product formula) is fulfilled by the majority of electrolyte solutions (except the most concentrated, where other factors come into force).

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Viscosity

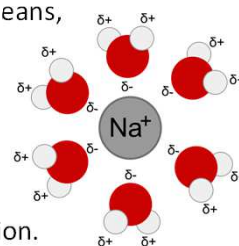
- As mobility is inversely proportional to the viscosity, so is the conductivity (molar as well).
- Viscosity is inversely related to temperature (when temperature increases, viscosity drops). Conductivity is directly proportional to temperature (conductivity increases with temperature).

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Ions' solvation

Presence of particle radius in formulae, e.g. diffusion formula (for the given viscosity) can be used to measure the hydration (solvation) degree.

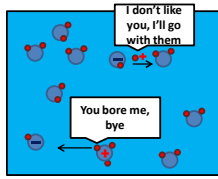
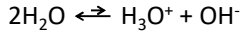
As the ions radii are known, then the higher value calculated from the formula means, that the real (practical) radius of an ion is bigger because of the solvation layer (solvent molecules). As their volume is also known, one can calculate (estimate) the number of molecules surrounding the ion.



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Water autodissociation

- Water as a ionic compound also dissociates – it is called water autodissociation.



- Due to identical properties of all water molecules, they are pulling each other with a same strength. But due to their ionic structure, statistically one in ten million molecules ($1/10000000 = 10^{-7}$) is torn apart by her neighbors into proton and OH^- group. Proton is immediately pulled to other water molecule to form H_3O^+ ion (solvation).

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Water autodissociation

- OH^- and H_3O^+ ions, if no other ions are present, quickly recombine into water molecules again (or they rip the counterion from a different water molecule to neutralize themselves), so the equilibrium is dynamic. In every moment in a pure water there is always one molecule for every ten million that is torn into ions.
- Hence, pure water (which is a solvent) also contains ions. Their number is too small to be seen as electric conductivity or melting point changes (it is already taken into account in standard water parameters, like resistance), but it can influence ionic reactions.

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Water autodissociation

- Equilibrium that sets certain concentration of OH^- and H_3O^+ ions ($1:10\,000\,000$) is shifted, when ions from different source appear. However, it shifts only in such a way that product of their concentrations is always equal to 10^{-14} (the more H_3O^+ ions number, the faster it finds and neutralize OH^- ions, but never can find them all, because water autodissociates all the time and always new H_3O^+ ions appear).

$$[\text{H}_3\text{O}^+]\cdot[\text{OH}^-] = 10^{-14}$$

- If we add hydrogen chloride (HCl) to water, the number of OH^- ions in a water decreases, e.g.: 0.1M HCl shifts the equilibrium to:
 $[\text{H}_3\text{O}^+] = 0.1 \text{ mol/dm}^3$ (10^{-1}) $[\text{OH}^-] = 10^{-13} \text{ mol/dm}^3$

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Water autodissociation

- H_2O dissociates into H_3O^+ i OH^-
- H_3O^+ not H^+ , because in reality H^+ is solvated by water molecule so fast, that it never exists as a solitary being ($<10^{-9}$ s).
- OH^- does not dissociate to O^{2-} i H^+ , because tearing apart one proton (intrinsically) is rare and energetically hard. When the first proton is torn apart from oxygen, the bond between second hydrogen and oxygen is even stronger.

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pH

- Equilibrium of water autodissociation is used to form **pH scale** – solution reaction (is it acidic or alkaline).
- pH is $-\log([\text{H}_3\text{O}^+])$ [in fact, $-\log(a_{\text{H}_3\text{O}^+})$], so 0.1 mol/dm³ is pH = 1, and 0.001 mol/dm³ to pH = 3
- In the same way one can use pOH scale ($-\log([\text{OH}^-])$), where OH^- concentration equal to 1 mol/dm³ is pOH = 0 and 0.01 mol/dm³ is pOH = 2.
- pH+pOH = 14, so at pH = 12 $[\text{H}_3\text{O}^+] = 10^{-12} \text{ mol/dm}^3$ and $[\text{OH}^-] = 0.01 \text{ mol/dm}^3$
- What will happen to pH value if we would infinitely dilute strong acid solution?
What about strong base solution?

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pH

0	Concentrated hydrofluoric acid (HF_{aq}), battery acid
1	Dilute hydrochloric acid (HCl_{aq}), the same acid in a stomach-secreted concentration
2	Lemon juice, vinegar, gastric juice
3	Grapefruit juice, orange juice, cola
4	Tomato juice, acid rain
5	Still mineral water, black coffee (no additives), sweat
6	Urine, saliva, sweat
7	Distilled water
8	Sea water
9	Baking powder solution
10	Brine, salt lake/Dead Sea water, antacid
11	Dilute ammonia solution
12	Potash soft soap solution
13	Bleach, cleaning agents for ovens and cookers
14	Draining agent for pipes

Is it better to have pH or pHD?

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What is the pH of pure water?

- Formally, pure water pH = 7.
In reality, when measured precisely, pH of pure water that has contact with the air is lower than 6.5. Air contains amounts of carbon dioxide (CO₂), some of which dissolves in water, where it is subject to the reaction

$$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$$
carbonic acid is dissociating in water

$$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$$
product of which cause the pH decrease.

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Buffered solutions

As a result from the example above, pH value is very sensitive towards any conditions change (CO₂ concentration in air for instance). Many chemical (whether reaction is possible or not), biochemical and biotechnological (fungi, algae or bacteria growth or metabolism) processes requires stable pH. In order to keep pH stable, so-called **buffer solutions** are used.

Buffer solutions are solutions of such composition, that they do not change their pH after addition (even on purpose) of acid or base (up to the certain limit of addition at least), or after dilution.

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Buffered solutions

In order to make buffer solution, one usually mix weak acid (HA) and its salt of the strong base (e.g. NaA). Then the equilibrium is formed:

- $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$
- $\text{NaA} \rightleftharpoons \text{Na}^+ + \text{A}^- \quad K_b = \frac{[\text{Na}^+][\text{A}^-]}{[\text{NaA}]}$

In which K_a is very small, and K_b is a very big.

- $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$
- $[\text{H}^+] = K_a \cdot \frac{[\text{HA}]}{[\text{A}^-]}$
- Upon taking the logarithm of the above:
 $\log[\text{H}^+] = \log(K_a) + \log[\text{HA}] - \log[\text{A}^-]$
 $-\log[\text{H}^+] = -\log(K_a) - \log[\text{HA}] + \log[\text{A}^-]$
 $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$

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Buffered solutions

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

[A⁻] is a result of the salt concentration (completely dissociated, as it is salt of the strong base) and [HA] is almost equal to acid concentration (as it is almost non-dissociated):

$$\text{pH} = \text{p}K_a + \log\left(\frac{c_{\text{salt}}}{c_{\text{acid}}}\right)$$

pH value kept by buffer depends on the acid constant of the acid and on salt and acid concentrations. Thus, it is possible to form buffer with a specific pH value.

Additionally, acid is weakly dissociating even compared to its self-contained solution as [A⁻] resulting from the salt is decreasing maximum [H⁺] resulting from the acid dissociation: $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$

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Buffered solutions

- Buffers can have any pH value from ca. 2 to ca. 12:
For instance: CH₃COOH+CH₃COONa (3.6-5.6), KH₂PO₄+Na₂HPO₄ (4.8-8.0), NH₃+NH₄Cl (8.0-10.0)
- How the buffer works:
 - Added acid is reacting with A⁻ and high concentration of A⁻ result in negligible change of pH of the final solution.
 - Added base is reacting with [H₃O⁺] (neutralization), but amount of H⁺ is reproduced by the weak acid dissociation; weak acid is waiting in non-dissociated state in large reserve.

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Buffered solutions

- How much acid or base can be added until pH value of the buffer solution is changing with a higher rate? It is defined by the **buffer capacity**:

$$\beta = \left| \frac{\Delta n_{\text{acid/base}}}{\Delta \text{pH}} \right|$$
- Buffer capacity is the highest when concentrations of salt and acid are equal and when pH=pK_a. One can calculate buffer capacity from the formula:

$$\beta = 2.303 \cdot (c_{\text{HA}} + c_{\text{A}^-}) \cdot K_a \cdot \frac{[\text{H}^+]}{(K_a + [\text{H}^+])^2}$$

E.g. buffer 0.5M CH₃COOH+0.5M CH₃COONa (pH ≈ 5) has β ≈ 0.57, so it is 0.06 moles of acid or base addition will change pH by ca. 0.1.

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