

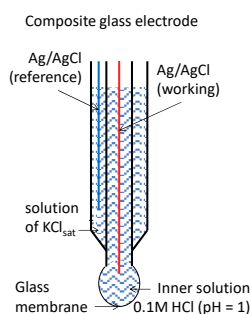
## EMF and potentials

### Practical applications of EMF

Measurement of pH can be performed with **composite glass electrode**. It is set of two electrodes forming a cell. Both of them are silver chloride electrodes (Ag|AgCl|Cl<sup>-</sup>), where one of them is immersed in the isolated solution containing chlorides. Second electrode is immersed in the inner solution that has a contact with a sample solution (external) through a ion-selective membrane. In the membrane, depending on the H<sub>3</sub>O<sup>+</sup> concentration in the sample solution, equilibrium forms between protons and sodium cations naturally occurring in the glass. It changes concentration of the inner solution, thus changing the potential of the whole cell.

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### pH measurements



EMF = E<sub>2</sub> - E<sub>1</sub>  
 $E_2 = E^0_{AgCl} + R \cdot T / (z \cdot F) \cdot \ln(1/a_{Cl-(1)})$   
 $E_1 = E^0_{AgCl} + R \cdot T / (z \cdot F) \cdot \ln(1/a_{Cl-(2)})$   
 thus:  
 $SEM = R \cdot T / (z \cdot F) \cdot \ln(a_{Cl-(2)} / a_{Cl-(1)})$   
 $EMF = 0.0592 \cdot \log(a_{Cl-(2)} / a_{Cl-(1)}) [V]$   
 where activity of anions in the solution at the reference electrode (2) is known and constant and that at the working electrode (1) depends on the H<sub>3</sub>O<sup>+</sup> ions concentration in the external solution.

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### Calculations

- Calculate EMF of the cell consisting of the silver chloride electrode immersed in the 1M KCl<sub>(aq)</sub> electrolyte and the lead electrode immersed in the 0.01M PbCl<sub>2(aq)</sub> electrolyte.
- Calculate EMF of the cell consisting of the silver chloride electrode and the lead electrode both immersed in the same electrolyte, which is 0.01M PbCl<sub>2(aq)</sub>.

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### Calculations

- Calculate EMF of the cell consisting of the cadmium electrode ( $E^0_{Cd/Cd^{2+}} = -0.81 V$ ) and electrode made of nickel oxide hydroxide ( $E^0_{NiOOH/Ni(OH)_2} = 0.49 V$ ) both immersed in the electrolyte containing necessary ions at the 1M concentration.
- Calculate EMF of the cell consisting of zinc electrode and manganese hydroxide electrode ( $E^0_{MnO_2/MnOOH} = 0.74 V$ ) both immersed in electrolyte with 0.1M ammonium chloride and zinc chloride.

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### Electrochemical series

Li <sup>+</sup> /Li	-3.045 V	AgCl/Ag	+0.222 V
Ca <sup>2+</sup> /Ca	-2.864 V	Hg <sub>2</sub> Cl <sub>2</sub> /2Hg	+0.268 V
Na <sup>+</sup> /Na	-2.711 V	Cu <sup>2+</sup> /Cu	+0.338 V
Mg <sup>2+</sup> /Mg	-2.370 V	I <sub>2</sub> /2I <sup>-</sup>	+0.536 V
Al <sup>3+</sup> /Al	-1.700 V	MnO <sub>4</sub> <sup>-</sup> /MnO <sub>4</sub> <sup>2-</sup>	+0.558 V
SO <sub>4</sub> <sup>2-</sup> /SO <sub>3</sub> <sup>2-</sup>	-0.932 V	Fe <sup>3+</sup> /Fe <sup>2+</sup>	+0.771 V
Zn <sup>2+</sup> /Zn	-0.763 V	Ag <sup>+</sup> /Ag	+0.799 V
Cr <sup>3+</sup> /Cr	-0.744 V	Pt <sup>2+</sup> /Pt	+0.963 V
Fe <sup>2+</sup> /Fe	-0.441 V	Cl <sub>2</sub> /Cl <sup>-</sup>	+1.358 V
Ni <sup>2+</sup> /Ni	-0.234 V	Au <sup>3+</sup> /Au	+1.498 V
Pb <sup>2+</sup> /Pb	-0.126 V	MnO <sub>4</sub> <sup>-</sup> /Mn <sup>2+</sup>	+1.531 V
H <sub>3</sub> O <sup>+</sup> /H <sub>2</sub>	0.000 V	F <sub>2</sub> /F <sup>-</sup>	+2.866 V
(SO <sub>4</sub> <sup>2-</sup> + H <sub>2</sub> O + 2e <sup>-</sup> → SO <sub>3</sub> <sup>2-</sup> + 2OH <sup>-</sup> )		(2H <sub>3</sub> O <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub> + 2H <sub>2</sub> O)	

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## Concentration and potential

Electrode potential dependence on the concentration stems from the concentration influence on electrode surroundings.

*E.g.* when ion reduces to metal at the electrode, low concentration of the ion results in low probability of this reaction occurrence and the high concentration results in high probability of it (the more ions, the higher probability of one of them reaching the electrode). When metal oxidizes to ions, low concentration of ions results in higher rate of oxidation (high chemical potential due to big concentration difference), and high concentration results in lower rate (if it is already high, the concentration gradient/difference is lower).

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## Exchange current

At the interphase a dynamic equilibrium is formed. During operation of the electrode/cell the interphase is crossed by ions in both directions. The movement of these ions is called the exchange current:

$$I_{\text{ech}} = |z_i| \cdot F \cdot N_i / N_A$$

( $z$  – charge,  $N_i$  – number of ions going through the interphase / s)

The value of the exchange current is directly related to the difficulty that ions experience to exit the crystalline structure of electrode (required energy). Ions in the structure are in equilibrium and local energy minimum. Thus, in order to exit, they need energy boost.

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## Exchange current

Thus the exchange current depends on:

- Electrode type (material) and ions arrangement in that material (in the same material the same ions can be arranged differently depending on the conditions)
- Electrolyte concentration ( $c \uparrow I_{\text{exch}} \downarrow$ )
- Temperature ( $T \uparrow I_{\text{exch}} \uparrow$ )
- Electrode state of aggregation (liquid ones have lower activation energy of the ion exit)
- Presence of other substances or impurities.

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## Polarizability of the interphase

The flow of the charge through the cell is causing unidirectional migration of ions through the interphase. It disturbs the equilibrium of the exchange current and temporarily changes the Galvani potential – the interphase polarization. Difference between equilibrium potential and potential resulting from the interphase polarization is called the **overpotential**.

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## Polarizability of the interphase

If the exchange current is very high compared to the resulting charge transfer through the cell, then this deviation from the equilibrium is negligible and interphase is not polarized. Such situation takes place with metallic electrodes (especially the liquid one, amalgam for instance) immersed in solution of that metal cation.

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## Polarizability of the interphase

If the exchange current is very low, especially if it is close to zero, then the electrode is polarizable, as at its boundary a high potential jump takes place. Electrodes that are blocking against ions in the solution are example of such situation. It is also a principle of capacitor operation: the lack of ion exchange, high potential and ions (charge) concentration at the electrode surface, which those ions cannot cross. It is a result of a very high energetic barrier for those ions entrance (exit) into the given electrode.

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## Diffusion potential

In order to connect half-cells using different electrolytes one can use ion-selective membranes or electrolytic bridges that are filled with good-conducting electrolyte (and has adequate ion-selective membranes at its ends). In reality, electrolytic bridges are more commonly used in measuring applications due to their structure thank to which they remove any differences resulting from the **diffusion potential**.

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## Diffusion potential

**Diffusion potential** is formed when there is an interphase between two electrolyte phases in one cell. In such situation, one of cations will be always faster than the other cation and one of anions will be faster than the other anion. Furthermore, cation and anion never have the same mobility, so one of the ions will be outdoing the other. Hence, there would be no local electroneutrality and an electric field will be formed due to the potential jump.

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## Diffusion potential

$$\Delta\Phi = (R \cdot T / F) \cdot (1 - 2t_+) \cdot \ln((c_1^+ \gamma_{\pm}^1) / (c_2^+ \gamma_{\pm}^2))$$

R – gas constant

T – temperature / K

$t_+$  - cation transference number

c – electrolyte concentration ( $c_1 > c_2$ )

$\gamma_{\pm}$  = mean activity coefficient (close to the activity coefficients of the individual ions, simplified by the assumption that activity of both ions is identical).

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## Overpotential

Reality is much more complex than it is presented in theory connected to the Nernst equation. Each process (chemical or physical) requires energy, thus all secondary processes are also requiring it. That means increase of energetic requirements of the main process. In case of cells it means higher required EMF in order to run process or diminished effective EMF compared to the theoretical calculations (by additional requirements not included in the theory).

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## Overpotential

- Decrease (increase of the required one) of the potential resulting from the electrolyte concentration change at the electrode due to consumption of its part can be an example of overpotential.
- Diffusion overpotential changes EMF due to the local deviations from electroneutrality.
- Process of the ion building into the electrode (or moving out of it) also requires crossing of the certain energetic threshold, thus it requires some energetic sacrifice to move out of the equilibrium state (local minimum). The harder is for an ion to build into the electrode or the stronger crystalline structure keeps this ion, the higher overpotential is required to run this process.

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