Electrochemistry

E1. Fundamental concepts

An electrolyte is a substance that leads electric current in solution or in form of melt.

Electrolytic dissociation: In solutions, neutral molecules decompose to charged particles – ions:

+: cation

- : anion

Fundamental units

Elementary charge: $e = 1.602 \cdot 10^{-19}$ C

(The charge of an electron is $-1.602 \cdot 10^{-19}$ C.)

The charge of one mol ions:

$z \cdot e \cdot N_A = z \cdot 1.602 \cdot 10^{-19}\ \mathrm{C} \cdot 6.022 \cdot 10^{23}\ \mathrm{mol}^{-1} =$

$= z \cdot 96485\ \mathrm{C\ mol}^{-1}$

N_A : Avogadro constant; z: charge number

Faraday constant: $F = 96485\ \mathrm{C\ mol}^{-1}$

E.g., Ca^{2+} : $z = +2$

PO_4^{3-}: $z = -3$

Fundamental concepts

The Faraday constant is equal to the charge of one mol singly charged positive ions (e.g., Na^+ or H^+)

Composition units used in electrochemistry

Concentration: c [mol dm^{-3}] (mol solute per dm^3 solution, molarity)

Molality: m [mol kg^{-1}] (mol solute per kg solvent, Raoult concentration)

Advantage of molality - more accurate

- does not change with T

E2. Equilibrium in electrolytes

Even very dilute solutions cannot be regarded ideal (because of the strong electrostatic interaction between ions).

Still K_c can be frequently used as equilibrium constant (it is assumed here that the activity coefficients are independent of the concentration, so K_γ is taken constant).

Dissociation equilibrium

C^+: cation

A^-: anion

$$\mathrm{CA} = \mathrm{C}^+ + \mathrm{A}^-$$

$$c_0(1-\alpha) \quad c_0 \cdot \alpha \quad c_0 \cdot \alpha$$

c_0 : initial concentration

α : degree of dissociation

$$K_c = \frac{\alpha^2 c_0}{1-\alpha} \qquad \text{(E1)}$$

The degree of dissociation (α) is the number of dissociated molecules per the number of all the molecules (before dissociation).

$$0 \le \alpha \le 1$$

α depends on concentration (it is higher in more dilute solutions).

Autoprotolitic equilibrium of water

$$H_2O + H_2O = H_3O^+ + OH^-$$

$$K_w = a(H_3O^+)\cdot a(OH^-) \qquad (E2)$$

The activity of water is missing because it is in great excess, its concentration is practically constant and can be absorbed in the equilibrium constant.

At 22 ^{0}C: $K_w \approx 10^{-14}$ $\qquad$ $pH = -\lg a(H_3O^+)$ (E3)

Ionization equilibrium of acids

$HA + H_2O = H_3O^+ + A^-$

Ionization constant:

$$K_a = \frac{a\left(H_3O^+\right) \cdot a\left(A^-\right)}{a\left(HA\right)} \qquad \text{(E4)}$$

Its negative decimal logarithm is used:

$$pK_a = -\lg K_a \qquad \text{(E5)}$$

Strong acids have small pK_a .

Ionization equilibrium of bases

$$B + H_2O = BH^+ + OH^-$$

Dissociation constant:

$$K_b = \frac{a(BH^+) \cdot a(OH^-)}{a(B)} \qquad \text{(E6)}$$

$$pK_b = -\lg K_b \qquad \text{(E7)}$$

K_a is also frequently used for bases:

$$BH^+ + H_2O = B + H_3O^+$$

$$K_a = \frac{a(H_3O^+) \cdot a(B)}{a(BH^+)} \qquad \text{(E8)}$$

Product of K_a and K_b: $K_a \cdot K_b = K_w$ (E9)

E3. Chemical potentials and activities in electrolytes

The definition of chemical potential:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j,j \neq i} \qquad \text{(E10)}$$

Its dependence on composition:

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad \text{(E11)}$$

Standard chemical potential *activity*

In dilute liquid solutions, molality (as already mentioned, m = mol solute per kg solvent) or concentration (molarity) (c = mol solute per dm^3 solution) are used instead of the mole fraction.

The activity a is expressed as the product of a quantity describing composition (m or c) and the corresponding activity coefficient (γ_m or γ_c, respectively).

Standard state: unit molality (or molarity) in the case of infinitely diluted solutions. So the standard state is a virtual state, result of an extrapolation to the infinitely diluted state.

Since the cations and anions are always together in the solution, the individual activities and therefore individual chemical potentials of the ions cannot be determined.

E.g., chemical potentials in NaCl solution:

$$\mu_{Na^+} = \left(\frac{\partial G}{\partial n_{Na^+}}\right)_{T,p,n_{Cl^-},n_{H_2O}}, \quad \mu_{Cl^-} = \left(\frac{\partial G}{\partial n_{Cl^-}}\right)_{T,p,n_{Na^+},n_{H_2O}}$$

$$\mu_{NaCl} = \left(\frac{\partial G}{\partial n_{NaCl}}\right)_{T,p,\ n_{H_2O}} = \left(\frac{\partial G}{\partial n_{Na^+}}\right)_{T,p,n_{Cl^-},n_{H_2O}} + \left(\frac{\partial G}{\partial n_{Cl^-}}\right)_{T,p,n_{Na^+},n_{H_2O}}$$

That is, $\mu_{NaCl} = \mu_{Na^+} + \mu_{Cl^-}$

Only the sum of the chemical potentials of the ions can be determined.

We can express the chemical potential as the sum of its standard value and a term describing the activity dependence (E11):

$$\mu_{Na^+} = \mu^0_{Na^+} + RT\ln a_{Na^+} \quad \mu_{Cl^-} = \mu^0_{Cl^-} + RT\ln a_{Cl^-}$$

$$\mu_{NaCl} = \mu^0_{Na^+} + RT\ln a_{Na^+} + \mu^0_{Cl^-} + RT\ln a_{Cl^-}$$

$$\mu_{NaCl} = \mu^0_{NaCl} + RT\ln\left(a_{Na^+} \cdot a_{Cl^-}\right)$$

The geometric mean of the activities of the two ions is called the mean activity:

$$a_\pm = \sqrt{a_{Na^+} \cdot a_{Cl^-}}$$

$$\mu_{NaCl} = \mu^0_{NaCl} + RT\ln a^2_\pm$$

Another example is a $CaCl_2$ solution:

$$\mu_{CaCl_2} = \mu_{Ca^{2+}} + 2\mu_{Cl^-}$$

$$\mu_{CaCl_2} = \mu^0_{CaCl_2} + RT\ln\left(a_{Ca^{2+}} a^2_{Cl^-}\right)$$

Introducing the mean activity

$$a_\pm = \sqrt[3]{a_{Ca^{2+}} \cdot a^2_{Cl^-}}$$

The chemical potential is

$$\mu_{CaCl_2} = \mu^0_{CaCl_2} + RT\ln a^3_\pm$$

In general, if the electrolyte dissociates to ν_A anions and ν_C cations:

$$A_{\nu_A} C_{\nu_C} = \nu_A A^{z_A} + \nu_C C^{z_C}, \quad \text{(E12a)}$$

where z_A and z_C are the charge numbers of anions and cations, respectively. The mean activity is

$$a_{\pm} = \sqrt[\nu]{a_A^{\nu_A} \cdot a_C^{\nu_C}}, \qquad \text{(E12b)}$$

where $\nu = \nu_A + \nu_C$.

The chemical potential:

(E13)

$$\mu = \mu^0 + RT \ln a_{\pm}^{\nu} = \mu^0 + \nu RT \ln a_{\pm}$$

The (dimensionless) activities can be expressed in the following way (examples):

$$a_A = \gamma_A \cdot \frac{m_A}{m^0}\ ,\ a_C = \gamma_C \cdot \frac{c_C}{c^0} \quad \text{(E14)}$$

γ_A, γ_C: *activity coefficients*

m°: *unit mola**l**ity* (1 mol kg^{-1}), c^0 *unit mola**r**ity*

The mean activity using molalities: (E15)

$$a_{\pm} = \sqrt[\nu]{\gamma_A^{\nu_A} \cdot \left(\frac{m_A}{m^0}\right)^{\nu_A} \gamma_C^{\nu_C} \left(\frac{m_C}{m^0}\right)^{\nu_C}} = \sqrt[\nu]{\gamma_A^{\nu_A} \gamma_C^{\nu_C} \frac{m_A^{\nu_A} m_C^{\nu_C}}{\left(m^0\right)^{\nu}}}$$

Introducing the mean activity coefficient $\gamma_{\pm}$ and the mean molality $m_{\pm}$:

$$\gamma_{\pm} = \sqrt[\nu]{\gamma_A^{\nu_A} \cdot \gamma_C^{\nu_C}} \qquad \text{(E16)}$$

$$m_{\pm} = \sqrt[\nu]{m_A^{\nu_A} \cdot m_C^{\nu_C}} \qquad \text{(E17)}$$

The mean activity:

$$a_{\pm} = \gamma_{\pm} \cdot \frac{m_{\pm}}{m^0} \qquad \text{(E18)}$$

Example:

Calculation of the mean molality of a 0.2 mol/kg $Al_2(SO_4)_3$ solution.

$$m_{\pm} = \sqrt[5]{0.4^2 \cdot 0.6^3} = 0.51\ mol \cdot kg^{-1}$$

E4. Debye-Hückel theory

The electrolytes do not behave ideally even if the solution is dilute. The reason is the electrostatic interaction between ions.

In 1923, Debye and Hückel developed a theory that explains the behavior of dilute electrolytes. We discuss only the main points of this theory.

Cations and anions are not distributed evenly in the solution. A selected anion is surrounded by more cations than anions and vice versa.

Around a cation there is an excess of anions. Around an anion there is an excess of cations.

The cloud of such ions has a spherical symmetry. It is called ionic atmosphere.

How does the cloud of ions of opposite charge influence the chemical potential?

The interionic attractive forces reduce the energy of ions, the chemical potential is reduced, too. So the activity coefficient is less than 1.

The result of a long derivation is a simple expression for the activity coefficient.

$$\lg \gamma_{\pm} = -|z_C \cdot z_A| \cdot A \cdot I^{1/2} \quad \text{(E19)}$$

where I is the ionic strength. It depends on the molalities (or concentrations) of all the ions in the solution.

$$I = 0.5 \cdot \sum m_i \cdot z_i^2 \quad \text{(E20a)}$$

$$I = 0.5 \cdot \sum c_i \cdot z_i^2 \quad \text{(E20b)}$$

The constant "A" depends on the permittivity (ε, D=εE), density, and temperature of the solvent. Its value is 0.509 in aqueous solutions at 25 °C.

$$\lg \gamma_{\pm} = -|z_C \cdot z_A| \cdot 0.509 \cdot I^{1/2}$$

25^oC, aqueous solution

According to equation E19, *the logarithm of the mean activity coefficient is a linear function of the square root of the ionic strength.*

This law is valid in dilute solutions only. Therefore E19 *is called the Debye-Hückel limiting law.*

E5. The electrochemical potential

The exact differential of the Gibbs free energy in an open system (material and energy exchange with the surroundings are allowed) at constant T and p:

$$dG_{p,T} = \sum_i \mu_i \, dn_i \qquad \text{(E21)}$$

If dn_i mol neutral component is added to the solution, the change of Gibbs free energy is $\mu_i dn_i$.

If ions are moved to a place where the electric potential is Φ, then electrical (non pV) work is performed:

$$dW = \Phi \cdot z_i \cdot F \cdot dn_i$$

Then, the exact differential of the Gibbs free energy is:

$$dG_{p,T} = \sum_i \left(\mu_i + z_i F \Phi \right) dn_i \qquad \text{(E22)}$$

The partial derivative of the Gibbs function with respect to the amount of substance in the presence of ions:

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j,i\neq j} = \mu_i + z_i F \cdot \Phi$$

This quantity is called the electrochemical potential:

$$\widetilde{\mu}_i = \mu_i + z_i \cdot F \cdot \Phi \qquad \text{(E23)}$$

If ions take part in the processes, the condition of equilibrium is expressed in terms of electrochemical potentials.

Of course, for neutral atoms and molecules (z_i=0), the electrochemical potential is equal to the chemical potential:

$$\tilde{\mu}_i = \mu_i$$

The condition of phase equilibrium is the equality of the electrochemical potential of the component that is present in two phases.

Chemical equilibrium:

$$\sum_A v_A \widetilde{\mu}_A = \sum_B v_B \widetilde{\mu}_B \qquad \text{(E24a)}$$

that is, $\Delta_r \widetilde{\mu} = 0$ (E24b)

where ν-s are the stochiometric coefficients, A-s stand for the reactants, B-s stand for the products.

Some practical applications of the electrochemical potential

1. Contact potential

Behavior of electrons in metals. *Their energies are different in different metals. Therefore, their electrochemical potentials are also different.*

If two metals are brought into contact (welding, soldering), electrons flow from the metal where their electrochemical potential is higher to the metal where their electrochemical potential is lower.

As a result, the metal that gains electrons acquires negative charge, while the metal that loses electrons acquires positive charge.

Thus, an electric potential difference $\Delta\Phi$ *occurs at the contact between the two metals.*

The condition of equilibrium is the equality of the electrochemical potential for the electrons in the two metals.

$$\tilde{\mu}_e^a = \tilde{\mu}_e^b$$ (E25) *where a and b denote the two metals.*

Substituting the expression E23 *into* E25, *and considering that for the electron,* $z_e = -1$,

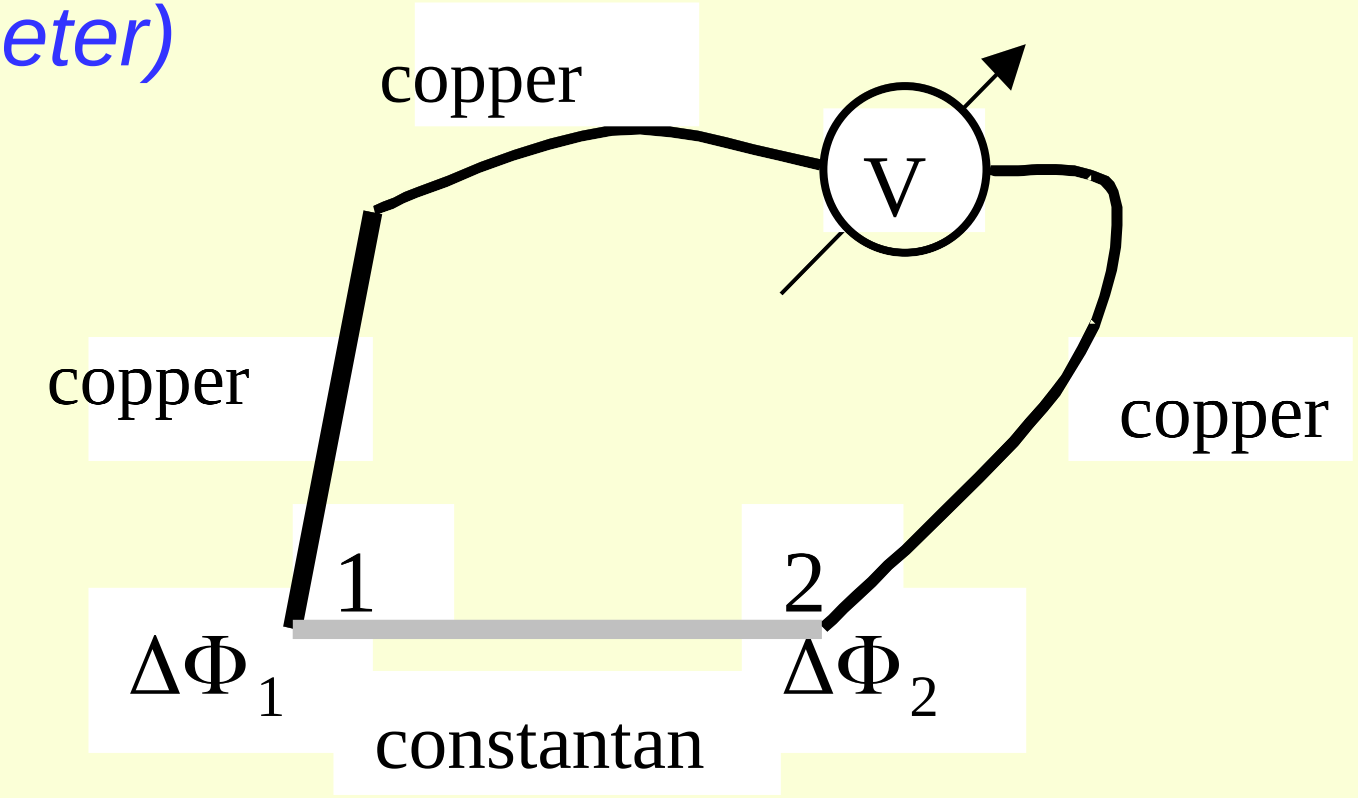
$$\mu_e^a - F \cdot \Phi_a = \mu_e^b - F \cdot \Phi_b$$

$$F \cdot \left(\Phi_b - \Phi_a \right) = \mu_e^b - \mu_e^a$$

$$\Delta\Phi = \Phi_b - \Phi_a = \frac{\mu_e^b - \mu_e^a}{F}$$ (E26)

$\Delta\Phi$ (E26) *is called the contact (electric) potential. It is proportional to the difference of the chemical potentials.*

A useful application of the contact potential is the thermocouple. Here, the contact potential can be measured directly. Consider for example a copper-constantan (60 % Cu, 40 % Ni) thermo-couple (copper cables connected to the voltmeter)



At the contact point of the two metals (1), the potential difference is $\Delta\Phi_1$. If we want to measure this, we have to attach a voltmeter. The voltmeter must have high internal resistance (high Ω/V value) for minimizing the electric current in the circuit.

Since the source of the current in the circuit is only the internal contact potential,

$$\Delta\Phi_2=-\Delta\Phi_1$$

The contact potential depends on the temperature (thermocouple!)

If points 1 and 2 are of different temperature, the resultant voltage is not zero any more.

It is the function of the temperature difference: $\Delta U = f(\Delta t)$.

Themocouples are used for temperature measurement. They always measure the temperature difference between two points. Practically, one of the two points has fixed temperature (cold point).

2. Electrode reaction

A piece of metal dips into a solution containing the ions of this metal. What happens in this case?

E.g., copper dips into $CuSO_4$ solution. The following equilibrium sets in:

$$Cu^{2+}(\text{solution}) + 2e^{-}(\text{metal}) = Cu$$

The condition for equilibrium is $\Delta_r \tilde{\mu} = 0$

That is, $\mu_{Cu} - \tilde{\mu}_{Cu^{2+}} - 2\tilde{\mu}_{e^-} = 0$ (E27)

For the neutral copper atoms, the chemical potential, for the charged particles (copper ions and electrons), the electrochemical potentials are used.

Substituting the expression of the electrochemical potential (E23) *into E27:*

$$\mu_{Cu} - \mu_{Cu^{2+}} - 2\mathrm{F}\cdot\Phi\left(solution\right) -$$
$$-2\mu_{e^{-}}\left(metal\right) + 2\mathrm{F}\cdot\Phi\left(metal\right) = 0$$

(E28)

Rearrange equation E28 so that the electric potential difference will be on the left:

$$2\mathrm{F}\cdot\left[\Phi\left(metal\right)-\Phi\left(sol.\right)\right]=2\mu_{e^{-}}\left(metal\right)+\mu_{Cu^{2+}}-\mu_{Cu} \tag{E29}$$

We cannot measure this electric potential difference because for that, we have to dip another metal in the solution, and the voltage of the entire circuit can only be measured.

E6. Electrochemical cells

Consider the following *redox reaction*:

$$CuSO_4 + Zn = ZnSO_4 + Cu$$

$$Cu^{2+} + Zn = Zn^{2+} + Cu$$

In this reaction, Cu^{2+} ions are reduced and Zn atoms are oxidized.

Two steps:

$Cu^{2+} + 2\ e^{-} = Cu$ reduction

$Zn = Zn^{2+} + 2\ e^{-}$ oxidation

In an electrochemical cell, the oxidation and reduction are separated in space: reduction means electron gain, oxidation means electron loss.

Galvanic cell: production of electrical energy from chemical energy.

Electrolytic cell: electrical energy is used to bring about chemical changes (e.g., production of chlorine from sodium chloride).

The following slide shows a Daniell cell.

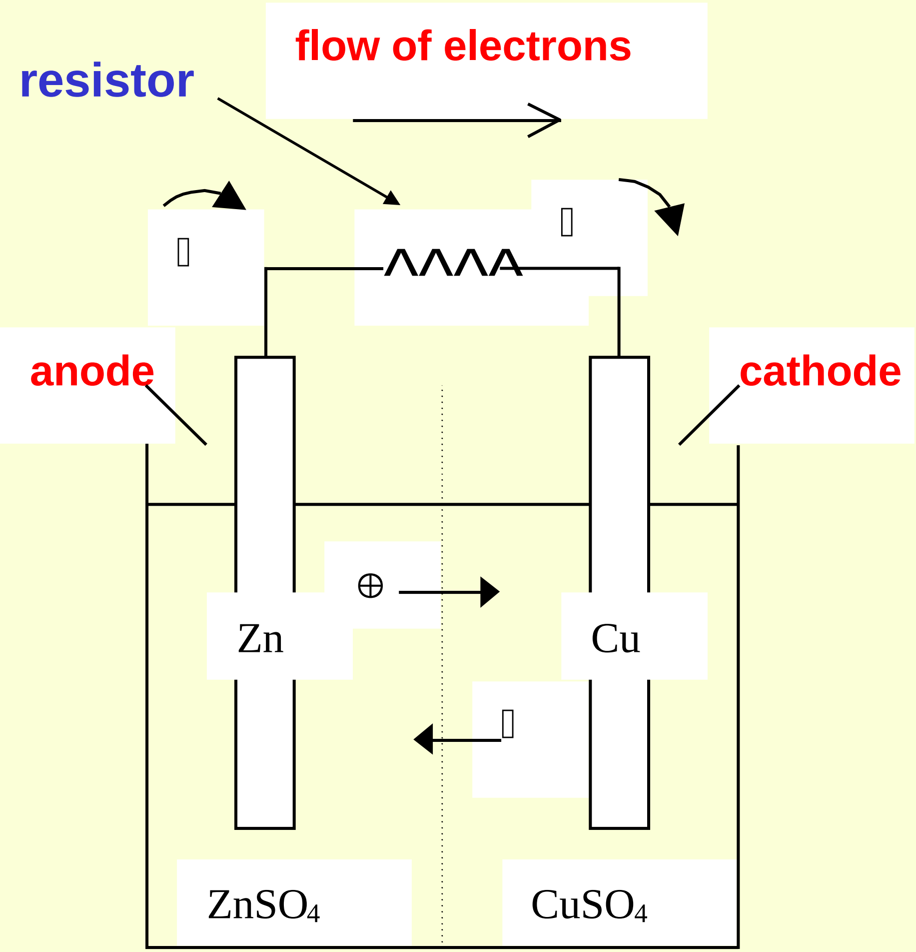
On the left, it works as a Galvanic cell and produces electric current (spontaneous process).

On the right, we use an external power source to reverse the process. In that case, the cell works as an electrolytic cell.

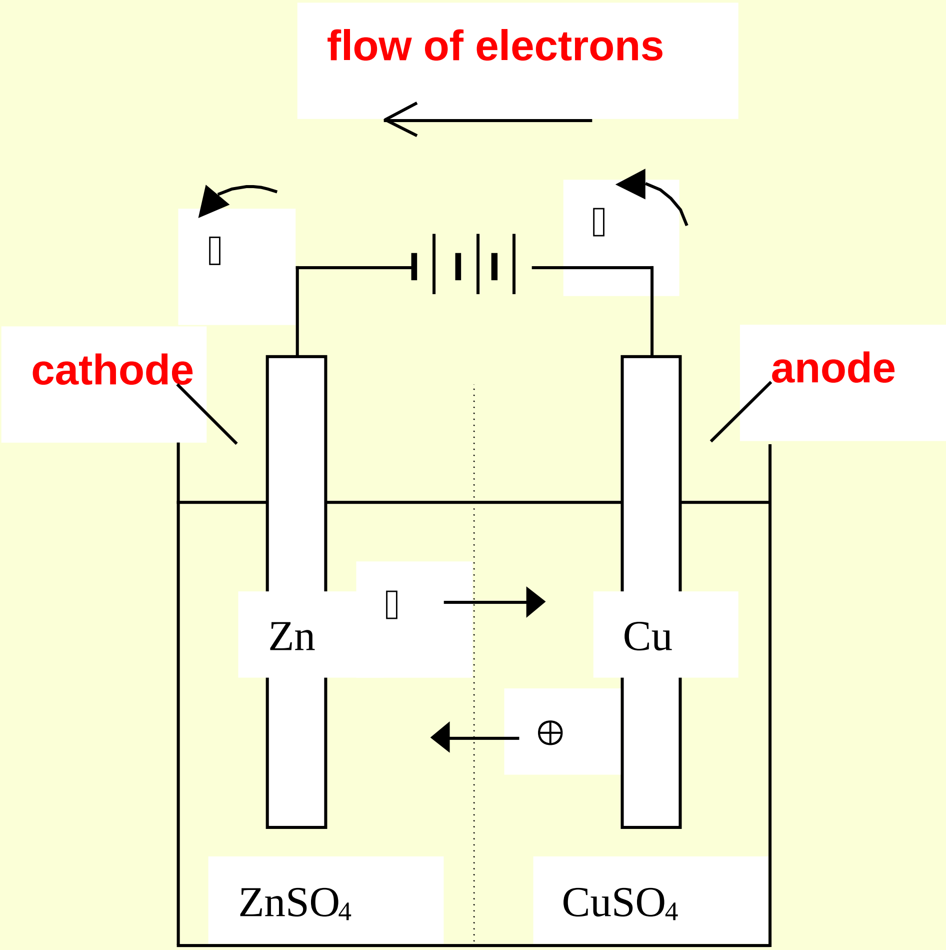
Cathodes and anodes are electrodes. Observe the change of anodic and cathodic functions in the case of the galvanic and electrolytic cells!

Daniell cell

Galvanic cell



Electrolytic cell



Cathodes and anodes are electrodes.

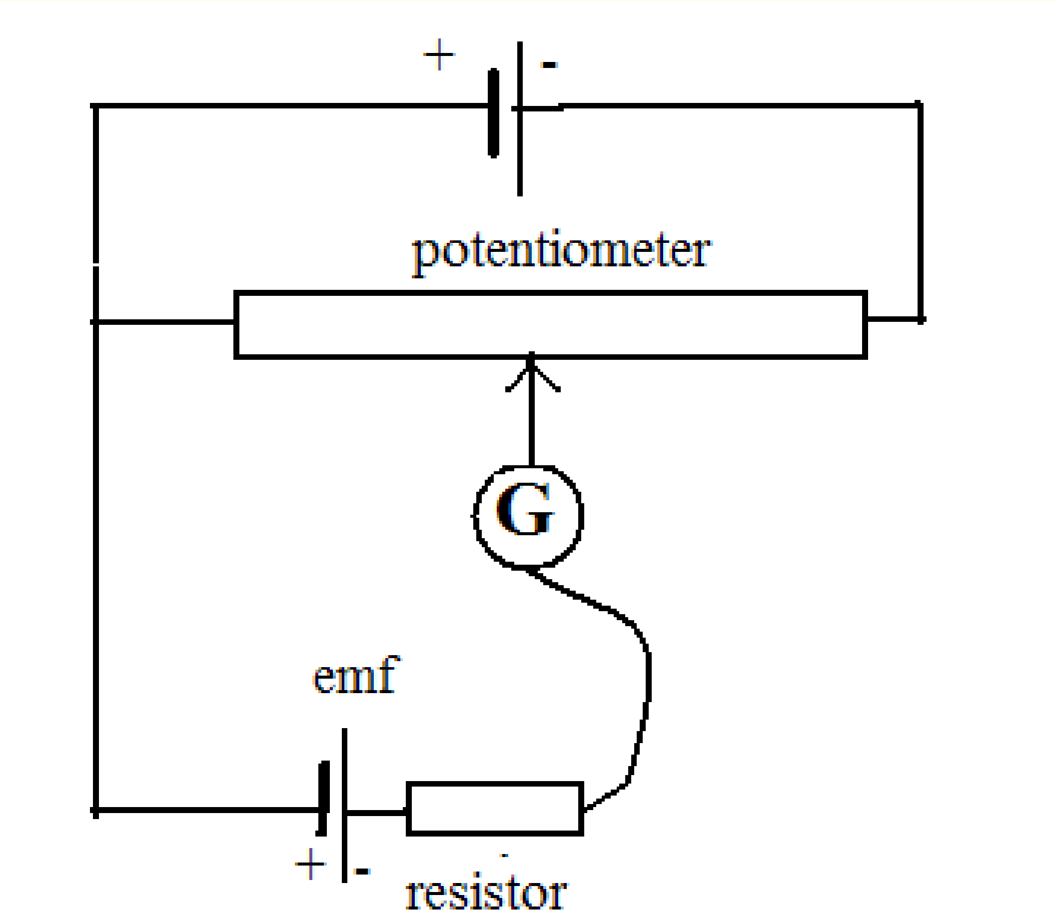
Galvanic cell	Electrolytic cell
$Zn \rightarrow Zn^{2+} + 2\,e^-$	$Zn^{2+} + 2\,e^- \rightarrow Zn$
$Cu^{2+} + 2\,e^- \rightarrow Cu$	$Cu \rightarrow Cu^{2+} + 2\,e^-$
$\Delta\Phi \approx 1.1\ V$	

Oxidation on anodes, reduction on cathodes.

The potential difference of a cell under equilibrium conditions is called the electromotive force (emf). The electromotive force E of the cell can be measured as the limiting value of the electric potential difference, $\Delta\Phi$, i.e., when the current through the cell goes to zero.

$$E = \Delta\Phi_{(I=0)} \qquad \text{(E30)}$$

Simple measurement of emf: the emf is compensated by a measurable and adjustable voltage source. If the G meter measures zero, the two voltages are equal.

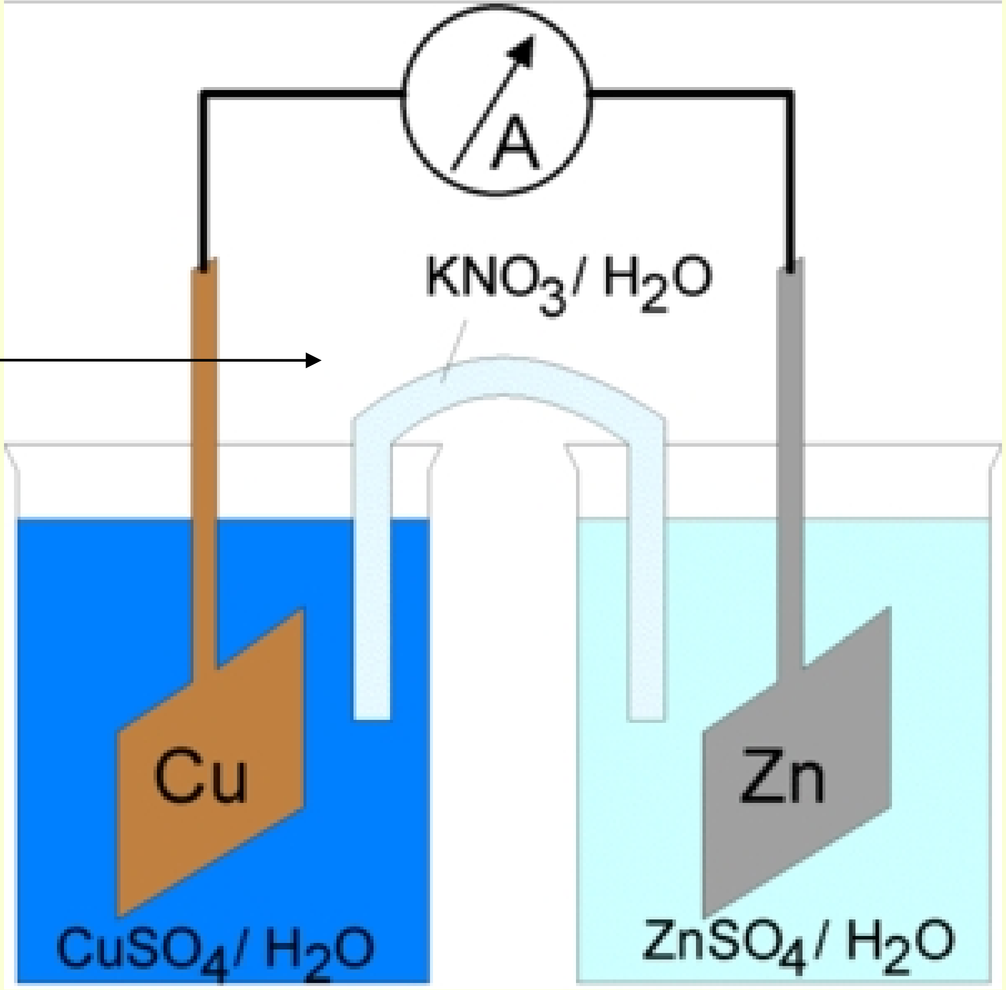


Cell diagram (description of the cell):

$$\mathrm{Zn}\ |\ \mathrm{Zn^{2+}(aq)}\ ||\ \mathrm{Cu^{2+}(aq)}\ |\ \mathrm{Cu}$$

Phase boundaries: vertical lines

Two vertical lines are used for the liquid junction. Usually a salt bridge is used to prevent the liquids from mixing (KNO_3/H_2O colloid in agar-agar gel, a sea kelp).



The electromotive force is the sum of the potential differences on the phase boundaries.

If the external leads are made of copper:

Cu /Zn - contact potential

Zn /Zn^{2+} - between solution and metal

Zn^{2+} / Cu^{2+} - between two solutions

Cu^{2+} /Cu - between metal and solution

Cu I Zn $2F [\Phi(Zn) - \Phi_{left}(Cu)] = 2\mu_e (Zn) - 2\mu_e (Cu)$

Zn I Zn^{2+} $2F [\Phi(sol) - \Phi(Zn)] = \mu_{Zn} - \mu_{Zn}{}^{2+} - 2\mu_e(Zn)$

Zn^{2+} I Cu^{2+} *diffusion potential (*ε_{diff}*, neglected, equation E40, section E8)*

Cu^{2+} I Cu $2F [\Phi_{right}(Cu) - \Phi(sol)] = 2\mu_e (Cu) + \mu_{Cu}{}^{2+} - \mu_{Cu}$

Summing up:

$$2F [\Phi_{right}(Cu) - \Phi_{left}(Cu)] = \mu_{Zn} + \mu_{Cu}{}^{2+} - \mu_{Cu} - \mu_{Zn}{}^{2+}$$

$$2F E = - \Delta_r \mu \; (= -\Delta_r G)$$

In general: $$\boxed{\Delta_r G = -|z|FE} \qquad \text{(E31)}$$

Left side of E31: Gibbs free energy change for the reaction. (It depends on the concentration of the participants.)

Right side of E31: *Electrical work* done by the system.

Sign dependence of the emf (E)

Positive E - The reaction goes spontaneously from left to right according to the reaction equation. ($\Delta_r G < 0$)

Negative E - The reaction goes spontaneously in the opposite direction. ($\Delta_r G > 0$)

$E = 0$ - Chemical equilibrium. ($\Delta_r G = 0$)

7. Thermodynamics of Galvanic cells, the Nernst equation

Find the relationship between the thermodynamic functions of reactions and the electromotive force.

1. $\Delta_r G$:

$$\boxed{\Delta_r G = -|z|FE} \qquad \text{(E31)}$$

2. $\Delta_r S$:

$$dG = V\,dp - S\,dT \qquad \text{(E32)}$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

Differentiating E31 (*$\Delta_r G$*) *with respect to the temperature:*

$$\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = -\Delta_r S$$

$$\Delta_r S = zF\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{(E33)}$$

According to E33, *for calculating $\Delta_r S$, we have to know the temperature dependence of the electromotive force.*

3. $\Delta_r H$ $\quad G = H - TS \longrightarrow H = G + TS$

Therefore $\Delta_r H = \Delta_r G + T\,\Delta_r S$ (E34)

Substituting E31 *and* E33 *into* E34

$$\Delta_r H = -zFE + zFT\left(\frac{\partial E}{\partial T}\right)_p \qquad \text{(E35)}$$

The changes of thermodynamic functions in chemical reactions can be accurately determined by measuring the electromotive force and its temperature dependence.

Nernst equation: Dependence of E on the composition

$$\Delta_r G = \sum \nu_B \mu_B - \sum \nu_A \mu_A \qquad \text{(E36)}$$

According to E11:

$$\mu_i = \mu_i^0 + R\,T\ln a_i$$

Substituting this equation into E36

$$\Delta_r G = \sum_B \nu_B \mu_B^0 - \sum_A \nu_A \mu_A^0 - RT \sum_B \nu_B \ln a_B - RT \sum_A \nu_A \ln a_A$$

$$\Delta_r G = \Delta_r \mu^0 + RT \ln \frac{\prod_B a_B^{\nu_B}}{\prod_A a_A^{\nu_A}} \qquad \text{(E37)}$$

Dividing both sides by $-|z| \cdot F$:

$$E = -\frac{\Delta_r \mu^0}{|z|F} - \frac{RT}{|z|F} \ln \frac{\prod_B a_B^{\nu_B}}{\prod_A a_A^{\nu_A}} \qquad \text{(E38a)}$$

$$E = E^0 - \frac{RT}{|z|F} \ln \frac{\prod_B a_B^{\nu_B}}{\prod_A a_A^{\nu_A}} \qquad \text{(E38b)}$$

products

reactants

E38b *is the original form of the* Nernst equation. E^0 *is the standard electromotive force, it is the value of* E *when the activities of all the participants are 1.*

From the equilibrium constant of the reaction, E^0 can be calculated (consider E11):

$\Delta_r\mu^0$ = - RT lnK

$$E^0 = -\frac{\Delta_r\mu^0}{|z|F} = \frac{RT}{|z|F}\ln K \qquad \text{(E39)}$$

If K > 1, $E^0 > 0$

If K < 1, $E^0 < 0$

Example: $Zn + Cu^{2+} = Cu + Zn^{2+}$

$$E = E^0 - \frac{RT}{2\mathrm{F}} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$E^0 \approx 1.1$ V, $z=2$

$$\frac{RT}{|z|F} \ln K = 1.1\ V$$

$$\frac{0.059}{2} \lg K = 1.1 \qquad \lg K = \frac{2.2}{0.059} = 37.29$$

$K \approx 2 \cdot 10^{37}$, i.e., the reaction is very strongly shifted in the direction of the products, Cu^{2+} ions do not exist practically in the solution.

E8. Electrode potentials

In a galvanic, cell oxidation and reduction are separated in space (figure in section E).

Anode - oxidation
Cathode - reduction

Many different electrodes can be constructed. Electrodes can be combined to form galvanic cells.

E.g., from 1000 different electrodes, nearly half a million different galvanic cells can be construted.

Instead of listing the electromotive forces of *all the galvanic cells, electrode potentials are defined. From the electrode potentials, the electromotive force can be calculated*.

$$E = \varepsilon_{right} - \varepsilon_{left}\ (+\varepsilon_{diff}) \qquad \text{(E40)}$$

ε_{diff} is the diffusion potential or junction potential. The anions or cations move with different (diffusion) velocity under the same electric potential. This causes local charge differences. This is the source of ε_{diff}.

We have seen that the absolute values of electrode potentials cannot be determined. Therefore, a relative electrode potential scale was defined.

One electrode was selected as a standard, and the electrode potentials of all the other electrodes are given relative to this standard.

The selected electrode is the standard hydrogen electrode.

In a standard hydrogen electrode, a platinum wire dips in a solution where the activity of hydrogen ions (H_3O^+ ions) is 1, and hydrogen gas of 10^5 Pa standard pressure bubbles around the platinum.

The adsorbed hydrogen molecules and the hydrogen (H_3O^+) ions in the solution take part in the electrode reaction.

So the electrode potential of the electrode X is defined as the electromotive force of the following cell (if the electrode X is the cathode) :

$$Pt\left|H_2\left(p^0\right)\right|H^+\left(a=1\right)\|X^+|X \qquad \text{(E41)}$$

$$\frac{1}{2}H_2=H^+ +e^-$$ oxidation

$$X^+ +e^- =X$$ reduction

The cell reaction is

$$\frac{1}{2}H_2+X^+ =H^+ +X \qquad \text{(E42)}$$

The electrode potential of an electrode (ε) is defined as the electromotive force of a cell constructed from that electrode and the standard hydrogen electrode. (The electrode in question is on the right side and the standard hydrogen electrode is on the left side in the cell diagram.)

$$\frac{1}{2}H_2 + X^+ = H^+ + X$$

X: metal

X^+: ion of the metal

$$E = E^0 - \frac{RT}{F}\ln\frac{a\left(H^+\right)}{a\left(X^+\right)\sqrt{\frac{p_{H_2}}{p^0}}} \qquad \text{(E43)}$$

In the standard hydrogen electrode,

$\left[a\left(H^{+}\right)\right]$ *and* $\dfrac{p_{H_2}}{p^{0}}$ are 1,

and therefore, considering E43,

$$E=E^{0}+\frac{RT}{F}\ln a\left(X^{+}\right) \qquad \text{(E44)}$$

$E^{0}=\varepsilon^{0}$ is the electrode potential when the activity of X^{+} ions is 1, it is called the standard electrode potential. These values are listed in electrode potential tables.

If the electrode potential is positive, the electrode oxidizes H_2.

If the electrode potential is negative, the electrode reduces H^+.

In general, the value of the electrode potential shows the oxidizing-reducing ability of the system.

A system having more positive electrode potential oxidizes the system having more negative electrode potential.

The expression for electrode potential for a general electrode process:

1. *Put down the electrode process, see (in the direction of reduction)*

$$\Sigma\, \nu_{ox}\, M_{ox} = \Sigma \nu_{red}\, M_{red}$$

(See E24a)

2. *Write down the Nernst equation (E38):*

$$\varepsilon = \varepsilon^{0} - \frac{RT}{|z|F} \ln \frac{\prod_{red} a_{red}^{\nu_{red}}}{\prod_{ox} a_{ox}^{\nu_{ox}}}$$

That is,

$$\varepsilon = \varepsilon^{0} + \frac{RT}{|z|F} \ln \frac{\prod_{ox} a_{ox}^{\nu_{ox}}}{\prod_{red} a_{red}^{\nu_{red}}}$$

← *oxidized form*

← *reduced form*

We apply the rules valid for the equilibrium of heterogeneous reactions.

The activities of pure metals and precipitates are left out.

For gases, the activity is p_i/p^o (ideal gas).

E.g., AgCl electrode (see metal-insoluble salt electrode, section E9).

$$\begin{array}{l}
\underline{\mathrm{AgCl}} = \mathrm{Ag}^+ + \mathrm{Cl}^- \\
\mathrm{Ag}^+ + e^- = \mathrm{Ag} \\
\hline
\underline{\mathrm{AgCl}} + e^- = \mathrm{Ag} + \mathrm{Cl}^-
\end{array}$$

ox *red*

$$\varepsilon = \varepsilon^{0}_{AgCl} + \frac{RT}{F} \ln \frac{1}{a_{Cl^-}} \qquad \varepsilon = \varepsilon^{0}_{AgCl} - \frac{RT}{F} \ln a_{Cl^-}$$

The electrode potentials at 25 °C:

$$\lg a = \frac{\ln a}{\ln 10}$$

ln a = lg a · ln 10, T = 298.15 K

$$\frac{RT}{F} \cdot \ln 10 = 0.05916\ [Volt]$$

$$\varepsilon = \varepsilon^{0} + \frac{0.05916}{|z|} \cdot \lg \frac{\prod_{ox} a_{ox}^{\nu_{ox}}}{\prod_{red} a_{red}^{\nu_{red}}} [V]$$ (E45)

E9. Types of electrodes

1. Metal electrodes

As already mentioned (section E6, electrode reactions), a metal dips into a solution containing the ions of the same metal (Me).

$Me^{z+} + z\cdot e^{-} = Me$ *z, charge number (positive integer)*

$$\varepsilon = \varepsilon^{0} - \frac{RT}{zF}\cdot\ln\frac{1}{a_{Me^{z+}}} = \varepsilon^{o} + \frac{RT}{zF}\cdot\ln a_{Me^{z+}} \quad \text{(E46)}$$

Amalgam electrode – metal dissolved in mercury.

2.Gas electrodes

Indifferent metal (e.g., Pt) is surrounded by a gas (in form of bubbles).

The electrode reaction is that of the gas molecules and ions.

E.g., $\mathrm{Pt}|\mathrm{Cl_2}|\mathrm{Cl^-(aq)}$

ε^0=1.36 V

$Cl_2 + 2\,e^- = 2\,Cl^-$

$$\varepsilon = 1.36 + \frac{0.05916}{2} \lg \frac{\frac{p_{Cl_2}}{p^0}}{a^2_{Cl^-}} [V]$$

at 25 ^{0}C

(E47)

The most important gas electrode is the ***hydrogen electrode*** *(see also equations E41, E42, and E43).*

The electrode: $H_2\ (Pt) | H^+\ (aq)$

The reaction: $H^+ + e^- = \frac{1}{2} H_2$

At 25 °C

$$\varepsilon = 0 + 0.05916 \cdot \lg \frac{a_{H^+}}{\sqrt{\frac{p_{H_2}}{p^0}}} \quad [V]$$

If $p_{H_2} = p^o \longrightarrow \varepsilon = -0.059 \cdot pH$

3.Redox electrodes

An indifferent metal dips in a solution containing a species in two oxidation states.

E.g. Sn^{2+}, Sn^{4+} $Sn^{4+} + 2e^- = Sn^{2+}$

$$\varepsilon = \varepsilon^0_{Sn^{2+}/Sn^{4+}} + \frac{RT}{2F} \ln \frac{a_{Sn^{4+}}}{a_{Sn^{2+}}} \qquad \text{(E48)}$$

4. Metal - insoluble salt electrodes

A metal electrode is covered by the layer of an insoluble salt of the metal. The electrolyte contains the anions of the insoluble salt.

E.g., Ag/AgCl electrode: Ag | AgCl(s) | KCl(aq)

$$\begin{array}{l} Ag = Ag^{+} + e^{-} \\ Ag^{+} + Cl^{-} = \underline{AgCl} \\ \hline Ag + Cl^{-} = \underline{AgCl} + e^{-} \end{array}$$

red ox

$$\varepsilon = \varepsilon^{0}_{AgCl} + \frac{RT}{F} \ln \frac{1}{a_{Cl^{-}}}$$

$$\varepsilon=\varepsilon^{0}_{AgCl}-\frac{RT}{F}\ln a_{Cl^{-}}$$

(E49)

The electrode potential depends on the anion activity, „Cl^- electrode”.

Calomel electrode, Hg | Hg_2Cl_2(s) | KCl(aq)

$\underline{Hg_2Cl_2}$ = Hg_2^{2+} + 2Cl^-

Hg_2^{2+} + 2 e^- = 2 Hg

$\underline{Hg_2Cl_2}$ + 2 e^- = 2 Hg + 2Cl^-

$$\varepsilon=\varepsilon^{0}_{Hg_2Cl_2}+\frac{RT}{2F}\cdot\ln\frac{1}{a^2_{Cl^{-}}}$$

$$\varepsilon = \varepsilon^{0}_{Hg_2Cl_2} - \frac{RT}{F} \cdot \ln a_{Cl^-} \qquad \text{(E50)}$$

The metal - insoluble salt electrodes are used as reference electrodes because their electrode potential is stable.

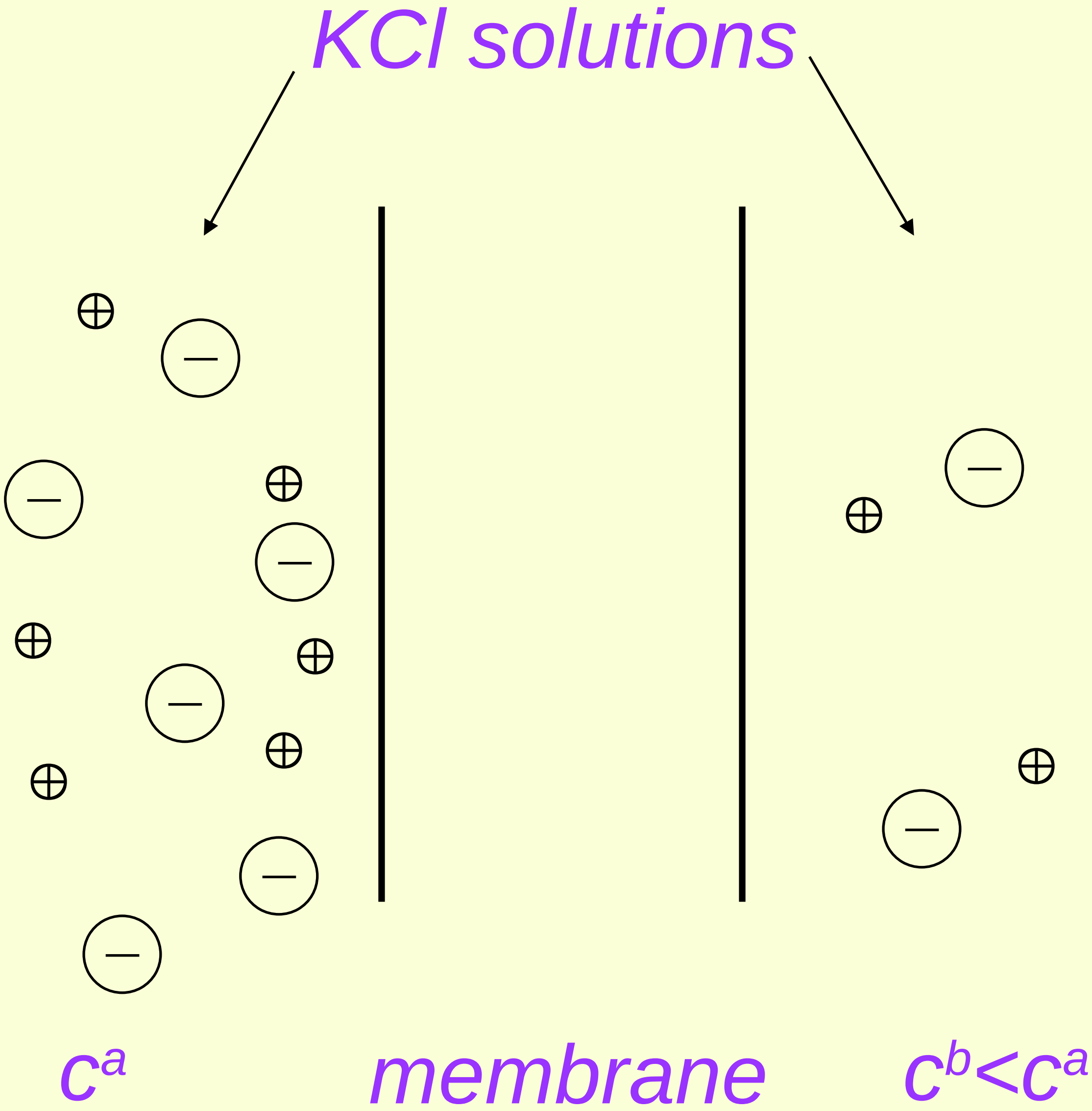
They are non-polarizable electrodes, their electrode potential does not change if the current changes.

E10. Membrane potentials, glass electrodes

Membranes are significant in biology. Walls of living cells behave as membranes.

Consider, e.g., two solutions of different concentrations of KCl, and let the membrane dividing them be permeable only to K^+!

The K^+ ions tend to diffuse into the more dilute solution, but the Cl^- ions cannot follow them.



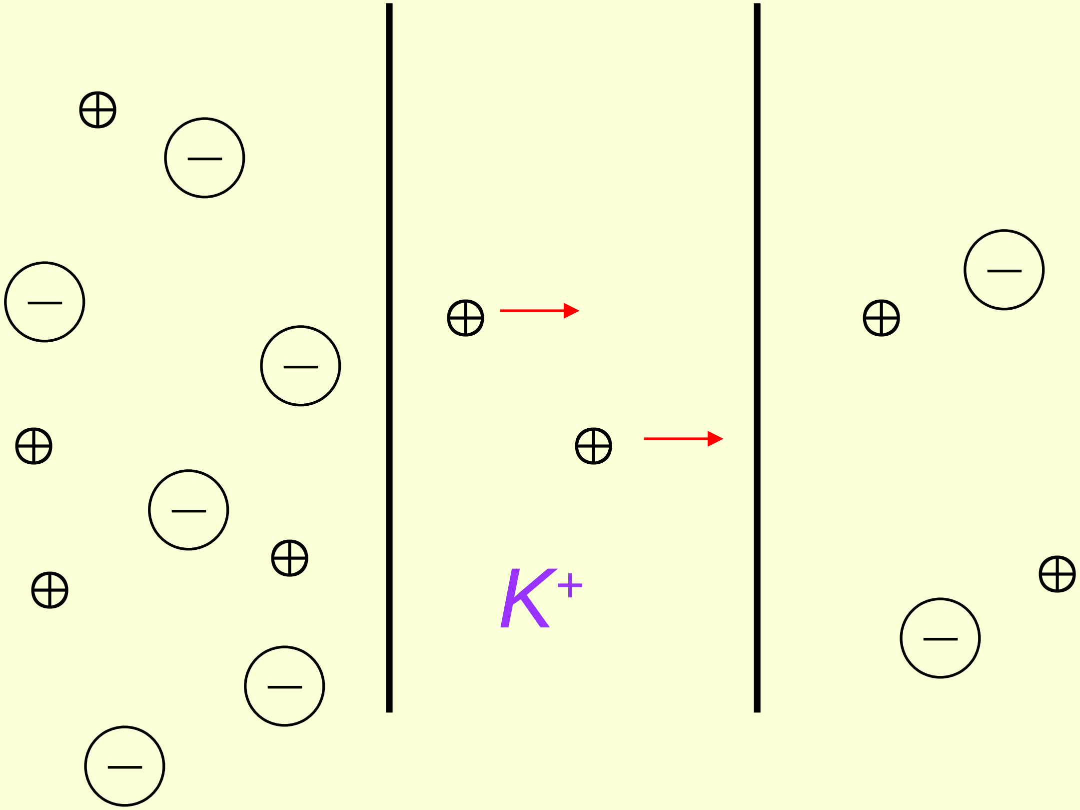
KCl solutions

c^a

membrane

$c^b < c^a$

Diffusion through the membrane



membrane

The diffusion does not continue infinitely since the charge separation causes retarded migration of the cations (repulsion of the anions).

The system reaches equilibrium when the electrochemical potentials of the K⁺ ions are the same on both sides of the membrane.

$$\tilde{\mu}^{a}_{K^{+}} = \tilde{\mu}^{b}_{K^{+}} \qquad \text{(E51)}$$

where the two solutions are denoted by superscripts a and b.

Considering E23 *and* E26:

$$\mu_{K^+}^{a} + F \cdot \Phi^{a} = \mu_{K^+}^{b} + F \cdot \Phi^{b}$$

$$\Delta\Phi = \Phi^{b} - \Phi^{a} = \frac{1}{F} \cdot \left(\mu_{K^+}^{a} - \mu_{K^+}^{b} \right)$$

$$\mu_{K^+} = \mu_{K^+}^{0} + RT \cdot \ln a_{K^+}$$

$$\mu_{K^+}^{a} - \mu_{K^+}^{b} = RT \ln \frac{a_{K^+}^{a}}{a_{K^+}^{b}}$$

$$\Delta\Phi = \frac{RT}{F} \ln \frac{a_{K^+}^{a}}{a_{K^+}^{b}} \qquad \text{(E52)}$$

Glass electrodes *are used for measuring pH.*

The main part of the glass electrode is a ***glass membrane*** *of special composition. It consists of a Si-O frame with the negative charges compensated by positive ions (Li^+,* ***Na^+,*** *Ca^{2+}).*

The positive ions are mobile so the membrane slightly conducts electricity.

Thickness ~0.05 mm.

Resistance 10^7 - 10^9 ohm.

Before its use, the glass electrode is soaked in water. Some of the sodium ions are replaced by hydrogen ions.

When we dip the glass electrode in a solution containing hydrogen ions, the equilibrium of H^+ ions is reached between the solution and the glass.

The condition for the equilibrium:

$$\tilde{\mu}_{H^+}(glass) = \tilde{\mu}_{H^+}(solution) \qquad \text{(E53)}$$

Applying E23 *and* E26

$$\mu_{H^+}(glass) + F\cdot\Phi(glass) = \mu_{H^+}(solution) + F\cdot\Phi(solution)$$

$$\Phi(solution) - \Phi(glass) = \frac{1}{F}\mu_{H^+}(glass) - \frac{1}{F}\mu_{H^+}(solution)$$

The chemical potential of the hydrogen ions in the solution depends on their activity:

since $\mu_{H^+} = \mu^0_{H^+} + RT\cdot\ln a_{H^+}$

$$\Delta\Phi = \frac{1}{F}\mu_{H^+}(glass) - \frac{1}{F}\mu^0_{H^+}(solution) - \frac{RT}{F}\ln a_{H^+}$$

At 25 °C $\frac{RT}{F}\ln a_{H^+} = 0.059\lg a_{H^+}$ *and* $-\lg a_{H^+} = pH$

$$\Delta\Phi = \Delta\Phi(0) + 0.059\,pH\,[V]$$

(E54)

The electrode potential of the glass electrode depends on the pH of the solution. 1 unit pH change causes 59 mV change in the electrode potential.

The system for measuring pH consists of a glass electrode and a reference electrode. The emf is measured. Solutions of known pH (buffers) are used for calibration.

E11. Conductivity of electrolytes

Ohm's law: $$I = \frac{\Delta\Phi}{R}$$ (E55)

I: *current [A]*
ΔΦ: *potential difference [V]*
R: *resistance [Ω]*

In the case of metallic conductors, the resistance depends on the kind of material, the geometry and, the temperature. For uniform cross section,

$$R = \frac{\rho \cdot l}{A}$$ (E56)

where l is the length, A is the cross section, and ρ is the resistivity, resistance for unit length and unit cross section

The resistivity ρ is the resistance of a conductor of unit length and unit cross section.

$$[\rho] = \frac{\Omega\, mm^2}{m} \quad \text{or} \quad \frac{\Omega\, m^2}{m} = \Omega\, m$$

In the case of electrolytes, the reciprocals of R and ρ are used:

$$G = \frac{1}{R}$$ Conductance [Ω^{-1}=S, Siemens] (E57)

$$\kappa = \frac{1}{\rho}$$ Conductivity [$\Omega^{-1}\ m^{-1}$=Sm^{-1}] (E58)

$$\frac{1}{R} = \frac{1}{\rho} \cdot \frac{1}{\left(\frac{l}{A}\right)}$$

Since for electrolytes, it is not easy to determine l and A separately, we introduce the C cell constant, which is their ratio.

$$G = \frac{\kappa}{C} \quad \text{and} \quad \kappa = G \cdot C \qquad \text{(E59)}$$

The cell constant is determined experimentally; the conductance of a solution of known conductivity (usually KCl solution) is measured.

Several parameters determine the values of G and κ:

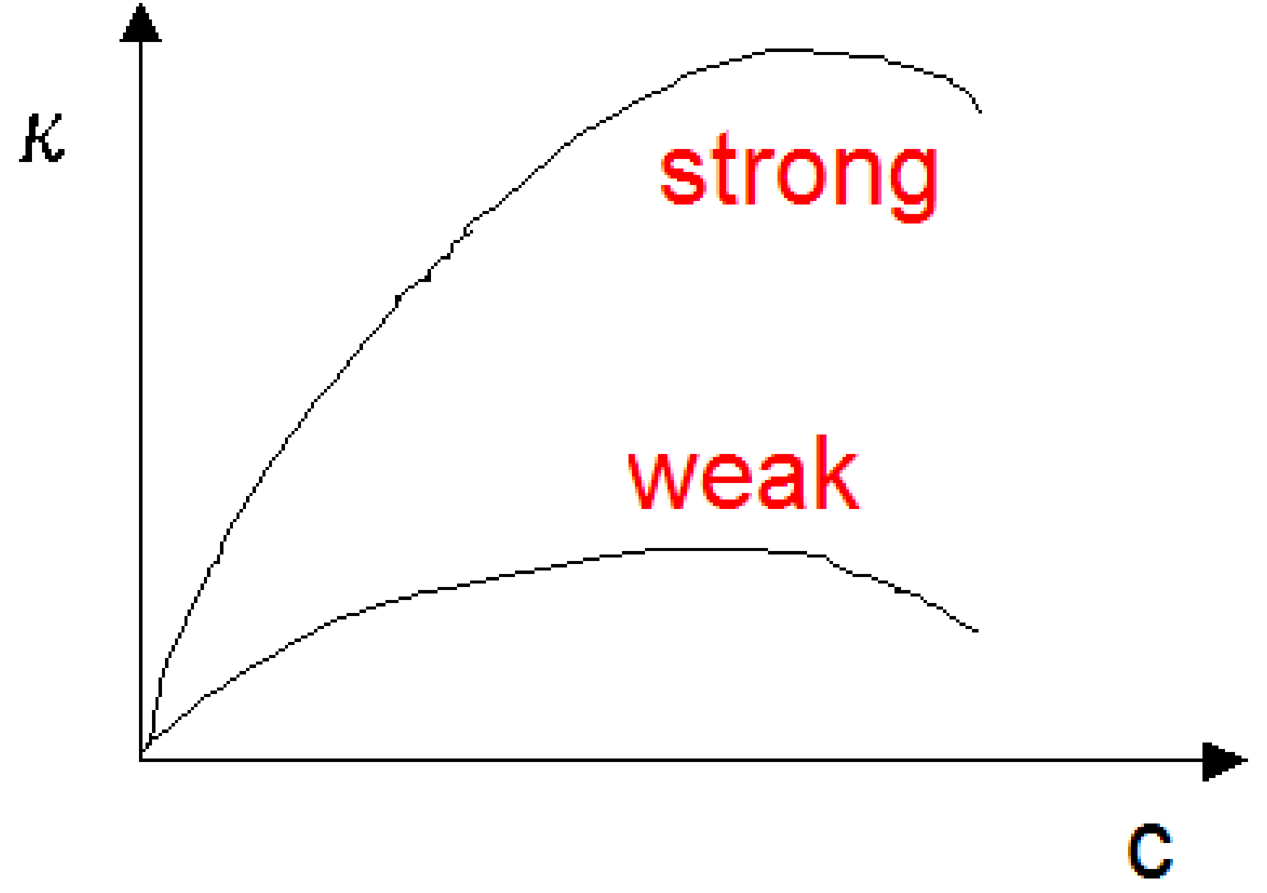
Conductance depends on

- *a) the type of electrolyte*
- *b) concentration*
- *c) temperature*
- *d) the geometry of the cell.*

Conductivity depends only on

- *a) the type of electrolyte*
- *b) concentration*
- *c) temperature*

*The concentration (**C**) depends also on the strength of the electrolyte. The curves often have maxima.*



What is the explanation for the decreasing conductivity at higher concentrations?

Weak electrolytes: *the degree of dissociation decreases. Fewer ions take part in carrying the electric charges.*

Strong electrolytes: *(the degree of dissociation is 100 %) the ions are too close and disturb one another in the migration.*

Temperature dependence of conductivity

In contrast to metals, the conductivity of electrolytes increases with increasing temperature (resistivity decreases).

Explanation: *The ions migrate with the solvent (water) molecules* attached to them. It is the viscosity of water (η) *that hinders the migration of the ions (for viscosity, see equation* T12 *and subsection "T4. Viscosity")*

T increases $\rightarrow$ η *decreases* $\rightarrow$ κ *increases*

Around room temperature, the viscosity of water decreases by 2-2.5 per cent per degree.

For the majority of electrolytes in aqueous solutions, the conductivity increases by 2-2.5 per cent per degree.

So one can assume for the first approximation that the temperature dependence of conductivity is independent of the type of the ion.

The conductivity of a solution is the sum of the conductivities of ions:

$$\kappa = \Sigma \kappa_{\text{ion}} \qquad \text{(E60)}$$

E12. Molar conductivity

Molar conductivity (Λ) is defined as the ratio of the conductivity and concentration:

$$\Lambda = \frac{\kappa}{c} = \kappa \cdot V$$

where V (m^3/mol) is the reciprocal of concentration, the molar volume.

(E61)

The unit of the molar conductivity is

$[\,\Lambda\,] = \Omega^{-1}\ m^{-1}\ m^{3}\ mol^{-1} = \Omega^{-1}\ m^{2}\ mol^{-1} = = Sm^{2}mol^{-1}$.

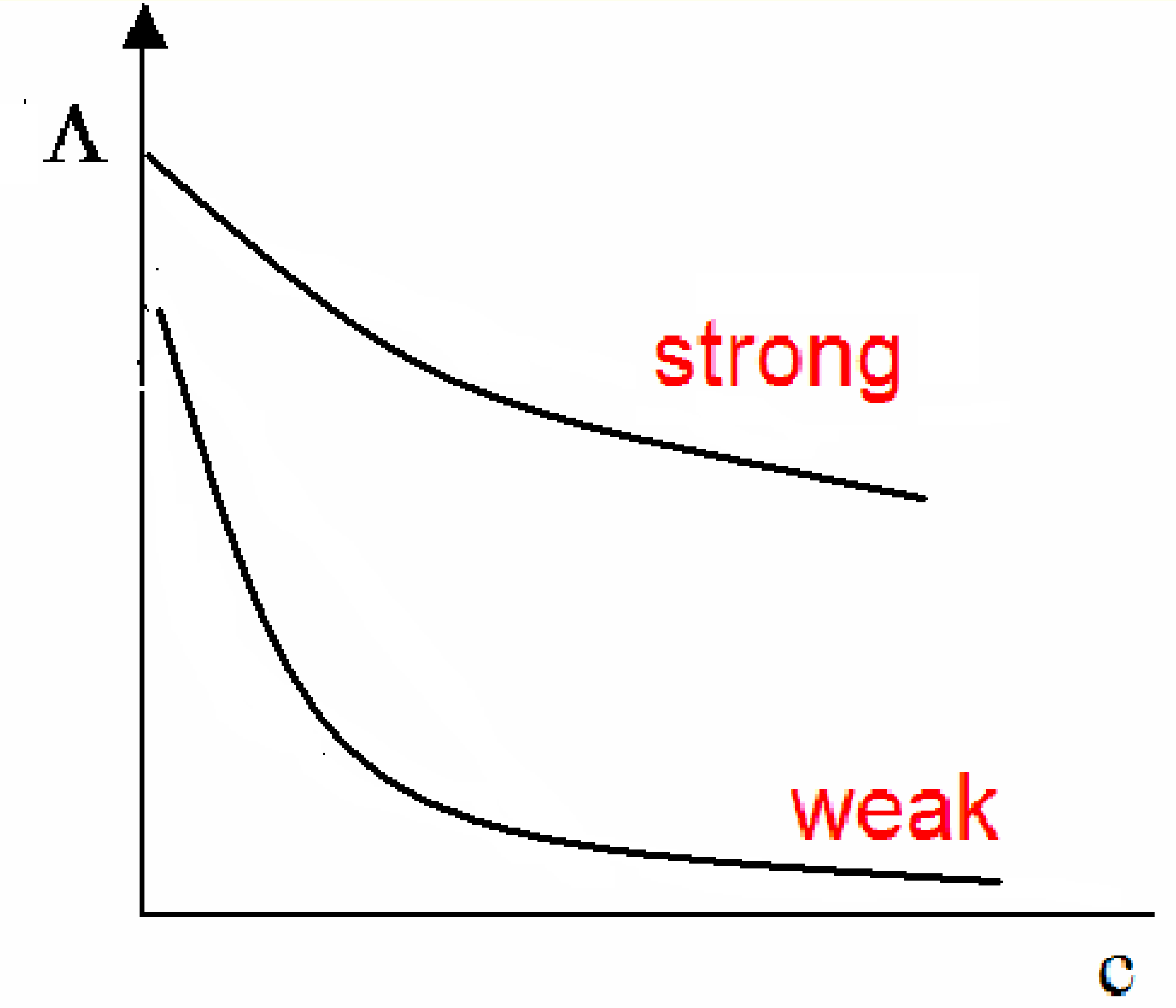
Siemens (S) in the unit of the electric conductivity $(1\mathrm{S} = 1\Omega^{-1})$.

Here, the concentration has to be expressed in $mol \cdot m^{-3}$ units.

Conductivity is the reciprocal of the measured resistance if electrodes of 1 m^2 area are placed at a distance of 1 m of each other. (Imagine a cube of 1 m edges filled with the electrolyte. Its two opposite faces are made of metal - these are the electrodes.)

Molar conductivity is the reciprocal of the measured resistance if the distance of two electrodes is 1 m, and a solution containing 1 mol solute is between them.

Molar conductivity increases with dilution and therefore decreases with concentration.

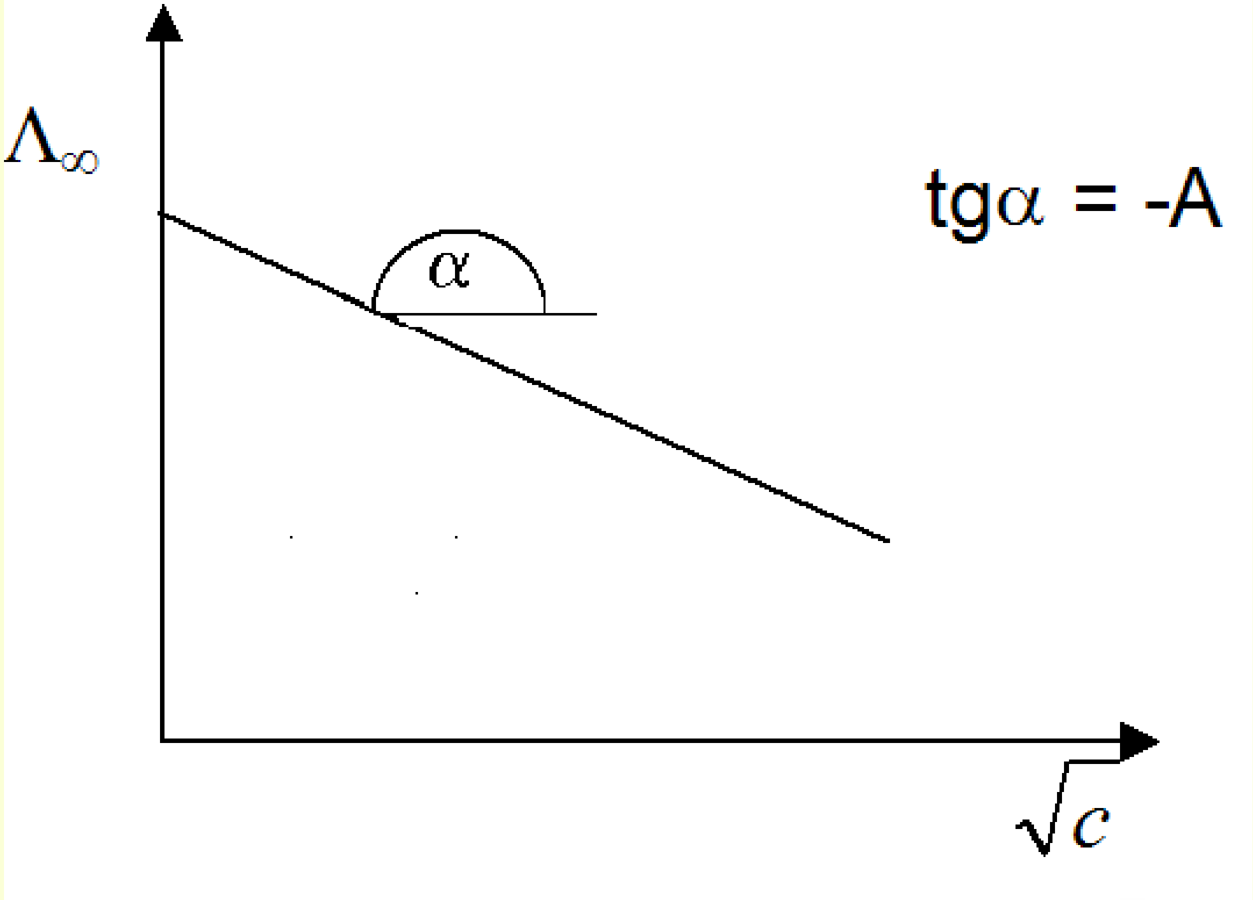


Weak electrolytes: The degree of dissociation increases with dilution, so the number of ions increases, too.

Strong electrolytes: The degree of dissociation is nearly 100 percent both in dilute and in concentrated solutions. At higher concentrations, the ions disturb one another in the migration.

Kohlrausch's law says that in the case of strong electrolytes, Λ is proportional to the square root of the concentration (next slide).

Strong electrolytes



$$\Lambda = \Lambda_\infty - A\sqrt{c}$$

(E62)

where Λ_∞ is the molar conductivity at infinite dilution.

The law of independent migration of ions

$$\Lambda_\infty = \nu_C \lambda_C + \nu_A \lambda_A \qquad \text{(E63)}$$

ν_C, ν_A: stoichiometric coefficients

λ_C, λ_A: molar conductivities of ions at infinitely diluted solution. They can be found in tables.

This law can be used as an approximation in dilute solutions, too (not only in infinitely dilute solutions).

Ostwald's dilution law

Consider the dissociation of a weak electrolyte producing singly charged cations and anions!

$$CA = C^+ + A^-$$

$c_0(1-\alpha)$ $c_0\cdot\alpha$ $c_0\cdot\alpha$

c_0 : *initial concentration*

α : *degree of dissociation*

$$K_c = \frac{\alpha^2 c_0}{1-\alpha}$$

(E1) *see section E2*

$\Lambda_\infty = \lambda_C + \lambda_A$

λ_C, λ_A: molar conductivity of ions at infinitely diluted solution.

$\Lambda = \alpha\ (\lambda_C + \lambda_A)$

$$\alpha = \frac{\Lambda}{\Lambda_\infty} \qquad \text{(E64)}$$

Substituting E64 into E1:

$$K_c = \frac{\alpha^2 \cdot c}{1-\alpha} = \frac{\dfrac{\Lambda^2}{\Lambda_\infty^2} \cdot c}{1 - \dfrac{\Lambda}{\Lambda_\infty}} = \frac{\dfrac{\Lambda^2 \cdot c}{\Lambda_\infty^2}}{\dfrac{\Lambda_\infty - \Lambda}{\Lambda_\infty}} = \frac{\Lambda^2 \cdot c}{\Lambda_\infty \left(\Lambda_\infty - \Lambda \right)}$$

The result is Ostwald's dilution law:

$$K_c = \frac{\Lambda^2 \cdot c}{\Lambda_\infty \left(\Lambda_\infty - \Lambda \right)} \qquad \text{(E65)}$$

Applications:

1) Determination of K_C from Λ and Λ_∞

2) Determination of Λ from K_C and Λ_∞

3) Determination of both Λ_∞ and K_C. To do this, Λ must be measured at various concentrations.