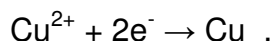# Electrochemistry

in biochemistry

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Processes on electrode

If a metallic electrode (e.g. made of copper) is immersed to a solution containing ions of the same metal (Cu^{2+} in given case) an oxidation-reduction reaction starts on the surface of the electrode:

$$Cu^{2+} + 2e^- \rightarrow Cu \quad .$$

In case of copper under common conditions, the equilibrium is on the right side (other metals, e.g. zinc, may behave in the opposite way). Thin layer of copper is formed on the surface of the electrode. The electrode also gets positively charged because free electrons from the electrode are spent in the reaction. On the other hand, the solution becomes negatively charged as cations Cu^{2+} are removed from it. The process stops after some time: electrostatic forces prevent further exchange of charged particles. Equilibrium characterised by certain electrical potential on the electrode it therefore established. Tendency of the electrode to accept or donate electrons can be expressed with *reducing potential* (E_{red}). In the special case that all components of the reaction are at activity of one or are in a state corresponding to standard situation (e.g. in solid state), the potential is called *standard reducing potential* (E_{red}^0).
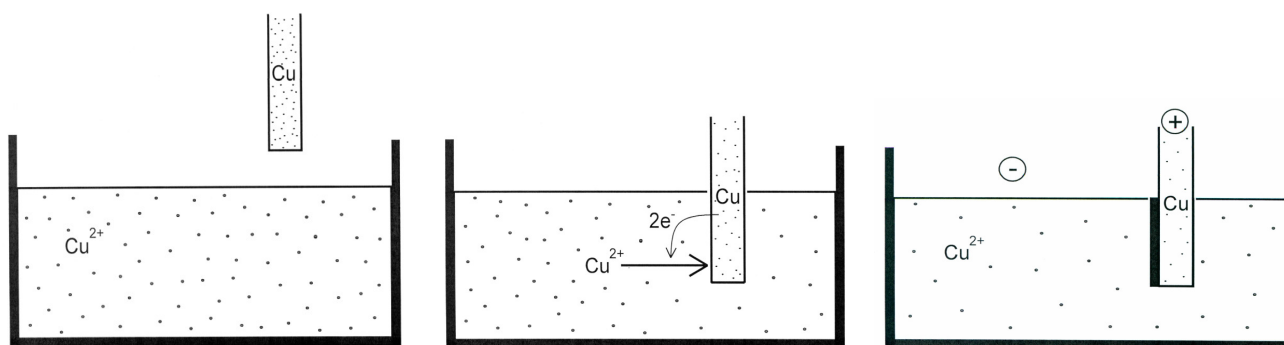

The potential formed on the electrode cannot be directly measured. It can be however compared with another electrode. In other words, a galvanic cell can be prepared using two electrodes, e.g. metals, and two electrolytes (in general, the cell is made of two half-cells). Daniel's cell may serve as an example: Cu immersed in solution of Cu^{2+} and Zn in solution of Zn^{2+}. Metals can be ordered according to their tendency to exist in oxidised or reduced form (so called Beketov's metal displacement series): K, Ca, Al, Zn, Fe, Ni, Pb, **H,** Bi, Cu, Hg, Ag, Au. Arbitrary, potential of standard hydrogen electrode[1] is considered zero. Metals with negative standard reducing potential (i.e. ones that easily donate electrons) are on left in the series (e.g. potassium tends to get oxidised to K^+). On the other hand, ions of metals placed in the series on right easily accept electrons (e.g. Ag^+ can be easily reduced to metallic silver) and their standard reducing potential is positive.

Daniel's cell mentioned above is schematically described Zn | Zn^{2+} ‖ Cu^{2+} | Cu (the more negative metal is on left). On the zinc electrode, reaction

$$Zn^{2+} + 2e^- \rightleftharpoons Zn,$$

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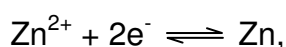
[1] Standard hydrogen electrode is an electrode made of platinum covered with platinum black, saturated with hydrogen gas under pressure of 101 325 Pa at temperature 273.15 K, immersed into solution with activity of hydrogen ions $a(H^+) = 1$. On the surface, the following reaction takes place:

$$\tfrac{1}{2}H_2 \Leftrightarrow H^+ + e^- .$$
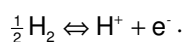
with equilibrium constant K_{Zn} takes place and is characterised by standard reducing potential $E_{red}^0(Zn)$. On the copper electrode, reaction

$$Cu^{2+} + 2e^- \rightleftharpoons Cu$$
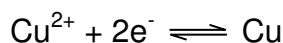
with equilibrial constant K_{Cu} and standard reducing potential $E_{red}^0(Cu)$ runs. In given case it applies that $K_{Cu} > K_{Zn}$, and $E_{red}^0(Cu) > E_{red}^0(Zn)$. In other words, copper is reduced and covers the electrode more readily than zinc. Thus, more electrons are spent from copper electrode than from zinc electrode. Copper electrode has therefore positive voltage with respect to zinc electrode and this voltage can be measured.
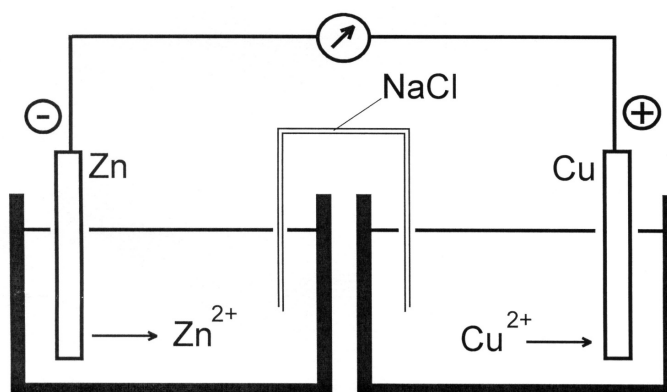
If both electrodes are electrically connected, "lacking" electrons are replenished to copper electrode from the zinc one and electric current runs. The whole process can be described as follows:

$$Zn \rightarrow Zn^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \rightarrow Cu$$
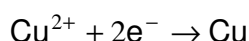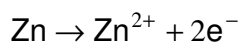
The current runs until either zinc electrode is completely dissolved or (more probably) all Cu^{2+} ions from electrolyte are spent, eventually the other electrolyte is completely saturated with Zn^{2+} – electrochemical cell is discharged.

Voltage on the cell equals to the difference of potentials of both electrodes. If the processes run spontaneously (it "produces" voltage) the cell is called galvanic cell ($\Delta G < 0$). If external power supply is connected to cell and processes are "forced" in this way the cell is called electrolytic ($\Delta G > 0$).

Described electrochemical processes are quite general and, in a similar way, can take place in various systems composed of different metals and ions.

Let's discuss the voltage between electrodes of an electrochemical cell. For simplicity, let's assume the cell is a system producing reversible electric work. This work must equal the difference in free enthalpy

$$\omega = -\Delta G .$$

Electric work is given by the charge Q and electric potential E in which the charge is transferred

$$\omega = -Q \cdot E .$$

With Faraday law, number of electrons n can be calculated from charge (F is Faraday constant 96 484,56 C·mol^{-1}).

$$Q = n \cdot F .$$

It follows

$$\Delta G = -\omega = Q \cdot E = -n \cdot F \cdot E .$$

We know from thermodynamics that

$$\Delta G = \Delta G^0 + RT \cdot \ln K$$

(R is universal gas constant = 8.314 41 J/mol/K).

After substitutions of $\Delta G = -nFE$ and $\Delta G° = -nFE°$, we get

$$E = E^0 - \frac{RT}{nF} \ln K \ .$$

It is useful to assume that the cell is composed of two half-cells (i.e. two electrodes in corresponding electrolytes). The previous equation can be written for each half-cell:

$$E_1 = E_1^0 - \frac{RT}{nF} \ln \frac{a_{1red}}{a_{1ox}}$$

and

$$E_2 = E_2^0 - \frac{RT}{nF} \ln \frac{a_{2red}}{a_{2ox}} \ .$$

Resulting voltage of the whole cell composed of the two half-cells is

$$U = E_1 - E_2 = E_1^0 - E_2^0 - \frac{RT}{nF} \ln \frac{a_{1red}}{a_{1ox}} + \frac{RT}{nF} \ln \frac{a_{2red}}{a_{2ox}} \ .$$

Note that electrode potential in general can be expressed as a sum of two terms. One of them, denoted with index ^{0}, depends only on temperature and properties of electrode itself. It corresponds to potential of the same electrode if activity of all components is unity (this means, it is the *standard reducing potential* mentioned above). This potential can be determined only in experiment – classically, comparing it with the potential of the *standard hydrogen electrode*. Standard reducing potentials of some electrodes are listed in the table 1.

Redox pair	E_{Red}^0 [V]	Redox pair	E_{Red}^0 [V]
Li^+/Li (s)	- 3.04	Co^{2+}/Co (s)	- 0.28
K^+/K (s)	-2.92	Ni^{2+}/Ni (s)	- 0.25
Na^+/Na (s)	- 2.71	Sn^{2+}/Sn (s)	- 0.14
Ca^{2+}/Ca (s)	-2.50	Pb^{2+}/Pb (s)	- 0.13
Al^{3+}/Al (s)	- 1.66	$2H^+$/H_2 (g)	+0.00
Mn^{2+}/Mn (s)	- 1.18	Sn^{4+}/Sn^{2+}	+0.15
Zn^{2+}/Zn (s)	- 0.76	Cu^{2+}/Cu (s)	+0.34
Cr^{3+}/Cr (s)	- 0.74	Ag^+/Ag (s)	+0.80
Fe^{2+}/Fe (s)	- 0.44	Cl_2/$2Cl^-$(g)	+1.36
Cd^{2+}/Cd (s)	- 0.40	Au^+/Au (s)	+1.50
Tl^+/Tl (s)	- 0.34		

The other term depends, besides temperature and number of exchanged electrons, on activites of components of the cell.

In general, voltage of a cell is the difference between potentials of the right (+, index 1) and left (-, index 2) electrode. If the standard reducing potential of copper electrode should be measured the copper half-cell would be connected as the positive pole against the standard hydrogen electrode (SHE). The resulting voltage would be

$$U = E_{red}^0 (Cu) - E_{red}^0 (SHE) = +0{,}34 - 0 = +0{,}34V$$

In case of Daniel's cell composed of standard copper and standard zinc electrode, the voltage is

$$U = E_{red}^0 (Cu) - E_{red}^0 (Zn) = +0{,}34 - (-0{,}76) = 1{,}1V$$

Potentiometry

Electrochemical cells can be used in analytical chemistry. Electrolyte of one of electrodes is usually directly the measured solution (*measuring, indicative electrode*). The other electrode (*referential* one) is constructed to have practically constant potential. The voltage between indicative and referential electrode typically depends only on concentration of one certain component of the measured solution; all the other dissolved compounds have almost no influence. It is said that the indicative electrode is *selective*. Potentiometry with ion selective electrodes (ISE) is employed for example in estimation of ions in blood (Na^+, K^+, Cl^-, Ca^{2+}).

pH-metry

The oldest and still the most widely used ion selective electrode is the glass electrode used for measuring of pH. Usually, both indicative and referential electrodes are built in one body. Many modifications of this electrode exist; hence, the principle will be demonstrated on the most general set-up.

With some simplification it can be said that glass membrane of the electrode (a bulb with very thin walls, blowed of a special glass) is permeable for H^+ but it cannot be crossed by other ions. The bulb is filled with an inner electrolyte in which a silver wire covered with AgCl is immersed. Depending on acidity of measured solution, H^+ concentration changes in the inner electrolyte. Cl^- ions cannot cross the glass membrane; to maintain electroneutrality of the solution, following reaction runs on the electrode:

$$AgCl + e^- \rightleftharpoons Ag^+ + Cl^-.$$
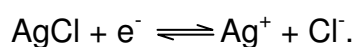
If the electrode is immersed to an acidic solution the excess of H^+ causes release of Cl^- from the paste of AgCl. Therefore, more electrons are spent from the silver wire and the electrode gets positive with respect to referential electrode. Analogically, in an alkaline solution is the electrode more negative.

The referential electrode for pH-metry is most frequently made of a silver wire covered with paste of AgCl too, it is however immersed in a solution of KCl of a precise concentration (i.e. a solution with constant Cl^- concentration, e.g. saturated, 1 mol·l^{-1}, 3 mol·l^{-1} etc.). Potential of the referential electrode is not influenced by H^+ concentration. The electrolyte of referential electrode is connected with the measured solution, usually by a bridge with fritted glass.

Description of pH-electrode above is much simplified. The processes on glass membrane are actually more complex. Ions, especially of hydrogen and alkaline metals (mostly sodium) are bound to relatively regular
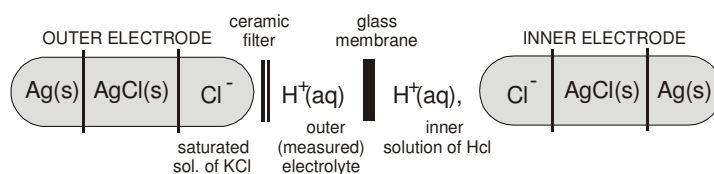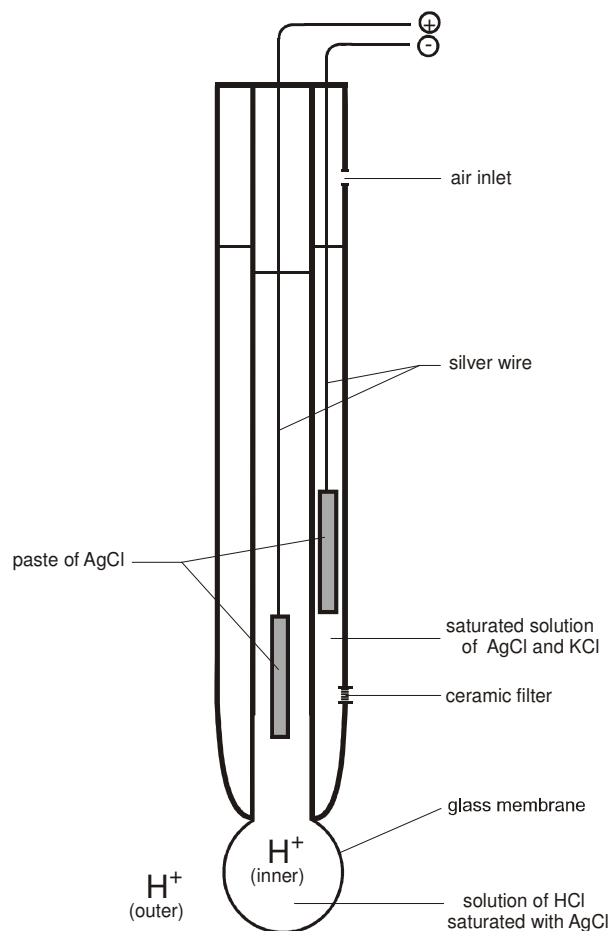
crystal lattice of silicate by electrostatic forces. In solution, the surface of glass is hydrated. In resulting solvated layer, hydrogen ions (but also e.g. sodium cations) are exchanged between glass and solution.

measured solution   inner electrolyte
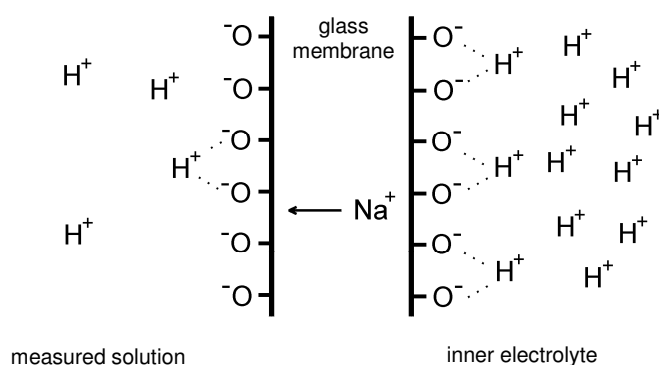
Glass electrode differs from most ISE – potential is not a result of redox processes but rather of exchange mechanisms between ions of glass and solution. For equilibrium on the glass membrane, it applies:

$$K_S = \frac{a_{H^+}^* \, a_{Na^+}}{a_{Na^+}^* \, a_{H_3O^+}}$$

where K_s is constant of selectivity. It shows how selectively the electrode reacts on one or another ion (* is phase of glass).

From the equations quoted above, we get for potential of indicative electrode (simplified):

$$E = const + \frac{RT}{F}\ln\left(a_{H_3O^+} + K_S a_{Na^+}\right) \doteq const + \frac{RT}{F}\ln a_{H_3O^+}$$

("const" corresponds not only to standard reducing potential – it involves type and composition of glass, construction of electrode, quality of its surface and inner filling, too). By algebraic derivations we get

$$E = const - 2.303 \times pH .$$

Hence, potential of indicative electrode is proportional to pH of measured solution. Under real conditions, voltage on the electrode grows a bit more slowly than assumed theoretically. To correct such deviations, pH-meters are routinely calibrated (for two or three pH values) and *slope* of calibration curve is automatically calculated. Measurement should be corrected for temperature at the same time. The ratio of real and theoretical slope is optimally about 98%. It decreases with detrition of the electrode or if it is dirty. If the slope drops bellow 95% of theoretical values the electrode should be cleaned and treated in a special procedure.
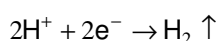
Having learned the function of glass electrode, errors of measurement can be readily explained. *Alkaline (positive) error* is caused by incomplete selectivity of glass electrode. If H^+ concentration is low, i.e. in alkaline solution, the role of Na^+ increases. Depending on the type of used glass and quality of the electrode, sodium error appears at pH values higher than 8 – 14. Measured pH is lower than the real one. Literally, in solution of pH about 10 and Na^+ concentration 0.1 mol·l^{-1} the error in pH is about 0.4. In strongly acidic environment (pH bellow 1 – 2) on the other hand, surface of the electrode is saturated with H^+ and the electrode loses its sensitivity to further increase of H^+ concentration. This is referred to as *acidic (negative) error.* It is also evident that exchange of ions on the electrode runs relatively slowly, especially when colloid solutions are measured. It leads to quite long response times of glass electrodes – typically about 15 to 60 s (glass electrode usually reacts faster in acidic solutions than in alkaline ones).

Other errors of measurement can be caused by properties of measured solutions and by the way in which the electrode is operated. If the electrode gets dry the surface layer of hydrated gel is disturbed; its reconstitution takes many hours. Some compounds can bind to the gel and change its behaviour (*"poisoning of electrode"*). Influence of mechanical impurities on the membrane is evident.
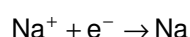
Electrolysis

It was assumed in the previous text that processes on the electrode are in equilibrium. Now, we will discuss what happens if voltage is connected to electrodes from external source (electrolytic cell, $\Delta G > 0$). The resulting processes are described by Farraday laws. We will use a system composed of two inert (platinum) electrodes in aqueous solution of sodium chloride.
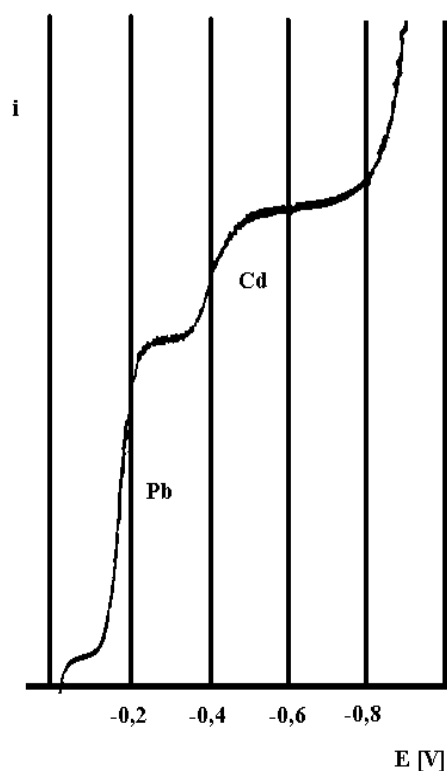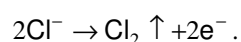
When voltage is connected, ions start moving in the solution according to their charge: cations Na^+ and H^+ migrate to the cathode and anions Cl^- and OH^- to the anode. In proximity of cathode the following reactions run:

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$

and (at higher voltage)

$$Na^+ + e^- \rightarrow Na$$
$$2Na + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2 \uparrow$$

In proximity of anode:

$$2Cl^- \rightarrow Cl_2 \uparrow + 2e^-.$$

Gaseous hydrogen and chlorine escape from the system (in this case, the process is irreversible). This example of electrolytic processes is well known: note the bubles released from electrodes during electrophoresis.

To start the electrolytic process, voltage on electrodes must exceed certain limit – so called *electrolytic voltage* (it corresponds to sum of standard electrode potentials for all reactions; it is about 1.4 V in the given example).

Polarography is based on this principle. Simply said, voltage between electrodes is subsequently increased. At the beginning, only little current flows through the electrolyte. When the electrolytic voltage is reached electrolytic processes on the surface of electrode start and the current rapidly increases. The reaction is very fast; thus, ions in proximity of the electrode are rapidly spent. New ions are transported to the electrode by diffusion which is quite slow. Therefore the intensity of current reaches a certain value. Plot of current intensity against voltage contains "steps", every step correspond to one redox pair.

Polarographic curve: dependence of current intensity on voltage. Solution of Pb^{2+} (0.39%) and Cd^{2+} (0.10%) ions. The value of half-wave potential (the middle of steep part) depends on properties of polarised compound. Intensity of limiting current (horizontal plateau) depends on concentration.

In fact, polarography is more complicated. To obtain reproducible results, intensity of current must depend on processes on only one electrode – the *polarised* one. The other, *non-polarised* electrode is similar to referential electrode in pH-metry or it is an electrode of very large surface area (e.g. mercury covering bottom of vessel). The surface of polarised electrode must be continuously renewed to eliminate products of the reaction. Mercury dropping from a capillary is one typical setup.

Today, polarography is widely replaced with voltametry. In voltametry, hanging drop of mercury usually is the indicative electrode, or solid electrodes renewed mechanically (by abrasion, wiping) or electrochemically are used. This technique allows accumulation of analysed compound

(e.g. by electrolysis at voltage higher than the electrolytic one) followed by its subsequent dissolution (so called "*stripping*"). Other techniques derived from classical polarography were developed. They differ in modulation of voltage and measuring of intensity of electric current. Pulse methods characterised by high sensitivity are the most important of them.
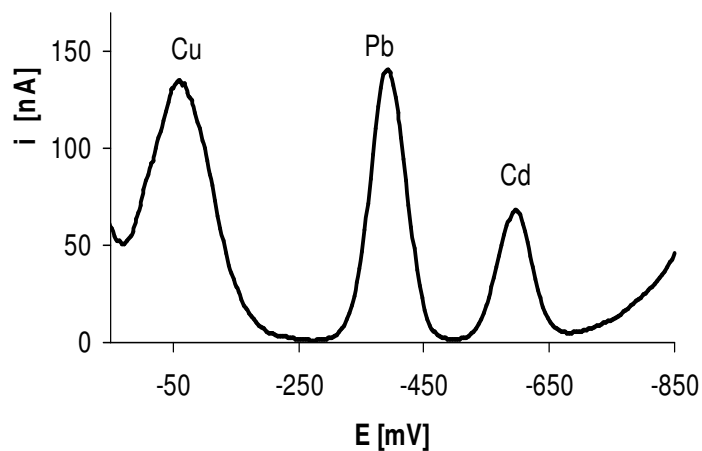
Polarography was invented by a Czech scientist, Jaroslav Heyrovský (1890 – 1967), in the year 1922. He was awarded with Nobel Prize in 1959.

Differential pulse voltamogram – estimation of Cu (26,4 mg/kg), Cd (3,6mg/kg) and Pb (5,1 mg/kg) in honey. The height of peaks (intensity of current) is proportional to concentration, positron determines the substance.