Electrode potential

When a metal object of any shape is embedded in an electrolyte solution (for example its salt), a so-called electrical double layer is formed on its surface. Metal ions show a tendency to be excreted into the electrolyte (eg $Cd \rightarrow Cd^{2+} + 2\ e^-$). Depending on the balance of the above reaction, it is also possible that the action takes place in the opposite direction. An example would be copper, where the surface is covered with a layer of reduced copper from copper ions from solution ($Cu^{2+} + 2\ e^- \rightarrow Cu$). When a cation leaves the electrode, it leaves behind its valence electrons and the electrode becomes negatively charged, thus attracting positively charged cations from the solution. An electric double layer is created here, formed on one side by a negatively charged electrode and on the other side by oppositely charged particles. In fact, the charges in the solution are surrounded by a layer of solvent (solvation shell), which partially "insulates" the direct contact of the ions. The resulting potential drop from the surface of the electrode to the volume part of the solution (electrolyte) is very high (~keV/m), but on a very thin layer. After a certain time, the reaction stops, because electrostatic forces prevent the further movement of charged particles, and an equilibrium is established, characterized by a certain electric potential at the electrode, in other words: an electric half-cell is formed. Each metal shows a greater or lesser effort to send its cations into solution, thus it has a certain "dissolving pressure". The more loosely bound the valence electrons are, the greater the tendency to emit their ions into the solution. Less noble metals with low values of ionization potentials have more pressure than noble metals. The so-called ``reduction potential *(E_{red}) characterizes the effort of the electrode to receive or give up electrons quantitatively. If all components electrode reactions have an activity equal to one or are in such a form to which the standard state is related (formation, modification), we speak of a* standard reduction potential *($E°_{red}$)*.

The size of the electrode potential, as already mentioned above, cannot be measured directly, but by comparison with another electrode, e.g. a so-called hydrogen electrode (platinum plate, coated with platinum black, saturated with hydrogen under a pressure of 101.325 kPa, immersed in a solution with a medium activity of hydrogen ions and (H^+) = 1), whose standard potential we consider equal to zero at all temperatures by definition. Using this electrode, the relative electrode potentials of some metals immersed in solutions of their own salts were determined and the so-called Beketov (N.N. Beketov 1827–1911) voltage series of metals was compiled: Li, Rb, K, Na, Ba, Sr, Ca, Mg, Al , Be, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, **H**, Sb, Bi, As, Cu, Hg, Ag, Pt, Au. Metals to the left of hydrogen have a negative potential, metals to the right of hydrogen have a positive potential. A few values of the common standard redox potentials of metals are given in the following Table I.a. Similar events also take place in various systems of reducible or oxidizable metals, non-metals or ions (e.g. the respiratory chain) (examples are given in Table I.b).

Table I.a: Standard redox potentials of selected metals

Redox couple	[In]	Redox Couple	[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	$2\ H^+$/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	Pt^+/Pt (s)	+1.19
Cd^{2+}/Cd (s)	−0.40	Cl_2/2 Cl^-(g)	+1.36
Tl^+/Tl (s)	−0.34	Au^+/Au (s)	+1.50

Table I.b: Standard redox potentials of selected redox couples

| Redox couple	[IN]
NAD^+ / NADH	−0.32
FMN or FAD / $FMNH_2$ or $FADH_2$	−0.20
Coenzyme Q10$_{ox}$ / Coenzyme Q10$_{red}$	+0.06
Cytochrome b$_{ox}$ / Cytochrome b$_{red}$	+0.12
Cytochrome c$_{ox}$ / Cytochrome c$_{red}$	+0.22
Cytochrome a$_{ox}$ / Cytochrome a$_{red}$	+0.29
O_2 / OH^-	+0.82

The value of the resulting electric voltage is very important when assessing the behavior of metals when they are in conductive contact with each other (a well-known example is the contact of an "aluminum fork with an amalgam filling of a tooth). Each metal from this series displaces from the solution all metals following, all metals to the left before hydrogen, it is displaced from the solutions.For example, an iron wire immersed in a solution of copper sulfate is covered almost immediately with displaced copper, i.e. the reaction takes place:

$$Fe + CuSO_4 \rightarrow Cu + FeSO_4$$

Zinc reduces hydrogen cations from hydrochloric acid to hydrogen gas and oxidizes itself to zinc ions:

$$Zn + HCl \rightarrow H_2 + ZnCl_2$$

Resp.

$$(Zn + H^+ + Cl^- \rightarrow H_2 \uparrow + Zn^{2+} + 2\ Cl^-)$$
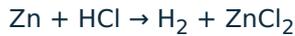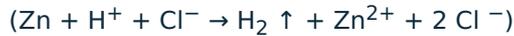
Caution: In acids that show oxidizing abilities, the events are considerably more complicated

eg: $Cu + 4\ HNO_3$ (conc.) $\rightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O$;

$Cu + 2\ H_2SO_4$ (conc.) $\rightarrow CuSO_4 + SO_2 + 2\ H_2O$;
$3\ Cu + 8\ HNO_3$ (dil.)$\rightarrow 3\ Cu(NO_3)_2 + 2\ NO + 4\ H_2O$.
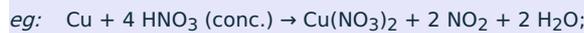
The more negative the potential of the metal, the more easily it oxidizes and has good reducing properties. Differences in metal voltage during electrochemical corrosion are very important.

The voltage of the whole cell formed by two half-cells (index (1) and index (2)) is defined as follows (Equation 8):

$$U = E_1 - E_2 = E_1^0 - E_2^0 - \frac{RT}{nF} ln \frac{a_1 red}{a_1 ox} + \frac{RT}{nF} ln \frac{a_2 red}{a_2 ox} \tag{8}$$

where U denotes electric voltage, E potential, R universal gas constant ($8.314\ J \cdot mol^{-1} \cdot K^{-1}$), T absolute temperature [K], F Faraday constant ($96\ 485\ C \cdot mol^{-1}$), n number of electrons, and activity (product of activity coefficient and molar concentration), indices 1, 2 indicate individual half cells.

It can therefore be seen that the electrode potential according to equation 8 can generally be expressed as the sum of two terms. The first of them is the *standard electrode potential*, which is denoted by the index 0, and is dependent only on the temperature and the properties of the electrode. It corresponds to the potential that the cell would have with the uniform activity of all components (it cannot be calculated, only determined by measurement and comparison with a standard hydrogen electrode). The second term depends on the temperature, the number of electrons and the activities of the components of the system.

A cell on which events take place spontaneously ("produces" voltage) is called a "galvanic" cell ($\Delta G<0$). If we apply a voltage to it and the events are "forced" by the applied voltage ($\Delta G>0$), we call such a cell '*electrolytic*. In other words, by applying voltage, a self-running event can be reversed.

Voltage measurement is dealt with by **potentiometry'** *realized using a* measuring (*indicative*) electrode. As mentioned above, to measure the voltage you need to have a second electrode available, whose potential is independent of the concentration of the measured substance - the so-called *reference* electrode, i.e. its potential is "almost" constant (this is not the case with so-called bipotentiometric measurements). With a suitable design, it can be achieved that the registered voltage between the indicator and reference electrode corresponds to the concentration of one specific component of the analyzed solution, while the other components have practically no influence (the measuring electrode is so-called selective). In clinical biochemistry, potentiometric measurements with ion-selective electrodes (ISE) are used, for example, to determine the concentration of some ions in the blood (Na^+, K^+, Cl^-, Ca^{2+}).

The most commonly used reference electrode is a silver wire covered with a layer of insoluble silver salt (silver chloride), immersed in a solution of soluble chloride salt (potassium chloride), i.e. a system: metal + insoluble metal salt (common cation with the metal) + soluble salt (common anion with insoluble salt). The concentration of the soluble salt must be constant for the selected measurement, but for different measurements it can be used to "set" the selected produced potential (e.g. saturated, $1\ mol \cdot l^{-1}$, $3\ mol \cdot l^{-1}$ etc. KCl solution). The potential of this reference electrode is not affected by the concentration of H^+ ions. The electrolyte is conductively connected to the measured solution by means of a bridge with a ceramic partition (frit), which prevents the exchange of KCl with the surrounding solution.