Electrochemical Equilibrium

Chemical reactions in which the oxidation numbers of elements change are called ***redox reactions***. During oxidation, the oxidation number increases, during reduction, it decreases. These changes usually involve the transfer of electrons from one atom or molecule to another.

If we immerse a zinc rod in a solution of zinc sulfate, a reaction is triggered in which the metallic zinc **gives up two electrons** *and changes to* Zn^{2+} *until equilibrium is restored. The process leads to the accumulation of electrical charge, which we refer to as electrode potential* (E). This can be measured indirectly, as a difference to another potential. We call the potential difference **voltage** and measure it in volts (V).

To overcome the problem of measuring absolute potential, chemists devised a little trick: they chose one of the electrodes and decided that its potential was considered zero. It is a so-called standard hydrogen electrode. Even the electrode potential is actually **a potential difference** (and is sometimes referred to as ΔE).

The amount of electric charge (also the value of the electrode potential) is related to the equilibrium constant of the reaction. Recall that ΔG corresponds to the maximum amount of work the system can do. In an electric field, work is done by moving charge across **a potential difference** (much like mechanical work is done by moving matter in a gravitational field). The relationship between ΔG and E is then expressed by the equation:

$$\Delta G = -n \cdot F \cdot E \tag{8}$$

where n is the number of electrons transferred in the redox reaction, F is Faraday's constant (equal to the charge of 1 mole of electrons, approximately $9.648\,530\,9 \cdot 10^4 \; C \cdot mol^{-1}$), E denotes the total potential difference between the two half-reactions.

For the standard electrode potential, we can derive the relation similarly:

$$\Delta E^0 = \frac{R \cdot T}{n \cdot F} \cdot lnK \tag{9}$$

Outside of standard conditions, this so-called Nernst equation (9) has the form:

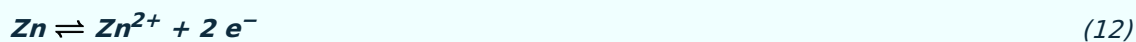$$E = \frac{R \cdot T}{n \cdot F} \cdot ln\frac{[reducedé]}{[oxidizedé]} \tag{10}$$

How can these equations be used to predict whether or not a certain redox reaction will occur? The decisive value is again represented by the ΔG value of the respective reaction. It can be calculated from equation (8).

Consider the reaction:

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu \tag{11}$$
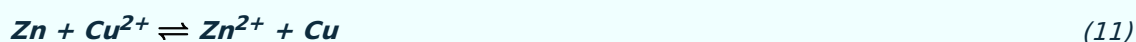
The two half-reactions that take place are:

$$Zn \rightleftharpoons Zn^{2+} + 2\,e^- \tag{12}$$

$$Cu^{2+} + 2\,e^- \rightleftharpoons Cu \tag{13}$$

*Zinc is **oxidized** while copper is **reduced**. Standard electrode potentials are usually given in tables as reductions, so the E^0 value for zinc oxidation must be multiplied by −1. Both half-reactions together form **the total reaction potential**. In this case, $E^0 Zn/Zn^{2+}$ = +0.76 V (after sign reversal) and $E^0 Cu^{2+}/Cu$ = +0.34 V. The total potential difference is therefore +1.1 V. For reaction (11) occurring under standard conditions, the total potential difference is positive, which means that ΔG (in our case $ΔG^0$) is negative and the reaction will proceed spontaneously. Under non-standard conditions, we must use the full Nernst equation for both half-reactions.*