

with $a_i = \text{activity}^4$ of the reacting components i (closely related to the concentration),
 $j_i = \text{number of equivalents of this component that take part in the reaction,}$
 $R = \text{molar gas constant for an ideal gas } (R = 8.3413 \text{ J/K/mole}),$
 $\Delta G_S = \text{standard value when all activities are unity.}$

From these equations, the Nernst equation describing the concentration dependence of the equilibrium voltage can be derived, where $E_{0,S}$ is the equilibrium potential in standard conditions.

$$E_0 = E_{0,S} + \frac{R \cdot T}{n \cdot F} \cdot \sum \ln[(a_i)^{j_i}]$$

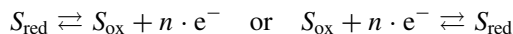
The temperature coefficient of the equilibrium cell potential can be derived from the following thermodynamic relation.

$$\frac{dE_0}{dT} = -\frac{\Delta S}{n \cdot F}$$

Thermodynamic calculations are always based on a complete cell, and the derived voltage refers to the potential difference between two electrodes. The potential difference between the electrode and the electrolyte, the “absolute potential”, cannot be determined. The name electrode potential always refers to a potential difference measured with the aid of a reference electrode. To get a basis for the electrode-potential scale, the zero point was arbitrarily equated with the potential of the standard hydrogen electrode (SHE⁵).

18.2.1.2 Electrode kinetics at current flow

When current flows through a cell, the reaction must take place at a corresponding rate. For each delivered ampere-second, a corresponding number of electron exchanges must have occurred. This means that at the electrodes the elementary processes



must take place $6.42 \cdot 10^{18}/n$ times (reciprocal of one elemental charge). To achieve this current flow, additional forces are required, which intensify the electron and ion flow in the required direction. These additional forces find their expression in deviations from the equilibrium data, which means irreversible energy loss.

⁴ Activity described the “effective concentration”. Thermodynamic rules are derived for dilute solutions. The activity is equivalent to the concentration in very dilute solutions, but the activity can be different at higher concentrations as interactions among the ions in the solution need to be taken into account.

⁵ The standard hydrogen electrode means a hydrogen electrode immersed in acidic solution with H^+ ion activity of 1 mole/dm³ and H_2 pressure of 1 atm. The specification of the electrolyte concentration is required because the potential of the hydrogen electrode depends on the H^+ ion concentration and is shifted by -0.0592 V when the H^+ concentration is reduced by one decade. The potential of the standard hydrogen electrode at 25°C is synonymous with the zero point of the potential scale. The temperature coefficient of the standard hydrogen electrode is $+0.871 \text{ mV/K}$.