

The laws of thermodynamics generally apply to the equilibrium, which means that all reactions are balanced. In the electrochemical cell, these data can only be measured when no current flows through the cell or the electrodes. On account of this balance, the thermodynamic parameters do not depend on the reaction path; they depend only on the difference between the final and initial components of the electrochemical reaction.

Because of the equilibrium conditions, the laws of thermodynamics describe the possible upper limit of the performance data. As soon as the current flows through the cell, energy losses occur due to kinetic restrictions and ohmic resistance.

The energy exchange, connected with electrochemical reactions, is described by the following thermodynamic parameters. As far as these parameters concern chemical or electrochemical reactions, they actually describe the difference between the parameters before the reaction started and after it was completed. Therefore, they are expressed as the difference between the initial and the final state of the reaction.

- *Enthalpy of the reaction* ΔH , which describes the amount of energy released or absorbed. It is derived from the energy content of the chemical compounds H .
- *Free enthalpy of the reaction* ΔG (also called the Gibbs free energy), which represents the (maximum) amount of chemical energy that can be converted into electrical energy, and vice versa.
- *Entropy* ΔS , which characterises the energy loss or gain connected with the chemical or electrochemical process. The product $T\Delta S$ represents the heat exchange with the surroundings when the process occurs reversibly. This is synonymous with minimal heat loss or gain of the system, which is true only when no current flows through the battery.

T is the absolute temperature. The most important relation among these parameters is given by the following formulae:

$$\Delta G = \Delta H - T \cdot \Delta S$$

As ΔG describes the amount of energy that can be converted into electrical energy, a simple relation between the Gibbs free energy and the equilibrium voltage³ E_0 of the cell can be derived.

$$\Delta G = -n \cdot F \cdot E_0$$

where n is the number of exchanges of electronic charges, F is the Faraday constant (96485 As) and nFE_0 describes the generated electrical energy.

Thermodynamic quantities like ΔH and ΔG depend on the concentration of the reacting components as far as these are dissolved according to the relation

$$\Delta G = \Delta G_S + R \cdot T \cdot \sum_i \ln[(a_i)^{j_i}]$$

³ Occasionally, the equilibrium voltage is called the open-circuit voltage. However, strictly speaking this term only means a voltage without external current flow, and may concern a mixed potential as well. On account of secondary reactions, the rest potential in batteries are usually mixed potentials, but this is not strictly observed in practical languages.