

Electrode events/Electrochemical potential

Let's deal with how big the voltage will be between the electrodes of an electrochemical cell. For simplicity, let's consider the cell as a system producing reversible electrical work. This work must be equal to the change in free enthalpy

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

The electrical work is given by the magnitude of the charge Q and the electric potential E through which this charge is transferred

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

Using Faraday's law, we can convert the charge into the number of electrons n (F is Faraday's constant 96,484.56 C·mol⁻¹).

$$Q = n \cdot F.$$

After substitution we get

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

We know from thermodynamics that

$$\Delta G = \Delta G^0 + R \cdot T \ln K$$

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

If we substitute $\Delta G = -n \cdot F \cdot E$ and $\Delta G^0 = -n \cdot F \cdot E^0$, we get

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

For practical reasons, it is useful to consider an electrochemical cell as a system composed of two half-cells (ie two electrodes in the corresponding electrolytes). We can break down the above equation for each half-term:

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

and

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

The resulting voltage between the terminals of the entire cell composed of these half-cells will be

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

Note that we can generally express the electrode potential as the sum of two terms. One, which we marked with the index ⁰, is dependent only on the temperature and the properties of the electrode. It corresponds to the potential that the cell would have if the activity of all components were equal to one (ie, it is the *standard reduction potential* mentioned above). The value of this term can only be determined experimentally - classically by comparison with the aforementioned *standard hydrogen electrode*. The standard reduction potentials of some electrodes are in the table:

Standard reduction potentials of selected electrodes

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

The second term, in addition to the temperature and the number of exchanged electrons, also depends on the activities of the individual components of the cell. The cell voltage is generally given by the difference in electrode potentials of the right (+, index ₁) and left (−, index ₂) electrodes. If the standard reduction potential of a copper electrode were to be measured, the copper half-cell would have to be connected as the positive pole of the cell against the standard hydrogen electrode (SVE). Its voltage would be

$$U = E^0_{\text{red}}(\text{Cu}) - E^0_{\text{red}}(\text{SVE}) = +0.34 - 0 = +0.34\text{V}$$

In the case of a Daniel cell composed of standard copper and standard zinc electrodes, the cell voltage is

$$U = E^0_{\text{red}}(\text{Cu}) - E^0_{\text{red}}(\text{Zn}) = +0.34 - (-0.76) = +1.1\text{V}$$

Links

References