3.4 Electrochemical equilibrium

In this section we will introduce the electrochemical potential into the Gibbs potential and discuss approaches to analyze electrochemical reactions by measurement of electrical potentials, or to change the equilibrium condition (e.g. equilibrium concentration of products and educts) by applying electrical potentials. These two aspects of electrochemical cells manifest themselves in the classification of cells as shown in Fig. 3.2. An electrochemical cell allowing for spontaneous reactions is called *galvanic cell* (cf. Fig. 3.2 a)) while a cell showing reactions due to the application of an external potential is called an *electrolytic cell* (cf. Fig. 3.2 b)).

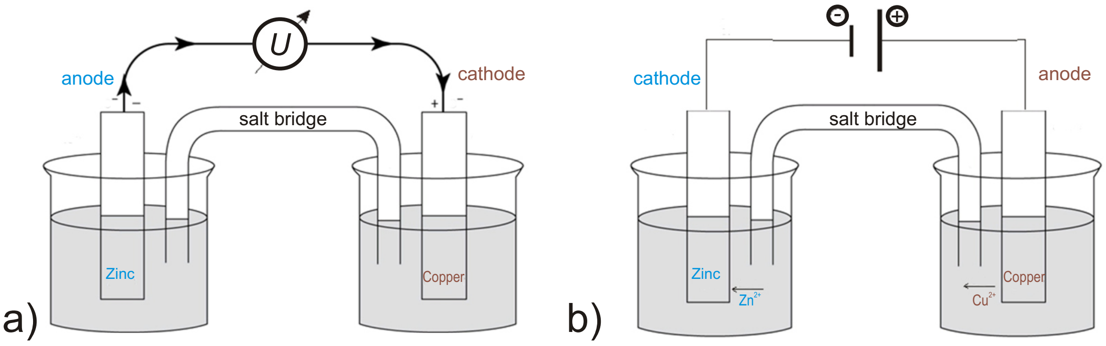

Figure 3.2: Daniel's cell as an example for an electrochemical cell. a) as galvanic cell (using the spontaneous process); b) as electrolytic cell driving reactions by external current, resp. by applying an external potential.

The Daniel's cell shown in Fig. 3.2 is an example for a heterogeneous cell with two different electrolytes in contact to metal electrodes connected by a salt bridge to close the electrical circuit. We will discuss the standard notation of electrochemical cells using this example:

$$\mathrm{Zn}(s)|\mathrm{Zn}^{2+}(aq)|\mathrm{Cu}^{2+}(aq)|\mathrm{Cu}(s) \quad , \tag{3.19}$$

where the vertical lines indicate phase boundaries. To complete the list of definitions:

- Oxidation: release of electrons (occurring at the anode) $\mathrm{Zn}(s) \rightarrow \mathrm{Zn}^{2+}(aq) + 2e^-$
- Reduction: uptake of electrons (occurring at the cathode) $\mathrm{Cu}^{2+}(aq) + 2e^- \rightarrow \mathrm{Cu}(s)$
- Overall reaction: $\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \rightleftarrows \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$

A further very important example of an electrochemical cell is the lead accumulator:

$$\mathrm{Pb} + \mathrm{PbO_2} + 2\mathrm{H_2SO_4} \rightleftarrows 2\mathrm{PbSO_4} + 2\mathrm{H_2O} \quad . \tag{3.20}$$

This is a typical example of a so called "comproportionation" reaction where one element (here Pb) just changes it's oxidation number.
Just as a reminder: Since oxidation is the removal of electrons from a species and reduction is the addition of electrons to species, a redox reaction is a couple Ox/Red of two half-reactions which can be written as

$$\mathrm{Ox} + \nu e^- \rightarrow \mathrm{Red} \quad . \tag{3.21}$$

Using the definition in Eq. (3.5) and introducing the additional electrical work for the electron transport from one electrode to the other we find

$$dG_{p,T} = \Delta_r G d\xi = dw_e = -\nu e N_A \Delta\Phi d\xi = -\nu F \Delta\Phi d\xi \quad . \tag{3.22}$$

The right hand side is just the work, related to the transport of an amount of electrons $\nu d\xi$ (in mole) with a charge per mole of $-eN_A := F = 9.64853 \times 10^4\ C$ (F: Faraday constant) through a potential difference $\Delta\Phi$.
We define the electromotive force E_{cell} by

$$E_{cell} = \lim_{I \to 0} \Delta\Phi = \Phi_{right} - \Phi_{left}; \tag{3.23}$$

here we have to take the limit of negligible current I to ensure reversibility (i.e. equilibrium condition). The right hand side of this equation just indicates that electrical potentials add up and it needs for an additional definition

for the zero of an electrochemical potential (see below) to define the electrical potential $\Phi_{left/right}$ of the left- or right-hand side of the cell.
Combining Eq. (3.22) and Eq. (3.23) we get

$$\Delta_r G = -\nu F E_{cell} \quad . \tag{3.24}$$

Nearly all relevant results related to electrochemical cells are extracted from this equation. Before discussing the consequences for the activities of the chemical species in terms of the famous Nernst equation we will exploit Eq. (3.24) to see how easily several thermodynamic (electro-) chemical parameter can be found from the measurement of the electromotive force, i.e. from the extremely accurate and easy measurement of electrical potential differences. By definition

$$\Delta_r S = -\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = \nu F \left(\frac{\partial E_{cell}}{\partial T}\right)_p \quad . \tag{3.25}$$

Correspondingly we find

$$\Delta_r H = \Delta_r G + T \Delta_r S = -\nu F \left[E_{cell} - T \left(\frac{\partial E_{cell}}{\partial T}\right)_p \right] \text{ , and } \quad \Delta_r V = -\left(\frac{\partial \Delta_r G}{\partial p}\right)_T = -\nu F \left(\frac{\partial E_{cell}}{\partial p}\right)_T \quad . \tag{3.26}$$

For standard pressure condition, i.e. $p^0 = p_{tot}$, we get $\frac{p_j}{p^0} = x_j$ which in it's generalized form reads $\frac{p_j}{p^0} = a_j$. Including this result in Eq. (3.7) and combining with Eq. (3.24) we find

$$E_{cell} = -\frac{\Delta_r G}{\nu F} = -\frac{\Delta_r G^0}{\nu F} - \frac{RT}{\nu F} \ln \prod \frac{a_{pr}^{|\nu^{prod}|}}{a_{ed}^{|\nu^{ed}|}} \quad \text{, and defining} \quad E^0 = -\frac{\Delta_r G^0}{\nu F} \quad , \tag{3.27}$$

we get the Nernst equation

$$E_{cell} = E^0 - \frac{RT}{\nu F} \ln \prod \frac{a_{pr}^{|\nu^{prod}|}}{a_{ed}^{|\nu^{ed}|}} \quad . \tag{3.28}$$

Since the actual potential of a half cell depends on the concentration of the redox couple the intrinsic properties are defined by the standard potentials E^0. As already mentioned before and shown in the following table it needs for a definition of one specially selected electrode which is the *standard hydrogen electrode* (SHE) as a reference for all other cell potentials.

Electrode	Reaction	E^0/ V
$Li^+\|Li$	$Li^+ + e^- \leftrightarrows Li$	-3.045
$Na^+\|Na$	$Na^+ + e^- \leftrightarrows Na$	-2.714
$OH^-\|H_2\|Pt$	$H_2O + e^- \leftrightarrows 1/2\ H_2 + OH^-$	-0.828
$Zn^{2+}\|Zn$	$1/2\ Zn^{2+} + e^- \leftrightarrows 1/2\ Zn$	-0.763
$Cd^{2+}\|Cd$	$1/2\ Cd^{2+} + e^- \leftrightarrows 1/2\ Cd$	-0.403
$Pb^{2+}\|Pb$	$1/2\ Pb^{2+} + e^- \leftrightarrows 1/2\ Pb$	-0.126
$H^+\|H_2\|Pt$	$H^+ + e^- \leftrightarrows 1/2\ H_2$	0
$Cl^-\|AgCl\|Ag$	$AgCl + e^- \leftrightarrows 1/2\ Ag + Cl^-$	0.222
$Cu^{2+}\|Cu$	$1/2\ Cu^{2+} + e^- \leftrightarrows 1/2\ Cu$	0.337
$OH^-\|O_2\|Pt$	$1/2\ O_2 + H_2O + e^- \leftrightarrows 2OH^-$	0.401
$Fe^{3+}\|F^{2+}\|Pt$	$Fe^{3+} + e^- \leftrightarrows Fe^{2+}$	0.771
$Hg^{2+}\|Hg$	$1/2\ Hg^{2+} + e^- \leftrightarrows 1/2\ Hg$	0.789
$H^+\|O_2\|Pt$	$2H^+ + 1/2\ O_2 + 2e^- \leftrightarrows H_2O$	1.229
$Au^{2+}\|Au$	$1/2\ Au^{2+} + e^- \leftrightarrows 1/2\ Au$	1.500

This table of increasing standard cell potentials defines the electrochemical series (including of course more elements than shown in the list):

Li, K, Ca, Na, Mg, ...

For the example of the silver chloride electrode we will discuss, how to extract E^0_{cell} from measurements of cell potentials E_{cell} for various molarities b of the chlorine concentration. For this example the Nernst equation is

$$E_{cell} = E^0(\mathrm{AgCl/Ag, Cl^-}) - \frac{RT}{F} \ln \frac{a_{\mathrm{H}^+} a_{\mathrm{Cl}^-}}{a_{\mathrm{H}_2}^{1/2}} \quad . \tag{3.29}$$

Since the hydrogen concentration is high and nearly not influenced by the electrochemical reaction we set $a_{\mathrm{H}_2} = 1$ and for simplicity write the standard potential of the $\mathrm{AgCl/Ag, Cl^-}$ electrode as E^0; so

$$E_{cell} = E^0 - \frac{RT}{F} \ln a_{\mathrm{H}^+} a_{\mathrm{Cl}^-} \quad . \tag{3.30}$$

As we learned in section (2.3) for ionic solutions even at very low concentration the activity coefficients do not reach 1. The activities can be described as $a_{\mathrm{H}^+} = \gamma_\pm b/b^0$ and $a_{\mathrm{Cl}^-} = \gamma_\pm b/b^0$ leading to

$$E_{cell} = E^0 - \frac{RT}{F} \ln(b/b^0)^2 - \frac{RT}{F} \ln \gamma_\pm^2 \quad , \tag{3.31}$$

which rearranges to

$$E_{cell} + \frac{2RT}{F} \ln(b/b^0) = E^0 - \frac{2RT}{F} \ln \gamma_\pm \quad . \tag{3.32}$$

From Eq. (2.17) we know that $\ln \gamma_\pm \propto -(b/b^0)^{1/2}$ which with an appropriate constant C allows to write Eq. (3.32) as

$$E_{cell} + \frac{2RT}{F} \ln(b/b^0) = E^0 + C(b/b^0)^{1/2} \quad . \tag{3.33}$$

Drawing the left hand side of Eq. (3.33) vs. $(b/b^0)^{1/2}$ (as shown in Fig. 3.3) a straight line is found and the extrapolation to $(b/b^0)^{1/2} = 0$ gives the standard cell potential E^0.

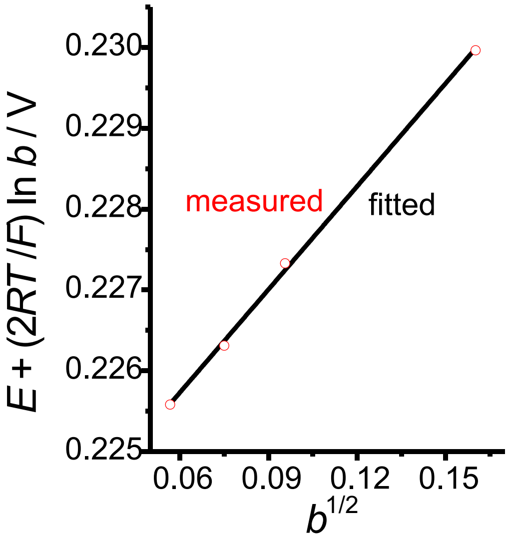

Figure 3.3: Plot and extrapolation used for the experimental measurement of standard cell potentials.

Once having found accurate values for E^0 Eq. (3.31) can be rearranged as

$$\ln \gamma_\pm = \frac{E^0 - E_{cell}}{2RT/F} - \ln(b/b^0) \quad , \tag{3.34}$$

i.e. mean activity constants can be extracted from cell potential and molarity measurements.

Electrochemical reactions dominate a large field of application including production (e.g. amalgam process for chlorine gas formation, galvanic purification of copper,...), energy storage (batteries), and characterization of (bio-) chemical reactions. One decisive aspect is related to the decomposition of water which according to the above table needs a potential of 1.23 V (the so called hydrogen over potential). For any electrochemical reaction which needs higher potentials than this over potential water can not be used as a solvent (it will be decomposed!). Batteries typically have voltages around 1.5 V; Li-ion batteries even voltages around 3.5 V. So a large part of battery science and technology just deals with the optimization and development of water free high voltage stable and "good enough" ion conducting electrolytes.

The standard hydrogen electrode (SHE) is an example of a gas - noble metal electrode. As shown in the principle setup in Fig. 3.4 it is described by $\mathrm{H}^+(aq)|\mathrm{H}_2(g)|\mathrm{Pt}$.
Thus

$$\mathrm{H}^+ + e^- \leftrightarrows 1/2\mathrm{H}_2(g) \quad , \tag{3.35}$$

and the Nernst equation (cf. Eq. (3.28)) reads

$$E_{cell} = E^0 + \frac{RT}{F}\ln\frac{a_{\mathrm{H}^+}}{\sqrt{f_{\mathrm{H}_2}/f^0}} \quad \text{, so} \quad \Delta E_{cell} = (E_{cell,p_1} - E_{cell,p_2})_{a_{\mathrm{H}_1^+}=a_{\mathrm{H}_2^+}} \approx \frac{RT}{F}\ln\sqrt{\frac{p_2}{p_1}} \quad . \tag{3.36}$$

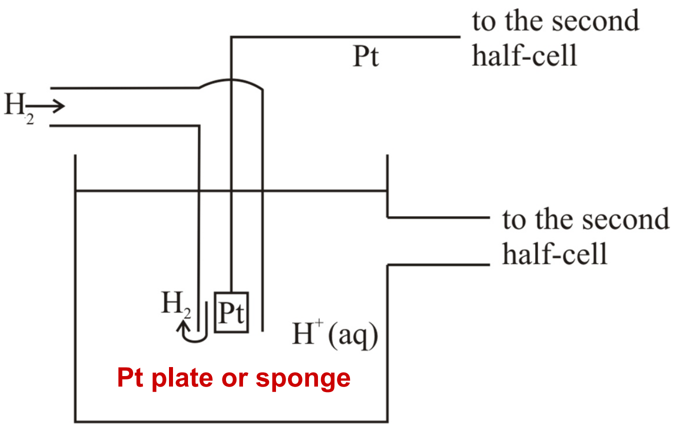

Figure 3.4: Plot and extrapolation used for the experimental measurement of standard cell potentials.

For the last equation we used the fact that for H_2 at 1 bar $f \approx p$. Actually the SCE electrodes is one of the most stable and most "ideal" electrochemical half cells. Due to this reason it has been chosen as a reference

$$E_{cell} = E^0 + \frac{RT}{F}\ln\frac{a_{\mathrm{H}^+}}{\sqrt{f_{\mathrm{H}_2}/f^0}} \equiv E^0(SHE) \overset{def}{=} 0 \quad , \tag{3.37}$$

implying that by definition $a_{\mathrm{H}^+} = f_{\mathrm{H}_2} = 1$.

Metal-ion electrodes are common electrochemical cells. The charge carriers are metal ions M^{z+}. The reaction transfers the metal ions from the solution to the interface of the pure metal

$$\mu_{M^{z+}} + z^+F\ E_{cell,sol} = \mu_M + z^+F\ E_{cell,M} \quad . \tag{3.38}$$

The decisive point is that the chemical potential of M^{z+} at the interface of pure metal is independent from the activity of the metal ion, i.e. $\mu_M = \mu_M^*$. Thus

$$\Delta E_{cell} = E_{cell,M} - E_{cell,sol} = \frac{\mu^0_{M_{z+}} - \mu^*_M}{z^+F} + \frac{RT}{z^+F}\ln a_{M^{z+}} \quad . \tag{3.39}$$

Often (in biological application) concentration differences of metal-salt solutions (α, β) separated by an ion selective membrane are measured by membrane potentials, i.e.

$$\mu^0_{M^+}(\alpha) + RT\ln a_{M^+}(\alpha) + FE_{cell}(\alpha) = \mu^0_{M^+}(\beta) + RT\ln a_{M^+}(\beta) + FE_{cell}(\beta) \quad . \tag{3.40}$$

Since $\mu^0_{M^+}(\alpha) = \mu^0_{M^+}(\beta)$ we finally get

$$\Delta E_{cell} = E_{cell}(\alpha) - E_{cell}(\beta) = \frac{RT}{F}\ln\left[\frac{a_{M^+}(\beta)}{a_{M^+}(\alpha)}\right] \quad . \tag{3.41}$$