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Electrochemical Methods for the Micro- and Nanoscale

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Solutions to the tasks: Chapter 4 – Electrochemical laboratory

Task 4.1 (Definitions of the normal hydrogen electrode (NHE))

The *standard hydrogen electrode* (SHE) is a hydrogen reference electrode with unit activity of protons (pH 0) and standard pressure for the hydrogen gas. The *normal hydrogen electrode* (NHE) is ambiguous. Either it relates to unit activity of protons (pH 0) or a proton concentration of $1\,\mathrm{mol\,l^{-1}}$, which is pH 0.13 in case of HCl.

At room temperature ($T = 273\,\mathrm{K} + 25\,\mathrm{K}$), the difference is:

$$\Delta E = \underbrace{\frac{RT}{F}\ln 1}_{\text{unit activity}} - \underbrace{\frac{RT}{F}\ln 10^{-0.13}}_{\text{unit concentration}} = 7.7\,\mathrm{mV}$$

Task 4.2 (Diffusion potentials in simple electrolytes)

Diffusion potentials may be counter-intuitive. Therefore, this task compares the potential between a phase with 0.1 M HCl and 1 M HCl to the situation with 0.1 M KCl and 1 M KCl.

For the same simple electrolyte in both phases, the diffusion potential at the liquid junction is:

$$E_{\mathrm{diff}} = \frac{\mu_+ - \mu_-}{\mu_+ + \mu_-} \cdot \frac{RT}{F} \ln \frac{a^\alpha}{a^\beta}$$

Approximating the ion mobilities by the values for infinite dilution according to Table 4.3, the diffusion potential for the HCl solutions

$$E_{\mathrm{diff}} = \frac{(362.4 - 79.1) \times 10^{-9}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}{(362.4 + 79.1) \times 10^{-9}\,\mathrm{m^2\,V^{-1}\,s^{-1}}} \cdot \frac{RT}{F} \ln \frac{0.1 \times 0.832\,\mathrm{mol\,l^{-1}}}{1 \times 0.741\,\mathrm{mol\,l^{-1}}} = -36\,\mathrm{mV}$$

at room temperature ($T = 273\,\mathrm{K} + 25\,\mathrm{K}$) is much higher compared to the case with KCl:

$$E_{\mathrm{diff}} = \frac{(76.2 - 79.1) \times 10^{-9}\,\mathrm{m^2\,V^{-1}\,s^{-1}}}{(76.2 + 79.1) \times 10^{-9}\,\mathrm{m^2\,V^{-1}\,s^{-1}}} \cdot \frac{RT}{F} \ln \frac{0.1 \times 0.785\,\mathrm{mol\,l^{-1}}}{1 \times 0.602\,\mathrm{mol\,l^{-1}}} = 0.98\,\mathrm{mV}$$

With a closer look, it is, of course, not counter-intuitive anymore that the KCl solutions with their similar ion mobilities show a much lower diffusion potential.

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