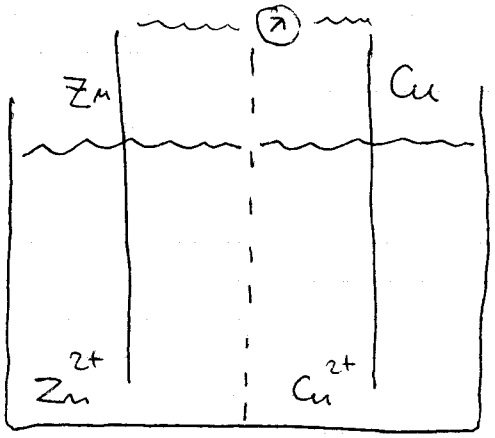
# Elektrokemi




$Zn^{2+} + 2e^- \rightarrow Zn$
$Cu^{2+} + 2e^- \rightarrow Cu$
} "slås om $e^-$"

$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$

elementskema:

$Zn \mid Zn^{2+} \,\vdots\, Cu^{2+} \mid Cu$

lodret streg adskiller forskellige faser

kontaktpotential $\Delta\phi$
kan elimineres (næsten, ~ 1 til 2 mV) med saltbro, f.eks mættet KCl:

$Zn \mid Zn^{2+} \,\vdots\vdots\, Cu^{2+} \mid Cu$

|| i gamle dage

Spændingsrækken:

$Pt \mid H_2(g) \mid H^+(aq) \,\vdots\vdots\, Cu^{2+}(aq) \mid Cu$

f.eks.

$E = E_h - E_v + \Delta\phi$

men $\Delta\phi \approx 0$ pga saltbro
$E_v = 0$ for standard H-elektrode:

$E = E_h$

Nernstligningen (udledes senere)

$$E_h = E^\ominus - \frac{N}{z} \log \frac{a(red)}{a(ox)}$$

"

$$N = \frac{RT \ln 10}{F} = 0{,}05916 \text{ V}$$

ved 25°C.

**Eks 1:** $Cu^{2+} + 2e^- \rightarrow Cu$

ox-form reel-form

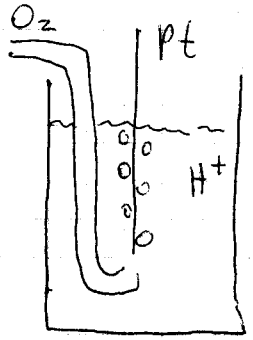
$$E = E^\circ - \frac{N}{2} \log \frac{a(Cu)}{a(Cu^{2+})}$$

$E^\circ = +0{,}34\,V$

$$\simeq 0{,}34 - \frac{0{,}05916}{2} \log\left(\frac{1}{\gamma_{Cu^{2+}} \cdot b(Cu^{2+})}\, b^\circ\right)$$

hvor vi har brugt $a(Cu) \simeq \chi(Cu) = 1$

**Eks 2**




$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(\ell)$$

$$E = E^\circ - \frac{N}{4} \log \frac{\chi^2_{H_2O}}{P_{O_2} \cdot a(H^+)^4} \; P^\circ b^{\circ 4}$$

$Pt \mid O_2 \mid H^+, H_2O \;\;::\;\;$ $E^\circ = 1{,}23\,V$

**Eks 3** $Fe^{3+} + e^- \rightarrow Fe^{2+}$ dvs $Pt \mid Fe^{2+}, Fe^{3+} \;::$

$$E = E^\circ - \frac{N}{1} \log \frac{\gamma_{Fe^{2+}} \cdot b(Fe^{2+})}{\gamma_{Fe^{3+}} \cdot b(Fe^{3+})} \qquad E^\circ = 0{,}771\,V$$

Pt bruges til at samle elektronerne op.

**Reference elektroder:**

Sølv/Sølvklorid: $Ag \mid AgCl(s) \mid Cl^- \;::$

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$$

$$E = E^\circ - \frac{N}{1} \log \frac{1 \cdot \gamma_{Cl^-} \cdot b(Cl^-)}{1} \; \frac{1}{b^\circ}$$

$E^\circ = +0{,}222\,V$

$E = 0{,}197\,V$ med mættet KCl.

Kalomel: $Pt \mid Hg(\ell) \mid Hg_2Cl_2(s) \mid Cl^- \;::$

indeholder $Hg_2^{2+}$-ionen: ~~$E = E^\circ$~~ $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(\ell) + 2Cl^-$

$$E = E^\circ - \frac{N}{2} \log \frac{1^2 \cdot \gamma(Cl^-)^2 \cdot b(Cl^-)^2}{1}$$

hvor vi har brugt $a(Hg(\ell)) \simeq \chi(Hg(\ell)) = 1$

og $a(Hg_2Cl_2(s)) \simeq \chi(Hg_2Cl_2(s)) = 1$

$E = +0{,}244\,V$ med mættet KCl.

Eks: Kalomel $::$ $Zn^{2+} \mid Zn$

$$E = E_h - E_v = \left(E^\circ_{Zn^{2+}/Zn} - \frac{N}{2} \log \frac{1}{a(Zn^{2+})}\right) - 0{,}244\,V$$