Lecture General Chemistry
Winter Term 2022/23

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- http://www.chemie.uni-siegen.de/pc/lehre/nanoscitec/

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21-19 The Nernst Equation

$$E = E^0 - \frac{2.303\ RT}{nF} \log Q$$

where

E = potential under the *nonstandard* conditions
E^0 = *standard* potential
R = gas constant, 8.314 J/mol · K
T = absolute temperature in K
n = number of moles of electrons transferred in the reaction or half-reaction
F = faraday, 96,485 C/mol $e^- \times$ 1 J/(V · C) = 96,485 J/V · mol e^-
Q = reaction quotient

"Ox" refers to the oxidized species and "Red" to the reduced species; x and y are their coefficients, respectively, in the balanced equation. The Nernst equation for any *cathode* half-cell (*reduction* half-reaction) is

$$E = E^0 - \frac{0.0592}{n} \log \frac{[\mathrm{Red}]^y}{[\mathrm{Ox}]^x} \qquad \text{(for reduction half-reaction)}$$

For the familiar half-reaction involving metallic zinc and zinc ions,

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad E^0 = -0.763\ \mathrm{V}$$

the corresponding Nernst equation is

$$E = -0.763\ \mathrm{V} - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]}$$

Example 21-5 The Nernst Equation for a Half-Cell Reaction

Calculate the potential, E, for the Fe^{3+}/Fe^{2+} electrode when the concentration of Fe^{2+} is exactly five times that of Fe^{3+}.

Solution

The reduction half-reaction is

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^0 = +0.771\ \mathrm{V}$$

We are told that the concentration of Fe^{2+} is five times that of Fe^{3+}, or $[Fe^{2+}] = 5[Fe^{3+}]$. Calculating the value of Q,

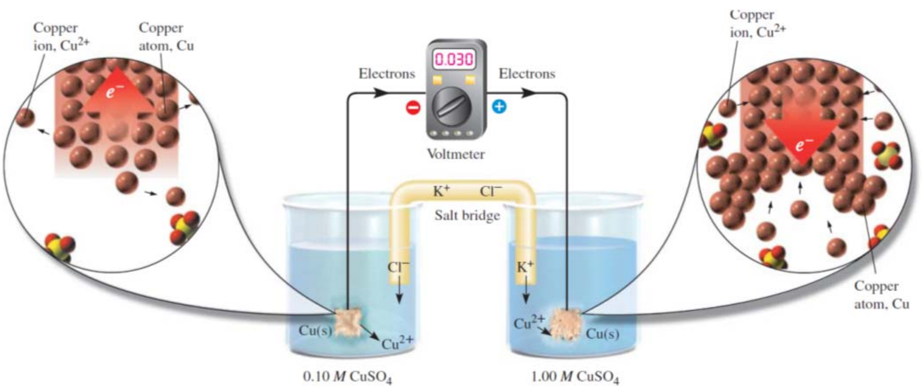
$$Q = \frac{[\mathrm{Red}]^y}{[\mathrm{Ox}]^x} = \frac{[Fe^{2+}]}{[Fe^{3+}]} = \frac{5[Fe^{3+}]}{[Fe^{3+}]} = 5$$

The balanced half-reaction shows one mole of electrons, or $n = 1$. Putting values into the Nernst equation,

$$E = E^0 - \frac{0.0592}{n} \log Q = +0.771 - \frac{0.0592}{1} \log 5 = (+0.771 - 0.041)\ \mathrm{V}$$

$$= +0.730\ \mathrm{V}$$

Concentration Cells



$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0592}{n} \log \frac{[\text{dilute solution}]}{[\text{concentrated solution}]}$$

$$= 0 - \frac{0.0592}{2} \log \frac{0.10}{1.00} = +0.030 \text{ V}$$

A cell is constructed at 25°C as follows. One half-cell consists of the Fe^{3+}/Fe^{2+} couple in which $[Fe^{3+}] = 1.00\ M$ and $[Fe^{2+}] = 0.100\ M$; the other involves the MnO_4^-/Mn^{2+} couple in acidic solution in which $[MnO_4^-] = 1.00 \times 10^{-2}\ M$, $[Mn^{2+}] = 1.00 \times 10^{-4}\ M$, and $[H^+] = 1.00 \times 10^{-3}\ M$. (a) Find the electrode potential for each half-cell with these concentrations, and (b) calculate the overall cell potential.

(a) For the MnO_4^-/Mn^{2+} half-cell *as a reduction*,

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + H_2O \qquad E^0 = +1.507 \text{ V}$$

$$E = E^0 - \frac{0.0592}{n} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= +1.507 \text{ V} - \frac{0.0592}{5} \log \frac{1.00 \times 10^{-4}}{(1.00 \times 10^{-2})(1.00 \times 10^{-3})^8}$$

$$= +1.507 \text{ V} - \frac{0.0592}{5} \log (1.00 \times 10^{22}) = +1.507 \text{ V} - \frac{0.0592}{5} (22.0)$$

$$= \boxed{+1.246 \text{ V}}$$

(b) For the Fe^{3+}/Fe^{2+} half-cell *as a reduction*,

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^0 = +0.771\ \text{V}$$

$$E = E^0 - \frac{0.0592}{n}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.771\ \text{V} - \frac{0.0592}{1}\log\frac{0.100}{1.00}$$

$$= +0.771\ \text{V} - \frac{0.0592}{1}\log(0.100) = +0.771\ \text{V} - \frac{0.0592}{1}(-1.00)$$

$$= \boxed{+0.830\ \text{V}}$$

The corrected potential for the MnO_4^-/Mn^{2+} half-cell is greater than that for the Fe^{3+}/Fe^{2+} half-cell, so we reverse the latter, balance the electron transfer, and add.

	E (corrected)
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$+1.246\ \text{V}$
$5(Fe^{2+} \longrightarrow Fe^{3+} + e^-)$	$-0.830\ \text{V}$
$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+}\ 4H_2O + 5Fe^{3+}$	$\boxed{E_{cell} = 0.416\ \text{V}}$