

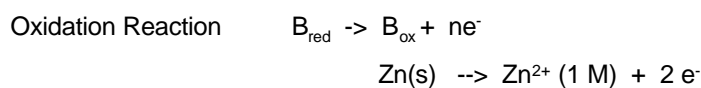
## Nernst Equation Example Problems

Note: all half reactions are written as reductions in this document. Standard cell potentials from Bard and Faulkner, Electrochemical Methods; New York: Wiley, 1980.

$$\begin{aligned} \text{Constants} \quad T &:= 298 \cdot \text{K} \\ R &:= 8.31441 \cdot \text{joule} \cdot \text{mole}^{-1} \cdot \text{K}^{-1} \\ F &:= 96484.6 \cdot \text{coul} \cdot \text{mole}^{-1} \end{aligned}$$

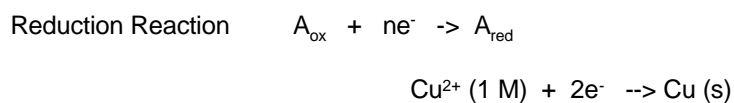
For the electrochemical system:  $\text{Zn} \mid \text{Zn}^{2+} (1 \text{ M}) \parallel \text{Cu}^{2+} (1 \text{ M}) \mid \text{Cu}$

Anode (oxidation occurs at the anode, on the left in the cell notation):



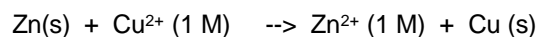
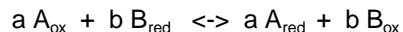
$$\begin{aligned} \text{Reduction potential for } B_{\text{ox}} \quad E_{\text{Zn}} &:= -0.763 \cdot \text{volt} \\ E_{\text{anode}} &:= E_{\text{Zn}} \end{aligned}$$

Cathode (reduction occurs at the cathode, on the right in cell notation):



$$\begin{aligned} \text{Reduction potential for } A_{\text{ox}} \quad E_{\text{Cu}} &:= 0.3402 \cdot \text{volt} \\ E_{\text{cathode}} &:= E_{\text{Cu}} \end{aligned}$$

Reaction: The overall electrochemical reaction has the form:



$E^\circ_{\text{cell}}$  (Calculate the standard cell potential for this system):

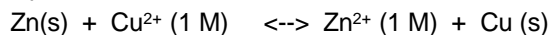
$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 1.1032 \text{ volt}$$

Next, change the concentrations so that the system is not at standard conditions:

$$M := \text{mole} \cdot \text{liter}^{-1} \quad C_{\text{Zn}} := 1.0 \cdot M \quad C_{\text{Cu}} := 0.1 \cdot M$$

Since the electrochemical system is an equilibrium system, changing the concentration of one of the species will shift the equilibrium. The cell potential is a measure of this equilibrium. Recall the balanced overall equation is:



Since the  $\text{Cu}^{2+}$  concentration is less than under standard conditions, the equilibrium will shift to the left. This means that the cell potential will be less positive (keep in mind that the cell potential is greater than 0 for a spontaneous reaction).

Use the Nernst equation to account for this shift in equilibrium. This calculation may be done several ways. I'll show two here:

Calculate the potential for each half reaction under these conditions:

The Anode:  $n := 2$

$$E_{\text{anode}} := E_{\text{Zn}} + \frac{R \cdot T}{n \cdot F} \cdot \ln(C_{\text{Zn}} \cdot M^{-1})$$

$$E_{\text{anode}} = -0.763 \text{ volt}$$

Notice that the Anode potential is unchanged ( $E_{\text{Zn}} = -0.763 \text{ volt}$ ), since the concentration of  $\text{Zn}^{2+}$  is the same as under standard conditions. Notice that the concentration of the solid is not included. Also, the value within the ln must be unitless. More detailed treatments use the activity coefficient ( $\alpha$ ).

The Cathode:  $n := 2$

$$E_{\text{cathode}} := E_{\text{Cu}} + \frac{R \cdot T}{n \cdot F} \cdot \ln(C_{\text{Cu}} \cdot M^{-1})$$

$$E_{\text{cathode}} = 0.31064 \text{ volt}$$

$$E_{\text{Cu}} = 0.3402 \text{ volt}$$

Notice that the Cathode potential has changed ( $E_{\text{Cu}} = 0.3402 \text{ volt}$ ), since the concentration of  $\text{Cu}^{2+}$  is different from the standard conditions.

The Cell:

$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 1.07364 \text{ volt}$$

We may also solve the entire equation in one step using a different form of Nernst equation.

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Zn}}}{C_{\text{Cu}}} \right)$$

$$E_{\text{cell}} = 1.07364 \text{ volt}$$

This equation is occasionally rearranged different ways, take a careful look at the following:

Flip values inside the log and change sign to add:

$$E_{\text{cell}} := E_{\text{std\_cell}} + \frac{R \cdot T}{n \cdot F} \cdot \ln \left( \frac{C_{\text{Cu}}}{C_{\text{Zn}}} \right) \quad E_{\text{cell}} = 1.07364 \text{ volt}$$

At 25 C, combine R, T, and F; switch from ln to log:

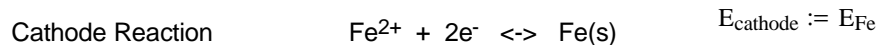
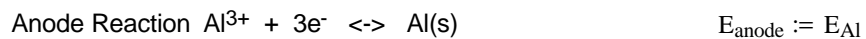
$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{0.05916 \cdot \text{volt}}{n} \cdot \log \left( \frac{C_{\text{Zn}}}{C_{\text{Cu}}} \right) \quad E_{\text{cell}} = 1.07362 \text{ volt}$$

Find the cell potential for the following:



$$E_{\text{Al}} := -1.706 \cdot \text{volt}$$

$$E_{\text{Fe}} := -0.409 \cdot \text{volt}$$



$$E_{\text{std\_cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{std\_cell}} = 1.297 \text{ volt}$$

Comments: Notice that the cathode reaction is more favorable as a reduction (higher reduction potential) and the anode reduction is more favorable as an oxidation (lower reduction potential). The reaction is spontaneous in the direction that is written so E is positive. Since all species are at their standard states (either solutions with 1M concentration or solids) the potential for this cell is the same as the standard state.

Find the cell potential for the following:



Since the cell is not in its standard state we need to pay attention to the concentrations. This requires using the balanced redox equation and the Nernst equation. The  $n$  used for the Nernst equation is from the number of electrons in the balanced redox reaction:



This redox reaction involves six electrons

The following constants are required:

$$T := 298 \cdot \text{K}$$

$$n := 6$$

$$F := 96484.6 \cdot \frac{\text{coul}}{\text{mole}}$$

$$R := 8.31441 \cdot \text{joule} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$$

$$C_{\text{Al}} := 0.1$$

Note, actually the activities are needed for the Nernst equation. We will assume that the activity coefficients are 1. In which case the activity is the same as the concentration but is unitless.

$$C_{\text{Fe}} := 0.1$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left[ \frac{(C_{\text{Al}})^2}{(C_{\text{Fe}})^3} \right]$$

$$E_{\text{cell}} = 1.28715 \text{ volt}$$

Notice that the cell potential does change in this example even though the concentrations of both species are the same. This only occurs for systems where different species have different coefficients. This result should make sense based on LeChatelier's principle since this equilibrium is more dependent upon the concentration of  $\text{Fe}^{2+}$ , as a result reducing its concentration has a greater effect and the equilibrium shifts backwards. So the cell potential decreases. The reaction is less spontaneous.

Next find the cell potential for the following:



We can solve this with the same setup used above:

$$C_{\text{Al}} := 0.1$$

$$C_{\text{Fe}} := 0.01$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left[ \frac{(C_{\text{Al}})^2}{(C_{\text{Fe}})^3} \right]$$

$$E_{\text{cell}} = 1.25758 \text{ volt}$$

Notice that reducing the  $\text{Fe}^{2+}$  concentration should shift the reaction backwards. It becomes less spontaneous. So the cell potential is reduced.

Alternatively this problem may be solved for each half reaction and then the half reactions combined. This is the procedure used in your textbook. For comparisons I will show the above problem worked this way.

$$E_{\text{anode}} := E_{\text{Al}} - \frac{R \cdot T}{3 \cdot F} \cdot \ln \left( \frac{1}{0.1} \right)$$

$$E_{\text{cathode}} := E_{\text{Fe}} - \frac{R \cdot T}{2 \cdot F} \cdot \ln \left( \frac{1}{0.01} \right)$$

$$E_{\text{cell}} := E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = 1.25758 \text{ volt}$$

Note that both of these methods work because of some unique properties of logs. These properties are shown in the rearrangements below:

$$\ln\left(\frac{a}{b}\right) \quad \text{expands to} \quad \ln(a) - \ln(b)$$

$$\ln(a^x) \quad \text{expands to} \quad x \cdot \ln(a)$$

$$\ln\left(\frac{1}{a^x}\right) \quad \text{expands to} \quad -x \cdot \ln(a)$$

As a result the following expressions are equivalent. Take a moment to convince yourself of this:

$$\frac{R \cdot T}{6 \cdot F} \cdot \ln\left[\frac{(C_{Al})^2}{(C_{Fe})^3}\right] \quad \text{expands to} \quad \frac{1}{3} \cdot R \cdot \frac{T}{F} \cdot \ln(C_{Al}) - \frac{1}{2} \cdot R \cdot \frac{T}{F} \cdot \ln(C_{Fe})$$

Or you can take the expressions used for the second solution and combine them since:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Where

$$E_{\text{anode}} = E_{Al} - \frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{C_{Al}}\right)$$

$$E_{\text{cathode}} = E_{Fe} - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{C_{Fe}}\right)$$

Substitutes in as

$$E_{\text{cell}} = \left(E_{Fe} - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{C_{Fe}}\right)\right) - \left(E_{Al} - \frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{C_{Al}}\right)\right)$$

This rearranges in the following steps

$$E_{\text{cell}} = (E_{Fe} - E_{Al}) + \left(\frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{C_{Al}}\right) - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{C_{Fe}}\right)\right)$$

Since  $E_{\text{std\_cell}} = E_{\text{Fe}} - E_{\text{Al}}$

$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{\text{Al}}\right) - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{\text{Fe}}\right) \right)$$

The common denominator is 6 for the number of moles. To change this need to change the power inside the log. See above identities to check how this step works.

$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{6 \cdot F} \cdot \ln\left(\frac{1}{\text{Al}^2}\right) - \frac{R \cdot T}{6 \cdot F} \cdot \ln\left(\frac{1}{\text{Fe}^3}\right) \right)$$

rearranges to

$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left[ \frac{R \cdot T}{6 \cdot F} \cdot \left( \ln\left(\frac{1}{\text{Al}^2}\right) - \ln\left(\frac{1}{\text{Fe}^3}\right) \right) \right]$$

rearranges to

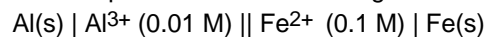
$$E_{\text{cell}} = (E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{6 \cdot F} \cdot \ln\left(\frac{\text{Fe}^3}{\text{Al}^2}\right) \right)$$

Check the numbers for these expressions:

$$\left( E_{\text{Fe}} - \frac{R \cdot T}{2 \cdot F} \cdot \ln\left(\frac{1}{C_{\text{Fe}}}\right) \right) - \left( E_{\text{Al}} - \frac{R \cdot T}{3 \cdot F} \cdot \ln\left(\frac{1}{C_{\text{Al}}}\right) \right) = 1.25758 \text{ volt}$$

$$(E_{\text{std\_cell}}) + \left( \frac{R \cdot T}{6 \cdot F} \cdot \ln\left(\frac{C_{\text{Fe}}^3}{C_{\text{Al}}^2}\right) \right) = 1.25758 \text{ volt}$$

Next find the cell potential for the following:



We can solve this with the same setup used above:

$$C_{\text{Al}} := 0.01$$

$$C_{\text{Fe}} := 0.1$$

$$E_{\text{cell}} := E_{\text{std\_cell}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \left[ \frac{(C_{\text{Al}})^2}{(C_{\text{Fe}})^3} \right]$$

$$E_{\text{cell}} = 1.30685 \text{ volt}$$

Notice that reducing the  $\text{Al}^{3+}$  concentration should shift the reaction forwards. It becomes more spontaneous. So the cell potential is increased.

This document was prepared by:

Scott Van Bramer  
Department of Chemistry  
Widener University  
Chester, PA 19013  
svanbram@science.widener.edu  
<http://science.widener.edu/~svanbram>