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.

Constants

$T := 298 \cdot K$

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

$F := 96484.6 \cdot coul \cdot mole^{-1}$

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

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

Oxidation Reaction B_{red} -> B_{ox} + ne^-

Zn(s) --> Zn^{2+} (1 M) + 2 e^-

Reduction potential for B_{ox} $E_{Zn} := -0.763 \cdot volt$

$E_{anode} := E_{Zn}$

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

Reduction Reaction A_{ox} + ne^- -> A_{red}

Cu^{2+} (1 M) + $2e^-$ --> Cu (s)

Reduction potential for A_{ox} $E_{Cu} := 0.3402 \cdot volt$

$E_{cathode} := E_{Cu}$

Reaction: The overall electrochemical reaction has the form:

a A_{ox} + b B_{red} <-> a A_{red} + b B_{ox}

Zn(s) + Cu^{2+} (1 M) --> Zn^{2+} (1 M) + Cu (s)

E^o_{cell} (Calculate the standard cell potential for this system):

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

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

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

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

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

$Zn(s) + Cu^{2+}$ (1 M) <--> Zn^{2+} (1 M) + Cu (s)

Since the Cu^{2+} concentration is less than under standard conditions, the equlibrium 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 equlibrium. This calculation may be done several ways. I'll show two here:

Calculate the potential for each half reaction under these conditions:

The Anode: $n := 2$

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

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

Notice that the Anode potential is unchanged ($E_{Zn} = -0.763\,volt$), since the concentration of 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 coefficeint (α).

The Cathode: $n := 2$

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

$E_{cathode} = 0.31064\,volt$ $\qquad E_{Cu} = 0.3402\,volt$

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

The Cell:

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

$E_{cell} = 1.07364\,volt$

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

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

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

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

Flip values inside the log and change sign to add:

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

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

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

Find the cell potential for the following:

Al(s) | Al^{3+} (1 M) || Fe^{2+} (1 M) | Fe(s)

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

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

Anode Reaction Al^{3+} + $3e^-$ <-> Al(s) $E_{anode} := E_{Al}$

Cathode Reaction Fe^{2+} + $2e^-$ <-> Fe(s) $E_{cathode} := E_{Fe}$

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

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

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 posative. 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:

Al(s) | A^{3+} (0.1 M) || Fe^{2+} (0.1 M) | Fe(s)

Since the cell is not in it's 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 equiation is from the number of electrons in the balanced redox reaction:

2 Al(s) + 3 Fe^{2+} <--> 2 Al^{3+} + 3 Fe(s)

This redox reaction involves six electrons

The following constants are required:

$T := 298 \cdot K$

$n := 6$

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

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

$C_{Al} := 0.1$

$C_{Fe} := 0.1$

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.

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

$E_{cell} = 1.28715 \, volt$

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 LeChatlier's principal since this equlibrium is more dependent upon the concentration of Fe2+, as a result reducing it's concentration has a greater effect and the equlibrium shifts backwards. So the cell potential decreases. The reaction is less spontaneous.

Next find the cell potential for the following:

$Al(s) \mid Al^{3+}$ (0.1 M) $\parallel$ Fe^{2+} (0.01 M) $\mid Fe(s)$

We can solve this with the same setup used above:

$$C_{Al} := 0.1$$

$$C_{Fe} := 0.01$$

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

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

Notice that reducing the 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.

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

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

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

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

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

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

$\ln\left(a^x\right)$ expands to $x\cdot\ln(a)$

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

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

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

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

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

Where

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

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

Substitues in as

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

This rearanges in the following steps

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

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

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

The comon 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.

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

rearanges to

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

rearanges to

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

Check the numbers for these expressions:

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

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

Next find the cell potential for the following:

$Al(s) \mid Al^{3+}$ (0.01 M) || Fe^{2+} (0.1 M) | Fe(s)

We can solve this with the same setup used above:

$C_{Al} := 0.01$

$C_{Fe} := 0.1$

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

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

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

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