2007 NERST MADE SIMPLE

What happens when the Daniell cell is used to do work?

- The zinc electrode becomes lighter as zinc atoms are oxidized to Zn^{2+} ions, which go into solution.
- The copper electrode becomes heavier as Cu^{2+} ions in the solution are reduced to copper metal.
- The concentration of Zn^{2+} ions at the anode increases and the concentration of the Cu^{2+} ions at the cathode decreases.
- Negative ions flow from the salt bridge toward the anode to balance the charge on the Zn^{2+} ions produced at this electrode.
- Positive ions flow from the salt bridge toward the cathode to compensate for the Cu^{2+} ions consumed in the reaction.

An important property of the cell is missing from this list. Over a period of time, the cell runs down, and eventually has to be replaced. Let's assume that our cell is initially a standard-state cell in which the concentrations of the Zn^{2+} and Cu^{2+} ions are both 1 molar.

$$Zn \mid Zn^{2+}(1.0\ M) \parallel Cu^{2+}(1.0\ M) \mid Cu$$

As the reaction goes forward — as zinc metal is consumed and copper metal is produced — the driving force behind the reaction must become weaker. Therefore, the cell potential must become smaller.

This raises an interesting question: When does the cell potential become zero?

The cell potential is zero if and only if the reaction is at equilibrium.

When the reaction is at equilibrium, there is no net change in the amount of zinc metal or copper ions in the system, so no electrons flow from the anode to the cathode. If there is no longer a net flow of electrons, the cell can no longer do electrical work. Its potential for doing work must therefore be zero.

In 1889 Hermann Walther Nernst showed that the potential for an electrochemical reaction is described by the following equation.

$$E = E^{\circ} - \frac{RT}{nF} \ln Q_c$$

In the **Nernst equation**, *E* is the cell potential at some moment in time, E° is the cell potential when the reaction is at standard-state conditions, *R* is the ideal gas constant in units of joules per mole, *T* is the temperature in kelvin, *n* is the number of moles of electrons transferred in the balanced equation for the reaction, *F* is the charge on a mole of electrons, and Q_c is the reaction quotient at that moment in time. The symbol *ln* indicates a natural logarithm, which is the log to the base *e*, where *e* is an irrational number equal to 2.71828...

Three terms in the Nernst equation are constants: *R*, *T*, and *F*. The ideal gas constant is 8.314 J/mol-K. The temperature is usually 25°C. The charge on a mole of electrons can be calculated from Avogadro's number and the charge on a single electron.

$$\frac{6.022045 \ x \ 10^{23} \ e^-}{1 \ mol} \ x \ \frac{1.6021892 \ x \ 10^{-19} \ C}{1 \ e^-} = 96{,}484.56 \ C/mol$$

Substituting this information into the Nernst equation gives the following equation.

$$E = E^\circ - \frac{0.02568}{n} \ln Q_c$$

Three of the remaining terms in this equation are characteristics of a particular reaction: n, E^o, and Q_c.

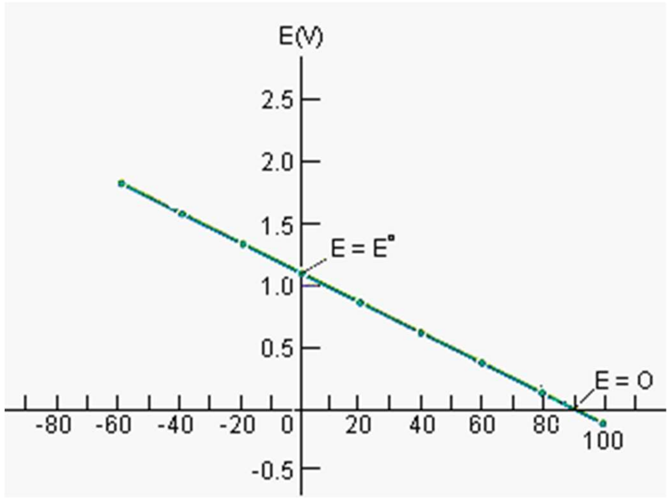
Example: The standard-state potential for the Daniell cell is 1.10 V. Two moles of electrons are transferred from zinc metal to Cu^{2+} ions in the balanced equation for this reaction, so n is 2 for this cell. Because we never include the concentrations of solids in either reaction quotient or equilibrium constant expressions, Q_c for this reaction is equal to the concentration of the Zn^{2+} ion divided by the concentration of the Cu^{2+} ion.

$$Q_c = \frac{(Zn^{2+})}{(Cu^{2+})}$$

Substituting what we know about the Daniell cell into the Nernst equation gives the following result, which represents the cell potential for the Daniell cell at 25°C at any moment in time.

$$E = E^\circ - \frac{0.02568}{2} \ln[\frac{(Zn^{2+})}{(Cu2+)}]$$

The figure below shows a plot of the potential for the Daniell cell as a function of the natural logarithm of the reaction quotient.



When the reaction quotient is very small, the cell potential is positive and relatively large. This isn't surprising, because the reaction is far from equilibrium and the driving force behind the reaction should be relatively large. When the reaction quotient is very large, the cell potential is negative. This means that the reaction would have to shift back toward the reactants to reach equilibrium.