
X. Electrochemistry.

F. The Nernst Equation.

Recall the equations:

\[ \Delta G = \Delta G^o + 2.303RT \log(Q) \]  
\[ \Delta G = -nF\Delta E \]  
\[ \Delta G^o = -nF\Delta E^o \]

Combining these equations gives the Nernst equation, which allows the calculation of cell potentials for non-standard state conditions:

\[ \Delta E = \Delta E^o - \frac{(2.303RT)}{(nF)} \log(Q) \]

where Q is the reaction quotient for the cell redox reaction, n is the # of electrons transferred in the redox reaction. **Note the - sign.** At 25°C, the collection of constants \((2.303RT/F)\) has the value of 0.05916 V (which will be provided on tests).

Problem Type 6: Calculate the cell potential for any set of concentrations.

Ex. What is \(\Delta E\) for the redox reaction: 
\[
\text{Cu}(s) + 2\text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + 2\text{Fe}^{2+}
\]
if \([\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M}, [\text{Fe}^{2+}] = 0.20 \text{ M}, \text{ and } [\text{Cu}^{2+}] = 0.25 \text{ M}\)?

Table:

<table>
<thead>
<tr>
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<th>(\text{Fe}^{3+})</th>
<th>(\text{Fe}^{2+})</th>
<th>(E^o)</th>
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<tbody>
<tr>
<td>(\text{Cu}^{2+}) + 2(e^-)</td>
<td>(\text{Cu}(s))</td>
<td>(+0.77) V</td>
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First, calculate \(\Delta E^o\), then Q, then use the Nernst equation. Since \(\text{Cu}(s)\) is oxidized to \(\text{Cu}^{2+}\), the 2nd half rxn is reversed and the sign of its \(E^o\) is changed.

\[
\Delta E^o = (+0.77) + (-0.34) = +0.43 \text{ V}
\]

\[
Q = \frac{([\text{Cu}^{2+}][\text{Fe}^{2+}]^2)}{([\text{Fe}^{3+}]^2)} = \frac{(0.25)(0.20)^2}{(1.0 \times 10^{-4})^2} = 1.0 \times 10^6
\]

Since \(n = 2\):

\[
\Delta E = (+0.43) - (0.05916/2) \log(1.0 \times 10^6) = (+0.43) - (+0.177) = +0.25 \text{ V}
\]

One of the most important consequences of the Nernst equation is the ability to determine the pH of a solution from a cell voltage. The only requirement is that the cell reaction contains \(\text{H}^+\) or \(\text{OH}^-\) explicitly. One way is to combine a half-reaction containing \(\text{H}^+\) or \(\text{OH}^-\) with another half-rxn not containing these ions to form a redox reaction and a cell:

Problem Type 7. Given a redox reaction (or cell notation) and a cell voltage, calculate the pH.

Ex. \(\text{Pt}(s)\) \(\text{H}_2(1 \text{ atm}), \text{H}^+ (\text{? M})\) \(\text{Pb}^{2+} (1 \text{ M})\) \(\text{Pb}(s)\)

What is the pH in the anode compartment if the cell voltage is +0.28 V?

Data:

\[
\begin{align*}
2\text{H}^+ + 2e^- & \rightarrow \text{H}_2(g) & E^o &= 0 \text{ V} & \text{(reverse and use as anode)} \\
\text{Pb}^{2+} + 2e^- & \rightarrow \text{Pb}(s) & E^o &= -0.13 \text{ V} & \text{(use as cathode)}
\end{align*}
\]
Redox reaction: \[ \text{Pb}^{2+} + \text{H}_2(g) \rightarrow \text{Pb}(s) + 2\text{H}^+ \]
\[ \Delta E^\circ = (-0.13) + (0) = -0.13 \text{ V} \]
\[ Q = [\text{H}^+]^2/[([\text{Pb}^{2+}]P_{\text{H}_2}) = [\text{H}^+]^2 \]
\[ \text{since } P_{\text{H}_2} = 1 \text{ atm and } [\text{Pb}^{2+}] = 1 \text{ M} \]
\[ \Delta E = \Delta E^\circ - (0.05916/2) \log([\text{H}^+]^2) = \Delta E^\circ - (0.05916/2)(2) \log([\text{H}^+]) \]
\[ = \Delta E^\circ + (0.05916)\text{pH} \]
\[ \text{since } \text{pH} = -\log([\text{H}^+]) \]
Note that there is a linear relationship between the cell potential and the pH.
\[ (+0.28) = (-0.13) + (0.05916)\text{pH}; \text{pH} = \{(+0.28) - (-0.13))/0.05916 = 6.9 \]

Comment on pH measurement: the modern pH electrode is not based on a half-reaction including \( \text{H}^+ \), an idea implied by M&F. Instead, the pH electrode contains a thin glass membrane. A voltage develops across the membrane, based on the relative concentrations of \( \text{H}^+ \) on each side. The changes in that membrane voltage are monitored by means of two reference electrodes (electrodes whose potentials are constant), one inside the pH electrode and one in contact with the sample. The cell voltage is also linearly related to the solution pH.

G. Electrolysis and Electrolytic Cells.
In an electrolytic cell, an external power supply is connected to the electrochemical cell. The direction of the current causes the cell redox reaction to run in the non-spontaneous direction. Again, reduction occurs at the cathode, oxidation at the anode.

Ex. Water electrolysis demo: \( \text{H}_2\text{O} \) plus an inert electrolyte (\( \text{Na}_2\text{SO}_4 \)), two Pt electrodes. Water is more easily reduced than \( \text{Na}^+ \), and is more easily oxidized than \( \text{SO}_4^{2-} \). The half-reactions are:
Cathode: \[ 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2(g) + 4\text{OH}^- \]
\[ E^\circ = -0.414 \text{ V at pH 7.00} \]
Anode: \[ 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{O}_2(g) + 4\text{H}^+ \]
\[ E^\circ = -0.815 \text{ V at pH 7.00} \]
Minimum cell voltage needed: \(-1.229 \text{ V} \). In practice, more than 2 V is needed.
Note that the cathode half-cell becomes more basic, and the anode half-cell more acidic. The cell reaction is:
\[ 6\text{H}_2\text{O} \rightarrow 2\text{H}_2(g) + 4\text{OH}^- + \text{O}_2(g) + 4\text{H}^+ \]
If the cell is not split (common electrolyte), the cell reaction is:
\[ 2\text{H}_2\text{O} \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \]

Electrolysis was used to isolate many elements for the first time (e.g., alkali metals). There are many commercially important electrolysis processes: production of alkali metals, sodium hydroxide, chlorine, aluminum (single largest user of electricity in the US), electorefining of metals, and electroplating (used to deposit very thin layers of silver, gold, chromium). Demo: electroplating of copper.
Quantitative aspects of electrolysis: Faraday (ca. 1830) observed that the amount of substance produced during electrolysis is proportional to the amount of charge passed through the cell. Charge (units coulombs) is the time integral of the current (i dt). If the current is constant, the charge in coulombs is the product of the current in amperes and time in seconds:

\[ Q \text{ (coul)} = i \text{ (A)} \times t \text{ (s)} \]

(Q is NOT the reaction quotient)

Faraday’s Law: \( \frac{Q}{nF} = \# \text{ moles of substance produced} \)
where F is Faraday’s constant (96,500 coul/mol) and n = \# moles electrons consumed per mole of product (look at the half-reaction).

Ex. The production of Al from aluminum ore can be represented simply as: \( \text{Al}^{3+} + 3e^- \rightarrow \text{Al(s)} \)
Hence, \( n = 3 \) mole of \( e^- \) consumed per mole of Al produced.

Ex. In water electrolysis, \( n = 2 \) per mol of \( H_2 \), and \( n = 4 \) per mole of \( O_2 \) - see the half-reactions above.

Problem Type 8: Be able to convert between charge (or current and time) and moles (or grams or liters) of product.

Ex. How many kg of Al can be produced by passing \( 10^5 \) Amps thru molten aluminum oxide + cryolite for 8 hours? The relevant half-reaction is: \( \text{Al}^{3+} + 3e^- \rightarrow \text{Al(s)} \)

Determine n, convert current to Amps and time to seconds, calculate \( Q \), and use Faraday’s Law.

\[ \begin{align*}
\text{Al}^{3+} + 3e^- & \rightarrow \text{Al(s)} \\
n & = 3 \text{ mol } e^- \text{ per mol Al} \\
t & = (8 \text{ hours})(60 \text{ min/hour})(60 \text{ s/min}) = 28,800 \text{ s} \\
Q & = (10^5 \text{ A})(28,800 \text{ s}) = 2.88 \times 10^9 \text{ coul.} \\
\frac{Q}{nF} & = \frac{2.88 \times 10^9 \text{ coul}}{3 \times 96,500} = 9.95 \times 10^3 \text{ mol Al} \\
(9.95 \times 10^3 \text{ mol Al})(26.98 \text{ g Al/mol}) & = 2.68 \times 10^3 \text{ g Al} = 2.68 \times 10^2 \text{ kg Al (about 600 lb)}
\end{align*} \]

Ex. A layer of silver is electroplated on a coffee server using a constant current of 0.100 A. How much time is required to deposit 3.00 g of Ag? \( \text{Ag}^+ + e^- \rightarrow \text{Ag(s)} \), hence, \( n = 1 \)

\[ \begin{align*}
(3.00 \text{ g Ag})(1 \text{ mol Ag/107.868 g}) & = 0.0278 \text{ mol Ag.} \\
Q & = nF(\# \text{ moles}) = (1)(96,500)(0.0278 \text{ mol}) = 2.68 \times 10^3 \text{ coul} \\
Q & = i t; 2.68 \times 10^3 \text{ coul} = (0.100 \text{ A})t; t = 2.68 \times 10^4 \text{ s} = 7.46 \text{ hours}
\end{align*} \]

The large value of Faraday’s constant is both a blessing and a curse. For example, it is possible to deposit very thin films of expensive metal with great control of thickness (look at the contacts in your computer). However, bulk production by electrolysis requires enormous amounts of electricity. That is why recycling aluminum is economically viable.
H. Batteries.

Batteries are galvanic cells designed to generate a lot of power (current times voltage) and have minimal internal resistance. The voltage is determined by the cell reaction. To get larger voltages, the cells must be connected in series. Current is a function of the surface area of the electrodes and the kinetics of the half-reactions, while the total charge delivered is a function of the amount of reactants present. Most batteries carry all of their reactants internally; fuel cells have external reservoirs of liquid or gas reactants that are fed to the electrodes.

Demo: the Daniel’s cell, an early battery with an output of 1.1 V per cell, based on:

\[
\text{Zn}(s) + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}(s).
\]

Many modern batteries use Zn/Zn\(^{2+}\) as the anode.

We will consider just one other type of battery, the lead-acid battery. During discharge, the reactions are:

**anode:** \(\text{Pb}(s) + \text{HSO}_4^- \rightarrow \text{PbSO}_4(s) + \text{H}^+ + 2\text{e}^-\) \(E^\circ = +0.296 \text{V}\)

**cathode:** \(\text{PbO}_2(s) + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}\) \(E^\circ = +1.628 \text{V}\)

**redox rxn:** \(\text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}^+ + 2\text{HSO}_4^- \rightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)\)

\[\Delta E^\circ = +1.924 \text{V} \text{ (about 2 V per cell; a 12 V battery has 6 cells in series)}\]

The electrolyte is concentrated H\(_2\)SO\(_4\) (which dissociates to H\(^+\) and HSO\(_4^-\)). Since all other reactants and products are solids, there is no salt bridge. Note that H\(_2\)SO\(_4\) is consumed during discharge; hence, the density of the electrolyte decreases. A measurement of electrolyte density is used to determine the state of charge in the battery.

The lead-acid battery is rechargeable; reversing the current flow reverses the cell reaction. In older batteries, the cathode (where PbSO\(_4\) is reduced to Pb) also generated hydrogen gas, which is an explosive hazard (hence, the warnings about avoiding sparks near a battery that is recharging).