Chapter 19: Electrochemistry II
Spontaneous electrochemical reactions

This reaction occurs spontaneously at room temperature:

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{e}^-$$
$$\text{Cu}^{2+}(aq) + 2\text{e}^- \rightarrow \text{Cu}(s)$$
Galvanic Cells (Voltaic Cells)

• Can we make use of those electrons as they are transferred? (electrical work)
• We could separate the two metals and connect them with a wire. Electrons would travel through the wire to make the reaction occur (metals conduct electricity).
• This type of arrangement is called a Galvanic or Voltaic cell
Potential (voltage) difference between two half-cells drives current.
Anatomy of a voltaic cell

- **Electrodes**: Solid metal (or graphite) surfaces placed in the solutions.
- The cell on the left will not produce current (or voltage) because the Ag\(^+\) can react directly with the Cd(s) electrode.
- **Must separate** the two half-cells to force the current through the wire (salt bridge).
Anatomy of a voltaic cell

**Salt bridge**: Porous gel that allows counter ions to flow from one solution to another (but not the other ions):

Counter ions are not involved in the redox reactions, but without them, charge would build up on each electrode, stopping the reaction.
Anatomy of a voltaic cell

**Anode**: The electrode, at which oxidation occurs

- “ox-an” you lose your electrons
- Can think of it as having a negative charge (-)
- Electrons flow **away** from the anode (it has a higher potential)
Anatomy of a voltaic cell

**Cathode**: The electrode, at which reduction occurs
- Can think of it as having a positive charge (+)
- Electrons flow **toward** the cathode (it has a lower potential)
Anatomy of a voltaic cell - salt bridge

• Anode solution would become more and more positively charged as reaction occurred (Zn is being converted to Zn\(^{2+}\) in the example below)

• Cathode would become more and more negatively charged as reaction occurred (Cu\(^{2+}\) is being converted to Cu in the example below)

• **Salt bridge**: Counter anions flow from salt bridge into anode solution

• **Salt bridge**: Counter cations flow from salt bridge into cathode solution
Electrochemical cell notation

It is annoying to draw the diagrams, so we use a notation instead:

\[
\text{Zn}(s) \mid \text{Zn}^{2+}(aq) \parallel \text{Cu}^{2+}(aq) \mid \text{Cu}(s)
\]

- **anode** (oxidation)
- **cathode** (reduction)
- **salt bridge**
- **phase change**
- **electrodes are written on the outsides**
Inert electrodes

Sometimes the electrode is not reacting, it is just a way for electrons to be transferred into the solution:

\[
\text{Fe}(s) \mid \text{Fe}^{2+}(aq) \  || \ \text{MnO}_4^-(aq), \ \text{H}^+(aq), \ \text{Mn}^{2+}(aq) \mid \text{Pt}(s)
\]
Standard electrode potentials

- Think of each half-cell as having its own potential (relative quantity)
- The standard potential of the cell, $E_{\text{cell}}^\circ$, is the resulting potential from combining the potentials of each half-cell

**Higher the cell voltage, higher potential energy for electrons**

- “Standard” means under standard conditions (1 M, 1 atm, 298 K)
Standard hydrogen electrode (SHE)

• Because the half-cell voltage is relative, we need a common scale to compare the electrodes

• Use SHE as the standard and define its potential to be zero at standard conditions

\[
2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2(g) \quad E^\circ = 0.00 \text{ V}
\]

• Compare everything to the SHE potential (reference point) so that everything is on the same scale
Standard cell potential

Consider this cell:

- Cathode is SHE so its standard potential is 0 V
- Anode is a Zn(s) electrode with a solution of Zn^{2+}(aq)
- The anode potential is -0.76 V (higher than the SHE potential)
- Reaction would be spontaneous and 2e^- would be transferred
- We could make such a measurement for any electrode (relat. to SHE)
Standard cell potential

• The overall cell potential can be calculated from how much higher the anode potential is vs. the cathode potential
• We can get the overall cell potential from:

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

“right - left”

• In the case of the Zn(s) | Zn\(^{2+}\)(aq) || H\(^+(aq)\) | H\(_2\)(g) | Pt(s) cell

-0.76 V 0.00 V

$$E_{\text{cell}}^\circ = 0.00 \, V - (-0.76 \, V) = 0.76 \, V$$

Cell notation: Oxidation on the left and reduction on the right!
Standard electrode potentials:

- Always written as reductions: **Standard reduction potentials**
- Substances at the top tend to undergo reduction; they are good oxidizing agents
- Substances at the bottom tend to undergo oxidation; they are good reducing agents
- Any reduction listed is spontaneous when paired with the reverse of any reaction listed below it
- **Do not multiply** $E_{\text{cell}}$ **by any factors when, e.g., balancing equations!**
SHE as the higher potential

• Now imagine you had a half-cell that had a positive standard potential relative to the SHE.

Example: \( \text{Cu}(s) \ | \ \text{Cu}^{2+}(aq) \ || \ \text{H}^+(aq) \ | \ \text{H}_2(g) \ | \ \text{Pt}(s) \)

• The way this cell is written, would be non-spontaneous (negative cell potential; -0.34 V).

The cell would be spontaneous in reverse direction:

\[ E_{cell}^\circ = 0.34 \text{ V} - 0.00 \text{ V} = 0.34 \text{ V} \]

(switch the sides of the electrodes above)
Two-electrode cell

Consider: Cu(s) | Cu^{2+}(aq)  and  Zn(s) | Zn^{2+}(aq)

Which electrode would be the anode and which the cathode?

According to the redox table:

C:  \[ \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E^o = +0.34 \text{ V} \]
A:  \[ \text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s) \quad E^o = -0.76 \text{ V} \]

The more positive standard potential will gain electrons (as written). Reduction (right) at cathode.

The more negative standard potential will lose electrons (reverse written reaction). Oxidation (left) at anode.

\[ E^o_{cell} = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V} \quad \text{Positive!} \]

“cathode - anode”
Summary of Standard Electrode Potentials

- The standard electrode potential (SHE) is (arbitrarily) defined to be 0 V (reference point).
- The electrode with greater $E^0$ (i.e., more positive value) will undergo reduction (cathode; polarity +) and the other electrode will undergo oxidation (anode; polarity -).
- Redox table written as reductions (reverse for oxidation).
- Calculate the standard cell potential using:

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

- $E_{\text{cell}}^0$ is positive for spontaneous reactions and negative for non-spontaneous reactions as written.

- **Do not multiply** $E_{\text{cell}}^0$ **by any factors when balancing chemical equations (stoichiometric coefficients)**
Example

Given the following two half-cell reactions, what reaction will occur at the anode, and what at the cathode? What is the $E_{cell}^0$ and the overall reaction? What is the cell notation?

\[
\begin{align*}
\text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni}(s) & \quad E^o = -0.23 \text{ V} \\
\text{Mn}^{2+}(aq) + 2e^- \rightarrow \text{Mn}(s) & \quad E^o = -1.18 \text{ V}
\end{align*}
\]

1. Based on the $E^0$ values, determine reduction (cathode; larger $E^0$) vs. oxidation (anode; smaller $E^0$) at the electrodes.

2. Calculate $E_{cell}^0$ by subtracting the $E^0$ values ("cathode – anode"). Positive value for spontaneous process.

3. Balance the number of electrons transferred, reverse the half-reaction that corresponds to oxidation, and add the two half-reactions to get the overall reaction.

4. Write the cell notation (oxidation on left; reduction on right)
Example

\[ \text{Mn}(s) \mid \text{Mn}^{2+}(aq) \ || \ \text{Ni}^{2+}(aq) \mid \text{Ni}(s) \]
Cell potential, Free energy, and $K$

- Positive $E_{cell}^0$
- Negative $\Delta G^0$
- $K > 1$ ($Q = 1$ at standard conditions)

- Negative $E_{cell}^0$
- Positive $\Delta G^0$
- $K < 1$ ($Q = 1$ at standard conditions)

There must be some relationship between cell potential, free energy, and equilibrium constant!
Relating $\Delta G^o_{\text{rxn}}$ to $K$ (equilibrium constant)

\[ \Delta G_{\text{rxn}} = \Delta G^o_{\text{rxn}} + RT \ln Q \]

At equilibrium, $Q = K$ and $\Delta G_{\text{rxn}} = 0$ (not spontaneous in either direction)

\[ 0 = \Delta G^o_{\text{rxn}} + RT \ln K \]

(\text{use } K_p \text{ for gases, and } K_c \text{ for solutions})

- If $K < 1$, $\Delta G^o_{\text{rxn}}$ is positive because $\ln(K)$ is negative
  - Under standard conditions ($Q = 1$), $Q > K$, spontaneous in reverse direction
- If $K > 1$, $\Delta G^o_{\text{rxn}}$ is negative because $\ln(K)$ is positive
  - Under standard conditions ($Q = 1$), $Q < K$, spontaneous in forward direction
- If $K = 1$, $\Delta G^o_{\text{rxn}}$ is zero, at equilibrium under standard conditions
Relationship between $\Delta G^\circ$ and $E_{cell}^\circ$

Electrical energy can be used to perform work:

$$w = -qE_{cell}^\circ$$  \hspace{1cm} (1 V = 1 J/C)

So, the (max) free energy available to do work:

$$\Delta G^\circ = -nFE_{cell}^\circ$$

$F = $ Faraday’s constant $= 96,485$ C/mol e$^-$

(total charge on 1 mole of electrons)

$n = $ number of moles of electrons transferred
Relationship between $E_{cell}^\circ$ and $K$

Recall:

\[ \Delta G_{rxn}^\circ = -RT \ln K \]

\[ -nF E_{cell}^\circ = -RT \ln K \]

\[ E_{cell}^\circ = \frac{RT}{nF} \ln K \]

At room temperature and converting natural log (ln) to log:

\[ E_{cell}^\circ = \frac{0.0592 V}{n} \log K \]
\[ \Delta G^\circ = -nF E_{\text{cell}}^\circ \]

\[ \Delta G^\circ = -RT \ln K \]

\[ E_{\text{cell}}^\circ = \frac{0.0592 \text{ V}}{n} \log K \]
Example

Use tabulated electrode potentials to calculate $\Delta G^o$ and $K$ for the reaction (temperature 298 K):

$$2 \text{Na}(s) + 2 \text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq) + 2 \text{Na}^+(aq)$$

Na is oxidized and $\text{H}_2\text{O}$ is reduced (2 el. transfer)

($E_{cell}^0 = 1.88$ V and use the equations on slide 26)
Calculation of $E_{cell}$ under non-standard conditions

We know that under standard conditions:

$$\text{Zn}(s) + \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) \rightarrow \text{Zn}^{2+}(\text{aq}, 1 \text{ M}) + \text{Cu}(s) \quad E_\text{o}^\circ = 1.10 \text{ V}$$

What if the concentrations were different? How would we calculate $E_{cell}$?

For example, with $[\text{Cu}^{2+}] = 1.5 \text{ M}$ and $[\text{Zn}^{2+}] = 0.5 \text{ M}$, the cell will be even more likely to go forward (Le Chatelier’s principle), which means that $E_{cell}$ should be $> 1.10 \text{ V}$. 
The Nernst Equation

\[ \Delta G = \Delta G^\circ + RT \ln Q \]

\[ -nF E_{cell} = -nF E_{cell}^\circ + RT \ln Q \]

\[ E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q \]

At room temp and converting natural log to log:

\[ E_{cell} = E_{cell}^\circ - \frac{0.0592}{n} \log Q \]
Calculation of $Q$ for redox reactions

For an overall reaction

$$aA(s) + bB(aq) \rightarrow cC(aq) + dD(s)$$

$$Q = \frac{[C]^c}{[B]^b}$$

Remember: Pure solids do not affect $Q$!
Example

Calculate the cell potential of a voltaic cell based on the following reaction (temperature 298 K):

$$2 \text{Fe}^{3+}(\text{aq}) + 3 \text{Mg}(s) \rightarrow 2 \text{Fe}(s) + 3 \text{Mg}^{2+}(\text{aq})$$

at a) standard condition

b) $[\text{Fe}^{3+}] = 1.0 \times 10^{-3} \text{ M}, [\text{Mg}^{2+}] = 2.50 \text{ M}$

(non-standard condition)

(use the Nernst equation in b)
Equilibrium and the Nernst Equation

\[ E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q \]

- \( Q = 1 \) (standard condition), \( E_{\text{cell}} = E_{\text{cell}}^\circ \)
- \( Q < 1 \), greater concentration of reactants vs. products: \( E_{\text{cell}} > E_{\text{cell}}^\circ \)
- \( Q > 1 \), greater concentration of products vs. reactants: \( E_{\text{cell}} < E_{\text{cell}}^\circ \)
Equilibrium and the Nernst Equation

\[ E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q \]

If \( Q = K \) then:
\[ E_{\text{cell}} = E_{\text{cell}}^\circ - E_{\text{cell}}^\circ = 0 \text{ V} \]

If the cell reaches equilibrium, the potential will be 0 V:

• No reaction will occur
• The cell is “dead”
Concentration cells

This property of cells to change potential based on concentration of the reactants is useful because you can create a cell with one reactant/product.

**Different concentrations for each half-cell**

\[
\text{Cu}(s) + \text{Cu}^{2+}(\text{aq}, 2.0 \ \text{M}) \longrightarrow \text{Cu}^{2+}(\text{aq}, 0.010 \ \text{M}) + \text{Cu}(s)
\]

\[
E^\circ_{\text{cell}} = 0 \ \text{V}
\]

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q
\]

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q = 0 - \frac{0.0592}{2} \log \left( \frac{0.010 \ \text{M}}{2.0 \ \text{M}} \right) = 0.068 \ \text{V}
\]
A Concentration Cell

**Standard conditions**
- Anode: Cu(s)
- Cathode: Cu(s)
- [Cu$^{2+}$] = 1 M

**Nonstandard conditions**
- Anode: Cu(s)
- Cathode: Cu(s)
- [Cu$^{2+}$] = 0.010 M
- [Cu$^{2+}$] = 2.0 M

Cu(s) $\rightarrow$ Cu$^{2+}$ (aq) + 2 e$^-$
Solution becomes *more concentrated* with flow of current.

Cu$^{2+}$ + 2 e$^-$ $\rightarrow$ Cu(s)
Solution becomes *less concentrated* with flow of current.

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