Chapter 19  Electrochemistry

Electrochemistry is the branch of chemistry that deals with the interconversion of electrical energy and chemical energy.

Oxidation-Reduction (Redox) Reactions

Loss of an electron - oxidation (LEO) charge increases
Gain of an electron - reduction (GER) charge decreases

Oxidation is loss - Reduction is gain (OIL-RIG)

\[
Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)
\]

Oxidation - the value of the charge increases

\[
Zn(s) \rightarrow Zn^{2+}(aq)
\]

Reduction - the charge decreases (it is reduced in size)

\[
2H^+(aq) \rightarrow H_2(g)
\]
Chemical Change Leading to an Electrical Current

**Voltaic cell**: a spontaneous redox reaction to do electrical work.

![Diagram of a voltaic cell showing electron flow, oxidized and reduced species, and electrode compartments.]

**Electrode** - a device for conducting electrons into and out of solutions in electrochemical cells.

Electric neutrality is maintained by migration of ions through a porous glass disc or through a salt bridge.

**Salt bridge** allows flow of non-reacting charged species between compartments.

car-boat (cathode reduction, anode oxidation)
Electrochemical Cells and Potentials

Electromotive force (emf, $E$): electrons move from an electrode of higher potential to one of lower potential (potential difference, in Volts).

**Electrical work** = charge $\times$ potential difference

charge in coulombs, $C$

charge of one electron: $1.6022 \times 10^{-19}$ C

\[
\text{Volt} = \frac{1 \text{ Joule}}{1 \text{ Coulomb}}
\]

or \[\text{Work (Joule)} = 1 \text{ volt} \times 1 \text{ coulomb}\]

**standard conditions,**
- pure solid, or
- 1.0 M solution, or
- gas at 1 bar., give **standard electrode potential, $E^\circ$**

Cell potentials for **product-favored** (spontaneous) electrochemical reactions have **positive** values.

cell potential, cell voltage, emf, potential difference
Calculating the Potential $E^\circ$ of an Electrochemical Cell

How I learned: \[ E_{cell}^\circ = E_{red}^\circ + E_{ox}^\circ \]

How the author does it: \[ E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ \], where both are reduction potentials.

standard half-cell, standard hydrogen electrode (SHE)

\[ 2 \text{H}_3\text{O}^+ (aq, 1 \text{ M}) + 2e^- \rightarrow \text{H}_2 (g, 1 \text{ bar}) + \text{H}_2\text{O}(l) \quad E^\circ = 0.00 \text{ V} \]

Tables list standard reduction potentials - potentials for reduction reactions:

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>$E^\circ$(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^-(aq)$</td>
<td>+2.87</td>
</tr>
<tr>
<td>$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$</td>
<td>+0.80</td>
</tr>
<tr>
<td>$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}(s)$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$</td>
<td>-3.05</td>
</tr>
</tbody>
</table>
Look at Zn, Cu cell

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

Zn is oxidized, use an oxidation potential, the opposite of reduction potential in table:

\[ \text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)} \quad E_{\text{cell}}^\circ = -0.76 \text{ V} \]

\[ \text{Zn(s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \quad E_{\text{cell}}^\circ = +0.76 \text{ V} \]

Cu is reduced, use reduction potential from table

\[ \text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)} \quad E_{\text{cell}}^\circ = +0.34 \text{ V} \]

\[ \text{Zn(s)} \rightarrow \text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \quad E_{\text{ox}}^\circ = +0.76 \text{ V} \]

\[ \text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)} \quad E_{\text{red}}^\circ = +0.34 \text{ V} \]

\[ \text{Zn(s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu(s)} \quad E_{\text{cell}}^\circ = +1.10 \text{V} \]

\[ E_{\text{cell}}^\circ = (+0.76 \text{ V}) + (+0.34 \text{ V}) = +1.10 \text{ V} \]

IMPORTANT: Changing the stoichiometric coefficients of a half-cell does not affect the value of \( E^\circ \)

\[ \text{F}_2(g) + 2\text{e}^- \rightarrow 2\text{F}^- (\text{aq}) \ (1 \text{ M}) \quad E^\circ = +2.87 \]

\[ 2\text{F}_2(g) + 4\text{e}^- \rightarrow 4\text{F}^- (\text{aq}) \ (1 \text{ M}) \quad E^\circ = +2.87 \]
**Shorthand notation**

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

Anode is written first, the cathode (alphabetical)

Calculate the standard cell potential of the following cells.

Mg(s) | Mg^{2+}(aq) || Ni^{2+}(aq) | Ni(s)

Zn(s) | Zn^{2+}(aq) || Ni^{2+}(aq) | Ni(s)

Ag(s) | Ag^{+}(aq) || Cu^{2+}(aq) | Cu(s)

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<td>Ag^{+}(aq) + e(^-) → Ag(s)</td>
<td>+0.80</td>
</tr>
<tr>
<td>Cu^{2+}(aq) + 2e(^-) → Cu(s)</td>
<td>+0.34</td>
</tr>
<tr>
<td>Ni^{2+} + 2e(^-) → Ni(s)</td>
<td>-0.25</td>
</tr>
<tr>
<td>Zn^{2+} + 2e(^-) → Zn(s)</td>
<td>-0.76</td>
</tr>
<tr>
<td>Mg^{2+} + 2e(^-) → Mg(s)</td>
<td>-2.37</td>
</tr>
</tbody>
</table>
Chang's diagonal rule, page 774
Under standard state conditions, any species on the left of a given half-cell reaction will react *spontaneously* ($E_{\text{cell}}^o$ will be positive) with a species that appears on the right of any half-cell reaction located below it in the table of standard reduction potentials.

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<th><strong>Half-Reaction</strong></th>
<th><strong>$E^o$ (V)</strong></th>
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<tr>
<td>$F_2(g) + 2e^- \rightarrow 2F^-(aq)$</td>
<td>+2.87</td>
</tr>
<tr>
<td>$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$</td>
<td>+1.36</td>
</tr>
<tr>
<td>$Br_2(g) + 2e^- \rightarrow 2Br^-(aq)$</td>
<td>+1.07</td>
</tr>
<tr>
<td>$Zn^{2+} + 2e^- \rightarrow Zn(s)$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$Mg^{2+} + 2e^- \rightarrow Mg(s)$</td>
<td>-2.37</td>
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</tbody>
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$F_2(g) + 2Cl^-(aq) \rightarrow 2F^-(aq) + Cl_2(g)$

$Br_2(g) + 2Cl^-(aq) \rightarrow 2Br^-(aq) + Cl_2(g)$
**Oxidizing and Reducing Agents**

The more positive the $E_{\text{red}}^\circ$ value for a half-reaction, the greater the tendency for the reactant of the half-reaction to be reduced, and therefore, to oxidize another species.

Look at the half-reactions in the table of reduction potentials.

\[
\begin{align*}
F_2(g) + 2e^- &\rightarrow 2F^-(aq) \quad E_{\text{red}}^\circ = 2.87 \text{ V} \\
2H^+(aq) &\rightarrow H_2(g) \\
Li^+(aq) + e^- &\rightarrow Li(s) \quad E_{\text{red}}^\circ = -3.05 \text{ V}
\end{align*}
\]

$F_2$ is most easily reduced and consequently the strongest oxidizing reagent.

\[
F_2(g) + 2e^- \rightarrow 2F^-(aq) \quad E_{\text{red}}^\circ = 2.87 \text{ V}
\]

Lithium ion, Li$^+$, is the most difficult to reduce and is therefore the poorest oxidizing reagent.

\[
Li^+(aq) + e^- \rightarrow Li(s) \quad E_{\text{red}}^\circ = -3.05 \text{ V}
\]

However, the reverse reaction is favorable, and makes Li(s) the strongest reducing agent on the table.

F$^-(aq)$ is the weakest reducing agent on the table.
Free Energy Change

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

Faraday’s constant, \( F \), 96,485 C/mol (J/V mol), charge on one mole of electrons

\[
F = \left(6.022 \times 10^{23} \text{ mol}^{-1}\right) \left(1.6022 \times 10^{-19} \text{ C}\right) = 96485 \text{ C mol}^{-1}
\]

\( n \), number of electrons transferred in the reaction

Calculate the standard free energy change for the cells on page 6.
Effect of Concentration on Cell EMF: The Nernst Equation

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

\[-nFE = -nFE^\circ + RT \ln Q \]

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

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

\[ E = \frac{RT}{nF} \left( \ln \frac{K}{Q} \right) \]

\[ E = E^\circ - \frac{0.0257V}{n} \ln Q \]

Q will be concentration of ions on right side over concentration of ions on left side. Must be given.

Calculate E, for the following cells:
Mg(s)| Mg^{2+}(aq)|| Ni^{2+}(aq)| Ni(s); \ [Mg^{2+}] = 0.10 \text{ M}, [Ni^{2+}] = 1.0 \text{ M}
Zn(s)| Zn^{2+}(aq)|| Ni^{2+}(aq)| Ni(s) \ [Zn^{2+}] = 0.50 \text{ M}, [Ni^{2+}] = 0.20 \text{ M}
**$E^\circ$ and the Equilibrium Constant**

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

$$\ln K = \frac{nFE^\circ}{RT} = \frac{nE^\circ}{0.0257V} \quad K = e^{nFE^\circ/RT} = e^{nE^\circ/0.0257\ V}$$

$$\frac{RT}{F} = 0.0257\ V$$

For the cells on page 6, calculate the value of $K$. 
Electrochemical Determination of pH

Pt|H₂(1 atm.)|H⁺(? M) || Reference cathode

\[ E_{cell} = E_{H_2 \rightarrow H^+} + E_{ref} \]

\[ H_2(g) \rightarrow 2H^+(aq) + 2e^- \]

\[ E_{H_2 \rightarrow H^+} = (E^\circ_{H_2 \rightarrow H^+}) - \left( \frac{0.0592 V}{n} \right) \left( \log \frac{[H^+]^2}{P_{H_2}} \right) \]

\[ E_{H_2 \rightarrow H^+} = -\left( \frac{0.0592 V}{2} \right) \left( \log [H^+]^2 \right) \]

\[ E_{H_2 \rightarrow H^+} = -\left( \frac{0.0592 V}{2} \right)(2)(\log [H^+]) = (0.0592 V)(-\log [H^+]) = (0.0592 V)(pH) \]

The overall cell potential is:

\[ E_{cell} = (0.0592 V)(pH) + E_{ref} \]

\[ pH = \frac{E_{cell} - E_{ref}}{0.0592 V} \]
**Batteries and Fuel Cells**

Primary Batteries (not easily reversed; at equilibrium "dead")

Secondary Batteries (easily reversed or "recharged")
car battery

Fuel Cells (reactants supplied from external source)

**Corrosion**

Oxidation of most metals by oxygen is favorable.

Iron:

Cathode:

\[ O_2 (g) + 4 H^+(aq) + 4e^- \rightarrow 2 H_2O(l) \]

\[ E_{\text{red}}^0 = -0.14 \text{ V} \]

Anode:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} (aq) + 2e^- \]

\[ E_{\text{red}}^0 = -0.44 \text{ V} \]

**anodic inhibition** - coat with inert material, paint or layer of oxide of metal protecting (Al_2O_3)

**cathodic inhibition** - make Fe the cathode, use Zn or Mg as the anode (sacrificial metal)
**Electrolysis** - use of an electrical current to bring about chemical change.

Direction of electron flow

Battery

[Diagram showing the flow of electrons, oxidation and reduction processes at anode and cathode, salt bridge, and movement of ions (cations and anions)].

ANODE compartment
OXIDATION occurs

CATHODE compartment
REDUCTION occurs

Reduced species
Oxidized species
Cations
Anions
Salt bridge
Electrode (+)
Electrode (−)
Battery

 ℝeализация электролиза - использование электрического тока для превращения химических веществ.
Quantitative Aspects of Electrolysis - Counting Electrons

Current, \( I \) (amperes, A) = \( \frac{\text{electric charge (coulombs, C)}}{\text{time (seconds, s)}} \)

- Current times time, in seconds, gives charge in coulombs, \( Q = It \)
- Divide charge by Faraday's constant to get moles of e-
- Divide moles of electrons by moles of electrons per mole of metal reduced
- Divide moles of metal by the atomic weight of the metal to get grams of metal

\[
\text{Current} \left( \frac{C}{s} \right) \times \text{time} \left( s \right) \times \frac{1}{96485 \text{ C}} \times \frac{1}{\text{mol}e^-} \times \frac{\text{mol metal}}{\text{mol}e^-} \times \frac{g \text{ metal}}{\text{mol metal}} = g \text{ metal}
\]

\[
m = \frac{QM}{nF}
\]

\[
m = \frac{\text{charge} \times \text{molecular weight}}{\text{charge of metal} \times \text{Faraday's constant}}
\]

Calculate the mass of aluminum produced in 1.00 hr by the electrolysis of molten AlCl\(_3\) if the electrical current is 10.0 A.