Consider the reaction between Zn and Cu$^{2+}$

$$
Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu
$$

This will take place spontaneously in solution (i.e., $\Delta G^o < 0$, $K_{eq} > 1$)

...electron transfer...
Oxidation-reduction reactions

- Oxidation: Loss of electrons
  (consider oxidation of Fe to Fe$^{3+}$ as in Fe$_2$O$_3$, rust)

- Reduction: Gain of electrons
  (Reduction of formal charge)

\[
\text{Zn}_{(s)} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}_{(s)}
\]
Electrochemical Terms

**Redox Rxn:** Reactions that involve the transfer of electrons from one species to another.

In an electrochemical reaction, both an oxidation and a reduction must occur.

**Oxidation:** A species loses electrons
Species that *are oxidized* are known as *reducing agents*

\[
\begin{align*}
\text{Al} & \rightarrow \text{Al}^{3+} + 3e^- \\
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^-
\end{align*}
\]

**Reduction:** A species gains electrons
Species that *are reduced* are known as *oxidizing agents*

\[
\begin{align*}
\text{Fe}^{3+} + 1e^- & \rightarrow \text{Fe}^{2+} \\
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu}
\end{align*}
\]

**Overall Rxn**—Both oxidation and reduction must occur…

2e\(^-\) net transferred

\[
2 \text{Fe}^{3+} + \text{Zn} \rightarrow 2 \text{Fe}^{2+} + \text{Zn}^{2+}
\]

Zn is reducing agent
Fe is oxidizing agent
Electric Potential (E) – work is needed to move electrons in a wire or to move ions through solution to an electrode. With electricity we need work to move charge from a region of high electrical potential (high electrical pressure) to a region at another potential (lower electrical pressure). The work needed to move an electric charge through a conductor (e.g. wire) depends on total charge moved and potential difference.

Work (Joules) = E (volts) x Q (coulombs) units: V=J/C

\[ E_p = (E)(e) \]

\[ E_p: \text{electrostatic potential energy in } J; \]
\[ e: \text{charge of an } e \text{ in } C; \]
\[ E: \text{potential in } V \]

The potential energy \((E_p)\) of an electron \((1.6 \times 10^{-19} \text{ C})\) in a 1 V field is \(1.6 \times 10^{-19} \text{ J} = 1 \text{ eV}\)
Electrochemical Terms

**Electric Charge (C)** – magnitude of charge on one mole of electrons is known as the Faraday constant, F.

\[ Q = n \times F \]

\[ F = 96500 \text{ C/mol e}^- \quad 1.6 \times 10^{-19} \text{ C per e}^- \]

**Current (A)** – quantity of charge that flows per second.

\[ i = \frac{\partial q}{\partial t} = C \frac{\partial E}{\partial t} A \]

**Ampere (A)** \( A = C/s \)

**Faraday’s Law:** mole of substance reacting = it/nF
The electrochemical cell

Implied reaction:
Zn + Cu$^{2+}$ → Zn$^{2+}$ + Cu

(Note: Reax may not proceed as written when switch is closed in circuit!)

Half cell reactions:

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^{-}
\]
\[
\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu}
\]
An electrochemical cell is a system consisting of two half cell reactions connected in such a way that chemical reactions either uses or generates an electric current.

A voltaic cell or galvanic cell is an electrochemical cell in which a spontaneous reaction generates an electric current.

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \]
An **electrolytic cell** is an electrochemical cell in which an *electric current drives* an otherwise *nonspontaneous reaction*.

\[ \text{Zn}^{2+} + \text{Cu} \rightarrow \text{Zn} + \text{Cu}^{2+} \]

Note that the reaction is reversed from previous slide, i.e., Cu is oxidized.
Anode (oxidation)

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

Cathode (reduction)

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

Cell potential (volts)

\[ 0.55 \text{ Vdc} \]

Overall reaction:

\[ \text{Zn(s)} + \text{Cu}^{2+} + 2e \rightarrow \text{Zn}^{2+} \text{Cu(s)} + 2e \]
Cell layout

Anode

Cd(s) $\rightarrow$ Cd$^{2+}$(aq) + 2e$^-$

Cathode

2Ag$^+(aq)$ + 2e$^-$ $\rightarrow$ 2Ag(s)
Shorthand notation

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \]

**Anode**

\[ \text{Zn} | \text{Zn}^{2+} (\text{___M}) \parallel \text{Cu}^{2+}(\text{___M}) | \text{Cu} \]

Phase boundary with junction potential

**Cathode**

NO liquid junction potential (e.g., salt bridge)

Other examples:

\[ \text{Pt} | \text{H}_2(\text{g}) \ (a=1) | \text{H}^+ \ (a=1) \parallel \text{Cu}^{2+}(0.01\text{M}) | \text{Cu} \]

\[ \text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{KCl} \ (\text{sat’d}) \parallel \text{Fe}^{2+}(0.001\text{M}) | \text{Pt} \]
Standard Potentials, $E^\circ$

ALWAYS written as reduction reactions

$$ Zn^{2+} + 2e^- \rightarrow Zn \quad E^\circ = -0.762 \text{ V} $$

$$ Cu^{2+} + 2e^- \rightarrow Cu \quad E^\circ = +0.339 \text{ V} $$

$$ Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^\circ = +0.771 \text{ V} $$

$E^\circ$ assumes unit activity for all species!

Potentials are relative to standard hydrogen electrode (SHE)

$$ 2H^+ + 2e^- \rightarrow H_2 \quad E^\circ = 0.000 \text{ V} $$

$E^\circ$ value is indication of driving force for reduction

$E^\circ$ is a constant!

Formal Potentials, $E^{\circ'}$

Potentials for unique conditions (all species NOT at unit activity)
\[
\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}
\]

Zn is reducing agent
Cu\(^{2+}\) is oxidizing agent
**E<sub>cell</sub> calculation**

\[ E^0_{\text{cell}} = E^0_{\text{cat}} - E^0_{\text{an}} \]

Zn | Zn<sup>2+</sup> (0.2 M) || Cu<sup>2+</sup> (0.3 M) | Cu

\[ \text{Zn}^2+ + 2e^- \rightarrow \text{Zn} \quad E^o = -0.762 \text{ V} \]

\[ \text{Cu}^2+ + 2e^- \rightarrow \text{Cu} \quad E^o = +0.339 \text{ V} \]

\[ E^0_{\text{cell}} = E^0_{\text{cat}} - E^0_{\text{an}} \]

= 0.339 - (-0.762) = +1.101 V
Electrochemical potentials and thermodynamics

$$\Delta G^o = -nFE^o$$ where $F = 96,500 \text{coul} / \text{eq}$;

$n = \text{number of e}^- \text{ transferred}$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{nFE^o}{RT}$$

$$E^o = \frac{RT}{nF} \ln K = \frac{0.059}{n} \log K$$

Nernst equation:

$$E = E^o - \frac{RT}{nF} \ln Q$$

or

$$E = E^o - \frac{0.059}{n} \log Q \quad (T = 298K)$$

at equilibrium: $Q=K$, $E=0$

E has units of volts (J/coul)
Determining $E_{\text{cell}}$

$$E = E^o - \frac{RT}{nF} \ln Q$$

or

$$E = E^o - \frac{0.059}{n} \log Q \ (T = 298K)$$

If $E$ is for whole cell, then $Q$ looks like “$K$” for the complete balanced reaction and $E^o$ is $E^o_{\text{cell}}$

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{0.059}{2} \log \left[ \frac{Zn^{2+}}{Cu^{2+}} \right]$$

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

This can also be for half cells! In this case, “$Q$” is the expression in the $E^o$ (reduction) equation, i.e., “reduced over oxidized”.

For example:

$$E_{Cu} = E^o_{Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$$E_{Zn} = E^o_{Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]}$$

$$E_{\text{cell}} = E^o_{Cu} - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]} - \left\{ E^o_{Zn} - \frac{0.059}{2} \log \frac{1}{[Zn^{2+}]} \right\}$$

$$E_{\text{cell}} = (E^o_{Cu} - E^o_{Zn}) - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$
### Table 14-2  Reduction potentials of biological interest

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( E^\circ ) (V)</th>
<th>( E^\circ' ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 + 4	ext{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} )</td>
<td>+1.229</td>
<td>+0.816</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} )</td>
<td>+0.771</td>
<td>+0.771</td>
</tr>
<tr>
<td>( \text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^- )</td>
<td>+0.535</td>
<td>+0.535</td>
</tr>
<tr>
<td>Cytochrome ( a ) (Fe(^{3+})) + \text{e}^- \rightleftharpoons \text{cytochrome} ( a ) (Fe(^{2+}))</td>
<td>+0.290</td>
<td>+0.290</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2 )</td>
<td>+0.695</td>
<td>+0.281</td>
</tr>
<tr>
<td>Cytochrome ( c ) (Fe(^{3+})) + \text{e}^- \rightleftharpoons \text{cytochrome} ( c ) (Fe(^{2+}))</td>
<td>+0.254</td>
<td></td>
</tr>
<tr>
<td>2,6-Dichlorophenolindophenol + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{reduced} 2,6-dichlorophenolindophenol</td>
<td></td>
<td>+0.22</td>
</tr>
<tr>
<td>Dehydroascorbate + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{ascorbate} + \text{H}_2\text{O}</td>
<td>+0.390</td>
<td>+0.058</td>
</tr>
<tr>
<td>Fumarate + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{succinate}</td>
<td>+0.433</td>
<td>+0.031</td>
</tr>
<tr>
<td>Methylene blue + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{reduced} product</td>
<td>+0.532</td>
<td>+0.011</td>
</tr>
<tr>
<td>Glyoxylate + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{glycolate}</td>
<td>-</td>
<td>-0.090</td>
</tr>
<tr>
<td>Oxaloacetate + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{malate}</td>
<td>+0.330</td>
<td>-0.102</td>
</tr>
<tr>
<td>Pyruvate + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{lactate}</td>
<td>+0.224</td>
<td>-0.190</td>
</tr>
<tr>
<td>Riboflavin + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{reduced} riboflavin</td>
<td>-</td>
<td>-0.208</td>
</tr>
<tr>
<td>FAD + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{FADH}_2</td>
<td>-</td>
<td>-0.219</td>
</tr>
<tr>
<td>(Glutathione-S)_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2 \text{glutathione-SH}</td>
<td>-</td>
<td>-0.23</td>
</tr>
<tr>
<td>Safranine T + 2\text{e}^- \rightleftharpoons \text{leucosafiranine T}</td>
<td>-0.235</td>
<td>-0.289</td>
</tr>
<tr>
<td>(C_6H_5S)_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2C_6H_5SH</td>
<td>-</td>
<td>-0.30</td>
</tr>
<tr>
<td>( \text{NAD}^+ + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{NADH} )</td>
<td>-0.105</td>
<td>-0.320</td>
</tr>
<tr>
<td>( \text{NADP}^+ + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{NADPH} )</td>
<td>-</td>
<td>-0.324</td>
</tr>
<tr>
<td>Cystine + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2 \text{cysteine}</td>
<td>-</td>
<td>-0.340</td>
</tr>
<tr>
<td>Acetooacetate + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{L-\beta-hydroxybutyrate}</td>
<td>-</td>
<td>-0.346</td>
</tr>
<tr>
<td>Xanthine + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{hypoxanthine} + \text{H}_2\text{O}</td>
<td>-</td>
<td>-0.371</td>
</tr>
<tr>
<td>2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2</td>
<td>0.000</td>
<td>-0.414</td>
</tr>
<tr>
<td>Gluconate + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{glucose} + \text{H}_2\text{O}</td>
<td>-</td>
<td>-0.44</td>
</tr>
<tr>
<td>( \text{SO}_3^- + 2\text{e}^- + 2\text{H}^+ \rightleftharpoons \text{SO}_3^- + \text{H}_2\text{O} )</td>
<td>-</td>
<td>-0.454</td>
</tr>
<tr>
<td>2\text{SO}_3^- + 2\text{e}^- + 4\text{H}^+ \rightleftharpoons \text{S}_2\text{O}_3^- + 2\text{H}_2\text{O}</td>
<td>-</td>
<td>-0.527</td>
</tr>
</tbody>
</table>
ΔG > 0 or E < 0 then reaction is nonspontaneous
ΔG < 0 or E > 0 then reaction is spontaneous

ΔG = -nFE

**Free Energy and Potential** – the maximum work obtainable from a balanced electrochemical rxn can be related to molar amounts of reactants. The sign and magnitude of the potential can be used to determine spontaneity of rxn and to measure total energy produced.
Ohm’s Law – current flowing through circuit is directly proportional to potential

\[ E = IR \]

**Power** – is the work done per unit time

\[ P = IE \quad \text{or} \quad P = I^2R \]

**Faraday’s Law:** mole of substance reacting = \( \frac{it}{nF} \)

**Electric Charge (C)** – magnitude of charge on one mole of electrons is known as the Faraday constant, F.

\[ Q = n F \quad \text{F} = 96500 \text{ C/mol e}^- \quad 1.6\times10^{-19} \text{ C per e}^- \]

**Current (A)** – quantity of charge that flows per second.

\[ i = \frac{\partial q}{\partial t} = C \frac{\partial E}{\partial t} A \quad \text{Ampere (A)} \quad A = \frac{C}{s} \]