Chapter 19
Electrochemistry

Review: Reduction-Oxidation Reactions (See Chapter 4) "REDOX"

Driving force: transfer/shift of electrons

“LEO the lion says GER”
Loss of Electrons is Oxidation; Gain of Electrons is Reduction

“OIL RIG”
Oxidation Is Loss; Reduction Is Gain

“ELMO”
Electron Loss Means Oxidation

The substance that is oxidized = the reducing agent.
The substance that is reduced = the oxidizing agent.

A reaction is a “redox reaction” if the oxidation numbers of one or more atoms changes.
e.g.,

\[
\begin{align*}
2\text{Zn}(s) + \text{O}_2(g) & \rightarrow 2\text{ZnO}(s) \\
\text{ON of Zn changes from 0 to +2} & \text{ON of O changes from 0 to } -2
\end{align*}
\]

∴ This is a redox reaction, and
Zn was oxidized and was the reducing agent, and
O\(_2\) was reduced and was the oxidizing agent.

Electrochemistry

• the study of interchange of chemical and electrical energy
• involves redox reactions

Goal: to be able to do useful things (work) by generating an electric current.

Much of the experimental evidence for thermodynamic concepts arose from electrochemical experiments!

Experimentally, this reaction is spontaneous (i.e., \(\Delta G^\circ\) is negative):

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

The problem is that the electron transfer occurs at the interface between the substances. To do useful electrical work, we need to force the electrons to travel through a wire; i.e., the reduction and oxidation processes must be separated!
We need to add an apparatus that will allow electrical neutrality to be maintained in both beakers without allowing the contents of the beakers to mix.

- **Salt bridge**
  - allows ions to flow, maintaining electrical neutrality
  - contains a strong electrolyte in a gelatinous matrix or a porous/absorbent substance saturated with a strong electrolytes solution, with the ends closed with a glass frit.
  - is an “external source” of ions.

- **Porous disk**
  - prevents solutions from mixing significantly but allows ions to cross, maintaining charge balance.
  - is an “internal source” of ions.

**voltaic (galvanic) cell**: device in which chemical energy is converted to electrical energy

**electrodes**: metallic conductors that make electrical contact with contents of half-cells

- **anode**: electrode at which oxidation occurs
- **cathode**: electrode at which reduction occurs

In the salt bridge: anions flow toward/into anode compartment
cations flow toward/into cathode compartment
**Cell Potential, \( E (E^\circ) \)**

measured in volts  
1 volt = 1 joule energy per coulomb charge transferred \([1 \text{ V} = 1 \text{ J} \cdot \text{C}^{-1}]\)

\[ E\text{\textsuperscript{\textdegree}}_{\text{CELL}} = E\text{\textsuperscript{\textdegree}}_{\text{OVERALL}} = E\text{\textsuperscript{\textdegree}}_{\text{OXIDATION}} + E\text{\textsuperscript{\textdegree}}_{\text{REDUCTION}} = E\text{\textsuperscript{\textdegree}}_{\text{CATHODE}} - E\text{\textsuperscript{\textdegree}}_{\text{ANODE}} \]

\[ E\text{\textsuperscript{\textdegree}}_{\text{OXIDATION}} = -E\text{\textsuperscript{\textdegree}}_{\text{ANODE}} \]

\[ E\text{\textsuperscript{\textdegree}}_{\text{REDUCTION}} = E\text{\textsuperscript{\textdegree}}_{\text{CATHODE}} \]

E.g., the two tabulated reductions \( \text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn} \quad E\text{\textsuperscript{\textdegree}}_{\text{RED}} = -0.76 \text{ V} \)

and \( \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} \quad E\text{\textsuperscript{\textdegree}}_{\text{RED}} = +0.34 \text{ V} \)

Reverse Zn half-reaction: \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \quad E\text{\textsuperscript{o}}_{\text{OX}} = +0.76 \text{ V} \) (\( = -E\text{\textsuperscript{\textdegree}}_{\text{ANODE}} = -(--0.76 \text{ V}) \))

Add to Cu half-reaction: \( \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} \quad E\text{\textsuperscript{\textdegree}}_{\text{RED}} = +0.34 \text{ V} \) (\( = E\text{\textsuperscript{\textdegree}}_{\text{CATHODE}} \))

For \( \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Zn}^{2+} \): \( E\text{\textsuperscript{\textdegree}}_{\text{CELL}} = +1.10 \text{ V} \)

We need a reference to measure half-cell \( E\text{\textsuperscript{\textdegree}} \) s…

**“Standard Hydrogen Electrode” (SHE)** (really a half-cell)

- Assigned exactly zero volts

\[ \text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^- \quad \text{OR} \quad 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \]

\[ \text{H}_2(\text{g}) \text{ atm} \]

Cell Shorthand Notation

| anode solid | species oxidized, if different | oxidation product | species reduced | reduction product | cathode solid, if different |

E.g., For \( \text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \): \( \text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)} \)

E.g., For \( 2\text{H}^+(\text{aq}) + \text{Fe(s)} \rightarrow \text{H}_2(\text{g}) + \text{Fe}^{2+}(\text{aq}) \): \( \text{Fe(s)} | \text{Fe}^{2+}(\text{aq}) || \text{H}^+(\text{aq}) | \text{H}_2(\text{g}) | \text{Pt(s)} \)

\( \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \) \( \text{ox} \) \( \text{anode} \)

\( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \) \( \text{red} \) \( \text{cathode (SHE)} \)

\[ E\text{\textsuperscript{\textdegree}} \text{ and Reaction Spontaneity—or—Predicting Redox Reactions} \]

- Redox reactions that have a positive overall \( E\text{\textsuperscript{\textdegree}} \) are spontaneous as written.

\[ \Delta G = -nFE\textsuperscript{\textdegree} \]

\( n \) = moles \( e^- \) transferred

\( F \) = Faraday constant

96,485 Coul/mol \( e^- \)

\( \Delta G = -\frac{nFE}{F} \)

\( n \), \( F \) always positive

\( \therefore \Delta G, \Delta G\text{\textsuperscript{\textdegree}} \) negative

if \( E \), \( E\text{\textsuperscript{\textdegree}} \) positive
Calculate $E^\circ$ for a galvanic cell using $\text{Ag}/\text{Ag}^+$ and $\text{Cr}/\text{Cr}^{3+}$ half-cells.

$\text{Ag}/\text{Ag}^+$  $E^\circ_{\text{red}} = +0.80\text{ V}$
$\text{Cr}/\text{Cr}^{3+}$  $E^\circ_{\text{red}} = -0.74\text{ V}$

$\text{Cr}(s) \rightarrow \text{Cr}^{3+}(aq) + 3e^-$  $E^\circ_{\text{ox}} = -E_{\text{anode}} = -(0.74\text{ V})$
$3 \text{ Ag}^+(aq) + 3e^- \rightarrow 3\text{ Ag}(s)$  $E^\circ_{\text{red}} = E_{\text{cathode}} = +0.80\text{ V}$

$3\text{ Ag}^+(aq) + \text{ Cr}(s) \rightarrow \text{ Cr}^{3+}(aq) + 3\text{ Ag}$

$\Sigma E^\circ = 1.54\text{ V} \quad (0.80\text{ V} - (-0.74\text{ V}))$

$2\text{ Cr} + 3\text{ Sn}^{2+} \rightarrow 3\text{ Sn} + 2\text{ Cr}^{3+}$

$3(\text{ Sn}^{2+} + 2e^- \rightarrow \text{ Sn})$

$2(\text{ Cr} \rightarrow \text{ Cr}^{3+} + 3e^-)$

$n = 6 \uparrow$

$\Delta G^\circ = -nFE^\circ = -6(96,485)(+0.60\text{ V})$

$= -350,000\text{ J}$

$= -350\text{ kJ}$