Electrochemical System

8-10 Electrochemical systems

- Electrochemical system and its thermodynamics
- Chemical reactions in electrochemical cells and the Nernst equation
- The relationship between the cell emf and the equilibrium constant, Gibbs energies and reaction entropies
- Thermodynamics of Galvanic cells and Fuel cell

It is expected that students are able to:

- Define the electrochemical system.
- Explain about electrochemical cell and differentiate galvanic cell and electrolyte cell
- Apply Nernst equation of thermodynamic principles to electrochemical cells.
- Determine $\Delta G^0$, $\Delta K^0$, $\Delta S^0$, $\Delta H^0$, $\Delta C p^0$ activity coefficient and pH of cell’s chemical reaction.
- Understand the cell emf in IUPAC convention.
- Estimate the liquid junction potential from emf measurement.
**Quick Review**

- **Redox**: Reduction-Oxidation, an electron transfer process
- **Oxidation**: loss one or more e⁻
- **Reduction**: gain one or more e⁻
- **Oxidation number**: the charge of the atom or molecule would have
  - Pure element and neutral compound → 0
  - Mono- and poly-atomic ions → sum of oxidation number is ionic charge

**Check your understanding**

- **CaBr₂**: Ca = +2, Br = -1, Oxidation number (pure element), 
  $$= (+2) + 2(-1) = 0$$

- **HCO₃⁻**: 
  - O = -2
  - H = +1
  - C = ?

- **K₂Cr₂O₇**: 
  - O = -2
  - K = +1
  - Cr = ?
# Redox Terminology

## Adding Zn(s) in acid solution

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>Zn(s) + 2H⁺(aq) → Zn²⁺(aq) + H₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OXIDATION</strong></td>
<td></td>
</tr>
<tr>
<td>- One reactant loses electrons</td>
<td>Zinc loses electrons.</td>
</tr>
<tr>
<td>- Reducing agent is oxidized</td>
<td>Zinc is the reducing agent</td>
</tr>
<tr>
<td>- Oxidation number increases</td>
<td>and becomes oxidized.</td>
</tr>
<tr>
<td>- Oxidation number decreases</td>
<td>The oxidation number of Zn</td>
</tr>
<tr>
<td></td>
<td>increases from 0 to +2.</td>
</tr>
</tbody>
</table>

**REDUCTION**

- Other reactant gains electrons
- Oxidizing agent is reduced
- Oxidation number decreases

- Hydrogen ion gains electrons.
- Hydrogen ion is the oxidizing agent and becomes reduced.
- The oxidation number of H⁺ decreases from +1 to 0.

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**Oil Rig**

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**Red Cat**
**Electrochemistry**: study of the interchange between chemical change and electrical work

**Electrochemical cells**: systems utilizing a redox reaction to produce or use electrical energy

Quick Review (Cont’d)

Zn(s) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(s)
Cell and Cell Notation

- **Anode**: Electrode site of oxidation
- **Cathode**: Electrode site of reduction
- Electrons flow from anode to cathode
- **Salt bridge**: Maintains electrical neutrality, allows current to flow, prevent solutions mixing
  - Positive ion migrates to cathode
  - Negative ion migrates to anode
- **Cell notation**: **Anode | Salt Bridge | Cathode**
Cell Potential

The difference in electrical potential between the anode and cathode is called:

- **cell voltage**
- **electromotive force (emf)**
- **cell potential**

\[ E_0^{Cell} = E_0^{oxidation} + E_0^{reduction} \]  
(Unit: Volts)

Note: Volt (V) = Joule (J) / Coulomb (C)

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### 19.1 Standard Reduction Potentials at 25°C

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^0 ) (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{O}_3(g) + 2\text{H}^+(aq) + 2e^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O} )</td>
<td>+2.07</td>
</tr>
<tr>
<td>( \text{Co}^{3+}(aq) + e^- \rightarrow \text{Co}^{2+}(aq) )</td>
<td>+1.82</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \rightarrow 2\text{H}_2\text{O} )</td>
<td>+1.77</td>
</tr>
<tr>
<td>( \text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O} )</td>
<td>+1.70</td>
</tr>
<tr>
<td>( \text{Ce}^{4+}(aq) + e^- \rightarrow \text{Ce}^{3+}(aq) )</td>
<td>+1.61</td>
</tr>
<tr>
<td>( \text{MnO}_4(aq) + 8\text{H}^+(aq) + 5e^- \rightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O} )</td>
<td>+1.51</td>
</tr>
<tr>
<td>( \text{Au}^{3+}(aq) + 3e^- \rightarrow \text{Au}(s) )</td>
<td>+1.50</td>
</tr>
<tr>
<td>( \text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq) )</td>
<td>+1.36</td>
</tr>
<tr>
<td>( \text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O} )</td>
<td>+1.33</td>
</tr>
<tr>
<td>( \text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O} )</td>
<td>+1.23</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O} )</td>
<td>+1.23</td>
</tr>
<tr>
<td>( \text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(aq) )</td>
<td>+1.07</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{Br}_2(l) + 2e^- & \rightarrow 2\text{Br}^-(aq) & +1.07 \\
\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- & \rightarrow \text{NO}(g) + 2\text{H}_2\text{O} & +0.96 \\
2\text{Hg}^{2+}(aq) + 2e^- & \rightarrow \text{Hg}^2+(aq) & +0.92 \\
\text{Hg}_2^{2+}(aq) + 2e^- & \rightarrow 2\text{Hg}(l) & +0.85 \\
\text{Ag}^+(aq) + e^- & \rightarrow \text{Ag}(s) & +0.80 \\
\text{Fe}^{3+}(aq) + e^- & \rightarrow \text{Fe}^{2+}(aq) & +0.77 \\
\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- & \rightarrow \text{H}_2\text{O}_2(aq) & +0.68 \\
\text{MnO}_4^-(aq) + 2\text{H}_2\text{O} + 3e^- & \rightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq) & +0.59 \\
\text{I}_2(s) + 2e^- & \rightarrow 2\text{I}^-(aq) & +0.53 \\
\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^-(aq) & +0.40 \\
\text{Cu}^{2+}(aq) + 2e^- & \rightarrow \text{Cu}(s) & +0.34 \\
\text{AgCl}(s) + e^- & \rightarrow \text{Ag}(s) + \text{Cl}^-(aq) & +0.22 \\
\text{SO}_3^{2-}(aq) + 4\text{H}^+(aq) + 2e^- & \rightarrow \text{SO}_2(g) + 2\text{H}_2\text{O} & +0.20
\end{align*}
\]
Standard reduction potential ($E^0$) is the voltage associated with a reduction reaction at an electrode when all solutes are 1 M and all gases are at 1 atm.

**Standard Electrode Potentials**

- $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $-0.83$
- $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ $-1.18$
- $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $-1.66$
- $Be^{2+}(aq) + 2e^- \rightarrow Be(s)$ $-1.85$
- $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $-2.37$
- $Na^+(aq) + e^- \rightarrow Na(s)$ $-2.71$
- $Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$ $-2.87$
- $Sr^{2+}(aq) + 2e^- \rightarrow Sr(s)$ $-2.89$
- $Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$ $-2.90$
- $K^+(aq) + e^- \rightarrow K(s)$ $-2.93$
- $Li^+(aq) + e^- \rightarrow Li(s)$ $-3.05$

**Reduction Reaction**

$2e^- + 2H^+ (1 \text{ M}) \rightarrow H_2 (1 \text{ atm})$

$E^0 = 0 \text{ V}$

Reference electrode

Standard hydrogen electrode (SHE)
Note: Copper reduction potential, $E^0 = +0.34$
(If copper is reduced (at cathode), voltmeter can give a reading- positive)

Note: Zn reduction potential is negative.
Change Zn as anode.
$E^0$ is for the reaction as written

The half-cell reactions are reversible; the sign of $E^0$ changes when the reaction is reversed

Changing the stoichiometric coefficients of a half-cell reaction does not change the value of $E^0$

The more positive $E^0$ the greater the tendency for the substance to be reduced

Spontaneity of Redox Reaction

$$E^0_{\text{Cell}} = E^0_{\text{oxidation}} + E^0_{\text{reduction}}$$

$E^0_{\text{reduction}} = -E^0_{\text{oxidation}}$

$+$ $E^0_{\text{CELL}}$: spontaneous reaction

$E^0_{\text{CELL}} = 0$: equilibrium

$-$ $E^0_{\text{CELL}}$: non-spontaneous reaction

More positive $E^0_{\text{CELL}}$ means stronger oxidizing agent or more likely to be reduced
Balance the Half-Cell Reactions

- Write separate equations (half-reactions) for oxidation and reduction
- For each half-reaction
  - Balance elements involved in e⁻ transfer
  - Balance number e⁻ lost and gained
  - To balance e⁻ multiply each half-reaction by whole numbers
- Add half-reactions/cancel like terms (e⁻)
- Check that all atoms and charges balance

Check your understanding

![Diagram of a Zn(s) | Zn²⁺ (1.0 M) solution | Cu²⁺ (1.0 M) solution | Cu(s) cell with electrons and ions]
Check your understanding

A half-cell reduction reaction is

$$\text{Fe(OH)}_2 (s) + 2e^- \rightarrow \text{Fe} (s) + 2\text{OH}^- (aq) \quad E^0 = -0.877 \text{ V}$$

Is to combine with another half-cell, which the reduction reaction is given as:

a) $$\text{Al}^{3+} (aq) + 3e^- \rightarrow \text{Al} (s) \quad E^0 = -1.66 \text{ V}$$

b) $$\text{AgBr} (s) + e^- \rightarrow \text{Ag} (s) + \text{Br}^- (aq) \quad E^0 = +0.071 \text{ V}$$

Determine $E^0_{\text{cell}}$, and whether Fe is oxidized or reduced.

Nernst Equation

$$\Delta G = \Delta G^0 + RT \ln Q$$

$$\Delta G^0 = -nFE^0_{\text{cell}}$$

$$-nFE_{\text{cell}} = -nFE^0_{\text{cell}} + RT \ln Q$$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT \ln Q}{nF}$$

Note: At equilibrium, $\Delta G = 0$, thus $E_{\text{cell}} = 0$.
Faraday, \( F \): charge on 1 mole e\(^-\)
\[ F = 96485 \text{ C/mole} \]

\[ \Delta G^0 = -nF \overline{E}_{\text{cell}} \]

\[ \Delta G^0 = -RT \ln K \]
\[ \Delta G^0 = -nF \overline{E}_{\text{cell}} \]

\[ E_{\text{cell}}^0 = \frac{RT}{nF} \ln K \]

\[ RT = \left( \frac{8.31}{\text{molK}} \right) (298K) = 0.0257 \]
\[ 96485 \text{ C/mole} \]

\[ E_{\text{cell}}^0 = \frac{0.0257}{n} \ln K = \frac{0.0592}{n} \log K \]

### Interrelationship of \( \Delta G^0, E^0, \) and \( K \)

- \( \Delta G^0 = -nF \overline{E}_{\text{cell}} \)
- \( \Delta G^0 = -RT \ln K \)

**Reaction at standard-state conditions**

<table>
<thead>
<tr>
<th>( \Delta G^0 )</th>
<th>( K )</th>
<th>( E_{\text{cell}}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0</td>
<td>&gt; 1</td>
<td>&gt; 0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>&lt; 1</td>
<td>&lt; 0</td>
</tr>
</tbody>
</table>
**Entropy Change**

To obtain the entropy change for the cell reaction

\[
\Delta S^o_R = -\left(\frac{\partial \Delta G^o_R}{\partial T}\right)_p = nF\left(\frac{\partial E^o}{\partial T}\right)_p 
\]

The reaction entropy related to \(\Delta G^o_R\)

Measurement of the \(T\) dependence of \(E^o\) can be used to determine \(\Delta S^o_R\)

**Enthalpy Change**

The reaction entropy related to \(\Delta G^o_R\)

\[
\Delta H^o = \Delta G^o + T\Delta S^o 
\]

\[
\Delta H^e = -nFE^o + nFT\left(\frac{\partial E^o}{\partial T}\right)_p 
\]
Example (from text book)

The half-cell reduction reactions,

\[ \text{Fe}^{3+} \text{(aq)} + e^- \rightarrow \text{Fe}^{2+} \text{(aq)} \quad E^o = +0.771 \text{ V} \]

\[ \text{Fe}^{2+} \text{(aq)} + 2e^- \rightarrow \text{Fe} \text{(s)} \quad E^o = -0.447 \text{ V} \]

Calculate \( E^o \) for half-cell reduction reaction

\[ \text{Fe}^{3+} \text{(aq)} + 3e^- \rightarrow \text{Fe} \text{(s)} \]

Example

Calculate \( \Delta G^o_r \) and the **equilibrium constant** at 298.15K for two half-cell reduction reactions:

\[ \text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l) \]

\( E^o = +1.232 \text{ V} \)

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

\( E^o = 0.00 \text{ V} \)
Example

The standard potential $E^\circ$ for a given cell in which a two electron transfer takes place is 1.10 V at 298.15 K and $(\partial E^\circ/\partial T) = -6.50 \times 10^{-5}$ V K$^{-1}$. Calculate $\Delta G^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, $\Delta H^\circ_{\text{rxn}}$. Assume that $n = 2$.

Check your understanding

Calculate the equilibrium constant at 298.15 K for the following half-cell reactions

a) Cathode: $\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$ \hspace{1cm} $E^\circ = +0.957$ V
   Anode: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ \hspace{1cm} $E^\circ = -1.229$ V

b) Anode: $\text{Cd(OH)}_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$ \hspace{1cm} $E^\circ = -0.809$V
   Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ \hspace{1cm} $E^\circ = +0.401$V
Example

Calculate the equilibrium constant at 25°C for the reaction occurring in the Daniell cell, if the standard EMF is 1.10 V.

Calculate the equilibrium constant for the reaction

\[ \text{H}_2 + 2\text{Fe}^{3+} \rightleftharpoons 2\text{H}^+ + 2\text{Fe}^{2+} \]

Galvanic cell vs. Electrolytic cell
The Basis of a Voltaic and an Electrolytic Cell

![Diagram of voltaic cell and electrolytic cell with reactions and components labeled.]

**A Voltaic Cell**
- Oxidation half-reaction: Sn(s) → Sn^{2+}(aq) + 2e^-
- Reduction half-reaction: Cu^{2+}(aq) + 2e^- → Cu(s)
- Overall reaction: Sn(s) + Cu^{2+}(aq) → Sn^{2+}(aq) + Cu(s)

**B Electrolytic Cell**
- Oxidation half-reaction: Cu(s) → Cu^{2+}(aq) + 2e^-
- Reduction half-reaction: Sn^{2+}(aq) + 2e^- → Sn(s)
- Overall reaction: Cu(s) + Sn^{2+}(aq) → Cu^{2+}(aq) + Sn(s)

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Voltaic vs. Electrolytic Cells

**Table 21.4 Comparison of Voltaic and Electrolytic Cells**

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>( \Delta G )</th>
<th>( E_{cell} )</th>
<th>Electrode</th>
<th>Name</th>
<th>Process</th>
<th>Sign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltaic</td>
<td>&lt;0</td>
<td>&gt;0</td>
<td>Anode</td>
<td>Oxidation</td>
<td>−</td>
<td></td>
</tr>
<tr>
<td>Voltaic</td>
<td>&lt;0</td>
<td>&gt;0</td>
<td>Cathode</td>
<td>Reduction</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Electrolytic</td>
<td>&gt;0</td>
<td>&lt;0</td>
<td>Anode</td>
<td>Oxidation</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Electrolytic</td>
<td>&gt;0</td>
<td>&lt;0</td>
<td>Cathode</td>
<td>Reduction</td>
<td>−</td>
<td></td>
</tr>
</tbody>
</table>
### Galvanic cell vs. Electrolytic cell

<table>
<thead>
<tr>
<th>Electrochemical cell (Galvanic Cell)</th>
<th>Electrolytic cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Converts chemical energy into electrical energy</td>
<td>Converts electrical energy into chemical energy</td>
</tr>
<tr>
<td>Redox reaction is spontaneous and is responsible for the production of electrical energy</td>
<td>Redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction</td>
</tr>
<tr>
<td>The two half-cells are set up in different containers, being connected through the salt bridge or porous partition</td>
<td>Both the electrodes are placed in a same container in the solution of molten electrolyte</td>
</tr>
<tr>
<td>Anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.</td>
<td>Here, the anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.</td>
</tr>
<tr>
<td>The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.</td>
<td>The external battery supplies the electrons. They enter through the cathode and come out through the anode.</td>
</tr>
</tbody>
</table>