**Unit 7: Reduction, Oxidation and Electrochemistry**

**Chapter 17: Electrochemistry**

**4.9: Oxidation-Reduction Reactions**

*Reduction-Oxidation Reactions (Redox Rxn):* - chemical reactions where there is a transfer of electron(s).

*Oxidation States (Oxidation Number):* - a number that is arbitrary assigned to an atom in an element, molecule, and polyatomic ions to account for the number of electrons in redox reaction.

**Rules for Assigning Oxidation Numbers:**

1. **Natural Elements (include diatomic and polyatomics) have an Oxidation Number of 0.**
   - Examples: Na\((s)\), O\(_2\)\((g)\), O\(_3\)\((g)\), H\(_2\)\((g)\), F\(_2\)\((g)\), P\(_4\)\((s)\), and Hg\((l)\) all have an oxidation number of 0.

2. **Single Atomic Ions have an Oxidation Number Equals to its Charge.**
   - Example: K\(^+\) has an oxidation number of +1.

3. **Oxygen in Binary Compound and Polyatomic Ions has an Oxidation Number of \(-2\).**
   - Examples: CO\(_2\), CO, SO\(_3\), SO\(_2\), CO\(_2\)\(^2-\), SO\(_2\)\(^2-\) and H\(_2\)O all have an oxidation number of \(-2\) for oxygen. 
     - An exception occurs in peroxides (compound containing O\(_2\)\(^2-\)) where the oxygen has an oxidation number of \(-1\).

4. **Hydrogen in Binary Compounds and Polyatomic Ions has an Oxidation Number of +1.**
   - Examples: H\(_2\)O, HCl, HBr, CH\(_4\), NH\(_4\)\(^+\) and H\(_2\)S all has an oxidation number of +1 for hydrogen.

5. **In Binary Compounds, the Atom that has the most attraction to electrons (HIGHER Electronegativity) is assigned the NEGATIVE Oxidation Number. This Negative Oxidation Number is the SAME as its Ionic Charge.**
   - Examples: HF: F is more electronegative. Thus, F has an oxidation number of −1.
     - NH\(_3\): N is more electronegative. Thus, N has an oxidation number of −3.
     - H\(_2\)S: S is more electronegative. Thus, S has an oxidation number of −2.

6. **The Sum of all Oxidation Numbers is 0 for all Electrically Neutral Compounds.**
   - Examples: CO: Oxidation numbers: O = −2; C = +2 \[ (+2) + (−2) = 0 \]
     - SO\(_2\): Oxidation numbers: O = −2; S = +4 \[ (+4) + 2(−2) = 0 \]

7. **The Sum of all Oxidation Numbers is Equal to the Overall Charge for all Polyatomic Ions.**
   - Examples: CO\(_3\)\(^2-\): Oxidation numbers: O = −2; C = +4 \[ (+4) + 3(−2) = −2 \]
     - SO\(_4\)\(^2-\): Oxidation numbers: O = −2; S = +6 \[ (+6) + 4(−2) = −2 \]

**Note:** Same Atom from different chemical species might NOT have the Same Oxidation Number.

We write the charges of ionic species as \(n^+\) or \(n^-\). Oxidation numbers are written as +\(n\) or −\(n\).
Example 1: Find the oxidation number for all atoms in each of the following elements or compounds:

a. NiO₂

Oxidation Numbers: O = −2  
Ni: \( n + 2(−2) = 0 \)  
\( n = +4 \)

b. P₄O₁₀

Oxidation Numbers: O = −2  
P: \( 4n + 10(−2) = 0 \)  
\( n = +5 \)
c. N₂

Oxidation Numbers: N₂ Diatomic Element  
\( n = 0 \)

d. SF₄

Oxidation Numbers: F = −1  
S: \( n + 4(−1) = 0 \)  
\( n = +4 \)
e. N₂H₄

Oxidation Numbers: H = +1  
N: \( 2n + 4(+1) = 0 \)  
\( n = −2 \)
f. Fe₃O₄

Oxidation Numbers: O = −2  
Fe: \( 3n + 4(−2) = 0 \)  
\( n = +\frac{8}{3} \)
g. KMnO₄

Oxidation Numbers: O = −2  
K = +1  
Mn: \((+1) + n + 4(−2) = 0 \)  
\( n = +7 \)
h. Na₂C₂O₄ or Na₂OOCOO

Oxidation Numbers: O = −2  
Na = +1  
C: \( 2(+1) + 2n + 4(−2) = 0 \)  
\( n = +3 \)
i. XeOF₄

Oxidation Numbers: O = −2  
Xe: \( n + (−2) + 4(−1) = 0 \)  
\( n = +6 \)

Example 2: Find the oxidation number for all atoms in each of the following polyatomic ions.

a. OCl⁻

Oxidation Numbers: O = −2  
Cl: \((−2) + n = −1 \)  
\( n = +1 \)
b. ClO₂⁻

Oxidation Numbers: O = −2  
Cl: \( n + 2(−2) = −1 \)  
\( n = +3 \)
c. ClO₃⁻

Oxidation Numbers: O = −2  
Cl: \( n + 3(−2) = −1 \)  
\( n = +5 \)
d. ClO₄⁻

Oxidation Numbers: O = −2  
Cl: \( n + 4(−2) = −1 \)  
\( n = +7 \)
e. NO₂⁻

Oxidation Numbers: O = −2  
N: \( n + 2(−2) = −1 \)  
\( n = +3 \)
f. NO₃⁻

Oxidation Numbers: O = −2  
Fe: \( n + 3(−2) = −1 \)  
\( n = +5 \)
g. UO₂²⁺

Oxidation Numbers: O = −2  
U: \( n + 2(−2) = +2 \)  
\( n = +6 \)
h. S₂O₃²⁻

Oxidation Numbers: O = −2  
S: \( 2n + 3(−2) = −2 \)  
\( n = +2 \)
i. Cr₂O₇²⁻

Oxidation Numbers: O = −2  
Cr: \( 2n + 7(−2) = −2 \)  
\( n = +6 \)

Oxidation Reactions: - reactions that **LOSE Electrons** (LEO – “Losing Electrons” – Oxidation) or an **INCREASE (Oxidation Number)**,  
- an **INCREASE in the number of Oxygen Atoms in the species** is a sign of oxidation reaction.  
- a **DECREASE in the number of HYDROGEN atoms in the species** is a sign of oxidation reaction.

Examples:  
\[ \text{Fe} (s) \rightarrow \text{Fe}^{3+} (aq) + 3e^- \]  
\( 0 \) to \(+3 \)  
(Lost 3 Electrons - Oxidation)  
(Increased Oxidation Number - Oxidation)

\[ 2 \text{Cr}^{3+} (aq) + 7 \text{H}_2\text{O} (l) \rightarrow \text{Cr}_2\text{O}_7^{2-} (aq) + 14 \text{H}^+ (aq) + 6e^- \]  
\(+3 \) to \(+6 \)  
(Lost 6 Electrons – Oxidation)  
(Increased Oxidation Number - Oxidation)
Reduction Reactions: - reactions that **GAIN Electrons (GER – “Gaining Electrons” – Reduction)** or a **DECREASE (Reduction)** in Oxidation Number.

**Examples:**

\[ \text{F}_2 (g) + 2e^- \rightarrow 2 \text{F}^- (aq) \]  
\[ \text{Gained 2 Electrons - Reduction} \]

\[ \text{MnO}_4^- (aq) + 8 H^+ (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + 4 \text{H}_2\text{O} (l) \]  
\[ \text{Gained 5 Electrons - Reduction} \]

**Half-Reactions:** - part of the redox reaction where it shows either the oxidation reaction or the reduction reaction.
- electrons are usually present in either side of the half-reaction.
- **Oxidation half-reaction** has **Electrons on the Product Side (Losing Electrons).**
- **Reduction half-reaction** has **Electrons on the Reactant Side (Gaining Electrons).**

**Oxidizing Agent:** - a chemical species that **Accepts (Gains) Electrons from an Oxidized species.**
- it **helps another species to oxidize** but itself being **reduced** (gained electrons or decreased in oxidation number).
- in another words, **Reducing Species = Oxidizing Agent (GER-OA)**

**Reducing Agent:** - a chemical species that **Donates (Lose) Electrons from a Reduced species.**
- it **helps another species to reduce** but itself being **oxidized** (lost electrons or increased in oxidation number).
- in another words, **Oxidizing Species = Reducing Agent (LEO-RA)**

**Example 1:** Classify if the following reactions are redox reaction. For each of the redox reaction identified, label the reducing agent and oxidizing agent. Propose a reduction half-reaction and oxidation half-reaction.

a. \[ 4 \text{Al} (s) + 3 \text{O}_2 (g) \rightarrow 2 \text{Al}_2\text{O}_3 (s) \]

  - **Oxidizing Agent = O}_2 (g)**  
  - **Reducing Agent = Al (s)**

  **Oxidation Half-Reaction:** \[ \text{Al} (s) \rightarrow \text{Al}^{3+} + 3e^- \]  
  **Losing Electrons**

  **Reduction Half-Reaction:** \[ \text{O}_2 (g) + 4e^- \rightarrow 2 \text{O}^2- \]  
  **Gaining Electrons**

b. \[ \text{HCl} (aq) + \text{NaF} (aq) \rightarrow \text{HF} (aq) + \text{NaCl} (aq) \]

  **Hydrogen Oxidation #:** \[ +1 \rightarrow +1 \]  
  **No Change**

  **Chlorine Oxidation #:** \[ -1 \rightarrow -1 \]  
  **No Change**

  **Sodium Oxidation #:** \[ +1 \rightarrow +1 \]  
  **No Change**

  **Fluorine Oxidation #:** \[ -1 \rightarrow -1 \]  
  **No Change**

  **(No Change in the Oxidation Number of any Atoms – NOT a Redox Reaction)**
c. \( \text{Cr(NO}_3\text{)}_3 \text{(aq)} + \text{Al(s)} \rightarrow \text{Al(NO}_3\text{)}_3 \text{(aq)} + \text{Cr(s)} \)

An initial examination reveals that \( \text{NO}_3^- \) did not change in oxidation numbers.

Complete Ionic Equation: \( \text{Cr}^{3+} \text{(aq)} + 3 \text{NO}_3^- \text{(aq)} + \text{Al(s)} \rightarrow \text{Al}^{3+} \text{(aq)} + 3 \text{NO}_3^- \text{(aq)} + \text{Cr(s)} \)

Net Ionic Equation: \( \text{Cr}^{3+} \text{(aq)} + \text{Al(s)} \rightarrow \text{Al}^{3+} \text{(aq)} + \text{Cr(s)} \)

Chromium Oxidation #: \( 0 \) to \( +3 \) (Reduction)
Aluminium Oxidation #: \( +3 \) to \( 0 \) (Oxidation)

**Oxidizing Agent** = \( \text{Cr}^{3+} \text{(aq)} \) **Reducing Agent** = \( \text{Al(s)} \)

**Oxidation Half-Reaction:** \( \text{Al(s)} \rightarrow \text{Al}^{3+} + 3e^- \) (Losing Electrons)
**Reduction Half-Reaction:** \( \text{Cr}^{3+} \text{(aq)} + 3e^- \rightarrow \text{Cr(s)} \) (Gaining Electrons)

d. \( \text{CH}_4 \text{(g)} + \text{O}_2 \text{(g)} \rightarrow \text{CO}_2 \text{(g)} + \text{H}_2\text{O(g)} \)

**Oxidation Half-Reaction:** \( \text{CH}_4 \text{(g)} + 2 \text{O}_2 \text{(g)} \rightarrow 2 \text{CO}_2 \text{(g)} + 2 \text{H}_2\text{O(g)} \) (Losing Electrons)
**Reduction Half-Reaction:** \( 4 \text{H}_2\text{O(g)} \rightarrow 8 \text{e}^- + \text{O}_2 \text{(g)} \) (Gaining Electrons)

**Oxidizing Agent** = \( \text{O}_2 \text{(g)} \) **Reducing Agent** = \( \text{CH}_4 \text{(g)} \)

### 4.10: Balancing Oxidation-Reduction Reactions

**Balancing Oxidation-Reduction Reaction by Half-Reaction Method:**

1. **Identify the atom that is undergoing a change in its oxidation number.** Find out the change in oxidation number. **Break up any Soluble Ionic Compound.**

2. **Balance the Oxidation Number by Adding Electrons to the side of the HIGHER Oxidation Number.** The Number of Electrons Added is the Difference in the Oxidation Number.

**Examples:**
- \( \text{Sn}^{2+} \text{(aq)} \rightarrow \text{Sn}^{4+} \text{(aq)} \) (Sn changes from +2 to +4. Hence, add 2 e\(^-\) to the right side.)
  (Charges and Elements are Balanced)
- \( \text{Fe}^{3+} \text{(aq)} \rightarrow \text{Fe}^{2+} \text{(aq)} \) (Fe changes from +3 to +2. Hence, add 1 e\(^-\) to the left side.)
  (Charges and Elements are Balanced)
- \( \text{Cl}_2 \text{(g)} \rightarrow \text{HClO}_4 \text{(aq)} \) (Cl changes from 0 to +7. Hence, add 7 e\(^-\) to the product side.)
  (Still need to Balance Hydrogen, Oxygen and the Charges)

3. **To balance the rest of the Half-Reaction (if necessary after step 2):**
   - **Balance the Chemical Species Containing the Atom undergoing the Change in Oxidation Number.** This is achieved by **Multiplying the BOTH the Chemical Species and the Number of Electrons just added by the New Coefficient.**
Example: \[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) \] (Cl changes from 0 to +7. Hence, add 7 \( e^- \) to the product side.)

\[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) + 7e^- \] (Multiply the HClO\(_4\) and \( e^- \) by 2 to balance Cl\(_2\).)

\[ \text{Cl}_2 (g) \rightarrow 2 \text{HClO}_4 (aq) + 14e^- \] (Still need to Balance Hydrogen, Oxygen and the Charges)

b. **Balance the Oxygen atom by adding H\(_2\)O\(_(l)\)** to the side that has less oxygen atom.

Example: \[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) \] (Cl changes from 0 to +7. Hence, add 7 \( e^- \) to the product side.)

\[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) + 7e^- \] (Multiply the HClO\(_4\) and \( e^- \) by 2 to balance Cl\(_2\).)

\[ \text{Cl}_2 (g) \rightarrow 2 \text{HClO}_4 (aq) + 14e^- \] (Since there are no oxygen on the left and we have 8 oxygen atom to balance, 2 HClO\(_4\), we need to add 8 H\(_2\)O to the reactant side.)

\[ \text{Cl}_2 (g) + 8 \text{H}_2\text{O} (l) \rightarrow 2 \text{HClO}_4 (aq) + 14e^- \] (Still need to Balance Hydrogen and the Charges)

c. **Balance the Hydrogen atom by adding H\(^+\)(aq) to the side that has less hydrogen atom.**

Example: \[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) \] (Cl changes from 0 to +7. Hence, add 7 \( e^- \) to the product side.)

\[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) + 7e^- \] (Multiply the HClO\(_4\) and \( e^- \) by 2 to balance Cl\(_2\).)

\[ \text{Cl}_2 (g) \rightarrow 2 \text{HClO}_4 (aq) + 14e^- \] (Since there are no oxygen on the left and we have 8 oxygen atom to balance, 2 HClO\(_4\), we need to add 8 H\(_2\)O to the reactant side.)

\[ \text{Cl}_2 (g) + 8 \text{H}_2\text{O} (l) \rightarrow 2 \text{HClO}_4 (aq) + 14e^- \] (We need 14 H\(^+\) on the right to balance the 16 H of the left.)

\[ \text{Cl}_2 (g) + 8 \text{H}_2\text{O} (l) \rightarrow 2 \text{HClO}_4 (aq) + 14 \text{H}^+ (aq) + 14e^- \] (In ACIDIC Environment: Charges and Elements are Balanced)

d. **In Basic Environment, Add the Same Number of OH\(^-\) as H\(^+\) to BOTH Sides. Combine H\(^+\) and OH\(^-\) that are on the Same Side into H\(_2\)O. Simplify the H\(_2\)O on Both Sides.**

Example: \[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) \] (Cl changes from 0 to +7. Hence, add 7 \( e^- \) to the product side.)

\[ \text{Cl}_2 (g) \rightarrow \text{HClO}_4 (aq) + 7e^- \] (Multiply the HClO\(_4\) and \( e^- \) by 2 to balance Cl\(_2\).)

\[ \text{Cl}_2 (g) \rightarrow 2 \text{HClO}_4 (aq) + 14e^- \] (Since there are no oxygen on the left and we have 8 oxygen atom to balance, 2 HClO\(_4\), we need to add 8 H\(_2\)O to the reactant side.)

\[ \text{Cl}_2 (g) + 8 \text{H}_2\text{O} (l) \rightarrow 2 \text{HClO}_4 (aq) + 14e^- \] (We need 14 H\(^+\) on the right to balance the 16 H of the left.)

\[ \text{Cl}_2 (g) + 8 \text{H}_2\text{O} (l) \rightarrow 2 \text{HClO}_4 (aq) + 14 \text{H}^+ (aq) + 14e^- \] (In BASIC Environment: Add 14 OH\(^-\) on Both Sides)

\[ \text{Cl}_2 (g) + 8 \text{H}_2\text{O} (l) + 14 \text{OH}^- (aq) \rightarrow 2 \text{HClO}_4 (aq) + 14 \text{H}^+ (aq) + 14 \text{OH}^- (aq) + 14e^- \] (Combine 14 H\(^+\) and 14 OH\(^-\) on the right into 14 H\(_2\)O)

\[ \text{Cl}_2 (g) + 8 \text{H}_2\text{O} (l) + 14 \text{OH}^- (aq) \rightarrow 2 \text{HClO}_4 (aq) + 14 \text{H}_2\text{O} (l) + 14e^- \] (Simplify the number of H\(_2\)O on either side.)

\[ \text{Cl}_2 (g) + 14 \text{OH}^- (aq) \rightarrow 2 \text{HClO}_4 (aq) + 6 \text{H}_2\text{O} (l) + 14e^- \] (In BASIC Environment: Charges and Elements are Balanced)

4. **Always CHECK if the half-reaction is Balanced for All Elements and Charges.**
5. Do Steps 1 to 4 again for the other atom that changes oxidation number.

6. Combine the redox half-reactions by balancing the electrons. There should be electrons on the product side of the oxidation half-reaction and the reactant side of the reduction half-reaction.

Example 1: Balance the following equation in acidic environment. Identify the oxidizing agent and reduction agent.

a. \( \text{KMnO}_4 (s) + \text{HBr} (aq) + \text{Sn}^{2+} (aq) \rightarrow \text{Mn}^{2+} (aq) + \text{Sn}^{4+} (aq) \)

<table>
<thead>
<tr>
<th>Manganese Oxidation Number:</th>
<th>( +7 ) to ( +2 ) (Reduction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin Oxidation Number:</td>
<td>( +2 ) to ( +4 ) (Oxidation)</td>
</tr>
</tbody>
</table>

**Oxidation Half-Rxn:**
\( \text{Sn}^{2+} (aq) \rightarrow \text{Sn}^{4+} (aq) + 2e^- \)

**Reduction Half-Rxn:**
\( \text{KMnO}_4 (s) + \text{HBr} (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + \text{K}^+ (aq) + \text{Br}^- (aq) \) (Add 5\( e^- \), \( K^+ \), and \( \text{Br}^- \))

\( \text{KMnO}_4 (s) + \text{HBr} (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + \text{K}^+ (aq) + \text{Br}^- (aq) + 4 \text{H}_2\text{O} (l) \) (Balance 4 O with 4 \( \text{H}_2\text{O} \))

\( \text{KMnO}_4 (s) + 8 \text{HBr} (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + \text{K}^+ (aq) + 8 \text{Br}^- (aq) + 4 \text{H}_2\text{O} (l) \) (Balance 8 H with 8 \( \text{H}_2\text{O} \) and 8 \( \text{Br}^- \) - H\(^+ \) is provided by \( \text{HBr} \))

**Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.**

**Ox Half-Rxn:**
\( 5 \) \( (\text{Sn}^{2+} (aq) \rightarrow \text{Sn}^{4+} (aq) + 2e^-) \)

**Red Half-Rxn:**
\( 2 \) \( (\text{KMnO}_4 (s) + 8 \text{HBr} (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + \text{K}^+ (aq) + 8 \text{Br}^- (aq) + 4 \text{H}_2\text{O} (l)) \)

\( \frac{2 \text{KMnO}_4 (s) + 16 \text{HBr} (aq) + 5 \text{Sn}^{2+} (aq) \rightarrow 5 \text{Sn}^{4+} (aq) + 2 \text{Mn}^{2+} (aq) + 2 \text{K}^+ (aq) + 16 \text{Br}^- (aq) + 8 \text{H}_2\text{O} (l)}{2 \text{KMnO}_4 (s) + 16 \text{HBr} (aq) + 5 \text{Sn}^{2+} (aq) \rightarrow 5 \text{Sn}^{4+} (aq) + 2 \text{Mn}^{2+} (aq) + 2 \text{K}^+ (aq) + 16 \text{Br}^- (aq) + 8 \text{H}_2\text{O} (l)} \)

**Oxidizing Agent** = \( \text{KMnO}_4 (s) \)

**Reducing Agent** = \( \text{Sn}^{2+} (aq) \)

b. \( \text{H}_2\text{SeO}_3 (aq) + \text{H}_2\text{S} (aq) \rightarrow \text{S} (s) + \text{Se} (s) \)

<table>
<thead>
<tr>
<th>Selenium Oxidation Number:</th>
<th>( +4 ) to ( 0 ) (Reduction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur Oxidation Number:</td>
<td>( -2 ) to ( 0 ) (Oxidation)</td>
</tr>
</tbody>
</table>

**Oxidation Half-Rxn:**
\( \text{H}_2\text{S} (aq) \rightarrow \text{S} (s) + 2 \text{H}^+ (aq) + 2e^- \) (Add \( 2e^- \) and \( 2 \text{H}^+ \))

**Reduction Half-Rxn:**
\( \text{H}_2\text{SeO}_3 (aq) + 4e^- \rightarrow \text{Se} (s) \) (Add \( 4e^- \))

\( \text{H}_2\text{SeO}_3 (aq) + 4e^- \rightarrow \text{Se} (s) + 3 \text{H}_2\text{O} (l) \) (Balance with 3 \( \text{H}_2\text{O} \))

\( \text{H}_2\text{SeO}_3 (aq) + 4 \text{H}^+ (aq) + 4e^- \rightarrow \text{Se} (s) + 3 \text{H}_2\text{O} (l) \) (Balance 6 \( \text{H}^+ \) with \( 4 \text{H}_2\text{O} \) - There are already \( 2 \text{H} \) in \( \text{H}_2\text{SeO}_3 \))

**Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.**

**Ox Half-Rxn:**
\( 2 \) \( (\text{H}_2\text{S} (aq) \rightarrow \text{S} (s) + 2 \text{H}^+ (aq) + 2e^-) \)

**Red Half-Rxn:**
\( \frac{\text{H}_2\text{SeO}_3 (aq) + 4 \text{H}^+ (aq) + 4e^- \rightarrow \text{Se} (s) + 3 \text{H}_2\text{O} (l)}{\text{H}_2\text{SeO}_3 (aq) + 4 \text{H}^+ (aq) + 4e^- \rightarrow \text{Se} (s) + 3 \text{H}_2\text{O} (l)} \)

**Oxidizing Agent** = \( \text{H}_2\text{SeO}_3 (s) \)

**Reducing Agent** = \( \text{H}_2\text{S} (aq) \)
Example 2: Balance the following equation in basic environment. Identify the oxidizing agent and reduction agent.

a. \( \text{NBr}_3(aq) \rightarrow \text{N}_2(g) + \text{Br}^-(aq) + \text{HOB}_r(aq) \)

Nitrogen Oxidation Number: \( +3 \rightarrow 0 \) (Reduction)
Bromine Oxidation Number: \( -1 \rightarrow (-1) \) \( +1 \) (Oxidation)

**Reduction Half-Rxn:**
\[ \text{NBr}_3(aq) + 3e^- \rightarrow \text{N}_2(g) + 3 \text{Br}^-(aq) \]
(Multiply \( e^- \), \( \text{NBr}_3 \) and \( \text{Br}^- \) by 2 to balance \( \text{N}_2 \))

**Oxidation Half-Rxn:**
\[ \text{Br}^- (aq) \rightarrow \text{HOB}_r(aq) + 2e^- \] (Balance \( O \) with \( \text{H}_2\text{O} \))
\[ \text{Br}^- (aq) + \text{H}_2\text{O} (l) + \text{OH}^- (aq) \rightarrow \text{HOB}_r(aq) + \text{H}_2\text{O} (aq) + \text{OH}^- (aq) + 2e^- \] (Balance \( H \) with \( \text{H}_2\text{O} \), but add equal \( \text{OH}^- \) to both sides – Basic Environment)

Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.

**Red Half-Rxn:**
\[ \text{2 NBr}_3(aq) + 6e^- \rightarrow \text{N}_2(g) + 6 \text{Br}^-(aq) \]

**Ox Half-Rxn:**
\[ 3 \left( \text{Br}^- (aq) + \text{OH}^- (aq) \rightarrow \text{HOB}_r(aq) + 2e^- \right) \]
\[ \text{2 NBr}_3(aq) + 3 \text{OH}^- (aq) \rightarrow \text{N}_2(g) + 3 \text{Br}^-(aq) + 3 \text{HOB}_r(aq) \] (Simplify \( \text{Br}^- \) on both sides)

\[ \text{Oxidizing Agent and Reducing Agent} = \text{NBr}_3(aq) \]

b. \( \text{Cl}_2(aq) \rightarrow \text{Cl}^-(aq) + \text{ClO}_3^-(aq) \)

Chloride Oxidation Number: \( 0 \rightarrow -1 \) (Reduction)
Chlorate Oxidation Number: \( 0 \rightarrow +5 \) (Oxidation)

**Oxidation Half-Rxn:**
\[ \text{Cl}_2(g) \rightarrow \text{ClO}_3^-(aq) + 5e^- \] (Add \( 5e^- \))
\[ \text{Cl}_2(g) \rightarrow 2 \text{ClO}_3^-(aq) + 10e^- \] (Multiply \( e^- \) and \( \text{ClO}_3^- \) by 2 to balance \( \text{Cl}_2 \))
\[ \text{Cl}_2(g) + 6 \text{H}_2\text{O} (l) \rightarrow 2 \text{ClO}_3^-(aq) + 10e^- \] (Balance \( 6 \text{O} \) with \( 6 \text{H}_2\text{O} \))
\[ \text{Cl}_2(g) + 6 \text{H}_2\text{O} (l) + 12 \text{OH}^- (aq) \rightarrow 2 \text{ClO}_3^-(aq) + 12 \text{H}^+(aq) + 12 \text{OH}^- (aq) + 10e^- \] (Balance \( \text{H}^+ \) with \( \text{H}_2\text{O} \), but add equal \( \text{OH}^- \) to both sides – Basic Environment)
\[ \text{Cl}_2(g) + 6 \text{H}_2\text{O} (l) + 12 \text{OH}^- (aq) \rightarrow 2 \text{ClO}_3^-(aq) + 12 \text{H}_2\text{O} (l) + 10e^- \] (Simplify \( \text{H}_2\text{O} \) on both sides)
\[ \text{Cl}_2(g) + 12 \text{OH}^- (aq) \rightarrow 2 \text{ClO}_3^-(aq) + 6 \text{H}_2\text{O} (l) + 10e^- \] (Check Balancing)

**Reduction Half-Rxn:**
\[ \text{Cl}_2(g) + e^- \rightarrow \text{Cl}^-(aq) \] (Add \( 1e^- \))
\[ \text{Cl}_2(g) + 2e^- \rightarrow 2 \text{Cl}^-(aq) \] (Multiply \( e^- \) and \( \text{Cl}^- \) by 2 to balance \( \text{Cl}_2 \))

Combine Oxidation and Reaction Half-Reactions by Equating the Number of Electrons.

**Ox Half-Rxn:**
\[ \text{Cl}_2(g) + 12 \text{OH}^- (aq) \rightarrow 2 \text{ClO}_3^-(aq) + 6 \text{H}_2\text{O} (l) + 10e^- \]

**Red Half-Rxn:**
\[ 5 \left( \text{Cl}_2(g) + 2e^- \rightarrow 2 \text{Cl}^-(aq) \right) \]
\[ 6 \text{Cl}_2(g) + 12 \text{OH}^- (aq) \rightarrow 10 \text{Cl}^-(aq) + 2 \text{ClO}_3^-(aq) + 6 \text{H}_2\text{O} (l) \]

\[ \text{Oxidizing Agent and Reducing Agent} = \text{Cl}_2(g) \]
Predicting Observations of a Redox Reaction:

1. Look for **new solid** form or **gas** evolved.
2. Some of the **metal ions and polyatomic ions have different colours** (see table below).
3. There might be **pH changes** as \([H^+]\) or \([OH^-]\) increases or decreases as the redox reaction proceeds forward.

**Some General Ions Colours in Solution for Row 1 of the Transition Metals**

<table>
<thead>
<tr>
<th>Ionic Species</th>
<th>Solution Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0 M</td>
</tr>
<tr>
<td>Dichromate</td>
<td>Cr₂O₇²⁻</td>
</tr>
<tr>
<td>Chromate</td>
<td>CrO₄²⁻</td>
</tr>
<tr>
<td>Chromium (III)</td>
<td>Cr³⁺</td>
</tr>
<tr>
<td>Cobalt (III)</td>
<td>Co³⁺</td>
</tr>
<tr>
<td>Hexa-cyano-cobalt (III)</td>
<td>Co(CN)₆³⁻</td>
</tr>
<tr>
<td>Hexa-ammine-cobalt (III)</td>
<td>Co(NH₃)₆³⁺</td>
</tr>
<tr>
<td>Cobalt (II)</td>
<td>Co²⁺</td>
</tr>
<tr>
<td>Copper (II)</td>
<td>Cu²⁺</td>
</tr>
<tr>
<td>Copper (I)</td>
<td>Cu⁺</td>
</tr>
<tr>
<td>Iron (III)</td>
<td>Fe³⁺</td>
</tr>
<tr>
<td>Tri-thiocyanate-iron (III)</td>
<td>Fe(SCN)₃</td>
</tr>
<tr>
<td>Hexa-cyano-iron (III)</td>
<td>Fe(CN)₆³⁻</td>
</tr>
<tr>
<td>Iron (II)</td>
<td>Fe²⁺</td>
</tr>
<tr>
<td>Hexa-cyano-iron (II)</td>
<td>Fe(CN)₆⁴⁻</td>
</tr>
<tr>
<td>Permanganate</td>
<td>MnO₄⁻</td>
</tr>
<tr>
<td>Manganese (IV)</td>
<td>Mn⁴⁺</td>
</tr>
<tr>
<td>Manganese (II)</td>
<td>Mn²⁺</td>
</tr>
<tr>
<td>Nickel (II)</td>
<td>Ni²⁺</td>
</tr>
<tr>
<td>Hexa-ammine-nickel (II)</td>
<td>Ni(NH₃)₆²⁺</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>V⁵⁺</td>
</tr>
<tr>
<td>Vanadium (IV)</td>
<td>V⁴⁺</td>
</tr>
<tr>
<td>Vanadium (III)</td>
<td>V³⁺</td>
</tr>
<tr>
<td>Vanadium (II)</td>
<td>V²⁺</td>
</tr>
</tbody>
</table>
Redox Titration: - a titration involving redox half reactions in order to determine the concentration of the ion in the analyte solution.
- does not need any indicator as the analyte ion tends to have a colour of its own.

Stoichiometry of Redox Titration:

2. Find the moles of the given reagent (usually with the titrant where the concentration and volume added are known).
3. Set up mole ratio and determine the number of moles of the analyte ion at equivalence point.
4. Calculate the concentration of the analyte ion.

Example 3: In a titration experiment, 10.0 mL of 0.0200 M acidified KMnO₄ (aq) is titrated with an unknown concentration of Sn²⁺ solution. The average volume of Sn²⁺ added was 32.42 mL. Determine the concentration of Sn²⁺. Use the answer of example 1a. in this section as the equation for this redox reaction. Comment on any qualitative observations involved with this titration.

Ox Half-Rxn: 5 (Sn²⁺(aq) → Sn⁴⁺(aq) + 2e⁻)
Red Half-Rxn: 2(KMnO₄(aq)) + 8 HBr(aq) + 5e⁻ → Mn²⁺(aq) + K⁺(aq) + 8 Br⁻(aq) + 4 H₂O(l)

\[ 2 \text{KMnO}_4(\text{aq}) + 10 \text{HBr(}aq\text{)} + 5 \text{Sn}^{2+}(\text{aq}) \rightarrow 5 \text{Sn}^{4+}(\text{aq}) + 2 \text{Mn}^{2+}(\text{aq}) + 2 \text{K}^+ (\text{aq}) + 16 \text{Br}^- (\text{aq}) + 8 \text{H}_2\text{O(l)} \]

\[ \frac{5 \text{ mol Sn}^{2+}}{2 \text{ mol KMnO}_4} \]

\[ \frac{0.5000 \text{ mmol}}{32.43 \text{ mL}} = 0.015417823 \text{ mol/L} \]

\[ [\text{Sn}^{2+}] = 0.0154 \text{ mol/L} \]

Qualitative Observations:
1. MnO₄⁻ is purple pink colour at around 0.0200 M. As Sn²⁺ is added from the buret, MnO₄⁻ in the flask will turn into Mn²⁺, which is colourless at low concentration.
2. The acidified Sn²⁺ solution initially had a low pH but the pH will increase as HBr(aq) is consumed.

Assignment
4.9 pg. 183–184 #57 to 62; pg. 867–868 #13 to 15
4.10 pg. 184 #63 to 68; pg. 868 #16
17.1: Galvanic Cells

**Electrochemistry**: - the branch of chemistry that studies the relationship between chemical energy and electrical energy.

**Electrochemical Cells**: - an apparatus that **Converts Chemical Energy to Electrical Energy**.
- commonly known as **Galvanic Cells** or **Voltaic Cells**.
- it consists of two containers of solutions (electrolytes) and the electrodes (usually metals called anode and cathode), as well as a connection between these two containers (salt bridge, porous cup, or porous disk), and a wire connecting the two electrodes.

**Electrodes**: - metals or other elements that serve as the site of redox reactions in a galvanic cell.
- in the case of a gaseous or liquid element, a carbon rod or platinum plating (inert material) is used as the solid electrode.

**Anode**: - the terminal where oxidation is taken place and commonly marked as the **Negative terminal**.
  (LEOA−RA: Losing Electrons Oxidation Anode – Reducing Agent)

**Cathode**: - the terminal where reduction is taken place and commonly marked as the **Positive terminal**.
  (GERC−OA: Gaining Electrons Reduction Cathode – Oxidizing Agent)

**Salt Bridge**: - an upside down U-tube filled with electrolytes like KCl (aq) to prevent charge build-up. (The ions in the salt bridge do NOT get mixed into the half-cells, nor do the electrolytes in the half-cells travelled into the salt bridge.)
- also serves as the separator between the two half cells.
- other equipment like **porous disk** and **porous cup (clay porcelain cup)** can be used instead of a salt bridge.

**Cell Potential** ($E_{\text{cell}}$): - sometimes called **electromotive force** (emf).
- the amount of electrical energy in terms of electric charges.

**Volts** ($V$): - the amount of work (energy) in J per charge ($q$) coulomb (unit symbol: C) of electrons transferred between two potentials (anode and cathode).
- commonly refer to as **potential difference**.

**Potentiometer**: - a electric device that measures potential difference between the cathode and anode.
- sometimes refer to as a **voltmeter**.

<table>
<thead>
<tr>
<th>Galvanic Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Electrons move from Anode (−) to Cathode (+).</td>
</tr>
<tr>
<td>2. Cations move towards the Cathode.</td>
</tr>
<tr>
<td>3. Anions move towards the Anode.</td>
</tr>
</tbody>
</table>

Anode (−): (LEOA−RA: Losing Electrons Oxidation Anode – Reducing Agent)
Cathode (+): (GERC−OA: Gaining Electrons Reduction Cathode – Oxidizing Agent)
**Galvanic Cell Step by Step**

1. $\text{Y}^{2+}$ leaves $\text{Y} (s)$ at the Anode.
2. Electrons produced at the Anode (−) move to Cathode (+) causing a potential difference that is measured by the voltmeter.
3. Electrons arrived at the Cathode combining with $\text{X}^{2+}$ to form $\text{X} (s)$.
4. $\text{Cl}^-$ from the salt bridge migrate towards the anode half-cells to counteract charge buildup by $\text{Y}^{2+}$.
5. As a result, $\text{K}^+$ from the salt bridge travel towards the cathode half-cell.
6. $\text{NO}_3^-$ (anions to bring in cations electrolytes into the half-cells) in the cathode half-cell moves toward the salt bridge (and thus towards the anode) because of $\text{K}^+$ charge buildup inside the salt bridge.
7. Similarly, $\text{NO}_3^-$ in the anode half-cell moves towards the anode because the anode metal is becoming too positive (electrons are leaving at the anode metal).
17.2: Standard Reduction Potentials

**Standard Hydrogen Potential**: the reduction potential of hydrogen ions to hydrogen gas is assigned a voltage of 0 at standard conditions (25°C and 1 atm).

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

**Standard Reduction Potential**: the electric potentials of reduction half-reactions as compared with hydrogen under standard condition (25°C and 1.0 mol/L of electrolytes or 1.0 atm of gaseous element (see Table on the next page). Since the table are of reduction half reactions, the **strongest oxidizing agent is listed on the left and decreasing in strength as one moves down the table**. (This makes sense, as we know F\(_2(g)\) is the most electronegative, and thereby is the strongest oxidizing agent – likes to gain electrons.) Conversely, the **weakest reducing agent is listed on the right and increasing as one moves down the table**. (This also makes sense, since Alkali metals like to lose electrons, they make excellent reducing agents.)

- Metals are reducing agents as they prefer to lose electrons to become cations (oxidation).
- Non-metals (especially halogens) are usually oxidizing agent as they tend to gain electrons to become anions (reduction).
- Strong oxidizing for common laboratory agents are acidify MnO\(_4^-\) and Cr\(_2O_7^{2-}\).

**Procedure to Predict Spontaneity Redox Reactions Under Standard Conditions**:

1. Locate the chemical species on the Table of Relative Strength of Standard Reduction Potentials. There should be one on the Left Side of the table and one on the right side. The reactions represent the reduction and oxidation half-reactions of the redox reaction.

2. **Spontaneous Reaction**: redox reactions that **will proceed forward** where chemical energy converts to electrical energy (galvanic cells).
   - the **Oxidizing Agent (OA) on the LEFT is HIGHER than the Reducing Agent (RA) on the RIGHT**.
   - FLIP the Reducing Agent – Oxidation Half-Reaction (LOWER Half-Reaction) and ADD the two half-reactions by balancing the electrons.

\[
\begin{align*}
\text{A}^{2+} \rightarrow 2e^- & \rightarrow \text{A(s)} \\
2 (\text{B(s)} & \rightarrow \text{B}^{+} + e^-) \quad \text{(Oxidation)}
\end{align*}
\]

\[
\text{A}^{2+} + 2 \text{B(s)} \rightarrow 2 \text{B}^{+} + \text{A(s)} \quad \text{(Spontaneous)}
\]

OA \quad RA

Flipped RA Half-Rxn
3. **Non-Spontaneous Reaction**: - redox reactions that **will NOT proceed forward** unless there is an eternal energy source to start and maintain the chemical reaction (electrolytic cell – see section 17.7)
- the **Oxidizing Agent (OA) on the LEFT is LOWER than the Reducing Agent (RA) on the RIGHT**.
- FLIP the Reducing Agent – Oxidation Half-Reaction (HIGHER Half-Reaction) and ADD the two half-reactions by balancing the electrons.

\[
\begin{align*}
X_{(s)} & \text{ will NOT react with } Y^+ \\
2 ( Y^+ + e^- & \rightarrow Y_{(s)} ) \quad \text{(Reduction)} \\
\frac{X_{(s)} \rightarrow X^{2+} + 2e^-}{\text{(Oxidation)}} \quad \text{Flipped RA Half-Rxn} \\
2 Y^+ + X_{(s)} & \rightarrow \text{Non-Spontaneous} \\
\text{OA} & \quad \text{RA}
\end{align*}
\]

### Standard Reduction Potentials in Aqueous Solution at 25°C

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>( E^*(V) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2(g) + 2e^- \rightarrow 2F^- )</td>
<td>2.87</td>
</tr>
<tr>
<td>( \text{Co}^{2+} + e^- \rightarrow \text{Co}^{2+} )</td>
<td>1.82</td>
</tr>
<tr>
<td>( \text{An}^{3+} + 3e^- \rightarrow \text{An}(s) )</td>
<td>1.50</td>
</tr>
<tr>
<td>( \text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^- )</td>
<td>1.36</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l) )</td>
<td>1.23</td>
</tr>
<tr>
<td>( \text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^- )</td>
<td>1.67</td>
</tr>
<tr>
<td>( 2 \text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}_2^{2+} )</td>
<td>0.92</td>
</tr>
<tr>
<td>( \text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}(l) )</td>
<td>0.85</td>
</tr>
<tr>
<td>( \text{Ag}^{+} + e^- \rightarrow \text{Ag}(s) )</td>
<td>0.80</td>
</tr>
<tr>
<td>( \text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}(l) )</td>
<td>0.79</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} )</td>
<td>0.77</td>
</tr>
<tr>
<td>( \text{I}_2(s) + 2e^- \rightarrow 2\text{I}^- )</td>
<td>0.53</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + e^- \rightarrow \text{Cu}(s) )</td>
<td>0.52</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}(s) )</td>
<td>0.34</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + e^- \rightarrow \text{Cu}^{2+} )</td>
<td>0.15</td>
</tr>
<tr>
<td>( \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} )</td>
<td>0.15</td>
</tr>
<tr>
<td>( \text{S}^{2-} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{S}(g) )</td>
<td>0.14</td>
</tr>
<tr>
<td>( 2\text{H}_2^+ + 2e^- \rightarrow \text{H}_2(g) )</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} + e^- \rightarrow \text{Pb}(s) )</td>
<td>0.13</td>
</tr>
<tr>
<td>( \text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}(s) )</td>
<td>0.04</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}(s) )</td>
<td>0.25</td>
</tr>
<tr>
<td>( \text{Co}^{2+} + 2e^- \rightarrow \text{Co}(s) )</td>
<td>0.28</td>
</tr>
<tr>
<td>( \text{Ti}^{4+} + e^- \rightarrow \text{Ti}(s) )</td>
<td>0.34</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}(s) )</td>
<td>0.40</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}(s) )</td>
<td>0.44</td>
</tr>
<tr>
<td>( \text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}(s) )</td>
<td>0.74</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}(s) )</td>
<td>0.76</td>
</tr>
<tr>
<td>( \text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}(s) )</td>
<td>1.18</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 3e^- \rightarrow \text{Al}(s) )</td>
<td>1.66</td>
</tr>
<tr>
<td>( \text{Be}^{2+} + 2e^- \rightarrow \text{Be}(s) )</td>
<td>1.70</td>
</tr>
<tr>
<td>( \text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}(s) )</td>
<td>2.37</td>
</tr>
<tr>
<td>( \text{Na}^{+} + e^- \rightarrow \text{Na}(s) )</td>
<td>2.71</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}(s) )</td>
<td>2.87</td>
</tr>
<tr>
<td>( \text{Sr}^{2+} + 2e^- \rightarrow \text{Sr}(s) )</td>
<td>2.89</td>
</tr>
<tr>
<td>( \text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}(s) )</td>
<td>2.98</td>
</tr>
<tr>
<td>( \text{Rb}^{+} + e^- \rightarrow \text{Rb}(s) )</td>
<td>2.92</td>
</tr>
<tr>
<td>( \text{K}^{+} + e^- \rightarrow \text{K}(s) )</td>
<td>2.92</td>
</tr>
<tr>
<td>( \text{Cs}^{+} + e^- \rightarrow \text{Cs}(s) )</td>
<td>2.92</td>
</tr>
<tr>
<td>( \text{Li}^{+} + e^- \rightarrow \text{Li}(s) )</td>
<td>3.05</td>
</tr>
</tbody>
</table>
Example 1: Predict whether the following reactions will react and write the complete redox reactions.

a. \( \text{Br}_2 (l) \) with \( \text{Ni} (s) \)

\[
\text{Br}_2(l) + 2e^- \rightarrow 2 \text{Br}^- (aq) \quad E^0 = 1.07 \text{ V} \\
\text{Ni}^{2+} (aq) + 2e^- \rightarrow \text{Ni}(s) \quad E^0 = -0.25 \text{ V}
\]

Since \( \text{Br}_2 \) (OA) is higher than \( \text{Ni} \) (RA), the reaction will be spontaneous.

\[
\text{Br}_2(l) + 2e^- \rightarrow 2 \text{Br}^- (aq) \\
\text{Ni} (s) \rightarrow \text{Ni}^{2+} (aq) + 2e^- \\
\text{Br}_2(l) + \text{Ni} (s) \rightarrow \text{Ni}^{2+} (aq) + 2 \text{Br}^- (aq)
\]

b. \( \text{Au} (s) \) with \( \text{Fe}^{3+} (aq) \)

\[
\text{Au}^{3+} (aq) + 3e^- \rightarrow \text{Au} (s) \quad E^0 = 1.50 \text{ V} \\
\text{Fe}^{3+} (aq) + e^- \rightarrow \text{Fe}^{2+} (aq) \quad E^0 = 0.77 \text{ V}
\]

Since \( \text{Fe}^{3+} \) (OA) is lower than \( \text{Au} \) (RA), the reaction will be non-spontaneous.

\[
3 ( \text{Fe}^{3+} (aq) + e^- \rightarrow \text{Fe}^{2+} (aq) ) \\
\text{Au} (s) \rightarrow \text{Au}^{3+} (aq) + 3e^- \\
3 \text{Fe}^{3+} (aq) + \text{Au} (s) \rightarrow \text{No Reaction}
\]

Because gold does not oxidize easily, this is the main reason why gold is so valuable!

Example 2: Four elements, \( A, B, C, \) and \( D \), form diatomic molecules and negative ions. Arranged the elements in order from most reactive to least reactive if the following observations are made

\[
\text{A}_2 + 2 \text{C}^- \rightarrow 2 \text{A}^- + \text{C}_2 \\
\text{B}_2 + 2 \text{D}^- \rightarrow \text{No Reaction} \\
\text{C}_2 + 2 \text{D}^- \rightarrow 2 \text{C}^- + \text{D}_2
\]

The diatomic elements undergo reduction to become anions. For example, \( \text{A}_2 + 2e^- \rightarrow 2 \text{A}^- \). Thus, the elements are oxidizing agents.

<table>
<thead>
<tr>
<th>Strength of Oxidizing Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{A}_2 &gt; \text{C}_2 )</td>
</tr>
<tr>
<td>( \text{B}_2 &lt; \text{D}_2 )</td>
</tr>
<tr>
<td>( \text{C}_2 &gt; \text{D}_2 )</td>
</tr>
</tbody>
</table>

Putting all the inequalities together, we have

\[
\text{A}_2 > \text{C}_2 > \text{D}_2 > \text{B}_2
\]

Example 3: As part of a laboratory procedure, a student recorded observations after placing strips of metal into aqueous solutions according to the following combinations. The results are recorded using representing a reaction and representing no reaction. Organize the oxidizing agents from the strongest to the weakest.

<table>
<thead>
<tr>
<th>Metals / Ions</th>
<th>( \text{A}^{2+} (aq) )</th>
<th>( \text{B}^{2+} (aq) )</th>
<th>( \text{C}^{2+} (aq) )</th>
<th>( \text{D}^{2+} (aq) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{A} (s) )</td>
<td>-----</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>( \text{B} (s) )</td>
<td>X</td>
<td>-----</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>( \text{C} (s) )</td>
<td>✓</td>
<td>✓</td>
<td>-----</td>
<td>✓</td>
</tr>
<tr>
<td>( \text{D} (s) )</td>
<td>X</td>
<td>✓</td>
<td>X</td>
<td>-----</td>
</tr>
</tbody>
</table>

The Oxidizing Agent are the ions because they Reduced (Gained Electrons) to produce their metal elements. For example, \( \text{A}^{2+} + 2e^- \rightarrow \text{A} (s) \).

The Strongest Oxidizing Agent is the ion that is MOST Reactive (look at the above table vertically). Thus, in order of decreasing strength (reactivity):

\[
\text{B}^{2+} > \text{D}^{2+} > \text{A}^{2+} > \text{C}^{2+}
\]

Chemical Species that are BOTH Oxidizing Agent and Reducing Agent: - some of the transition metals have more than one monoatomic ionic charges can have the intermediate charge species act as reducing agent as well as oxidizing agent.

Examples: Iron (II), Chromium (II) and Tin (II)

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

Fe$^{3+} + e^{-} \rightarrow$ Fe$^{2+}$ $E^\circ = +0.77$ V

Fe$^{2+} + 2e^{-} \rightarrow$ Fe$^{(s)}$ $E^\circ = -0.44$ V

Cr$^{3+} \rightarrow$ Cr$^{2+} \rightarrow$ Cr$^{(s)}$

Cr$^{3+} + e^{-} \rightarrow$ Cr$^{2+}$ $E^\circ = -0.41$ V

Cr$^{2+} + 2e^{-} \rightarrow$ Cr$^{(s)}$ $E^\circ = -0.91$ V

Sn$^{4+} \rightarrow$ Sn$^{2+} \rightarrow$ Sn$^{(s)}$

Sn$^{4+} + 2e^{-} \rightarrow$ Sn$^{2+}$ $E^\circ = +0.15$ V

Sn$^{2+} + 2e^{-} \rightarrow$ Sn$^{(s)}$ $E^\circ = -0.14$ V

H$_2$O$^{(l)}$ as an Oxidizing Agent (Left Side of the Table)

H$_2$O$^{(l)}$ as a Reducing Agent (Right Side of the Table)

2 H$_2$O$^{(l)} + 2e^{-} \rightarrow$ H$_2$($g$) + 2 OH$^-$ $E^\circ = -0.83$ V

O$_2$($g$) + 4 H$^+$ + 4e$^-$ $\rightarrow$ 2 H$_2$O$^{(l)}$ $E^\circ = +1.23$ V

Standard Cell Potential: - the cell potential under standard conditions ($E^\circ_{cell} = E^\circ_{cathode} + E^\circ_{anode}$)

- when Flipping the Reducing Agent’s Half-Reaction, reverse the Sign of $E^\circ$ to obtain $E^\circ_{anode}$.
- do NOT Multiply $E^\circ$ when using electrons to balance complete redox reactions.

Line Notation: - a notation using lines to represent the electrode and electrolytes as well as the half-cell separations of a galvanic cell.

- single line, |, separates electrode and its electrolyte; double line, ||, represents salt bridge, porous cup or porous disk.

- ALWAYS write the Anode on the LEFT hand side.

Line Notation and Standard Cell Potential of Galvanic Cells

| Anode | Anode’s Electrolyte || Cathode’s Electrolyte | Cathode |
|-------|---------------------|-----------------|-----------------|
| $E^\circ_{cell}$ = $E^\circ_{cathode} + E^\circ_{anode}$ |

(E$^\circ_{cell}$ > 0 means Spontaneous Reaction)

Example 4: For a galvanic cell using copper and aluminum electrodes as shown below, identify anode and cathode. Indicate movements of ions and electrons. Write the line notation and calculate the standard cell potential.

Cu$^{2+}_{(aq)} + 2e^- \rightarrow$ Cu$^{(s)}$ $E^\circ = 0.34$ V

Al$^{3+}_{(aq)} + 3e^- \rightarrow$ Al$^{(s)}$ $E^\circ = -1.66$ V

Since the half-reactions for Cu$^{(s)}$ is higher than Al$^{(s)}$, Cu$^{2+}$ will be reduced (Cu$^{(s)}$ is the Cathode) and Al$^{(s)}$ will be oxidized (Anode – flipped half-reaction and voltage).

3 (Cu$^{2+}_{(aq)} + 2e^- \rightarrow$ Cu$^{(s)}$) $E^\circ = 0.34$ V

2 (Al$^{(s)} \rightarrow$ Al$^{3+}_{(aq)} + 3e^-$) $E^\circ = +1.66$ V

3 Cu$^{2+}_{(aq)} + 2$ Al$^{(s)} \rightarrow$ 2 Al$^{3+}_{(aq)} + 3$ Cu$^{(s)}$ $E^\circ_{cell} = 2.00$ V

Note: We do NOT multiply $E^\circ$.

Line Notation: Al$^{(s)}$ | Al$^{3+}_{(aq)}$ || Cu$^{2+}_{(aq)}$ | Cu$^{(s)}$
17.3: Cell Potential, Electrical Work and Free Energy

Faraday Constant ($F$): - the amount of charge (coulomb) in one mole of electrons. ($F = 96,500 \text{ C/mol } e^-$)

Free Energy and Cell Potential: - we can relate $E^\circ_{\text{cell}}$ with $\Delta G^\circ$ in order to predict spontaneity.

$$E^\circ_{\text{cell}} = -\frac{w}{q}$$  \hspace{1cm} ($E^\circ_{\text{cell}}$ as emf is defined as the ability to do work ($-w$) per charge.)

$$w = -qE^\circ_{\text{cell}}$$  \hspace{1cm} (Manipulate Equation)

$$\Delta G^\circ = -qE^\circ_{\text{cell}}$$  \hspace{1cm} ($\Delta G^\circ = w_{\text{max}} = w$ Free Energy is maximum useful work obtained, assuming 100% efficiency of the cell.)

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$  \hspace{1cm} ($F = \frac{q}{n}e$ or $q = ne_{\text{electrons}}F$)

Free Energy and Cell Potential

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$\Delta G^\circ = $ Standard Free Energy (J)  \hspace{1cm} $n =$ moles of electrons transferred

$F = $ Faraday Constant ($9.65 \times 10^4 \text{ C/mol } e^-$)  \hspace{1cm} $E^\circ_{\text{cell}} =$ Standard Cell Potential (V)

$E^\circ_{\text{cell}} > 0$ means $\Delta G^\circ < 0$ (Spontaneous Reaction)

$E^\circ_{\text{cell}} < 0$ means $\Delta G^\circ > 0$ (Non-Spontaneous Reaction)

Example 1: Using the aluminum-copper galvanic cell in example 4 of section 17.2, determine the $\Delta G^\circ$ of under standard conditions and verify the reaction is spontaneous.

$$3 (\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu(s)}) \hspace{1cm} E^\circ = 0.34 \text{ V}$$

$$2 (\text{Al(s)} \rightarrow \text{Al}^{3+}(aq) + 3e^-) \hspace{1cm} E^\circ = +1.66 \text{ V}$$

$$3 \text{ Cu}^{2+}(aq) + 2 \text{ Al(s)} \rightarrow 2 \text{ Al}^{3+}(aq) + 3 \text{ Cu(s)} \hspace{1cm} E^\circ_{\text{cell}} = 2.00 \text{ V}$$

$\Delta G^\circ =$ \hspace{1cm} $n =$ 6 moles of $e^-$ ($3 \times 2e^-$ or $2 \times 3e^-$)

$F = 9.65 \times 10^4 \text{ C/mol } e^-$  \hspace{1cm} $E^\circ_{\text{cell}} = 2.00 \text{ V}$

$\Delta G^\circ = -nFE^\circ_{\text{cell}} = - (6 \text{ mol})(9.65 \times 10^4 \text{ C/mol } e^-)(2.00 \text{ V})$

$\Delta G^\circ = 1,158,000 \text{ J}$

Since $\Delta G^\circ < 0$ and its magnitude is quite large, we would expect this galvanic cell to be very spontaneous.

Assignment

17.1 pg. 868 #25 and 26
17.2 pg. 868–869 #27 to 36
17.3 pg. 869 #37 to 50

Page 338.  

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17.4: Dependence of Cell Potential on Concentration

**Equilibrium Quotient and Cell Potential**: when the equilibrium quotient of the redox reaction, $Q > K$, the electrochemical cell has its $E_{\text{cell}} > 0$ (anode is lower than the oxidizing agent in the Standard Reduction Potential Table), **making it spontaneous**.

**The Nernst Equation**: an equation to calculate cell potential ($E_{\text{cell}}$) at other conditions BESIDES 1.0 M and 25°C with the equilibrium quotient.

$$\Delta G = \Delta G^\circ + RT \ln Q$$  
$$-nF E_{\text{cell}} = -nF E_{\text{cell}}^\circ + RT \ln Q$$  
$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$$

(Replace $\Delta G$ with $-nF E_{\text{cell}}$ and $\Delta G^\circ$ with $-nF E_{\text{cell}}^\circ$)

(Divide each term on both sides by $-nF$)

### The Nernst Equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q \quad \text{or} \quad E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ mol} \cdot \text{V}}{n} \log Q \quad \text{(at 25°C)}$$

- $E_{\text{cell}}$ = Cell Potential (V) at Other Conditions
- $E_{\text{cell}}^\circ$ = Standard Cell Potential (V) at 1.0 M and 25°C
- $n$ = moles of electrons transferred per redox reaction
- $R$ = Gas Constant [8.31 (V • C) / (mol • K)]
- $T$ = Temperature in Kelvin
- $F$ = Faraday Constant ($9.65 \times 10^4$ C/mol)
- $Q = \frac{[B^{n+}]}{[A^{m+}]} = \frac{[\text{Anode Electrolyte}]}{[\text{Cathode Electrolyte}]} = \text{Equilibrium Quotient for } aA^{b+} + bB \rightarrow bB^{n+} + aA$

Using the Nernst Equation to Explain Operation of a Galvanic Cell:

1. One way to **Increase the $E_{\text{cell}}$ from $E_{\text{cell}}^\circ$** is to setup the galvanic cell such that $[B^{n+}] < [A^{m+}]$ ([Anode Electrolyte] < [Cathode Electrolyte]), $E_{\text{cell}} > E_{\text{cell}}^\circ$ ($E_{\text{cell}}$ is elevated from $E_{\text{cell}}^\circ$).

2. Initially, when the electrochemical reaction operates under standard condition, $E_{\text{cell}} = E_{\text{cell}}^\circ$. This is because $Q = 1$ (ln $Q$ or log $Q = 0$) and [Anode Electrolyte] = [Cathode Electrolyte] = 1.0 M.

3. As the electrochemical cell operates (battery is discharging), the **concentration of ions will change** ($E_{\text{cell}}$ decreases from $E_{\text{cell}}^\circ$). $[B^{n+}] > [A^{m+}]$ ([Anode Electrolyte] > [Cathode Electrolyte]), $E_{\text{cell}} < E_{\text{cell}}^\circ$.

4. Eventually, when $Q = K$, $E_{\text{cell}} = 0$. Then, the **flow of electrons will stop** (battery is completely discharged). (Therefore $K$ of redox reaction is usually very large to begin with. Equilibrium Position is favouring the product side).
Calculating $K$ of a Redox Reaction:

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

\[
\ln K = \frac{nFE^{\circ}_{\text{cell}}}{RT} \quad \text{or} \quad \log K = \frac{nE^{\circ}_{\text{cell}}}{0.0592} \quad \text{(at } 25^\circ\text{C)}
\]

**Example 1:** Using Example 4 of Section 17.2, the $E^{\circ}_{\text{cell}}$ for Al (s) | Al$^{3+}$ || Cu$^{2+}$ | Cu (s) is 2.00 V. Rewrite the net-ionic redox equation, and determine the $E_{\text{cell}}$ of the following at 25°C. Include a diagram and label anode, cathode, electron flow, and ion migrations and their concentrations.

a. Al (s) | Al$^{3+}$ (1.0 M) || Cu$^{2+}$ (0.075 M) | Cu (s)

\[
\begin{align*}
E^{\circ}_{\text{cell}} = 2.00 \text{ V} & \quad n = 6 \text{ moles of } e^- (3 \times 2e^- \text{ or } 2 \times 3e^-) \\
T = 25^\circ\text{C} & \\
E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ mol} \cdot \text{V}}{n} \log Q \\
E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ mol} \cdot \text{V}}{n} \log \left[ \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3} \right] \\
E_{\text{cell}} &= (2.00 \text{ V}) - \frac{0.0592 \text{ mol} \cdot \text{V}}{6 \text{ mol}} \log \left( \frac{(1.0)^2}{(0.075)^3} \right) \\
E_{\text{cell}} &= 1.97 \text{ V}
\end{align*}
\]

Since the [Al$^{3+}$ = anode electrolyte] > [Cu$^{2+}$ = cathode electrolyte], the $E_{\text{cell}}$ is lowered from $E^{\circ}_{\text{cell}}$.  

---

**Equation 7.7: Nernst Equation**

\[
E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{nFE^{\circ}_{\text{cell}}}{RT} \ln K
\]

**Rearrange equation:**

\[
\ln K = \frac{nFE^{\circ}_{\text{cell}}}{RT}
\]

**Solve for $K$:**

\[
\log K = \frac{nE^{\circ}_{\text{cell}}}{0.0592} \quad \text{(at } 25^\circ\text{C)}
\]
Example 2: Determine the equilibrium constant for the galvanic cell \( \text{Al} \mid \text{Al}^{3+} \ (0.025 \text{ M}) \parallel \text{Cu}^{2+} \ (1.0 \text{ M}) \mid \text{Cu} \) at standard conditions. Include a diagram and label anode, cathode, electron flow, and ion migrations and their concentrations.

\[
\begin{align*}
3 \text{ ( Cu}^{2+} \ (aq) + 2e^{-} \rightarrow \text{Cu} (s) ) & \quad E^\circ = 0.34 \text{ V} \\
2 \text{ ( Al} (s) \rightarrow \text{Al}^{3+} \ (aq) + 3e^{-}) & \quad E^\circ = +1.66 \text{ V} \\
3 \text{ Cu}^{2+} \ (aq) + 2 \text{ Al} (s) \rightarrow 2 \text{ Al}^{3+} \ (aq) + 3 \text{ Cu} (s) & \quad E^\circ_{\text{cell}} = 2.00 \text{ V}
\end{align*}
\]

\[E_{\text{cell}} =? \quad n = 6 \text{ moles of } e^- (3 \times 2e^- \text{ or } 2 \times 3e^-) \]

\[E^\circ_{\text{cell}} = 2.00 \text{ V} \quad T = 25^\circ \text{C}\]

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{n}{E_{\text{cell}}} \log \left[ \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]} \right]
\]

Since the \([\text{Al}^{3+} = \text{anode electrolyte}] < [\text{Cu}^{2+} = \text{cathode electrolyte}], the E_{\text{cell}} is elevated from E^\circ_{\text{cell}}.\]

\[
\begin{align*}
\text{Anode (−)} & \quad \text{Cathode (+)} \\
\text{e}^- \text{ flow} & \quad \text{Cations (Cu}^{2+} \text{ and Al}^{3+}) \\
& \quad \text{Anion (NO}_3^-) \\
0.025 \text{ M Al(NO}_3^-)_3 \ (aq) & \quad 1.0 \text{ M Cu(NO}_3^-)_2 \ (aq)
\end{align*}
\]

\[
\begin{align*}
3 \text{ ( Sn}^{2+} \ (aq) + 2e^{-} \rightarrow \text{Sn} (s) ) & \quad E^\circ = -0.14 \text{ V} \\
2 \text{ ( Al} (s) \rightarrow \text{Al}^{3+} \ (aq) + 3e^{-}) & \quad E^\circ = +1.66 \text{ V} \\
3 \text{ Sn}^{2+} \ (aq) + 2 \text{ Al} (s) \rightarrow 2 \text{ Al}^{3+} \ (aq) + 3 \text{ Sn} (s) & \quad E^\circ_{\text{cell}} = 1.52 \text{ V}
\end{align*}
\]

\[K =? \quad n = 6 \text{ moles of } e^- (3 \times 2e^- \text{ or } 2 \times 3e^-) \]

\[E^\circ_{\text{cell}} = 2.00 \text{ V} \quad T = 25^\circ \text{C}\]

\[
\log K = \frac{nE^\circ_{\text{cell}}}{E_{\text{cell}}} = \frac{(6 \text{ mol})(1.52 \text{ V})}{0.0592 \text{ mol} \cdot \text{V}}
\]

\[\log K = 154.0540541 \quad \text{Too Large for Calculator to Handle}\]

\[K = 10^{154.0540541} \]

\[K = 1.13 \times 10^{154}\]

As we can see, the values of \(K\) for redox reactions are usually quite large.
**Concentration Cells**: - electrochemical cells where both electrodes are of the same material but the concentration of the electrolytes are different.

- under standard condition, concentration cell has a $E^\circ_{\text{cell}}$ of 0 ($E^\circ_{\text{cathode}} = E^\circ_{\text{anode}}$).
- the half-cell that contains the lower concentration electrolytes becomes the anode (When $[\text{Anode Electrolyte}] < [\text{Cathode Electrolyte}]$), $E_{\text{cell}} > E^\circ_{\text{cell}}$ ($E_{\text{cell}}$ is elevated from $E^\circ_{\text{cell}}$).

**Concentration Cells**

$$E_{\text{cell, conc}} = E^\circ_{\text{cell}} = \frac{RT}{nF} \ln Q$$

or

$$E_{\text{cell, conc}} = -\frac{RT}{nF} \ln Q$$

$$Q = \text{Equilibrium Quotient for } aA^{b+}_{(\text{high conc})} + aA_{(s)} \rightarrow aA^{b+}_{(\text{low conc})} + aA_{(s)}$$

or

$$E_{\text{cell, conc}} = -\frac{0.0592 \text{ mol } \cdot \text{ V}}{n} \log Q$$

**Example 3**: Calculate the $E_{\text{cell}}$ of the following at 25°C. Draw a diagram and label the anode, cathode, and electron flow if applicable.

a. Cu$_{(s)}$ | Cu$^{2+}$ (1.0 M) || Cu$^{2+}$ (1.0 M) | Cu$_{(s)}$

$\text{Cu}^{2+}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)}$ \hspace{1cm} $E^\circ = 0.34 \text{ V}$

$\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2e^-$ \hspace{1cm} $E^\circ = -0.34 \text{ V}$

When the two half-cells are Identical, there is no reaction and $E^\circ_{\text{cell}} = 0 \text{ V}$

b. Cu$_{(s)}$ | Cu$^{2+}$ (0.0050 M) || Cu$^{2+}$ (1.0 M) | Cu$_{(s)}$

$0.0050 \text{ M Cu(NO}_3\text{)}_2_{(aq)} \rightarrow 1.0 \text{ M Cu(NO}_3\text{)}_2_{(aq)}$

$E_{\text{cell}} = ?$ \hspace{1cm} $n = 2 \text{ moles of } e^-$ \hspace{1cm} $T = 25^\circ \text{C}$

$$E_{\text{cell, conc}} = -\frac{0.0592 \text{ mol } \cdot \text{ V}}{n} \log Q$$

$$E_{\text{cell, conc}} = -\frac{0.0592 \text{ mol } \cdot \text{ V}}{n} \log \left(\frac{[\text{Cu}^{2+}_{\text{low conc}}]}{[\text{Cu}^{2+}_{\text{high conc}}]}\right)$$

$$E_{\text{cell, conc}} = -\frac{0.0592 \text{ mol } \cdot \text{ V}}{(2 \text{ mol})} \log \left(\frac{0.0050}{(1.0)}\right)$$

$$E_{\text{cell, conc}} = 0.068 \text{ V}$$

The bigger the difference between the concentrations of the electrolytes in the half-cells, the higher the $E_{\text{cell, conc}}$. 

\[\text{Page 342.} \quad \text{Copyrighted by Gabriel Tang B.Ed., B.Sc.}\]
Ion-Selective Electrode: - a glass electrode with a tin-walled membrane containing a metal wire (coated with specialized crystal sensitive to certain ion concentration) enclosed within a reference solution.
- is used to measured selected ion concentration (most commonly H⁺ for pH, but can be modified to measure concentrations of Cd²⁺, Ca²⁺, Cu²⁺, K⁺, Ag⁺, Na⁺, Br⁻, Cl⁻, CN⁻, F⁻, NO₃⁻ and S²⁻).

A typical pH Meter (above) and its inner working (right)

### Assignment
17.4 pg. 869–871 #51 to 61, 63 to 69

17.5: Batteries

Batteries: - portable galvanic cells that are commonly in series (cells that connect in a way such that the potential difference can be added to yield a greater voltage).

```
<table>
<thead>
<tr>
<th>Anode (−)</th>
<th>Cathode (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 ( Cu²⁺(aq) + 2e⁻ → Cu(s) )</td>
<td>E° = 0.34 V</td>
</tr>
<tr>
<td>2 ( Al(s) → Al³⁺(aq) + 3e⁻ )</td>
<td>E° = +1.66 V</td>
</tr>
<tr>
<td>3 Cu²⁺(aq) + 2 Al(s) → 2 Al³⁺(aq) + 3 Cu(s)</td>
<td>E°cell = 2.00 V</td>
</tr>
<tr>
<td>3 ( Cu²⁺(aq) + 2e⁻ → Cu(s) )</td>
<td>E° = 0.34 V</td>
</tr>
<tr>
<td>2 ( Al(s) → Al³⁺(aq) + 3e⁻ )</td>
<td>E° = +1.66 V</td>
</tr>
<tr>
<td>3 Cu²⁺(aq) + 2 Al(s) → 2 Al³⁺(aq) + 3 Cu(s)</td>
<td>E°cell = 2.00 V</td>
</tr>
</tbody>
</table>
```

Total Voltage = 2.00 V + 2.00 V = 4.00 V
Different Types of Batteries:

1. **Lead-Acid Battery**: a rechargeable battery commonly used in automobiles to start and maintain the sparks needed for the combustion of the gasoline engine.
   - consists of \( \text{Pb} \) as the anode and \( \text{PbO}_2 \) as the cathode in an acidic \( \text{H}_2\text{SO}_4(aq) \) environment. (Since solid lead is used, the lead-acid battery tends to be heavy. The sulfuric acid used in this type of battery is commonly known as battery acid.)
   - the battery is in series with six identical galvanic cells giving it \( 6 \times 2V = 12V \) of total potential difference.

2. **Dry Cell**: a non-rechargeable battery commonly used in electronic devices such as, radios, calculators, and electronic toys.
   a. **Zinc-Carbon Dry Cell**: consists of \( \text{Zn} \) as the anode and both \( \text{MnO}_2 \) (cathode with a carbon rod) and the acid \( \text{NH}_4\text{Cl}(s) \) are in a dry paste – hence the term “dry” cell.
   b. **Alkaline Dry Cell**: in a basic environment, the \( \text{NH}_4\text{Cl} \) is replaced with \( \text{NaOH} \) or \( \text{KOH} \), and zinc oxidized to \( \text{ZnO} \) at the anode.
   - some dry cell battery is in series with six identical Zn-C or alkaline dry cells, giving it \( 6 \times 1.5V = 9V \) of total potential difference.
c. **Nickel Cadmium Battery**: - a dry cell with the same set up as alkaline dry cell but it can be **recharged** (a lot lighter than lead-acid batteries).
- it can developed a "memory" problem, so after each recharged cycled, the battery tends to have a shorter "life-span". This can be corrected by completely discharging the battery before recharging it fully for the next usage cycle.
- cadmium is an expensive metal, and cannot be disposed easily due to its toxicity. Special care must be taken to recycle Ni-Cd batteries.

**Redox Reaction for a Ni-Cd Dry Cell Battery**

\[
\begin{align*}
\text{(Reduction)} & \quad \text{NiO}_2 (s) + \text{Cd} (s) + 2 \text{H}_2\text{O} (l) \rightarrow \text{Cd(OH)}_2 (s) + \text{Ni(OH)}_2 (s) & E^{\circ}_{\text{cell}} &= 1.25 \text{ V} \\
\text{(Oxidation)} & \quad \text{NiO}_2 (s) + 2 \text{H}_2\text{O} (l) + 2\text{e}^- \rightarrow \text{Ni(OH)}_2 (s) + 2 \text{OH}^- (aq) & E^{\circ}_{\text{cathode}} &= -0.49 \text{ V} \\
& \quad \text{Cd} (s) + 2 \text{OH}^- (aq) \rightarrow \text{Cd(OH)}_2 (s) + 2\text{e}^- & E^{\circ}_{\text{anode}} &= +1.74 \text{ V}
\end{align*}
\]
d. **Nickel Metal-Hydride Battery**: a rechargeable dry cell that does not have a “memory” problem and can last 40 times longer than the Ni-Cd battery. The expensive and toxic cadmium is replaced by an inexpensive and environmentally friendly metal-hydride (a mixture of many metals alloys, including V, Ti, Zr, Ni, Cr, Co, and Fe). Ni-MH batteries are used in cellular phones, digital cameras, laptop computers, emergency backup lightings, power tools and even electric vehicles. Its design is similar to that of the Ni-Cd battery and yields the same $E^\circ_{\text{cell}}$.

Ni-MH batteries are a popular power source for portable electronic devices such as digital cameras.

**Redox Reaction for a Ni-MH Dry Cell Battery**

\[
\begin{align*}
\text{(Reduction)} & \quad \text{NiOOH} (s) + \text{H}_2\text{O} (l) + e^- & \rightarrow & \quad \text{Ni(OH)}_2 (s) + \text{OH}^- (aq) & \quad E^\circ_{\text{cathode}} = -0.52 \text{ V} \\
\text{(Oxidation)} & \quad \text{MH} (s) + \text{OH}^- (aq) & \rightarrow & \quad \text{M} (s) + \text{H}_2\text{O} (l) + e^- & \quad E^\circ_{\text{anode}} = +0.73 \text{ V} \\
\text{NiOOH} (s) + \text{MH} (s) & \rightarrow & \quad \text{M} (s) + \text{Ni(OH)}_2 (s) & \quad E^\circ_{\text{cell}} = 1.25 \text{ V}
\end{align*}
\]

**d. Mercury Oxide Battery**: a non-rechargeable dry cell due to its small size has found its uses in small electronic devices like watches. It consists of amalgamated zinc-mercury Zn(Hg) (s) as the anode and both HgO (s) (cathode) and the bases (KOH (s) and Zn(OH)2 (s)) are in a dry paste. Commonly known as the button battery due to its small size.

Ni-Cd Rechargeable Batteries has $E^\circ_{\text{cell}} = 1.2 \text{ V}$ (above). The cell constructions of various Ni-Cd batteries (left).
3. **Fuel Cell**: a galvanic cell where there is a continuous supply of reactants.

- the **hydrogen-oxygen fuel cell** produces water as a product and hence is an ideal power source for zero-emission vehicles

**Redox Reaction for a Mercury Oxide Battery**

**(Reduction)**\[ \text{HgO} (s) + \text{H}_2\text{O} (l) + 2e^- \rightarrow \text{Hg} (l) + 2 \text{OH}^- (aq) \]

**(Oxidation)**\[ \text{Zn(Hg)} (s) + 2 \text{OH}^- (aq) \rightarrow \text{ZnO} (s) + \text{H}_2\text{O} (l) + \text{Hg} (l) + 2e^- \]

**E°_cathode = 0.10 V**

**E°_anode = +1.25 V**

**E°_cell = 1.35 V**

**Schematic of a Hydrogen Fuel Cell (above).**

**Redox Reaction for a Hydrogen Fuel Cell**

**(Reduction)**\[ \text{O}_2 (g) + 2 \text{H}_2\text{O} (l) + 4e^- \rightarrow 4 \text{OH}^- (aq) \]

**(Oxidation)**\[ 2 (\text{H}_2 (g) + 2 \text{OH}^- (aq) \rightarrow 2 \text{H}_2\text{O} (l) + 2e^-) \]

\[ \text{E°_cathode = 0.40 V} \]

\[ \text{E°_anode = +0.83 V} \]

\[ \text{E°_cell = 1.23 V} \]

Ford Hydrogen Fuel Cell Vehicle (FCV): The hydrogen tank (at 5000 psi) is stored inside the trunk (above). Under the hood with the fuel cell engine (below).

(Left) The Hydrogen Fueling Station at the city of Chicago. Shown in the photo is Chicago’s Fuel Cell Public Transit Vehicle. The solar panel, next to the hydrogen storage tank (vertical column), is used to supply power needed to decompose water into hydrogen and oxygen. Hence, from the production of hydrogen gas to its usage in the fuel cell vehicles, it is 100% environmentally friendly.
17.6: Corrosion

**Corrosion:** - oxidation of metal into metal-oxides.
- from the Standard Reduction Potential Table, metals are generally strong reducing agent (bottom right side). Because metals tend to have low electronegativity, they lose electrons easily to form cations (oxidation).
- since solid gold is the weakest of all metal reducing agents, it lacks the ability to oxidize and hence gold is considered a precious metal where all currencies are based on.

**Ways to Prevent Corrosion:**

1. **Painting:** - putting a protective coating like paint on metals covers the metal surfaces so oxidation of the metal cannot take place.
   - if the paint coating is scratched, oxidation will occur on the metal. Any rust needs to be removed before a fresh coat of paint is put on.

2. **Alloys:** - by mixing metals in various percentages to form an alloy, the reduction potential increases.
   - stainless steel is composed of iron and carbon, which has a higher reduction potential than iron metal. Therefore, stainless steels do not rust.
   - **Surface Alloy:** - when alloy is coated of the metal surface by bombardment of alloy metals in gaseous ions form (alloying plasma – ion gas that consists of alloys to be coated). This makes a cheaper alternative than making the entire material out of alloy.
3. **Galvanization**: the plating of a metal with a lower reduction potential (higher oxidizing potential – stronger reducing agents like zinc or magnesium) on the metal intended for protection.
- the oxygen will likely react with the stronger reducing agent metal, leaving the other metal unreacted.
- the metal with the lower reduction potential is in effect protecting the other metal, hence we call this the galvanizing metal **sacrificial metal**.
- galvanized metal last longer than zinc and does not need reapplication because it is “self-healing” when scratched (see below).

**Example**: Zinc is often used to galvanize iron metal.

\[
\begin{align*}
\text{O}_2 + 2 \text{H}_2\text{O} + 4e^- & \rightarrow 4 \text{OH}^- \\
\text{Fe}^{2+} + 2e^- & \rightarrow \text{Fe(s)} \\
\text{Zn}^{2+} + 2e^- & \rightarrow \text{Zn(s)} \quad \text{(SRA)}
\end{align*}
\]

\[
E^\circ \text{ reduction} = 0.40 \text{ V} \\
E^\circ \text{ reduction} = -0.44 \text{ V} \\
E^\circ \text{ reduction} = -0.76 \text{ V}
\]

Zinc will be oxidized first (sacrificed) before iron.

\[
\begin{align*}
\text{O}_2 + 2 \text{H}_2\text{O} + 4e^- & \rightarrow 4 \text{OH}^- \\
2 (\text{Zn(s)}) & \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{(SRA)} \\
\text{O}_2 + 2 \text{H}_2\text{O} + 2 \text{Zn(s)} & \rightarrow 2 \text{Zn}^{2+} + 4 \text{OH}^- \\
E^\circ \text{ cell} & = 1.16 \text{ V}
\end{align*}
\]

\[
\text{O}_2-\text{Zn(s)} \text{ has a Higher Voltage than } E^\circ \text{cell of } \text{O}_2-\text{Fe(s)}. \text{ Therefore, it is More Spontaneous.}
\]

(Above) Deep-sea structures like offshore oil drilling platforms used sacrificial metals to protect the main structure from corrosion.

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4. **Cathodic Protection**: - it is similar to galvanization, in an electrolytic environment (sea water and underground water), the sacrificial metal – the most active metal (anode) will oxidize first. Electrons flow to the protected less reactive metal (cathode). When the anode supplies current, it will gradually dissolve into ions in the electrolyte, and at the same time produce electrons, which the cathode will receive through the metallic connection with the anode. The result is that the cathode will be negatively polarised and hence be protected against corrosion.
- unlike galvanization, we do not need to “coat” the protected metal. However, the anode metal has to be replaced over time.
- find its usage for any metal placed underground (gas pipes and gas tanks) and structures or marine transport over the seas and oceans (like bridges, offshore oil rigs and ships)

The basic principle behind cathodic protection (top left). Sacrificial metals are placed on columns of the sea-bridge (above) and underground with a metal pipe (left). All are connected by wires to facilitate the process of cathodic protection.
Determining the Redox Reaction for Electrolytic Cell

1. **List ALL ions** in the solution as well as **water**.
2. **Identify the strongest oxidizing and reducing reagents**.
3. **Balance** each of the reduction and oxidation **half reactions**.
4. **Add both half reactions** to form a complete redox reaction.
5. **Calculate the** $E^\circ_{\text{cell}}$ **of the overall reaction.**

**Example 1**: Determine the redox net-ionic reaction and the $E^\circ_{\text{cell}}$ for the following solutions when two inert electrodes (carbon) are connected with an operating power supply. Draw and label a diagram for the set up. Suggest any possible observations for these electrolytic cells.

- **SOA** | **OA**
  - $\text{Pb}^{2+}$, $\text{Br}^-$, $\text{H}_2\text{O}$
  - $\text{SRA}$ | $\text{RA}$

\[
\begin{align*}
\text{O}_2(\text{g}) + 4 \text{H}^+_{(aq)} + 4e^- & \rightarrow 2 \text{H}_2\text{O}(\text{l}) \quad E^\circ = 1.23 \text{ V} \\
\text{Br}_2(\text{l}) + 2e^- & \rightarrow \text{Br}^-_{(aq)} \quad E^\circ = 1.07 \text{ V} \\
\text{Pb}^{2+}_{(aq)} + 2e^- & \rightarrow \text{Pb}(\text{s}) \quad E^\circ = -0.13 \text{ V} \\
2 \text{H}_2\text{O}(\text{l}) + 2e^- & \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-_{(aq)} \quad E^\circ = -0.83 \text{ V}
\end{align*}
\]

We can see that this is a **Non-Spontaneous Rxn** because the half-reactions for $\text{Br}^-_{(aq)}$ is higher than $\text{Pb}^{2+}_{(aq)}$. $\text{Pb}^{2+}$ will be **reduced** (Cathode) and $\text{Br}^-$ will be **oxidized** (Anode – half-rxn needs to flip).

\[
\begin{align*}
\text{Pb}^{2+}_{(aq)} + 2e^- & \rightarrow \text{Pb}(\text{s}) \quad E^\circ = -0.13 \text{ V} \\
2 \text{Br}^-_{(aq)} & \rightarrow \text{Br}_2(\text{l}) + 2e^- \quad E^\circ = -1.07 \text{ V} \\
\text{Pb}^{2+}_{(aq)} + 2 \text{Br}^-_{(aq)} & \rightarrow \text{Br}_2(\text{l}) + \text{Pb}(\text{s}) \quad E^\circ_{\text{cell}} = -1.20 \text{ V}
\end{align*}
\]

**Minimum Voltage Needed** = 1.20 V

**Possible Observations**:
1. $\text{Pb}(\text{s})$ will be plated on the cathode.
2. $\text{Br}_2(\text{l})$ (brown liquid) can be found near the anode.
Determining the Redox Reaction for Electrolytic Cell

1. **List ALL ions** in the solution as well as **water**.
2. Identify the **strongest oxidizing** and reducing reagents.
3. **Balance** each of the reduction and oxidation half reactions.
4. **Add both half reactions** to form a complete redox reaction.
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**Example 1**: Determine the redox net-ionic reaction and the $E^{\circ}_{\text{cell}}$ for the following solutions when two inert electrodes (carbon) are connected with an operating power supply. Draw and label a diagram for the set up. Suggest any possible observations for these electrolytic cells.

- **SnBr$_2$**

**SOA**

<table>
<thead>
<tr>
<th>Major Species</th>
<th>OA</th>
<th>SRA</th>
<th>RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pb}^{2+}$, $\text{Br}^-$, $\text{H}_2\text{O}$</td>
<td>$\text{S}_{\text{RA}}$</td>
<td>$\text{O}_{\text{OA}}$</td>
<td></td>
</tr>
<tr>
<td>$\text{O}_2(g) + 4 \text{H}^+(aq) + 4e^- \rightarrow 2 \text{H}_2\text{O}(l)$</td>
<td>( E^\circ = 1.23 \text{ V} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Br}_2(l) + 2e^- \rightarrow \text{Br}^-(aq)$</td>
<td>( E^\circ = 1.07 \text{ V} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s)$</td>
<td>( E^\circ = -0.13 \text{ V} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2 \text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$</td>
<td>( E^\circ = -0.83 \text{ V} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

We can see that this is a **Non-Spontaneous Rxn** because the half-reactions for $\text{Br}^-(aq)$ is higher than $\text{Pb}^{2+}(aq)$. $\text{Pb}^{2+}$ will be **reduced** (Cathode) and $\text{Br}^-$ will be **oxidized** (Anode – half-rxn needs to flip).

\[
\begin{align*}
\text{Pb}^{2+}(aq) + 2e^- & \rightarrow \text{Pb}(s) \quad E^\circ = -0.13 \text{ V} \\
2 \text{Br}^-(aq) & \rightarrow 2 \text{Br}(l) + 2e^- \quad E^\circ = -1.07 \text{ V} \\
\text{Pb}^{2+}(aq) + 2 \text{Br}^-(aq) & \rightarrow \text{Br}_2(l) + \text{Pb}(s) \quad E^\circ_{\text{cell}} = -1.20 \text{ V}
\end{align*}
\]

**Minimum Voltage Needed** = **1.20 V**

**Possible Observations**:
1. $\text{Pb}(s)$ will be plated on the cathode.
2. $\text{Br}_2(l)$ (brown liquid) can be found near the anode.
Possible Observations:
1. Ni(s) will be plated on the cathode.
2. O₂(g) will be bubbling out of the anode.
3. pH of the solution will decrease as [H⁺] increases.

**Table:**

<table>
<thead>
<tr>
<th>Major Species</th>
<th>SOA</th>
<th>OA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₂⁺, NO₃⁻, H₂O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

NO₃⁻ is neither an oxidizing agent because the solution has no H⁺. We can see that this is a Non-Spontaneous Rxn because the half-reactions for H₂O(l) is higher than Ni²⁺(aq). Ni²⁺ will be reduced (Cathode) and H₂O will be oxidized (Anode – half-rxn needs to flip).

2 ( Ni²⁺(aq) + 2e⁻ → Ni(s) )  
2 H₂O(l) → O₂(g) + 4 H⁺(aq) + 4e⁻  

Minimum Voltage Needed = 1.49 V

Possible Observations:
1. H₂(g) bubbles out at the cathode.
2. O₂(g) bubbles out of the anode.
**Example 2**: If a 30.0 A of current flow through an electrolytic cell containing molten aluminum oxide for 1.00 hour. What mass of aluminum will be deposited at the cathode?

\[
\begin{align*}
I &= 30.0 \text{ A} = 30.0 \text{ C/s} \\
\tau &= 1.00 \text{ hour} = 60.0 \text{ min} = 3600 \text{ s} \\
F &= 9.65 \times 10^4 \text{ C/mol} \\
n_{e^-} &= \frac{It}{F} = \frac{(30.0 \text{ C/s})(3600 \text{ s})}{(9.65 \times 10^4 \text{ C/mol})} = 1.119170984 \text{ mol} \\
\text{Al}^{3+} &\rightarrow 3e^- \\
1.119170984 \text{ mol} &\rightarrow ? \text{ g} \\
M_{\text{Al}} &= 26.98 \text{ g/mol} \\
m_{\text{Al}} &= ? \\
n_{\text{Al}} &= 1.119170984 \text{ mol} \times \frac{1 \text{ mol Al}}{3 \text{ mol e}^-} = 0.3730569948 \text{ mol Al} \\
m_{\text{Al}} &= (0.3730569948 \text{ mol Al})(26.98 \text{ g/mol}) = 10.1 \text{ g} \\
\end{align*}
\]
Example 3: A student wishes to plate 11.74 g of Ni (s) onto a piece of metal using 2.00 mol/L solution of NiBr₂. How long should the student run a 0.500 A current in order to produce the desire mass of nickel?

\[ I = 0.500 \text{ A} = 0.500 \text{ C/s} \]
\[ F = 9.65 \times 10^4 \text{ C/mol} \]
\[ m_{Ni} = 11.74 \text{ g} \]
\[ M_{Ni} = 58.69 \text{ g/mol} \]

\[ n_{Ni} = \frac{11.74 \text{ g} \text{ Ni}}{58.69 \text{ g/mol}} = 0.2000340774 \text{ mol Ni} \]

\[ n_{e^-} = \frac{2 \text{ mol e}^-}{1 \text{ mol Ni}} \times 0.2000340774 \text{ mol Ni} = 0.4000681547 \text{ mol e}^- \]

\[ t = \frac{n_{e^-} F}{I} = \frac{(0.4000681547 \text{ mol})(9.65 \times 10^4 \text{ C/mol})}{(0.500 \text{ C/s})} = 77213.15386 \text{ s} \times \frac{1 \text{ hr}}{3600 \text{ s}} = 21.4 \text{ hours} \]

Example 4: A certain electrolytic cell produced 39.00 g of Cl₂ from molten NaCl. The time it took for this process was 80.0 minutes. What was the average current ran during this time?

\[ m_{Cl_2} = 39.0 \text{ g} \]
\[ M_{Cl_2} = 70.906 \text{ g/mol} \]
\[ t = 80.0 \text{ min} = 4800 \text{ s} \]
\[ F = 9.65 \times 10^4 \text{ C/mol} \]

\[ n_{Cl_2} = \frac{39.0 \text{ g} \text{ Cl}_2}{70.906 \text{ g/mol}} = 0.5500239754 \text{ mol Cl}_2 \]

\[ n_{e^-} = \frac{2 \text{ mol e}^-}{1 \text{ mol Cl}_2} \times 0.5500239754 \text{ mol Cl}_2 = 1.100047951 \text{ mol e}^- \]

\[ I = \frac{n_{e^-} F}{t} = \frac{(1.100047951 \text{ mol})(9.65 \times 10^4 \text{ C/mol})}{(4800 \text{ s})} = 22.1 \text{ A} \]

Assignment
17.7 pg. 871–872 #73 to 88