Chapter 12
Redox reactions and Electrochemistry

• 12-1 Balancing Redox Equations
• 12-2 Electrochemical Cells
• 12-3 Stoichiometry in Electrochemical Cells
• 12-4 Metals and Metallurgy
• 12-5 Electrometallurgy

Note: See course website for text book error corrections Chapter 12 p. A-63 problem 29
• This entire Chapter deals with Oxidation, Reduction, electrochemistry and electron transfer
• Balancing Redox Reactions
• Practice, Practice, Practice
• All reactions take place in either Acid (H\(^+\)) or Basic (OH\(^-\)) conditions
• Very important to remember the problem you are working. Is it acidic or basic conditions?
• We will be adding H\(_2\)O and H\(^+\) for acid reactions or H\(_2\)O and OH\(^-\) for basic reaction in order to properly balance the reactions
• Practice, Practice, Practice
<table>
<thead>
<tr>
<th>Term</th>
<th>Oxidation Number Change</th>
<th>Electron Change</th>
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<tbody>
<tr>
<td>Oxidation</td>
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<td>Loss of Electrons</td>
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<td>Reduction</td>
<td>Decrease</td>
<td>Gain of Electrons</td>
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<tr>
<td>Oxidizing Agent, does the oxidizing</td>
<td>Decrease</td>
<td>Picks Up electrons</td>
</tr>
<tr>
<td>Reducing Agent, does the reducing</td>
<td>Increase</td>
<td>Supplies Electrons</td>
</tr>
<tr>
<td>Substance Oxidized</td>
<td>Increase</td>
<td>Loses Electrons</td>
</tr>
<tr>
<td>Substance Reduced</td>
<td>Decrease</td>
<td>Gains Electrons</td>
</tr>
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• **Step 1** Write two unbalanced half-equations, one for the species that is oxidized and its product and one for the species that is reduced and its product.

• **Step 2** Insert coefficients to make the numbers of atoms of all elements except oxygen and hydrogen equal on the two sides of each half-equation.

• **Step 3** Balance oxygen by adding $H_2O$ to the side deficient in O in each half-equation.

• **Step 4** Balance hydrogen.
  - For half-reaction in acidic solution, add $H^+$ on to the side deficient in hydrogen.
  - For a half-reaction in basic solution, add $H_2O$ to the side that is deficient in hydrogen and an equal amount of $OH^-$ to the other side.
• **Step 5** *Balance charge* by inserting $e^-$ (electrons) as a reactant or product in each half-reaction.

• **Step 6** *Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication*

• **Step 7** *Check for balance*
Balancing Redox Reactions

- Dithionite ion reacting with chlorous acid in aqueous acidic conditions

\[ \text{S}_2\text{O}_6^{2-}(aq) + \text{HClO}_2(aq) \rightarrow \text{SO}_4^{2-}(aq) + \text{Cl}_2(g) \]

Will have:
- Oxidation half reaction
- Reduction half reaction
• **Step 1** Write two unbalanced half-equations, one for the species that is oxidized and its product and one for the species that is reduced and its product

\[ \text{Dithionate} \\
(\text{we will see eventually that this is the oxidation reaction}) \]

\[ \text{Chlorous acid} \\
(\text{we will see eventually that this is the reduction reaction}) \]

\[ \text{S}_2\text{O}_6^{2-}(aq) + \text{HClO}_2(aq) \]
\[ \rightarrow \text{SO}_4^{2-}(aq) + \text{Cl}_2(g) \]
**Step 2** Insert coefficients to make the numbers of atoms of all elements except oxygen and hydrogen equal on the two sides of each half-equation.

\[ S_2O_6^{2-} \rightarrow SO_4^{2-} \]

\[ HClO_2 \rightarrow Cl_2 \]
• **Step 3** Balance oxygen by adding $H_2O$ to the side deficient in $O$ in each half-equation

\[
\begin{align*}
S_2O_6^{2-} & \rightarrow 2 SO_4^{2-} \\
2HClO_2 & \rightarrow Cl_2
\end{align*}
\]
• **Step 4** *Balance hydrogen.*
  
  – *For half-reaction in acidic solution, add $H^+$ on to the side deficient in hydrogen.*
  
  – *For a half-reaction in basic solution, add $H_2O$ to the side that is deficient in hydrogen and an equal amount of $OH^-$ to the other side*

Dithionate ion reacting with chlorous acid in aqueous **acidic** conditions

\[ 2H_2O + S_2O_6^{2-} \rightarrow 2SO_4^{2-} \]

\[ 2HClO_2 \rightarrow Cl_2 + 4H_2O \]
• Step 5 Balance charge by inserting $e^-$ (electrons) as a reactant or product in each half-reaction.

$$2\text{H}_2\text{O} + \text{S}_2\text{O}_6^{2-} \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+$$

$$6\text{H}^+ + 2\text{HClO}_2 \rightarrow \text{Cl}_2 + 4\text{H}_2\text{O}$$
Step 6 Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication.

\[
2H_2O + S_{2}O_6^{2-} \\
\rightarrow 2SO_4^{2-} + 4H^+ + 2e^-
\]
• **Step 6** Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication

**3 times**

\[
\begin{align*}
2H_2O + S_2O_6^{2-} & \rightarrow 2SO_4^{2-} + 4H^+ + 2e^- \\
\end{align*}
\]

equals

\[
\begin{align*}
H_2O + S_2O_6^{2-} & \rightarrow SO_4^{2-} + H^+ + e^- \\
\end{align*}
\]

Now add both Re-Ox reactions
Step 6 Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication.

\[
6H_2O + 3S_2O_6^{2-} \rightarrow 6SO_4^{2-} + 12H^+ + 6e-
\]

\[
6H^+ + 2HClO_2 + 6e- \rightarrow Cl_2 + 4H_2O
\]
• **Step 7 Check for balance**

\[
2\text{H}_2\text{O} + 3\text{S}_2\text{O}_6^{2-} + 2\text{HClO}_2 \\
\rightarrow 6\text{SO}_4^{2-} + 6\text{H}^+ + \text{Cl}_2
\]

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<tr>
<td>Cl</td>
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If it doesn’t balance, look for simple mistakes first

- Omitted subscripts
- Omitted superscripts
Typical Exam Question

• Find the (integer) stoichiometry coefficients for the correctly balanced version of the following reaction

\[ \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ + \text{I}^- \rightarrow \text{Cr}^{+3} + \text{H}_2\text{O} + \text{I}_3^- \]
Step 1 Write two unbalanced half-equations, one for the species that is oxidized and its product and one for the species that is reduced and its product.

\[
\text{Cr}_2\text{O}_7^{2-} + \text{H}^+ + \text{I}^- \rightarrow \text{Cr}^{3+} + \text{H}_2\text{O} + \text{I}_3^-
\]
Step 2: Insert coefficients to make the numbers of atoms of all elements except oxygen and hydrogen equal on the two sides of each half-equation.

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{+3} \]

\[ \text{I}^- \rightarrow \text{I}_3^- \]
• **Step 3** Balance oxygen by adding $H_2O$ to the side deficient in $O$ in each half-equation

\[
\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{+3}
\]

\[
3\text{I}^- \rightarrow \text{I}_3^-
\]
• **Step 4** *Balance hydrogen.*
  
  – *For half-reaction in acidic solution, add* $H^+$ *on to the side deficient in hydrogen.*
  
  – *For a half-reaction in basic solution, add* $H_2O$ *to the side that is deficient in hydrogen and an equal amount of* $OH^-$ *to the other side*

Dichromate ion reacting with iodide ion in aqueous *acidic* conditions

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} & \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \\
3\text{I}^- & \rightarrow \text{I}_3^-
\end{align*}
\]
• **Step 5** Balance charge by inserting $e^-$ (electrons) as a reactant or product in each half-reaction.

\[
14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O
\]

\[
3I^- \rightarrow I_3^-
\]
Step 6 Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication.

Reduction reaction has 6 electrons

Oxidation Reaction has 2 electrons

Multiply the oxidation reaction by 3 this will give 6 electrons on both sides of the reaction

$$3I^- \rightarrow I_3^- + 2e^-$$
• **Step 6** Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication.

\[
\begin{align*}
3 &\text{ times} \\
3I^- &\rightarrow I_3^- + 2e^- \\
\text{equals} \\
\end{align*}
\]

Now add both Re-Ox reactions
• **Step 6** Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication.

\[
6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O
\]

\[
9I^- \rightarrow 3 I_3^- + 6 e^-
\]

**equals**

\[
\text{cancel out the duplication}
\]

\[
\text{cancel out the duplication}
\]

\[
6e^- + 14H^+ + Cr_2O_7^{2-} + 9I^- \rightarrow 2Cr^{3+} + 7H_2O + 3 I_3^- + 6 e^-
\]
• **Step 7 Check for balance**

\[
14H^+ + Cr_2O_7^{2-} + 9I^- \rightarrow 2Cr^{3+} + 7H_2O + 3 I_3^-
\]

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<td>I</td>
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<td>9</td>
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Basic Solution
Method 1

• At Step 4
  – Instead of adding H\(^+\) on the deficient side as did with the acid solution method
  – Add H\(_2\)O on the H deficient side and add an equal amount of OH\(^-\) on the other side.
Typical Exam Question

• Note: this is not Example 12-2, which is similar

• Find the (integer) stoichiometry coefficients for the correctly balanced version of the following reaction conducted in a basic solution

$$\text{Ag}_2\text{S} + \text{Cr(OH)}_3 \rightarrow \text{Ag}^0 + \text{HS}^- + \text{CrO}_4^{2-}$$
• **Step 1** Write two unbalanced half-equations, one for the species that is oxidized and its product and one for the species that is reduced and its product.

\[
\begin{align*}
\text{Ag}_2\text{S} + \text{Cr(OH)}_3 & \rightarrow \text{Ag}^0 + \text{HS}^- + \text{CrO}_4^{2-} \\
\text{Ag}_2\text{S} & \rightarrow \text{Ag} + \text{HS}^- \\
\text{Cr(OH)}_3 & \rightarrow \text{CrO}_4^{2-}
\end{align*}
\]
• **Step 2** Insert coefficients to make the numbers of atoms of all elements except oxygen and hydrogen equal on the two sides of each half-equation.

\[
\text{Ag}_2\text{S} \quad \rightarrow \quad \text{Ag} + \text{HS}^- \\
\text{Cr(OH)}_3 \quad \rightarrow \quad \text{CrO}_4^{2-}
\]
• **Step 3** Balance oxygen by adding $H_2O$ to the side deficient in $O$ in each half-equation

\[
\text{Ag}_2\text{S} \rightarrow 2\text{Ag} + \text{HS}^- \\
\text{Cr(OH)}_3 \rightarrow \text{CrO}_4^{2-}
\]
• **Step 4** *Balance hydrogen.*
  
  – *For half-reaction in acidic solution, add $H^+$ on to the side deficient in hydrogen.*
  
  – *For a half-reaction in basic solution, add $H_2O$ to the side that is deficient in hydrogen and an equal amount of $OH^-$ to the other side.*

This problem is in aqueous **basic** conditions

```
Ag_2S

→ 2Ag + HS^-
```

```
H_2O + Cr(OH)_3

→ CrO_4^{2-}
```
• **Step 5** Balance charge by inserting $e^-$ (electrons) as a reactant or product in each half-reaction.

\[
\begin{align*}
\text{H}_2\text{O} + \text{Ag}_2\text{S} & \quad \rightarrow \quad 2\text{Ag} + \text{HS}^- + \text{OH}^- \\
\text{5OH}^- + \text{H}_2\text{O} + \text{Cr(OH)}_3 & \quad \rightarrow \quad \text{CrO}_4^{2-} + 5\text{H}_2\text{O}
\end{align*}
\]
• **Step 6** *Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If H⁺ ion, OH⁻ ion, or H₂O appears on both sides of the final equation, cancel out the duplication*

Reduction reaction has 2 electrons

Oxidation Reaction has 3 electrons
Step 6. Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If H\(^+\) ion, OH\(^-\) ion, or H\(_2\)O appears on both sides of the final equation, cancel out the duplication.

\[
\begin{align*}
\text{Reduction reaction} & = 6e^- + 3H_2O + 3Ag_2S \\
& \rightarrow Ag + HS^- + OH^- \\
\text{Oxidation reaction} & = 10OH^- + 2H_2O + 2Cr(OH)_3 \\
& \rightarrow CrO_4^{2-} + H_2O + e^-
\end{align*}
\]
• **Step 6** Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal to the number taken up by the reduction. Then add the two half-equations and cancel out the electrons. If $H^+$ ion, $OH^-$ ion, or $H_2O$ appears on both sides of the final equation, cancel out the duplication.

Now add both Re-Ox reactions

\[
\begin{align*}
6e^- + 3H_2O + 3Ag_2S & \rightarrow 6Ag + 3HS^- + 3OH^- \\
10OH^- + 2H_2O + 2Cr(OH)_3 & \rightarrow 2CrO_4^{2-} + 10H_2O + 6e^-
\end{align*}
\]
Now add both Re-Ox reactions

\[
6e^- + 3H_2O + 3Ag_2S \\
\rightarrow 6Ag + 3HS^- + 3OH^- \\
10OH^- + 2H_2O + 2Cr(OH)_3 \\
\rightarrow 2CrO_4^{2-} + 10H_2O + 6e^-
\]

equals

\[
6e^- + 3H_2O + 3Ag_2S + \\
10OH^- + 2H_2O + 2Cr(OH)_3 \\
\rightarrow 6Ag + 3HS^- + 3OH^- + \\
2CrO_4^{2-} + 10H_2O + 6e^-
\]
simplify

\[ 6e^- + 3H_2O + 3Ag_2S + 10OH^- + 2H_2O + 2Cr(OH)_3 \rightarrow 6Ag + 3HS^- + 3OH^- + 2CrO_4^{2-} + 10H_2O + 6e^- \]

\[ 3Ag_2S + 7OH^- + 2Cr(OH)_3 \rightarrow 6Ag + 3HS^- + 2CrO_4^{2-} + 5H_2O \]
Step 7 Check for balance

\[
3\text{Ag}_2\text{S} + 7\text{OH}^- + 2\text{Cr(OH)}_3 \rightarrow 6\text{Ag} + 3\text{HS}^- + 2\text{CrO}_4^{2-} + 5\text{H}_2\text{O}
\]

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<td>9</td>
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</tr>
</tbody>
</table>

**NOTE:** This problem is the reverse reaction of Example 12-2
Typical Exam Question

Answer

• Note: this is not Example 12-2, which is similar

• Find the (integer) stoichiometry coefficients for the correctly balanced version of the following reaction conducted in a basic solution

\[
3 \text{Ag}_2\text{S} + 2 \text{Cr(OH)}_3 + 7 \text{OH}^- \rightarrow 6 \text{Ag} + 3 \text{HS}^- + 2\text{CrO}_4^{2-} + 5\text{H}_2\text{O}
\]
Chapter 12
Redox reactions and Electrochemistry
Balancing Disproportionation Reactions

- Same Steps
- For example

\[ \text{Cl}_2 \rightarrow \text{ClO}_3^- + \text{Cl}^- \]

- Step 1
  - Oxidation:
  - Reduction:
### Chapter 12
Redox reactions and Electrochemistry

- **Review of Common Terms**

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<tr>
<th>Term</th>
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<th>Electron Change</th>
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</thead>
<tbody>
<tr>
<td>1 Oxidation</td>
<td>increase</td>
<td>loss of electrons</td>
</tr>
<tr>
<td>2 Reduction</td>
<td>decrease</td>
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<td>3 Oxidizing Agent</td>
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<td>increase</td>
<td>supplies electrons</td>
</tr>
<tr>
<td>5 Substance Oxidized</td>
<td>increase</td>
<td>loses electrons</td>
</tr>
<tr>
<td>6 Substance Reduced</td>
<td>decrease</td>
<td>gains electrons</td>
</tr>
</tbody>
</table>

1. **Oxidation increase**
   - e.g., Cu to Cu\(^{2+}\) (0 to +2)

2. **Reduction decrease**
   - e.g., Ni\(^{+}\) to Ni (+1 to 0)

3. **Oxidizing Agent decrease**
   - e.g., O\(_2\) to oxide (0 to -2)

4. **Reducing Agent increase**
   - e.g., H\(_2\) to H\(_2\)O (0 to +1)

5. **Substance Oxidized increase**
   - e.g., Mg to MgO (0 to +2)

6. **Substance Reduced decrease**
   - e.g., CuO to Cu (+2 to 0)
Electrochemical Cells

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

Silver plates spontaneously

\[ \therefore \Delta G_f < 0 \]

Called a galvanic or voltaic cell
Cu(s) + 2Ag⁺(aq) → Cu⁺⁺(aq) + 2Ag(s)

Chemical energy converted to Electrical Energy. This potential difference can be measured.
\[ \text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{++}(\text{aq}) + 2\text{Ag(s)} \]

Convention for this reaction

\[ \text{Cu(s)} \mid \text{Cu}^{+2}(\text{aq}) \parallel \text{Ag}^+(\text{aq}) \mid \text{Ag(s)} \]
If an opposing electric force is applied the reverse reaction occurs, called an electrolytic cell

$$\text{Cu}^{++}(aq) + 2\text{Ag}(s) \rightarrow \text{Cu}(s) + 2\text{Ag}^{+}(aq)$$
Stoichiometry in Electrochemical Cells

• Faraday’s Law
  – The quantities of substances produced or consumed at the electrodes are directly proportional to the amount of electric charge passed through the cell.
  – When a given amount of electric charge passes through a cell, the quantity of a substance produced or consumed at an electrode is proportional to its molar mass divided by the number of moles of electrons required to produce or consume one mole of the substances.
**Faraday Constant** \((F)\) = the electric charge carried by 1 mole of electrons.

Charge 1 \(e\) = \(1.602 \times 10^{-19}\) Coulombs

\(\times\) Avogadro’s number

1 **Faraday** = 96,485 Coulombs of charge per mole of electrons
Problem 12-30
What number of coulombs of electricity is produced in each of the following oxidations?

- 1.00 mol of $\text{H}_2\text{O}_2(\text{aq})$ to $\text{O}_2(\text{g})$

\[
1.00\text{mol } \text{H}_2\text{O}_2 \times \left( \frac{2\text{ mol e}^-}{\text{mol } \text{H}_2\text{O}_2} \right) \times \left( \frac{96,485\text{C}}{\text{mol e}^-} \right) = 1.93 \times 10^5 \text{C}
\]
Problem 12-30
What number of coulombs of electricity is produced in each of the following oxidations?

• 1.70 mol of H₂S (aq) to 0.850 mol of H₂S₂O₃(aq)

\[
H₂S \rightarrow H₂S₂O₃
\]

\[
1.7\text{mol H}_₂\text{S} \times \left( \frac{8\text{ mol e}^-}{2\text{ mol H}_₂\text{S}} \right) \times \left( \frac{96,485\text{C}}{\text{mol e}^-} \right) = 6.56 \times 10^5 \text{C}
\]
Stoichiometry in Electrochemical Cells

M = Molar Mass
\( \frac{M}{n_e} = \text{molar mass per \# electrons} \)

\[
\begin{align*}
\text{Ag}^+ + e^- & \rightarrow \text{Ag} \\
\frac{M}{n_e} & = \frac{107.87}{1}
\end{align*}
\]

\[
\begin{align*}
\text{Cu} & \rightarrow \text{Cu}^{++} + 2e^- \\
\frac{M}{n_e} & = \frac{63.54}{2}
\end{align*}
\]
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Redox reactions and
Electrochemistry

Example

How many grams of Cl\(_2\) can be produced by the electrolysis of molten NaCl at a current of 10.0 amps for 5 minutes?

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \]

\[
\text{mass} = \frac{I \cdot t \cdot \frac{M}{n_e}}{96,485}
\]

\[
\text{Cl}_2 (\text{grams}) = \frac{10.0 \text{amps} \cdot 5 \text{ min} \cdot 60 \text{ sec/ min} \cdot \frac{70.9}{2}}{96,485}
\]

\[
\text{Cl}_2 \text{ produced} = 1.11 \text{ grams}
\]
Reminder

1 mole electrons
  reduces 1 mol of Ag$^+$
2 moles electrons
  reduces 1 mole of Mg$^{2+}$
3 moles electrons
  reduces 1 mole of Al$^{3+}$
Example (not in book)
Suppose a current of 100 amps is passed through a bath of molten alumina and cryolite (a mineral Na₃AlF₆) for 10 minutes. How many grams of elemental aluminum are produced? The molar mass of aluminum is 26.90 g/mol.

What is the oxidation number of Al in Na₃AlF₆?
Example

How long would it take to plate 5.43 grams Nickel on to an electrode from a solution of NiCl$_2$ at a current of 12.34 amps? Molar mass of Nickel is 58.693 g mol$^{-1}$.

\[\text{Ni}^{+2} + 2\text{e}^- \rightarrow \text{Ni}\]
Chapter 12
Redox reactions and
Electrochemistry

Summary

• Balancing Redox reactions

• Understand electrochemical cells and the Faraday law calculations
Chapter 12
Redox reactions and
Electrochemistry

Examples / Exercises
12-1, 12-2, 12-3, 12-4, 12-5

Problems
1, 3, 7, 9, 11, 13, 29, 31, 33

Note: see website for Problem 29 correct answers