CHAPTER 12: Redox Reactions and Electrochemistry

• Recall “GERtrude and LEO”
• Gain of Electrons Reduction
• Loss of Electrons Oxidation
• Goals of Chapter:
  – Understand redox reactions in detail
  – Review oxidation numbers
  – Learn electrochemical techniques
• Application of Redox Chemistry – extracting metals from ores, e.g.

\[
\text{Cu}_2\text{CO}_3\text{(OH)}_2(s) + C(s) \rightarrow 2\text{Cu(s)} + 2\text{CO}_2(g) + \text{H}_2\text{O(g)}
\]

“azorite”

• Need to learn to balance tricky redox reactions

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Balancing Redox Equations

• Book provides a very schematic, step-by-step approach. Take a look at it.
• We’ll take a more freestyle approach.
• Let’s do the first example in the book.
• Balance:

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

\[
S_2O_6^{2-} (aq) + HClO_2 (aq) \rightarrow SO_4^{2-} (aq) + Cl_2(g)
\]

• General Strategy
  – Divide equation into two **half-reactions**
  – One reaction for reduction
  – One reaction for oxidation
  – Balance each separately then recombine

• Another Trick
  – Assuming reactions in aqueous solution, \( H_2O \) can be thrown in to the equation when needed (might not be given!!)
  – \( H^+ \) can be helpful for acidic solutions
  – \( OH^- \) can be of use in basic solutions
Back to the Example

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

- First break into half-reactions … What element is reduced? What is oxidized?

Reduced: ________________________________

Oxidized: ________________________________
Begin the Balancing Act

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

- Now balance the non-H, non-O atoms for each half-reaction:

  **Reduction:**
  \[ \text{HClO}_2 \rightarrow \text{Cl}_2 \]

  **Oxidation:**
  \[ \text{S}_2\text{O}_6 \rightarrow \text{SO}_4^{2-} \]
Balance H and O’s

\[
S_{2}O_{6}^{2-} (aq) + HClO_{2} (aq) \rightarrow SO_{4}^{2-} (aq) + Cl_{2}(g)
\]

- Now throw in H$_{2}$O, H$^{+}$ (if acidic), OH$^{-}$ (if basic) as needed to balance the H and O atoms. Here acidic (HClO$_{2}$).

Reduction:

\[
2HClO_{2} \rightarrow Cl_{2}
\]

Oxidation:

\[
S_{2}O_{6} \rightarrow 2SO_{4}^{2-}
\]
Overview

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

Break into half-reactions:

- Reduced: \[ \text{HClO}_2 \rightarrow \text{Cl}_2 \]
- Oxidized: \[ \text{S}_2\text{O}_6^{2-} \rightarrow \text{SO}_4^{2-} \]

Balance Cl, S:

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

Balance H, O:

\[ 6\text{H}^+ + 2\text{HClO}_2 \rightarrow \text{Cl}_2 + 4\text{H}_2\text{O} \]
\[ 2\text{H}_2\text{O} + \text{S}_2\text{O}_6^{2-} \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+ \]

Combine the halves … balance electrons first!

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Balancing Electrons

• Add and subtract electrons to make charge balance on both sides of equation (seem strange? Don’t worry, just temporary for book keeping!)

\[
6H^+ + 2\text{HClO}_2 \rightarrow \text{Cl}_2 + 4\text{H}_2\text{O}
\]

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

• Multiply one of the equations to obtain equal number of electrons. Then, add to cancel out electrons.

  Reduction: \[
6H^+ + 2\text{HClO}_2 \rightarrow \text{Cl}_2 + 4\text{H}_2\text{O}
\]

  Oxidation: \[
\text{H}_2\text{O} + \text{S}_2\text{O}_6^{2-} \rightarrow 2\text{SO}_4^{2-} + 4\text{H}^+
\]

Final:

• Check: everything balanced?
Another Practice Problem

AsO$_3^{3-}$ (aq) + Br$_2$ (aq) $\rightarrow$ AsO$_4^{3-}$ (aq) + Br$^-$ (aq)  **assume basic

I. Identify what’s oxidized and what’s reduced
II. Split oxidation and reduction reaction, balance for all atoms but O,H
III. Add H$_2$O, H$^+$, OH$^-$ to balance H,O
IV. Add electrons to balance charge for half-reaction
V. Add half-reactions together to cancel electrons
Another Practice Problem

AsO$_3^{3-}$ (aq) + Br$_2$ (aq) $\rightarrow$ AsO$_4^{3-}$ (aq) + Br$^-$ (aq)  **assume basic
Disproportionation

• The same chemical species is both oxidized and reduced. e.g.,

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

[unbalanced]

• In these cases, a single species is allowed to appear in both half-reactions.

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

[unbalanced]

\[ \text{Cl}_2 \rightarrow \text{Cl}^- \]  

[unbalanced]
Application to Batteries

• Batteries work by using redox reactions.
• Example of an electrochemical cell:
  \[ \text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)} \]
• Above equation is balanced – recall example of deposition of Ag(s) on copper wire in AgNO₃ solution.
• Batteries harness the flow of electrons in redox reactions to perform electrical work.
A Look Inside a Battery

- Electrons are produced at the anode by oxidation. They flow to the (+) cathode, where they promote reduction.
- Salt bridge allows flow of ions to keep charge neutrality of solutions.
- Amount of charge flow can be measured by:
  \[ I = \frac{Q}{t} \]
  current = charge/time  amperes (A) = Coulombs/sec
Example Problem

• How many amps would be needed to reduce 1 mol of Ag\(^+\) ions in one hour? \(I = \frac{Q}{t}\)

• To reduce a mol of Ag\(^+\), one mol of e\(^-\) is needed.
Example Problem 2

- A galvanic cell generates an average current of 0.121 A for 15.6 min. The cathode half-reaction in the cell is \( \text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s) \). What mass of lead is deposited at the cathode?
Electrometallurgy

• Electrochemical methods to produce metals from compounds (often ores)
• Uses redox reactions. e.g.,

\[
2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Al} + 3\text{CO}_2 \\
\text{MgCl}_2(\text{l}) \rightarrow \text{Mg(}\text{l}) + \text{Cl}_2(\text{g})
\]

Dangerous process!!
Converted to HCl.

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Electrorefining

• Purify metals by electrochemistry.
• Metals leave anode (where they’re oxidized) as ions and re-deposit on cathodes.
• Impurities are more likely to stay in solution.
Electroplating

- Use of electrochemistry to deposit a thin film of a metal (like Ag, Au) on top of another substance.