CHAPTER 12: Redox Reactions and Electrochemistry

- Recall “<u>GER</u>trude and <u>LEO</u>”
- <u>G</u>ain of <u>E</u>lectrons <u>R</u>eduction
- <u>L</u>oss of <u>E</u>lectrons <u>O</u>xidation
- Goals of Chapter:
  - Understand redox reactions in detail
  - Review oxidation numbers
  - Learn electrochemical techniques
- Application of Redox Chemistry – extracting metals from ores, e.g.

$$\overset{+2}{Cu}_2\overset{+4}{C}O_3(OH)_2(s) + \overset{0}{C}(s) \rightarrow 2\overset{0}{Cu}(s) + 2\overset{+4}{C}O_2(g) + H_2O(g)$$

“azurite”

- Need to learn to balance tricky redox reactions

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:

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

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

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

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

Reduced: ______________________________________

Oxidized: ______________________________________

Begin the Balancing Act

$S_2O_6^{2-}$ (aq) + $HClO_2$ (aq) → SO_4^{2-} (aq) + Cl_2(g)

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

Reduction: $HClO_2 \rightarrow Cl_2$

Oxidation: $S_2O_6 \rightarrow SO_4^{2-}$

Balance H and O's

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

- Now throw in H_2O, 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:

$S_2O_6 \rightarrow 2SO_4^{2-}$

Overview

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

Break into half-reactions:

Reduced: $\overset{+1\,+3\,-2}{HClO_2} \rightarrow \overset{0}{Cl_2}$

Oxidized: $\overset{+5\;\;-2}{S_2O_6^{2-}} \rightarrow \overset{+6\;\;-2}{SO_4^{2-}}$

Balance Cl, S:

$$2HClO_2 \rightarrow Cl_2$$

$$S_2O_6^{2-} \rightarrow 2SO_4^{2}$$

Balance H, O:

$$6H^+ + 2HClO_2 \rightarrow Cl_2 + 4H_2O$$

$$2H_2O + S_2O_6^{2-} \rightarrow 2SO_4^{2} + 4H^+$$

Combine the halves … balance electrons first!

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!)

$$6H^+ + 2HClO_2 \rightarrow Cl_2 + 4H_2O$$

$$H_2O + S_2O_6^{2-} \rightarrow 2SO_4^{2} + 4H^+$$

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

Reduction: $6H^+ + 2HClO_2 \rightarrow Cl_2 + 4H_2O$

Oxidation: $H_2O + S_2O_6^{2-} \rightarrow 2SO_4^{2} + 4H^+$

Final:

- Check: everything balanced?

Another Practice Problem

AsO_3^{3-} (aq) + Br_2 (aq) → 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_2O, 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.,

Cl_2 (aq) → ClO_3^- (aq) + Cl^- (aq)   [unbalanced]

- In these cases, a single species is allowed to appear in <u>both</u> half-reactions.

Cl_2 → ClO_3^-

Cl_2 → Cl^-

[unbalanced]

Application to Batteries

- Batteries work by using redox reactions.
- Example of an electrochemical cell:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

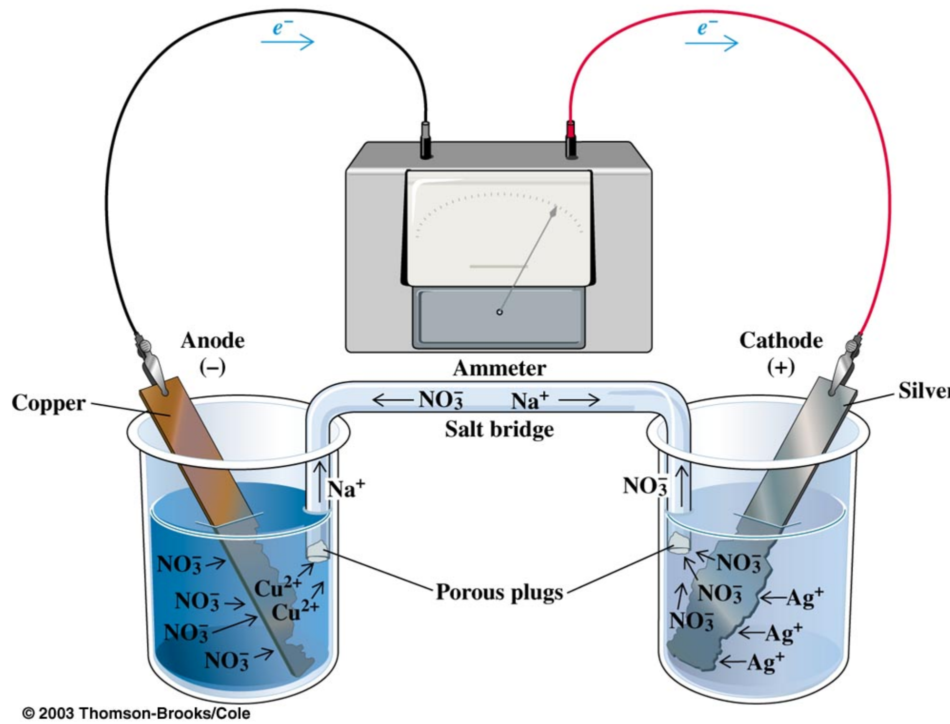
- Above equation is balanced – recall example of deposition of Ag(s) on copper wire in $AgNO_3$ solution.
- Batteries harness the flow of electrons in redox reactions to perform electrical work.

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:

$$I = Q/t$$

$$\text{current} = \text{charge/time}$$



$$\text{amperes (A)} = \text{Coulombs/sec}$$

Example Problem

- How many amps would be needed to reduce 1 mol of Ag^+ ions in one hour? $I = Q/t$
- 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 $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$. What mass of lead is deposited at the cathode?

Electrometallurgy

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

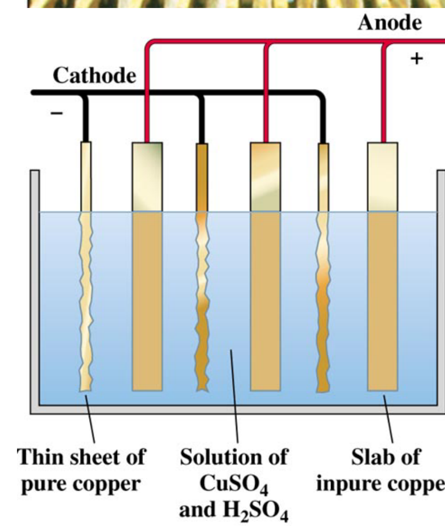
$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$

$$MgCl_2(l) \rightarrow Mg(l) + Cl_2(g)$$

Dangerous process!!
Converted to HCl.

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.