Lecture #2 of 26

Looking forward... our review of Chapter "0"

- Cool applications
- Redox half-reactions
- Balancing electrochemical equations
- History of electrochemistry
- IUPAC terminology and $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$
- Thermodynamics and the Nernst equation
- Common reference electrodes
- Standard and Absolute potentials
- Latimer and Pourbaix diagrams
- Calculating $E_{\text{cell}}$ under non-standard state conditions
- Conventions

From M3C: Oxidation and reduction

An oxidation-reduction, or "redox" reaction is one in which one or more electrons are transferred.
Redox reactions

2Na(s) + Cl₂(g) → 2NaCl(s)

Oxidation states

**Ionic compound**: the oxidation state of an atom is equal to its charge.

- KCl: K^+1, Cl^-1

**Covalent compound, different types of atoms**: the oxidation state equals the charge that would result if the electrons were given to the most electronegative atom.

- NH₃: N^-3, H^+1

**Covalent compound, same type of atoms**: charge that the compound would have if the electrons were divided evenly among atoms of the same type.

- N₂H₄ (H₂NNH₂): N^-2, H^+1

Closed (filled) orbital shells are most stable...

... in general H (+1), O (-2), halides (-1), etc.

- Zn (s) + 2HCl (aq) → ZnCl₂ (aq) + H₂ (g)
- CH₄ (g) + 2O₂ (g) → CO₂ (g) + 2H₂O (l)
Oxidation and Reduction

Oxidizing agent (oxidant) ⇒ molecule that gains electrons
Reducing agent (reductant) ⇒ molecule that loses electrons

\[ \text{Mg (s)} + \text{O}_2 (g) \rightarrow \text{MgO (s)} \]

This reaction can be split into two half-reactions

**Oxidation** half-reaction
reactant (= reducing agent) loses e−
\[ \text{2 Mg} \rightarrow \text{2 Mg}^{2+} + \text{4 e}^- \]

**Reduction** half-reaction
Reactant (= oxidizing agent) gains e−
\[ \text{O}_2 + \text{4 e}^- \rightarrow \text{2 O}^{2-} \]

Oh (silly) acronyms...

OIL RIG

- Oxidation
- Is
- Loss. (of electrons)

- Reduction
- Is
- Gain. (of electrons)

Redox reactions, or not?

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

\[ \text{Cu}^{2+} (aq) + 4\text{NH}_3 (l) \rightarrow \text{Cu(NH}_3)_4^{2+} (aq) \]
Redox reactions

Zinc metal reacts with aqueous hydrochloric acid to form zinc chloride in solution and hydrogen gas. Is this a redox reaction? If yes, identify the oxidizing agent, the reducing agent, and the substances being oxidized and reduced.

1. Write a balanced chemical equation (not always easy).

\[
\text{Zn (s) + 2HCl (aq) } \rightarrow \text{ZnCl}_2 (aq) + H_2 (g)
\]

2. Assign oxidation states.

3. Determine whether atomic oxidation states change. Yes

4. Use the changes in oxidation state for each atom to determine what is being oxidized and reduced.

\[
\begin{align*}
\text{Zn: 0} & \rightarrow +2 & \text{oxidized, reducing agent} \\
\text{H: +1} & \rightarrow 0 & \text{reduced, oxidizing agent} \\
\text{Cl: -1} & \rightarrow -1 & \text{spectator ion}
\end{align*}
\]

Half-reactions

Redox reactions are often difficult to balance by inspection. Instead, we can use the method of half-reactions. Half-reactions don’t actually exist all that often… (read on)…
Writing half-reactions

1. Assign oxidation states for each element in the reactants and products.
2. Determine what is being oxidized, what is being reduced, and how many electrons are transferred.
3. Write balanced half-reactions, using electrons as reactants or products, as appropriate.

Method of half-reactions

Each redox reaction can be separated into two half-reactions, one for oxidation and one for reduction.

\[ \text{CH}_4 (g) + 2\text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2\text{H}_2\text{O} (g) \]

- Oxidation half-reaction:
  \[ \text{CH}_4 \rightarrow \text{CO}_2 + 8\text{e}^- \]
  \[ \text{CH}_4 \rightarrow -4 \quad \text{CO}_2 \rightarrow 4 \quad \text{e}^- \rightarrow 8 \]

- Reduction half-reaction:
  \[ 2\text{O}_2 + 8\text{e}^- \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]
  \[ 2\text{O}_2 \rightarrow 2 \quad \text{e}^- \rightarrow 8 \quad \text{CO}_2 \rightarrow -2 \quad \text{H}_2\text{O} \rightarrow -2 \]

In half-reactions, electrons are written as reactants or products depending on whether they are gained or lost.

Balancing redox equations

The oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) by Cr\(_2\)O\(_7\)\(^{2-}\) (becomes Cr\(^{3+}\)) in acid solution?

1. Write the unbalanced equation for the reaction in ionic form.
   \[ \text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+} \]

2. Separate the equation into two half-reactions.
   - Oxidation:
     \[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]
     \[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]
   - Reduction:
     \[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]
     \[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]

3. Balance the atoms other than O and H in each half-reaction.
   \[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]
   \[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]
Balancing redox equations

4. For reactions in acid, add \( H_2O \) to balance O atoms and \( H^+ \) to balance H atoms.

\[
\begin{align*}
\text{Cr}_2O_7^{2-} & \rightarrow 2\text{Cr}^{3+} + 7H_2O \\
14H^+ + \text{Cr}_2O_7^{2-} & \rightarrow 2\text{Cr}^{3+} + 7H_2O
\end{align*}
\]

5. Add electrons to one side of each half-reaction to balance the charges on the half-reaction.

\[
\begin{align*}
6e^- + 14H^+ + \text{Cr}_2O_7^{2-} & \rightarrow 2\text{Cr}^{3+} + 7H_2O \\
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + e^-
\end{align*}
\]

6. If necessary, equalize the number of electrons in the two half-reactions by multiplying the half-reactions by appropriate coefficients.

\[
\begin{align*}
6\text{Fe}^{2+} & \rightarrow 6\text{Fe}^{3+} + 6e^- \\
6e^- + 14H^+ + \text{Cr}_2O_7^{2-} & \rightarrow 2\text{Cr}^{3+} + 7H_2O
\end{align*}
\]

Balancing redox equations

7. Add the two half-reactions together and balance the final equation by inspection. The number of electrons on both sides must cancel.

\[
\begin{align*}
\text{Oxidation:} & \quad 6\text{Fe}^{2+} \rightarrow 6\text{Fe}^{3+} + 6e^- \\
\text{Reduction:} & \quad e^- + 14H^+ + \text{Cr}_2O_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7H_2O \\
14H^+ + \text{Cr}_2O_7^{2-} + 6\text{Fe}^{2+} & \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7H_2O
\end{align*}
\]

8. Verify that the number of atoms and the charges are balanced.

\[
14 \times 1 - 1 \times 2 + 6 \times 2 = 24 = 6 \times 3 + 2 \times 3 + 7 \times 0
\]

9. For reactions in basic solutions, add \( OH^- \) to both sides of the equation for every \( H^+ \) that appears in the final equation…

Method of half-reactions
(under basic/alkaline conditions)

1. Use the half reaction method for acidic solution to balance the equation as if excess \( H^+ \) ions were present.

2. To both sides of the equation, add the number of \( OH^- \) ions needed to balance the \( H^+ \) ions added in the last step.

3. Form \( H_2O \) on the side containing both \( H^+ \) and \( OH^- \) ions, and cancel out the number of \( H_2O \) molecules appearing on both sides of the equation.

4. Check to make sure that the equation is balanced.
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A Short History Lesson...

Electrochemistry is associated with Luigi Galvani who discovered "animal electricity," while trying to Frankenstein frogs legs (1791)

Luigi Galvani (1737-1798) from Wiki

Physician, Physicist, Philosopher

Voltaic pile

Invented by Alessandro Volta (1800) but the elements of the pile (galvanic cells) were named after Galvani.

What are the combined half-reactions?

Volta presenting his "Voltaic Pile" to Napoleon and his court... and now he is a Count!

http://en.wikipedia.org/wiki/Voltaic_pile

http://en.wikipedia.org/wiki/Alessandro_Volta
**Galvanic Cells**

Every non-equilibrium cell is a galvanic cell (in one direction, i.e. the spontaneous direction)

Physically separating the half-reactions allows the electrons to go over a long distance, from the anode to the cathode via a (solid) conductor: basis for conversion of chemical energy into electricity = "Electrochemistry!"

Salt bridge is an ionic conduit to prevent buildup of charge in both compartments and also to prevent bulk mixing of the two solutions.

**Electrolysis of water**

Volta's results were shared with the scientific community and then, *boom*, many people demonstrated electrolysis the same year, and later electroplating!

- William Nicholson (1753–1815)
- Sir Anthony Carlisle (1768–1840)
- Johann Wilhelm Ritter (1776–1810)
- William Cruickshank (1777–1810(1))


**Daniell (galvanic) Cell (1836)**

No more $\text{H}_2$ from the (primary) battery!

- John Frederic Daniell (1790–1845)

$\text{Zn (s)} \rightarrow \text{Zn}^{2+} (aq) + 2e^-$

$\text{Cu}^{2+} (aq) + 2e^- \rightarrow \text{Cu (s)}$

**NET REACTION:** $\text{Zn (s)} + \text{Cu}^{2+} (aq) \rightarrow \text{Zn}^{2+} (aq) + \text{Cu (s)}$