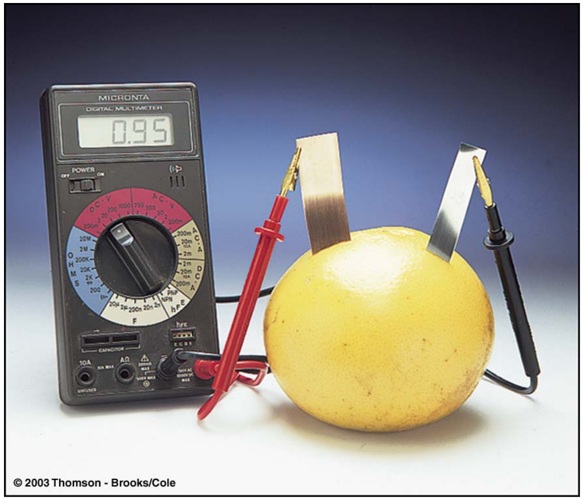
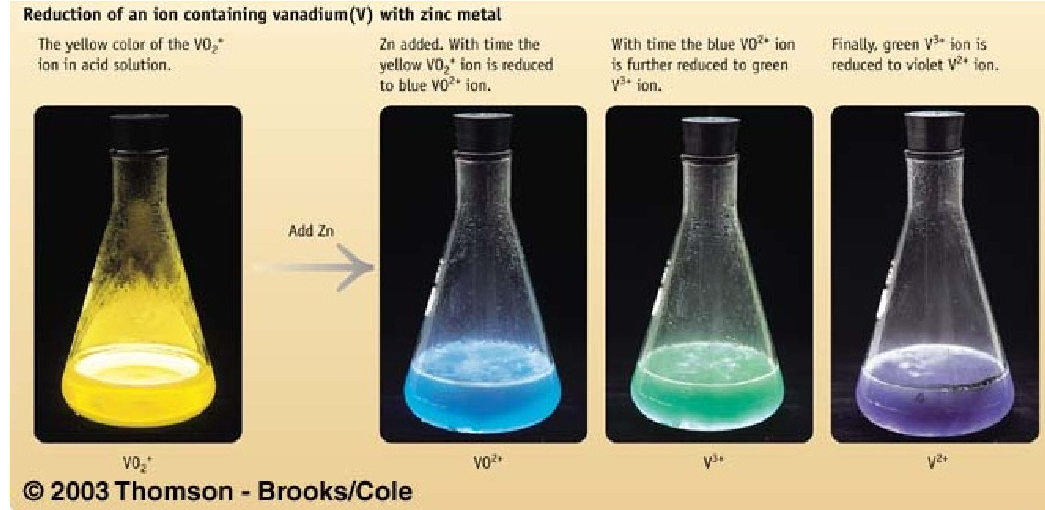




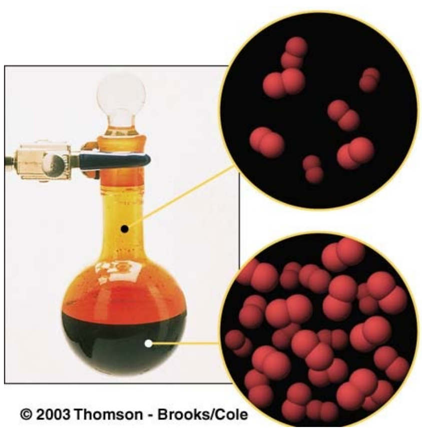
CHEMISTRY 2000

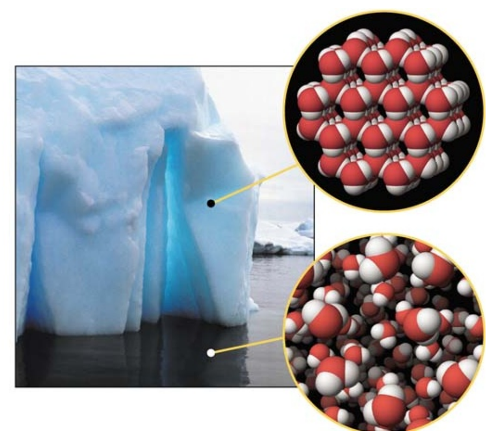
Topic #2: Thermochemistry and Electrochemistry – What Makes Reactions Go?

Fall 2020

Dr. Susan Findlay

See Exercises 9.1 and 9.2





Oxidation States

- **Oxidation states** are used as a means to track the movement of electrons in a reaction. An atom's oxidation state is the charge it would have if all bonds in the molecule were 100% ionic *(except bonds between atoms of the same element).*
- To determine oxidation states for atoms in a molecule or ion:
  - Draw the Lewis structure.
  - Assume that any bond between atoms of the same element is 100% covalent – so give half the electrons in the bond to each atom.
  - Assume that any bond between atoms of different elements is 100% ionic – so give all electrons in the bond to the more electronegative atom.

Oxidation State = # valence electrons in neutral atom - # valence electrons atom has in molecule

  - The sum of the oxidation states for every atom in the molecule/ion must equal the net charge of the molecule/ion.

Oxidation States

- To clearly illustrate the difference between calculating formal charge and calculating oxidation state, let's do both for water…

The real picture of water is, of course, somewhere in the middle of these two pictures. But "somewhere in the middle" is a whole lot more complicated to calculate! Oxidation state is a LOT easier to calculate and is an effective tool for assessing whether the electron density on any given atom increases or decreases in a reaction.

Oxidation States

- Determine the oxidation state for each atom in the sulfate ion.

- Determine the oxidation state for each atom in acetic acid. *(Acetic acid is CH_3CO_2H, and C is more electronegative than H.)*

Redox Reactions

- When an atom **L**oses **E**lectrons in a reaction, its oxidation state increases, and the compound is said to be **O**xidized.

- When an atom **G**ains **E**lectrons in a reaction, its oxidation state decreases, and the compound is said to be **R**educed.

- Since an atom can only lose electrons if another atom gains them, oxidation and reduction go hand-in-hand in what we call **redox reactions**. A common mnemonic device to remind us that oxidation and reduction go together (and which is which) is the saying that "LEO the lion says GER".

Some of you may have learned an Alberta version of this mnemonic:
OIL RIG (Oxidation Is Loss; Reduction is Gain)
Either works.

Redox Reactions

- Consider a simple redox reaction:

$$2\ H_{2(g)}\ +\ O_{2(g)}\ \rightarrow\ 2\ H_2O_{(g)}$$

  - The oxidation state of the hydrogen atoms goes from ___ to ___.
  - The oxidation state of the oxygen atoms goes from ___ to ___.
  - Thus, the hydrogen atoms are ____________ and the oxygen atoms are _______________.

- Note that the _________________ of oxygen is only possible because hydrogen is being _______________. This makes hydrogen the **reducing agent** in this reaction.

- Similarly, the __________________ of hydrogen is only possible because oxygen is being __________________. This makes oxygen the **oxidizing agent** in this reaction.

Redox Reactions

- When copper roofs tarnish, they turn green (like the Parliament buildings or Statue of Liberty). This is because the copper reacts with oxygen, carbon dioxide and water in the atmosphere to produce a green solid, $Cu_2(OH)_2CO_3$:

$$2\ Cu_{(s)} + O_{2(g)} + CO_{2(g)} + H_2O_{(g)} \rightarrow Cu_2(OH)_2CO_{3(s)}$$

______ is oxidized. _____ is reduced.

______ is the reducing agent. _____ is the oxidizing agent.

- When the $Cu_2(OH)_2CO_3$ reacts with acid rain (dilute sulfuric acid), a second, more permanent green solid, $Cu_2(OH)_2SO_4$ is produced:

$$Cu_2(OH)_2CO_{3(s)} + H_2SO_{4(aq)} \rightarrow Cu_2(OH)_2SO_{4(s)} + H_2CO_{3(aq)}$$

Is this a redox reaction too? If so, what is oxidized and what is reduced?

Half Reactions

- Most redox reactions can be separated into two **half-reactions**:
  - In the oxidation half-reaction, electrons are products.
  - In the reduction half-reaction, electrons are reactants.

- In the CHEM 1000 lab, you used zinc metal to precipitate copper metal from a clear blue solution of copper(II) sulfate. The net ionic equation for this reaction was:

  It can be divided into two half-reactions, one describing the ________________ of zinc and one describing the ________________ of copper:

Balancing Redox Reactions

- Balancing redox reactions is generally easiest if you divide the reaction into the two half-reactions, balance each of those then recombine them, making sure that all of the electrons cancel.

- In acid:
  1. Separate the half-reactions and balance all elements except O and H.
  2. Balance oxygen in each half-reaction by adding $H_2O_{(l)}$.
  3. Balance hydrogen in each half-reaction by adding $H^+_{(aq)}$.
  4. Balance the charge in each half-reaction by adding electrons.
  5. Multiply each half-reaction by whatever coefficient will make the electrons cancel when the two half-reactions are added.
  6. Add the two half-reactions, canceling electrons (and possibly $H_2O_{(l)}$ and/or $H^+_{(aq)}$) as necessary.

Balancing Redox Reactions

- In base, follow the above steps then add enough $OH^-_{(aq)}$ (same amount to each side) to exactly cancel all $H^+_{(aq)}$. By definition, a basic solution never has a significant concentration of $H^+_{(aq)}$.

- Under neutral conditions, $H^+_{(aq)}$ is acceptable as a product; however, $OH^-_{(aq)}$ should be added to neutralize any $H^+_{(aq)}$ on the reactant side of the equation (adding the same amount of $OH^-_{(aq)}$ to each side of the equation).

- Neither $H^+_{(aq)}$ nor $OH^-_{(aq)}$ are allowed to be listed as reactants if a redox reaction is performed under neutral conditions. What is the approximate concentration of these two ions in a neutral aqueous solution at $25\ ℃$?

Balancing Redox Reactions

- Sodium dichromate ($Na_2Cr_2O_7$) is an excellent oxidizing agent that is bright orange in colour. When sodium dichromate reacts with potassium bromide **in aqueous acid**, the products are bromine and the Cr^{3+} cation. Write a balanced chemical equation for this reaction.

Balancing Redox Reactions

- Permanganate ions (MnO_4^-) react with cyanide ions (CN^-) under **basic** aqueous conditions to give manganese(IV) oxide $\left(MnO_{2(s)}\right)$ and cyanate ions (OCN^-). Write a balanced chemical equation for this reaction.

Balancing Redox Reactions

- In a fuel cell, a fuel is oxidized in a controlled manner to produce electricity. Common fuel cells operate under basic conditions. Write a balanced chemical equation (and both half reactions) for the oxidation of methane in a methane fuel cell.