Experiment 6

Synthesis und Analysis uff ein Magical Green Crystal

Part Deux: Oxalate Content Analysis by Redox Titration Using a Vile Purple Fluid

CH 204 Fall 2007

Dr. Brian Anderson

But first...

Last week:

- Synthesis of $K_x[Fe_y(C_2O_4)_x]\cdot zH_2O$
- Metal complex coordination compounds
- Calculating limiting reagent, theoretical yield, and percent yield

This week:

- Oxidation-Reduction (Redox) chemistry

What is redox chemistry?

Moving electrons between different atoms:

$$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$$

$$Cu^{2+}_{(aq)} + 2\,e^{-} \longrightarrow Cu_{(s)}$$

Cu^{2+} gains electrons.
Cu^{2+} is REDUCED.

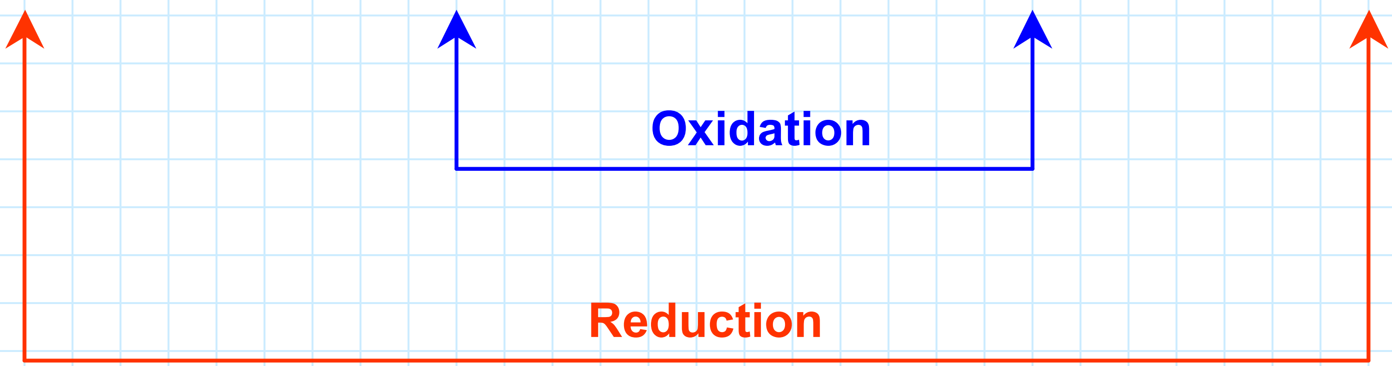
$$Zn_{(s)} \longrightarrow 2\,e^{-} + Zn^{2+}_{(aq)}$$

$Zn_{(s)}$ loses electrons.
$Zn_{(s)}$ is OXIDIZED.

Our redox reaction

We will use MnO_4^- to oxidize the oxalate ligands surrounding the Fe^{3+}. The carbon in the oxalate ions will be oxidized, and the oxalate will change from $C_2O_4^{2-}$ to $CO_{2(g)}$.

$$MnO_4^-{}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \longrightarrow CO_{2(g)} + Mn^{2+}{}_{(aq)}$$



Hey! This reaction is not balanced!

Balancing redox reactions

Separate the overall equation into two half-reactions. For each half-reaction:

1. Balance the main atom.
2. Add H_2O to balance O.
3. Add H^+ to balance H.
4. Balance the charge using electrons.

When you're done, add the two half-reactions and cancel out the electrons.

Let's try a few. To the Doc Cam!

Oxidation half-reaction

Oxidation of $C_2O_4^{2-}$ to CO_2 is simple enough:

(Remember, half-reactions do not include the other reactant)

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

Reduction half-reaction

The oxidizing agent, MnO_4^-, gets reduced to Mn^{2+}

$$MnO_4^- \rightarrow Mn^{2+} + ???$$

Balance Mn

Balance O using H_2O

Balance H using H^+

Balance charge using e^-

Reduction half-reaction solved!

The oxidizing agent, MnO_4^-, gets reduced to Mn^{2+}

$$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$$

Balance Mn

Balance O using H_2O

Balance H using H^+

Balance charge using e^-

Add the two half reactions

First multiply the equations in order to balance out the electrons:

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \quad \times 5$$

$$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \times 2$$

$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

$$16H^+ + 2MnO_4^- + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$

The equation for the overall reaction is:

$$16H^+ + 2MnO_4^- + 5C_2O_4^{2-} \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Always balance in acidic solution

As easy as 1-2-4.

1) Balance the oxidized/reduced atoms
2) Balance oxygens using H_2O
3) Balance hydrogens using H^+
4) Balance charge using e^-

What if the solution is basic?

Here's what Whitten, Davis, Peck, and Stanley say:

To balance in a basic solution, for each O needed

(1) Add *two* OH^- to the side needing O

and

(2) Add *one* H_2O to the other side

Then, for each H needed,

(1) Add *one* H_2O to the side needing H

and

(2) Add *one* OH^- to the other side.

Here's what the current book suggests

"In basic solution, balance O by using H_2O; then balance H by adding H_2O to the side of each half reaction that needs H and adding OH^- to the other side.

"When we add . . . OH^- . . . → . . . H_2O . . . to a half-reaction, we are effectively adding one H atom to the right. When we add . . . H_2O . . . → . . . OH^- . . . We are effectively adding one H atom to the left. Note that one H_2O molecule is added for each H atom needed."

Do it the E-Z way instead

Balance the equation in acidic solution,
and if it's supposed to be in basic solution,
just add enough OH^- to both sides
to get rid of all the H^+.

Just like this...

Permanagante is reduced to manganese (IV) oxide in basic solution:

$$MnO_4^- \rightarrow MnO_2$$

Balance O using H_2O: $MnO_4^- \rightarrow MnO_2 + \mathbf{2H_2O}$

Balance H using H^+: $MnO_4^- + \mathbf{4H^+} \rightarrow MnO_2 + 2H_2O$

Balance charge using e^-: $MnO_4^- + \mathbf{3e^-} + 4H^+ \rightarrow MnO_2 + 2H_2O$

Add one OH^- for every H^+. Add OH^- to both sides!

$$MnO_4^- + 3e^- + 4H^+ + \mathbf{4OH^-} \rightarrow MnO_2 + 2H_2O + \mathbf{4OH^-}$$

Combine waters and delete redundant waters:

$$MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$$

Balancing redox reactions review

- Separate the reactants into half reactions.
- Balance the main atom.
- Balance the half-reactions using H_2O to balance O, then use H^+ to balance H. Balance the charge with electrons.
- Add the two half-reactions — electrons must cancel.
- If necessary, convert acidic solution to basic by adding OH^- to both sides and crossing out spectator water molecules.

Today: Sample prep and three titrations

Land mine! 1:1 mixture of ethanol/water means mix them together in a beaker BEFORE you pour them in!

The $KMnO_4$ solution is already standardized and ready to go. Make sure you record the concentration: 0.0369 M.

Take no more than 60 ml of $KMnO_4$

Step 10: Start titrating while sample is heating, don't wait for 70°

Back to College Station

I will be gone again this week from Wednesday through Friday.

I will not have office hours on Wednesday.

You can go to Dr. Leytner's office hours on Thursday from 4:00 to 5:00

I will have e-mail access in the evenings.