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 Spring 2008

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But first...

Last week:

- Synthesis of $K_x[Fe_y(C_2O_4)_x]\cdot zH_2O$
- Coordinate covalent bonds and metal complex ions
- Calculating limiting reagent and theoretical 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.

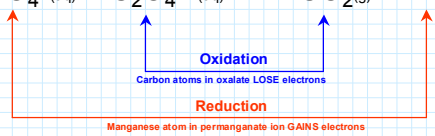
$$Zn_{(s)} \longrightarrow 2\ e^- + Zn^{2+}_{(aq)}$$

$Zn_{(s)}$ 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.
5. Equalize electrons between the half-reactions.

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

Here's our overall reaction again:

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

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

Overall reaction:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow CO_2(g) + Mn^{2+}(aq)$$

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!

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

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 equalize the electrons between the two half-reactions:

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \quad \times 5$$
$$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \times 2$$

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

Es gibt keine Elektronen, ja?
They all cancel out!
Sehr gut?
Ja, sehr gut!

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

Balancing redox half-reactions is as easy as 1-2-4.

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

What if the solution is basic?

Always balance the equation in acidic solution,
and if it's supposed to be in basic solution,
just add one OH^- to both sides
For each H^+ in the reaction.

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

We got 4 H^+, so add 4 OH^- to both sides!

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

4 H^+ + 4 OH^- → 4 H_2O, so delete spectator water molecules:

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

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.
- Equalize electrons and 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: 0.0376 M.

Take only about 50 ml of $KMnO_4$

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

Solution goes from yellow to colorless to endpoint.

Quiz Time

Mini-Final part 5 of 9 — we're past the halfway mark.

You will have a quiz covering redox chemistry when you return from spring break.