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 $K_x[Fe_y(C_2O_4)_z]$·$H_2O$
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:

$\text{Cu}^{2+}_{(aq)} + \text{Zn}_{(s)} \rightarrow \text{Cu}_{(s)} + \text{Zn}^{2+}_{(aq)}$

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

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

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

Zn$^{2+}$ loses electrons. Zn$^{2+}$ is OXIDIZED.
Our redox reaction

We will use $\text{MnO}_4^-$ to oxidize the oxalate ligands surrounding the $\text{Fe}^{3+}$. The carbon in the oxalate ions will be oxidized, and the oxalate will change from $\text{C}_2\text{O}_4^{2-}$ to $\text{CO}_2(\text{g})$.

$$\text{MnO}_4^{-}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{Mn}^{2+}(\text{aq})$$

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 $\text{H}_2\text{O}$ to balance O.
3. Add $\text{H}^+$ 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:

$$\text{MnO}_4^{-}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{Mn}^{2+}(\text{aq})$$

Oxidation of $\text{C}_2\text{O}_4^{2-}$ to $\text{CO}_2$ is simple enough:

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

$$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2e^-$$
Reduction half-reaction

Overall reaction:
\[ \text{MnO}_4^- (aq) + C_2O_4^{2-} (aq) \rightarrow CO_2 (g) + \text{Mn}^{2+} (aq) \]

The oxidizing agent, \( \text{MnO}_4^- \), gets reduced to \( \text{Mn}^{2+} \):
\[ \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + \text{???} \]

Balance Mn
Balance O using \( \text{H}_2\text{O} \)
Balance H using \( \text{H}^+ \)
Balance charge using \( e^- \)

Reduction half-reaction solved!

\[ \text{MnO}_4^- + 8 \text{H}^+ + 5 e^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O} \]

Balance Mn
Balance O using \( \text{H}_2\text{O} \)
Balance H using \( \text{H}^+ \)
Balance charge using \( e^- \)

Add the two half reactions

First multiply the equations in order to equalize the electrons between the two half-reactions:

\[ \begin{align*}
\text{C}_2\text{O}_4^{2-} & \rightarrow 2\text{CO}_2 + 2e^- & \times 5 \\
8\text{H}^+ + \text{MnO}_4^- + 5e^- & \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} & \times 2 \\
5\text{C}_2\text{O}_4^{2-} & \rightarrow 10\text{CO}_2 + 10e^- \\
16\text{H}^+ + 2\text{MnO}_4^- + 10e^- & \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O}
\end{align*} \]

The equation for the overall reaction is:
\[ \begin{align*}
16\text{H}^+ + 2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} & \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}
\end{align*} \]
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 $\text{H}_2\text{O}$
3) Balance hydrogens using $\text{H}^+$
4) Balance charge using $\text{e}^-$

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 $\text{OH}^-$ to both sides for each $\text{H}^+$ in the reaction.

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

$$\text{MnO}_4^- \rightarrow \text{MnO}_2^-$$

Balance $O$ using $\text{H}_2\text{O}$:
$$\text{MnO}_4^- \rightarrow \text{MnO}_2^- + 2\text{H}_2\text{O}$$

Balance $H$ using $\text{H}^+$:
$$\text{MnO}_4^- + 4\text{H}^+ \rightarrow \text{MnO}_2^- + 2\text{H}_2\text{O}$$

Balance charge using $e^-$:
$$\text{MnO}_4^- + 3e^- + 4\text{H}^+ \rightarrow \text{MnO}_2^- + 2\text{H}_2\text{O}$$

We get 4 $\text{H}^+$, so add 4 $\text{OH}^-$ to both sides:
$$\text{MnO}_4^- + 3e^- + 4\text{H}^+ + 4\text{OH}^- \rightarrow \text{MnO}_2^- + 2\text{H}_2\text{O} + 4\text{OH}^-$$

4 $\text{H}^+ + 4$ $\text{OH}^- \rightarrow 4$ $\text{H}_2\text{O}$, so delete spectator water molecules:
$$\text{MnO}_4^- + 3e^- + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2^- + 4\text{OH}^-$$
Balancing redox reactions review

- Separate the reactants into half reactions.
- Balance the main atom.
- Balance the half-reactions using H₂O 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 KMnO₄ solution is already standardized and ready to go.
Make sure you record the concentration: 0.0376 M.
Take only about 50 ml of KMnO₄.

Step 10: Start titrating while the sample is heating — don’t wait for 70º.
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.