Exp. 2: The 1-2-3 Superconductor $YBa_2Cu_3O_7$ (Text #1)

Last week:

- Performed high-temperature, solid-state reaction to prepare $YBa_2Cu_3O_x$

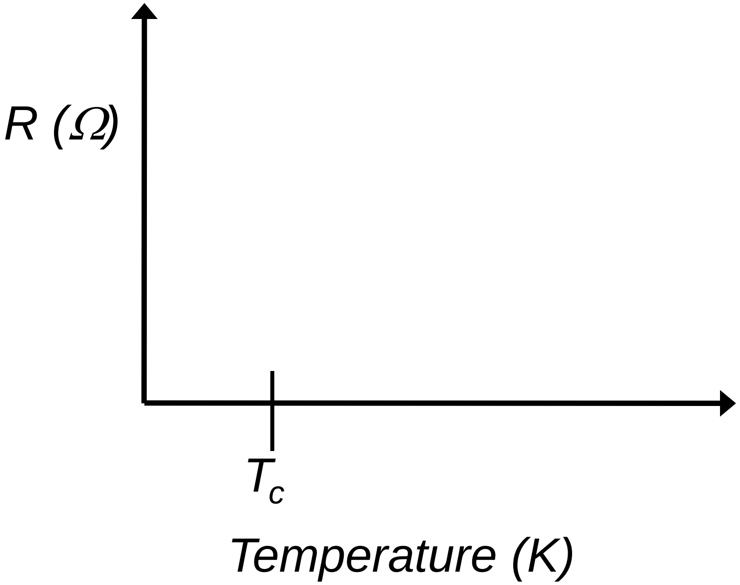
Thursday:

- Determine product stoichiometry (“x”)
  - *based on lost mass after heating*
  - from an iodometric titration
- Test your product for superconductivity

Superconductivity

Definition?

Conductivity with zero electrical resistance*, observed at temperatures* ***below the critical temperature (T******$_c$*** ***)***



For comparison, what do you expect the R vs. T plot to look like for a metal, and why?

Recall: Lattice vibrations increase with increasing T, causing decreased carrier mobility and lower conductivity.

Superconductors: Limitations

A. No materials are known to display superconductivity at room temperature.

Early superconductors had T_c values approaching 0 Kelvin.

$YBa_2Cu_3O_7$ was the first "high-temperature" superconductor with $T_c \sim 93$ K. (Nobel Prize 1986)

B. "High-temperature" superconductors are ceramics

Superconductivity, continued

BCS Theory – Cooper pairs

- Electrons travel through the material in pairs with opposite spins.
- As one e- moves past, a nearby lattice atom (“cation”) is attracted to it
  - The increase in local positive charge attracts the second e-
- Below T_c, the lattice aids in e- flow. Above T_c, vibrations of lattice atoms are disruptive and superconductivity ceases.

Meissner Effect

- Superconductors exclude magnetic fields. Below T_c, a superconductor will repel a small magnet, causing it to levitate above the surface.

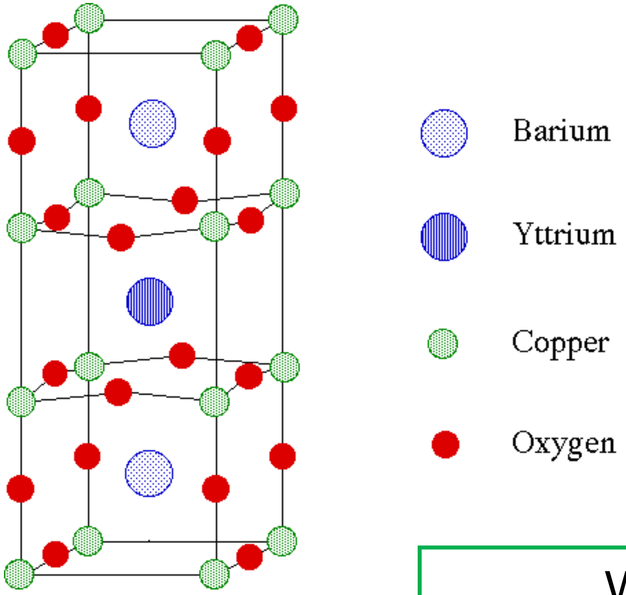
Stoichiometry of $YBa_2Cu_3O_x$: Determining *x*

$$\tfrac{1}{2}\,Y_2O_{3\,(s)} + 2\,BaCO_{3\,(s)} + 3\,CuO_{(s)} \rightarrow YBa_2Cu_3O_{x\,(s)} + 2\,CO_{2\,(g)}$$

What value of ‘x’ is expected from stoichiometry? 6.5

Desired for superconductivity? 7

Unit cells of $YBa_2Cu_3O_x$ and $CaTiO_3$



What would $CaTiO_3$ (Perovskite) look like?

http://imr.chem.binghamton.edu/labs/super/superc.html

Determining *x*: From Lost Mass

$\frac{1}{2}\ Y_2O_{3\ (s)} + 2\ BaCO_{3\ (s)} + 3\ CuO_{\ (s)} \rightarrow YBa_2Cu_3O_{x\ (s)} + 2\ CO_{2\ (g)}$

Mass before heating – Mass after heating = ?? Mass of CO_2 lost

How can you use the lost mass of CO_2 to determine *x*?

- *Find moles of O present in lost CO_2.*
- *Use your masses of reactants to find moles of O in each; then determine moles of O in your product.*
- *Set up a proportion to relate moles of O to equivalents of O*

What are some potential sources of inaccuracy in this method for determining *x*?

Determining *x*: From Iodometric Titration

Superconductor $YBa_2Cu_3O_7$: Average Cu oxidation state?

What does this mean, practically?

Formally, there are two are Cu(II) ions for every one Cu(III).

(Cu(III) represents Cu centers with missing electrons in Cu-O bonds.)

In your compounds, we don't know *x*. We will determine the average oxidation state of Cu by titration and use it to find *x*.

Iodometric Titrations

Cu(II) and Cu(III) both oxidize iodide, I^-, to molecular iodine, I_2.

$Cu^{3+} + 2\ I^- \rightarrow Cu^+ + I_2$ 2 oxidizing equivalents

$Cu^{2+} + I^- \rightarrow Cu^+ + \frac{1}{2}\ I_2$ 1 oxidizing equivalent

In your final titration (the one using your $YBa_2Cu_3O_x$ product), you will determine the amount of I_2 formed in these reactions and use it to find the total # of oxidizing equivalents, the average Cu oxidation state, and *x*.

The I_2 formed will be titrated with sodium thiosulfate, $Na_2S_2O_3$:

$$\frac{1}{2}\ I_2 + S_2O_3^{2-} \rightarrow I^- + \frac{1}{2}\ S_4O_6^{2-}$$

Titrations – Three Total

Precise determination of titrant concentration

Titrations 1 and 2 – Standardization of $Na_2S_2O_3$:

You will generate I_2 from reaction of I^- (KI) with IO_3^- (KIO_3)

a) $5\ I^- + \boxed{IO_3^-} + 6\ H^+ \rightarrow \boxed{3\ I_2} + 3\ H_2O$

Limiting reagent

b) $\boxed{\tfrac{1}{2}\ I_2} + S_2O_3^{2-} \rightarrow I^- + \tfrac{1}{2}\ S_4O_6^{2-}$

Reaction (a) prepares the I_2 that is reacted in the titration (Reaction (b)),

KIO_3 is a standard solution of known normality, 0.1 N.

$[KIO_3] = 0.1/6 \sim 0.0167\ M$

You will react a known volume of this KIO_3 solution. To find concentration of $Na_2S_2O_3$:

- Use moles of KIO_3 to determine moles of I_2 produced in rxn (a).
- Determine moles and concentration of $S_2O_3^{2-}$ required to reach equivalence (rxn (b)). **Repeat titration; use the average $[S_2O_3^{2-}]$.**

Titrations, continued

Titration 3: Reaction with $YBa_2Cu_3O_x$ product

Here, I_2 is generated by reaction of the Cu^{2+}/Cu^{3+} in your product with I^-.

Recall:
$$\left\{ \begin{array}{ll} Cu^{3+} + 2\,I^- \rightarrow Cu^+ + I_2 & \text{2 oxidizing equivalents} \\ Cu^{2+} + I^- \rightarrow Cu^+ + \tfrac{1}{2}\,I_2 & \text{1 oxidizing equivalent} \end{array} \right\}$$

The I_2 formed is titrated with $S_2O_3^{2-}$, as before:

$$\tfrac{1}{2}\,I_2 + S_2O_3^{2-} \rightarrow I^- + \tfrac{1}{2}\,S_4O_6^{2-}$$

Using the known concentration and volume of $S_2O_3^{2-}$, you will determine the moles of I_2 reacted in the titration and the total moles of I^- that were oxidized by your product (i.e., the total number of oxidizing equivalents).

(For every mole I_2, 2 moles I^- were oxidized.)

Determining *x* from Iodometric Titrations

1. Use your average concentration of $Na_2S_2O_3$ to find the **total # of oxidizing equivalents (total moles I^-)** present in your "superconductor" sample (Titration 3).

$$\frac{1}{2} I_2 + S_2O_3^{2-} \rightarrow I^- + \frac{1}{2} S_4O_6^{2-}$$

2. Approximate the **number of moles of Cu in your sample** using the mass of $YBa_2Cu_3O_x$ reacted in Titration 3 and an approximate molecular weight for the compound, assuming x = 7.

3. Find the number of **oxidizing equivalents per mole of Cu** atoms, and use this value to determine the average oxidation state of copper in your sample:

Avg Cu ox. state = (# ox. equiv. per mole Cu) + 1

4. Use oxidation states (including your average for copper) to calculate x; report to 2 significant figures.

“Report” Due Thurs., 2/10

You will **not** write a formal lab report for this experiment. Instead, please answer each of the following questions:

1. Briefly characterize the appearance of your $YBa_2Cu_3O_x$ product and describe the results of your Meissner test for superconductivity.

2. Calculate ‘x’ in $YBa_2Cu_3O_x$ using each of the two methods below, showing all your calculations:
   a) Lost mass after heating
   b) Iodometric titration

3. Briefly discuss the results described in your answers to Questions 1 and 2. Which value of ‘x’ is more reliable and why? Did your compound display superconductivity? Are its appearance and stoichiometry consistent with the results of the Meissner test?

4. You assumed x=7 to calculate the moles of your superconductor. How much impact does this have on the subsequent steps in the calculation?

Procedural Tips

1. Remember to use the same balance to determine the “post-heating” mass of your crucible and product.

2. Weigh out the ~0.11 g of $YBa_2Cu_3O_x$ to be used in titration 3 first (record exact mass). The remainder of your product may be used for superconductivity testing.

3. All solutions have been prepared for you. Note the molar concentration or normality provided on each bottle.

4. Take your time with titrations. You will look for disappearance of blue color. Swirl the flask and wait between drops of titrant.

   a) Don’t add as much titrant initially (prior to adding indicator) as is suggested in the text. This is **especially important for Titration 3**. Instead of adding 10 mL of $S_2O_3^{2-}$, try 7-8 mL, instead (so as not to overshoot the endpoint).