

**Due Thursday:** Exp. 1 Report, Exp. 2 Pre-Lab

**Due Thurs., 2/8 :** Exp. 2 “Report”

Exp. 2: The 1-2-3 Superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Text #1)

**Last week:**

- Performed high-temperature, solid-state reaction to prepare  $\text{YBa}_2\text{Cu}_3\text{O}_x$

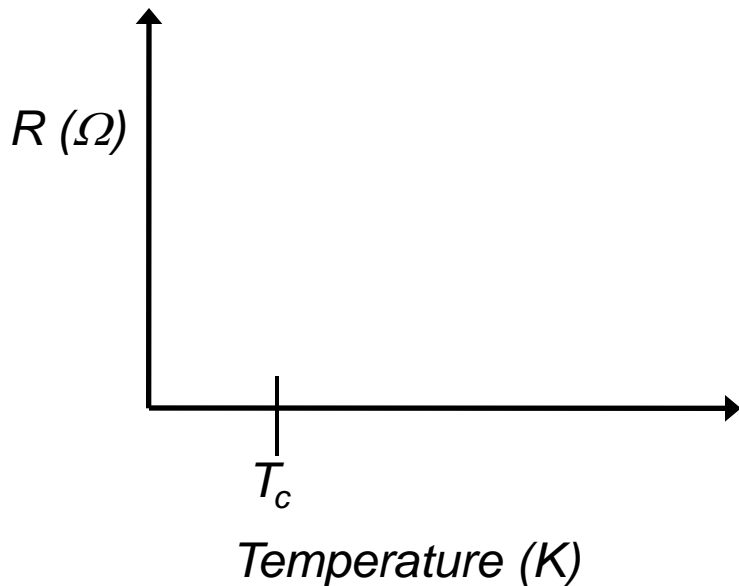
**Thursday:**

- 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.*

*$\text{YBa}_2\text{Cu}_3\text{O}_7$  was the first “high-temperature” superconductor with  $T_c \sim 93 \text{ K}$ . (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<sup>-</sup> moves past, a nearby lattice atom (“cation”) is attracted to it
  - The increase in local positive charge attracts the second e<sup>-</sup>
- Below  $T_c$ , the lattice aids in e<sup>-</sup> 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.

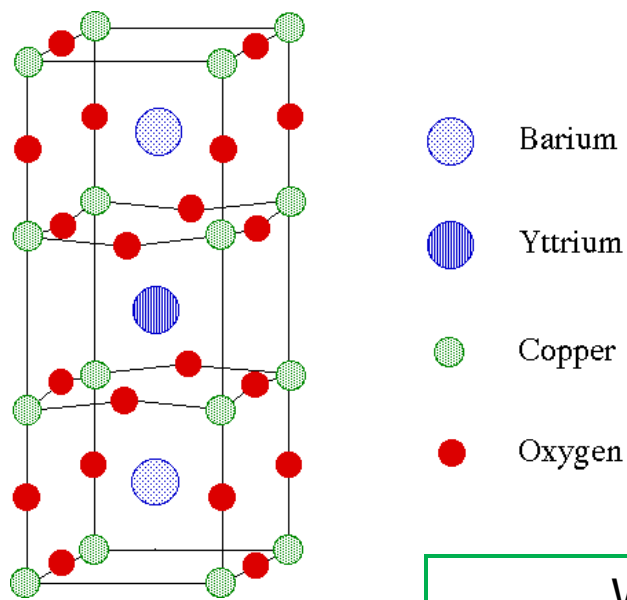
# Stoichiometry of $\text{YBa}_2\text{Cu}_3\text{O}_x$ : Determining $x$



What value of 'x' is expected from stoichiometry? 6.5

Desired for superconductivity? 7

Unit cells of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and  $\text{CaTiO}_3$



What would  $\text{CaTiO}_3$  (Perovskite) look like?

## Determining $x$ : From Lost Mass



Mass before heating – Mass after heating = ??      Mass of  $\text{CO}_2$  lost

How can you use the lost mass of  $\text{CO}_2$  to determine  $x$ ?

- *Find moles of O present in lost  $\text{CO}_2$ .*
- *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  $\text{YBa}_2\text{Cu}_3\text{O}_7$ : Average Cu oxidation state?

What does this mean, practically?

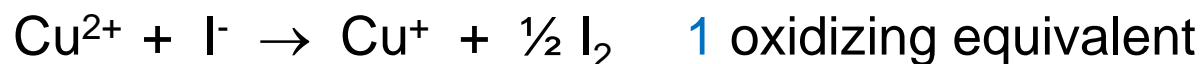
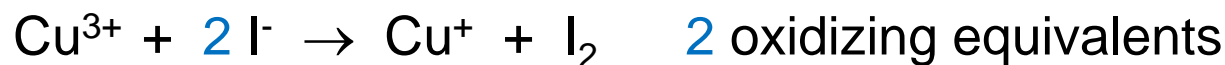
Formally, there are two Cu(II) ions for every one Cu(III).

(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  $x$ .**

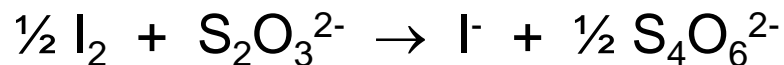
# Iodometric Titrations

Cu(II) and Cu(III) both oxidize iodide, I<sup>-</sup>, to molecular iodine, I<sub>2</sub>.



In your final titration (the one using your YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> product), you will determine the amount of I<sub>2</sub> formed in these reactions and use it to find the total # of oxidizing equivalents, the average Cu oxidation state, and x.

The I<sub>2</sub> formed will be titrated with sodium thiosulfate, Na<sub>2</sub> S<sub>2</sub>O<sub>3</sub>:



starch

deep  
blue

white

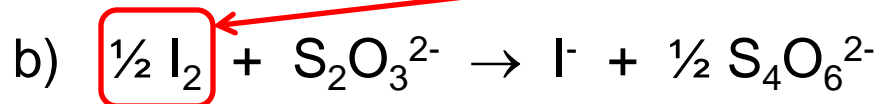
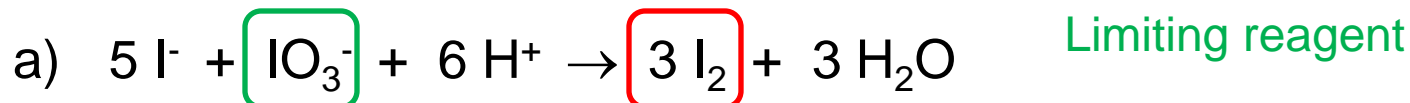


# Titration – Three Total

Precise determination of  
titrant concentration

## Titration 1 and 2 – Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ :

You will generate  $\text{I}_2$  from reaction of  $\text{I}^-$  (KI) with  $\text{IO}_3^-$  ( $\text{KIO}_3$ )



Reaction (a) prepares the  $\text{I}_2$  that is reacted in the titration (Reaction (b)),

$\text{KIO}_3$  is a standard solution of known normality, 0.1 N.

$$[\text{KIO}_3] = 0.1/6 \sim 0.0167 \text{ M}$$

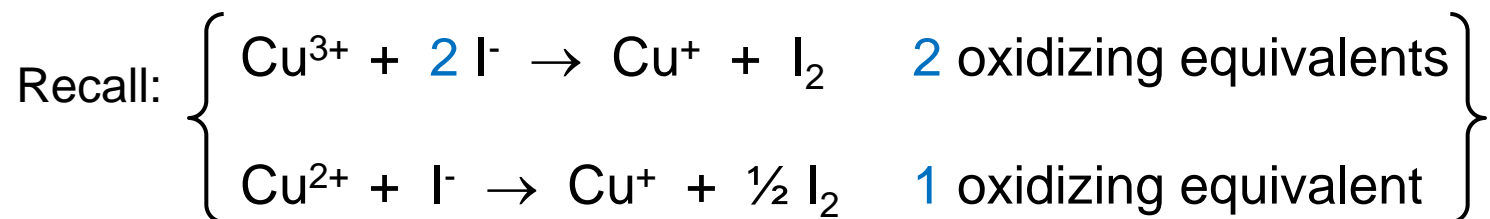
You will react a known volume of this  $\text{KIO}_3$  solution. To find concentration of  $\text{Na}_2\text{S}_2\text{O}_3$ :

- Use moles of  $\text{KIO}_3$  to determine moles of  $\text{I}_2$  produced in rxn (a).
- Determine moles and concentration of  $\text{S}_2\text{O}_3^{2-}$  required to reach equivalence (rxn (b)). **Repeat titration; use the average  $[\text{S}_2\text{O}_3^{2-}]$ .**

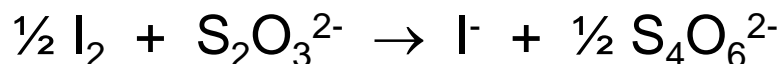
## Titration, continued

### Titration 3: Reaction with $\text{YBa}_2\text{Cu}_3\text{O}_x$ product

Here,  $\text{I}_2$  is generated by reaction of the  $\text{Cu}^{2+}/\text{Cu}^{3+}$  in your product with  $\text{I}^-$ .



The  $\text{I}_2$  formed is titrated with  $\text{S}_2\text{O}_3^{2-}$ , as before:

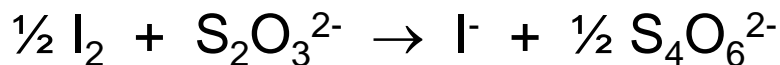


Using the known concentration and volume of  $\text{S}_2\text{O}_3^{2-}$ , you will determine the moles of  $\text{I}_2$  reacted in the titration and the total moles of  $\text{I}^-$  that were oxidized by your product (i.e., the total number of oxidizing equivalents).

(For every mole  $\text{I}_2$ , 2 moles  $\text{I}^-$  were oxidized.)

## Determining $x$ from Iodometric Titrations

1. Use your average concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  to find the **total # of oxidizing equivalents (total moles  $\text{I}^-$ )** present in your “superconductor” sample (Titration 3).



2. Approximate the **number of moles of Cu in your sample** using the mass of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  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:

$$\text{Avg Cu ox. state} = (\# \text{ ox. equiv. per mole Cu}) + 1$$

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  $\text{YBa}_2\text{Cu}_3\text{O}_x$  product and describe the results of your Meissner test for superconductivity.
2. Calculate ‘x’ in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  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  $\sim 0.11$  g of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  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  $\text{S}_2\text{O}_3^{2-}$ , try 7-8 mL, instead (so as not to overshoot the endpoint).