

ELECTROLYTIC TITRATION

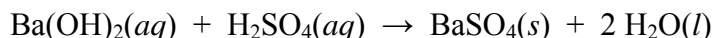
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CHEMICAL CONCEPTS

- Stoichiometry
- Limiting reagents
- Use of the complete ionic equation
- Electrolytes
- Acid-base neutralization reactions
- Precipitation reactions

HOW DEMONSTRATION ADDRESSES THE CONCEPTS

When reactions of ionic compounds in aqueous solution are introduced to General Chemistry students, it is critical for students to understand that the dissociated ions are the reactive species. The “electrolyte light bulb” is a convenient visual indicator of conductivity, and hence, the total concentration of ions in solution. But it will typically remain illuminated throughout the course of a reaction, even if the reaction product is a non-electrolyte, due to the presence of spectator ions. The reaction of aqueous barium hydroxide with aqueous sulfuric acid, described in the Chemical Demonstrations sourcebook by Summerlin, Borgford, and Ealy, is an exception:



This is both an acid-base neutralization and a precipitation reaction. Hence, no ions are present at the equivalence point, so the light bulb dims.

An acid-base indicator such as phenolphthalein shows when hydroxide ion is in excess. A white emulsion indicates the barium sulfate precipitate. These three dependent variables have different functional forms with respect to the independent variable of increasing volume of sulfuric acid solution: the conductivity goes to zero and then goes back up, the hydroxide ion concentration decreases monotonically, and the quantity of precipitate increases to the equivalence point. All this is quite predictable to those experienced with stoichiometry and ionic equations, but it must be a mystery to neophytes. Students forced to confront these disparate responses occurring simultaneously may realize that they must think things through more carefully. Only a good operational understanding of the complete ionic equation, coupled with an understanding of limiting reagents, allows students to correctly explain all observations.

PREPARING AND PERFORMING THE DEMONSTRATION

Assemble the following:

- Electrolyte light bulb
- 500-mL Erlenmeyer flask
- Phenolphthalein indicator solution in dropper bottle
- Magnetic stirrer and stir bar
- 50-mL buret
- Ring stand with buret clamp
- 40 mL of 0.4 molar sulfuric acid (prepared by diluting 0.9 mL of reagent sulfuric acid to 40mL with distilled water; preparing a larger quantity and saving the excess is more practical)
- 200 mL of 0.04 molar barium hydroxide (prepared by dissolving 2.5 g of barium hydroxide octahydrate in distilled water and diluting to 200 mL) in a stoppered 200-mL Erlenmeyer flask

The barium hydroxide solution rapidly picks up carbon dioxide from the air to form insoluble barium carbonate, which detracts from the demo, so I prepare it in a tightly-stoppered 200-mL Erlenmeyer flask with a minimum of air space. Then I pour it into a 500-mL flask just as I begin the demo. This flask should have a magnetic stirring bar and sit atop a magnetic stirrer. The buret and electrolyte light bulb are supported by a ring stand with a pole of small enough diameter to hold the light bulb. The barium hydroxide solution with a drop of phenolphthalein is then "titrated" with the sulfuric acid solution, monitoring the pink color, light bulb, and opacity, pausing occasionally to ask the class what will happen next. The net ionic equation is written on the board to help explain the observations.

Safety

- Concentrated sulfuric acid causes burns, but once diluted, it can be handled without gloves.
- Solid barium hydroxide causes irritation, but once diluted, it can be handled without gloves.
- Running water and paper towels should be available in case of spills.
- Demonstrator should wear safety goggles.

Disposal

The final mixture is 240 mL of 0.03 molar sulfuric acid with barium sulfate in suspension. It may be stored for disposal in a bottle with that label.

HOW THE DEMONSTRATION IS USED IN THE CLASSROOM TO FOSTER LEARNING AND UNDERSTANDING OF THE CONCEPTS

- The "prerequisite" is that students be familiar with the electrolyte light, the bulb that illuminates when its electrodes are immersed in an electrolyte solution. Several weeks earlier, when introducing electrolytes in lecture, I immerse the electrodes in distilled water, first soliciting a vote, "How many think the bulb will

light up?” Several hands go up. It doesn't. “I know! Let's add sugar!” A vote, several hands rise, sugar added from a familiar-looking packet, still no light. “I know! Salt!” A vote, many hands, sprinkle salt from shaker and stir, light goes on.

- In the fifth week of General Chemistry I, I am covering solution stoichiometry from chapter 4 of Zumdahl and Zumdahl, following the text closely. The students have known about limiting reagents for about a week but are still pretty shaky on the concept. In this lecture and the previous one, I have introduced molecular, complete ionic, and net ionic equations. Precipitation and acid-base neutralization reactions are used for illustration. Students are told to memorize simple rules for solubility, and one of my examples is the precipitation of barium sulfate.
- The aqueous barium hydroxide is kept in a stoppered flask to minimize reaction with carbon dioxide in the air to form a barium carbonate “scum.” It is transferred to a beaker and the electrodes are immersed, but not before soliciting a vote, “How many think the light will go on?” It does.
- The indicating property of phenolphthalein is described, and a couple of drops are added, but not before soliciting a vote, “How many think it will turn pink?” It does.
- Aqueous sulfuric acid is added from the buret, but not before more questions: “I am only going to add a little bit, not very much at all.” I will add about 4 mL. “How many think the light will go out?” It doesn't. “How many think the pink will disappear?” It doesn't. “Will anything else happen? Anything at all? An explosion, perhaps?” The immediate milkiness is a surprise, even to the few who expected a precipitate.
- When I say that milkiness can be the form taken by a precipitate and ask what it is, someone knows it is barium sulfate. “How did Katie know that?” I put the reactants on the board in molecular form, then beneath that, in ionic form. We can see why the precipitate formed by looking at the chart of solubilities. We complete the ionic equation. “So why did the light remain on? Why is it still pink?” I put in some ballpark numbers for concentrations and show that the barium and hydroxide ions are in excess.
- “Now I will add a lot more sulfuric acid. How many think the light will eventually go out? How many think the pink will eventually disappear?” I open the stopcock, and there's not much change for about a minute, but then the light dims. All at once at about 20 mL, the light goes out, the pink disappears, and I close the stopcock.
- “What's going on?” I go to the board and ask what species are present in solution when I have added a stoichiometric amount of sulfuric acid (just the right amount to react with all of the barium hydroxide, no limiting reagent, no excess reagent). There are no ions in solution (lights out) and no excess of hydroxide (phenolphthalein colorless). “What type of reaction is this, precipitation or acid-base neutralization? Trick question! It's both!”
- “So what will happen when I add more sulfuric acid? How many think the light will go back on?” It does. “How many think the pink color will return?” It does not. “How many think the precipitate will re-dissolve?” Nobody falls for that

- one. "Use the balanced equation to explain these observations." I then do that, with any help the audience can offer.
- "How many people answered every question correctly?" A few hands go up, but I am skeptical. "If you got every question right, then you really understand this stuff. And people say the hard part of chemistry is the math?"
 - Follow up with homework and/or exam questions such as the following:
 - a. Write the balanced molecular, complete ionic, and net ionic equations for the reaction between sulfuric acid and sodium hydroxide.
 - There was a demonstration in class in which aqueous sulfuric acid from a buret was added to aqueous barium hydroxide. Suppose we did that demonstration instead with sulfuric acid and sodium hydroxide as in part a of this problem.
 - b. The barium hydroxide solution turned opaque white as soon as sulfuric acid was added. Would the sodium hydroxide solution also turn opaque white when sulfuric acid was added? Explain.
 - c. The barium hydroxide solution turned pink when phenolphthalein was added, but the pink disappeared when excess sulfuric acid was added. Would the same thing happen when excess sulfuric acid was added to sodium hydroxide solution? Why or why not?
 - d. When sulfuric acid was added to barium hydroxide, the light went out at the equivalence point. Would the same thing happen when sulfuric acid was added to sodium hydroxide? Explain.

REFERENCE

Summerlin, L.R.; Borgford, C.L.; and Ealy, J.B. *Chemical Demonstrations: A Sourcebook for Teachers* (Vol. 2), Washington, D.C.: The American Chemical Society (1988), 132-133.