Using Limiting-Excess Stoichiometry to Introduce Equilibrium Calculations: A Discrepant Event Laboratory Activity Involving Precipitation Reactions

ARTICLE *in* JOURNAL OF CHEMICAL EDUCATION · APRIL 2002

Impact Factor: 1.11 · DOI: 10.1021/ed079p474

1 AUTHOR:

Stephen Demeo
City University of New York - Hunter College

Using Limiting–Excess Stoichiometry to Introduce Equilibrium Calculations: A Discrepant Event Laboratory Activity Involving Precipitation Reactions

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Stephen DeMeo

Department of Curriculum and Instruction, Hunter College of CUNY, New York, NY 10021; *svd2@columbia.edu*

One important type of reaction that is studied by introductory chemistry students is a precipitation reaction. This laboratory activity gives students an opportunity to qualitatively investigate two precipitation reactions as they relate to stoichiometry and equilibrium: the precipitation of lead carbonate from aqueous lead nitrate and sodium carbonate, and the formation of lead iodide from aqueous lead nitrate and potassium iodide. Students performing this activity are asked the simple question, "What reactants remain in the filtrate after precipitation has occurred?" To answer this, students use their knowledge of stoichiometry gained earlier in their first semester of general chemistry to calculate which reactant should be limiting and which should be in excess. By performing qualitative tests, students find that their calculated prediction for one of the precipitation reactions is not supported by their observations; instead of one excess reactant there are two. This "discrepant event" provides a reasonable context for introducing the concept of equilibrium and the necessity of a new way to calculate the amounts of chemical species after a reaction. The use of discrepant events to uncover students' prior knowledge is widely found in laboratory activities not only in chemistry but in the other sciences as well (*1*).

Since the purpose of this experiment is to introduce equilibrium, the activity is best used in the second semester of a college chemistry laboratory program or after students have mastered net ionic equations, stoichiometry, and molarity problems. Although precipitation reactions are commonly used in laboratory activities (*2–4*), their use as a vehicle of transition between limiting–excess stoichiometry and equilibrium is novel in the chemical education literature.

A Prelaboratory Assignment

Before coming into the lab, students are asked to make predictions, based on stoichiometric calculations, about the identity and quantity of the limiting species in the filtrate. In the first precipitation reaction

$$Pb^{2+}(aq) + CO_3^{2-}(aq) \rightarrow PbCO_3(s) \qquad (1)$$

students are told that they will mix 25 mL of 0.05 M lead nitrate with 1.4 mL of 0.125 M sodium carbonate. From these values, they predict that the carbonate ion is limiting and the lead ion should theoretically be left over. In the second reaction

$$Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s) \qquad (2)$$

instructions state that 25 mL of a 0.05 M lead nitrate solution is mixed with 1.4 mL of 0.25 M potassium iodide solution. In this case, the iodide ion is calculated to be the limiting reactant and the lead should be in excess. Once students have completed this assignment they are ready to work in the lab.

Experimental Summary

Reaction I

Mix 25 mL of 0.05 M lead nitrate with 1.4 mL of 0.125 M sodium carbonate. Separate the precipitate from the filtrate using a vacuum filtration flask with a Hirsch funnel. Decant the filtrate evenly between two 50-mL beakers. To one of the beakers test for excess lead ion by adding 1 mL of 0.1 M potassium phosphate. The formation of a white precipitate of lead phosphate indicates a positive test. In the other beaker test for excess carbonate ion by adding 1 mL of 0.1 M nickel(II) nitrate. The formation of a pale green precipitate of nickel(II) carbonate indicates a positive test.

Reaction II

Mix 25 mL of 0.05 M lead nitrate with 1.4 mL of 0.25 M potassium iodide. Using the Hirsch funnel again, collect the filtrate and decant it evenly between two 50-mL beakers. In one of the beakers test for excess lead ion by adding 1 mL of 0.1 M potassium phosphate. The formation of a white precipitate of lead phosphate indicates a positive test. In the other beaker test for excess iodide ion by adding 1 mL of 0.1 M silver nitrate. The formation of a pale yellow precipitate of silver iodide indicates a positive test.

To formulate a hypothesis concerning any unexpected behavior seen in the reactions described above, take a spatula and remove the filter paper containing the yellow lead iodide solid and place it in a large beaker. Add 50 mL of water and mix well. Filter this mixture through a cleaned Hirsch funnel and then decant the filtrate evenly between two 50-mL beakers. In one of the beakers test for excess lead ion by adding 1 mL of 0.1 M potassium phosphate. The formation of a white precipitate of lead phosphate indicates a positive test. In the other beaker test for iodide ion by adding 1 mL of 0.1 M silver nitrate. The formation of a pale yellow precipitate of silver iodide indicates a positive test. What conclusions can you make based on the outcome of these tests?

Hazards

None of the substances used in this activity at the concentrations described pose an unacceptable health hazard for students working safely in an academic laboratory.

Lead and nickel are heavy metal ions and all solutions of these ions should be appropriately placed in separate marked containers and not allowed to be disposed of down the drain. Sittig recommends that solutions containing these ions should be precipitated as carbonate compounds before disposing of the solutions (*5*).

The small pieces of filter paper containing lead iodide or precipitated lead carbonate respectively should be placed in labeled beakers under the hood and then disposed of following local and state laws. Lead iodide and lead carbonate should not be thrown into the laboratory garbage pails.

Sample Observations and Results

A. Descriptions of all substances before and after reaction.

Reaction 1:

1. Lead nitrate and sodium carbonate are colorless solutions.
2. Upon mixing, a white precipitate forms.

Reaction 2:

1. Lead nitrate and potassium iodide are colorless solutions.
2. Upon mixing, a bright yellow precipitate forms.

B. Observations of all qualitative tests

Reaction 1:

1. When potassium phosphate was added to the filtrate a white precipitate formed.
2. When nickel nitrate was added to the filtrate no green precipitate formed.

Reaction 2:

1. When potassium phosphate was added to the filtrate a white precipitate formed.
2. When silver nitrate was added to the filtrate a yellow precipitate formed.

Tests on Filter Paper:

1. When potassium phosphate was added to the filtrate resulting from washes of the filter paper a white precipitate formed.
2. When silver nitrate was added to the filtrate resulting from washes of the filter paper a yellow precipitate formed.

C. Results tables

Table 1. Results of Reaction 1

Ion	Present?
Excess Lead Ion	Yes
Excess Carbonate Ion	No

Table 2. Results of Reaction 2

Ion	Present?
Excess Lead Ion	Yes
Excess Iodide Ion	Yes

Table 3. Tests on Filter Paper

Ion	Present?
Excess Lead Ion	Yes
Excess Iodide Ion	Yes

The above results indicate that in the first reaction the excess reactant, lead ion, is correctly predicted from student calculations. With regard to the second reaction, students' prediction of only the lead ion being in excess is incorrect; instead of only one excess reactant, both are present as indicated by the qualitative tests. To explain to students why the second reaction produces positive tests for both ions necessitates the introduction of the concept of equilibrium; if a quantitative discussion is planned then equilibrium calculations can be taught. This experiment exploits the K_{sp}'s of precipitation reactions; for example, a metal cation will precipitate with a designated anion when the K_{sp} of that reaction is lower than the K_{sp} of a competing reaction involving another cation. This topic, commonly referred to as selective precipitation, is discussed in many introductory chemistry textbooks and therefore will not be taken up here (*6*).

The test for lead and iodide ions on the filter paper containing lead iodide is performed to challenge students' idea that precipitates are static. The positive tests for lead and iodide ions help create an argument for the concept of equilibrium. While other precipitation reactions could be used, these two were chosen because they provide students with safe, colorful, and distinguishable transformations upon which to base their decisions.

Conclusion

Based on selective precipitation, this activity motivates students by providing a result that challenges their preconceived notions of what should take place. In the five years that we have used this experiment it has never failed to create conjecture: some students perform the experiment multiple times to make sure they did it correctly, while others redo their calculations. The conflict between theory and observation is clearly visible through this laboratory activity. Resolution of this conflict when it arises provides students with an acceptable explanation of their results. In other words, this "discrepant event" opens students up to alternative explanations, thus giving them a purpose for learning about equilibrium and subsequent concepts.

[W]Supplemental Material

Details of the procedure and a complete list of materials and chemicals are available in this issue of *JCE Online*.

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