Simplest Formula of Copper Iodide: A Stoichiometry Experiment

D. J. MacDonald
U.S. Bureau of Mines, Reno Research Center, Reno, NV 89512

Experiments in stoichiometry or experiments to demonstrate the Law of Definite Proportions are often included in the general chemistry laboratory course. Unfortunately, some of the traditional stoichiometry experiments give results that do not convincingly demonstrate the concept. For example, the copper sulfide produced by reaction of copper metal with excess sulfur is not stoichiometric but is, on the contrary, a good example of a *non*stoichiometric compound.[1,2]

A suitable stoichiometry experiment which involves a pure compound having simple stoichiometry was developed by adapting to freshman use the procedure described by Kauffman and Pinnell[3] for preparation of copper(I) iodide.

The experiment involves the dissolution in nitric acid of a weighed quantity of copper metal. The resulting solution is partially neutralized with aqueous ammonia (to approximately pH 4), then boiled to expel the dissolved oxides of nitrogen which would otherwise oxidize the iodide that is to be added subsequently. The solution is then cooled to room temperature or lower and treated with a pre-mixed solution of potassium iodide and sodium thiosulfate which is dispensed from a buret. If the solution is too acidic or too warm when the iodide-thiosulfate reagent is added, undesired oxidation of iodide by nitrate will occur which yields a product contaminated with elemental iodine. The iodide-thiosulfate solution is prepared by dissolving 36.5 g of KI together with 28.0 g of $Na_2S_2O_3 \cdot 5H_2O$ to make 100 ml of solution. The proportion of KI to $Na_2S_2O_3 \cdot 5H_2O$ is critical, but the concentration is not. About 8 ml of the solution is required for a typical 0.6-g sample of copper metal.

A turbid brown precipitate forms immediately. But the color changes to a creamy pale violet or pale yellow when exactly enough of the iodide-thiosulfate solution has been added to consume the cupric ions.

The reactions occurring are

$$Cu + 2NO_3^- + 4H^+ \rightarrow Cu^{2+} + 2NO_2\uparrow + 2H_2O$$

and

$$2Cu^{2+} + 2I^- + 2S_2O_3^{2-} \rightarrow 2CuI\downarrow + S_4O_6^{2-}$$

Iodide alone will convert cupric ions to cuprous iodide, but the cuprous iodide produced in that way is contaminated with elemental iodine. The thiosulfate serves to reduce that elemental iodine to soluble iodide, thereby ensuring the production of a pure cuprous iodide precipitate.

Because copper(I) forms soluble complex ions with thiosulfate as well as with iodide, it is necessary to use an iodide-thiosulfate solution which contains both reagents in the correct proportions, so that neither reagent is present in excess. To avoid using an excessive volume of the mixed reagent is simple. The color change occurring upon addition of the stoichiometric quantity of reagent solution is so distinct that most students can readily detect it. In testing the experiment before it was assigned to students, it was found that purposely stopping short in the addition of the iodide-thiosulfate solution produces in either case an error on the low side, proportional to the deviation from the correct volume. The error occurs in this way because the use of either too much or too little of the reagent leaves some of the copper in solution; as copper(I) complex ions in one case, or as Cu^{2+} ions in the other.

The student filters the precipitate onto a preweighed filter paper, washes out any soluble matter, and allows the residue to dry in the open air or in a desiccator until the next laboratory period. In the dry climate of Nevada, drying for about 48 hr in open air is adequate. Drying the soggy precipitate in a desiccator is slower than drying in open air. Kauffman and Pinnell mention that copper(I) iodide retains moisture tenaciously, but the mass of the strongly held portion of the total moisture is insignificant for this experiment. Drying overnight in an oven at 100°C is also satisfactory. Then from the mass of copper metal taken, the mass of copper iodide produced, and the given atomic masses of copper and of iodine, the student calculates the empirical formula of his copper iodide preparation.

The experiment is presented to the student as a problem in determining the stoichiometry of "copper iodide" in order to decide whether it is cuprous iodide (I/Cu atom ratio = 1.00) or cupric iodide (I/Cu atom ratio = 2.00).

In actual use by a total of 58 General Chemistry students at the University of Nevada, Reno, (an entire class, of random composition with regard to ability), student results for the coefficient n in the empirical formula CuI_n averaged 1.02 with a standard deviation of 0.16. In terms of the problem posed to the student by the experiment, i.e., distinguishing between CuI and CuI_2, the results are clear cut even in the presence of the usual minor imperfections of technique. The largest errors were on the high side, presumably the result of insufficient drying. A student who works carefully can come within one or two percent of the theoretical value.

In addition to illustrating principles of stoichiometry, the experiment teaches a number of important laboratory techniques, including filtration, use of a buret, and safe handling of corrosive liquids; it also provides practice in numerical computation.

A detailed outline of the experiment, written for student use, can be obtained from the author.

[1] Dingledy, David, and Barnard, Walther M., J. CHEM. EDUC., **44**, 242 (1967).

[2] Strong, Laurence E., and Kreider, James, *in* 'Current Topics," (CBA), (Arthur S. Welch, *Editor*), Webster Div., McGraw-Hill Book Co., Manchester, MO, **1965**, Vol. 5, No. 2.

[3] Kauffman, G. B., and Pinnell, R. P., *in "Inorganic Syntheses,"* **6**, 3 (1960); Kauffman, *in* "Inorganic Syntheses," **11**, 215 (1968).