

# An Experimental Approach to the Precipitation Reaction of Basic Zinc Carbonate

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**Abstract:** An investigative approach to the stoichiometry of the precipitation reaction of basic zinc carbonate is proposed as a suitable laboratory activity for an advanced chemistry course at secondary schools and for an introductory chemistry experiment at universities and colleges. Practical experimental procedures of the students' activity are described together with several complementary data of instrumental analyses to support the interpretation of the experimental results. The present experimental approach can be utilized as an investigative students' activity for the following two reasons: first, students are not familiar with the formula of basic zinc carbonate, and, second, the composition of the precipitated basic zinc carbonate can not be deduced directly from the stoichiometry of pH titration for the precipitation reaction.

## Introduction

It is well known that in many cases basic salts are precipitated when a solution of a base is added to an aqueous solution of a transition-metal salt. Because such precipitates are usually treated as normal hydroxides of transition metals for simplicity in secondary school chemistry courses [1], students are not familiar with the composition of the basic salts of transition metals. This led us to design some attractive teaching materials for an advanced chemistry course in secondary schools or an introductory chemistry experiment at universities or colleges.

Various teaching materials for laboratories have been developed by utilizing basic salts of transition metals [2–8]. For example, a reaction cycle for copper(II) compounds was established via various basic copper(II) compounds [5]. In this cycle, students observe various changes in the color of solutions and solid compounds due to different types of chemical reactions, such as dissolution in acid, precipitation, thermal decomposition of solids, oxidation–reduction, complex formation, etc. Experimental approaches to the reaction stoichiometry of the precipitation reaction and the composition of the precipitated basic salts have also been proposed as effective teaching materials [2–4, 6, 7]. By titrating a copper(II) solution with a solution of sodium hydroxide, the reaction stoichiometry of the precipitation reaction of copper(II) hydroxide sulfate,  $\text{Cu}_4(\text{OH})_6\text{SO}_4$ , can be estimated through pH and/or temperature titrations [2, 3]. The estimated composition of the precipitate is confirmed through quantitative analysis of  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  as  $\text{BaSO}_4$  by iodometry and gravimetry, respectively [3]. Students draw unambiguous conclusions about the stoichiometry of the precipitation reaction and the composition of the precipitate on the basis of the close agreement of the results of the pH and/or temperature titrations with the quantitative analysis of the precipitate.

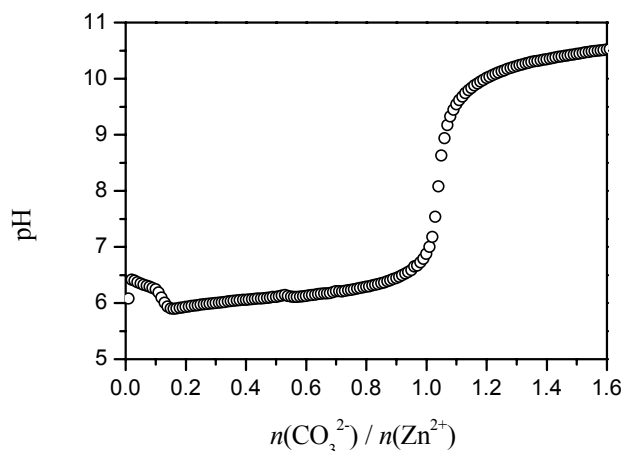
In order to develop more investigative teaching materials for students' laboratory work, we focus on the precipitation reaction of basic zinc carbonate by reacting an aqueous solution of zinc salts with a solution of sodium carbonate [9,

10]. It was shown in our previous study [9] that an apparent disagreement between the reaction stoichiometry of the precipitation reaction measured by pH titration and the composition of the precipitate was observed due to evolution of  $\text{CO}_2$  during the course of the precipitation reaction. While on the one hand such characteristics of the reaction make it difficult to deduce the reaction stoichiometry of the precipitation reaction directly from the result of pH titration, the reaction provides us with the possibility of developing a new teaching material that promotes an investigative approach to the reaction stoichiometry through the comprehensive interpretation of experimental results. In the present study, experimental procedures for determining the chemical equation of the precipitation reaction of basic zinc carbonate are designed for practical use in an advanced chemistry course at secondary schools or in an introductory chemistry experiment at universities and colleges. The experimental procedures of such an investigative activity are described together with the interpretation of typical experimental results. Several complementary data of instrumental analyses are also presented in order to support interpretations of the experimental results. The educational usefulness of the present activity is evaluated by drawing a scenario of a phased student approach to reveal the correct reaction stoichiometry of the precipitation reaction of basic zinc carbonate.

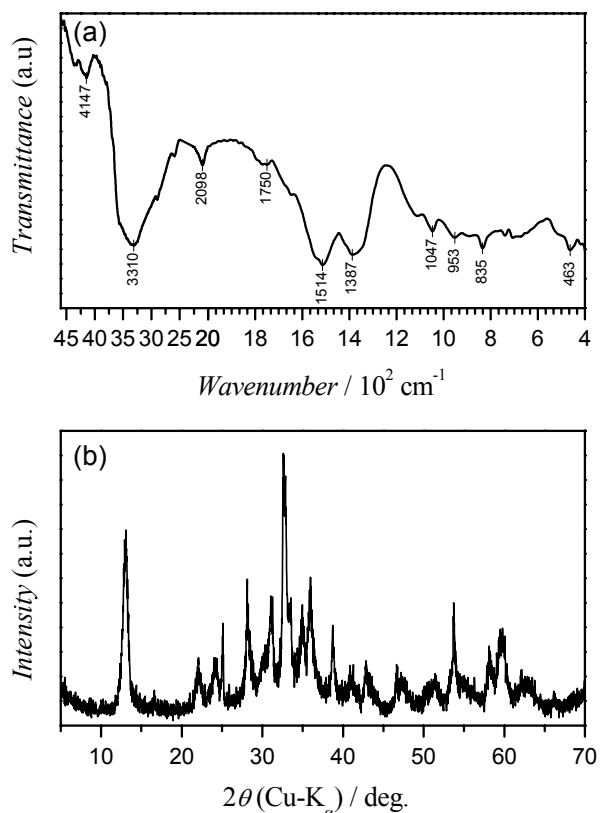
## Experimental

The students' experimental activities consist of a pH titration to estimate the reaction stoichiometry of the precipitation reaction and several qualitative and quantitative analyses to determine the composition of the precipitate.

**pH Titration and Preparation of the Sample.** With stirring at room temperature, 100 mL of  $\text{Zn}(\text{NO}_3)_2$  solution of a known concentration (0.1–1.0 M) is titrated slowly ( $\sim 1 \text{ mL min}^{-1}$ ) with a solution of  $\text{Na}_2\text{CO}_3$  of a similar known concentration. During the titration, the pH of the solution is recorded against the volume of  $\text{Na}_2\text{CO}_3$  solution added. Upon completion of the titration at pH 8, the precipitate is collected by filtration and washed and dried in an



**Figure 1.** A typical pH titration curve for the reaction of 0.1 M  $\text{Zn}(\text{NO}_3)_2$  with 0.1 M  $\text{Na}_2\text{CO}_3$  solution.



**Figure 2.** Typical FTIR spectrum (a) and powder XRD pattern (b) of the precipitate.

electric oven at 100 °C in air for 3 h [11]. The precipitate is used as the sample for a series of determinations of the composition.

**Reaction of the Sample with Hydrochloric Acid.** The sample is added slowly into 1 M HCl (~5 mL) in a test tube. The reactivity of the sample with HCl is observed by focusing on the evolution of gas.

**Qualitative Analysis of the Gaseous Products through the Thermal Decomposition of the Sample.** A small amount of sample (~1 g) is placed in a test tube, which is fixed horizontally to a support stand with a clamp. A glass tube is connected to the test tube in order to introduce the product gases released by the thermal decomposition of the sample into lime water in a test tube. By heating the sample

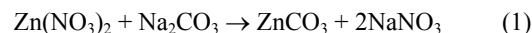
over a burner flame, the change in the condition near the lip of the test tube and the reaction taking place in lime water are carefully observed.

**Simplified Quantitative Analysis of the Products through the Thermal Decomposition of the Sample** [6]. A known amount of the sample (~1 g) is weighed into a test tube. The total mass of the sample and test tube is also weighed. An apparatus similar to that used in the above experiment for the qualitative analyses of evolved gases is used, but  $\text{CO}_2$  evolved during the thermal decomposition of the sample is collected in a measuring cylinder over water in a tank by substituting evolved  $\text{CO}_2$  for water in the measuring cylinder [12]. The sample is heated over a burner flame until the evolution of gases is finished. The volume of the evolved  $\text{CO}_2$  is measured by leveling the water surfaces inside and outside of the measuring cylinder. After cooling the test tube to room temperature, the total mass of the solid product and the test tube is weighed.

**Hazards and Disposal.** All the solutions in this activity should be discarded according to local laws. It is recommended that zinc oxide produced by the thermal decomposition of the sample be recovered and reused for other experiments in student laboratories.

## Results and Discussion

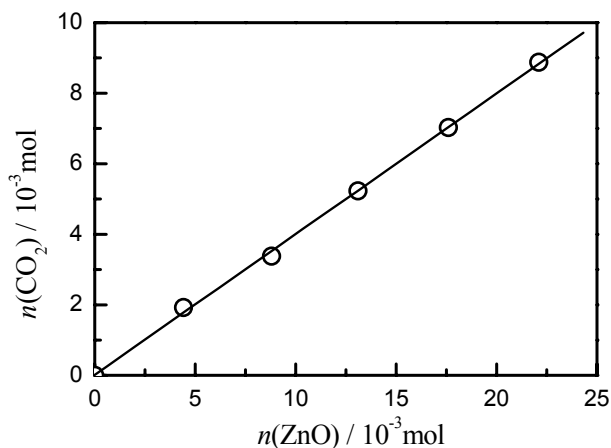
Figure 1 shows a typical pH titration curve for the reaction of 0.1 M  $\text{ZnSO}_4$  solution with 0.1 M  $\text{Na}_2\text{CO}_3$  solution. An abrupt increase in the pH value is observed at a molar ratio of  $\text{CO}_3^{2-}/\text{Zn}^{2+}$  about equal to unity. From this result, students may suspect the following chemical reaction by assuming the white precipitate produced during the titration is  $\text{ZnCO}_3$ .



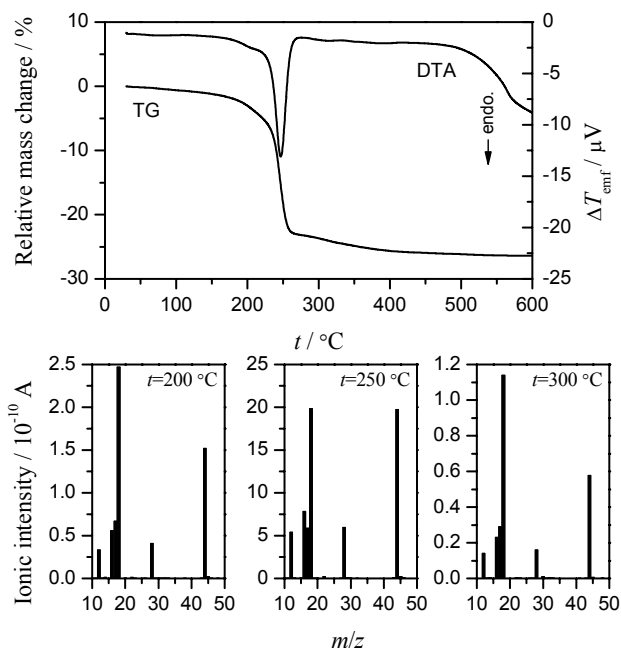
However, as is seen from the FTIR spectrum and powder X-ray diffraction (XRD) patterns of the precipitate that are shown in Figure 2(a) and (b), this assumption turns out to be incorrect. In the FTIR spectrum, the characteristic O–H stretching band centered at 3310  $\text{cm}^{-1}$  is observed in addition to the  $\nu_3$  mode of carbonate at 1514 and 1387  $\text{cm}^{-1}$  [9, 13] and all the major diffraction peaks in the powder XRD pattern correspond to  $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$  [9, 14]. The content of  $\text{Zn}^{2+}$  in the precipitate, determined by chelatometry using xylenol orange as the indicator, is ca. 60 % [9], which is in good agreement with the calculated value for  $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ . All these data support the formation of the basic salt.

Having made an incorrect assumption for the precipitation reaction, the students' activity moves to an analysis of the precipitate composition. Observing bubble formation upon reaction of the sample with HCl solution, students confirm the existence of carbonate ion in the precipitate. At this stage, it is also possible to test for the existence of  $\text{NO}_3^-$  in the solution using an ordinary detection method for  $\text{NO}_3^-$ , such as the precipitation reaction with a nitron solution [15]. The assumed equation for the precipitation reaction, eq 1, would be supported at least qualitatively by confirming the existence of  $\text{CO}_3^{2-}$  and nonexistence of  $\text{NO}_3^-$ .

Students should realize the necessity to modify eq 1 for the precipitation reaction through the identification of the gaseous products formed during the course of the thermal decomposition of the sample. By heating the sample in a test tube, the formation of water vapor and carbon dioxide can be identified by observing water droplets appearing inside of the test tube and the clouding of lime water due to the evolved gases. Because the formation of water vapor cannot be expected from the assumed composition of the precipitate,



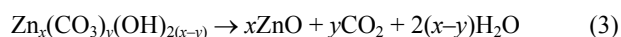
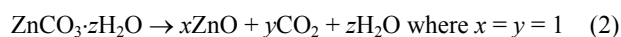
**Figure 3.** A typical plot of the molar amount of CO<sub>2</sub> versus that of ZnO produced by the thermal decomposition of the precipitate.



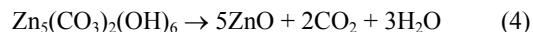
**Figure 4.** Typical TG-DTA curves for the thermal decomposition of the precipitate together with the mass spectra of the evolved gases at different temperatures.

ZnCO<sub>3</sub>, the students now have to reconsider the composition of the precipitate.

Students should consider two possible compositions to replace that of ZnCO<sub>3</sub>. One consideration is that hydrated water is included in the precipitate, that is, the precipitate is ZnCO<sub>3</sub>·zH<sub>2</sub>O. A second consideration is that a basic salt, Zn<sub>x</sub>(CO<sub>3</sub>)<sub>y</sub>(OH)<sub>2(x-y)</sub> is formed. The thermal decomposition of these two compounds can be expressed by the following equations:



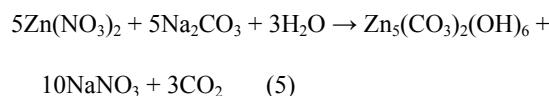
The sample composition can be determined by simplified quantitative analyses of the solid and gaseous products of the thermal decomposition [6]. The coefficients  $x$  and  $y$  in eqs 2 and 3 are evaluated by weighing the solid product and by measuring the volume of the evolved CO<sub>2</sub> collected in a measuring cylinder over water. By converting these measured values to molar amounts, the molar ratio of  $x$  to  $y$  can be determined. Figure 3 shows the plot of the molar amount of CO<sub>2</sub> versus that of ZnO measured using various amounts of the sample in the thermal decomposition. The slope of the plot is close to 0.4, indicating the molar ratio,  $x:y$ , is 5:2. Accordingly, the thermal decomposition of the sample is expressed by the following chemical equation.



The mass loss due to the thermal decomposition measured by weighing the sample and the solid product in the test tube is ca. 26.0 %, which is also in agreement with the calculated value based on eq 4.

Additionally, Figure 4 shows typical curves for thermogravimetric (TG) and differential thermal analysis (DTA) of the decomposition of the sample together with the mass spectra of the evolved gases at various temperatures. The thermal decomposition of the sample takes place in a temperature range of 150 to 400 °C with mass loss corresponding to eq 4. Only the fragment ions of H<sub>2</sub>O and CO<sub>2</sub> can be detected in the mass spectra during the course of the thermal decomposition. It has already been discovered by the quantitative analyses of the mass chromatograms [9, 10] that the molar ratio of evolved CO<sub>2</sub> and H<sub>2</sub>O is 2:3.

Knowing the correct composition of the precipitate, students can now modify the chemical equation for the precipitation reaction. The following chemical equation can be obtained for the precipitation reaction as the final stage of the experiment.



The stoichiometric evolution of CO<sub>2</sub> during the precipitation reaction can be confirmed by mixing equal volumes of 1 M ZnSO<sub>4</sub> and 1 M Na<sub>2</sub>CO<sub>3</sub> solutions and measuring the mass loss of the mixed solution.

## Conclusion

The approach described above to the reaction stoichiometry of the precipitation reaction of basic zinc carbonate and the composition of the precipitate is used as a challenging experimental project for students. This approach is possible due to the two important characteristics of the selected reaction system. First, the formula for basic zinc carbonate, as is also true of many other basic salts of transition metals, is not familiar to students. Second, the composition of the precipitate, Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub>, cannot be deduced directly from the stoichiometric molar ratio of Zn<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> during the precipitation reaction. Despite this, students can reach the proper conclusion concerning the reaction stoichiometry of the precipitation reaction and the composition of precipitate by integrating the results of rather simple experiments. Students experience the process of a scientific investigation by

proposing a hypothesis, verifying the hypothesis experimentally, and, finally, modifying the hypothesis. In this sense, the precipitation reaction of basic zinc carbonate can be used to design a discovery-based experiment to determine the stoichiometry of chemical reaction.

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### References and Notes

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11. When the sample is dried for longer than 3 h, we recommend setting the drying temperature at 80 °C in order to avoid possible thermal decomposition of the sample.
12. Although the gases evolved by the thermal decomposition of the sample are composed of H<sub>2</sub>O and CO<sub>2</sub>, only CO<sub>2</sub> is collected in the measuring cylinder by passing the evolved gases through water.
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15. The nitron solution is C<sub>20</sub>H<sub>16</sub>N<sub>4</sub> dissolved in diluted acetic acid. See, for instance, Hioki, A.; Watanabe, T.; Terajima, K.; Fudagawa, N.; Kubota, M.; Kawase, A. Accuracy of Gravimetric Determination of Nitrate and Nitrite as Nitron Nitrate. *The Japan Society for Analytical Chemistry*. <http://www.rminfo.nite.go.jp/common/pdfdata/4-005.24.pdf> (accessed Nov 2005).