Separation of Cations by Thiourea⁽¹⁾

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The alkaline solution of thiourea, when boiled, decomposes and some sulfide ions are formed. The substance is also known to yield precipitates with some cations,⁽²⁾ from which their sulfides are produced.⁽³⁾ The authors found that such a property of thiourea makes it possible to separate the ions belonging to the copper sub-group from other cations.

Thermal Decomposition of Thiourea in Aqueous Phase.—The neutral solution of thiourea decomposes very gradually only when it is kept in boiling state for some time; but the decomposition takes place even at a comparatively lower temperature i. e., *ca.* 80° when the solution is made alkaline. For instance, when a solution prepared by adding 1 g. of thiourea to 200 cc. of 0.05 *N* sodium hydroxide was boiled gently for 5 minutes, the decomposition took place. It was found on qualitative test that the product contained, beside traces of carbonate-, sulfate-, sulfite- and nitrate-ions, a considerable amount of sulfide ion. The evolution of sulfur dioxide gas, though very little, was also recognized by its odor.

The Amount of Thiourea Necessary for the Formation of Sulfide Precipitate.—The ions which can be precipitated with the sulfide ion produced by the decomposition of thiourea in an alkaline medium are copper, cadmium, lead, mercury and bismuth, while other cations form no sulfide precipitate under the same condition. The boiling changes almost all sulfur in thiourea into sulfide ion, precipitating the metals of the copper sub-group quantitatively. This may be illustrated by the following example.

A series of copper sulfate solutions were prepared and buffered by a mixture of sodium chloride, sodium hydroxide and glycocol so that their pH was 11.29 at 10°. To each of the solutions containing 0.0144 g. of CuO were added different volumes of the thiourea solution⁽⁴⁾ and they were made up to 40 cc. with distilled water respectively. The solution was then boiled gently for 2 minutes when a black precipitate was formed. The precipitate, after filtered through Toyo filter paper No. 5 A, was ignited to constant weight.

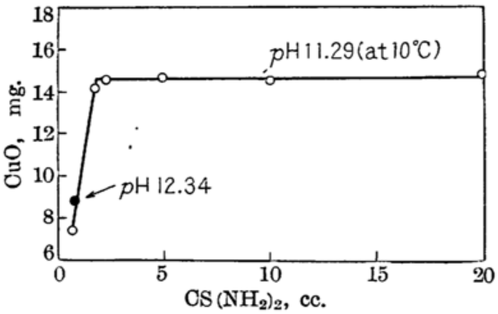

Fig. 1.

The results are summarized in Fig. 1 which shows that the precipitation of copper was complete when as much as 2 cc. of the thiourea solution was added. The theoretical amount of thiourea necessary for the quantitative separation of copper from the said solution is 1.67 cc., provided that all the sulfur in thiourea is available for the purpose. As illustrated in Fig. 1, the addition of 1.7 cc. of thiourea gave 0.0144 g. of CuO, the experimental results being in close agreement with the theoretical values.

The precipitate thus obtained is crystalline and adsorbs little foreign substances. It can be filtered easily with Toyo filter paper No. 5 A or even No. 1 etc., which have larger size of pores. This may be due to the fact that the velocity of precipitation is rather small and also that the precipitate once formed partly as hydroxide changes into sulfide very gradually.

Influence of pH on Sulfide Formation by Thiourea.—Thiourea does not produce sulfides in an acid medium. Our investigation has revealed that even when the solution is made alkaline, the precipitation is not complete unless $p\text{H} > 12$. This is confirmed by the following experiments.

To 20 cc. of the thiourea solution whose sulfur content was 3.5 mg. per cc. was added the buffer together with a solution containing copper or other ions of the sub-group. The total volume was made up to 55 cc., and the

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(1) Read before the Hokkaido meeting of the Chemical Society of Japan, on July 31, 1949.

(2) J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem., Anal. Ed.*, **14**, 435 (1942).

(3) Beilstein, Vol III, 180.

(4) 1 cc. of the solution contains 3.5 mg. of sulfur.

solution was heated until it boiled gently for 2 minutes. The liquid was then cooled and filtered through Toyo filter paper No. 3. The precipitate was washed thoroughly and ignited to constant weight.(5) The results are shown in Fig. 2. The values are the means of several experments in which about 50 mg. and 100 mg. of the copper sub-group ions were taken. These data show that the velocity of sulfides precipitation depends upon pH of the system and also the concentration of thiourea as well as cations. In consequence, the best result should be expected when pH of the solution is kept 12.

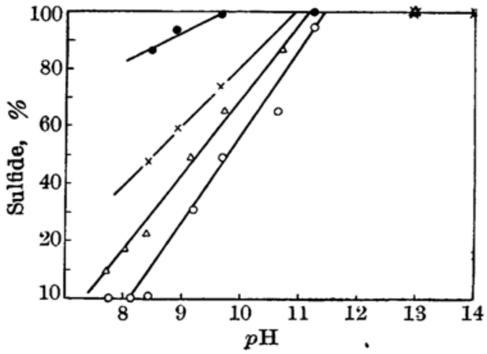

Fig. 2.

•, Cu; △, Pb; ×, Hg; ○, Cd

Separation of the Copper Sub-group Ions from Other Cations by Thiourea.— The results obtained above suggest us a new means of separation of the copper sub-group ions from other cations. In case where Cu^{++} and Fe^{+++}, for example, coexist in a solution, both metals precipitate as hydroxides when the solution is made alkaline. In presence of thiourea, Cu^{++} changes into sulfide while ferric hydroxide remains as such. When a sufficient amount of acetic acid is added, the hydroxide dissolves on boiling(6) whereas the sulfide remains as precipitate. The experiments were carried out in the following way.

To a solution containing one of the copper group ions, e. g., Cu^{++} as copper sulfate, was added three to five times as much another ion. Thiourea was present in the solution in such a ratio as $Cu : CS(NH_2)_2 = 1 : 5$ (in gram equivalent). Sodium hydroxide was added so that the solution was approximately 0.5 N. The mixture was heated and boiled for 2 minutes. After adding 10 cc. of acetic acid, the solution was allowed to stand on the water-bath for about 10 minutes. The precipitate was collected on Toyo filter paper No. 3, washed first with acetic acid and then with water and finally ignited to constant weight. The results are shown in Table 1.

Table 1

Influence of Coexisting Ions on the Precipitation of the Cu Sub-group Ions

Co-existing ions	Cu Sub-group Ions				
	Cu	Cd	Pb	Hg	Bi
Fe	85.3%	93.7%	91.6%	101%	95.3%
Al	92.8	96.4	96	83.2	96
Co	92.8	103.5	93.6	102.4	94.3
Ni	92.8	99.4	109	101.6	101
Mn	76.6	76.4	102.3	101.5	99
Zn	101.1	85.7	106	102.5	96
Cr	86.3	97.6	110	89	86

The values in the table are the separability of the copper sub-group ions from the coexisting ions which are found in the first column. They are the figures found with the solutions containing 0.05 g. and 0.1 g. of copper, cadmium and lead and also with the saturated solutions of mercury and bismuth.

Lead sulfide thus produced adheres to the inner wall of the vessel in which the reaction took place, forming a brilliant mirror. The deposit comes off easily from the wall in its early stage of formation. When the solution is allowed to stand for some time, however, the deposition becomes so firm that the mirror can be removed only on heating with nitric acid.

That the solubility to acetic acid of the sulfides obtained in this manner is very small is illustrated by the following experiments. A sulfide was precipitated in 50 cc. of the solution containing approximately 30 mg. of a copper sub-group ion, and the mixture, together with 30 cc. of acetic acid, was allowed to stand on the water-bath for 1 hour. The precipitate was then filtered and ignited to constant weight. The percentage by which the metal sulfides dissoved in acetic acid is as follows:

Cu 2.1%, Cd 2.8%, Pb 8.6%,(7) Hg 2.3%, Bi 4%

The separability of all the copper sub-group ions from the mixture of the ions of the third

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(5) The mercury precipitate was dried at 110° and weighed.

(6) If the solution containing ferric hydroxide is boiled for some time, the hydroxide becomes less soluble.

(7) The error is considered to be large in case of lead because of its nature of adhering to the wall.

group as well as the fourth group was next studied. The experimental procedure is as follows.

To the mixture of copper, cadmium, lead, mercury and bismuth salts, the total amount of which was 0.1114 g. as sulfide, was added approximately five times as much Fe^{+++}, Al^{+++}, Co^{++}, Ni^{++}, Mn^{++}, Zn^{++} and Cr^{+++}. The solution was made up to 100 cc. and treated with sodium hydroxide and thiourea in the same manner as in the previous experiments. It was boiled gently for 5 minutes and, after adding 50 cc. of acetic acid, allowed to stand on the water-bath for 10 minutes. The precipitate was then filtered and weighed. The separations of the copper sub-group from the fourth group, and the third group + the fourth group were also investigated. The results are summarized in Table 2.

Table 2

Separability of the Cu Sub-group Ions from Other Group Ions

	Co-existing ions	Separability
(1)	the third group	106.3%
(2)	the fourth group	103.4
(3)	the third group and the fourth group	106.4
(4)	tin sub-group, the third group and fourth group	168.3
(5)	the same as (4), but the precipitate was washed with conc. NaOH	94

When the ions of the tin sub-group exist in the system, they precipitate as hydroxide insoluble in acetic acid, the separation being made difficult. In this case the sulfides are filtered, washed with acetic acid and treated with conc. sodium hydroxide solution. The precipitates of the tin sub-group metals then dissolve and a fairly good separation is performed. This is understood by the figures given at the bottom of the table.

It is thus confirmed that the ions of the copper sub-group can be separated nearly quantitatively from many other cations by thiourea. The present operation suggests us a new scheme of qualitative analysis without hydrogen sulfide which is under investigation in our laboratory. In such a plan, the effect of the excess of thiourea after the separation of copper sub-group ions should by no means be ignored. For instance, because of its reducing nature, thiourea, if present, positively retards the oxidation of Mn^{++} to MnO_2 by means of nitric acid and potassium chlorate. The excess of thiourea must therefore be decomposed by evaporating up the solution with nitric acid to dryness before the solution is subjected to analysis of the fourth group.

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