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The Quantitative Separation of
Antimony and Tin

Chemical Engineering

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THE QUANTITATIVE SEPARATION OF
ANTIMONY AND TIN

BY

Carl J. Lauter
CARL J. LAUTER

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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In Chemical Engineering

S. W. Parr

Instructor in Charge

APPROVED:

W. A. Hayes

HEAD OF DEPARTMENT OF Chemistry

THE QUANTITATIVE SEPARATION OF
ANTIMONY AND TIN

By the term alloy, is meant a metal made by the fusion of two or more elementary metals for the purpose of obtaining some particular property, peculiar to the mixture alone.

This art of making alloys was known in the earliest ages, for there have been found in the old tombs and ruins all kinds of articles and weapon made of bronze and similar alloys.

Since that time the production of alloys has rapidly increased, until at the present time we have an almost infinite number of such metals. Especially noteworthy have been the advances made in the production of various steels, containing small amounts of the rare metals, imparting certain valuable properties to the former; and in the manufacture of babbitt or bearing metals. The demand for good metals of this latter type has been following the rapid growth of the automobile industry, where the best babbitt metal obtainable is used, since efficiency and life of such high speed engines depends greatly upon the nature of the bearings. Most of these alloys contain the metals tin, antimony, zinc and generally some copper. These are present in varying amounts depending upon where they are used; for small amounts of one or the other will greatly change the properties of the resultant alloy. Thus, antimony gives a certain hardness whereas too much would make it brittle. Antimony, also imparts to the metal its peculiar property of expansion upon cooling which insures a snug fit for bearings.

It is therefore evident that the problem in hand is the quantitative separation of this metal from its group metal, tin, which is consistently present in all brasses, bronze and similar alloys. Among the many methods the following may be mentioned:



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(1)

In Willer's method, the metals are both in the higher state of oxidation. The solution is then treated with Hydriodic acid, whereby, the antimonie chloride is reduced to antimonous chloride, while the stannic chloride remains unchanged. The equivalent amount of iodine which is thus liberated is then distilled into a potassium iodide solution and titrated with a dilute solution of sulphurous acid. Great care must be taken in this distillation; therefore making the analysis difficult and not attractive to the industrial chemist.

(2)

In Garnot's method antimony is precipitated from tin by the addition of sodium thiosulphate, to a neutral solution of tin and antimony, after an excess of oxalic acid had been added to the mixed chlorides of the metals. Oxalic acid must be in considerable excess or tin will also be precipitated. In precipitating, antimony in this way I found some antimony in the filtrate and results obtained with this method are widely variant.

(3)

Brensen's method deals with the separation of antimony and arsenic. The metals are precipitated as the sulphides which are then dissolved in an excess of potassium hydroxide, after which a stream of chlorine is passed through the solution, volatilizing the arsenic. This method does not take into account the difficulty of getting the antimonie sulphide dissolved in potassium hydroxide or the fact that the arsenic is not completely volatilized. He also says nothing about the separation of tin, with which we are chiefly interested.

(4)

In Karsner's method the sulphides of antimony, arsenic, and tin are treated with sodium peroxide. This dissolves the sulphides but partially

(1) Chemical News Vol. 46, p. 172

(2) Zeit. fur Anal. Chemie. Vol. 27, p. 651

(3) Anal. Chemie, Vol. 192, p. 317

(4) Zeit. fur Anal. Chemie Vol. 34, p. 596.

re-precipitates some of the tin. If the solution is boiled the tin is all reprecipitated while the antimony stays in solution, which is later precipitated as pyro-antimonic acid, by the addition of alcohol. The objection to the use of this method is that the tin is not completely precipitated in boiling and some of the antimony likewise stays in solution, after the alcohol treatment.

(5)

In McCays method the mixture of the higher sulphides of antimony and tin are redissolved in five cubic centimeters of hydrochloric acid and after expelling the hydrogen sulphide a solution of tartaric acid is added and the filtrate then neutralized with sodium hydroxide. Five cubic centimeters of a 48 per cent hydrofluoric acid solution are then added and an excess of sodium acetate. The solution is then diluted to about three hundred cubic centimeters and the antimony precipitated with hydrogen sulphide, the fluoride present prevents precipitation of stannic tin. The antimony precipitate is converted, as usual, into the black anhydrous sulphide. The filtrate is evaporated in a platinum dish on the water bath with an addition of sulphuric acid to expel the fluorine, and after dissolving the residue in water, the tin is precipitated with hydrogen sulphide and treated in the usual way.

(6)

(6)

By Vortmann and Metyl's method, antimony may be quantitatively separated from tin by dissolving the mixed sulphides in a little hydrochloric acid, neutralizing by addition of sodium hydroxide and diluting to a volume of about sixty cubic centimeters. An equal volume of phosphoric acid of specific gravity 1.3 and about twenty five cubic centimeters of concentrated hydrochloric acid are then added and the solution treated at boiling temperature with hydrogen sulphide. The black precipitate of antimony trisulphide is collected and weighed. The filtrate containing all the tin in solution is

(5) Journal American Chem. Society 31, 373-38.

(6) Zeit. fur Anal. Chemie 1905- pages 525-535

nearly neutralized; diluted with an equal volume of water, warmed and the tin precipitated as sulphide and weighed in the usual way. This method is untrustworthy if nitric acid or other oxidizing agents are present.

(7)

In Warren's method the antimony and tin are precipitated as sulphides along with the other metals and separated from them by dissolving in sodium hydroxide. The sulphides are then reprecipitated by an addition of hydrochloric acid and they are then dissolved in aqua regia. The nitric acid is driven off and the tin precipitated as ferrocyanide; no such compound being known for antimony. The objection to this method is in the use of sodium hydroxide in dissolving the sulphides of antimony and tin. Unless certain precautions not given under this method are taken the tin is partially reprecipitated and antimony, if in the higher state of oxidation is very difficultly soluble in alkalies.

(8)

Low's method is the direct titration of both metals in the presence of each other. The solution of the metals or sulphides in sulphuric acid is titrated with potassium permanganate, whereby the antimony is oxidized. The tin is then reduced with metallic antimony and titrated with a solution of iodine. This method usually gives low results for tin.

(9)

Vietz's method is a modification of Low's. Here the tin and antimony or sulphides are dissolved in concentrated sulphuric acid. This is diluted to about two hundred cubic centimeters and the antimony which is present in the antimonous state is titrated with standard permanganate solution. After titrating with permanganate, about one gram of finely powdered antimony per 3/10 grams of alloy and 25 cubic centimeters of concentrated hydrochloric acid are added to reduce the tin. Carbon dioxide is then passed through the flask, while it is being boiled, to prevent re-oxidation of the tin. The

(7) Chem. News Vol. 57, p. 124

(8) Jour. American Chem. Society Vol. 29, p. 66

(9) Chem. Engineer Vol. XII, p. 116.

solution is then rapidly cooled, continually passing carbon dioxide and then quickly titrated with iodine, standardized against tin and carried out in the same manner as above described.

The analysis is reliable only when the process is carefully carried out, the titrations require a little practice before reliable results can be obtained.

(10)

Clarke's method depends upon the fact that antimony is completely precipitated from an oxalic acid solution while stannic tin is not. The alkaline solution of the sulphides of antimony and stannic tin are placed in a flask and treated with six grams of pure potassium hydroxide (.3 grams of the combined metals being present). To this mixture enough 30 per cent hydrogen peroxide is added to completely oxidize the tin and any thiosulphate which may have been formed. The excess of hydrogen peroxide is boiled off and the solution cooled, after which five times the weight of the combined metals, of oxalic acid is slowly added and then vigorously boiled to remove any surplus hydrogen peroxide. Through this volume of the solution, which is about 100 cubic centimeters, a rapid stream of hydrogen sulphide is passed. After a short time the volume is increased and hydrogen sulphide passed for fifteen to twenty minutes longer.

The antimony pentasulphide is filtered through a Gooch crucible, dried in a stream of carbon dioxide at 300° for an hour and weighed as antimonious sulphide. The filtrate is evaporated to about 200 cubic centimeters transferred to a platinum dish and electrolyzed at 60° with a current of .2 amperes, and weighed as metallic tin.

(EXPERIMENTAL WORK)

It has been found possible to get a clear solution and a clean separation

of antimony and tin from the rest of the sulphides of group two by the use of potassium hydroxide. The mixed sulphides are filtered and transferred to a beaker, a little hydrochloric acid is added and this is then heated. A mixture consisting of 100 cubic centimeters of 5 per cent potassium hydroxide and one cubic centimeter of 30 per cent hydrogen peroxide, is then added until just faintly alkaline to litmus. The mixture of sulphides and alkali is then heated to boiling upon which the red coloration disappears, and more of the potassium hydroxide can be added without fear of reprecipitating any tin. If larger amounts of hydrogen peroxide are used, some of the copper sulphide, if present, will be oxidized and go along into solution with the antimony and tin sulphides. Having the sulphides of antimony and tin dissolved completely in potassium hydroxide, the next question was to get a good separation of the two.

I first tried the application of Clarke's method. As the sulphides were dissolved in potassium hydroxide and hydrogen peroxide it was not necessary to add any more peroxide and boil to oxidize sulpho salts, as the antimony and tin are both present as oxy salts. The solution of the sulphides was strongly acidified with Oxalic acid and boiled to remove any free peroxide. A stream of hydrogen sulphide was then passed through the hot solution and the antimony precipitated out as a dark reddish granular precipitate, which filtered rapidly and clearly. A test for tin in the precipitate showed its absence then. The filtrate was then neutralized with ammonia and ammonium acetate added which precipitated the tin as hydroxide. The precipitate was very gelatinous and occupied a large volume which made it difficult to filter and wash. This difficulty was overcome by the use of a filter pump, using a gentle suction.

In order to find a quicker way for the determination, the reactions of various reagents upon the alkaline solutions were tried out.

Separate solutions containing only tin and only antimony were tried, and give the following tabulated results:

Reagent	Tin Sulphide in		Antimony Sulphide in	
	Potassium Hydroxide		Potassium Hydroxide	
	To neutral point	Excess of reagent	To neutral point	Excess of reagent
	white ppt.	no change	no ppt.	no ppt.
Acetic acid	" "	" "	" "	" "
Sodium bicarbonate	" "	" "	" "	" "
Potassium persulphate	" "	" "	" "	" "
Ammonium persulphate	" "	" "	" "	" "
Oxalic acid	" "	" "	" "	" "
Potassium ferricyanide	green "	" "	" "	" "
Potassium ferrocyanide	white "	" "	" "	" "
Phosphoric acid	" "	redissolves	" "	" "
Hydrochloric acid	" "	"	" "	" "
Nitric acid	" "	"	" "	" "
Aluminium	no action		metallic Sb. metallic Sb.	

From these facts we seem to have reached an ideal separation, for acetic acid, potassium and ammonium persulphate, sodium bicarbonate, and phosphate all give a complete separation of tin, leaving none in solution, while they are without absolutely any visible action at all upon the antimony solutions.

A mixture of the two metals was then analyzed using about .1 grams of each metal. This was precipitated with hydrogen sulphide, filtered and dissolved in the usual way in a 5 per cent solution of potassium hydroxide containing 1 cubic centimeter of 30 per cent hydrogen peroxide in one hundred cubic centimeters of solution.

After obtaining a clear solution about one cubic centimeter more of hydrogen peroxide and 25 cubic centimeters of potassium hydroxide was added, so as to be sure to have the tin and antimony both completely oxidized. This was then boiled to completely expel the excess of peroxide, after which acetic acid was added until the solution was distinctly acid. A white precipitate was formed which quickly settled to the bottom and filtered easily and clear.

This precipitate was then dried and ignited and weighed as stannic oxide, but the results were all much higher than the amounts of tin taken, although somewhat close to each other.

Results of the Analysis.

Tin taken	Tin found
.0974 grams	.1217 grams
.0974 "	.1208 "
.0974 "	.1298 "
.0974 "	.1107 "

The fact that the weights of tin found agreed as closely as they did gave a suggestion that perhaps a compound of antimony and tin was found. This may have been a tin antimonate having a definite composition, in which case this would have been as good as a clean separation of the two metals as the antimony remaining in solution could be determined later. If not enough antimony were present in the beginning a known amount of a standard solution could be added to combine with all the tin present.

In order to verify this, another series of analyses were run using a fresh solution of tin and antimony. The results were as follows:

	Tin taken	Tin found
I	.0689 grams	.0818 grams
II	.0689 "	.0795 "
III	.0689 "	.0808 "

Here again the weights of tin found were higher than amounts taken but the percentage difference was not the same as in the first set of determinations and results were not as concordant. This proves beyond a doubt that the antimony must be carried down mechanically with the tin.

Potassium persulphate and ammonium persulphate and sodium bicarbonate all behaved similarly with the mixed sulphides in potassium hydroxide; all bringing down antimony with the tin precipitate. Phosphoric acid when tried on the mixtures gave a precipitate which was impossible to filter and upon heating went back into solution.

From the results obtained it seems sure that there is no definite compound formed between antimony and tin as the percentage increase in weight is not constant under similar conditions. It may, however, be possible to find a way to get a complete separation with varying conditions or by reprecipitation. Otherwise the long method of Clarke's is applicable to the conditions in which the two sulphides are left, after separating from the other elements of the same group.

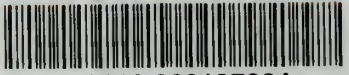
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