6. The activity coefficients calculated from the measurements with thallous chloride show satisfactory agreement with those calculated from solubility measurements.

7. The values of the activity coefficients calculated from measurements of the freezing-point lowering, electromotive force and solubility agree among themselves, but do not agree with the theoretical equation of Debye and Hückel and the modification of that equation by Brönsted and La Mer.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF MICHIGAN]

A REVISION OF THE ATOMIC WEIGHT OF ANTIMONY
THE ANALYSIS OF ANTIMONY TRICHLORIDE

BY PHILIP F. WEATHERILL

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Clarke, in the 4th edition of his "Recalculation of Atomic Weights"[1] gives a summary of the work on the atomic weight of antimony up to that time. Willard and McAlpine have since then published the results of their work on the analysis of antimony tribromide,[2] and have critically discussed previous work on this problem. The results obtained by Willard and McAlpine indicate that the value of 120.2, which has appeared in the tables for a number of years, is much too low, and that 121.77 is nearer the truth.

After the present research was completed, Professor O. Hönigschmid stated that in a recent investigation,[3] he had obtained the value 121.76 from the analysis of both the trichloride and the tribromide, confirming the results obtained by Willard and McAlpine.

In the present work antimony trichloride was prepared in a vacuum, purified by repeated distillation in a vacuum, and compared with pure silver. Since previous work indicated that the exclusion of all moisture is of greatest importance, all apparatus was dried with great care.

The fact that the ratio given by the trichloride is more favorable than in the case of the tribromide is about balanced by the fact that the end-point in the latter case can be determined more accurately. However, since the trichloride has a lower melting point, it is much easier to handle in the type of apparatus used here for its purification. By cooling the solution the sharpness of the end-point was increased so that the error here was probably no greater than that in other parts of the process.

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[1] Clarke, "Recalculation of Atomic Weights," Third Memoir, *Nat. Acad. Sci.*, **16,** 247 (1920).

[2] Willard and McAlpine, THIS JOURNAL, **43,** 797 (1921).

[3] Hönigschmid, personal communication. The work will appear in *Z. anorg. allgem. Chem.*

The Preparation of Antimony Trichloride

Kahlbaum's purest metallic antimony was broken up in a mortar and fused in a Pyrex tube in a current of hydrogen. The hydrogen, from a tank, was first passed through a small Pyrex glass tube heated to redness, and then dried by passing through a U-tube filled with phosphorus pentoxide. The resulting buttons were broken up and again fused in the same manner. No discoloration of the glass occurred during the second fusion.

This twice-fused material was then placed in a Pyrex glass tube and dried in a current of hydrogen at 500°, after which the tube was sealed into position in the apparatus for making the trichloride, as shown at D, Fig. 1.

The chlorine was generated in a large Pyrex flask by the interaction of 1:1 hydrochloric acid with c.p. potassium permanganate. The hydrochloric acid had previously been fractionated and the middle fraction boiled for a short time with a small amount of potassium permanganate. The chlorine thus produced was passed through two towers containing pure water, three towers containing concd. sulfuric acid, and finally through a tower containing layers of phosphorus pentoxide separated by glass wool. All connections were made by fusing the glass together.

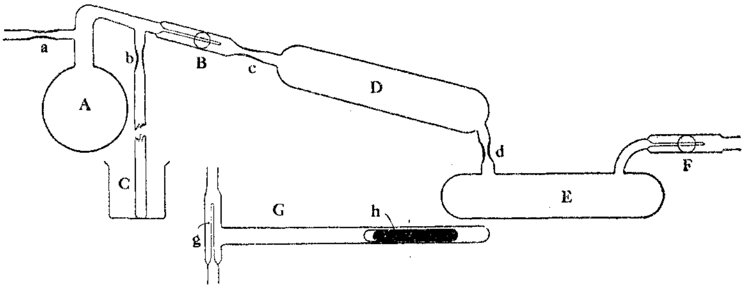

Fig. 1.

The reaction was carried out in the all-Pyrex glass apparatus, shown in Fig. 1. After the tube D, containing the antimony, was sealed into place, the system from B to F was completely exhausted by a Langmuir diffusion pump, through a side tube not shown in the figure, and sealed off from the pump. The tube a was now sealed onto the chlorine generator and drying train, and the generator train and Bulb A were swept out with the gas for about 12 hours, the gas passing out through the tube C which dipped under concd. sulfuric acid.

The bulb A was then cooled with a mixture of carbon dioxide snow and alcohol and the chlorine collected as a liquid, any gas not condensed escaping through C. Near the end of the reaction, when the generating flask had to be heated by a water-bath, a small amount of gas passed off through C. This was probably hydrogen chloride which had not been absorbed by the water in the towers. After about 12 hours, sufficient chlorine had been collected in A and the system was sealed off from the generating train at the constriction a. The cooling mixture was now removed from the bulb A for a short time and about a quarter of the chlorine allowed to boil off through C to remove any gaseous impurities that might have been present, such as hydrogen chloride. The bulb was then cooled again, and the trap sealed off at the constriction b.

The construction of the Bruner and Bekier[4] valves used at B and F in Fig. 1 is shown in detail in the figure at G. The small, thin-walled capillary, g, forms a seal at that point, but connection can readily be made by tipping the whole apparatus so that the mercury-weighted glass tube, h, will slide down the T-tube and break the capillary. This valve has been used by a number of different investigators in recent years,[5] and is a very useful piece of apparatus in vacuum distillation.

The bulb A was then cooled with liquid air so that the chlorine could not pass too rapidly into the evacuated tube D, and the capillary in the valve B was broken. The reaction between the chlorine and the antimony was very vigorous and the freezing mixture was not, at first, sufficient to keep the reaction under control. As the reaction went on, it became less violent and the carbon dioxide mixture could be used. The heat of reaction kept the antimony trichloride in a liquid state, so that it flowed into the tube F as fast as it was formed in D. When all except a small amount of the antimony had been used up the bulb A was sealed off from the rest of the system at the constriction c.

In order to remove the excess of chlorine from the antimony trichloride, the melted material was poured from E into D and allowed to stand, in a liquid state, over the metallic antimony for many hours. During this time the liquid was frequently poured into tube E and back to D to insure thorough mixing. Finally all of the liquid was poured into E and a small fraction was distilled back into D so as to remove a part of the more volatile impurities. D was then sealed off from the system, and the material in E used as the starting point of the distillation in a vacuum which was depended on to remove the impurities that might have been present at this stage of the procedure. The trichloride in E was not quite water-clear when melted, and probably contained a trace of chlorine together with other impurities in small amounts, derived for the most part from the metallic antimony.

The Purification of Antimony Trichloride

The tube E, Fig. 1, was sealed onto a similar tube, also ending in a Bruner and Bekier valve, and connected through a side arm to a Langmuir

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[4] Bruner and Bekier, *Z. Elektrochem.*, **18**, 369 (1912).

[5] See, for example, Baxter, Weatherill and Scripture, *Proc. Am. Acad. Arts. Sci.*, **58**, 245 (1923).

diffusion pump. The tube sealed on contained a small amount of *very pure* metallic antimony, prepared by Willard and McAlpine.[2] This antimony was to remove any free chlorine that might have been present. The system between the two valves was then thoroughly exhausted, and the pump sealed off. In pumping out the system the glass was heated with a free flame in order to drive off as much of the moisture from the walls as possible, and a high vacuum was maintained for about half an hour. The apparatus was then tipped and the capillary in the valve F, Fig. 1, broken, establishing a passage between the tube E and the evacuated tube. The antimony trichloride was then melted and distilled into the evacuated tube, a small heavy fraction being left. E was then allowed to cool, and a small light fraction distilled back into it, after which it was sealed off from the system and discarded. The material was kept fused over the metallic antimony for about 12 hours to allow any free chlorine to react with the metal.

The whole distillation of the material is shown diagrammatically in Fig. 2. The distillation just described is that from A to B. In a similar manner the material was distilled from B to C, from C to D, and so on, discarding a heavy and a light fraction at each step. Metallic antimony was used only in B, as there, and in all succeeding distillations, the liquid was water-clear when melted and pure white when solid.

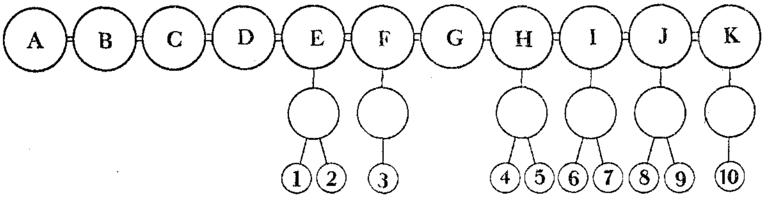

Fig. 2.

In distilling from B to C, Fig. 2, a very small amount of air leaked into the apparatus through an extremely minute pinhole in one of the fused points. This leak was so small that the pump produced a vacuum of about 0.0001 mm., but after the tube had been sealed off the distillation did not proceed as well as it had in previous cases. So in the next distillation, from C to D, Fig. 2, the joint was broken while the system was still connected to the pump, and the material was melted and poured from C to D, and D sealed off from the pump. After this no trouble was experienced with air leaks.

Fig. 2 shows that before E was distilled into F, a small amount was distilled into a small bulb, not marked, and that from this bulb the two samples, 1 and 2, were obtained. Similarly, Samples 6 and 7 were obtained from the material in I before the trichloride was distilled into J.

The method of obtaining the samples for analysis, which has not been in general use in this kind of work, is shown in detail in Fig. 3. The material was distilled from H, Fig. 2, for example, into the bulb A, Fig. 3, connected to the valve B, and then sealed off as shown at the top of A. Now the rest of the system shown in Fig. 3 was sealed on, the system evacuated through c and sealed off from the pump at the constriction b. The bulbs for receiving the samples, shown at D, were connected to the rest of the system by small ground points which were very carefully made and finally polished in with rouge. In order to be sure that they would be perfectly tight, since of course no grease could be used, a mercury seal, shown on the bulb on the left, was used. This consisted simply of a small glass tube held in place by a small cork, so that it could be removed easily. No mercury came in contact with the material in the bulbs. The system having been exhausted, the capillary in valve B was broken and the trichloride distilled into the bulb C, and A was sealed off. From C the trichloride was distilled directly into the sampling bulbs, which were immersed in hot water to keep the material from solidifying, and these were sealed off, giving the samples as shown at F. The construction of apparatus shown in Fig. 3 prevented the fragments of glass from the broken capillary in B from being carried into the sampling bulbs.

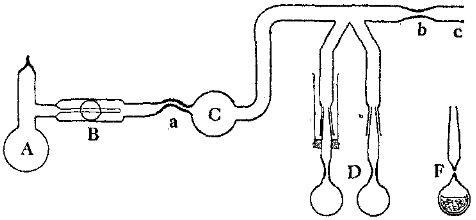

Fig. 3.

Purification of Other Materials

Water.—Water from the laboratory still was twice redistilled, once from alkaline permanganate and once from very dilute sulfuric acid. The condensers were constructed of block tin tubes fitted to Pyrex flasks with constricted necks, which served as stills. The connections were made by a water seal, no cork or rubber being used. The water was collected in Pyrex flasks a short time before it was used.

Nitric Acid.—Concd. nitric acid was distilled through a quartz condenser, the middle third being collected.

Tartaric Acid.—The best C.P. material was once recrystallized, the crystals being drained in a centrifuge in platinum baskets, washed with a small amount of chilled water and drained again. Tests gave no indication of the presence of the halogens.

Silver.—The silver used in these analyses was prepared by R. K. McAlpine for his work on the analysis of antimony tribromide.[2] Since the silver had been prepared for some time, it was etched twice with purest nitric acid, with thorough washing after each etching, and dried in a high vacuum at about 300°. A large trap cooled with a mixture of carbon dioxide snow and alcohol was used between the mercury pump and the drying tube. The drying tube was of Pyrex glass.

Phosphorus Pentoxide.—The ordinary C.P. material was sublimed in the usual manner in a current of pure oxygen.

Weighing

All weighings were made on a No. 10 Troemner balance with weights standardized to 0.01 mg. All weights were corrected to a vacuum, the weight of the air at the time of weighing being determined by weighing a standardized globe.[6] In the case of silver, the vacuum correction was so small that an average value of 0.00114 g. for the weight of 1 cc. of air was taken. This value was obtained from a series of readings taken during the past year. The density of Pyrex glass was taken to be 2.23 from determinations made in this Laboratory, and the density of the weights was assumed to be 8.4. The density of the bulbs containing the samples was of course determined for each individual bulb. All weighings were made by the method of substitution.

Analysis

The method used in the present work for finding the weight of glass in the sampling bulb is rather different from that generally used in atomic-weight investigations of this kind. Usually the fragments of glass are filtered off and weighed after the bulb has been broken.

In order to avoid this filtration of the solution the weight of glass was determined in the following manner. The clean, empty bulb, sealed to the ground joint as shown at D, Fig. 3, was weighed before being attached to the system. After the bulb had been filled and sealed off, and the ground joint detached from the system, the two parts shown at F in the figure remained. By weighing the part with the ground joint and subtracting this weight from the weight of the original "bulb plus joint," the weight of glass in the bulb was found.

In order to be sure that this gives accurate results, it is necessary to know (1) that no glass is lost during the fusion when the bulb is sealed off; (2) that no glass is ground off at the joint; (3) that the mercury and antimony trichloride can be completely removed from the joint before it is weighed.

The first point was investigated by weighing a small tube of Pyrex glass about the size of the capillary in the system, sealing this off in the usual manner and weighing the two parts. The two weights found were identical to 0.01 mg.

In work done by the usual method of breaking the bulb in a glass-stoppered flask and filtering off the glass fragments, it has been shown that no weighable amount of glass is detached from a well-ground stopper. Considering the care with which the very small joints used in the present method were ground, it seems impossible that any appreciable error could occur in this manner.

The small amount of mercury adhering to the joint could be wiped off with a cloth until none could be seen with the eye, so the amount remaining after cleaning with nitric acid must have been negligible. Antimony trichloride was readily removed by hydrochloric acid.

In order to check the method as a whole, a trial system, containing no antimony trichloride, was set up and evacuated, and the empty bulb sealed

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[6] Baxter, This Journal, **43**, 1317 (1921).

off and weighed. The computed weight varied from that actually found by only 0.01 mg. It is not to be hoped that this accuracy was obtained in all cases, but the result indicates that any error in the method is very small.

When the weight of glass in the bulb is known, only the weight of the bulb containing the sample is necessary to determine the weight of the antimony trichloride present. The volume of the bulb, necessary for the computation of the vacuum correction, was found by weighing under water in the usual manner.

An amount of tartaric acid, such that 4.8 g. was present for each gram of the trichloride, was then weighed out, dissolved in water and filtered into a 2-liter heavy-walled Pyrex precipitating flask fitted with a well-ground stopper. The bulb containing the sample was placed in the flask and broken by shaking. Ample time was allowed for all the sample to dissolve, and the solution was then diluted to a volume such that it was equivalent to a solution of silver containing not more than 10 g. per liter.

The amount of silver, computed on the basis of Sb = 121.77, was now weighed out in the form of buttons, dissolved in purest nitric acid in a flask fitted with a Richards bulb tower, and then diluted so that there was less than 10 g. per liter. This silver nitrate was added quantitatively in small portions to the trichloride solution, swirling the liquid gently after each addition, and the flask was then shaken vigorously for some time. All operations involving silver chloride were carried out in a dark room lighted by a ruby light.

After the first long shaking, the solutions were shaken five or six times a day for at least a week; then they were cooled in ice for several hours, shaken and allowed to settle for 12 hours or more. Samples were then drawn off in a pipet and tested in a nephelometer with silver nitrate and potassium chloride solutions. Small amounts of these solutions, which were equivalent to a solution containing 1.0000 g. of silver per liter, were added to the flasks from 5cc. burets which could be read to 0.01 cc., until equilibrium was reached.

When the solutions were cooled in ice, 0.2 mg. of silver (or chloride, as the case might be) gave a perfectly definite change from one side of the equilibrium to the other, and it is believed that the end-point was accurate to within 0.1 mg. of silver. The estimates from the ratios observed were recorded to 0.05 mg. Table 1 shows the small amounts of silver that were necessary to reach the end-point.

After the end-point had been reached, the solutions were allowed to stand for at least a week, and shaken several times each day, in order to be sure that no more "soaking out" took place. In only one case did any change occur, and tests after an additional week showed that this solution had reached equilibrium.

It is to be noted that in this method of analysis, only one transfer of material takes place, namely, the transfer of silver nitrate from the dissolving flask to the precipitating flask—an operation that is not subject to much uncertainty.

TABLE I

THE ATOMIC WEIGHT OF ANTIMONY

Analysis	$SbCl_3$ G.	Ag weighed out G.	Ag added Mg.	Total Ag G.	Ratio $SbCl_3$: 3 Ag	At. wt. of Sb
1	2.22658	3.15853	+0.60	3.15913	0.704808	121.730
2	2.17394	3.08407	+ .05	3.08412	.704882	121.754
3	2.97080	4.21468	+ .10	4.21478	.704853	121.745
4	2.27024	3.22083	.00	3.22083	.704862	121.747
5	3.55903	5.04901	+ .35	5.04936	.704848	121.743
6	2.52017	3.57491	+ .40	3.57531	.704881	121.754
7	1.98530	2.81671	− .10	2.81661	.704854	121.745
8	2.75200	3.90404	+ .25	3.90429	.704865	121.749
9	2.57051	3.64662	+ .20	3.64682	.704863	121.748
10	3.15055	4.46931	+ .40	4.46971	.704867	121.749
			Av. of all 10		.704858	121.746
			Av., omitting No. 1		.704864	121.748

Ag = 107.880 Cl = 35.458

Results

Table I is a complete list of the analyses made. Every analysis started was carried to completion, and is recorded in the table. The atomic weights of silver and chlorine are assumed to be 107.880 and 35.458, respectively.

The first analysis was in the nature of a preliminary analysis, and is included only for the sake of completeness. It was made some time before any of the others were started, in order to secure experience in carrying out the process. For these reasons it seems best to omit it from the final computations, although its inclusion causes a difference of only two units in the third decimal place of the atomic weight of antimony.

The absence in the results of any definite trend following the course of distillation indicates that further distillation would have given material of no greater purity. If any impurity was present it formed a constant-boiling mixture with the antimony trichloride. The presence of such an impurity is possible, but highly improbable.

Taking the mean of Analyses 2 to 9 we get 0.704864 ± 0.0000026 as the ratio of $SbCl_3$ to 3Ag, and 121.748 ± 0.00086 as the atomic weight of antimony. This result is slightly lower than that obtained by Willard and McAlpine[2] from the analysis of antimony tribromide, 121.77, and also a little under the result, 121.76, obtained by Hönigschmid[3] from the analysis of both the trichloride and the tribromide. Considering the three independent researches, a value of 121.76 seems close to the truth.

Dr. Willard and Dr. McAlpine were very generous in placing at my disposal much material and many valuable suggestions. Their coöperation and interest have added to the pleasure of carrying out the work, and to the value of the results obtained.

Summary

Antimony trichloride, prepared from pure antimony and chlorine in a vacuum, was repeatedly distilled in a vacuum in an all-glass apparatus, dissolved in a solution of pure tartaric acid, and compared with pure silver. The mean of nine analyses gave 0.704864 ± 0.0000026 as the ratio of $SbCl_3$ to 3Ag, and 121.748 ± 0.00086 as the atomic weight of antimony.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS WESLEYAN UNIVERSITY]

THE SOLUBILITY OF BENZOIC ACID IN BENZENE AND IN TOLUENE

BY JOHN CHIPMAN

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The data on the solubility of benzoic acid in benzene quoted by Landolt, Börnstein and Roth[1] and by Seidell[2] are based on the work of Roloff.[3] The values of the logarithm of the mole fractions of solute calculated from these data plotted against the reciprocal of the absolute temperature do not form a smooth curve. The solubility at 25° is reported by several observers. Reduced to percentage by weight the data recorded are as follows: Seidell,[4] 10.9%, Marden and Dover,[5] 10.4%, von Euler and Lowenhamn,[6] 8.65%; Szyszkowski,[7] 10.85%. The only data available on the system, benzoic acid-toluene, are a single observation by Seidell[4] at 25° and a series of observations obtained in this Laboratory[8] which are not in as good agreement with the solubility in benzene as might be predicted from the close similarity in internal pressures of the two solvents. It has appeared worth while therefore to redetermine the solubilities over the entire temperature range.

Experimental Part

Materials.—Benzene was shaken repeatedly with sulfuric acid, then successively with water, dil. sodium hydroxide, water and saturated calcium chloride solution. It was then fractionally distilled over solid calcium chloride; about two-thirds of the liquid was

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[1] Landolt, Börnstein and Roth, "Phys.-Chem. Tabellen," J. Springer, **1912**, p. 523.

[2] Seidell, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., **1919**, p. 135.

[3] Roloff, *Z. physik. Chem.*, **17**, 333 (1895).

[4] Seidell, *U. S. Pub. Health Service Hyg. Lab. Bull.*, **67** (1910).

[5] Marden and Dover, THIS JOURNAL, **38**, 1239 (1916).

[6] von Euler and Lowenhamn, *Z. Elektrochem.*, **22**, 199 (1916).

[7] Szyszkowski, *Medd. Vetenskapsakad. Nobelinst.*, **3**, No. 4, 1 (1915).

[8] Mortimer, THIS JOURNAL, **45**, 633 (1923).