[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A Revision of the Atomic Weight of Thallium. The Analysis of Thallous Chloride

BY GREGORY PAUL BAXTER AND JOSEPH SMITH THOMAS

Three recent determinations of the atomic weight of thallium have shown beyond question that the value 204.04 obtained by Crookes[1] by conversion of metal to nitrate is too low. Hönigschmid, Birckenbach and Kothe[2] determined the ratio of thallous chloride to silver and silver chloride with the result 204.39. The vacuum corrections given in their paper are ten times larger than the correct values, but since the effect of this error upon the atomic weight of thallium would be 0.12 unit it seems likely that the correct values actually were used. Hönigschmid and Striebel[3] carried out a similar investigation with thallous bromide and obtained the same result as with the chloride. Briscoe, Kikuchi and Peel[4] also compared thallous chloride with silver using instead of the conventional equal-opalescence method of titration, that of adding a very slight excess (2–3 mg.) of silver and then, after evaporation of the solution (6–7 liters), titrating the excess of silver with dilute standard thiocyanate. As has already been pointed out (Report of the International Committee on Atomic Weights)[5] this method could scarcely be expected to give reliable results, for the dissolved silver chloride in the solution must have amounted to many milligrams. In fact since the silver found in the solution fell between 2.0 mg. and 4.1 mg. in all but one experiment, it seems by no means certain that a real excess was added in any case. Their result, 204.34, is appreciably lower than that of the German experimenters. Aston[6] from mass spectrographic data calculates the chemical atomic weight 204.41 ± 0.02, using the conversion factor 1.000125. With the factor 1.00022 his value for thallium becomes 204.39.

Our own efforts were first directed toward an attempt to determine the thallium content of thallous chloride by electrolytic deposition in a weighed mercury cathode. We were unable to find, however, any liquid for washing the amalgams under which rusting did not occur so extensively that correction for the difficulty was hopelessly impossible. We therefore turned to the method used in the investigations cited above, of comparing thallous chloride with silver.

Purification of Materials

Water and acids were purified by distillation; silver was prepared by a standard procedure.[7]

---

(1) Crookes, *Phil. Trans.*, **163**, 277 (1874).

(2) Hönigschmid, Birckenbach and Kothe, *Sitzungsb. Bayer Akad.*, 179 (1922).

(3) Hönigschmid and Striebel, *Z. anorg. Chem.*, **194**, 293 (1930).

(4) Briscoe, Kikuchi and Peel, *Proc. Roy. Soc.*, **A133**, 440 (1931).

(5) THIS JOURNAL, **55**, 447 (1933).

(6) Aston, *Proc. Roy. Soc.*, **A134**, 577 (1932).

(7) For an outline see Baxter and Ishimaru, THIS JOURNAL, **51**, 1730 (1929).

Commercial metallic thallium served as a starting point for the preparation of thallium material. When examined in a pure graphite arc with a Féry quartz spectrograph this metal appeared to be already comparatively pure, the chief impurities being copper, lead and aluminum to the extent of a few hundredths of a per cent. The metal was dissolved in sulfuric acid, and, after the solution had been filtered, the sulfate was fractionally crystallized in Pyrex vessels with centrifugal drainage and washing. The first fraction received five crystallizations, the others a larger number. Spectroscopic examination showed that the impurities disappeared slowly during this process, but not entirely.

Thallous chloride was next precipitated by dissolving recrystallized sulfate, filtering through a platinum sponge crucible, and adding hydrochloric acid. The product after solution and filtration was recrystallized in quartz vessels. Sample A of thallous chloride was prepared from one of the less pure fractions of sulfate and after precipitation was recrystallized once. This material contained a spectroscopic trace of silver, owing to accidental contamination, but no other impurity could be detected. Sample B was prepared from sulfate which had been obtained from the mother liquors of the best sulfate by seven crystallizations, and was recrystallized three times after precipitation. Sample B contained no impurities which could be detected spectroscopically. Sample C was prepared from the best five times crystallized sulfate and was recrystallized twice after precipitation. It was not tested spectroscopically. The solution from which Sample B had been precipitated was evaporated to dryness and the residue when tested spectroscopically was found to contain appreciable amounts of copper, lead, aluminum and gallium which had escaped the sulfate crystallization.

Method of Analysis

The preparation of the salt for analysis followed the procedure described by Hönigschmid, Birkenbach and Kothe.[2] The chloride was first sublimed in a quartz tube in a current of pure nitrogen, in order to eliminate organic matter and silica. Removal of the distilled salt from the tube was facilitated by allowing the fused material to run into a cold portion of the tube.

The distilled salt was then re-fused in a weighed quartz boat in a current of nitrogen and was transferred to the weighing bottle in dry air by means of a Richards bottling apparatus. Since the melted chloride adheres to quartz, a sturdy boat was necessary to avoid fracture during solidification.

The quartz boat from which the chloride was distilled in the course of time showed signs of attack, although the quartz tube remained unchanged in appearance. On the other hand, the quartz boat in which the chloride was finally fused showed no evidence of reaction with the chloride. In seven experiments in which the weight of the boat and weighing bottle was obtained both before and after an experiment the average difference in weight was found to be −0.08 mg. Since this difference includes any change caused by the boiling in nitric acid to which the boat and weighing bottle were subjected preparatory to each experiment, it did not seem to be a cause for alarm.

After being weighed the salt was dissolved in hot water. This required several days. In the meantime a very nearly equivalent amount of the purest silver was weighed and dissolved in nitric acid, and when the chloride was dissolved, was added to the solution. Adjustment of the end-point by means of hundredth normal solutions of silver and chloride was effected with the use of a nephelometer. Precipitation was carried out with the solutions at room temperature or with the chloride solution slightly warm. In all except Analysis 7 the chloride solution was about 0.03 normal and the silver solution 0.05 normal during precipitation. In Analysis 7 the concentrations were about one-half as large. Ordinarily the silver solution was added to the chloride solution, but in Analyses 6 and 12 the reverse method of precipitation was used. The final adjustment of the end-point was effected only after an analysis had stood for several months. After the first few weeks there was ordinarily no drift of the end-point, several of the analyses showing no change over a period of six months. In Analysis 3

VACUUM CORRECTIONS APPLIED

	Density	Vac. corr. per g.
Air	0.00120	
Weights	8.3	
TlCl	7.0	+0.000026
Ag	10.49	−0.000031

THE ATOMIC WEIGHT OF THALLIUM

TlCl:Ag

Ag = 107.880 Cl = 35.457

No.	Sample of TlCl	TlCl in vacuum, g.	Ag in vacuum, g.	Ag added, g.	Corr. wt. of Ag in vacuum, g.	Ratio TlCl:Ag	At. wt. of Thallium
1	A	6.03004	2.71239	0.00030	2.71269	(2.22290)	(204.349)
2	A	7.16504	3.22260	.00005	3.22265	2.22334	204.397
3	A	7.26645	3.26817	.00015	3.26832	2.22330	204.393
4	B	11.54708	5.19388	−.00031	5.19357	2.22334	204.397
5	B	11.94726	5.37368	−.00010	5.37358	2.22333	204.396
6	B	9.87039	4.43951	−.00020	4.43931	2.22341	204.404
7	B	13.11388	5.89858	−.00040	5.89818	2.22338	204.401
8	C	8.97358	4.03753	−.00117	4.03636	2.22319	204.381
9	C	9.71404	4.36906	−.00008	4.36898	2.22341	204.404
10	C	10.23369	4.60220	.00050	4.60270	2.22341	204.404
11	B	12.79964	5.75631	.00050	5.75681	2.22339	204.402
12	C	9.97133	4.48474	−.00015	4.48459	2.22347	204.411
					Average excluding Analysis 1	2.22336	204.399
					Average excluding Analyses 1–3	2.22337	204.400
					Average of Analyses 2 and 3	2.22332	204.395
					Average of Analyses 4–7 and 11	2.22337	204.400
					Average of Analyses 8–10 and 12	2.22337	204.400

the final fusion atmosphere was pure air. The silver chloride of Analysis 3 after being thoroughly washed was tested spectroscopically and found to be free from all but the merest trace of thallium.

Summary

Samples B and C of thallium chloride, which were undoubtedly the purest, give identical results for the atomic weight of thallium, while the difference between these two samples and Sample A is no larger than the experimental error.

The atomic weight of thallium found in this work, 204.40, confirms very closely the work of Hönigschmid, Birckenbach and Kothe, and Hönigschmid and Striebel, as well as that of Aston.

CAMBRIDGE, MASSACHUSETTS RECEIVED JANUARY 18, 1933
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. IV. The Conductance Minimum and the Formation of Triple Ions Due to the Action of Coulomb Forces[1]

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

I. Introduction

In the first paper[2] of this series, we presented the results of an experimental study of the influence of the dielectric constant of the solvent medium on the conductance of electrolytic solutions. It was shown that the general conductance–concentration curve includes four fairly well-defined regions whose location depends upon the structure of the salt and the properties of the solvent: (1) starting from zero concentration, the conductance initially decreases proportionally to the square root of concentration, in accordance with Onsager's equation; (2) for weaker electrolytes, or for strong electrolytes in solvents of intermediate and low dielectric constant, the conductance begins to fall much more rapidly than corresponds to the coefficient computed on the basis of the interionic attraction theory; (3) an inflection point appears in the conductance curve and, in solvents of sufficiently low dielectric constant, a minimum may eventually appear; (4) and finally, after the minimum, the conductance increases very rapidly as the concentration increases. The stronger the electrolyte or the higher the dielectric constant, the fewer are the number of the above regions which appear in the accessible concentration range. In our second paper[3] we showed that the second region may be accounted for on the basis of an equilibrium between ions and neutral

---

(1) Presented at the Symposium on Electrolytes during the Washington Meeting of the American Chemical Society, March 28, 1933.

(2) Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

(3) Fuoss and Kraus, *ibid.*, **55**, 476 (1933).