

The present work thus completes a connected chain of data, and furnishes striking evidence in favor of the low values for silver and nitrogen which have recently found support in so many other different ways.

It is not without interest also to note that if one chooses the value for silver, 107.93, and for chlorine, 35.473, the present work makes nitrogen 14.017—a value inconsistent with the value 14.037 calculated from silver nitrate, if silver is assumed as 107.93. Thus the present results are incompatible with the work of Stas, both as regards silver and as regards nitrogen.

### Summary.

In the present paper is described a series of analyses of ammonium chloride. These analyses were superior to any other that have ever been made in respect, first, to the purity of the material; second, to the choice of conditions for subliming the salt; and third, to the accuracy of the analyses. The ammonium salt was prepared in such a way as to render the presence of amines very unlikely; the sublimation was conducted first in a current of ammonia, and then the same substance was resublimed in a vacuum; the analysis was carried out with all the care used in the recent work in Harvard University, taking due account of the solubility of silver chloride. As a result, it was found that if oxygen is taken as 16.000 and hydrogen as 1.0076, the three following values result: Ag = 107.881, Cl = 35.457, and N = 14.008.

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## THE ATOMIC WEIGHT OF TELLURIUM.

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The atomic weight of tellurium has received an unusual amount of study ever since attention was directed to it by the statement of Mendeleef in his memorable paper before the Russian Chemical Society in 1869. In outlining the principles of the periodicity of the elements he observed that "The atomic weight of tellurium must be between 123 and 126 and cannot be 128."

Various lines of experimentation have been followed to test the validity of this assertion: (a) Critical studies have been on the elementary character of tellurium but nothing thus far has developed which would warrant a belief in its complexity from the character of the experimental evidence produced. (b) The spark spectrum of the element has been studied, especially by Köthner<sup>1</sup> who purified his material by various processes, and who used tellurium from various sources. His results show no differences in the spectrum. (c) Numerous atomic weight

<sup>1</sup> *Ann.*, 319, 1.

determinations have been published from time to time with tellurium from various sources, but the results of all the experiments seem to indicate that the figure is higher than that of iodine.

It is the purpose of this paper to describe a series of atomic weight determinations made with three specimens of tellurium from widely different sources and by the use of a method different in principle from any previously used with tellurium.

The salt chosen for the work has been the double bromide of tellurium and potassium,  $K_2TeBr_6$ , a salt readily obtained in a high degree of purity and one of the most strongly crystalline derivatives of tellurium. This salt when heated in a current of chlorine is converted into potassium chloride, tellurium tetrachloride and bromine. The latter two substances, being volatile, are driven off and the last trace of tellurium can be expelled from the potassium chloride by heating in a current of hydrochloric acid gas. In this method potassium tellurium bromide is originally weighed and later potassium chloride. It is thus possible to obtain a tellurium figure through the ratios of bromine, chlorine and potassium and to eliminate the possibility of an error in the weighing of tellurium, which may contain oxygen when precipitated from solution and dried. It also does not require the formation of insoluble silver bromide by double decomposition with this salt, a reaction to be avoided if possible inasmuch as the tellurous acid formed by dissolving the salt in water tends to form insoluble silver tellurite which would contaminate to a greater or less extent the silver bromide formed. By this method of weighing potassium tellurium bromide and subsequently weighing potassium chloride any question of the ratio of tellurium and oxygen would be removed.

*Preparation of Material. Tellurium from Colorado.*—Through the courtesy of Professor C. W. Stoddart, a quantity of tellurium gold ore was obtained from the Clarissa Tunnel, Boulder County, Colorado. The ore is graphic tellurium containing about three per cent. of gold and a little silver in a vein rock of quartz.

The ore was extracted with hot nitrohydrochloric acid, the extract was converted into hydrochloric acid solution free from nitric by repeated evaporation with hydrochloric acid, after which sodium acid sulphite was added and the impure tellurium precipitated. The dried precipitate was fused with potassium cyanide in order to separate the heavy metals and to allow of the separation of the sulphur and selenium from the tellurium. After extraction with water and filtration from the gold and other heavy metals, a current of air was passed through the solution and the tellurium precipitated, the sulphur and selenium remaining in the cyanide solution. One hundred grams of tellurium thus obtained were precipitated from the chloride solution by means of sulphur dioxide gas,

after which it was converted into basic nitrate. The recrystallized basic nitrate was converted by ignition into the oxide.

*Tellurium from Bohemia.*—50 grams of tellurium from the Transylvania gold ores were precipitated by sulphur dioxide from hydrochloric acid solution, fused with potassium cyanide to remove sulphur, selenium and any heavy metals; again precipitated from chloride solution by sulphur dioxide. It was then transformed into the basic nitrate, which was recrystallized and ignited to oxide.

*Tellurium from Copper Ores.*—A quantity of tellurium residues from the electrolytic tanks of the Baltimore Copper Smelting and Rolling Co. was treated in alkaline solution with grape sugar. The tellurium obtained was purified by precipitation from chloride solution by means of sulphur dioxide; this product was fused with potassium cyanide to separate it from sulphur, selenium and the heavy metals, twice distilled in hydrogen and after recrystallization as basic nitrate was converted to oxide.

*Potassium Bromide.*—The potassium used was prepared from Kahlbaum's pure material. It was repeatedly crystallized and in each crystallization the first portions and last portion were rejected.

*Hydrobromic Acid.*—The acid used was prepared from potassium bromide and sulphuric acid, the small amount of bromine formed being removed by means of phosphorus and the resulting colorless acid repeatedly distilled.

*Preparation of the Double Bromide of Tellurium and Potassium.*—The tellurium oxide was dissolved in hydrobromic acid and the molecular proportion of potassium bromide added. The bright red anhydrous salt was crystallized from boiling solution, redissolved in pure water containing a small quantity of hydrobromic acid and repeatedly crystallized from boiling solution.

In order to remove the last traces of moisture and hydrobromic acid, the salt was finely powdered and dried in vacuum desiccators over soda lime for a period of eight months. Tests made showed that the salt prepared in this manner is anhydrous.

*Procedure.*—The double bromide was weighed into a porcelain boat. The boat was covered with a loosely fitting piece of glass and placed in a tube of Jena glass. A current of chlorine was passed through the tube and heat was applied immediately below the boat. A low temperature was maintained for a short time, after which the temperature was gradually raised. After conducting a brisk current of chlorine over the salt for an hour, the chlorine was replaced by hydrochloric acid gas and the boat and the salt heated for an hour longer. Treatment of the material with hydrochloric acid gas is essential after the treatment with chlorine. Small amounts of tellurium oxide are produced in the potassium chloride by the action of the oxygen of the air remaining in the tube on the tellu-

rium chloride first formed by the action of the chlorine on the original salt. It is impossible to volatilize this oxide from the resulting potassium chloride by heating in chlorine alone but with hydrochloric acid gas,  $\text{TeO}_2 \cdot 2\text{HCl}$  is formed with the oxide and is driven out of the boat. That any oxychloride is formed by heating tellurium tetrachloride in air or oxygen is highly improbable, and its doubtful existence will be shown in another place.

All weighings were made on a balance constructed by Troemner, having a capacity of two hundred grams and a sensibility with a minimum load of one fifty-fifth of a milligram. All weighings are reduced to zero and vacuum. The slight change in weight of the porcelain boats used was constantly watched and corrections duly made. The following atomic weights were used: (1) Bromine, 79.96; chlorine, 35.45; potassium, 39.11. (2) The revised weights of the atomic weight commission for 1909: chlorine, 35.46; bromine, 79.92; potassium, 39.095.

## SERIES I.—TELLURIUM FROM BOHEMIA.

	Wt. $\text{K}_2\text{TeBr}_6$ .	Wt. $\text{KCl}$ .	At. wt. $\text{Te}$ .	
			(1)	(2)
1.....	2.33360	0.50779	127.31	127.54
2.....	1.27372	0.27716	127.32	127.54
3.....	1.47573	0.32111	127.33	127.56
4.....	1.65715	0.36059	127.33	127.55
5.....	1.54006	0.33513	127.29	127.51
Mean.....			127.32	127.54

## SERIES II.—TELLURIUM FROM COPPER ORES.

	Wt. $\text{K}_2\text{TeBr}_6$ .	Wt. $\text{KCl}$ .	At. wt. $\text{Te}$ .	
			(1)	(2)
6.....	1.82810	0.39778	127.34	127.56
7.....	1.87342	0.40765	127.33	127.55
8.....	1.48045	0.32214	127.33	127.55
9.....	2.24775	0.48911	127.31	127.54
Mean.....			127.33	127.55

## SERIES III.—TELLURIUM FROM COLORADO.

	Wt. $\text{K}_2\text{TeBr}_6$ .	Wt. $\text{KCl}$ .	At. wt. $\text{Te}$ .	
			(1)	(2)
10.....	2.37899	0.51767	127.31	127.54
11.....	1.79926	0.39146	127.41	127.64
12.....	0.94102	0.20476	127.33	127.56
13.....	1.55357	0.33806	127.31	127.54
14.....	1.95038	0.42440	127.31	127.54
15.....	1.73248	0.37698	127.33	127.55
16.....	1.81923	0.39586	127.32	127.55
Mean.....			127.33	127.55
Mean of the three series			127.33	127.55

It will be observed that the atomic weight of tellurium as given by use of 1909 figures for chlorine, bromine and potassium appears as 127.55, which figure the author considers to be very close to the true ratio for tellurium.

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## THE REACTION BETWEEN FUSED POTASSIUM NITRATE AND TELLURIUM DIOXIDE.

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In the preparation of telluric acid by the fusion of tellurium dioxide with potassium nitrate, there are two distinct stages: First, the transformation of the white dioxide into a yellow or brown substance which swims undissolved in the fused mass; second, the solution of this brown material in the fusion and its complete transformation to alkaline tellurate.

Berzelius<sup>1</sup> has assumed this yellow substance to be a tetratellurate and describes it as insoluble in water, acids and alkalies. In the recent work of Baker and Bennet<sup>2</sup> this same substance is described as a tetratellurate.

In preparing telluric acid by the fusion process in our laboratory this brown substance has been repeatedly observed. By examination with the microscope and by use of polarized light it appears homogeneous. It may be formed by heating potassium nitrate to 390°–400°, the temperature at which oxygen is evolved from the fused salt, and adding finely powdered tellurium dioxide in small portions. The dioxide first turns yellow, then brown, and finally red-brown, all the while remaining undissolved. During these color changes considerable effervescence and loss of the oxides of nitrogen ensues. When the mass is allowed to cool, the substance appears yellow-brown. If, however, the process of heating be continued, the brown substance is further oxidized by the fused nitrate and the tellurium is completely converted into normal tellurate.

The brown substance appears, therefore, to be an intermediate product between tellurium dioxide and potassium tellurate.

Its composition is dependent upon the length of time of heating and on the quantities of nitrate and dioxide used. A series of intermediate products have been obtained by extracting such fusions with boiling water until no more soluble matter is removed, and analyzing the resulting substance.

*Analysis.*—In order to arrive at the composition of the brown material, the potassium content was determined by heating a weighed portion in a porcelain boat in a combustion tube in a current of hydrochloric acid gas and weighing the potassium chloride. The tellurium existing in the

<sup>1</sup> *Pogg. Ann.*, 28, 460. *Ibid.*, 32, 584.

<sup>2</sup> *J. Chem. Soc.*, 91, 1849.