

ART. LVIII.—*On Thallium Triiodide and its Relation to the Alkali-Metal Triiodides*; by H. L. WELLS and S. L. PENFIELD.

THE well-known resemblance between the thalious salts and many of the corresponding alkali-metal salts has led us to prepare thallium triiodide and to compare its crystalline form with that of the alkali-metal triiodides.* As a result, it has been found that TII_3 agrees, with remarkable closeness, in form with RbI_3 and CsI_3 , and thus a case of isomorphism is established between the higher iodides of thallium and the alkali-metals.

This isomorphism is of special interest because our study of the trihalogen compounds of caesium has led us to the conclusion that these have the structure of double-salts. We consider the evidence of this double-salt structure as very strong, and since it seems necessary to infer that isomorphism indicates the same arrangement of the atoms, we are obliged, in spite of the apparent trivalence of thallium in thallic compounds, to conclude that TII_3 is also a double-salt, to which the formula $\text{TII} \cdot \text{I}_2$ should be given. It is not safe to assert at present that all thallic salts must be similarly constituted, for it is possible that thallium triiodide is not a true thallic compound at all, and that thallic sulphate, nitrate, etc., have an entirely different kind of structure. If it is granted that

* This Journal, III, xliii, 17 and 475.

thallium triiodide is a double-salt, it seems probable that many other compounds, which are considered as showing higher valence of elements, may in reality have the structure of double-salts or "addition products."

Thallium triiodide was first described by Nicklès* who prepared it by evaporating an ethereal solution of thallos iodide and iodine. Nicklès states that he did not obtain it in a pure condition, but that his product always contained an excess of iodine. He described its crystalline form, and his results will be mentioned beyond.

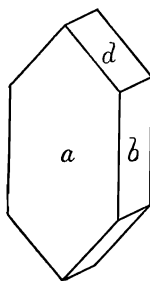
We have modified Nicklès' method by using alcohol as a solvent and have encountered no difficulty in obtaining a pure product. The amount of iodine used was slightly in excess of the calculated quantity, and the solution, produced after long digestion, was evaporated over sulphuric acid until crystallization took place. The resulting crystals were frequently of large size, perfectly black with a magnificent luster which was slowly lost upon exposure. A sample of the salt, simply pressed upon paper, gave the following results upon analysis:

	Found.	Calculated for TlI_3 .
Thallium	34.22	34.87
Iodine	64.80	65.13

An examination of the crystals has shown that they are orthorhombic and isomorphous with the orthorhombic alkali-metal trihalides. Moreover, all the forms which have been observed have also been found on the alkali-metal salts, and are as follows:

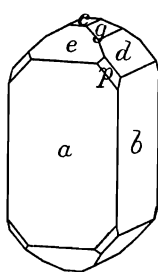
$$\begin{array}{l} a, 100, i\bar{i} \\ b, 010, i\bar{i} \end{array}$$

1.



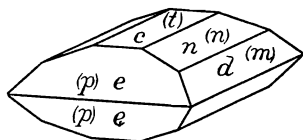
$$\begin{array}{l} c, 001, o \\ g, 012, \frac{1}{2}i\bar{i} \end{array}$$

2.



$$\begin{array}{l} d, 011, 1\bar{i} \\ e, 102, \frac{1}{2}i\bar{i} \end{array}$$

3.



The habit is shown in figures 1 and 2, the latter being remarkably like that of CsI_3 when this had been crystallized

* J. Pharm. [4], 1, 25.

from alcohol. The measurements which were chosen as fundamental are $d \wedge \bar{d}$, $011 \wedge 0\bar{1}1 = 96^\circ 34'$ and $e \wedge \bar{e}$, $102 \wedge \bar{1}02 = 78^\circ 48'$ giving the axial ratio:

$$\bar{a} : \bar{b} : \bar{c} = 0.6828 : 1 : 1.1217$$

The dome g was determined by the measurement $g \wedge g$, $012 \wedge 0\bar{1}2 = 58^\circ 34'$, calculated $58^\circ 34'$ and the pyramid p by its position in the zones $a-d$ and $\bar{d}-e$.

A description of this salt, including a figure, has been given by Nicklès. His salt, crystallized from ether, had the habit shown in fig. 3, the letters in brackets being those used by him and the position being changed to correspond with the orientation of the alkali metal trihalides. He considered p as a prism, t as a macropinacoid and m and n as brachydomes. No calculations are given and only the following four measurements:

Nicklès.	Measured.	Calculated from author's measurement.
$p \wedge p = 100^\circ 15'$,		$101^\circ 12'$ for $e \wedge \bar{e}$, $102 \wedge 10\bar{2}$
$p \wedge t = 39^\circ 22'$,		$39^\circ 24'$ " $e \wedge \bar{c}$, $102 \wedge 001$
$p \wedge m = 61^\circ$,		$59^\circ 3'$ " $e \wedge \bar{d}$, $102 \wedge 011$
$n \wedge t = 19^\circ 25'$,		$20^\circ 30'$ " $013 \wedge 001$

The agreement between the measured and calculated angles is not very close, but Nicklès' measurements cannot be very exact, for if we take $p \wedge t = 39^\circ 22'$ and $n \wedge t = 19^\circ 25'$ as fundamental, we find by calculation $p \wedge p = 101^\circ 16'$ and $p \wedge m = 57^\circ 55'$, which vary considerably from his measurements. Nicklès crystals differ from ours not only in habit but in having the one-third brachydome n , 013, which has not been observed either in the ThI_3 , prepared from alcohol or on any of the alkali-metal trihalides prepared by us.

The very close agreement between the forms of rubidium, caesium and thallium triiodides is to be seen from the following table of axial ratios:

RbI_3	$\bar{a} : \bar{b} : \bar{c} = 0.6858 : 1 : 1.1234$
CsI_3	" " " = $0.6824 : 1 : 1.1051$
ThI_3	" " " = $0.6828 : 1 : 1.1217$

Our previous observation, that the exchange of one metal for another in the trihalogen compounds usually has little or no effect upon the crystalline form, is strongly confirmed by these ratios, and the remarkable agreement between the rubidium triiodide and the thallium compound is very striking when the great difference between the atomic weights of the two metals is considered.

It was hoped that a pentaiodide of thallium could be prepared in order that its form might be compared with that of

cæsium pentaiodide, but by the use of increasing proportions of iodine with thallium triiodide in alcoholic solutions no evidence of the existence of such a compound could be obtained.

The remarkably close relations of thallium to the alkali-metals as far as the thallous compounds are concerned, and the additional resemblance which has been pointed out in the present communication, have led us to consider the possibility that thallium has been wrongly placed in the periodic system of the elements and that it really belongs to the alkali-metals. There are two vacancies in Mendeléeff's table in the alkali-metal group corresponding to atomic weights of about 170 and 220. One of these is smaller, the other larger than the accepted atomic weight of thallium, so that, as far as these numbers are concerned thallium might be composed of two alkali-metal elements. Although the probability that thallium was composed of two elements seemed very slight from other considerations, we have deemed it desirable to test the question experimentally.

About 200 grms. of thallium were converted into the nitrate and this was systematically fractionated by crystallization until about one-twentieth of the salt remained as a repeatedly re-crystallized portion and about another twentieth was contained in a final mother-liquor. From each of these two fractions thallous chloride was prepared by converting into sulphate, precipitating impurities with hydrogen sulphide, and finally precipitating thallous chloride by means of hydrochloric acid. The preparations were carefully washed, dried at 100°, and the chlorine was determined as silver chloride in order to get the atomic weight of the metal in each fraction. The silver chloride was weighed in the Gooch crucible, a method which can be most highly recommended for accurately weighing this substance. The following results were obtained, the weights being given as taken in air.

	Crystallized End.	Soluble End.
TlCl taken	3.9146 g.	3.3415 g.
AgCl obtained	2.3393	1.9968
Atomic weight of Tl, ($O = 16$),	204.5	204.5

It was not expected that absolute accuracy in the atomic weight of thallium would be attained, but since the same method of purification and analysis was used in both cases the two results are comparable with each other, and their exact agreement shows that the fractionation of the nitrate gives no change in the atomic weight of thallium, and no evidence has been obtained that thallium is not homogeneous.

Sheffield Scientific School, New Haven, Conn., January, 1894.