ART. XXIX.—*On the Cæsium-Mercuric Halides*; by H. L.
WELLS.

It is to be expected that more complete series of double-halides can be made with cæsium than with the other alkali-metals, because it is the extreme member of the potassium group and the most electro-positive element known, and because cæsium double-salts in general are less soluble than the corresponding compounds of the other alkali-metals. A thorough

study of these compounds seems desirable since very little work has been done in this direction, and therefore the present investigation of the cæsium-mercuric chlorides, bromides and iodides has been undertaken.

The following is a complete list of the previously described mercuric double-halides containing the alkali-metals and ammonium, as far as I have been able to find them :

Na_2HgCl_4	NH_4HgCl_3	RbHg_2Cl_5
Rb_2HgCl_4	RbHgCl_3	$\text{KHg}_2\text{Cl}_5 \cdot 2\text{H}_2\text{O}$
Cs_2HgCl_4	KHgBr_3	
$(\text{NH}_4)_2\text{HgBr}_4$	$\text{NH}_4\text{HgCl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	
K_2HgBr_4	$\text{KHgCl}_3 \cdot \text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Hg}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}$
Na_2HgI_4	$\text{KHgBr}_3 \cdot \text{H}_2\text{O}$	
K_2HgI_4	$\text{NaHgCl}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	
$(\text{NH}_4)_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$	$\text{NH}_4\text{HgI}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Hg}_3\text{Cl}_{10}$
$\text{K}_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$	$\text{KHgI}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	
$\text{Rb}_2\text{HgCl}_4 \cdot 2\text{H}_2\text{O}$		
$(\text{NH}_4)_2\text{HgI}_4 \cdot 3\text{H}_2\text{O}$		

The greater number of these arrange themselves into two types with varying water of crystallization or with none. There are two compounds of a third type, while the two remaining, more complicated salts, stand alone. The last two were described by Holmes.*

An effort has been made to make the examination of the cæsium-mercuric salts very complete, but it is not safe to say that every possible compound has been prepared, for negative results are uncertain. It will not be necessary to describe the unsuccessful experiments where mixtures or uncertain products were obtained. It is sufficient to say that other double-halides were repeatedly looked for in every direction, and every indication of a new salt was followed up until a homogeneous product was obtained and analyzed.

The following table gives a list of the salts that are to be described. One of them, Cs_2HgCl_4 , has already been prepared by Godeffroy.†

I.	II.	III.
Cs_2HgCl_5	Cs_2HgCl_4	$\text{CsHgCl}_3\ddagger$
Cs_3HgBr_5	Cs_2HgBr_4	$\text{CsHgBr}_3\ddagger$
Cs_3HgI_5	Cs_2HgI_4	CsHgI_3
$\text{Cs}_2\text{HgCl}_3\text{Br}_2$	$\text{Cs}_2\text{HgCl}_2\text{Br}_2$	$\text{CsHgClBr}_2\ddagger$
$\text{Cs}_3\text{HgBr}_3\text{I}_2$	$\text{Cs}_2\text{HgBr}_3\text{I}_2\ddagger$	CsHgBrI_2
	$\text{Cs}_2\text{HgCl}_2\text{I}_2$	
IV.	V.	VI.
	CsHg_2Cl_5	$\text{CsHg}_2\text{Cl}_{11}$
$\text{Cs}_2\text{Hg}_3\text{I}_8$	CsHg_2Br_5	
	CsHg_2I_5	
	$\text{CsHg}_2\text{ClBr}_4$	$\text{CsHg}_3\text{ClBr}_{10}$

* Chem. News, v, 351.

† These compounds are dimorphous.

† Berichte, viii, 9.

These salts confirm the composition of all the previously known alkaline-mercuric halides, as given in the preceding table, except the single compound $(\text{NH}_4)_2\text{Hg}_5\text{Cl}_{20}$. It is extremely probable, however, that the correct formula for this is $\text{NH}_4\text{Hg}_5\text{Cl}_{11}$, for Holmes obtained results slightly lower than his theory in his ammonium determinations, and it would be scarcely possible to distinguish between the two formulas by analysis, as will be seen from the following numbers:

	Calculated for $(\text{NH}_4)_2\text{Hg}_5\text{Cl}_{20}$.	Calculated for $\text{NH}_4\text{Hg}_5\text{Cl}_{11}$.	Differences.
Mercury.....	70.70	71.00	0.30
Ammonium.....	1.41	1.27	0.14

The differences between the amounts of mercury and cæsium for the corresponding formulas are 0.80 and 0.85, so that it is evident that the cæsium compound furnishes a far better means of determining the composition of the salts.

The first type, Cs_2HgHl_6 , is a new one. These compounds are interesting as exceptions to Remsen's law concerning the composition of double-halides.*

The salt $\text{Cs}_2\text{Hg}_3\text{I}_8$, although standing alone among the cæsium compounds, is a very well characterized body; and the compound $(\text{NH}_4)_2\text{Hg}_5\text{Cl}_8 \cdot 4\text{H}_2\text{O}$, made by Holmes, belongs to the same type.

The results of the work on the cæsium-mercuric salts fulfill the expectations concerning the value of cæsium as a means of studying alkaline double-halides, for all the previously discovered types have been made with this metal, and one besides that had never been discovered.

Preparation.

The compounds were made by dissolving mercuric halides in hot solutions of cæsium halides and cooling, or in some cases evaporating at ordinary temperatures, to crystallization. The relative amounts of the two halides and the dilution both have an important influence in determining the salt produced. In most cases dilution with water is equivalent to the addition of mercury, while concentration produces the same effect as the addition of a cæsium halide. It has been noticed, where more than one salt is deposited from a solution by cooling, that the salts with more mercuric halides are formed first. This shows that cooling a solution may be equivalent to the addition of cæsium.

There are only a few of the salts that can be recrystallized unchanged from water, most of them requiring the presence of an excess of cæsium halide, or in two or three cases mercuric

* Am. Chem. Jour., xi, 296; xiv, 85.

halide, for their formation. Crystallization from water can therefore often be used for preparing one salt from another.

All the compounds were made with solutions of the normal salts without the use of acids. Some of them have been made with alcoholic solutions, but this solvent has not been found to possess any advantages except for preparing CsHg_2I_2 .

Analytical Methods.

The salts were always carefully examined to be sure that they were not mixtures. Many mixed crops of crystals were obtained, but I am confident that the products analyzed were pure. The crystals for analysis were always quickly and thoroughly freed from the mother-liquor by pressing repeatedly between smooth filter-papers, and, at the same time, they were crushed to remove included liquid. During this drying process the substances were exposed to the air as little as possible to avoid any evaporation of the adhering liquid before its removal. After the products had been dried as thoroughly as possible in this way, they were usually exposed to the air for an hour or two to remove the last traces of moisture, but this was not done in a few cases where I wished to be certain that no easily-lost water of crystallization was present.

Portions of about one gram of substance were usually taken for analysis. In no case was the analysis hampered from lack of material. The chlorides and bromides were readily dissolved in water, but it was necessary in analyzing the iodine compounds to dissolve them in water containing alcohol. Mercury was invariably determined as sulphide, the precipitate being collected, dried at 100° and weighed on an asbestos filter in a Gooch crucible. Cæsium was usually determined in the filtrate from the mercuric sulphide and was always weighed as sulphate. In this operation the excess of sulphuric acid was removed by ignition in a current of air containing ammonia, as suggested by Krüss for potassium sulphate. In some cases where cæsium alone was to be determined, the substance was weighed out directly into a platinum crucible, sulphuric acid was added, the excess of this and the mercury were removed by evaporation and heating and normal cæsium sulphate was weighed. The halogens were invariably determined in separate portions and were weighed as silver salts. In the cases where two were present, they were determined by heating the mixed silver halides to constant weight in chlorine.

The Double-chlorides.

These are all white in color and are permanent when exposed to the air. On recrystallizing from water all of them finally yield CsHgCl_2 .

Cs_2HgCl_6 is made by dissolving a comparatively small quantity of mercuric chloride in a nearly saturated cæsium chloride solution. It is deposited on cooling, but the best crystals are obtained by spontaneous evaporation. If too much of the mercuric compound is added or if too much water is present, other double salts or mixed products will be obtained. On the other hand, if too little mercuric chloride is present, cæsium chloride crystallizes out. The limits of the conditions under which it is formed are narrow, but by repeated trials, with slight variations suggested by previous results, a pure product is readily obtained. It forms slender, radiating prisms which are easily distinguished from the compounds with which it is liable to be mixed.

The following analysis was made of a sample which was rapidly dried on paper, but not air-dried. The small amount of water found was probably simply moisture. It was determined by direct weighing in a calcium-chloride tube.

	Found.	Calculated for Cs_2HgCl_6 .
Cæsium	51.15	51.38
Mercury	24.84	25.76
Chlorine	21.79	22.86
Water	1.69	0.00
	<hr/> 99.47	<hr/> 100.00

Cs_2HgCl_4 is produced, by cooling a hot solution, when a little more mercuric chloride or water is used than in the case of the last salt. The conditions for its formation are narrow. It forms large but usually very thin plates which are readily distinguished from the other double-chlorides. A sample was dried on paper for analysis.

	Found.	Calculated for Cs_2HgCl_4 .
Cæsium	44.06	43.75
Mercury	----	32.90
Chlorine	22.87	23.35
Water	0.52	0.00
		<hr/> 100.00

$CsHgCl_3$ is dimorphous, forming, according to circumstances, cubic or orthorhombic crystals. The cubic form is produced, under widely varying conditions by cooling dilute aqueous solutions, when cæsium chloride is considerably in excess. The orthorhombic form is deposited when cæsium chloride is not in great excess and by one or more recrystal-

lizations from water of all the double chlorides. This form can be recrystallized from water indefinitely.

The compound is practically insoluble in absolute alcohol, but it dissolves in alcohol diluted with about one-third of its volume of water, and it is remarkable that the *cubic form* is deposited from such a solution on cooling.

The cubes often form peculiar aggregates, apparently of a pyramidal shape. The orthorhombic crystals are very brilliant and highly modified, usually forming groups of spear-shaped individuals joined end to end.

Three samples were analyzed; A, cubes simply dried on paper; B, cubes from alcohol; C, orthorhombic crystals, air-dry.

	A	Found. B	C	Calculated for CsHgCl_3
Cæsium.....	30.29	30.26	29.92	30.26
Mercury	44.80		45.63	45.51
Chlorine	28.40		24.03	24.23
Water.....	1.42			0.00
	<hr/> 99.91		<hr/> 99.58	<hr/> 100.00

Since the orthorhombic form of this compound is not decomposed by water its solubility could be determined. This was done by analyzing the mother-liquor from a third recrystallization at about 17° . Of this solution, 100 parts contained 0.4255 parts of cæsium, corresponding to 1.406 parts of CsHgCl_3 .

CsHg_2Cl_5 was made by dissolving 24 g. of CsHgCl_3 and 16 g. of HgCl_2 (a little more than one molecule of the latter) in about 150 c. c. of hot water and cooling. A large crop of needles was obtained which were undoubtedly homogeneous.

	Analysis gave.	Calculated for CsHg_2Cl_5
Cæsium.....	18.13	18.72
Mercury.....	56.32	56.30
Chlorine.....	24.68	24.98
	<hr/> 99.13	<hr/> 100.00

The salt is not very readily decomposed by water, but by repeated recrystallization the orthorhombic form of CsHgCl_3 is obtained.

$\text{CsHg}_6\text{Cl}_{11}$ was prepared by making a nearly saturated solution of 12.5 g. of HgCsCl_3 and 38.5 g. of HgCl_2 (about one molecule of CsCl to six of HgCl_2) in boiling water and cooling. The compound was obtained in prisms, so well formed

that there was no doubt about their homogeneity. Two crops were analyzed.

	Found.		Calculated for $\text{CsHg}_2\text{Cl}_{11}$.
Cæsium	8.68	8.51	8.73
Mercury	65.59	----	65.64
Chlorine	24.97	----	25.63
	<hr/> 99.24		<hr/> 100.00

A single recrystallization of this salt from water gave a mixed crop of crystals and this, on repeating the operation, gave CsHg_2Cl_5 still containing a little of the original compound. This last crop was analyzed.

	Found.	Calculated for CsHg_2Cl_5 .
Cæsium	15.57	18.72

The Double Bromides.

All of these salts are white, or nearly so, except CsHgBr_4 , which has a lemon-yellow color. This color is remarkable since CsBr and HgBr_2 are both pure white.

All of the double bromides yield CsHg_2Br_6 on recrystallizing them one or more times from water. It is to be noticed that this salt belongs to a different type from the double-chloride which is stable with water, but if alcohol is used for recrystallizing this bromide, the salt corresponding to the chloride just mentioned is deposited.

Cs_2HgBr_6 .—The preparation of this salt is exactly analogous to that of the corresponding chloride, and it has the same appearance.

	Found.	Calculated for Cs_2HgBr_6 .
Cæsium	39.83	39.94
Mercury	19.50	20.02
Bromine	39.60	40.04
	<hr/> 98.93	<hr/> 100.00

Cs_2HgBr_4 is prepared similarly to the chloride, but the limits of the conditions under which it is formed are much wider. Like the chloride it usually forms very thin plates, but they can sometimes be produced of sufficient thickness for measurement. Three separate crops, made under considerably different conditions were analyzed.

	Found			Calculated for Cs_2HgBr_4 .
Cæsium	33·84	34·43	33·69	33·84
Mercury	25·68	25·11	25·45	25·45
Bromine	40·48	40·40	40·52	40·71
	100·00	99·94	99·66	100·00

CsHgBr_3 .—This compound is dimorphous, but while one form is cubic, like one of the chlorides, the other is monoclinic and has no apparent relation to the orthorhombic chloride. Just as in the case of the chlorides, the cubic form is produced when an excess of the cæsium halide is present, while the second form is deposited when this excess is not as great. Unlike the corresponding chloride, the second form of the bromide is decomposed by recrystallization from water, the salt CsHg_2Br_6 being formed, but, as will be noticed beyond, the opposite transformation can be produced by recrystallizing the last mentioned salt from alcohol. The limits of formation of the cubic salt are wide, but it is difficult to produce the other form in a pure state, and it is possible that the monoclinic crystals analyzed were mixed with a small quantity of the cubes.

	Found		Calculated for CsHgBr_3 .
	Cubic.	Monoclinic.	
Cæsium	23·18	22·89	23·21
Mercury	34·95	35·54	34·90
Bromine	41·70	41·63	41·89
	99·83	100·06	100·00

CsHg_2Br_6 .—The recrystallization of any of the other double-bromides from water produces this salt, and it can be recrystallized indefinitely without decomposition. It forms very small, thin plates which have a very faint tinge of yellow. By spontaneous evaporation of a mother-liquor from a recrystallization of this salt somewhat larger crystals were formed. Three separate crops were analyzed.

	Found.		Calculated for CsHg_2Br_6 .
Cæsium	14·60	14·69	14·26
Mercury ...	42·71	----	42·87
Bromine ...	42·55	----	42·87
	99·86		100·00

The mother-liquor from a third recrystallization from water at about 16° was found to contain 0·1151 per cent of cæsium, corresponding to solubility of 0·807 parts of CsHg_2Br_6 in 100

parts of the solution. The salt dissolves rather sparingly in hot, strong alcohol and, on cooling this solution, the compound CsHgBr_3 separates out.

	Found.	Calculated for CsHgBr_3 .
Cæsium	22.68	23.21

The crystals thus obtained were not large enough to measure, but it was probable, from microscopic examination, that they were the monoclinic form of this compound. This is interesting from the fact that it is the cubic form of CsHgCl_3 , which crystallizes from alcoholic solutions.

No satisfactory crops of crystals were obtained from solutions made with CsHg_2Cl_6 and HgBr_2 together.

The Double Iodides.

These salts are all yellow, CsHg_2I_6 and $\text{Cs}_2\text{Hg}_2\text{I}_6$ having a color nearly like that of normal potassium chromate, while the others become paler as the cæsium chloride increases. All of them are decomposed by water, forming compounds containing more mercuric iodide than the original salt, or, at last, mercuric iodide itself. It is therefore possible to take any one of these double-salts, and, by recrystallizing from water and evaporating the resulting solutions, to prepare the complete series of five double-iodides, as well as the component simple iodides, without the use of any new material. It is noticeable that the iodides differ from the chlorides and bromides in not including a salt that can be recrystallized continually from water. This peculiarity is doubtless due to the comparative insolubility of mercuric iodide. In most cases, the analyses of the salts containing iodine show an excess of mercury and a deficiency of the halogen (or halogens). It is not known whether this was due to some impurity in the salts or to analytical errors. It is not considered probable that inaccuracies in the analyses could have caused so much variation from theory, for the methods used were the same as for the chlorides and bromides, except that alcohol was used as a solvent, and, while halogens and mercury were always determined in separate portions, the summations of the analyses were usually satisfactory.

Cs_2HgI_6 .—This salt, like the corresponding chloride and bromide, requires for its preparation a very concentrated solution of the cæsium halide containing a relatively small amount of the mercuric compound. It crystallizes well and may be obtained either by cooling or spontaneous evaporation. The crystals form peculiar, steep pyramids.

	Found.	Calculated for Cs_3HgI_6 .
Cæsium	33.02	32.33
Mercury	16.33	16.21
Iodine	50.42	51.46
	<hr/> 99.77	<hr/> 100.00

Its specific gravity taken in benzol was found to be 4.605.

When this salt is dissolved in a small quantity of hot water the compound Cs_2HgI_4 crystallizes out on cooling, but with a larger quantity of water everything remains in solution.

Cs_2HgI_4 .—This salt is produced under wide limits of conditions by cooling solutions of the component salts when cæsium iodide is in excess. The monoclinic crystals vary in habit, forming long prisms, nearly square plates or intermediate forms. They are often obtained of very large size, sometimes extending completely across the bottom of the vessel containing the solution and turning upwards at the ends besides.

	Found.		Calculated for Cs_2HgI_4 .
Cæsium	27.32	27.39	27.31
Mercury	21.57	21.21	20.53
Iodine	51.41	51.49	52.16
	<hr/> 100.30	<hr/> 100.09	<hr/> 100.00

Two determinations of the specific gravity, taken in benzol, gave the numbers 4.799 and 4.812.

The salt is decomposed by water, giving, according to the quantity used, either one of the salts containing more mercuric iodide or mercuric iodide itself. It is not dissolved or decomposed by alcohol.

CsHgI_3 (H_2O ?).—This salt is formed only within very narrow limits from solutions containing a little more mercuric iodide or water than those from which the preceding salt is obtained. These conditions are perhaps most easily reached by dissolving the last salt in a small amount of hot water and cooling. It often happens that the three salts $\text{Cs}_2\text{Hg}_3\text{I}_8$, CsHgI_3 and Cs_2HgI_4 are successively deposited as a solution cools, and it is consequently difficult to obtain the salt under consideration in a pure state, but this was accomplished after a great many trials with varying conditions. The compound forms very thin transparent plates which usually radiate from a point and are often of large size. By pressing on paper they rapidly become opaque. Whether this is caused by molecular re arrangement or loss of water of crystallization is not certain, for, on account of the extreme thinness of the crystals, it was

impossible to decide whether a small amount of moisture or a molecule of very unstable water of crystallization was present. Two samples were analyzed. A was air-dried after pressing on paper; B was quickly dried on paper.

	Found. A.	Calculated for CsHgI_3 .	Found. B.	Calculated for $\text{CsHgI}_3 \cdot \text{H}_2\text{O}$.
Cæsium ----	18.81	18.63	18.25	18.17
Mercury ----	29.29	28.01	28.74	27.33
Iodine ----	51.50	53.36	50.98	52.05
Water ----	----	0.00	2.51*	2.45
	<hr/> 99.60	<hr/> 100.00	<hr/> 100.48	<hr/> 100.00

Like all the other iodides, this salt is decomposed by water.

$\text{Cs}_2\text{Hg}_3\text{I}_8$ is formed under widely different conditions. It is most convenient to prepare it by dissolving Cs_2HgI_4 in the proper amount of hot water and cooling. It is also formed, in a finely divided condition, by treating the same salt with not too much cold water. The crystals vary considerably in habit, but they can be readily distinguished from the other iodides. A characteristic form is a triangular plate, but plates of different shape and more or less elongated prisms often occur. The following analyses were made of separate crops. Sample C was made by treating Cs_2HgI_4 with cold water.

	Found.			Calculated for $\text{Cs}_2\text{Hg}_3\text{I}_8$.
	A.	B.	C.	
Cæsium -----	13.89	14.14	14.07	14.13
Mercury -----	33.76	---	33.83	31.88
Iodine -----	52.07	52.10	52.96	53.99
	<hr/> 99.72		<hr/> 100.86	<hr/> 100.00

Specific gravity, taken in benzol, 5.14. The salt dissolves in alcohol. It is decomposed by water with the separation of a part of the mercuric iodide. From the solution thus obtained, the salts containing less mercuric iodide can be prepared by evaporation.

CsHg_2I_6 .—When a hot aqueous solution of cæsium iodide is saturated with mercuric iodide, this compound is formed on cooling, but, under these conditions, the substance is usually mixed with HgI_2 and often with $\text{Cs}_2\text{Hg}_3\text{I}_8$. When weak alcohol is used as a solvent, however, a pure product is obtained without difficulty. It forms slender yellow prisms which become red on standing in an aqueous mother-liquor. They are more permanent in the solution when it is alcoholic, but, on drying them by pressing on paper, they quickly assume the

* By loss at 100°.

red color of of mercuric iodide without losing their form. It is probable that the spontaneous decomposition results in the formation of $\text{Cs}_2\text{Hg}_2\text{I}_8$ and HgI_2 . It was necessary to analyze the material which had become red.

	Found.	Calculated for CsHg_2I_8 .
Cæsium	11.47	11.39
Mercury	35.73	34.25
Iodine	52.93	54.36
	<hr/> 100.13	<hr/> 100.00

The Mixed Double-halides.

A great deal of labor has been devoted to a study of these compounds in order to find to what extent they could be prepared. The results show that cæsium chloride and mercuric bromide unite readily although there is a tendency towards an exchange of halogens and the formation of unmixed salts. It is also noteworthy that, while there is a double chloride as well as a double bromide which is not decomposed by recrystallization from water, all the chloro-bromides finally yield mercuric bromide when so treated.

The number of bromo-iodides is less than that of the unmixed salts, for, when attempts are made to prepare compounds containing the larger amounts of mercuric iodide, there is an exchange of halogens and almost pure double iodides are produced.

Only one compound of mercuric iodide with cæsium chloride could be prepared. This is $\text{Cs}_2\text{HgCl}_2\text{I}_2$, and the type to which it belongs may probably be considered, on this account, the most stable one of the cæsium-mercuric halides.

It is evident that the mixed salts are not as readily formed as the unmixed, and that the more dissimilar the two halogens are, the less tendency there is to form the mixed compounds.*

In preparing these salts, containing two different halogens, the halogen of higher atomic weight was always added in combination with the mercury. The methods of preparation are exactly analogous to those by which the unmixed salts are made, so that most of these details will be omitted in describing them.

The Chloro-bromides.

In form these all resemble the unmixed salts between which they are intermediate, and all of them are colorless except CsHgClBr , which is pale yellow.

* This point is discussed in connection with the cæsium trihalides. (Wells and Peuffield, this Journal, III, xliii, pp. 31 and 32.)

Cs₃HgCl₃Br₂.—

	Found.	Calculated for Cs ₃ HgCl ₃ Br ₂ .
Cæsium	48.12	46.10
Mercury	23.80	23.11
Chlorine	16.24	12.30
Bromine	11.82	18.49
	<hr/> 99.98	<hr/> 100.00

The product was made with a very large excess of cæsium chloride, and it contained a considerable amount of the double chloride. The analysis corresponds nearly to the formula $2\text{Cs}_3\text{HgCl}_3\text{Br}_2 + \text{Cs}_3\text{HgCl}_3$.

Cs₂HgCl₂Br₂.—Two products, which were made under different conditions, were analyzed.

	Found.		Calculated for Cs ₂ HgCl ₂ Br ₂ .
Cæsium	40.34	38.86	38.16
Mercury	28.79	28.58	28.69
Chlorine	12.94	10.48	10.19
Bromine	17.43	22.07	22.96
	<hr/> 99.50	<hr/> 99.99	<hr/> 100.00

One of these crops corresponds very closely to the formula, while the other, made in the presence of a greater excess of cæsium chloride, contains a little Cs_3HgCl_3 .

CsHgClBr₂.—This has been obtained, like the chloride and bromide, in dimorphous forms. One of these is cubic like the other salts, while the second form crystallizes like the chloride and not like the bromide. The color of both varieties is pale yellow.

		Found.				
	Cubic form.	Orthorhombic form. Separate products.				Calculated for CsHgClBr ₂ .
Cæsium	26.50	26.97	26.74	26.01		25.17
Mercury	38.75	40.21	40.05	38.91		37.84
Chlorine	9.23	11.32	11.42	8.53		6.72
Bromine	25.21	21.63	21.94	26.65		30.27
	<hr/> 99.69	<hr/> 100.13	<hr/> 100.15	<hr/> 100.10		<hr/> 100.00

These products evidently contain some of the chloride. The analyses of the first two samples of the orthorhombic salt correspond closely to the formula, $2\text{CsHgClBr}_2 + \text{CsHgCl}_3$.

CsHg₂ClBr₄.—Two separate products, made under different conditions, were analyzed.

	Found.		Calculated for $\text{CsHg}_5\text{ClBr}_4$.
Cæsium	15.48	15.23	14.97
Mercury	45.72	45.06	45.02
Chlorine	5.75	3.71	3.99
Bromine	32.30	36.06	36.02
	<hr/> 99.25	<hr/> 100.06	<hr/> 100.00

$\text{CsHg}_5\text{ClBr}_{10}$.—This compound was prepared by recrystallizing the preceding salt from water.

	Found.	Calculated for $\text{CsHg}_5\text{ClBr}_{10}$.
Cæsium	6.23	6.76
Mercury	52.77	50.80
Chlorine	2.85	1.80
Bromine	38.19	40.64
	<hr/> 100.04	<hr/> 100.00

There is a chloride corresponding to this compound, but no bromide was obtained of this type. It forms elongated crystals much smaller than the chloride. The final product, when this salt is recrystallized from water, is mercuric bromide.

The Bromo-iodides.

Only three of these compounds have been prepared. When attempts were made to obtain compounds containing larger amounts of mercuric iodide, there was an interchange of halogens and nearly pure double iodides were formed. Two such products were analyzed.

	Found.	Calculated for $\text{Cs}_2\text{Hg}_3\text{I}_8$.	Found.	Calculated for CsHg_2I_5 .
Cæsium	14.69	14.13	11.62	11.39
Mercury	33.72	31.88	36.09	34.25
Bromine	2.19	0.00	2.43	0.00
Iodine	49.58	53.99	49.45	54.36
	<hr/> 100.18	<hr/> 100.00	<hr/> 99.59	<hr/> 100.00

$\text{Cs}_3\text{HgBr}_3\text{I}_2$.—This salt resembles the iodide, not the bromide, in form. Its color is a pale yellow, intermediate between the brighter iodide and the colorless bromide.

	Found.	Calculated for $\text{Cs}_3\text{HgBr}_3\text{I}_2$.
Cæsium	37.21	36.50
Mercury	19.39	18.30
Bromide	25.18	21.96
Iodine	18.24	23.24
	<hr/> 100.02	<hr/> 100.00

Cs₂HgBr₂I₂.—This compound has a very faint tinge of yellow. It is apparently dimorphous, although no other salt of this type has been made in more than one form. It occurs in very thin plates, like the chloride, bromide and chlorobromide, and in stout monoclinic crystals like the iodide. The limits of the conditions under which the plates are made are very narrow, and it is difficult to obtain them free from the dimorphous crystals. As the solution cools, however, the plates are deposited first, and, with the proper dilution, it is possible to remove them and get the mother-liquor pressed out with paper before the other crystals begin to form. There is no difficulty in preparing the other modification of the compound.

	Found.		
	Thin plates.	Orthorhombic crystals.	Calculated for Cs ₂ HgBr ₂ I ₂ .
Cæsium ----	30·71	30·26	30·23
Mercury ...	24·14	23·86	22·73
Bromine ...	21·05	17·91	18·18
Iodine	24·23	28·50	28·86
	<hr/> 100·13	<hr/> 100·47	<hr/> 100·00

It is noticeable that the plates, which resemble the bromide in form, contain a small excess of bromine and a corresponding deficiency of iodine.

CsHgBrI₂.—Only one form of this compound has been prepared, although three other salts of this type are dimorphous. Its form is monoclinic, like one modification of the bromide, and it is pale yellow in color.

	Found.	Calculated for CsHgBrI ₂ .
Cæsium	20·26	19·94
Mercury	31·44	29·99
Bromine	13·35	11·99
Iodine	34·39	38·08
	<hr/> 99·44	<hr/> 100·00

The Chloro-iodide, Cs₂HgCl₂I₂.

This is the only combination of cæsium chloride and mercuric iodide that could be produced. It is formed only in very concentrated solutions containing a great excess of cæsium chloride. Its form is different from any other salt of the type, for it occurs in slender, radiating needles. It is snow-white in color, and when it is brought in contact with water it instantly becomes bright red from the formation of mercuric iodide. Two entirely separate crops were analyzed

	Found.		Calculated for $\text{CsHgCl}_2\text{I}_2$.
Cæsium	33.38	32.14	33.63
Mercury	26.71	----	25.28
Chlorine	8.87	9.01	8.98
Iodine	30.85	30.17	32.11
	<hr/> 99.81		<hr/> 100.00

When it was attempted to make a chloro-iodide containing more mercuric iodide than this, a nearly pure double-iodide was formed by exchange of halogens.

	Found.	Calculated for $\text{Cs}_2\text{Hg}_2\text{I}_8$.
Cæsium	13.76	14.13
Mercury	33.49	31.88
Chlorine	0.16	0.00
Iodine	50.74	53.99
	<hr/> 98.15	<hr/> 100.00

The investigation of double-halides will be continued in this laboratory, and it is hoped that a further study of the cæsium salts will lead to a better knowledge of this class of compounds in general than we now possess.

In conclusion, it gives me pleasure to express my gratitude to my colleague, Professor Penfield, for his hearty coöperation in undertaking the crystallographic examination of the compounds which have been described. His results have been freely used in the foregoing descriptions, and they will be given in detail in a future article.

Sheffield Scientific School, New Haven,
Conn., May, 1892.