ART. IV.—*On a Series of Caesium Trihalides*; by H. L. WELLS. *Including their Crystallography*; by S. L. PENFIELD.

IN the course of some experiments with caesium compounds, bromine was added to a concentrated solution of caesium chloride with an astonishing result. There was instantly formed a bright yellow precipitate, so dense as to nearly solidify the liquid. The substance readily dissolved on warming the liquid, and, on cooling it, large crystals of a yellowish-red color were formed which were found to be CsClBr_2 .

In view of the fact that KI_3 was already known,* this discovery made it probable that a series of caesium trihalides could be obtained. An attempt was accordingly made to prepare each of the following possible members of such a series containing chlorine, bromine and iodine.

1. CsI_3	6. CsCl_2I
2. CsBrI_2	7. CsBr_3
3. CsBr_2I	8. CsClBr_2
4. $[\text{CsClI}_2]$	9. CsCl_2Br
5. CsClBrI	10. $[\text{CsCl}_3]$

As a result, all the members of the series except the two enclosed in brackets were isolated.

These eight trihalides are easily made, being much less soluble than the normal halides. They crystallize beautifully, have remarkably brilliant colors and some of them possess an unexpected degree of stability.

Method of preparation.

Each of these compounds can be made by dissolving, with the aid of heat, the appropriate normal caesium halide and the halogen or halogens indicated by the formula in the proper amount of water, or, in the single case of CsBrI_2 , in weak alcohol, and cooling to crystallization. The caesium salt used in making the mixed trihalides is preferably the one which is not decomposed by the halogen or halogens added. In most cases the presence of an excess of the normal halide is desirable in order that the halogens, especially iodine, may readily dissolve and not separate out again on cooling, but the same result may also be obtained by the use of weak alcohol. Details of preparation will be given for each body separately.

* Jörgensen, J. pr. Ch., II, ii, 357; Johnson, J. Chem. Soc., 1877, 249.

Color.

In the following list the compounds are arranged in order, from the darkest to the lightest. The colors given, unless otherwise specified, are for crystals of considerable size, for when the bodies are obtained as precipitates or when the crystals are pulverized they are lighter in color.

CsI_3	Brilliant black, nearly opaque ; powder brown.
CsBrI_2	Dark reddish-brown ; thin crystals transmit deep red light ; powder dark red.
CsBr_2I	Deep cherry-red.
CsClBrI	} { Yellowish-red each having a somewhat yellower tint than the one preceding it.
CsBr_3	
CsClBr_2	
CsCl_2I	} { Orthorhombic variety, deep orange. Rhombohedral variety, pale orange.
CsCl_2Br	
	Bright yellow.

Stability on exposure.

The five bodies containing iodine are much more stable than the others, and will bear long exposure to the air at ordinary temperatures with very slight superficial change. This exposure in some cases may be continued for a week or more in warm weather without producing any marked alteration of color, but they constantly give off a slight odor and finally begin to whiten. The three compounds containing no iodine usually become white in a few hours on exposure, but even these can be preserved indefinitely in tightly corked tubes. Experiments showed that CsBrI_2 whitened more rapidly than CsBr_2I , also that CsClBr_2 decomposed more rapidly than CsCl_2Br . This indicates that their stability does not entirely depend upon the volatility of the halogens contained in them, a point which has a bearing on the constitution of this group of bodies, and which will be considered subsequently.

Behavior when heated.

The following table shows the temperatures of complete decomposition as determined by the change of color to white. They are only approximate since they represent gradual changes which vary somewhat with the rapidity of heating. The melting-points are also given. In open tubes these are usually sharp, but in sealed tubes often very gradual.

	Melts in open tube. (uncorr.)	Melts in sealed tube. (uncorr.)	Becomes white in open tube. (approximate.)
CsI ₃ -----	210°	201°–208°	330°
CsBr ₂ I -----	246°	243°–248°	320°
CsClBrI -----	238°	225°–235°	290°
CsCl ₂ I -----	238°	225°–230°	290°
CsBrI ₂ -----	208°	155°–190°	260°
CsBr ₃ -----	whitens	180°	160°
CsCl ₂ Br ...	whitens	205°	150°
CsClBr ₂ ...	whitens	191°	150°

Behavior with solvents.

All these bodies except CsBrI₃, which is almost completely decomposed by water, can be recrystallized by treating with warm water and cooling the solution. There is usually some decomposition during this operation, accompanied by the separation of iodine or the volatilization of this or the other halogens.

All the trihalides containing iodine can be dissolved in alcohol and recrystallized from it. There is usually a slight deposition of normal halide at the same time, which can be avoided by adding a little water to the alcohol. CsI₃ is much more soluble in alcohol than in water. The other iodine compounds, with the exception of CsBrI₂, which decomposes with water, are apparently more soluble in water. Those bodies containing no iodine are all decomposed by alcohol, leaving a white residue. Mixtures of alcohol and water are good solvents for all the trihalides.

Ether has no immediate action on the more stable compounds, CsI₃, CsBr₂I, CsClBrI and CsCl₂I, but it decomposes all the others with separation of normal halides. When CsBrI₃ is thus decomposed, pure CsBr is left.

Crystallography.

The crystallization of the caesium trihalides is orthorhombic. The salts form an isomorphous group, the chief features of which will first be given, followed by a brief description of the different individuals.

The forms which have been observed are :

<i>a</i> , 100, <i>i</i> - $\bar{i}$	<i>g</i> , 012, $\frac{1}{2}$ - $\bar{2}$
<i>b</i> , 010, <i>i</i> - $\bar{i}$	<i>d</i> , 011, 1- $\bar{1}$
<i>c</i> , 001, <i>O</i>	<i>f</i> , 021, 2- $\bar{2}$
<i>m</i> , 110, <i>I</i>	<i>e</i> , 102, $\frac{1}{2}$ - $\bar{2}$

Of these *m*, *d* and *e* are the most prominent and usually determine the habit of the crystals. Either *m* or *d* usually predominates to such an extent that the crystals are prismatic in the direction of the vertical or the brachy-axes. The dome

f is very common but is usually too small to give a characteristic habit, and is therefore omitted from most of the figures. The face *g* was observed only on CsI_3 . The pinacoids are variable in their development, but commonly one and frequently all three can be found on a single crystal. Pyramidal faces are practically wanting. In the examination of a great many crystals but one was found (of CsBr_2I) on which a single pyramidal face occurred; this replaced the edge between *m* and *d* and had the symbol $132, \frac{3}{2}-\bar{3}$. The cleavage is perfect parallel to *c*.

An idea of the similarity of the different salts may be obtained from the following table, in which the axial ratios* and three of the prominent angles are given. The angles which were chosen as fundamental are marked by an asterisk, the others are calculated, and in all cases the measurements showed close agreement.

		I		II	
		<i>a</i> : <i>b</i> : <i>c</i>		<i>a</i> : <i>b</i> : <i>c</i>	
Series with iodine	$\left\{ \begin{array}{l} \text{CsI}_3 \\ \text{CsBrI}_2 \\ \text{CsBr}_2\text{I} \\ \text{CsClBrI} \\ \text{CsCl}_2\text{I} \end{array} \right.$	0.6824	1 : 1.1051	1 : 1.4655	1.6196
		0.6916	1 : 1.1419	1 : 1.4460	1.6511
		0.7203	1 : 1.1667	1 : 1.3882	1.6196
		0.7230	1 : 1.1760	1 : 1.3831	1.6268
		0.7373	1 : 1.1920	1 : 1.3563	1.6167
Series without iodine	$\left\{ \begin{array}{l} \text{CsBr}_3 \\ \text{CsClBr}_2 \\ \text{CsCl}_2\text{Br} \end{array} \right.$	0.6873	1 : 1.0581	1 : 1.4550	1.5395
		0.699	1 : -----	1 : 1.430	-----
		0.7186	1 : 1.1237	1 : 1.3917	1.5638
<i>m</i> $\wedge$ <i>m</i> , 110 $\wedge$ 1 $\bar{1}$ 0 <i>d</i> $\wedge$ <i>d</i> , 011 $\wedge$ 0 $\bar{1}$ 1. <i>e</i> $\wedge$ <i>e</i> , 102 $\wedge$ 102.					
	CsI_3	*68° 37'	*95° 43'	78° 0'	0'
	CsBrI_2	*69 20	97 34	*79 5	
	CsBr_2I	*71 32	*98 48	78 0	
	CsClBrI	*71 44	*99 15	78 15	
	CsCl_2I	72 48	*100 1	*77 54	
	CsBr_3	*69 0	*93 14	75 10	
	CsClBr_2	*69 56			
	CsCl_2Br	*71 24	*96 40	76 0	

CsI_3 and CsBr_3 are almost identical in axial ratios, but it is surprising that the chemically intermediate compounds, CsBrI_2 and CsBr_2I , are not crystallographically intermediate.

A very remarkable relation exists between the first five compounds in the table, all of which contain iodine and are arranged in the order of their molecular weights. The ratio of two axes remains nearly constant throughout, while the third varies.† Exactly the same relation exists between the

* The ratios are given in two ways: I, with $\bar{b}$ as unity, as is customary; and II, with $\bar{a}$ as unity, in order to show more clearly the relation between $\bar{a}$ and $\bar{c}$.

† Several series of organic compounds with analogous axial relations have been observed by Groth (Berichte, iii, 449) and by Hintze (Berichte, vi, 593.)

three compounds containing no iodine, but in this series the ratio between the two constant axes varies slightly from the corresponding ratio in the iodine compounds.

If an arrangement according to molecular weights is made with all the compounds containing bromine, or in like manner with all those containing chlorine, a symmetrical series of axial ratios is not formed. This leads to the conclusion that the two series given in the table have a special significance, and that iodine, with the highest atomic weight, plays an important part in the constitution of the first, while bromine acts in the same way in the second. Since several of the compounds contain only a single halogen atom of highest atomic weight, it follows that a single atom throughout exerts an influence on the symmetry of the series. This peculiar part played by an iodine or bromine atom may be explained by supposing it to be closely united either with the caesium or with one of the other halogen atoms. It seems probable from these considerations that the three halogen atoms in these compounds do not have similar positions in the molecule, and consequently that the trihalides are not compounds of trivalent caesium but have some other structure.

CsI₃.—Of this salt, crystals from both aqueous and alcoholic solutions were examined. On the former the forms *a*, *c*, *m*, *d* and *f* were observed. The habit was different from anything else in the series, being needle-like, with *a* and *m* in the prismatic zone, terminated by *d*, fig. 1, or by *c*, *d*, and *f*, fig. 2. The crystals did not give very satisfactory reflections, but the best measurements, from a number of selected crystals, agreed closely with those given in the table. The crystals examined were 20–30^{mm} in length and seldom over 2^{mm} in diameter. On the crystals from alcohol, the forms *a*, *b*, *c*, *m*, *g*, *d*, *f* and *e* were observed. The habit is shown in fig. 3. There was a tendency in the crystals to arrange themselves in parallel position forming plates, showing large *a* faces, but the separate individuals were small, scarcely over 3^{mm} in greatest diameter. The faces gave excellent reflections. The crystals are black, transmit a brownish red light only on the thinnest edges, and are too opaque for optical examination.

CsBrI₂.—On two separate samples of this salt the forms *a*, *b*, *c*, *m*, *d*, *f* and *e* were ob-

served. The crystals are thin tables somewhat lengthened in the direction of the brachy-axis, fig. 4. On examining the

general table, it will be seen that this is the only one of the first five salts, in which the angle $e \wedge e$ varies considerably from 78° . Here, the variation amounts to a little over one degree, but, in all probability, this is not to be accounted for by imperfections in the crystals or inaccuracy in the observation, for from two different crops of crystals good reflections and almost identical measurements were obtained. The crystals were only a fraction of a millimeter in thickness and not over 10^{mm} long in the direction of the brachy-axis. With the polarizing microscope the tables show a decided pleochroism. For rays vibrating parallel to the c axis the color is dark brown, almost opaque, while for vibrations parallel to a it is a rich reddish brown. A similar, though less marked, pleochroism was observed in the remaining salts of the series, but owing to the inability to obtain orientated pinacoid sections, it could not be studied satisfactorily. In convergent polarized light, the phenomena were not very distinct, but with the tables of CsBrI_2 apparently an obtuse bisectrix could be seen, the optical axis being in the macro-pinacoid a .

CsBr₂I.—On this salt the forms a, c, m, d, f and e were observed. The habit is shown in fig. 5. The crystals were brilliant and gave excellent reflections. Those submitted for measurement were about 3^{mm} in greatest diameter.

CsClBrI.—On this salt the forms b, c, m, d, f and e were observed. The habit is like fig. 5, but much longer, or prismatic, in the direction of the brachy-axis. The crystals were about 2^{mm} in diameter

and 10 in length.

CsCl₂I.—This compound is dimorphous.

On the orthorhombic modification the forms a, c, m, d, f and e were observed, but m and f are usually wanting. The habit is shown in fig. 6. The crystals were about 2^{mm} in diameter.

The hexagonal, rhombohedral, variety occurred in curious saddle-shaped scales, with bright crystal faces only along the edges. The forms which were observed are $r(1, 10\bar{1}1), f(-2, 02\bar{2}1)$ and a

($i\bar{2}, 11\bar{2}0$), fig. 7. Only that portion is perfect which is included between the irregular dotted lines, the upper and lower angles of the rhombohedrons being truncated by irregular warped surfaces. In their growth the individuals of a whole series of crystals, with similar orientation, are piled upon one another in the direction of the vertical axis. The scales are about 6^{mm} in diameter.

The measurement which was taken as fundamental is:

$$r \wedge r, \text{ over } a, 10\bar{1}1 \wedge 01\bar{1}\bar{1} = 99^\circ 48'$$

giving for the length of the vertical

axis, $c = 0.96363$. The following measurements were also made:

$a \wedge a = 60^\circ 0', 60^\circ 1', 59^\circ 59'$	Calculated $60^\circ 0'$
$a \wedge f, \bar{1}2\bar{1}0 \wedge 02\bar{2}1 = 37^\circ 45'$	" $37^\circ 49'$

The remaining compounds containing no iodine, were much more unstable than those previously described. By making the measurements in a cold room very satisfactory results were obtained, the crystals retaining enough luster to give good reflections, even after they had suffered considerable decomposition.

CsBr₃.—The forms observed on this salt are *b*, *m* and *d*. The habit is short prismatic, with either *m* or *d* predominating, while *b* is usually wanting. Single crystals are sometimes 10^{mm} in length; but groups of small crystals are more apt to occur.

CsClBr₂.—The only forms observed on this salt are *m* and *c*. The habit is short and stout prismatic. Single crystals are sometimes 15^{mm} in length.

CsCl₂Br.—The forms observed on this salt are *c*, *m* and *d*. It crystallized in stout prisms, over 10^{mm} long, terminated like fig. 1.

Method of analysis.

The samples were prepared for analysis by pressing on paper. The drying was not always very good, both on account of the haste sometimes necessary to avoid too much decomposition, and on account of the great tendency of the crystals to contain cavities filled with liquid.

Caesium was invariably determined by weighing the normal halide produced by heating. In some cases where the resulting normal halide was slightly contaminated by a higher halogen, this was replaced by the proper one before weighing.

Where two halogens were present they were determined in the usual way by weighing their silver salts and determining the loss in weight of these when heated in chlorine. In the cases where all three halogens were present, use was made of the extremely satisfactory method described by Gooch and Ensign.*

CsI₃.

This can be made by dissolving about one-fourth the theoretical amount of iodine in a solution of one part of caesium iodide in ten parts of water. It generally gives a crop of brilliant, slender crystals. If a larger proportion of iodine is used, the substance generally separates in the form of crystalline plates without distinct faces. They are possibly a dimorphous form of the substance. If weak alcohol is used as a solvent instead of water, the theoretical amount of iodine can be taken and a well-crystallized product is obtained.

The following numbers show the composition :

	Found		Calculated for
	Slender Crystals.	Plates.	CsI ₃ .
Caesium	25.41	23.71	25.88
Iodine	72.67	----	74.12

When iodine is being dissolved in a warm aqueous solution of CsI, or when an attempt is made to dissolve CsI₃ in warm water, a heavy black liquid is formed at about 73° which solidifies on cooling to a crystalline mass. It is much richer in iodine than CsI₃ and probably contains a higher polyiodide. Analyses of the substance gave varying results, and although most of these approached the composition CsI₃, it is still uncertain what body this is. The low melting point of the substance is remarkable since CsI₃ melts at 210° and iodine at 114°.

To find the solubility of CsI₃ in an aqueous solution of CsI, the mother-liquor from a crop of crystals deposited at about 20° was analyzed. It gave :

CsI   16.99 per cent.
I (free) 0.416 per cent or CsI₃ 0.842 per cent.

The specific gravity of this mother-liquor was 1.154, hence 1 c.c. contained 0.0097gCsI₃. The body is so insoluble that, were we to use CsI in the place of KI in making a volumetric iodine solution, we could only obtain, at ordinary temperatures, a solution which would be about $\frac{1}{24}$ normal.

* This Journal, III, xl. 145, 1890.

CsBrI₂.

Iodine dissolves in considerable quantity in a hot aqueous solution of caesium bromide, but it nearly all separates on cooling. It is therefore necessary to use a mixture of alcohol and water in preparing this trihalide. A good crop of crystals was obtained by dissolving one-half the theoretical iodine in a solution of one part of caesium bromide dissolved in two parts of water and one part (by volume) of alcohol.

The following numbers show the composition of the crystals.

	Found.	Calculated for CsBrI ₂ .
Caesium	28.54	28.48
Bromine	18.11	17.13
Iodine	52.01	54.39

CsBr₂I.

This may be made by dissolving the theoretical amounts of iodine and bromine in a solution of one part of caesium bromide in ten parts of water. A considerable excess of bromine does not interfere with its formation.

The crystals have the following composition :

	Found.	Calculated for CsBr ₂ I.
Caesium	31.32	31.67
Bromine	37.63	38.09
Iodine	29.57	30.24

The solubility of this substance in water was approximately determined by estimating the free halogens volumetrically in the mother-liquor from a recrystallization at about 20°. The amount found corresponded to 4.45 per cent of CsBr₂I.

[*CsClI₂*.]

Repeated attempts to make this substance, by using concentrated solutions of caesium chloride and iodine in mixtures of water and alcohol and cooling to low temperatures, invariably failed.

CsClBrI.

This may be made by dissolving about one-fourth of the theoretical bromine and iodine in a solution of one part of caesium chloride in five parts of water. If an excess of caesium chloride is not taken the product will contain too little chlorine and too much bromine.

An analysis of the product, properly prepared, gave :

	Found.	Calculated for CsClBrI.
Caesium	34.24	35.42
Chlorine	9.36	9.45
Bromine	19.96	21.30
Iodine	32.36	33.83

If a large excess of bromine is used, an impure product results as is shown by the following analysis of a sample thus made:

	Found.
Caesium	36.11
Chlorine	9.36
Bromine	27.70
Iodine	24.83

On attempting to recrystallize the CsClBrI a product of a darker red color is formed, sometimes accompanied by the separation of some iodine. The following analyses were made of products of recrystallization:

“A” was from a single recrystallization. “B” was recrystallized three times, a little alcohol being added the last time to keep iodine in solution. “C” was recrystallized five times, each time with the addition of a large excess of bromine.

	A.	B.	C.	Calculated for CsClBrI.	Calculated for CsBr ₂ I.
Caesium...	32.69	33.22	----	35.42	31.67
Chlorine ..	3.32	5.02	2.70	9.45	0.
Bromine ..	31.56	28.30	32.50	21.30	38.09
Iodine	30.91	31.78	30.99	33.83	30.24

These analyses show that the recrystallized body approaches CsBr₂I, but that a part of the chlorine is very tenaciously held. The excess of bromine used in the case “C” had apparently no effect, probably because caesium and iodine were present in equivalent quantities, whereas, in the case previously given, in which an excess of bromine was used in presence of much caesium chloride in preparing the body, there was evidently a contamination with CsClBr₂.

CsCl₂I.

This body is dimorphous, the form apparently depending upon the presence or absence of a large excess of caesium chloride in the solution from which it crystallizes.

The rhombohedral variety is usually obtained by adding iodine in the proportion of one atom to one molecule of caesium chloride dissolved in about ten parts of water, then passing chlorine into the liquid heated nearly to boiling until the iodine just dissolves, and finally cooling. If an excess of

chlorine is used, the body CsCl_2I is formed corresponding to KCl_2I discovered by Filhol.* This new caesium compound will be described in a future article in connection with several other new bodies of the same class.

The orthorhombic variety of CsCl_2I can be obtained by using three or four times as much caesium chloride as in the other case, the other conditions remaining unchanged.

The following analyses of two separate products of each of the two varieties were made.

	Rhombohedral. Found.		Orthorhombic. Found.		Calculated for CsCl_2I .
Caesium ----	39.20	39.92	38.43	40.00	40.18
Chlorine ----	20.72	21.08	19.78	20.75	21.45
Iodine -----	37.81	38.21	38.97	38.88	38.37

On recrystallizing either form of this substance, from solution in hot water, the rhombohedral variety is usually formed, owing to the lack of an excess of caesium chloride. It is not unusual, however, to obtain at first, as the solution cools, slender needles evidently of the orthorhombic variety, which afterward become surrounded by rhombohedral crystals.

CsBr_3 .

To make this substance, one half the calculated amount of bromine is added to a solution of one part of caesium bromide in three parts of water, the whole is heated with vigorous shaking until the liquid bromine disappears and then slowly cooled. Crystals gave on analysis:

	Found.	Calculated for CsBr_3
Caesium	35.12	35.66
Bromine	61.53	64.34

In preparing this body, there usually remains, when the liquid bromine disappears on heating the solution, a heavy reddish liquid much lighter in color than bromine. It is without doubt a higher polybromide and it probably corresponds to the easily fusible substance already mentioned as a probable higher polyiodide. An investigation of its composition will soon be made.

CsClBr_2 .

The formation of this body was mentioned at the beginning of this article in connection with the discovery of the new series of salts. It can be made by adding about one half the theoretical bromine to a solution of caesium chloride in about five parts of water, dissolving by heat and cooling.

* Michälis, "Anorgan. Chem.," 3, 102; Gmelin-Kraut, II, 1, 82.

The analyses of two products are given below. The "precipitate" resulted from adding bromine to a cold caesium chloride solution, and, being finely divided as well as the most unstable compound of the series, it suffered a considerable amount of decomposition although time was not taken to dry it thoroughly.

	Found.		Calculated for CsClBr ₂ .
	Precipitate.	Crystals.	
Caesium	40·62	42·14	40·49
Chlorine	12·64	13·24	10·81
Bromine	39·61	42·93	48·70
Water	6·45	1·72	0·
	99·32	100·03	100·00

Cs Cl₂ Br.

This substance may be made by adding the calculated amount of bromine to a solution of caesium chloride in five parts of water, warming enough to keep CsClBr₂ in solution, and passing chlorine in excess.

	Analysis gave	Calculated for
		CsCl ₂ Br.
Caesium	46·25	46·83
Chlorine	24·15	25·00
Bromine	26·05	28·17

[*Cs Cl₃*]

Efforts to prepare this substance by passing chlorine into saturated aqueous solutions of caesium chloride cooled by a freezing-mixture did not succeed. It was noticeable that the compound Cl 5H₂O was not formed under these circumstances.

Other Trihalides.

Johnson's KI₃* is undoubtedly analogous to the caesium compounds. An investigation of this and other potassium trihalides as well as the corresponding rubidium compounds is now in progress in this laboratory, and an effort will be made to prepare similar compounds with still other metals.

The compound KI₂(CN)† and the body NH₄I₃, which Johnson describes‡ as very similar to KI₃, should be mentioned in this connection.

There have been described a great number of trihalides of both natural and artificial organic bases. These are mostly triiodides but there are among them a number of tribromides

* J. Chem. Soc., 1877, i, 249.

† Langlois, Ann. Chim. Phys., [III] lx, 220.

‡ J. Chem. Soc., 1878, 397.

and also mixed trihalides, especially of the type RCl_2I . These organic bodies* are evidently analogous to the caesium compounds under consideration, but since they have not been sufficiently studied to throw any light on the structure or crystalline form of trihalides in general, they will not be described in detail here.

Theoretical Considerations.

Thus far in this article the simplest possible formulæ have been used. The probable structure of the compounds will now be discussed.

The trihalides previously known have been usually considered as weakly combined addition-products. Mendelejeff,† for example, says that the instability with which I_2 unites with KI and $\text{N}(\text{CH}_3)_3\text{I}$ is analogous to the instability of many crystal-hydrates, e. g., $\text{HCl} \cdot 2\text{H}_2\text{O}$. It must be noticed that some of the caesium trihalides are very stable, but this fact is evidently due to the strong positive character of the metal, and, since others among them are comparatively unstable, it can have no important bearing on their structure.

Johnson‡ advances the formula K_2I_3 for potassium triiodide with no better reason than the existence of a higher iodide of mercury, HgI_4 .§ This formula may be dismissed at once, for there is no more ground for it than for writing K_2I , because HgI_2 exists, and moreover if the caesium salts were Cs_2X_3 we should expect to find in the series such compounds as $\text{Cs}_2\text{Cl}_3\text{I}$, $\text{Cs}_2\text{Cl}_2\text{I}_2$, etc., none of which were discovered.

Since the members of the caesium series are crystallographically isomorphous they must all have the same structure, and, as has just been shown, no multiple of the formula CsX_3 is probable.

A possible explanation of the caesium trihalides may be made by supposing the metal to act trivalently, and the following arguments seem to favor this view:

1st. Caesium has the highest atomic weight of the alkali-metals, and it is a noticeable fact that, among the elements in general, those with higher atomic-weights in a group have the greater tendency to act with variable quantivalence. 2d. Caesium is univalent in its ordinary compounds, and, following

* See the following articles: Weltzien, *Ann. Ch. Ph.*, xci, 33; xcix, 1. Müller, *ibid.*, cviii, 5. Hubner, *ibid.*, ccx, 368. Ladenburg, *ibid.*, ccxvii, 122. Zinke and Lawson, *ibid.*, ccxi, 123. Zinke and Artzberger, *ibid.*, ccxlix, 366. Jörgensen, *J. pr. Ch.*, II, vols. ii, iii, xiv and xv. Dafert, *Monatshefte*, iv, 496. Dittmar, *Berichte*, xviii, 1612. Ostermayer, *ibid.*, xviii, 2298. Kamensky, *ibid.*, xi, 1600. Tilden, *J. Chem. Soc.*, xviii, 99. Hoogewerff and Dorp, *Rec. Trav. Chim.*, iii, 361.

† "Grundlagen der Chemie," p. 563, foot-note 63.

‡ *J. Chem. Soc.*, 1878, 183.

§ Jörgensen, *J. pr. Ch.*, II, ii, 357.

the general rule, the next higher quantivalence should be three. 3rd. Caesium is in the same group as gold, in Mendelejeff's periodic system of the elements, and it is well known that this element acts univalently and trivalently.

On the other hand, the following arguments are in favor of considering the bodies double salts: 1st. The compounds IBr , ICl and BrCl are definite bodies and all the trihalides may be considered as molecular compounds of these, and also the molecules I_2 and Br_2 , with normal halides. 2d. The fact that CsBr_2I is more stable than CsBrI_2 , and that CsCl_2Br is more so than CsClBr_2 , showing that the stability of these bodies does not entirely depend upon the volatility of the halogens contained in them, indicates that the halogen atoms have much influence on each other, and that at least two of them are probably bound together. A consideration of the fact that CsCl_2I is a very stable body while CsClI_2 probably cannot be prepared leads to the same conclusion. 3d. It has been pointed out by Godeffroy* that the simple salts of caesium are as a rule more soluble than the corresponding rubidium and potassium salts, while with the double-salts the reverse is true. Work now in progress in this laboratory shows that the rubidium and potassium trihalides, as far as they have been investigated, increase in solubility towards potassium, hence, if the rule holds true, they must be double-salts. 4th. The new salt CsI.AgI ,† an undoubted double-salt, shows a close relation to the trihalides in its system of crystallization, in the ratio of the two axes, which alone were determined, and in its cleavage.‡ The salt $\text{KI.AgI}\S$ has been prepared, but it has not yet been procured in crystals fit for measurement. Work will be continued on this class of compounds.

* Berichte, ix, 1365.

† This was made by dissolving AgI in a concentrated, hot solution of CsI and cooling. It forms tufts of hair-like crystals, very seldom large enough to measure.

	Analysis gave	Calculated for CsI.AgI .
Silver	19.03	21.82
Iodine	50.91	51.32
Caesium	----	26.86

‡ CsI.AgI crystallizes in the orthorhombic system. It was obtained in long needles, not over $\frac{1}{8}$ mm. in diameter and too small to show distinct end faces. A pinacoid and two other forms occur in the prismatic zone which correspond to $c(001)$, $g(012)$ and $d(011)$ of the trihalide series. Of these c and g are the best developed while d is very small. Five independent measurements of $c \wedge g$ gave values varying between $27^\circ 29'$ and $27^\circ 44'$, the average being $27^\circ 36'$ which gives the ratio $b:c = 1:1.0456$. The crystals show a imperfect cleavage parallel to $a(100)$ and probably a second parallel to c , but they were too small to allow of this being determined with certainty. Under the polarizing microscope they show parallel extinction.

§ Boullay, Ann. Chim. Phys., II, xxxiv, 377.

The evidence which has just been given points strongly towards considering the trihalides as double-salts. The considerations based on the axial relations of the crystals, which have been given in the crystallographic part of this article, also indicate that these bodies cannot be viewed as compounds of trivalent caesium, and, moreover, that a single halogen atom of highest atomic weight plays an important part in their structure. One view of the possible position of this peculiar atom may be that it is a trivalent atom united to the others in the manner indicated by the general formulæ $\text{Cs}-\text{I} < \frac{\text{X}}{\text{X}}$ and $\text{Cs}-\text{Br} < \frac{\text{X}}{\text{X}}$. This view may be objected to because the strongest halogen atom is not directly united to the caesium. The structure $\text{Cs}-\text{X} < \frac{\text{X}}{\text{X}}$ is scarcely admissible in the compound $\text{CsI}.\text{AgI}$ on account of the probable invariable univalence of silver.

Another view of the position of the peculiar iodine or bromine atom may be based upon the idea, so ably advocated by Remsen,* that a bivalent group of two halogen atoms acts the same part in double halides that oxygen takes in ordinary oxygen salts. Supposing that a halogen atom of highest atomic weight is linked to the caesium atom by means of the other two halogen atoms, acting as a bivalent group, the trihalides have the following formulæ:

These formulæ allow the supposition that the most negative halogen atom is in direct union with the caesium. They are consistent with the view that there are two symmetrical series of compounds, one with an iodine atom, the other with a bromine atom in a special position. On these grounds they seem quite plausible.

Assuming that the structure of the trihalides is represented by the above formulæ, a comparison of their relative stability leads to the view that the linking group of two halogen atoms causes greater stability when composed of like atoms than when these atoms differ. The groups (II) (BrBr) and (ClCl) occur in the comparatively stable compounds, while (ClBr) is in the most unstable body of the "bromine series," (BrI) is in

* On the Nature and Structure of Double Halides, *Am. Chem. Jour.*, xi, 291.

the least stable one of the "iodine series" and the compound which should contain (ClI) , with the least closely related halogens, could not be prepared. There is a possible exception in the body $\text{Cs}-(\text{ClBr})-\text{I}$, for it has not been noticed that the stability of this varies to any marked extent from $\text{Cs}-(\text{ClCl})-\text{I}$. The same view of the effect of the identity of the linking halogen atoms will probably apply to all double halides, for it is certain that very few of these containing different halogens are known, although this may be partly due to the fact that mixed double halides have not been sufficiently studied. An investigation of the double halides of caesium and mercury, now in progress, indicates that the generalization will apply in this case. Whatever may be the true structure of double halides, this influence of the identity of the halogens in the combining simple salts probably depends upon the same broad chemical law which causes, for example, two oxides or two sulphides to combine more readily than an oxide and a sulphide of the same elements, and which causes sulphates to combine with other sulphates more readily than they combine with nitrates and other dissimilar salts.

The present communication may be considered as preliminary to a wider study of polyhalides and double halogen salts. It is hoped that other series, studied chemically and crystallographically, may give valuable results.

Sheffield Scientific School, December, 1891.