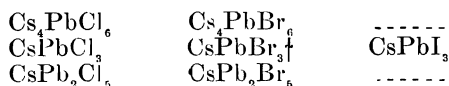


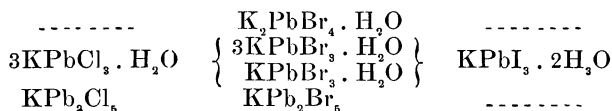
ART. XVI.—*On the Cæsium- and the Potassium-Lead Halides*; by H. L. WELLS.

As a continuation of the work on double halides, in this laboratory,* a study of the cæsium-lead salts has been undertaken by Messrs. G. F. Campbell, P. T. Walden and A. P. Wheeler. These gentlemen have carried out the investigation with much enthusiasm and skill, and I take pleasure in expressing my obligations to them. They have established the following salts:



These results showed the existence of three types of lead double halides, the first of which fails to conform with Remsen's law‡ concerning the composition of this class of bodies.

Since the recent investigations of Remsen and Herty§ had indicated the existence of only a single type of potassium-lead halides, a new investigation of these seemed desirable, especially since these authors had denied the existence of Boullay's salt,|| K_4PbI_6 , which corresponds to one type of the new cæsium compounds. I have, therefore, undertaken this work and, as a result, have obtained the following salts:



It is to be noticed that neither Boullay's iodide nor any corresponding chloride or bromide was obtained among these salts. On the other hand, the compound $\text{K}_2\text{PbBr}_4 \cdot \text{H}_2\text{O}$ belongs to a type which had not been discovered among the cæsium salts, so that, taking the cæsium and potassium series together, the existence of four types of double lead halides is shown.

The compound K_2PbBr_4 , the anhydrous form of the salt just mentioned, is ascribed to Löwig,¶ but although iodides belonging to the same type have been described, $\text{K}_2\text{PbI}_4 \cdot 4\text{H}_2\text{O}$ by Ditte** and $\text{K}_2\text{PbI}_4 \cdot 2\text{H}_2\text{O}$ by Berthelot,†† neither Remsen

* This Journal, III, xlv, 155, 157 and 221.

† This compound is dimorphous.

‡ Am. Chem. Jour., xi, 296.

§ Am. Chem. Jour., xiv, 107.

|| Ann. Chim. Phys., II, xxxiv, 336 (1827).

¶ Gmelin's "Handbook," English Ed. of 1850, v. 162.

** Ann. Chim. Phys., V, xxiv, 226, 1881.

†† Ann. Chim. Phys., V, xxix, 289, 1883.

and Herty nor I have been able to prepare them. Although these iodides and Boullay's salt, K_2PbI_4 , belong to types which certainly exist, I am inclined to believe, with Remsen and Herty, that the products which gave these formulæ were mixtures of $KPbI_3 \cdot 2H_2O$ and KI . The absence of more than one iodide in the cæsium series strengthens this view.

Remsen and Herty obtained the salt $KPbI_3 \cdot 2H_2O$ under wide variations of conditions and I have confirmed their results. This salt was first obtained by Boullay* and analyzed by him, after drying over lime, in an anhydrous condition. Berthelot† has described a compound, $K_2Pb_3I_{10} \cdot 6H_2O$, which differs but slightly in required composition from the above salt, and his description of it agrees with that compound. There is no doubt, therefore, that he really obtained the compound $KPbI_3 \cdot 2H_2O$ and that his analyzed products were slightly contaminated with potassium iodide. Berthelot attributes $K_2Pb_3I_{10}$ to Boullay. The latter chemist, however, derived the correct formula, equivalent to $KPbI_3$, from his analysis, but since this did not agree closely with theory, Gmelin‡ derived the above-mentioned formula from it, and this has been frequently copied in more recent chemical literature.

Schreinemakers,§ in connection with an investigation on the equilibrium of the double salt of iodide of lead and potassium in aqueous solution, has assumed that Ditte's formula was correct as far as the composition of the anhydrous compound was concerned. By making a number of water determinations, without determining lead, potassium or iodine, he arrived at the formula $K_2PbI_4 \cdot 2\frac{1}{2}H_2O$. It is absolutely certain, from his description of the salt and his method of preparing it, that he had the compound $KPbI_3 \cdot 2H_2O$; moreover, his water determinations, 5.52, 5.72, 5.89, 5.93 and 5.16 per cent, agree satisfactorily with the calculated amount, 5.90, for this salt.

Remsen and Herty made only a single chloride, and likewise only one bromide. The other chloride, and the two bromides belonging to other types crystallize beautifully and are as easily made as the salts which they prepared, and it is a strange coincidence that the latter happened to correspond in type to the iodide which they had obtained. I have confirmed the composition of their bromide, $KPbBr_3 \cdot H_2O$, but their chloride, to which they gave the formula $KPbCl_3$, is evidently identical with the compound which I have found to be undoubtedly hydrous, $3KPbCl_3 \cdot H_2O$.

* Ann. Chim. Phys., II, xxxiv, 336, 1827.

† Ann. Chim. Phys., V, xxix, 289, 1883.

‡ "Handbook." English ed., 1850, v, 161.

§ Zeitschr. Physikal. Chem., ix, 57, 1892.

Löwig, as already mentioned, has described the compound K_2PbBr_4 . I have been unable to find his original article, but from the fact that I have not obtained an anhydrous form of this compound, I believe that he overlooked the water of crystallization or dehydrated the salt before analyzing it.

A bromide, $K_2Pb_3Br_8$ is mentioned by Berthelot.* He does not give any analysis or description of it, and I am convinced from my own experiments that he obtained a mixture of $KPbBr_3 \cdot \frac{1}{3}H_2O$ and KPb_2Br_5 .

Strohecker† states that he produced three different chlorides of potassium and lead by mixing potassium chloride and lead nitrate solutions. It is remarkable, considering the abundance and cheapness of the materials and the ease with which large quantities of the double salts can be made, that he did not obtain them in sufficient quantities for exact analyses. Since I have succeeded in making only two double chlorides, I believe that one of Strohecker's salts, which he describes as feathery, was simply lead chloride.

The results of previous investigators may be summed up by saying that it is probable that no potassium lead halides have been correctly described, if water of crystallization is taken into consideration, except two of Remsen and Herty's salts, $KPbBr_3 \cdot H_2O$ and $KPbI_3 \cdot 2H_2O$.

Method of Preparation.

Both the cæsium and potassium salts have been investigated, in every case, by making hot, aqueous solutions of the component halides and cooling to crystallization. Some previous investigators had used solutions of lead nitrate and an alkaline halide for the purpose, but their example has not been followed, because it was not believed that the presence of an alkaline nitrate would in any way facilitate the operation, and it was feared that it might incur contamination in some cases. The conditions were gradually varied from a point where the alkaline halide crystallized out, to a point where the lead halide was deposited uncombined, and the experiments were so carefully carried out and so frequently repeated that it seems scarcely possible that any double salt was overlooked.

The salts have been made on a rather large scale. In the case of the cæsium compounds, the rarity of the material made it necessary to perform the separate experiments with only about 50 or 75 grams of a cæsium halide, but in making the potassium salts 400 or 500 grams of a potassium halide were frequently used.

* Ann. Chim. Phys., V. xxix, 289, 1883.

† Jahresbericht, 1869, 282.

Solutions which were neutral or slightly acid were generally used. The effect of the presence of a large amount of free acid, hydrochloric, hydrobromic or hydroiodic, as the case required, was also carefully studied, but these had no apparent effect upon the results.

Very large crops of the potassium salts were sometimes formed, so that the homogeneity of the mass was doubtful. In such cases the greater part of the crop was removed and satisfactory crystals were obtained by dissolving the remainder in the mother-liquor by the aid of heat and cooling.

The cæsium material used was wholly from the pollucite of Hebron, Maine.* The salts were carefully purified for this investigation. Godeffroy's method† was found to be very satisfactory for the purpose of separating cæsium from the sodium and potassium which accompany it in the mineral.

Kahlbaum's potassium chloride, bromide and iodide were usually used for making the potassium salts, but for a few experiments the ordinary medicinal potassium bromide was substituted. Since some of the analyses of the double bromides show an excess over 100 per cent, it is suspected that the salts contained a little chlorine. Calculation shows that one per cent of chlorine replacing bromine would cause an excess of 0.71 per cent if the chlorine was weighed as silver chloride and calculated as bromine.

The lead halides which were used were prepared by ourselves from reliable materials.

General Properties.

The lead double halides are all decomposed by water, and the presence of a large excess of the alkaline halide is necessary for the formation of all the compounds to be described except CsPb_2Cl_6 and CsPb_2Br_6 , which are almost stable with water. The concentration of the alkaline halide solution evidently determines, in the cases of the chlorides and bromides, the type of salt produced. Since the simple cæsium halides are much more soluble than those of potassium, it is possible to use them in much more concentrated solutions, and the salts Cs_3PbCl_6 and Cs_3PbBr_6 are readily obtained. In the case of potassium bromide the solution becomes saturated with the simple salt by concentration just beyond the point where $\text{K}_2\text{PbBr}_4 \cdot \text{H}_2\text{O}$ is obtained, and with potassium chloride, which is less soluble than the bromide, the limit is reached at the compound $3\text{KPbCl}_5 \cdot \text{H}_2\text{O}$. The apparent existence of only a single double iodide, both with cæsium and potassium, is remarkable since cæsium iodide is

* This Journal, III, xli, 213.

† Berichte d. Chem. Ges., vii, 375.

very soluble and potassium iodide is much more soluble than the bromide and chloride.

On account of their decomposition by water, no determinations of the solubility of the double halides have been made, but it was noticed that the cæsium compounds were much less soluble in the saline solutions than the corresponding potassium salts. This relation corresponds with the observation of Godeffroy,* that while the simple salts increase in solubility from potassium to cæsium, the double and complicated salts show a decrease in this direction.

All the chlorides and bromides described in this article are colorless, or in one case nearly so, except two cæsium salts, CsPbCl , and one modification of CsPbBr_3 . The first of these is pale yellow and the other bright orange. These colors are very remarkable since the simple halides from which they are made are all colorless. I have previously observed a similar case, where a colored double halide was formed from two colorless halides, in the compound CsHgBr_3 .† Both double iodides are yellow, the hydrous potassium salt being the paler of the two.

Analytical Methods.

Great care was used in selecting homogeneous material for analysis. The crystals were dried as rapidly and thoroughly as possible by pressing them between smooth filter-papers, and where the substance did not lose its luster by the operation, it was then exposed to the air for several hours.

Water was determined by collecting and weighing it in a calcium-chloride tube, the substance being ignited in a combustion-tube, behind a layer of dry sodium carbonate, in a current of dry air. The water lost over sulphuric acid or at certain temperatures was determined by the usual methods.

Lead was determined in two ways. With all the cæsium salts the substance was dissolved in hot water (an easy operation with all these salts, but impracticable in the case of some of the potassium compounds), and all except a trace of lead was precipitated by ammonium carbonate in presence of ammonium hydroxide. The precipitate of lead carbonate was removed by filtration and the remaining trace of lead was precipitated by passing hydrogen sulphide into the alkaline solution. The lead sulphide was collected and ignited by itself in a porcelain crucible. The amount of this was so small that it was evident that no appreciable error would arise from any lead sulphate that the ignited residue might contain, so that the main precipitate of lead carbonate was ignited in the same

* *Berichte d. Chem. Ges.*, ix, 1365.

† *This Journal*, III, xlv. 227.

crucible and the whole was weighed and calculated as lead oxide. A different method was selected for the determination of lead in the potassium compounds, for the reason that some of them could not be readily dissolved in hot water, and it was found to be more convenient and expeditious than the other. About one gram of substance was dissolved in about 10^{cc} nitric acid (sp. gr. 1.20), about 2^{cc} concentrated sulphuric acid, previously diluted with water were then added and the nitric acid was removed by evaporation. After diluting with about 25^{cc} of water and cooling, the lead sulphate was collected in a Gooch crucible, washed with very dilute sulphuric acid, ignited and weighed.

In order to determine cæsium, the alkaline solution from which the lead had been removed was concentrated until the ammonium carbonate, hydroxide and sulphide had been nearly or quite removed, a small excess of sulphuric acid was added, and, after evaporation and ignition, normal cæsium sulphate was obtained by igniting in a current of air containing ammonia and this was weighed.

The filtrates from the lead sulphate did not contain an appreciable amount of lead. Normal potassium sulphate was obtained from these solutions by evaporating, igniting and heating in an ammoniacal atmosphere.

The halogens were determined as silver halides. Where the substance could be completely dissolved in hot water, an excess of silver nitrate was added to the hot solution and it was afterwards acidified with nitric acid. When it happened that the lead halide remained partly undissolved, the nitric acid was not added until this had been completely decomposed by long digestion on the water-bath with an excess of silver nitrate. The precipitates were collected and weighed in Gooch crucibles.

The Cæsium-Lead Chlorides; by G. F. Campbell.

Cs₄PbCl₆.—When lead chloride is dissolved, by the aid of heat, in a solution of cæsium chloride which is so concentrated as to be nearly saturated when cold, this salt is deposited on cooling in the form of brilliant, white rhombohedrons. Crystals having a diameter of 2 or 3^{mm} were sometimes obtained. Two entirely separate crops were analyzed, both of which were undoubtedly free from other compounds.

	Found.		Calculated for Cs ₄ PbCl ₆ .
Cæsium	55.60	56.03	55.90
Lead	----	21.63	21.75
Chlorine	21.97	22.23	22.35
		<hr/> 99.89	<hr/> 100.00

CsPbCl₃.—On gradually diluting the concentrated solution of cæsium chloride, such as was used in making the previous salt, and dissolving lead chloride in it as before, a point is soon reached where short prismatic crystals of small size and of a pale yellow color are deposited on cooling. Three different crops of apparently pure crystals were analyzed.

		Found.		Calculated for CsPbCl ₃ .
Cæsium . . .	31.33	30.54	30.13	29.79
Lead	44.99	45.28	46.29	46.36
Chlorine . . .	23.85	23.75	23.71	23.85
	<hr/>	<hr/>	<hr/>	<hr/>
	100.17	99.57	100.13	100.00

CsPb₂Cl₅.—Experiments with still more dilute solutions, carried out in a similar manner, gave, under wide variations of conditions, this salt in the form of thin white plates which were often several millimeters in diameter. These plates presented marked variations in habit, which were apparently due to changes in the conditions under which they were made. In two crops, of which A and B are the analyses, the plates were uniformly rhomboidal in form. Two other crops, C and D, were made up of lengthened plates, so twinned as to form feathery aggregates. In another crop, E, made from a more dilute solution than the others, the plates were apparently square.

	A.	B.	Found. C.	D.	E.	Calculated for CsPb ₂ Cl ₅ .
Cæsium . .	19.99	18.44	18.27	----	18.45	18.36
Lead	57.14	57.16	57.06	56.98	57.08	57.16
Chlorine . .	----	24.47	----	24.52	24.35	24.48
	<hr/>	<hr/>			<hr/>	<hr/>
		100.07			99.88	100.00

The three different habits in which this salt crystallizes are so distinct in appearance that, before the samples were analyzed, it was supposed that they were separate compounds. It appears probable that the compound is at least dimorphous.

The Cæsium-Lead Bromides; by P. T. Walden.

Cs₂PbBr₆.—This salt is produced, in concentrated solutions, similarly to the corresponding chloride. Like the latter salt it forms white rhombohedrons. The crystals were usually not over 1 or 2^{mm} in diameter. Two separate crops were prepared and analyzed.

	Found.		Calculated for Cs_4PbBr_6 .
Cæsium	43.61	43.42	43.64
Lead	16.83	16.83	16.98
Bromine	39.24	39.33	39.38
	<hr/> 99.68	<hr/> 99.58	<hr/> 100.00

CsPbBr_3 .—This compound is dimorphous. One modification forms small prisms of a bright orange color, the other is pure white and crystallizes in slender needles. The orange salt is obtained when lead bromide is dissolved in somewhat more dilute solutions of cæsium bromide than those required for the formation of Cs_4PbBr_6 , and there is a narrow range of conditions where it crystallizes upon the latter salt. There is, therefore, no evidence of the existence of an intermediate compound, Cs_2PbBr_4 , corresponding to one of the potassium-lead bromides. Whenever solid lead bromide is added to a concentrated solution of cæsium bromide, it instantly loses its white color and takes on that of the orange salt. The white needles are formed in solutions which are slightly more dilute than those required for the orange modification. The limits of the conditions, under which this white salt is formed, are very narrow and a great many trials were necessary before satisfactory crops were obtained. Two distinct samples of each salt were analyzed. The white needles were not absolutely free from the orange compound, but there is no doubt that they were sufficiently pure to show their composition accurately.

	Found.				Calculated for CsPbBr_3 .
	Orange salt		White salt.		
Cæsium...	23.19	23.13	23.02	22.49	22.93
Lead	35.69	35.39	35.24	35.88	35.69
Bromine ..	41.37	41.34	41.47	41.45	41.38
	<hr/> 100.25	<hr/> 99.86	<hr/> 99.73	<hr/> 99.82	<hr/> 100.00

On heating the white modification to about 140° , it gradually assumes the exact color of the orange salt, without changing its external form, and this color is permanent on cooling.

CsPb_2Br_5 .—This salt is produced in solutions which are still more dilute than those from which the preceding compounds are obtained. It was first noticed at a volume of about 160° of a solution containing about 50% of cæsium bromide. It continued to form, on further dilution and the addition of lead bromide, until the volume reached 1250° , when lead bromide began to be deposited. The conditions under which the salt is formed are, therefore, very wide. The

compound crystallizes in thin, white plates, which, like the corresponding chloride, present considerable differences in habit. Plates having a diameter of about 5^{mm} were sometimes obtained. Three separate crops of crystals were analyzed.

		Found.		Calculated for CsPb ₂ Br ₃ .
Cæsium	14.13	14.35	----	14.05
Lead	43.39	43.72	43.45	43.71
Bromine	42.23	42.21	----	42.24
		<hr/>		<hr/>
		99.75	100.28	100.00

*The Cæsium-Lead Iodide, and some Mixed Double-Halides ; by
A. P. Wheeler.*

CsPbI₃.—Under a great variety of conditions this was the only double iodide that could be produced. The compound is but slightly soluble in hot cæsium iodide solutions, so that the crops obtained were always small. It forms very slender, rectangular prisms which are yellow in color. The following analyses were made on separate products :

		Found.		Calculated for CsPbI ₃ .
Cæsium	17.90	----		18.45
Lead	28.38	27.40		28.71
Iodine	52.83	52.57		52.84
		<hr/>		<hr/>
		99.11		100.00

Three double salts have been made by dissolving lead bromide in solutions of cæsium chloride. The analyses show that the two salts do not combine unchanged, but that there is usually an extensive exchange of halogens. Each of the products must be considered, therefore, as a mixture of a double chloride with the corresponding double bromide.

Cs₄Pb(Cl, Br)₆.—This was produced in rhombohedrons, like the chloride and bromide. Two crops were analyzed.

		Found.	
Cæsium	54.65	55.50	
Lead	19.30	18.61	
Chlorine	15.89	19.90	
Bromine	9.52	4.03	
		<hr/>	<hr/>
		99.36	98.04
Ratio, Br : Cl	1 : 3.8		1 : 11.2

$CsPb(Cl, Br)_3$.—This occurred in small rectangular prisms, like the chloride and bromide and having a yellow color intermediate between them. Two crops gave the following analyses:

	Found.	
Cæsium	30.24	30.50
Lead	44.23	43.55
Chlorine	21.44	18.94
Bromine	4.00	8.79
	<hr/>	<hr/>
	99.91	101.96
Ratio Br : Cl	1 : 12	1 : 4.8

$CsPb_2(Cl, Br)_5$.—This was obtained in white plates resembling the two double salts. Two products were analyzed.

	Found.	
Cæsium	18.94	---
Lead	51.40	51.97
Chlorine	16.29	19.31
Bromine	13.27	8.62
	<hr/>	
	99.90	
Ratio Br : Cl	1 : 2.8	1 : 5

The Potassium Lead Halides.

In studying these bodies care has been taken to record the conditions under which they were made. These conditions, in many cases are only approximately given, because uncertain quantities of salts had often been removed from the solutions, either for analysis or in order to obtain smaller and better crops of crystals. A large number of analyses have been made in some cases. This was due to the fact that the salts often varied so little in appearance that it was necessary to analyze many products in order to identify them and to be certain that they were not different compounds.

$3K Pb Cl_4 \cdot H_2 O$.—When lead chloride is dissolved in a hot solution of potassium chloride which is so concentrated as to be nearly saturated when cold, this double salt is deposited on cooling. It forms brilliant prismatic crystals which are largest in the most concentrated potassium chloride solutions. The largest crystals obtained had a length of more than 10^{mm} and a diameter of 1 or 2^{mm}. It was noticed that, when sufficiently concentrated solutions were used, pure potassium chloride crystallized upon this compound, and no evidence was obtained of the existence of a double salt containing a larger proportion of potassium chloride than this.

The following table gives the approximate conditions under which the five samples which were analyzed were made.

	KCl.	PbCl ₂ .	Volume.	Volume for 1gKCl.
A	400 ^g	30 ^g	1100 ^{cc}	2 $\frac{3}{4}$ ^{cc}
B	400	80	1200	3
C	150	40	450	3
D	100	25	350	3 $\frac{1}{2}$
E	300	55	1300	4 $\frac{1}{3}$

The results of the analyses are as follows :

	A.	B.	C.	D.	E.	Calculated for 3KPbCl ₃ · H ₂ O.
K	11·38	11·10	10·79	-----	-----	10·90
Pb ...	57·46	57·68	57·43	57·94	57·14	57·73
Cl ...	29·91	29·87	29·81	-----	-----	29·70
H ₂ O ..	1·45	1·39	-----	1·51	1·88	1·67
	<hr/> 100·20	<hr/> 100·04				<hr/> 100·00

All the samples were thoroughly air-dried before they were analyzed. By this treatment the crystals did not lose any of their luster. A finely pulverized portion of sample A lost only 0·02 per cent in weight after standing over concentrated sulphuric acid for eight days. The same sample suffered an additional loss of 0·23 per cent when heated for twelve hours in a steam drying-oven. The water was not rapidly given off until a temperature of about 200° was reached. The salt decrepitates when heated rapidly to about 200°, corresponding in this respect to the salt which Remsen and Herty described as anhydrous and to which they gave the formula KPbCl₃. There can be no doubt, therefore, that Remsen and Herty's formula is incorrect.

KPb₂Cl₅.—This salt is formed in more dilute solutions than those which produce the previously described compound. It occurs, like that compound, in white prismatic crystals, but it differs considerably from it in luster and form, so that the two salts can be distinguished by microscopic examination. The salt under consideration is anhydrous, and this fact makes it easy to distinguish this compound, when pure, from the other.

Four analyzed crops were made under the following conditions :

	KCl.	PbCl ₂ .	Volume.	Volume for 1gKCl.
A	200 ^g	50 ^g	1500 ^{cc}	7 $\frac{1}{2}$ ^{cc}
B	150	30	1100	7 $\frac{1}{3}$
C	150	20	1100	7 $\frac{1}{3}$
D	250	55	1200	4 $\frac{8}{10}$

The analyses were as follows:

	A.	B.	C.	D.	Calculated for KPb_2Cl_3 .
Potassium..	6.14	5.97	6.18	6.07	6.20
Lead	64.74	66.43	65.85	65.72	65.65
Chlorine ...	28.11	----	28.13	28.08	28.15
Water	0.11	----	----	----	0.00
	99.10		100.16	99.87	100.00

There was no indication of the formation of any other double chloride as the dilution was increased beyond that given for the above products, and when a solution containing 1^g of KCl in 11^{cc} was used pure lead chloride was deposited.

$K_2PbBr_4 \cdot H_2O$.—This salt is obtained by dissolving lead bromide in the most concentrated solutions of potassium bromide. It forms brilliant, prismatic crystals which are permanent in the air. The largest of these which were obtained were about 1^{mm} in diameter and 5^{mm} in length. A number of crops were made under the following conditions:

	KBr.	PbBr ₂ .	Volume.	Volume for 1gKBr.
A	400 ^g	70 ^g	700 ^{cc}	1 $\frac{3}{4}$
B	400	90	700	1 $\frac{3}{4}$
C	400	120	800	2
D	400	130	650	1 $\frac{6}{10}$
E	500	130	850	1 $\frac{7}{10}$
F	500	130	775	1 $\frac{6}{10}$

These products gave the following analyses:

	K.	Pb.	Br.	H ₂ O.
A	12.51	34.25	51.47	2.50 = 100.73
B	12.21	34.59	51.21	2.51 = 100.52
C	11.89	34.47	51.14	2.44 = 99.94
D	12.37	34.50	51.35	----
E	----	34.26	51.40	2.61
F	12.70	33.89	51.46	2.57 = 100.62
Calculated for } $K_2PbBr_4 \cdot H_2O$ }	12.55	33.21	51.35	2.89 = 100.00

This salt is apparently stable in the air, but it loses water very slowly over sulphuric acid. A finely powdered sample of A lost 0.23 per cent after remaining 12 hours in the desiccator, and the same portion suffered an additional loss 0.33 after eight days. A sample which was not pulverized lost only 0.09 per cent in 12 hours and, in addition, 0.17 per cent in eight days. About one-half of the water went off when the substance was heated for 12 hours in a steam drying-oven. At 200° the water is rapidly and completely expelled.

$3K Pb Br_2 \cdot H_2O$.—The conditions under which this salt can be made are rather narrow, and these conditions encroach upon those of the preceding compound, so that small differences in the amounts of lead chloride used or in the temperature of the solution are sufficient to cause the formation of the other salt. It forms brilliant, colorless, lozenge-shaped crystals which can be easily distinguished from the other compound. The crystals which were obtained sometimes had a diameter of 2 or 3^{mm}.

The crops analyzed were made under the following conditions:

	KBr.	PbBr ₂ .	Volume.	Volume for 1g KBr.
A	500 ^g	130 ^g	950 ^{cc}	$1\frac{9}{10}$
B	500	130	1050	$2\frac{1}{10}$
C	500	140	900	$1\frac{8}{10}$
D	500	120	1050	$2\frac{1}{10}$
E	500	120	1125	$2\frac{1}{4}$

The analyses were as follows:

	K.	Pb.	Br.	H ₂ O.
A	8.44	41.91	—	1.29
B	8.02	42.71	48.95	1.62 = 101.30
C	8.60	41.61	49.16	1.60 = 100.97
D	8.08	42.69	48.91	1.14 = 100.82
E	—	42.61	—	1.17
Calculated for } 3KPbBr ₂ · H ₂ O }	7.95	42.06	48.77	1.22 = 100.00

The salt is stable in the air. A sample, after standing seven days over sulphuric acid, lost only 0.04 per cent. The water is given off very slowly at 100°.

$K Pb Br_2 \cdot H_2O$.—This salt was described by Remsen and Herty. At summer temperature, about 25°, I was unable to obtain it, but by placing the mother-liquors from the preceding salt in an ice-chest, beautifully crystallized crops of it were obtained.

Its formation was also noticed at laboratory temperatures when the weather was somewhat cooler than in mid-summer. It forms prismatic crystals. Some of those obtained were about 10^{mm} long and 2^{mm} in diameter. Two crops were analyzed.

	Found.	Calculated for KPbBr ₂ · H ₂ O.
Potassium	8.24	7.90
Lead	41.23	41.20
Bromine	47.81	—
Water	3.28	3.64
	100.56	100.00

The salt is usually permanent in the air, but in dry weather the crystals gradually become opaque, and over sulphuric acid about two thirds of the water is rapidly given off.

KPb₂Br₅.—This salt crystallizes in square plates, sometimes 3 or 4^{mm} in diameter. It can be readily distinguished from the other double bromides, not only by its form, but from the fact that it quickly assumes a pale green color when exposed to daylight. On long exposure, or in direct sunlight, this color changes to a pale dirty-brown. I have observed that lead bromide itself becomes nearly black on long exposure to daylight. This fact does not appear to be generally known.

The samples analyzed were made under the following conditions :

	KBr.	PbBr ₂ .	Volume.	Volume for 1gKBr.
A	400 ^g	130	1050 ^{cc}	2 $\frac{2}{3}$
B	400	150	1250	3 $\frac{1}{8}$
C	200	75	1000	5

The results of the analyses are as follows :

	A.	B.	C.	Calculated for KPb ₂ Br ₅ .
Potassium	4.75	4.75	4.71	4.58
Lead	49.22	49.11	48.48	48.53
Bromine	47.03	46.98	46.89	46.89
	<hr/> 101.00	<hr/> 100.84	<hr/> 100.08	<hr/> 100.00

KPbI₃ . 2H₂O.—It has already been mentioned that this is the only double iodide that either Remsen and Herty or I have been able to make. It forms slender, pale yellow needles, and is produced under a great variety of conditions. Two samples were analyzed. A was made with about 450^gKI, 75^gPbI₂, and 600^{cc} volume. For B about 400^gKI, 45^gPbI₂, and 280^{cc} volume were used.

	A.	B.	Calculated KPbI ₃ . 2H ₂ O.
Potassium	6.03	6.07	5.90
Lead	30.73	30.13	31.21
Iodine	57.57	56.99	57.46
Water	5.26	6.04	5.43
	<hr/> 99.59	<hr/> 99.23	<hr/> 100.00

The salt is apparently stable in the air, but it loses water in the desiccator.

Sheffield Scientific School.
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