ART. XXVIII.—*On some Peculiar Halides of Potassium and Lead*; by H. L. WELLS.

IN a preceding article I have described a series of double chlorides of the type M_2PbCl_6 , where M is NH_4 , K, Rb and Cs. It has seemed desirable to extend the investigation by attempting to prepare bromides and iodides corresponding to these salts. A thorough search has been made, using the metals of the potassium group and sodium, with the result that no double bromides or iodides containing extra halogen could be prepared except in the case of potassium. It is remarkable that the potassium-lead bromide and iodide which have been discovered do not correspond in composition to the chlorides. The failure to prepare double salts of rubidium and caesium corresponding to the new potassium compounds was unexpected, for, as a general rule, the insolubility and stability and the consequent ease of preparation of such compounds become greater from potassium towards caesium. The explanation of the anomaly probably lies in the fact that extremely concentrated rubidium and caesium solutions containing a lead halide and the corresponding halogen cannot be obtained, in the case of the bromides and iodides, on account of the slight solubility of caesium triiodide, and of the double halides which are formed with $PbBr_2$ and PbI_2 .

The compounds to be described probably have the composition represented by the following formulæ:

* Method of Godeffroy, *Berichte*, vii, 375.

These formulæ may be also written,

The composition of these salts is very remarkable on account of the small amount of the extra halogen that they contain. They apparently do not correspond to any other chemical compound that is known.

The Iodide, $\text{K}_3\text{Pb}_2\text{I}_3 \cdot 4\text{H}_2\text{O}$:— This salt forms brilliant, black, prismatic crystals, sometimes a centimeter or two in length and three or four millimeters in diameter. Although the crystals have fine prismatic faces, they never appear to have definite terminations. The ends usually appear fibrous, as though made up of numerous small crystals in parallel position. When the crystals are crushed on paper it is evident that they enclose much mother-liquor. The salt is deposited from nearly or quite saturated solutions of potassium iodide containing lead iodide and iodine. It is deposited at ordinary temperature, usually slowly, after the lapse of several hours or even after several days. In preparing the compound, the lead iodide and the iodine can be varied considerably, but it is formed only in very concentrated potassium iodide solutions and it is difficult to obtain crops of it which are not evidently contaminated with this salt in the form of crystals. The salt is stable in the air but it is instantly decomposed by water or alcohol, so that it cannot be washed.

Six separate crops have been analyzed, and great care has been used in selecting them and in drying them on paper for analysis. In two cases the product was rapidly and finely pulverized during the drying operation, but without any effect upon its composition. The results of the six analyses agree with remarkable closeness, but in spite of this fact it must be assumed, from considerations which will be given subsequently, that all these products were seriously contaminated with potassium iodide. The fibrous nature of the crystals and the concentration of the mother-liquor make the possibility of such a contamination very evident, but the constancy of this contamination, as indicated by the uniformity of the analyses, is very remarkable in view of the fact that some of the products were made at wide intervals of time, covering a period of about six months, so that there were considerable variations in the laboratory temperature.

The products were made under the following conditions:

	KI	PbI ₂	I	Volume.
A	450 ^g	30 ^g	15 ^g	?
B	425	30	50	450 ^{cc}
C	445	40	70	470
D	445	40	100	470
E	445	40	150	460
F	200	15	15	200

They gave the following results on analysis:

	K	Pb	I	H ₂ O
A	9.31	22.03	64.00	4.69 = 100.03
B	9.25	22.30	----	4.81
C	9.07	22.03	63.98	4.89 = 99.97
D	9.21	21.98	64.09	4.71 = 99.99
E	9.20	22.13	64.17	----
F	9.27	22.02	63.84	----

In these analyses and those which follow, water was determined by weighing it directly in a calcium-chloride tube. The other determinations were made according to the methods mentioned in the preceding article on the double salts of lead tetra-chloride.

The above analyses correspond closely to the formula $K_3Pb_4I_{10} \cdot 10H_2O$, but it will be shown beyond that the probable formula of the pure compound is $K_3Pb_4I_6 \cdot 4H_2O$. This requires $K=7.25$, $Pb=25.56$, $I=62.74$ and $H_2O=4.45$. If this is the true composition, it must be assumed that all of the analyzed products were contaminated with about 16.5 per cent of potassium iodide, and that an excess of water was present, possibly on account of the hygroscopic properties of that salt.

It is to be noticed that the products were prepared under great variations in the amount of iodine present, and it can be safely assumed, from the care with which the products were examined, that they were not contaminated with the salt $KPbI_3 \cdot 2H_2O$ nor any similar compound. The amount of lead iodide in the solutions was comparatively small, and a large part of it was used in forming the salt under consideration, so that any contamination must have been chiefly potassium iodide. It is therefore evident, since the salt is not decomposed on exposure, and since the analyses show a constant amount of extra iodine in spite of the variations of this ingredient in the solutions, that the analyses must show the true ratio between the lead iodide and the extra iodine in the pure compound. This ratio is $2PbI_2:I$ in both $K_3Pb_4I_{10}$ and $K_3Pb_4I_6$.

The Bromide, $K_3Pb_4Br_6 \cdot 4H_2O$.—This compound forms dark brown, prismatic crystals which are solid and definitely terminated, so that they do not have the tendency to hold in-closed mother-liquor which the iodide has. The salt is easily

prepared and it crystallizes well, but it is extremely unstable. When exposed to the air it begins to whiten almost instantly, giving off bromine. It is stable, however, in air containing a considerable amount of bromine vapor, so that it can be dried by pressing on paper in such an atmosphere. It is sufficiently stable, when corked up in a weighing-tube, to be rapidly weighed in a cold room without serious decomposition.

Three crops of the double bromide were analyzed. A and B were made, in each case, by adding 20^{cc} of bromine to 400^{cc} of a cold solution which was saturated with potassium bromide and lead bromide and allowing the mixture to stand over night. C was made like the other crops, except that 30^{cc} of bromine were used.

	A	Found. B	C	Calculated for $K_2Pb_2Br_8 \cdot 4H_2O$
Potassium ----	10.33	10.41	10.24	9.43
Lead -----	32.05	31.90	32.49	33.30
Bromine -----	51.96	52.15	52.05	51.48
Water -----	----	5.59	5.28	5.79
		<hr/> 100.05	<hr/> 100.06	<hr/> 100.00

The analyses agree with the formula as well as could be expected, considering the instability of the compound. The analyses show almost exactly one atom of extra bromine for two atoms of lead, so that the compound is closely related to the iodide if not exactly analogous to it.

The satisfactory crystals of the bromide and the stability of the iodide suggested the possibility that, if the two compounds were really analogous as suspected, isomorphous mixtures of the two could be made which would retain the desirable qualities of both, so as to be solidly crystallized and stable enough to be accurately analyzed. Experiments showed that isomorphous mixtures could be readily obtained which crystallized satisfactorily, and it was found that even small amounts of iodine had the effect of greatly increasing the stability of the compound. It was noticed that when a product was made from a solution containing free bromine and iodine in nearly atomic proportions (BrI), an almost perfectly stable, bright red salt was obtained. The color of this salt is far from being intermediate between that of the black iodide and the dark brown bromide, but, since the analyzed products contain about 23 atoms of bromine to one of iodine, it does not seem probable that any definite relation between the two halogens exists. It is remarkable that such a small proportion of iodine should have so great an influence upon the color and stability of the product, but it is to be noticed that only one eighth of the

halogens in these compounds is in excess, so that, if all the iodine is in this condition it amounts to about one-third of this excess.

The crops A and B had a dark bronze color. They were successive crops made by adding bromine to a strong solution of potassium iodide containing lead iodide. The exact conditions are unknown, but it is probable that insufficient bromine was used to set free all the iodine which the solution contained. These products were apparently as stable as the iodide.

C and D were successive crops made by continuing the addition of bromine to a somewhat similar solution until a change of color showed that the free iodine had been converted into PbI_2 . These salts were red. An analysis of the mother-liquor from D gave, $\text{KBr} = 31.3$, $\text{PbBr}_2 = 1.8$, $\text{Br} = 6.7$, $\text{I} = 8.3$, $\text{H}_2\text{O}(\text{difference}) = 51.9$.

E was made by adding 31% of bromine to 430% of the above-mentioned, analyzed solution. This crop was also red, but it was not quite as bright in color and not as stable as the others. On continuing the addition of bromine, still less stable crops were obtained which approached the pure bromide in color. These were not analyzed.

The analyses of the five crops are as follows:

	K	Pb	Br	I	H_2O
A	9.41	31.57	41.40	12.06	$5.09 = 99.53$
B	9.24	31.55	39.27	14.57	----
C	9.90	32.88	48.66	3.40	$5.24 = 100.08$
D	9.99	32.74	48.70	3.30	$5.02 = 99.75$
E	10.24	32.26	49.97	2.07	----

The ratios calculated from the above analyses are as follows:

	K	:	Pb	:	Br + I	:	H_2O
A	1.57		1.		3.99		1.83
B	1.55		1.		3.99		----
C	1.59		1.		4.00		1.82
D	1.61		1.		4.00		1.76
E	1.68		1.		4.16		----

The ratio required for the formula $\text{K}_3\text{Pb}_2(\text{Br}, \text{I})_8 \cdot 4\text{H}_2\text{O}$ is,

K	:	Pb	:	Br + I	:	H_2O
1.50		1.		4.		.2.

The analyses agree well with this formula, except that the water is somewhat low. Although $3\frac{1}{2}$ molecules of water would correspond more closely to these analyses than 4, the latter number is considered more probable on account of the fact that the analyses of the iodide show some excess over four molecules.

It is to be seen that these mixed salts correspond in composition to the bromide. The analogous mode of formation of the iodide, the identical relation of the lead to the extra halogen in the iodide and the other products, as well as the existence of these mixed salts, make it appear certain that the analyzed iodide was invariably impure and that the pure compound should be considered as analogous to the other salts. This view has been confirmed by a crystallographic examination of the iodide and the red bromo-iodide, which Prof. S. L. Penfield has kindly undertaken. He has found that both these salts crystallize in prisms of the tetragonal system. Unfortunately the crystals of the iodide were without terminations, so that a more detailed comparison of the two salts could not be made.

The nature of these peculiar salts is not clear. If they are, strictly, hydrous "double salts," such higher halides as Pb_2I_6 or K_3I_4 must be assumed. If they are formed from such compounds as PbI_4 or KI_3 , they must be considered as hydrous triple salts.

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