

A STUDY OF THE DOUBLE CHLORIDS OF
POTASSIUM AND ARSENIC.

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Setterberg, in 1882, (Ofversigt K. Vetensk-Akad, Fofhandl., 1882.) succeeded in preparing a black salt of antimony and caesium, a double chlorid, the emperical formula of which was found to be Cs_2SbCl_6 or $4 CsCl.SbCl_3.SbCl_5$. His method was to treat a boiling solution of antimony trichlorid in concentrated hydrochloric acid with anequally strong solution of antimony pentachlorid also in conc. hydrochloric and an excess of a saturated solution of caesium chlorid. He described the crystals as short prisms. Later work by Wells and Metzger, (Amer. Chem. Jour. 26, 1901, p. 268.) however, leaves us in doubt as to the true form, as the salt prepared by them in the same way, crystallized in octahedra. This seems more likely to be correct.

As the antimony in the black salt of Setterberg has the valence of four, it appears to be a member of the series of hexahalids, such double chlorids as Cs_2PtCl_6 , Cs_2PbCl_6 , Cs_2SnCl_6 etc. The primary object of this work was to prepare, if possible, the corresponding salt of potassium amd arsenic. Previous work along the same line has been done in the Washington and Lee labratory, except that the efforts have been to precipitate the salts from cold solutions while in this case the solutions were all hot. All these earlier attempts have been for the most part, unsuccessful, altho in one instance on record a very dark brown salt having the octahedra form was prepared. But as these crystals were very closely associated with some extremely minute other crystals as arsenious oxid and probably an arsenate, their composition could not be definately established. The work was done with rubidium chlorid so there is a

possibility that their formula was Rb_2AsCl_6 , a member of the same series. All efforts in connection with this paper were in the main, unsuccessful, but several very interesting facts were brought out regarding the equilibrium of arsenic acid and potassium chlorid in a hot solution of hydrochloric acid.

The general method used was to prepare an absolutely saturated solution of potassium chlorid in hydrochloric acid at boiling temperature. Then while still hot, arsenic acid, concentrated to over 90%, was added and a strong stream of hydrochloric acid gas led in. The proportions and other details were varied in every case. Each time a considerable quantity of white crystals came down. These were analyzed qualitatively for chlorin with $AgNO_3$ and for pentavalent arsenic with both magnesia mixture and $AgNO_3$, the latter giving a brown precipitate soluble in nitric acid.

A quantitative determination then was carried out. First the arsenic was titrated with uranium acetate standardized with pure arsenious oxid in nitric acid. This titration for the AsO_4 group — for the pentavalent arsenic is in this form in solution due to hydrolysis — is quite different. The indicator is a freshly prepared solution of potassium ferro-cyanid and is external. As the brown shade given this by uranium acetate varies with the concentration of the indicator and also of the solution titrated, it was hard to get the same end-point in the several analysis run, especially as the indicator could not be saved from day to day. To remedy this as far as possible

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the samples were put into solution in the same quantity of water each time. A little ammonium hydroxid was added to just alkaline reaction to neutralize any mineral acid present, and then acetic acid added to slightly acid reaction for titration. Also the uranium acetate was made quite weak to facilitate accuracy.

The chlorine was then determined by titration with silver nitrate, standardized against potassium chlorid. It was found that this analysis could be carried out with the same samples after the arsenic had been precipitated as uranium arsenate. The red color of the potassium chromate indicator was sufficiently strong to be efficient even with the yellow arsenate present. In a few cases the results were verified with new samples using an excess of silver nitrate in nitric acid solution and titrating back with potassium thio-cyanid solution. The indicator in this case was ferric-nitrate.

In the preparation of most of the salts made, the crystallization was allowed to take place on cooling. In two cases, however, the solutions after the mixture was made were kept boiling until almost dry. SO_2 gas was let in after the mixture in several cases to see if it would reduce part of the arsenic. None was reduced as shown by the absence of trivalent arsenic when tested in a sodium bicarbonate solution with iodine.

Another method was tried using trivalent arsenic as well as the pentavalent. The results are given in the table which

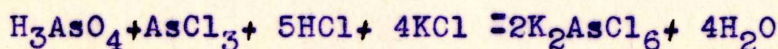
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follows. One very interesting fact should be noted, however. The arsenious oxid used was put in solution in concentrated HCl leading the gas in the while. It was not very soluble. in this even when boiling. But when a saturated solution KCl was added to the boiling mixture, the solubility of the As_2O_3 was markedly increased. The reason for this is probably due to the formation of a double chlorid of arsenic and potassium.

The following table will show the results in brief of a number of the preparations. Many others were made but qualitative analysis proved them to be valueless.

	$\frac{KCl}{H_3AsO_4}$	%As	%AsO ₄	%Cl	%KCl	Remarks
1	1:1	6.5	12.0	42.9	90.5	Boiled down to almost dryness.
2	1:1	3.0	5.5	43.8	92.0	"
3		4.7	8.7	54.0	81.0	\swarrow NH_4Cl used in place of KCl
4	1:2	3.4	6.6	43.3	91.0	
5	1:1	3.5	6.5	43.9	90.4	Led in a little SO_2 while boiling.
6	1:2	3.6	6.6	43.0	90.5	"
7	1:3	3.0	5.6	43.0	90.9	
8		1.8	3.3	43.2	91.1	As_2O_3 also used.

The proportions in number 8 were $As_2O_3 : H_3AsO_4 : KCl$ as 1:1.43:0.75, calculated from the supposed equation,



It was found that there was no trivalent arsenic in the crystals that came down.

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A detailed account of the preparation of one of the samples will be sufficient for all as the several variations have been indicated already. Take for example # 1. The proportions were 1 : 1, which seemed the best supposing the factor to be for the weighed quantities, 2 KCl/H₃AsO₄ and the acid to be between 90% and 100% pure. So 4 gms. of each were taken. The KCl was put in conc. HCl and boiled until dissolved. Then HCl gas was led in. It was generated by sulfuric acid, dilute, on common salt and washed thru conc. hydrochloric. The boiling of the potassium chlorid solution was continued until the crystals started to come out. Then a few drops of water were added to dissolve these. This assured an absolutely concentrated solution at the boiling temperature, a thing desired to prevent hydrolysis as far as possible. The arsenic acid was then added, the HCl gas being continued the while. In # 1, the boiling was continued until the volume of the solution had become so small that spattering commenced. The crystals were then removed from the beaker onto filter paper, washed with very concentrated HCl and dried thoroughly in a sulfuric acid dessicator. They were then ready for analysis.

While the above percentages are probably a little high, owing to a slight difference of end-points taken in the standardization of the uranium acetate and the titrations of the salts, they suffice to show without a doubt, that the numerous salts formed were not double chlorids but merely mixtures of KCl and probably K₃AsO₄. The greater part of the arsenic

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acid remained in solution as was shown by the fact that several samples of the solutions when boiled down after the salt had been removed, became very viscous, due to the almost pure acid.

Looking at the last column in the table of percentages, ~~the~~ the amounts of potassium chlorid considering all the chlorin to be in this form, we see that the figures are nearly constant and are quite high. This indicates that the equilibrium is upset in such a way, on cooling, that the potassium chlorid is nearly completely precipitated taking with it a small amount of the arsenic. It is interesting to note that the amounts of chlorin in the several mixtures are so constant. This may be accounted for by the great excess of Cl^- ions present from the hydrochloric acid.

After the crystals had been filtered from sample # 8 in which the trivalent arsenic was used with the pentavalent, SO_2 gas (generated by conc. H_2SO_4 on charcoal) was led in to the solution to reduce any As^{V} , and the solution partially evaporated. On standing, a few regular crystals separated out. The amount was not sufficient for a quantitative determination. A microscopic examination showed their form to be isometric, octahedra, truncated by cube. Then a very careful qualitative examination showed the presence of chlorin, trivalent arsenic and potassium. The formula was likely $3 \text{KCl} \cdot 2 \text{AsCl}_3$ or $\text{K}_3\text{As}_2\text{Cl}_9$, a salt described by H. L. Wheeler. (Jour. of Chem. Society, 64-II 1893.) This indicates that the equilibrium of the trivalent arsenic is not disturbed until after the new equilibrium of

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the potassium chlorid and the arsenate is established.