III.—*Note on some Double Thiosulphates.*

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Hydrated Potassium Cuprous Thiosulphate.

RAMMELSBERG found that when cupric sulphate or acetate is added to a solution of potassium thiosulphate, and the resulting green liquid is allowed to stand, sulphur-yellow crystals are deposited, consisting of a double thiosulphate of copper and potassium of the formula $K_2S_2O_3, Cu_2S_2O_3, 2H_2O$. These crystals are needles grouped in clusters, and are readily decomposed on warming with water, copper sulphide being deposited. If, however, the addition of potassium thiosulphate be continued until the green colour disappears and gives place to a pale yellow tint (1 part of hydrated cupric sulphate requires about 2 parts of potassium thiosulphate), the resulting solution may be boiled for a long time, and only a very slight deposition of a brown precipitate occurs. On standing, this solution deposits a small quantity of brilliant orange-coloured crystals, which consist of groups of six-sided prisms, terminated by basal planes, and belong to the hexagonal system. The crystals were washed with cold water, dried in the air, and analysed with the following results:—

Calculated for		Found.				
$Cu_2S_2O_3, 2K_2S_2O_3, 3H_2O$.		I.*	II.	III.	IV.	V.
H ₂ O.....	8.03	7.53	—	—	—	—
K.....	23.21	—	23.27	23.34	—	—
Cu.....	18.74	—	19.62	—	19.51	19.67
S.....	28.57	—	—	27.57	—	—

The substance cannot be recrystallised from water, as it is scarcely soluble in the cold, and dissolves with slight decomposition in hot water. Hydrochloric acid decomposes it with evolution of sulphur dioxide and the formation of copper sulphide. Caustic soda precipitates cuprous oxide, and, if exposed to the air in contact with ammonia, it dissolves, forming a blue solution. It may be distinguished from Rammelsberg's salt by its crystalline form, its greater stability in hot aqueous solution, and by the fact that the slight decomposition which then occurs is not accompanied by the formation of sulphate. It may be kept unaltered in the air for several days, but slowly blackens after several weeks, even in a well-closed vessel. It immediately turns black when heated to 100—110°.

* Each number denotes a fresh preparation of the salt.

Anhydrous Potassium Cuprous Thiosulphate.

If 1 part hydrated copper sulphate be added to rather less than 4 parts potassium thiosulphate in hot concentrated aqueous solution, the liquid remains colourless, and, on cooling, a mass of colourless silky needles is deposited. The purification of this salt is attended with some difficulty, as, although almost insoluble in excess of potassium thiosulphate, it is very soluble in the cold in pure water. Nor can the substance be reprecipitated with alcohol, as in this case almost the whole is converted into the yellow modification described above, which separates out in minute hexagonal plates. The needles were therefore freed from mother-liquor by washing them with small quantities of cold water on the filter-pump; there was considerable loss, however. The air-dried substance gave the following results on analysis, corresponding with the formula $\text{Cu}_2\text{S}_2\text{O}_3, 2\text{K}_2\text{S}_2\text{O}_3$:—

	Calculated for $\text{Cu}_2\text{S}_2\text{O}_3, 2\text{K}_2\text{S}_2\text{O}_3$.	Found.	
		I.	II.
Cu	20.38	20.65	20.02

Its behaviour with reagents is similar to that of the yellow salt. It does not change colour nor lose weight at 100 — 110° ; but begins to blacken at 120° with evolution of sulphur dioxide.

Barium Cuprous Thiosulphate.

The colourless and yellow salts both give with barium chloride the same white curdy precipitate of a barium cuprous thiosulphate, which dissolves readily in boiling water, but is scarcely soluble in cold water. The analyses of the barium salt, dried at 100 — 110° , gave results which apparently do not correspond with any simple formula.

	Found.		
	I.	II.	III.
Ba	34.08	34.36	33.78
Cu	16.85	—	—
S	17.84	—	—

Nos. 1 and 2 are analyses of the barium compound obtained from different preparations of the yellow potassium salt; No. 3 is obtained from the anhydrous white salt.

Potassium Silver Thiosulphate.

A double thiosulphate of silver and potassium has been prepared by Herschel by adding to a solution of silver chloride in sodium thio-

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sulphate a strong solution of potash or a potassium salt. If 2 parts of potassium thiosulphate in solution is added to 1 part of silver nitrate in solution and boiled, a black precipitate of silver sulphide is formed and sulphur dioxide evolved. On the other hand, if the solution whilst boiling be kept slightly alkaline with potassium carbonate, the amount of black precipitate is very much diminished, and the filtrate on standing deposits long colourless transparent prisms of the double salt, some of them an inch long. Analyses of the compound gave the following results, corresponding approximately with the formula $\text{Ag}_2\text{S}_2\text{O}_3, 2\text{K}_2\text{S}_2\text{O}_3$.

	Calculated for $\text{Ag}_2\text{S}_2\text{O}_3, 2\text{K}_2\text{S}_2\text{O}_3$.	Found.	
		I.	II.
K	22·03	—	22·19
Ag.....	30·50	33·14	33·12
S	27·11	26·62	26·58

The salt does not lose weight at 100—110°, but a few brown specks make their appearance. It is decomposed by acids and alkalis, but does not change in the air nor on keeping for a length of time.