ART. XXXI.—*On the Separation of Cæsium and Rubidium by the Fractional Crystallization of the Aluminium and Iron Alums and its Application to the Extraction of these Elements from their Mineral Sources;* by PHILIP E. BROWNING and S. R. SPENCER.

[Contribution from the Kent Chemical Laboratory of Yale Univ.—cclxxxi.]

ROBINSON and Hutchins* have recommended the crystallization of the aluminium alums for the separation of cæsium and rubidium from potassium and lithium in lepidolite after the decomposition of that mineral by fluorspar and sulphuric acid. They have also called attention to the difference in solubility between the cæsium and the rubidium alums† and have suggested fractional crystallization for the separation of these elements. The marked difference in solubility between the potassium alum and the alums of cæsium and rubidium makes the method quite satisfactory for the separation of potassium from these rare alkalies, but the difference in solubility between the alums of cæsium and rubidium is not sufficiently great to bring about a rapid separation of these elements.

The work to be described was undertaken to obtain some definite information as to the value of the process of fractional crystallization when applied to the problem of separating the alkalies.

The process may be briefly described as follows:

A solution obtained from the decomposition of lepidolite by heating with fluorspar and sulphuric acid after the removal of the calcium sulphate was evaporated until on standing the mixed alums crystallized out. The mother liquor was poured off into a second flask and this liquid was evaporated until another crop of crystals was obtained and the new mother liquor poured into a third flask, and so on. The crystals in the first flask were dissolved in a small amount of water, by warming, and again allowed to crystallize, the supernatant liquid being poured into the second flask upon the crystals which had formed there; these crystals, in turn, were dissolved in this liquid and allowed to recrystallize; and the process was continued through all the series of flasks. The crystals separating in flask number one were repeatedly dissolved in fresh water and allowed to recrystallize in this way, and the mother liquor was kept moving along the series of flasks in succession.

By this method the more insoluble alum was concentrated at the upper end of the series while the more soluble alum moved toward the lower end.

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* Amer. Chem. Jour., vi. 74.

† Note: 100 parts of water at 15–17° C. will dissolve 0·62 parts of cæsium alum, 2·3 parts of rubidium and 13·5 parts of potassium alum.

After six such crystallizations applied to a solution of the alkalies from lepidolite, the crystals in the first flask showed only cæsium and rubidium when examined before the spectroscope on a platinum wire, and the crystals in the sixth flask gave a decided test for potassium and a very strong test for lithium, and showed only traces of cæsium and rubidium.

A mixture of cæsium and rubidium alums obtained by the above process was subjected to this same crystallization method. After about seven crystallizations, the crystals in the first flask were found to be pure cæsium alum but the crystals in the sixth flask, while strong in rubidium, still gave evidence of the presence of cæsium. The process of crystallization was continued until twenty-two fractions had been obtained before the cæsium had been completely removed. The crystals in the twenty-second flask proved to be pure rubidium alum, no evidence of the presence of cæsium being found.

Locke,* in studying the properties of the alums, has called attention to the differing solubilities of these interesting compounds, and notes in particular the great difference of solubility of the cæsium and rubidium iron alums† as compared to that of the corresponding aluminium alums; and it has been suggested that this difference might be of analytical value.

In order to investigate this point a mixture of cæsium and rubidium iron alums was prepared and subjected to the same process described above. After four crystallizations, the crystals in flask number one gave no test for rubidium but showed abundance of cæsium; and after the process had been continued until eight fractions were obtained, the eighth fraction was found to be free from cæsium and contained pure rubidium alum.

A further experiment was made as follows: Ten grams of the mixed cæsium and rubidium alums from lepidolite were dissolved in water and the aluminium hydroxide was precipitated by ammonium hydroxide and filtered off. The filtrate, evaporated to about 130 cm^3, was poured upon some crystals of ammonium ferric alum in quantity somewhat in excess of the amount necessary to allow the replacement of the ammonium by the cæsium and rubidium. The solution was then warmed until the crystals were dissolved. On cooling, crystals separated which, when examined, gave abundant evidence of cæsium but no test for rubidium.

This experiment suggested a convenient method for the formation of cæsium alum and also seemed to show that the more insoluble alums were readily thrown out of solution by treatment with strong solutions of the more soluble alums.

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* Amer. Chem. Jour., xxvi. 166.

† 100 parts of water at 25° C. dissolve 2·7 parts of cæsium alum and about 17 parts of rubidium alum.

This method was applied quite successfully to the extraction of cæsium from pollucite as follows:

The mineral was decomposed by hydrochloric acid, and after evaporation and the removal of silica the acid extract was poured upon crystals of ammonium aluminium alum and warmed until the crystals had dissolved. On cooling, cæsium alum separated in abundance; and the mother liquor, although not free from cæsium, after one treatment consisted mainly of ammonium chloride. After about two recrystallizations the crystals obtained in the first treatment were found to give no test for either ammonium or chlorine and to be pure cæsium alum. The remainder of the cæsium was easily obtained by a few crystallizations of the mother liquor.

This method has advantages over the other methods for the extraction of cæsium from pollucite which involve the precipitation of the cæsium as the double lead or antimony chloride and the decomposition of these compositions by hydrogen sulphide or ammonium hydroxide.

A few experiments were made to determine the insolubility of the cæsium and rubidium in a saturated solution of ammonium aluminium alum. It was found that 1 cm^3 of a solution of RbCl containing 0·0002 grams Rb would give a perceptible precipitate when treated with 5 cm^3 of a saturated solution of ammonium alum, and that 1 cm^3 of a solution of CsCl containing 0·00005 grams Cs would give a precipitate of cæsium alum.

By the careful study of conditions and the use of the other alums it is hoped that these observations may lead to some advances in the analytical study of these elements, and we hope to give further attention to this problem.