

sodium, and no compounds of the chiolite type are formed by the first-mentioned metals. The structures for all these compounds are based on aluminum fluoride octahedra, arranged in chains for penta-fluoaluminates and layers for tetra-fluoaluminates. Chiolite is similar to the tetra-fluoaluminates except that one octahedron in every four is replaced by a sodium ion.¹ While the ionic radii of potassium, rubidium and univalent thallium lie within the limits 1.33 to 1.60 Å., it is evident that the much lower value (0.95 Å.) for sodium is incompatible with the tetra- or penta-fluoaluminate structures. On the other hand, the ionic radii of potassium, rubidium, etc., are apparently too great to enable these ions to occupy the positions of missing aluminum fluoride octahedra, as occurs with sodium ions in the chiolite lattice.

Compounds such as $\text{NaAlF}_4 \cdot \text{H}_2\text{O}$ and Na_2AlF_6 , described by Yatlov,³ are thus mixtures of chiolite with aluminum fluoride and cryolite, respectively. Samples 1 (cryolite) and 4 (chiolite) represent attempts to obtain sodium penta-fluoaluminates by his methods. Yatlov also claimed that sodium tetra-fluoaluminate dissolved in water to give solutions of the same composition as the solid, but this is at variance with the observations of the present authors. A washed sample of the tetra-fluoaluminate made according to his directions gave diffraction patterns for chiolite only and had the sodium-aluminum ratio of 1.33 (sample 7). It is most probable that the so-

called tetra-fluoaluminate ($\text{NaAlF}_4 \cdot \text{H}_2\text{O}$) is a mixture of chiolite (1 mole) with aluminum fluoride trihydrate (2 moles), a combination which reduces to the empirical formula $\text{NaAlF}_4 \cdot 1.2\text{H}_2\text{O}$.

Conclusions

In precipitates obtained from aqueous solutions, the only sodium fluoaluminates which can be detected by X-ray diffraction methods are cryolite and chiolite. Although both compounds contain combined water ($> 5\%$), the crystal structures are the same as those of the corresponding anhydrous compounds obtained in the binary melt, aluminum fluoride-sodium fluoride, except for a small increase in the volume of the unit cell in the case of chiolite. The compounds $\text{NaAlF}_4 \cdot \text{H}_2\text{O}$ and Na_2AlF_6 , previously mentioned in the literature, are probably mixtures of chiolite with aluminum fluoride and cryolite, respectively.

Summary

A study has been made of the sodium fluoaluminates precipitated from aqueous solutions. Examination of X-ray diffraction patterns has shown that the only fluoaluminates obtained are cryolite (Na_3AlF_6) and chiolite ($\text{Na}_5\text{Al}_3\text{F}_{14}$). Variation in the chemical position (as shown by sodium-aluminum ratios) is caused by admixture of chiolite with either cryolite or hydrated aluminum fluoride. No evidence has been found for the existence of penta- or tetra-fluoaluminates of sodium.

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The Heat of Formation and Free Energy of Chlorous Acid

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The free energy of chlorous acid as quoted by Latimer¹ was based upon the Bichowsky and Rossini² value for the heat of formation of the acid. These authors used the heat of solution of chlorine dioxide (g) in water obtained by Booth and Bowen³ and assumed that the heat resulted from the reaction



However, Bray⁴ made a careful study of the distribution of chlorine dioxide between water and carbon tetrachloride in the presence of H^+ and ClO_3^- and concluded that the water solution was practically unhydrolyzed. It seemed desirable, therefore, to obtain a new value for the heat of formation of chlorous acid and to recalculate the free energy values. The general experimental

procedure adopted was the determination of the heat of solution of NaClO_2 and the heat of reduction by iodide.

Experimental

Analysis of $\text{NaClO}_2(\text{s})$.—We are indebted to Mr. Herbert Fleischman for a sample of NaClO_2 of unusual purity for this material. The compound was analyzed by dissolving 0.1-g. samples in ~ 300 cc. of $\sim 0.1 M$ potassium iodide, $0.03 M$ sulfuric acid (or perchloric acid) solution. The liberated iodine was titrated with standard $\text{S}_2\text{O}_3^{2-}$ after standing five to ten minutes.

Average of four analyses gave 43.60 ± 0.03 milliequivalents per gram (98.6% of theoretical).

Calorimetric Measurements.—The calorimeter used was that of Latimer and Zimmerman⁵; however, a new copper resistance thermometer and manganin heater were constructed. The resistance thermometer measuring circuit of Pitzer⁶

(1) Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 48.

(2) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 181.

(3) Booth and Bowen, *J. Chem. Soc.*, **127**, 342 (1925).

(4) Bray, *Z. physik Chem.*, **54**, 583 (1906).

(5) Latimer and Zimmerman, *This Journal*, **61**, 1550 (1939).

(6) Pitzer, *ibid.*, **59**, 2365 (1937).

