As in the combustion of pyrite the rate of sulfur dioxide production varied linearly with the time. Maxima in the weight loss curves were again observed. Also as with pyrite the rate of oxide formation did not change with the temperature between 425 and 500°. Pore closing was again observed, for the reaction stopped at $x = 0.7$ at 500° and at $x = 0.45$ at 400°. Sulfate formation amounting to 15.5% should just prevent pore formation in this case.

Application of equations I, II and III to this reaction gave results similar to those obtained with pyrite. Evaluation of the absolute reaction velocity by means of equation I gave $k = 0.0017$ min.$^{-1}$ and S/σ were found to be 1.2×10^{-4}. Hence D is of the same order of magnitude as in the oxidation of pyrite and the analogy between the two reactions is complete. The question as to whether ferrous sulfide is an intermediate in the oxidation of pyrite cannot be determined from these experiments, for both phenomena are diffusion processes controlled as to rate by geometry, their chemical mechanisms being inaccessible because of their great rapidity.

Summary

The thermal decomposition, reduction by hydrogen and air oxidation of iron pyrite and the air oxidation of ferrous sulfide have been investigated kinetically by measuring continuously the weight losses of the solids during the course of the reaction with an all-glass balance enclosed within the apparatus. The course of the air-oxidation reactions was further followed by measurements of the sulfur dioxide produced and by analyses of the final solid products.

The thermal decomposition of pyrite begins at the homogeneous surface, proceeding at active spots until at about 20% reaction ferrous sulfide separates as a new phase. The phase boundaries thus formed cause an autocatalytic acceleration of the reaction at temperatures below 615°. An activation energy of 30 kcal. per mole or more is required.

The rate of reduction of pyrite by hydrogen is proportional to the fraction of pyrite remaining to be reduced and has an activation energy of 30 kcal. per mole. All surface anions hit by hydrogen molecules and possessing the requisite activation energy react.

The air oxidation of pyrite yields largely ferric oxide along with small quantities of ferric sulfate which amount to about 10% of the reaction product at 400° and decrease with increasing temperature. The rate of the reaction is almost independent of temperature between 400 and 500° and apparently is controlled by the rate of diffusion of oxygen through pores in the ferric oxide layers produced. Formation of sulfate tends to close the pores and stop the reaction short of completion.

The air oxidation of ferrous sulfide proceeds kinetically in exactly the same way as the air oxidation of pyrite. The principal product is ferrous oxide, along with some ferrous sulfate.

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[CONTRIBUTION FROM DIVISION OF INDUSTRIAL CHEMISTRY COUNCIL FOR SCIENTIFIC INDUSTRIAL RESEARCH, MELBOURNE, AUSTRALIA]

The Nature of Precipitated Sodium Fluoaluminates

BY J. M. COWLEY AND T. R. SCOTT

Introduction

In a study of the complex fluorides of aluminum, Brosset[1] has described, *inter alia*, the preparation and crystal structure of the alkali fluoaluminates precipitated from aqueous solutions. Although both penta- and hexa-fluoaluminates of potassium were characterized, he found no evidence for the existence of corresponding sodium salts other than cryolite (Na_3AlF_6). In both instances the hexafluoaluminates were deficient in alkali fluoride, which was replaced by water. Nikolaev,[2] however, has described the preparation of a compound, approximating in composition to chiolite (5NaF, $3AlF_3$), by the addition of stipulated quantities of sodium sulfate and hydrofluoric acid to aluminium fluosulfate solutions, while Yatlov[3] has cited analyses for compounds having the formulas $NaAlF_4 \cdot H_2O$ and Na_2AlF_5, produced by the partial neutralization of solutions of "fluoaluminic acid" (H_3AlF_6) with sodium carbonate. Reference to "pseudo-cryolite" ($NaAlF_4 \cdot nH_2O$) has been made by Caglioti,[4] who claims that "the structure...is identical with that of cryolite save for a slight widening perpendicular to the c axis."

In an attempt to clarify the position, the work described in the present paper has been undertaken. Compounds obtained by methods similar to those of Nikolaev and Yatlov have been analyzed and the crystal structure determined by X-ray diffraction methods.

Experimental

All materials used in the preparation of the sodium fluoaluminates were of A. R. grade, with the exception of Laboratory Reagent aluminum metal used for the prepara-

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[1] Brosset, "Electro-chemical and X-Ray Crystallographic Investigation of Complex Aluminium Fluorides," Stockholm, 1942.

[2] Nikolaev, *J. Chem. Ind. U. S. S. R.*, **14**, 1087 (1937).

[3] Yatlov, *J. Gen. Chem. U. S. S. R.*, **7**, 2439 (1937).

[4] Caglioti, *Chim. industria Italy*, **20**, 274 (1938).

tion of aluminum fluoride solutions. Samples 1, 4 and 7 (Table I) were prepared according to the directions given by Yatlov,[3] using molar solutions of aluminum fluoride to which had been added sufficient concentrated hydrofluoric acid to bring the empirical formula to H_3AlF_6. Addition of 0.1 mole of sodium carbonate per mole of aluminum fluoride, at room temperature, yielded sample 1 (Na_2AlF_5 according to Yatlov), while the same procedure at 75° gave sample 7 ($NaAlF_4 \cdot H_2O$ according to Yatlov). Sample 4 was obtained by adding 0.5 mole of sodium fluoride per mole of "fluoaluminic acid" at 70°. This procedure was claimed by Yatlov to yield sodium pentafluoaluminate. All precipitates were allowed to settle, filtered with difficulty, washed sparingly with distilled water and dried at 130°.

The remaining samples were prepared by adding hydrofluoric acid to aqueous solutions containing both sodium and aluminum sulfates, according to the general equation

$$x\mathrm{Na_2SO_4} + \mathrm{Al_2(SO_4)_3} + (2x + 6)\mathrm{HF} \rightleftarrows (x + 3)\mathrm{H_2SO_4} + 2\mathrm{Na_xAlF_{x+3}}$$

Solutions were approximately 0.25 *M* with respect to aluminum sulfate. The reaction mixture was usually boiled for forty-five minutes and allowed to settle for ten hours, as directed by Nikolaev[2]; the precipitate was then removed by filtration, washed with water and dried at 130°. The boiling and washing with water was omitted in the preparation of samples 3, 8 and 9. The precipitates were generally crystalline and easy to handle but, since the reaction is reversible, yields were from 50–80% of the theoretical. To obtain compounds with sodium–aluminum ratios lower than 1.3, it was necessary to add aluminum sulfate and hydrofluoric acid in excess of the theoretical quantities determined from the above equation.

X-Ray diffraction patterns were obtained from all samples with the 14.3-cm. powder camera of the General Electric XRD equipment, using filtered cobalt Kα radiation. The specimen was packed in the form of a wedge, using a dilute solution of collodion in amyl acetate as binder, and rocked through an angle of 20° during exposure.

Results

The results given in Table I show that cryolite and chiolite are the only sodium fluoaluminates which can be identified in precipitates obtained from aqueous solutions.

TABLE I

NATURE OF SODIUM FLUOALUMINATES

Sample	Ratio Na:Al	Ratio H_2O:Al	Phases identified
1	2.71	0.23	Cryolite
2	2.24	.32	Cryolite + chiolite
3[a]	1.51	n. d.	Chiolite
4	1.49	.44	Chiolite
5	1.48	.40	Chiolite
6	1.34	.46	Chiolite
7	1.33	0.5–0.6	Chiolite
8[a]	0.90	.8–0.9	Chiolite
9[a]	.49	1.0–1.2	Chiolite + $AlF_3 \cdot 3H_2O$

[a] Unwashed samples: ratios corrected for ingredients introduced by the wetting solutions.

Powder photographs give the dimensions of the tetragonal unit cell of the precipitated chiolite as $a = 7.02$, $c = 10.30$ Å. For the chiolite formed by fusion of the component fluorides the dimensions were found to be $a = 6.97$, $c = 10.38$ Å. The volume of the unit cell, which contains $2Na_5Al_3F_{14}$,[1] is thus 0.7% greater for the precipitated chiolite. This greater volume, and the differences in relative intensities observed in the powder patterns, are probably due to the incorporation of 1 or 2 molecules of water per unit cell. Not all the water shown in Table I is present in this form, some being combined as hydroxyl groups replacing fluorine in the aluminum fluoride octahedra. The fluorine deficiency amounts to approximately 4% of the total fluorine present and analyses by Yatlov of similar compounds show a fluorine deficiency of the same order.

The fact that samples 3–8 show only the chiolite pattern might be taken to indicate that the composition of precipitated chiolite varies over a considerable range of sodium–aluminum ratios while retaining the same crystal lattice. Such variation in composition should be reflected, however, by changes in the unit cell dimensions and the intensity distribution of the lines of the corresponding diffraction patterns, but no such changes have been observed. It is more probable that samples 3–8 consist of chiolite of fixed composition ($Na_5Al_3F_{14}$), contaminated with varying quantities of aluminum fluoride trihydrate, which indeed is present in sample 9 in sufficient amount to yield its characteristic diffraction pattern. The increase in the content of aluminum fluoride, as the sodium–aluminum ratio decreases, is illustrated by the considerable increase in water content of samples 7, 8 and 9. Precise figures cannot be given for these samples, since drying at 130° causes a partial dehydration of aluminum fluoride trihydrate, the extent of which varies with the time of heating.

Further confirmation of the presence of aluminum fluoride in samples 6–9 is afforded by washing tests, the trihydrate being nearly ten times more soluble in water than chiolite. Sample 9, for example, was filtered and dried without washing, but an identical preparation after washing with water showed an increase in the sodium–aluminum ratio from 0.49 to 0.73. After boiling with water for thirty minutes, and further drying, the ratio had risen to 0.95. The latter process was also used to prepare sample 7, the sodium–aluminum ratio of which was originally 1.18; with removal of aluminum fluoride trihydrate, the water content of this sample fell from 10.0 to 5.6%. As the composition of the precipitates approaches that of chiolite, washing causes only minor changes in the sodium–aluminum ratio, as indicated by the identical preparations, 3 (unwashed) and 5 (washed).

It is evident that washing with water does not merely cause decomposition of hypothetical compounds such as $NaAlF_4 \cdot H_2O$, since the diffraction patterns of unwashed samples show only the lines of chiolite (and, in sample 9, aluminum fluoride trihydrate).

Discussion

Although potassium, rubidium, thallium and ammonium form tetra-fluoaluminates and, with the exception of rubidium, penta-fluoaluminates also, no analogous compounds are formed with 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 $NaAlF_4 \cdot H_2O$ and Na_2AlF_5, 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 ($NaAlF_4 \cdot H_2O$) is a mixture of chiolite (1 mole) with aluminum fluoride trihydrate (2 moles), a combination which reduces to the empirical formula $NaAlF_4 \cdot 1.2H_2O$.

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 ($\not> 5\%$), 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 $NaAlF_4 \cdot H_2O$ and Na_2AlF_5, 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_3) and chiolite ($Na_5Al_3F_{14}$). Variation in the chemical position (as shown by sodium–aluminum ratios) is caused by admixture of chiolite with either cryolite or hydrated alumium fluoride. No evidence has been found for the existence of penta- or tetra-fluoaluminates of sodium.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Heat of Formation and Free Energy of Chlorous Acid

BY B. J. FONTANA AND WENDELL M. LATIMER

The free energy of chlorous acid as quoted by Latimer[1] was based upon the Bichowsky and Rossini[2] 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 Bowen[3] and assumed that the heat resulted from the reaction

$$2ClO_2(g) + H_2O = HClO_3(aq.) + HClO_2(aq)$$

However, Bray[4] 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 $NaClO_2$(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 $\sim$ 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 $S_2O_3^=$ 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 Zimmerman[5]; however, a new copper resistance thermometer and manganin heater were constructed. The resistance thermometer measuring circuit of Pitzer[6]

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(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).