[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES]

Some Physical and Chemical Properties of a New Sodium Aluminum Fluoride

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The existence of a new compound in the sodium fluoride–aluminum fluoride system has been established by chemical and X-ray powder diffraction methods. The compound consists of 1 mole of sodium fluoride and 1 mole of aluminum fluoride. Procedures for preparing this compound in appreciable quantities have been developed and some of its chemical and physical properties have been investigated.

Introduction

Cold zone sublimates, which gave X-ray powder diffraction patterns not associated with any known compound, were found in experiments consisting of the passage of a rapid stream of gas over NaF–AlF_3 mixtures that contained 3 or less moles of sodium fluoride to one mole of aluminum fluoride, heated above their fusion points. A typical experiment in which argon gas at 50 liters/hour was passed over a mixture of 45.5% sodium fluoride and 54.5% aluminum fluoride, held in a copper boat inside of a 1.5 in. diameter copper-lined ceramic tube at 1000°, yielded a deposit on the Seitz filter outside the furnace that gave, upon chemical analysis for sodium, aluminum and fluoride, a composition of 33.0% sodium fluoride and 67.0% aluminum fluoride. This composition corresponds to a NaF-AlF_3 weight ratio of approximately 0.50 and NaF: AlF_3 molar ratio of about 1:1.

A similar material was obtained when 50 liters/hour of nitrogen or hydrogen was passed over a charge of 33.5% NaF and 66.5% AlF_3 at 1000°, and when 50 liters/hour of air, argon or carbon monoxide was passed over a mixture of 15% Na_3AlF_6 and 85% AlF_3 at 1000°.

The new compound was found to be quite volatile at temperatures above 900°. For example, a few grams, contained in a copper boat in a copper-lined ceramic tube through which about 3 liters/hour of argon gas was passed, showed weight losses in four hours of 0.7% at 750°, 3.25% at 900° and 100% at 1000°. With the gas flow increased to about 50 liters/hour, the weight losses in one hour were 2.3% at 400°, 4.3% at 600°, 13.7% at 700° and 100% at 1000°. Because of a solid phase transformation described later, the residues from each of the above experiments, with the exception of the one at 400°, were found by X-ray powder diffraction analysis to have changed from the new material to chiolite and aluminum fluoride.

The formula of this new compound is $NaF \cdot AlF_3$ or $NaAlF_4$, analogous to other compounds of the type $MAlF_4$, where M may be ammonium, potassium, rubidium or thallium.[1] This new material may be named sodium tetrafluoroaluminate.[2]

Thermal analyses of the NaF–AlF_3 system[3] have previously shown the existence of no other compounds than $3NaF \cdot AlF_3$ and $5NaF \cdot 3AlF_3$, although Boner[4] has recently discussed the hypothetical existence of undissociated $NaAlF_4$ in molten cryolite without offering concrete evidence. From studies in aqueous systems, the supposed existence of $2NaF \cdot AlF_3$ and $NaAlF_4 \cdot H_2O$ has been mentioned.[5]

Experimental

Preparation.—Sodium tetrafluoroaluminate may be prepared by quenching vapors above molten mixtures of NaF and AlF_3 in a cold zone. A suitable method consisted of heating a charge of 30% NaF and 70% AlF_3 by weight to 1000° in a graphite-lined retort equipped with a collection train consisting of a water-cooled condenser followed by several glass flasks. In this system a gas or air flow rate of about 700 liters/hour has proved satisfactory. As would be expected, the gas flow rate required to produce appreciable yields of the product depends on the size and shape of the generating and collecting equipment.

Table I summarizes a few experiments conducted in such an apparatus using a charge temperature of 1000° and a nitrogen gas flow rate of 700–800 liters/hour. In this system a 1000-g. charge yielded approximately 100 g. of product in a two-hour period. Table I contains nominal charge composition and the weight ratio of NaF/AlF_3 in the product as determined by chemical analysis. The sodium tetrafluoroaluminate sublimate was sometimes contaminated with small amounts of chiolite ($5NaF \cdot 3AlF_3$), as shown by X-ray powder diffraction analysis. The product

TABLE I

PREPARATION OF SODIUM TETRAFLUOROALUMINATE FROM NaF–AlF_3 MIXTURES HELD AT 1000° IN A NITROGEN GAS STREAM OF 700–800 LITERS/HOUR

Expt.	Nominal charge composition Wt. % NaF	Nominal charge composition Wt. % AlF_3	Product Wt. ratio NaF/AlF_3
1	33.3	66.7	0.51
2	33.0	67.0	.49
3	30.0	70.0	.50
4	28.5	71.5	.50
5	30.0	70.0	.50
6	30.0	70.0	.49
7	45.5	54.5	.50

TABLE II

X-RAY DIFFRACTION PATTERN OF $NaAlF_4$

d, Å.	Intensity	d, Å.	Intensity
7.47	w	1.970	m
5.25	vw	1.880	w
4.73	vvw	1.850	vvw
4.33	s	1.817	vs
3.76	w	1.775	vw
3.54	s	1.745	ms
3.07	vs	1.672	vw
2.93	s	1.565	m
2.51	w	1.321	w
2.34	vw	1.302	w
2.26	w	1.285	w
2.17	vvw	1.170	w
2.12	m	1.149	w

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[1] C. Brosset, *Z. anorg. Chem.*, **235**, 139; **239**, 301 (1938).

[2] W. Conard Fernelius, Chemical Nomenclature, Advances in Chemistry Series No. 8, A.C.S., p. 9, 1953.

[3] P. P. Fedotieff and W. P. Iljinski, *Z. anorg. Chem.*, **80**, 132 (1913).

[4] J. E. Boner, *Helv. Chim. Acta*, **33**, 1137 (1950).

[5] J. H. Simons, "Fluorine Chemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1950, p. 41.

obtained in the collection flasks was a fine, fluffy powder of low apparent density. The particle size distribution was about 75% in the 0–10 μ range and 25% in the 10–20 μ range. The particle shape was rather evenly distributed between short rods and spheres. In still larger scale work with very high gas velocities, 10,000 liters/hour, the particle size distribution was 90% in the 0–2 μ range and 10% in the 2–4 μ range. Table II contains X-ray diffraction data for this new compound.

Properties of Sodium Tetrafluoroaluminate

Solid Phase Transformation.—When a slow gas stream was used in the experiments carried out in the small diameter tubes, crystalline deposits were obtained on the copper liner in the hot zone downstream from the charge and no deposit on the Seitz filter. Chemical analysis showed the weight ratio of NaF/AlF_3 to be about 0.50 or a 1:1 molar ratio. X-Ray powder diffraction analysis, however, showed the crystalline phases present to be largely chiolite mixed with small to medium amounts of aluminum fluoride. This suggested that the vapor phase above the charge consisted of molecules having a 1:1 molar ratio of NaF to AlF_3. If these vapors were rapidly swept from the hot zone, they could be condensed in a cold zone as sodium tetrafluoroaluminate. On the other hand, if the vapors were cooled slowly, a solid phase transformation occurred so that the hot zone deposits consisted of chiolite and aluminum fluoride. The reaction may be expressed by the equation

$$5(NaF{\cdot}AlF_3) \longrightarrow 5NaF{\cdot}3AlF_3 + 2AlF_3$$

This theory was substantiated by an X-ray powder diffraction analysis of the deposits collected along the entire length of the tube from experiments using high gas velocities. A typical distribution of the crystalline deposits would be 50% chiolite and 50% aluminum fluoride in the hot zone, 10% chiolite plus 90% sodium tetrafluoroaluminate in the condenser and 100% sodium tetrafluoroaluminate on the Seitz filter. The amount of sodium tetrafluoroaluminate increased toward the cold zone, even though the chemically-determined ratio of NaF/AlF_3 was found to be approximately 0.5 in all cases.

Further substantiation was obtained by showing that sodium tetrafluoroaluminate exhibited a solid phase transformation. The thermal analysis equipment was not sensitive enough to detect the transformation. Therefore, the transformation temperature was bracketed by heating samples of sodium tetrafluoroaluminate containing a trace of chiolite at various temperatures for different time intervals. Examination of the product by the X-ray powder diffraction method showed that the samples held at 470–480° for a very short period of time were almost completely transformed to chiolite and aluminum fluoride, while samples held below 470° showed no change in the crystalline composition over a period of several hours. These experiments showed a transformation temperature above 470°. There is a possibility that the small chiolite impurity may have nucleated the transformation.

To determine whether sodium tetrafluoroaluminate could be formed from the liquid phase, samples at about the 1:1 molar ratio of NaF/AlF_3 composition were fused and the melts quenched by pouring into a large quantity of cold water. X-Ray powder diffraction analyses showed that the quenched samples consisted of approximately 75% sodium tetrafluoroaluminate and 25% chiolite. Slowly cooled melts of the same composition were found to consist only of chiolite and aluminum fluoride.

Thermal Analysis.—Thermal analyses of some of the sodium tetrafluoroaluminate samples and of mixtures of NaF and AlF_3 at about this composition were made by determining heating and cooling curves. A specially-constructed furnace in which the rate of heating or cooling was controlled by differential temperature measurements was used. The charges were held in platinum crucibles and the temperature continuously recorded from a platinum, platinum–10% rhodium thermocouple encased in a platinum tube.

The liquidus temperatures of separate fusions starting with sodium tetrafluoroaluminate and with the 1:1 molar mixture of NaF and AlF_3 were found to be 690 ± 3°. A heat effect presumed to be the solidus was found in the system in both cases at 664 ± 3°. Because of the solid phase transformation previously described, the residue from the sample which was initially sodium tetrafluoroaluminate was chiolite and AlF_3 by X-ray powder diffraction analysis. The residue from the fusion of NaF and AlF_3 also consisted of chiolite and AlF_3.

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The Fluorides of Permanganic[1] and Perrhenic Acids, MnO_3F and ReO_3F

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Pure permanganyl fluoride and perrhenyl fluoride were isolated, some of their physical constants determined, and their chemical behavior investigated. Permanganyl fluoride, MnO_3F, forms dark green crystals, melting at −38° to a dark green liquid and vaporizing to an intense green gas. The boiling point, extrapolated from its vapor pressure at low temperature, is near 60°. It is stable only below 0°. Above this temperature it decomposes, often explosively, to MnF_2, MnO_2 and O_2. It is extremely reactive with organic matter and hydrolyzes instantaneously on exposure to moist air to give deep purple vapors of $HMnO_4$. Perrhenyl fluoride, ReO_3F, forms a yellow glass or very fine crystalline powder, melting at 147° and boiling at 164° at 760 mm. It is very easily reduced to blue colored rhenium compounds of lower valence states and is immediately hydrolyzed by water to perrhenic and hydrofluoric acids.

Neither one of the acid fluorides of heptavalent manganese and rhenium, MnO_3F or ReO_3F, has been isolated in a pure state. The suitable names of these oxyfluorides as derivatives of the corresponding acids, $HMnO_4$ and $HReO_4$, are permanganyl fluoride and perrhenyl fluoride.

Many rather conflicting statements have been made about these compounds. More than a century ago, Wöhler[2] observed that the green vapors turned purple violet in air while heating a mixture of potassium permanganate, calcium fluoride and concentrated sulfuric acid in a platinum retort. Since then several chemists[3–6] have confirmed the formation of a green volatile manganese compound when permanganates reacted with anhydrous hydrogen fluoride or fluorosulfonic acid. None of them, however, was able to separate it from hydrogen fluoride and isolate this extremely reactive compound in a pure state. Ruff[4] questioned even whether the gas *contained fluorine* and suggested

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[1] Presented before the Chemistry Section of the American Association for the Advancement of Science at Philadelphia, Pa., on December 26, 1951; see General Program of the 118th Meeting of the American Association for the Advancement of Science, 1951, p. 140.

[2] F. Wöhler, *Ann. chim. phys.*, [2] **37**, 101 (1828), *Ann. Miner.*, [2] **3**, 163 (1828).

[3] J. Gore, *J. Chem. Soc.*, **22**, 368 (1869).

[4] O. Ruff, *Ber.*, **47**, 658 (1914); "Chemie des Fluors," 1920, p. 115.

[5] K. Fredenhagen, *Z. Elektrochem.*, **37**, 684 (1931).

[6] K. Fredenhagen, *Z. anorg. allgem. Chem.*, **242**, 23 (1939).