

entropies of iron and rhombic sulfur and the measured entropy of ferrous sulfide, the value $-23,600$ cal. was calculated as the free energy of ferrous sulfide.

Sabatier¹⁰ determined the heat of formation of calcium sulfide by direct union of calcium and rhombic sulfur. He gives the value of $\Delta H_{298}^{\circ} = -111,200$ cal. Using this value and the values of the entropies of calcium and rhombic sulfur as given by Lewis and Randall, and the entropy obtained for calcium sulfide, the free energy of calcium sulfide was calculated as $-109,800$ cal.

Summary

The heat capacities of manganese sulfide, ferrous sulfide and calcium sulfide from about 60 to 300°K. have been determined, and their corresponding entropies and free energies calculated.

The following table contains the summarized results.

	S_{298}°	ΔF_{298}°	ΔH_{298}°
MnS	18.7	-64,000	-62,900
FeS	16.1	-23,600	-23,070
CaS	13.5	-109,800	-111,200

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND THE UNIVERSITY OF OKLAHOMA]

THE DECOMPOSITION OF REFRACTORY SILICATES BY FUSED AMMONIUM FLUORIDE AND ITS APPLICATION TO THE DETERMINATION OF SILICA IN GLASS SANDS

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For years the opening of silicates, preparatory to the analysis of the alkali metals, has been a serious problem. The method of J. Lawrence Smith, though satisfactory as to accuracy, is laborious in technique, consequently the hydrofluoric-sulfuric acid process often has been proposed to supplant it but has been unqualifiedly rejected by Hillebrand² as unsuitable because of the difficulty of removing fluorides. Lundell³ proposes to substitute perchloric acid for sulfuric to obviate this difficulty, especially with reference to soda-lime glasses. While working along the same lines, but using crystallized ammonium fluoride, the writers noticed that fusion took place and it occurred to them that possibly a molten reagent might be more ef-

¹⁰ Sabatier, *Ann. chim. phys.*, [5] 22, 22 (1881).

¹ Recipient of "The J. T. Baker Fellowship in Analytical Chemistry" at the University of Illinois for the year 1930-31. Assistance is further gratefully acknowledged as a result of a leave of absence granted by the University of Oklahoma.

² U. S. Geol. Survey Bull., 700, 99 (1919).

³ Lundell and Knowles, *J. Am. Ceramic Soc.*, 10, 849 (1927).

fective than the aqueous solutions commonly employed. Such proved to be the case, as will be shown later.

On looking up the literature, it was found that Berzelius⁴ noted the fusibility of ammonium fluoride, and that it had been employed by Jannasch⁵ to decompose andalusite, but in such a way as to obscure and nullify the peculiar advantages of the reagent. For instance, the flux was formed in the reaction crucible from the aqueous reagents, ammonia and hydrofluoric acid, with the latter in large excess, necessitating the removal of at least 20.0 ml. of water, and leaving in doubt whether the mineral had been decomposed by the excess of hydrofluoric acid used or by the subsequent fusion. Jannasch apparently realized the value of the molten fluoride but his interest was intrigued by his boric oxide flux—this fact and, possibly, a faulty translation, referring to his work, seem to have left this phase of the problem unnoticed ever since.

H. Rose⁶ had previously proposed the following scheme, which had apparently been unfamiliar to Jannasch. To a mixture of ammonium fluoride and water in the form of a semi-fluid mass in a platinum crucible is added the finely ground sample of quartz or silicate. The mixture is then evaporated to dryness and ignited. It was stated (contrary to our experience with the dry reagent) that the process has to be repeated three to four times in the case of quartz but is more effective in the case of silicates. Rose's method is undesirable because of the time required in each treatment and the necessary repetition of the operation for complete reaction and because of loss from spattering due to the addition of water to the reaction mixture. Rose did not apply the method quantitatively.

Qualitative tests on finely powdered minerals—among them quartz, orthoclase feldspar, beryl, iron tourmaline—have shown that silica is rapidly eliminated in presence of molten ammonium fluorides. These results encouraged the writers to undertake a quantitative study on the extent of the decomposition. The quartz of glass sand was selected because of its simplicity of composition, its comparative resistance, among the silicon compounds, to attack by hydrofluoric acid, the availability of excellent analyzed samples, and the usefulness of a quick and accurate method of analysis for the commercial product. The samples analyzed were Bureau of Standards glass sand sample No. 81 and one that had been carefully analyzed, using the sodium carbonate fusion method, by one of the writers.⁷

Method of Analysis.—A weighed sample, previously dried at 110°, was thoroughly mixed with five grams of C. P. crystalline ammonium fluoride

⁴ J. J. Berzelius, *Lehrbuch der Chemie*, 3, 282 (1856), Dresden.

⁵ Jannasch, *Z. anorg. Chem.*, 12, 220 (1896).

⁶ Rose, *Pogg. Ann.*, 108, 19 (1859).

⁷ A. C. Shead, "Chemical Analyses of Oklahoma Mineral Raw Materials," Study No. 32, University of Oklahoma, Analysis No. 171.

in a tared 25.0 ml. platinum crucible, provided with a well-fitting lid which is kept in place during the subsequent decomposition. The crucible was placed in a hole through a heavy asbestos board of such a size that about a third of the surface of the crucible is exposed to the flame of an adjustable burner of the Tirrill type, and fixed at such a height that the bottom of the empty crucible will be maintained at a dull red heat. The fusion and expulsion of the excess reagent should require about ten minutes. Experience shows that about a gram of quartz of one hundred mesh or finer will be volatilized within this time but that a very small amount of silica will generally remain, necessitating the repetition of the process. The smallest residue of unattacked mineral is easily seen as it tends to segregate itself. The amount left will be large, even in the case of precipitated silica, unless the flux be thoroughly mixed with the sample, in the first place. The fusion is remarkably quiet and the small amount of residue spattering upon the lid can generally be easily removed by the following technique. The lid is heavily coated with ammonium salt upon which some of the residue may be projected. Toward the end of the fume evolution this coat is heated with the burner held in the hand and the flame impinging on the lid; this causes the detachment of the deposit, which falls into the crucible carrying the residue with it.

Before the crucible is allowed to come to redness, after the excess fluoride has been volatilized, it is advisable to add a drop or two of concentrated sulfuric acid, or a few fragments of ammonium bisulfate to prevent the escape of traces of iron or aluminum, as halide. Perchloric acid cannot be used, as ignition forms these halides.

TABLE I
TYPICAL RESULTS

Sample of glass sand	Sample, g.	Residue, g.	Residue, %	SiO ₂ by difference, %
B. S. 81 ^a	1.1741	0.0097	0.83	99.17
B. S. 81	1.0856	.0091	.84	99.16
B. S. 81	1.7514	.0057	.27	99.73
		Average	.65	99.35
B. S. 8174	99.26
Okla. 171	1.0088	.0017	.17	99.83
Okla. 171	1.2756	.0020	.16	99.84
Okla. 171	1.3905	.0021	.15	99.85
Okla. 171	0.7569	.0013	.17	99.83
		Average		99.84
Okla. 171	(By sodium carbonate fusion, etc.)			99.63

^a Analysis of B. of S. sample No. 81: Fe₂O₃, 0.073; Al₂O₃, 0.265; TiO₂, 0.095; ZrO₂, 0.031; CaO, 0.029; MgO, 0.016; loss on ignition, 0.23. This gives a total of 0.74% impurities in the form finally weighed in these experiments. The indicated silica content is therefore 99.26%.

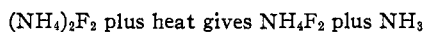
The time required for the expulsion of silica and excess reagents need not exceed twenty minutes, for both evaporations.

The residue is preponderantly oxides of iron, aluminum and titanium, with but negligible amounts of alkali and alkali earth oxides, and the loss can safely be attributed to silica in this particular case.

The data in Table I are typical of the results obtained.

Discussion

As ammonia fumes are given off copiously on heating ammonium fluoride, and a more fusible compound seems to be formed, it is suggested that the following reaction takes place



Experiments with the technical grades of the bifluoride lead to the conclusion that previously fused pieces of this flux would probably afford prompter fusion, greater fluidity, a more acid nature and an even quieter melt than the normal salt.

Summary

Molten ammonium fluoride rapidly decomposes powdered quartz and silicates. This reaction has been proved to be quantitative, in the case of glass sand, and shows the possibility of opening silicates preliminary to determining other constituents therein, particularly the alkali metals.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]
**OXYGEN FILMS ON TUNGSTEN. I. A STUDY OF STABILITY BY
MEANS OF ELECTRON EMISSION IN PRESENCE OF
CESIUM VAPOR**

BY I. LANGMUIR AND D. S. VILLARS

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In this paper we wish to describe a powerful method of studying the properties and detecting the presence of adsorbed films of oxygen on a tungsten surface. This method, not in general use, seems to us to be capable of much wider application than we are making of it here, and for that reason we wish to call it to the attention of chemists. We shall, at the same time, present evidence obtained by it to show that adsorbed oxygen films are held on a tungsten surface by enormous binding forces,¹ very much greater even than those corresponding to the heat of dissociation of the oxygen molecule.

The experimental work on which this paper is based was done by Dr.

¹ Cf. Langmuir, Chandler Lecture, *Ind. Eng. Chem.*, **22**, 393 (1930).