the lower range (10 to ~50°) is so slow, however, that all that could be reasonably read from the results is a curve attributable to a form stable above ~50–60°. This form, crystallizing in small octahedra, persists metastably evidently down to 10°, and its solubility curve, with some points approached from undersaturation, some from supersaturation, and a few from both directions, was determined from 10 to 95°. For each point the solid phase was examined microscopically and found to be always the same. The values, listed in Table IV, fall on a smooth curve with a minimum solubility near 85°. These values represent measurements agreeing on repeated analysis with continued stirring at each temperature. The density of the solution at 24.95°, with 45.33% $LiIO_3$, was 1.587. Many widely scattered and unreproducible "solubilities" lower than the values on this curve were observed at temperatures below 55°, and one higher than the curve at 60° but none below the curve at temperatures above 50°. It is probable, therefore, that the form involved is stable above and unstable below ~50–60°.

TABLE IV

SOLUBILITY OF ONE FORM OF $LiIO_3$ (OCTAHEDRAL CRYSTALS)

U, undersaturation; S, supersaturation; *m*, metastable

Temp., °C.	Solubility wt. % $LiIO_3$	Approach from
9.93	47.19 (*m*)	U
20.24	45.86 (*m*)	S
24.95	45.33 (*m*)	U & S
29.94	44.89 (*m*)	U
34.95	44.45 (*m*)	U
40.00	44.12 (*m*)	U
45.00	43.84 (*m*)	U & S
50.06	43.51 (*m*)	S
55.1	43.35 (?)	U
60.2	43.10	U
65.3	43.00	U
75.5	42.82	U
85.5	42.76	S
95.1	42.85	U

Most attention was given to 25°, where a long-constant value of 43.86% was obtained with several different samples of starting material. This is lower than the value in Table IV, and therefore must pertain to a form stable (relatively) at 25°. Whether it is the most stable form at 25°, however, cannot be said, although its solubility does agree fairly well with the value (~44.0%) extrapolated from the solubility curve of $LiIO_3$ in the system $LiIO_3$–HIO_3–H_2O as presented in Table III and Fig. 2. It also agreed in crystalline appearance with the $LiIO_3$ solid phase obtained in the ternary system, in the form of long hexagonal rods, as already mentioned. It is probably the form studied crystallographically by Zachariasen and Barta.[22] Since this solid is definitely anhydrous according to Fig. 2, we may infer that the higher temperature form involved in Table IV must also be anhydrous.

For comparison, we note that the solubility values in the literature are few, at scattered temperatures, and sometimes with no information concerning the purity of the salt and the attainment of equilibrium. Lühdemann[23] reported 42.18% at 10°; Heydweiler[24] gave values of 23.5 and 38.3%, for two forms, at 18°; Grüneisen[25] reported 38% at 18°; Mylius and Funk[26] reported 44.6% at 18°. In addition a hydrate of the salt was also reported ($LiIO_3 \cdot H_2O$, at ~60°) by Ditte,[16] although it has not again been mentioned.

[22] W. H. Zachariasen and F. A. Barta, *Phys. Rev.*, **36**, 1693 (1930); **37**, 1326 (1931).

[23] R. Lühdemann, *Z. physik. Chem.*, **B29**, 133 (1935).

[24] A. Heydweiler, *Ann. Physik*, **37**, 741 (1912).

[25] E. Grüneisen, *Wissensch. Abh. Phys.-Techn. Reichsanst.*, **4**, 246 (1905).

[26] F. Mylius and R. Funk, *Ber.*, **30**, 1716 (1897).

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Some Aqueous Salt Systems Involving Fluosilicates

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The solubility relations in several aqueous systems, some ternary and one quaternary, involving fluosilicates are reported for 25°. The isotherm of the system K_2SiF_6–KBr–H_2O shows the saturating solid K_2SiF_6 to be anhydrous. The three ternary systems involving the salt pairs $(NH_4)_2SiF_6$–$MgSiF_6$, $SrCl_6$–$SrSiF_6$, and $(NH_4)_2SiF_6$–$SrSiF_6$ were studied with 0.5% aqueous H_2SiF_6 as solvent, to prevent hydrolytic precipitations. The first two are simple, with $(NH_4)_2SiF_6$, $MgSiF_6 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $SrSiF_6 \cdot 2H_2O$ as sole solid phases. The third pair forms a congruently soluble double salt the formula of which seems to be $(NH_4)_2SiF_6 \cdot 6SrSiF_6$. In connection with these systems the solubilities of $(NH_4)_2SiF_6$ and $SrSiF_6 \cdot 2H_2O$ in presence of H_2SiF_6, up to ~30%, were also determined. The three systems containing the pairs NH_4–NH_4Cl, NH_4Cl–$(NH_4)_2SiF_6$, and NH_4F–$(NH_4)_2SiF_6$ were studied with pure water as solvent. The first two are simple, the only solids being the anhydrous salts. The third involves the already known incongruently soluble double salt $NH_4F \cdot (NH_4)_2SiF_6$. The 25° isotherm of the quaternary system NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O has two solutions of threefold saturation. One is a transition point in isothermal evaporation, with the phase reaction $(NH_4)_2SiF_6 + \text{liquid} \rightleftarrows NH_4Cl + NH_4F \cdot (NH_4)_2SiF_6 + H_2O\nearrow$, and the other is the congruent drying-up point for the solids $NH_4F + NH_4Cl + NH_4F \cdot (NH_4)_2SiF_6$.

The literature contains little information on solubility equilibria of the fluosilicates. Solubilities of a number of fluosilicates, some of them of uncertain dependability, are cited in Mellor's "Treatise,"[1] in Seidell's "Solubilities,"[2] and in a compilation by Carter of values known to 1930.[3] Carter also reported some further measurements, in particular the solubilities of the sodium, potassium and barium salts from 0 to ~80°. No double salts of the fluosilicates are mentioned other than the compound $NH_4F \cdot (NH_4)_2SiF_6$. This was first prepared

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[1] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York, N. Y., 1925, Vol. VI, pp. 944–958.

[2] A. Seidell, "Solubilities of Inorganic and Organic Substances," D. Van Nostrand Co., New York, N. Y., 1940, Vol. I, pp. 810, 970, 1098. A few further individual solubilties have since been reported in the literature.

[3] R. H. Carter, *Ind. Eng. Chem.*, **22**, 886 (1930).

by Marignac,[4] and its crystal structure has been studied by Hoard and Williams.[5] The only study of aqueous salt systems involving fluosilicates seems to be that of the system Na_2SiF_6–$NaCl$–H_2O reported by Anosov and Chirkov,[6] in which the solid phases are the separate, single anhydrous salts at the temperature 15°.

Some of the difficulties involved in such studies are the hydrolytic instability of many of the salts with precipitation of silica or metallic fluoride or both, the corrosive action of the solutions on glass ware, and the lack of rapid and accurate analytical methods for fluosilicates, fluorides and silica in the presence of each other. The systems here reported, dealing principally with the fluosilicates of ammonium, strontium and magnesium, are presented as a possible start for the more systematic investigation of the aqueous solubility relationships of the fluosilicates among themselves and with other related salts.

Ammonium fluosilicate is a stable compound easily prepared and purified by recrystallization from water. It was planned to investigate a number of systems at 25° with it as a component in conjunction with some of the more stable fluosilicates as well as with other salts, with the aim of determining any double salt formation. Fluosilicates other than those of the alkali metals suffer hydrolytic precipitation in pure water solution, because of the reaction $SiF_6^{=} + 4H_2O \rightarrow Si(OH)_4 + 4H^+ + 6F^-$.[7] Exploratory experiments on the alkaline earth fluosilicates showed that such precipitation could be prevented by the use of 0.5% fluosilicic acid as solvent in the case of both strontium and magnesium fluosilicates at room temperature. Since the over-all phase diagram with such a solvent would hardly differ from that with pure water, the ternary systems of each of these salts with ammonium fluosilicate were investigated as a starting point. The salts $(NH_4)_2SiF_6$ and $SrSiF_6$ were found to form a congruently soluble anhydrous double salt $(NH_4)_2SiF_6 \cdot 6SrSiF_6$ as one of the solid phases at 25°. In connection with this isotherm the simpler system $SrCl_2$–$SrSiF_6$–H_2O was also studied for the purpose of confirming the dihydrate of $SrSiF_6$ as the equilibrium solid phase for strontium fluosilicate at 25°. The barium salt of fluosilicic acid is only slightly soluble,[3] while the calcium salt was found to hydrolyze to such an extent as to require too high a concentration of acid to prevent precipitation of calcium fluoride and silica. Ternary systems involving these salts were therefore not attempted.

In order to add to the scanty information about the stability relations of the double salt $NH_4F \cdot (NH_4)_2SiF_6$, the ternary system NH_4F–$(NH_4)_2SiF_6$–H_2O was studied, together with the corresponding system with NH_4Cl in place of NH_4F, in which, however, no double salt appeared at 25°. With the additional simple system NH_4F–NH_4Cl–H_2O these ternary systems were then used in the study of the quaternary system NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O at 25°.

In addition, the system K_2SiF_6–KBr–H_2O was also investigated in order to determine if precipitated gelatinous potassium fluosilicate was hydrated. When a solution of a potassium salt is added to fluosilicic acid, a slightly opalescent, almost transparent, gelatinous precipitate forms.[8] When filtered, it is still gelatinous but dries to a fine white powder. Upon resuspension of this amorphous powder in water the material regains its former appearance. It seemed possible that the gelatinous material was an unstable hydrate, but the phase diagram with KBr shows it to be anhydrous.

Materials.—Five general methods are available for the preparation of the fluosilicates[9]: (a) reaction of gaseous SiF_4 with a solid metallic fluoride; (b) solution of the metallic fluoride together with silicic acid in hydrofluoric acid and evaporation; (c) digestion of $BaSiF_6$ with a solution of the metallic sulfate, filtration of the $BaSO_4$, and evaporation of the filtrate; (d) neutralization of fluosilicic acid with either the carbonate or the hydroxide, and evaporation; (e) precipitation of the fluosilicate by the addition of alcohol to a solution containing fluosilicic acid and the metallic chloride. The first two of these methods were not used in the present work. Although the other three methods were tried in the preparation of strontium and magnesium fluosilicates, the last was found to be the most convenient. This method avoids the evaporation of solution, a process requiring chemically resistant non-glass apparatus if a pure product is to be obtained. Moreover, the use of the carbonate to neutralize the fluosilicic acid is a slow process involving persistent foaming, while the use of the hydroxide causes precipitation of silica before complete neutralization.

Ammonium Fluosilicate.—This salt was prepared by the treatment of 30% fluosilicic acid (Baker and Adamson) containing 0.3 to 0.4% hydrofluoric acid, with 28% aqueous ammonia. The hydrofluoric acid was added to prevent precipitation of gelatinous silica which otherwise occurs before the calculated amount of ammonia is added (such precipitation was observed by Berzelius, ref. 8, p. 192). The neutralization was carried out in a special pot cooled in an ice-water mixture, the pot being a one-liter cylindrical container made of a plastic material chemically resistant to hydrofluoric acid. During the dropwise addition of the ammonia, the solution was stirred by means of a motor-driven, waxed glass stirrer. The small crop of ammonium fluosilicate crystals forming after sufficient cooling was collected by suction on a filter paper in a büchner funnel, and the mother liquor was immediately returned to the plastic pot and evaporated by heating until again saturated. Cooling to room temperature then gave a second crop of crystals. The mother liquor from this was combined with that from another neutralization, evaporated, and cooled, yielding a third crop. This cycle of processes was repeated several times before the liquid was discarded. The solid ammonium fluosilicate was recrystallized once from water by the cooling of a saturated solution at 50° to room temperature. A final yield of 80–90% was possible in preparation of a pound of the salt. The final crystals were collected on a büchner funnel, washed with a small amount of water, and given a preliminary air drying. Then they were placed in a large platinum dish, heated for several hours in an oven at 60°, pulverized, and finally heated at 80° for 24 hours. The salt thus prepared gave a clear solution in water, and was 99.9% pure on the basis of ammonia, determined by distillation into standard H_2SO_4 followed by NaOH titration with methyl red as indicator. Determination of fluosilicate by the method described later under the system NH_4F–$(NH_4)_2SiF_6$–H_2O gave 79.6% SiF_6 against a theoretical value of 79.75%.

Magnesium Fluosilicate.—About 90 g. of C.P. $MgCl_2 \cdot 6H_2O$ was added to 500 ml. of 95% alcohol together with the

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[4] J. C. G. de Marignac, *Annales de Mines*, [5] **15**, 224 (1859).

[5] J. L. Hoard and M. B. Williams, THIS JOURNAL, **64**, 633 (1942); also, H. Baker, *J. Chem. Soc.*, **35**, 762 (1879).

[6] V. Y. Anosov and S. K. Chirkov, *J. Applied Chem., U. S. S. R.*, **6**, 224 (1938).

[7] (a) I. G. Ryss and N. P. Bakina, *Compt. rend.* (*Doklady*) *Acad. Sci. U. R. S. S.*, (*N. S.*), **2**, 21 (1936), cited in *C. A.*, **30**, 7058 (1936), give $K = 1.2 \times 10^{-27}$ for this reaction at 20°. (b) I. G. Ryss, *J. Phys. Chem., U. S. S. R.*, **21**, 197 (1947), cited in *C. A.*, **41**, 6112 (1947), gives $K = 5.4 \times 10^{-27}$ at 11°.

[8] J. J. Berzelius, *Ann. Phys. Chem.*, **1**, 188 (1824).

[9] Summarized from Mellor's "Treatise," ref. 1.

minimum amount of water needed for complete solution. The filtered solution was added dropwise with stirring to 250 ml. of 30% H_2SiF_6 in the plastic pot. The final alcohol concentration was about 50% by volume. Well formed white crystals of $MgSiF_6 \cdot 6H_2O$ settled out leaving a clear supernatant liquid. After decantation the crystals were collected by suction on filter paper on a büchner funnel. They were then redissolved in a minimum amount of 5% H_2SiF_6 and reprecipitated by the very slow, dropwise addition of an equal volume of 95% alcohol, with stirring. The crystals were again filtered and the process repeated twice more. During the final precipitation the stirring was done manually with a hard rubber spatula rather than with the waxed stirrer. After a final washing with 95% alcohol containing a little H_2SiF_6, the crystals were placed in an evacuated desiccator over $CaCl_2$ for removal of alcohol and surface moisture.

A solution of the salt thus prepared gave no turbidity when tested with $AgNO_3$ in presence of HNO_3. Because of the insolubility of MgF_2 in water the turbidity of a solution of magnesium fluosilicate in pure water was used as a criterion of purity as well as of the extent of hydrolysis. The dry, well formed, free-flowing crystals gave only a very slight turbidity when dissolved in water at room temperature. Upon standing this turbidity increased a bit. But it was found that with 0.3% H_2SiF_6 as solvent no turbidity developed with standing overnight. Ten grams of the crystals was dissolved in 40 ml. of each of a series of fluosilicic acid solutions with concentrations varying from 0.1 to 1.0%. The solutions were allowed to stand in beakers coated lightly with wax. The decreasing turbidity with increasing acid concentration was easily observed, and it was decided to work with 0.5% acid as solvent to provide a margin of safety, inasmuch as the 0.3% solution remained clear for the 24 hours of the test.

No attempt was made to prepare a salt having the exact composition of the hexahydrate. Instead, the hydrated salt was thoroughly mixed and analyzed for magnesium when complexes of known composition were to be made up. The ratio of Mg to SiF_6 was 1:1.005, with, originally, a content of 63.5% $MgSiF_6$ on the basis of the magnesium determination (precipitation with oxine as described later under the system $(NH_4)_2SiF_6$–$MgSiF_6$–H_2O). The theoretical value is 60.63% for $MgSiF_6 \cdot 6H_2O$. On standing in air, covered by a watch glass, the water content rose, later analyses giving 62.1 and then 61.5% $MgSiF_6$. As observed by others,[10] moreover, dehydration at 105° caused considerable decomposition. The heated product gave a very turbid solution, apparently precipitating MgF_2.

Strontium Fluosilicate.—The procedure was the same as that for the magnesium salt, with recrystallized $SrCl_2 \cdot 6H_2O$ as the starting material. Tests again showed that 0.5% H_2SiF_6 was more than enough to prevent turbidity in a solution of 5 g. of the salt ($SrSiF_6 \cdot 2H_2O$) in 40 ml. Analysis of the hydrated salt gave 13.00% loss of weight (as H_2O) at 105°, 47.59% residue on ignition (as SrF_2), a value of 1:1.003 for the ratio Sr:SiF_6 (strontium being determined as the sulfate by the method described under the system $SrCl_2$–$SrSiF_6$–H_2O), and a negative test for chloride. Theoretical values for $SrSiF_6 \cdot 6H_2O$, are 13.56% H_2O and 47.28% SrF_2. In contrast to $MgSiF_6 \cdot 6H_2O$, this hydrate loses its water at 105° without significant decomposition. The anhydrous salt so obtained was 99.7% pure by strontium determination, while the determination of both strontium and fluosilicate gave 1:0.99 for the ratio Sr:SiF_6. In addition, the slight turbidity of its aqueous solution cleared up in 0.5% H_2SiF_6. The analyzed hydrated and anhydrous materials were both used for the making up of complexes of definite composition.

Calcium Fluosilicate.—The same method was again used, with calcium nitrate as starting material. A gelatinous precipitate, difficult to filter, formed if a large excess of H_2SiF_6 was not present. When the well formed crystalline salt was treated with water a very turbid solution was obtained together with a gelatinous precipitate not easily dissolved by addition of H_2SiF_6. If this is the behavior of pure $CaSiF_6$ (see also ref. 10, p. 369), the aqueous solubility reported in the literature[3] has little meaning.

Potassium Fluosilicate.—Since this salt is only slightly soluble the use of alcohol is unnecessary. A dilute solution of C.P. KCl was added to a large volume of dilute (~5%) H_2SiF_6. The transparent potassium fluosilicate was allowed to settle and the solution decanted. The precipitate was washed thoroughly by decantation and then again repeatedly, with water, on filter paper in a büchner funnel. It was finally washed with 95% alcohol and dried at 100°. By conversion to K_2SO_4 with sulfuric acid a purity of 99.7% was calculated, while direct titration of $SiF_6^=$ with 0.1 *N* NaOH and phenolphthalein as indicator, in a hot solution of the salt, gave 100.0%.

Ammonium Fluoride.—For the preparation of complexes of definite composition this salt was used in the form of an analyzed solution of C.P. material (J. T. Baker), which was first adjusted to the methyl red end-point by addition of a small amount of HF. The neutralized solution, preserved in a waxed bottle, contained 21.54% ammonium, determined by distillation and titration, and 22.70% fluoride, determined as PbClF.[11] These values give 1:1.001 for the ratio NH_4:F, corresponding very closely to pure NH_4F. The original solid salt, dried for several weeks over solid KOH in an evacuated desiccator, was used when exact total compositions were not required; the KOH was intended to take up CO_2 from decomposition of ammonium carbonate probably accounting for the original alkalinity.

Other Materials.—C.P. NH_4Cl was used without further purification. C.P. KBr was recrystallized from water, ground after preliminary drying at 105°, and heated finally at 150°. Strontium chloride was used as recrystallized C.P. $SrCl_2 \cdot 6H_2O$.

Procedure and Preliminary Tests.—Mixtures of the components were brought to equilibrium in closed tubes rotated in a large water-bath maintained at 25 ± 0.02°. The solubility tubes and bottles were carefully waxed with material obtained by melting down the fluosilicic acid bottles. The stoppers were of rubber. For analysis the saturated solutions were sampled by means of waxed pipets fitted with filter paper tips.

In all cases the samples were rotated for at least two or three weeks, after which time several of the complexes in each system studied were reanalyzed on consecutive days to verify equilibrium. In each system equilibrium was approached from both directions, *i.e.*, some complexes from undersaturation, others from supersaturation. In the latter cases the mixtures were first shaken at temperatures not exceeding 35°, because of the unstable nature of the metallic fluosilicates.

Specific analytical procedures are described under the individual systems.

As already mentioned, 0.5% H_2SiF_6 was used as solvent in systems involving magnesium and strontium fluosilicates, to prevent hydrolytic precipitation. That slow hydrolysis of $SrSiF_6$ did not occur in the 0.5% acid was ascertained by the constancy of the density of the saturated solution with time. The measurements were made directly in the solubility tube, without removing it from the bath, by means of a Westphal balance constructed from an analytical balance set over the bath. The specific gravities observed varied from 1.14798 by +3, −3, −3, +2, 0 in the last place after 1, 2, 3, 10, 15 days of stirring. The solid was then filtered and analyzed, and the ratio Sr:SiF_6 was found to be 1:1.002 indicating no appreciable hydrolysis.

In addition parts of the isotherms of the systems $(NH_4)_2SiF_6$–H_2SiF_6–H_2O and $SrSiF_6$–H_2SiF_6–H_2O were also studied in order to determine that the solid phases involved would not be affected by the 0.5% fluosilicic acid, or that the presence of the acid would cause no unusual behavior in the ternary phase relations to be investigated.

The measurements for the system $(NH_4)_2SiF_6$—H_2SiF_6—H_2O are listed in Table I, in terms of weight percentage. For the analysis, both of saturated solutions and of wet residues, $(NH_4)_2SiF_6$ was determined as ammonia after distillation with alkali, while H_2SiF_6 was titrated directly with NaOH with phenolphthalein as indicator. This was done in ice-cold solution saturated with KNO_3 to precipitate K_2SiF_6 and prevent reaction of $SiF_6^=$ with the alkali. To check the method, 10-ml. aliquots of ~15% H_2SiF_6 were pipetted into each of six beakers

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(10) Fr. Stolba, *Sitzber. böhm. Ges. Wiss.*, 290 (1877).

(11) Procedure as in W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand, Co., Inc., New York, N. Y., 1939, Vol. I, p. 405.

containing various amounts (0.0 to 5.0 g.) of $(NH_4)_2SiF_6$. The volumes were adjusted to 100 ml., finely divided KNO_3 was added with stirring until in slight excess, and the mixtures were cooled in an ice-water bath for an hour, with frequent thorough stirring. They were then titrated to the methyl red end-point with 1 *N* NaOH, phenolphthalein was added, and the titration was continued to the first pink color. Another aliquot of the fluosilicic acid was treated in the same manner but in platinum for the purpose of standardization. In cold titration with phenolphthalein as indicator the titer was 22.90 ml. of 1 *N* NaOH, while continuation of the titration hot required an additional 45.79 ml. The second titration corresponds to the reaction $SiF_6^= + 4OH^- \rightarrow Si(OH)_4 + 6\ F^-$ and should require twice the volume for the cold titration. Blanks run on the KNO_3 and indicators were found to be negligible. The six test aliquots required 22.79 ml. (with average deviation of 0.02) with methyl red, and 22.91 ± 0.04 with phenolphthalein as indicator. Phenolphthalein was therefore chosen as the indicator.

TABLE I

PARTIAL SYSTEM $(NH_4)_2SiF_6(=A)–H_2SiF_6(=B)–H_2O$ AT 25°; SOLID PHASE, $(NH_4)_2SiF_6$

Wet residue		Saturated solution	
% A	% B	% A	% B
		18.75	0.00
71.44	2.58	16.31	6.67
73.29	4.48	13.75	13.09
72.80	6.04	12.29	17.65
60.97	10.3	10.16	22.57
60.93	11.9	8.54	27.39

Graphical and algebraic consideration of the tie-lines fixed by the compositions of saturated solutions and wet residues[12] shows that the solid phase is anhydrous $(NH_4)_2SiF_6$ from pure water up to a concentration of ~27% H_2SiF_6. The algebraic extrapolation gives an average error of +0.6(±0.2)% H_2SiF_6 at 100% $(NH_4)_2SiF_6$. For the solubility of $(NH_4)_2SiF_6$ at 25°, here observed as 18.75%, Jatlov and Pinaevskaya[12a] report two values, 18.75 and 18.32%.

For the partial isotherm of the system $SrSiF_6$–H_2SiF_6–H_2O the measurements are listed in Table II. The complexes were prepared from $SrSiF_6 \cdot 2H_2O$, analyzed (~30%) H_2SiF_6, and water. For the analysis of the saturated solution, H_2SiF_6 was determined as described in the preceding system and total fluosilicate was determined on a separate sample, usually smaller, by direct titration of the solution with NaOH, first neutralizing the acid at room temperature, then heating, and completing the titration of the fluosilicate ion. The $SrSiF_6$ was calculated by difference. This analytical scheme was checked in various ways. Solutions with known percentages of $SrSiF_6$ (3.16 and 3.74) in presence of fluosilicic acid, gave 3.17 and 3.77%, respectively. Aliquots of a solution of H_2SiF_6 requiring 25.42 (average) ml. of 1 *N* NaOH for cold titration in presence of KNO_3 and phenolphthalein as previously described, required 25.46, 25.43 and 25.45 ml. in the presence, in addition, of 1, 3 and 5 g. $SrSiF_6$, respectively. Finally, the direct (hot) titration of total fluosilicate in presence of strontium was verified by analysis of samples of strontium fluosilicate both in this manner and by the method described later for the system NH_4F–$(NH_4)_2SiF_6$–H_2O, involving precipitation of K_2SiF_6 and hot titration of the filtered precipitate with NaOH. The two procedures gave values differing by only 3/1000.

TABLE II

PARTIAL SYSTEM $SrSiF_6(=A)–H_2SiF_6(=B)–H_2O$ AT 25°; SOLID PHASE $SrSiF_6 \cdot 2H_2O$

Original complex		Saturated solution	
% A	% B	% A	% B
		(14.9)[a]	0.00
		14.58	0.42
19.89	3.95	11.39	4.52
21.52	7.84	8.22	9.53
22.83	12.03	5.10	15.49
23.63	16.25	2.45	21.87
26.45	19.44	1.44	27.82
(48.68	13.37)[b]	1.18	29.93

[a] Estimated by extrapolation to 0% H_2SiF_6. [b] Wet residue.

The tie-lines fixed by compositions of solutions and original complexes indicated, both graphically and by algebraic extrapolation,[13] that the solid phase is $SrSiF_6 \cdot 2H_2O$ throughout. The average extrapolation error is −0.5 (±0.1)% H_2SiF_6 at the line representing the theoretical percentage of $SrSiF_6$ in the dihydrate. The lowest concentration of H_2SiF_6 in the saturated solution was 0.42%, calculated from the observed weight percentage of $SrSiF_6$ and the fact that the complex was prepared from 0.5% H_2SiF_6 and solid $SrSiF_6 \cdot 2H_2O$. The solubility of $SrSiF_6 \cdot 2H_2O$ in pure water, by extrapolation to 0% H_2SiF_6, is then ~14.9% in terms of $SrSiF_6$. The only value in the literature, for comparison, is that of 3.22% at 15°.[14]

System K_2SiF_6–KBr–H_2O.—The saturated solutions were analyzed for total solid by evaporation and drying at 105° (in platinum), and for KBr by the Mohr method. The calculation of the percentage of K_2SiF_6 by difference has, of course, little numerical significance, since the quantity found was of the order of magnitude of the uncertainties involved. The precise value of the low concentration of K_2SiF_6 in solution, however, does not affect the indirect determination of the composition of the solid phase, which was the purpose in studying this isotherm. Tests showed the Mohr titration of bromide in presence of K_2SiF_6, which gives an acidic reaction, to be satisfactory.

The measurements are listed in Table III. Graphical and algebraic extrapolation of the tie-lines shows that the solid potassium fluosilicate is anhydrous. The average deviation from pure K_2SiF_6, by extrapolation, is +0.27 (±0.26)% KBr at 100% K_2SiF_6. The solubility of K_2SiF_6, ~0.15%, was determined only roughly. Carter[8] reported 0.177 g./100 ml. solution at 25°, while in-

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[12] F. A. H. Schreinemakers, *Z. phys. Chem.*, **11**, 75 (1893).

[12a] V. S. Jatlov and E. N. Pinaevskaya, *J. Gen. Chem. U. S. S. R.*, **16**, 259 (1945).

[13] A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

[14] R. Fresenius, *Z. anal. Chem.*, **29**, 145 (1890).

terpolation of Ryss's values at 20 and 40° (ref. 7b) gives ~0.134% at 25°.[15]

TABLE III

SYSTEM K_2SiF_6(A)–KBr(B)–H_2O AT 25°

Complex		Solution		Solid	%B at
% A	% B	% A	% B	phase	100% A
...	0.00	0.15	0.00	A	
10.01	5.90	.02	6.58	A	−0.22
9.99	7.13	.02	7.92	A	.00
10.04	9.92	.01	11.05	A	+ .68
9.76	15.50	.09	17.14	A	+ .20
9.98	20.33	.07	22.56	A	+ .07
9.87	23.82	.19	26.30	A	+ .73
9.72	25.87	.09	28.61	A	+ .18
9.03	30.28	.05	33.26	A	+ .09
6.52	34.07	.07	36.42	A	+ .22
8.11	36.88	.09	40.05	A	+ .56
10.06	39.48	.14	40.47	A + B	
0.00	...	.00	40.51	B	

System $(NH_4)_2SiF_6$–$MgSiF_6$–0.5% H_2SiF_6 at 25°.—For the analysis of the saturated solution, the ammonium salt was determined by ammonia distillation, and the magnesium salt in a separate sample by the quinolate method for magnesium. For this purpose the sample was weighed in a small platinum dish covered with a watch glass. A platinum cover was then substituted for the glass one and sulfuric acid was added carefully to the sample. The solution was evaporated to fumes of SO_3 to drive off HF and SiF_4, cooled, and transferred to a Pyrex beaker. It was again evaporated to fumes of SO_3, fumed strongly, cooled, diluted with water and just neutralized with ammonia. After filtration to remove suspended material, the solution was aliquoted if necessary and the magnesium was precipitated and weighed as the quinoline dihydrate.

The results are listed in Table IV. Since the complexes were made up from $(NH_4)_2SiF_6$, $MgSiF_6 \cdot 6H_2O$ and 0.5% H_2SiF_6, the actual weight percentage of H_2SiF_6, both in the complexes and in the saturated solutions, is not uniform; $\%H_2SiF_6 = 0.5 - \%(NH_4)_2SiF_6/200 - \%\,MgSiF_6(0.00825)$, in which the factor 0.00825 represents $(MgSiF_6 \cdot 6H_2O/MgSiF_6)/200$. The average percentage of H_2SiF_6 in the solution is therefore close to ~0.3. The solubility of the magnesium salt in absence of the ammonium salt is 23.54% $MgSiF_6$ with ~0.3% H_2SiF_6 in solution. Roughly, by analogy with $SrSiF_6$ in Table II, one may estimate a solubility of ~23.7% in pure water. This is to be compared with 24.1%, interpolated from the measurements by Jatlov and Pinaevskaya[16] at 20 and 40°; these authors also reported the solubility at 20° in presence of up to 46% H_2SiF_6.

TABLE IV

SYSTEM $(NH_4)_2SiF_6$–$MgSiF_6$–0.5%H_2SiF_6 AT 25°

A = $(NH_4)_2SiF_6$, B = $MgSiF_6$, W = H_2O

Complex		Solution		Solid
% A	% B	% A	% B	phase
25.33	6.96	15.85	7.85	A
24.77	9.64	14.77	10.91	A
24.95	10.70	14.36	12.23	A
25.64	12.07	13.61	14.01	A
23.74 71.96[a]	15.08 5.55[a]	12.48	17.32	A
17.98	18.73	11.62	20.19	A
17.07	20.35	11.39	20.85	A + B·6W
10.94	25.72	11.35	20.96	A + B·6W
9.46	25.04	10.45	21.28	B·6W
6.80	25.87	7.51	22.08	B·6W
3.82	25.81	4.14	22.85	B·6W
1.90	30.35	2.37	23.06	B·6*W*
0.00	...	0.00	23.54	B·6W

With the small percentage of H_2SiF_6 disregarded, the percentages listed in Table IV may be plotted in the usual fashion on a triangular diagram with the corners representing $(NH_4)_2SiF_6$, $MgSiF_6$ and "H_2O." The plot shows clearly that the solid phases are pure $(NH_4)_2SiF_6$ and $MgSiF_6 \cdot 6H_2O$. For precise algebraic verification of these exact solid phases, the three components may be taken strictly as $(NH_4)_2SiF_6$, $MgSiF_6 \cdot 6H_2O$ and 0.5% H_2SiF_6. Algebraic extrapolation of the tie-lines then gives errors of +0.09, +0.29, +0.06 and −0.05% $(NH_4)_2SiF_6$ at 100% $MgSiF_6 \cdot 6H_2O$, and an average error of −0.03 (±0.11)% $MgSiF_6 \cdot 6H_2O$ at 100% $(NH_4)_2SiF_6$.

System $SrCl_2$–$SrSiF_6$–0.5% H_2SiF_6 at 25°.—The saturated solutions were analyzed for total strontium and for chloride. The preparation of samples for strontium determination was the same as that already described for magnesium, up through their evaporation practically to dryness in beakers to expel excess H_2SO_4. After addition of 100 ml. of water and 100 ml. of 95% alcohol, the precipitate of $SrSO_4$ was allowed to settle overnight. It was filtered through asbestos in an ignited gooch crucible, being washed and transferred with 50% alcohol containing a little H_2SO_4. The strontium sulfate was finally washed with small portions of 95% alcohol, dried at 110°, and ignited to constant weight at ~800°. Chloride was determined by the Volhard method, the excess of $AgNO_3$ being titrated with KCNS in suitable aliquots after filtration of AgCl. Tests were made showing that $SrSiF_6$ did not interfere with the chloride determination.

TABLE V

SYSTEM $SrCl_2$–$SrClF_6$–0.5%H_2SiF_6 AT 25°

A = $SrCl_2$, B = $SrSiF_6$, W = H_2O

Complex		Solution		Solid
% A	% B	% A	% B	phase
...	0.00	35.82[a]	0.00	A·6W
42.10	0.66	35.23	.39	A·6W + B·2W
41.71	3.01	35.30	.39	A·6W + B·2W
30.81	17.80	35.27	.64	A·6W + B·2W
28.33	17.96	35.20	.60	A·6W + B·2W
27.89	17.90	34.81	.65	B·2W
27.31	17.94	34.20	.64	B·2W
26.87	17.90	33.60	.93	B·2W
25.90	18.16	32.36	1.22	B·2W
20.70	19.30	26.10	2.20	B·2W
15.55	20.41	19.35	4.23	B·2W
10.36	21.50	12.83	6.45	B·2W
5.25	23.27	6.41	9.68	B·2W

[a] In pure water.

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(15) There is considerable disagreement at other temperatures also. While Carter (ref. 3) gives 0.132 g./100 ml. at 16°, A. A. Wassilieff and N. N. Martianoff, *Z. anal. Chem.*, **103**, 103 (1935), give 0.115 at 17° and M. Pierrat, *Compt. rend.*, **172**, 1041 (1921), gives 0.09 at 14°.

(16) V. S. Jatlov and E. N. Pinaevskaya, *J. Gen. Chem., U. S. S. R.*, **8**, 1665 (1938), cited in Seidell, Ref. 2, p. 970.

The data are listed in Table V. The complexes were made up from $SrCl_2 \cdot 6H_2O$, $SrSiF_6 \cdot 2H_2O$ and 0.5% H_2SiF_6, so that %H_2SiF_6, both in mixtures and in solution, is 0.5 − %$SrCl_2$(0.00841) − %$SrSiF_6$ (0.00557). A triangular plot of the tabulated percentages disregarding the small and slightly variable percentage of H_2SiF_6, and with "H_2O" as one of the corners, shows that the solid phase for the fluosilicate is $SrSiF_6 \cdot 2H_2O$. Algebraic extrapolation on the basis of $SrCl_2 \cdot 6H_2O$, $SrSiF_6 \cdot 2H_2O$ and 0.5% H_2SiF_6 as components, gives −0.21 (±0.39)% $SrCl_2 \cdot 6H_2O$ at 100% $SrSiF_6 \cdot 2H_2O$ as the extrapolation error.

System $(NH_4)_2SiF_6$–$SrSiF_6$–0.5% H_2SiF_6 at 25°.—The solutions were analyzed by separate determinations of ammonium and of strontium. The procedure for strontium was a slightly different earlier technique later replaced by the method already described for the system $SrCl_2$–$SrSiF_6$–H_2O. The sample was evaporated to dryness with HCl several times, in a small platinum dish, and then transferred to a beaker. After repeated evaporations with HNO_3 and HCl the silica was dehydrated at 110° and the residue treated again with dil. HCl. The filtrate from the silica was treated with a small excess of H_2SO_4 and evaporated to fumes of SO_3. Water and alcohol were then added, with separation of $SrSO_4$ as before.

The complexes were made up from $(NH_4)_2SiF_6$ and 0.5%H_2SiF_6, with either $SrSiF_6$ or $SrSiF_6 \cdot 2H_2O$. In some cases the solids initially dissolved completely, and upon rotation in the bath overnight a silky white solid precipitated, which was quite different in appearance from the starting materials. When the correct quantities of the filtered saturated solutions of pure $(NH_4)_2SiF_6$ and pure $SrSiF_6$ at 25° were mixed, this same silky solid appeared upon rotation for a few hours. The new solid phase also formed in presence of HNO_3, HCl or as much as 10% H_2SiF_6.

The measurements are listed in Table VI and are plotted in Fig. 1 in terms of $(NH_4)_2SiF_6$, $SrSiF_6$ and 0.5% H_2SiF_6 as components. The deviations from strict ternary relations caused by the neglect of the slight variation of the solvent composition is here very small because of the generally low solubility of the strontium salt. Accordingly, the tie-lines for saturation with $(NH_4)_2SiF_6$ meet the corner of the diagram with small extrapolation errors, namely, −0.07, −0.22 and −0.05% $SrSiF_6$, respectively, at 100% $(NH_4)_2SiF_6$. The tie-lines for the next branch of the solubility curve indicate a 1:6 anhydrous compound, or $(NH_4)_2SiF_6 \cdot 6SrSiF_6$, as solid phase. The nine tie-lines involved intersect the base at an average value of 11.56% $(NH_4)_2SiF_6$; with exception of the first, extrapolating to 10.1%, the values range from 11.44 to 11.76%. The theoretical value for the 1:6 molar ratio is 11.45%.

TABLE VI

SYSTEM $(NH_4)_2SiF_6$–$SrSiF_6$–0.5%H_2SiF_6 AT 25°

A = $(NH_4)_2SiF_6$, B = $SrSiF_6$, W = H_2O

Complex		Solution		Solid phase
% A	% B	% A	% B	
35.29	1.37	18.60	1.73	A
25.83	2.94	18.54	3.25	A
34.71	4.56	18.55	5.70	A[m]
33.44	9.74	18.72	4.88	A + A·6B
23.81	11.03	18.71	4.85	A + A·6B
22.00	12.78	18.68	5.03	A + A·6B
18.89	11.75	18.60	4.94	A + A·6B
21.73	15.82	18.71	4.91	A + A·6B
Average		18.68	4.92	A + A·6B
18.00	11.87	18.71	4.87	A·6B
17.87	12.96	18.55	4.97	A·6B
16.84	12.87	17.37	5.02	A·6B
12.11	16.33	12.18	5.02	A·6B
10.92	12.31	10.86	5.19	A·6B
7.92	14.77	7.45	5.73	A·6B
4.98	19.65	3.75	7.02	A·6B
2.90	20.47	1.48	9.44	A·6B
2.19	22.60	0.63	11.49	A·6B
1.01	22.27	0.20	14.66	A·6B + B·2W

[m] Metastable.

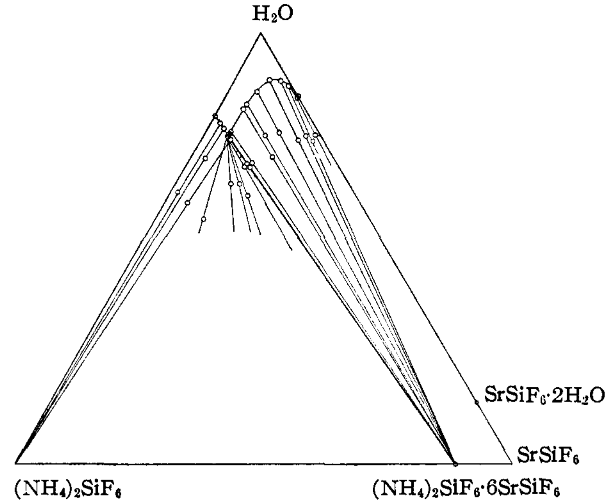

Fig. 1.—System $(NH_4)_2SiF_6$–$SrSiF_6$–0.5% H_2SiF_6 at 25°.

The double salt is seen to be congruently soluble, and an attempt was made to check its composition by direct analysis of the filtered solid. Although the material filtered easily, however, it could not be separated well from the mother liquor even when centrifuged, but remained pasty and moist. When rubbed between the fingers it did not feel gelatinous but seemed to have a somewhat fibrous texture. A solution of the material in water was only slightly turbid while a solution in 0.5% H_2SiF_6 was clear. A sample of the centrifuged solid lost ∼30% of its weight at 100°. Another sample was dissolved in dil. HCl and aliquoted for analysis, giving 2.26% NH_3, 20.36% Sr and 42.4% SiF_6, corresponding to the molar ratios NH_3:Sr:SiF_6 = 0.133:0.232:0.299, a result which makes the composition accountable in terms of fluosilicates of ammonium and strontium. In view of the low solubility of SrF_2, the fact that the aqueous solution of the centrifuged material had only a slight turbidity, which may be attributed to a slight hydrolysis, indicates further that the salts are present as fluosilicates only. Moreover, when the centrifuged material was washed with alcohol, it dried to a fine white powder which lost very little weight when heated at 110°; it was therefore apparently anhydrous, in agreement with the tie-line extrapolations. Finally, one of the original wet residues was washed with water and then with alcohol, sucked as dry as possible, and placed in an evacuated desiccator with $CaCl_2$ overnight. Analysis showed 11.51% $(NH_4)_2SiF_6$ by ammonia determination, and 87.52% $SrSiF_6$ by strontium determination (use of 0.5% HNO_3 as wash water gave 87.76%), compared to the theoretical values of 11.45 and 88.55%, respectively, for the formula $(NH_4)_2SiF_6{\cdot}6SrSiF_6$; for the 1:5 formula, the values would be 13.43 and 86.57%, respectively.

The solution saturated with $(NH_4)_2SiF_6$ and double salt contains 18.68% $(NH_4)_2SiF_6$, 4.92% $SrSiF_6$, and 0.38% H_2SiF_6; that saturated with double salt and $SrSiF_6{\cdot}2H_2O$ contains 0.20% $(NH_4)_2SiF_6$, 14.66% $SrSiF_6$ and 0.43% H_2SiF_6.

The Quaternary System NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O **at 25°.**—The quaternary isotherm requires the study of its three ternary aqueous systems, which are therefore presented first. Since the only fluosilicate involved is the ammonium salt, the solvent in this work is pure water. All mixtures, both ternary and quaternary, were rotated in wax-lined bottles.

For brevity in discussion, the solid phases will be represented by the symbols A for NH_4F, B for NH_4Cl, C for $(NH_4)_2SiF_6$, and D for $NH_4F{\cdot}(NH_4)_2SiF_6$.

System NH_4F–NH_4Cl–H_2O.—The solutions were analyzed for total ammonia and for chloride, so that NH_4F was calculated by difference. Chloride was determined by precipitation with excesss of standard $AgNO_3$, filtration of the AgCl, and determination of the excess of $AgNO_3$ in ammoniacal solution by the cyanide method. Neither the Mohr titration nor the Volhard method gave good results in the presence of NH_4F at concentrations encountered in this system, according to various tests on known samples. Despite careful adjustment of the *p*H to 6.5–7.0 in the Mohr method, the concentration of free ammonia may have been high enough to interfere by complex ion formation. In the Volhard titration with KCNS the ferric alum indicator failed to give the characteristic color change because of complex ion formation with fluoride. Addition of boric acid or aluminum nitrate to bind the fluoride did not help. In the procedure used, a 100-ml. aliquot of the filtrate containing the excess of $AgNO_3$ was treated, in ammoniacal solution, with an excess of standard KCN, and titrated with standard $AgNO_3$ in presence of 0.2 g. of KI as indicator (Liebig-Dénigès method). Tests for determination of 0.25 g. of KCl in presence of up to 5 g. of NH_4F showed no interference on the part of the fluoride.

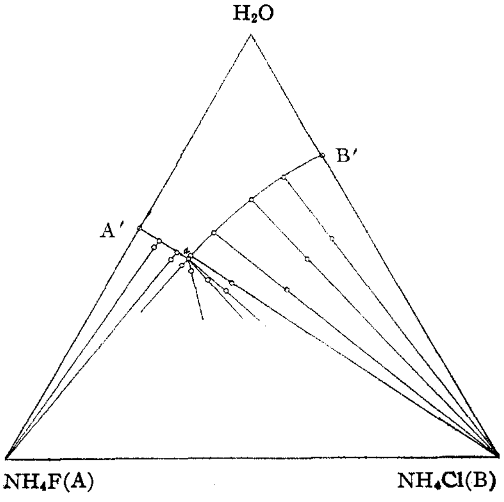

Fig. 2.—System NH_4F–NH_4Cl–H_2O at 25°.

The data, listed in Table VII and plotted in Fig. 2, show that the only solid phases are the pure anhydrous salts, NH_4F and NH_4Cl, on the basis of graphical and algebraic extrapolation of the tie-lines. The solubility observed for NH_4F at 25° (45.1%) is lower than two values in the literature, both ~46.1%.[16a]

TABLE VII

SYSTEM NH_4F(A)–NH_4Cl(B)–H_2O AT 25°

Complex		Solution		Solid phase
% A	% B	% A	% B	
...	0.00	45.12	0.00	A
44.51	5.20	42.73	5.36	A
42.35	10.02	40.42	10.32	A
40.95	12.80	38.97	13.48	A + B
39.79	15.26	38.97	13.50	A + B
37.49	20.16	38.96	13.47	A + B
25.13	25.17	38.98	13.48	A + B
Average (*a*)		38.97	13.48	A + B
33.21	25.07	38.18	13.61	B
23.06	36.93	30.94	15.43	B
15.16	37.45	19.62	19.16	B
7.99	40.19	10.30	23.14	B
0.00	...	0.00	28.37	B

System NH_4Cl–$(NH_4)_2SiF_6$–H_2O.—The analysis in this system consisted of determination of total ammonia and determination of chloride by the usual Volhard method, $(NH_4)_2SiF_6$ being calculated by difference. The fluosilicate does not interfere with the chloride determination, as shown by experiments on known mixtures with varying amounts of $(NH_4)_2SiF_6$. The data are given in Table VIII and plotted in Fig. 3. Again the tie-lines indicate that the solid phases are simply the anhydrous salts, NH_4Cl and $(NH_4)_2SiF_6$.

TABLE VIII

SYSTEM NH_4Cl(B)–$(NH_4)_2SiF_6$(C)–H_2O AT 25°

Complex		Solution		Solid phase
% B	% C	% B	% C	
45.28	0.79	27.97	0.78	B
35.21	1.30	27.81	1.47	B
44.84	1.58	27.52	2.21	B
47.87	3.13	27.35	2.73	B + C
43.09	4.61	27.40	2.59	B + C
40.58	6.91	27.42	2.56	B + C
41.20	9.01	27.37	2.62	B + C
Average (*b*)		27.39	2.63	B + C
20.20	25.17	26.17	3.00	C
15.03	27.04	19.73	4.32	C
10.40	29.13	13.73	6.30	C
5.70	30.56	7.36	10.21	C

System NH_4F–$(NH_4)_2SiF_6$–H_2O.—The saturated solutions were analyzed for total ammonia, and for fluosilicate by titration of precipitated K_2SiF_6, so that NH_4F was calculated by difference. For the fluosilicate determination the sample was

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[16a] W. M. Spurgeon, Dissertation, University of Michigan, Publication No. 1079 (1941); V. S. Jatlov and E. M. Poliakova, *J. Gen. Chem., U. S. S. R.*, **15**, 724 (1945).

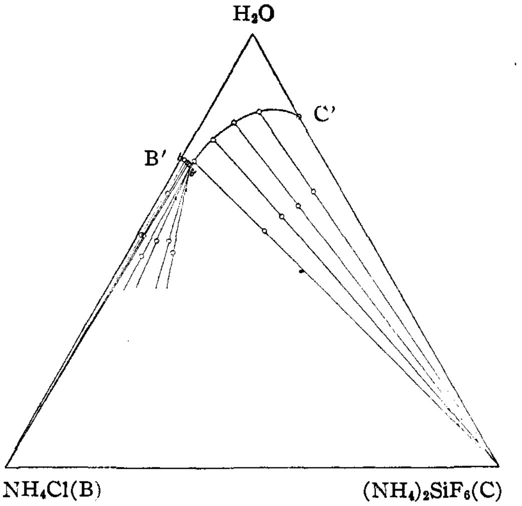

Fig. 3.—System NH_4Cl–$(NH_4)_2SiF_6$–H_2O at 25°.

weighed in a 150-ml. platinum dish and the volume adjusted to ~50 ml. with water. Finely divided KNO_3 was added with stirring until a small excess was present. A heavy platinum wire was used as a stirring rod. The mixture was cooled in an ice-water bath for about two hours and stirred thoroughly several times. After decantation through asbestos in a gooch crucible the K_2SiF_6 was transferred and washed with ice-cold saturated KNO_3 solution. Washings were limited to ~50 ml. to cut down solubility losses. After its outside and bottom had been carefully rinsed the crucible was placed in 150 ml. of nearly boiling water. Phenolphthalein indicator was added and the solution titrated with 1 N NaOH to a permanent pink. The final temperature of the solution was ~70°.

The principal error in the determination is the incomplete precipitation of the fluosilicate as the potassium salt. The solubility of K_2SiF_6 in saturated KNO_3 at room temperature is reported to be 5.0 mg. per 100 ml. solution.[17] The solubility loss is relatively small for large samples, being only 5/1000 for 1 g. of K_2SiF_6 precipitated in a volume of 100 ml. Also, since $(NH_4)_2SiF_6$ is in general the minor component in the saturated solutions under consideration, the error in its determination causes very little relative error in the percentage of NH_4F, which is determined by difference.

The measurements are reported in Table IX and plotted in Fig. 4. The formation of the 1:1 compound $NH_4F\cdot(NH_4)_2SiF_6$ is clearly indicated by the diagram. The four tie-lines for the double salt branch of the solubility curve intersect the base, by algebraic extrapolation, at 83.3, 83.5, 83.2, 83.0% $(NH_4)_2SiF_6$, respectively, while the theoretical value for the 1:1 double salt is 82.79%. From the plot it is evident that the double salt is incongruently soluble in water at this temperature; while solution *d* is congruently saturated with the solids NH_4F and $NH_4F\cdot(NH_4)_2SiF_6$, solution *c* is incongruently saturated with its two solids, the double salt and $(NH_4)_2SiF_6$.

TABLE IX

SYSTEM NH_4F(A)–$(NH_4)_2SiF_6$(C)–H_2O AT 25°

D = $NH_4F\cdot(NH_4)_2SiF_6$

Complex % A	Complex % C	Solution % A	Solution % C	Solid phase
53.85	1.99	44.62	1.55	A + D
44.00	14.12	44.66	1.53	A + D
Average (*d*)		44.64	1.54	A + D
37.43	15.40	41.62	1.71	D
31.71	16.94	35.01	2.54	D
25.59	20.12	27.81	4.14	D
20.57	21.87	21.42	7.15	D
18.45	30.25	20.13	8.19	D + C
16.86	27.68	20.13	8.16	D + C
Average (*c*)		20.13	8.18	D + C
15.48	25.24	19.04	8.31	C
11.17	27.10	13.94	9.27	C
6.33	29.71	7.94	11.54	C

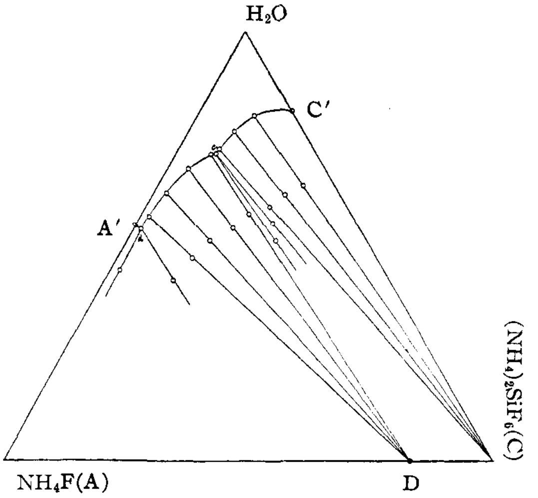

Fig. 4.—System NH_4F–$(NH_4)_2SiF_6$–HO_2 at 25°; D = $NH_4F\cdot(NH_4)_2SiF_6$

The Quaternary Isotherm.—Each of the quaternary isothermal curves for solutions saturated with two solids was investigated by addition of the third salt component to mixtures calculated to give one of the ternary isothermally invariant solutions of twofold saturation. Thus the addition of A to mixtures giving point *c* of Fig. 4 leads to the quaternary curve for saturation with solids D and C. The intersections of these curves constitute isothermally invariant quaternary solutions saturated with three solids. No points were obtained on the very short curve for saturation with solids A and B.

The compositions of the saturated quaternary solutions are presented in Table X. The isothermally invariant points alone (binary, ternary and quaternary) are summarized in Table XI.

The mixtures were rotated for at least two weeks before analysis of the saturated solutions. A check on the percentage of chloride in solution 9 of Table X, after three more days of stirring, showed that equilibrium had been reached. The agreement of the compositions of invariants approached with different total compositions (solutions 8, 9, 10 as also solutions 15, 16), is further proof of equilibrium. The presence of the expected solid phases was in each case verified through the characteristic appearance of each solid, already familiar from the ternary work. NH_4F was easily recognized be-

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[17] Wassilieff and Martianoff, ref. 15.

TABLE X

SYSTEM NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O AT 25°

Point or curve	Weight percentage				Solid phases
	NH_4F	NH_4Cl	$(NH_4)_2SiF_6$	H_2O	
c → *1*	18.06	5.66	6.19	70.09	C + D
c → *1*	17.17	10.97	4.46	67.40	C + D
c → *1*	16.33	15.77	3.39	64.51	C + D
b → *1*	4.88	24.67	3.12	67.33	B + C
b → *1*	(11.9?)	21.15	(3.5?)	63.44	B + C
b → *1*	13.13	20.88	3.19	62.80	B + C
b → *1*	14.06	20.55	2.98	62.41	B + C
1	15.47	19.92	2.73	61.88	B + C + D
1	15.43	19.96	2.73	61.88	B + C + D
1	15.69	19.88	2.73	61.70	B + C + D
1 → *2*	17.41	19.34	2.44	60.81	B + D
1 → *2*	34.30	14.16	1.20	50.34	B + D
d → *2*	42.90	3.58	1.37	52.15	A + D
d → *2*	41.32	6.85	1.24	50.59	A + D
2	38.58	13.34	1.07	47.01	A + B + D
2	38.52	13.40	1.07	47.01	A + B + D

TABLE XI

INVARIANT POINTS AT 25°

Point	Weight percentage				Solids
	NH_4F	NH_4Cl	$(NH_4)_2SiF_6$	H_2O	
A'	45.12			54.88	A
a	38.97	13.48		47.55	A + B
B'		28.37		71.63	B
b		27.39	2.63	69.98	B + C
C'			18.75	81.25	C
c	20.13		8.18	71.69	C + D
d	44.64		1.54	53.82	D + A
1	15.53	19.92	2.73	61.82	B + C + D
2	38.55	13.37	1.07	47.01	A + B + D

cause its crystals floated to the top instead of settling. $(NH_4)_2SiF_6$ had a glassy appearance while the crystals of NH_4Cl were lustrous and opaque. The double salt crystals were unlike both of these, being dull and opaque, like oven-dried powdered silver nitrate; it was not as white as the other two. Analyses were run in duplicate, separate samples being used for determination of total ammonia by distillation, chloride by the cyanide method described, and fluosilicate by (hot) titration with NaOH of the precipitate of K_2SiF_6. NH_4F was calculated by difference, and the percentage of water as 100 − Σ(% salt). In the chloride determination, partial removal of fluosilicate was necessary in samples containing larger amounts of $(NH_4)_2SiF_6$ because of the precipitation of silica when the filtrate containing excess of $AgNO_3$ was made alkaline with ammonia. It was otherwise difficult to detect the turbidity at the end-point when AgI is first precipitated, in the already turbid mixture. The weighed sample was therefore treated with excess KNO_3, and the clear supernatant liquid was aliquoted for the chloride determination. In this case the solution remained clear when made ammoniacal. Tests of the method with varying amounts of NH_4F and $(NH_4)_2SiF_6$ present showed it to be without error.

The four percentages in Table X may be represented in a regular tetrahedral isothermal figure. The orthogonal projection of the relations upon the base (three salts) of this tetrahedron appears as in Fig. 5. On this figure the salt percentages are plotted directly, each augmented by one-third the percentage of water. Figure 5 is not the full dia-

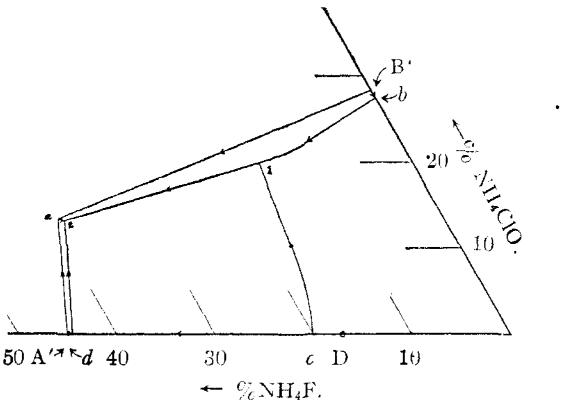

Fig. 6.—System NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O at 25°; Schreinemakers diagram showing % NH_4F and % NH_4Cl. Point O = H_2O or $(NH_4)_2SiF_6$.

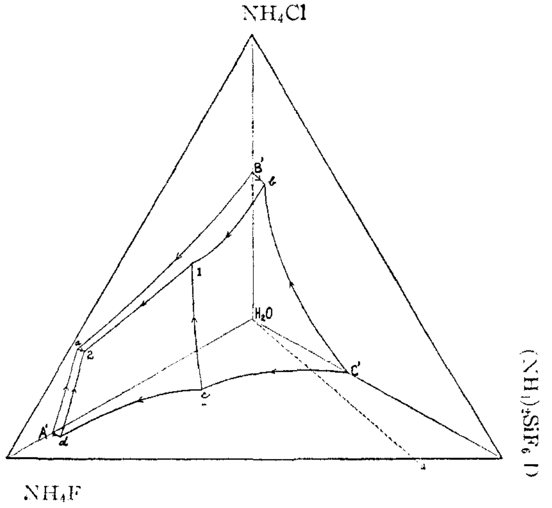

Fig. 5.—System NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O at 25°; orthogonal diagram to 70% salt; D = $NH_4F \cdot (NH_4)_2SiF_6$.

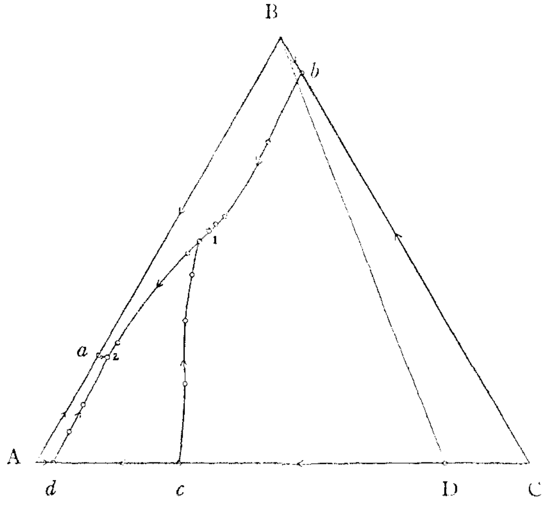

Fig. 7.—System NH_4F–NH_4Cl–$(NH_4)_2SiF_6$–H_2O at 25°; Jänecke diagram.

gram, but is cut off at the limit of 70% for each salt.

A different view of the tetrahedron, bringing out something of the water content of the saturated solution, is shown in Fig. 6, which is a Schreinemakers projection,[18] obtained by superimposing the H_2O and $(NH_4)_2SiF_6$ corners of the tetrahedron and projecting parallel to the edge H_2O–$(NH_4)_2SiF_6$. Finally, the salt proportions (water neglected) of the saturated solutions are projected, radially from the H_2O corner upon the salt base, in the Jänecke diagram of Fig. 7. This represents the relative weight percentage of each salt in the total salt content.

Of the two 3-solid invariant points, point *2*, lying, as seen in Fig. 7, in the triangle of its three solids, A, B, D, is congruently saturated with them and is the congruent drying-up point, at equilibrium, for all solutions with salt proportions in the triangle ABD, with the phase reaction Liquid → A + B + D + $H_2O\uparrow$ in isothermal evaporation. Point *1*, lying outside the triangle of its solids, B, C, D, is incongruently saturated. Its phase reaction is of the transition type, Liquid + C → B + D + $H_2O\uparrow$. It is, therefore, the incongruent drying-up point, at equilibrium, for isothermal evaporation of solutions with salt proportions in triangle BCD. Solutions reaching point *1* from the region D*1*B would lose solid C in the invariant reaction (for complete equilibrium) and then travel on curve *1* → *2* to point *2*, to dry up to A + B + D. With a rate too high for complete equilibrium, solid C will not be consumed at point *1*, and all liquids reaching point *1* proceed to point *2*, which is therefore the practical drying-up point for the whole system. Point *2* is therefore the only minimum of vapor pressure of the isothermal solubility surfaces and curves, and the arrows on the curves indicate the direction followed during isothermal evaporation of the solutions saturated with two solids. The phase reaction on curve *c* → *1* is the same as that at the ternary point *c* itself, Liquid + C → D + $H_2O\uparrow$, except that the liquid now contains NH_4Cl in addition. This transition curve is therefore crossed, in isothermal evaporation with complete equilibrium, only by solutions with original salt proportions in the region *c1*D, when, with the liquid traveling on the curve, C comes to be completely consumed. For practical conditions, however, it is crossed by any solution reaching it, or from the region *c1*C, and the unchanged C takes hardly any part in the ensuing phase reactions.

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[18] F. A. H. Schreinemakers, *Z. physik. Chem.*, **59**, 642 (1907).

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, ANGLO-IRANIAN OIL CO., LTD.]

The Preparation and Properties of Sulfur Compounds Related to Petroleum. I. The Dialkyl Sulfides and Disulfides[1]

BY D. T. MCALLAN, T. V. CULLUM, R. A. DEAN AND F. A. FIDLER

The preparation of fourteen dialkyl sulfides and eleven dialkyl disulfides is given, together with some of their physical properties. For purposes of characterization, mercuric chloride derivatives and sulfones have been prepared from the sulfides. It has been shown that under certain conditions, a mixture of two symmetrical disulfides will disproportionate to give an equilibrium mixture containing the unsymmetrical compound. This reaction is extremely useful for the preparation of certain unsymmetrical disulfides.

Introduction

The growing interest which the petroleum industry is taking in the gradually increasing production of high sulfur crude oils has been pointed out recently in numerous articles in the scientific press. An examination of the tables of physical properties of sulfur compounds recently compiled by the Bureau of Mines,[2] shows that the data for even the simplest members are far from complete and of questionable accuracy. Although the deleterious effects of some of the sulfur compounds in petroleum products are well known and many refinery processes have been developed for their removal, yet the fundamental knowledge of their chemical properties is extremely limited. A program designed to assist in filling this gap was therefore begun in these laboratories. The present program has been confined to the synthesis of those sulfur compounds which have been identified in straight run distillates, which means that thiophenes and unsaturated sulfur compounds have not been included. A quantity of 500 g. of the pure compound in each case was aimed at, of which 200 g. was allocated as a standard sample.

Discussion

Dialkyl Sulfides.—Fourteen dialkyl sulfides have been prepared and their physical properties determined. These include all the possible members, both symmetrical and unsymmetrical, having methyl, ethyl, *n*-propyl and isopropyl radicals attached to the sulfur atom. In addition, all the four possible ethyl butyl sulfides were synthesized.[3] Of these four isomers, ethyl *s*-butyl sulfide is a new compound and has not been described previously.

In order to avoid the possibility of the final sulfides being seriously contaminated with impurities which might prove difficult to remove, care was taken to ensure that the starting materials were of an extremely high degree of purity. Even so, it was found that some purification, before final fractionation through 100-plate columns, was beneficial in giving compounds whose purity could be guaranteed.

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[1] Presented before the Petroleum Division of the American Chemical Society at the 117th National Meeting, Houston, Texas (March, 1950).

[2] W. E. Haines, W. J. Wenger, R. V. Helm and J. S. Ball, U. S. Bureau of Mines, Report of Investigation 4060.

[3] The ethyl rather than the methyl radical was chosen for this series since the necessary starting materials were more readily available.