

## THE SOLUBILITY OF GROUP I AND GROUP II FLUOROSULFATES IN FLUOROSULFURIC ACID

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### SUMMARY

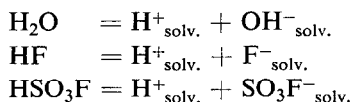
The solubilities at 25° of some Group I and Group II fluorosulfates in fluorosulfuric acid have been determined. The solubilities (g fluorosulfates/100 g fluorosulfuric acid) are LiSO<sub>3</sub>F, 33.78; NaSO<sub>3</sub>F, 80.21; KSO<sub>3</sub>F, 63.83; RbSO<sub>3</sub>F, 89.43; CsSO<sub>3</sub>F, 132.4; MgSO<sub>3</sub>F, 0.12; CaSO<sub>3</sub>F, 16.39; SrSO<sub>3</sub>F, 14.52 and BaSO<sub>3</sub>F, 4.67.

These results can be rationalized on the basis of lattice and solvation energy considerations. These solubility trends are consistent with those of the corresponding fluorides in hydrogen fluorides.

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### INTRODUCTION

Many studies of the solubilities of salts in their parent acids have been carried out. In most cases, the rationale has been a study of the solvents as analogues of water. For example, the solubilities of fluorides in hydrogen fluorides have been determined and compared with the solubilities of hydroxides in water<sup>1</sup>. In this study the solubilities of Group I and Group II fluorosulfates in fluorosulfuric acid have been determined and have been compared with those of the corresponding fluorides in hydrogen fluoride. These compounds are all bases in their own solvent systems.



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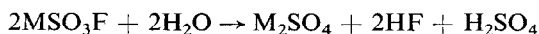
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## EXPERIMENTAL

All fluorosulfuric acid (B and A Code 1071) used in this work was purified before use by distillation in a dry glass apparatus well protected from moisture. It was stored in tightly closed Teflon bottles.  $\text{KSO}_3\text{F}$  was furnished by the Ozark Mahoning Company. The other Group I and II fluorosulfates were prepared by carefully reacting the appropriate metal chlorides with a stoichiometric amount of  $\text{HSO}_3\text{F}$  in Teflon bottles. After the evolution of  $\text{HCl}$  had largely subsided, a stream of dry nitrogen was passed through the bottle to ensure complete removal of  $\text{HCl}$ . All products were tested for the presence of chloride (aqueous solution) using a  $\text{AgNO}_3$  test. They all gave negative tests before they were used. Enough metal fluorosulfate was placed into a Teflon bottle containing  $\text{HSO}_3\text{F}$  to ensure that a considerable amount of solid would remain after saturation. These tightly closed bottles were placed into a constant temperature water bath regulated at  $25 \pm 0.05^\circ$ . These samples experienced mild agitation while they were in the bath and were vigorously agitated by hand several times a day. Usually, they were not sampled for at least 3 days, and samples were then taken at daily intervals. Consistency in determination was interpreted as meaning that equilibrium was attained.

The following sampling and analytical procedures were followed.

A small amount of the saturated solution (liquid phase) was transferred, by decanting, into a small Teflon sample bottle. This bottle was weighed and a small amount of sample was transferred to a weighed ignited platinum crucible. The sample bottle was re-weighed and the weight of the portion in the crucible determined by difference. Three samples were taken from the sample bottle in this way. The samples in the platinum crucibles were treated with several drops of distilled water in order to convert the metal fluorosulfate to metal sulfate



The samples were then placed in a muffle furnace and warmed to  $250^\circ$ . When the sample had been evaporated to dryness, several drops of 1:1 sulfuric acid were added to ensure that all of the metal fluorosulfate had been converted to metal sulfate. After evaporation to dryness a second time, a pea-sized piece of ammonium carbonate was added to volatilize any residual acid. The samples were then heated for approximately 15 h (constant weight), and then cooled and weighed.

An attempt to gain some insight into the identity of the solid phase in equilibrium with the liquid phase was made. Some of the solid was removed and placed into weighed platinum crucibles and treated in a manner similar to that of the liquid. While an attempt was made to free the solid of as much liquid phase as possible, it should be pointed out that many of the solids were fine powders and fluorosulfuric acid other than that involved in solvation was carried along. This would, of course, raise the apparent degree of solution.

## DISCUSSION AND RESULTS

The solubilities of the fluorosulfates in fluorosulfuric acid at 25° is given in Table 1, both in terms of grams per 100 g of fluorosulfuric acid and in terms of moles per 100 g of solvent. It is a convenient coincidence that 100 g of solvent is essentially 1 mole (mol. wt. 100.07) whereas 100 g of hydrogen fluoride is essentially 5 moles (mol. wt. 20.01).

TABLE 1  
SOLUBILITIES OF FLUOROSULFATES IN FLUOROSULFURIC ACID

Fluorosulfate	Solubility (g/100 g HSO <sub>3</sub> F)	Solubility (mole/100 g HSO <sub>3</sub> F)
Li	33.78 ± 0.64	0.319
Na	80.21 ± 0.99	0.658
K	63.83 ± 0.51	0.461
Rb	89.48 ± 0.99	0.486
Cs	132.4 ± 1.5	0.992
Mg	0.12 ± 0.04	5.4 × 10 <sup>-4</sup>
Ca	16.39 ± 0.46	6.86 × 10 <sup>-2</sup>
Sr	14.52 ± 0.33	5.10 × 10 <sup>-2</sup>
Ba	4.67 ± 0.35	1.39 × 10 <sup>-2</sup>

It is interesting to note that in Group I the smooth trend of increasing solubilities with increasing atomic number is spoiled by sodium fluorosulfate (or potassium fluorosulfate, if one thinks of solubilities on a gram basis) and at sodium fluorosulfate (or potassium and rubidium fluorosulfate) on a mole basis. One would expect that the solvation energies for the atoms would follow the same trends as the hydration energies, *i.e.*, decrease with increasing atomic numbers. On this basis alone, one would expect that the solubilities would decrease with increasing atomic number. On the other hand, one would expect, on the basis of lattice energy considerations, that the solubilities should increase with increasing atomic number. Lattice energies in the Group should decrease with increasing atomic size and number. The results of this work suggest that a cross-over of the predominance of one effect over the other occurs between sodium and potassium fluorosulfate.

The solubilities of calcium, strontium and barium fluorosulfates drop off with increasing atomic number. The deviation for magnesium fluorosulfate, perhaps, is to be excused since the high charge/size ratio may bring in a considerable degree of covalency. Magnesium compounds frequently show difference from those of similar compounds of other members of Group II. The solubilities in water, of sulfates, nitrates and chlorides (not fluorides) of calcium, strontium and barium also decrease with increasing atomic number. This is

consistent with a decrease in hydration energy of the metal ion. It may also be that within the Group lattice energies may be bigger with bigger cations than with the very small cation reflecting a more desirable radius ratio (anion, anion repulsion).

A comparison with the solubilities of fluorides in HF (Table 2) shows rather similar relationships. In this series, the solubility of  $\text{SrF}_2$  seems to be out of line. Perhaps a cross-over of effects occurs at this point.

TABLE 2  
SOLUBILITIES OF FLUORIDES IN HYDROGEN FLUORIDE

Fluoride	Solubility (g/100 g HF)	Solubility (moles/100 g HF)	Temperature (°C)
Lj <sup>a</sup>	10.3	$3.97 \times 10^{-1}$	12.2
Na <sup>a</sup>	30.1	$7.16 \times 10^{-1}$	11.0
K <sup>b</sup>	36.5	$6.28 \times 10^{-1}$	8
Rb <sup>c</sup>	110	$6.67 \times 10^{-1}$	20
Cs <sup>d</sup>	199	$13.1 \times 10^{-1}$	10
Mg <sup>a</sup>	0.025	$4.8 \times 10^{-3}$	12.2
Ca <sup>a</sup>	0.817	$10.5 \times 10^{-3}$	12.2
Sr <sup>a</sup>	14.83	$118 \times 10^{-3}$	12.2
Ba <sup>a</sup>	5.60	$31.9 \times 10^{-3}$	12.2

<sup>a</sup> Ref. 1; <sup>b</sup> Ref. 2; <sup>c</sup> Ref. 3; <sup>d</sup> Ref. 4.

Data obtained in attempting to gain some insight into the composition of the solid phases are given in Table 3. The ratio of fluorosulfuric to unsolvated salt acid for the wetted solid is reported. The samples were all wet with solute. The degree of wetting differs from sample to sample. The results may then set upper limits of solvation. One could interpret the data for  $\text{NaSO}_3\text{F}$  as indicating the composition of the solid phase was  $\text{NaSO}_3\text{F} \cdot \text{HSO}_3\text{F}$  or conceivably  $4\text{NaSO}_3\text{F} \cdot 5\text{HSO}_3\text{F}$ . We prefer the former.

TABLE 3  
COMPOSITION OF WET SOLID

Fluorosulfate	Composition (moles $\text{HSO}_3\text{F}$ /mole salt)
Li	2.7
Na	1.25
K	0.65
Rb	1.45
Cs	1.65
Mg	3.35
Cd	1.9
Sr	4.1
Ba	4.3

Fluorosulfuric acid is another solvent system in which rather few solubilities have been quantitatively determined. The solubilities of the Group I and II fluorosulfates can be rationalized and follow a pattern similar to that of fluorides in hydrogen fluoride.

#### ACKNOWLEDGEMENT

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