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⑭ Research in Fluorine Chemistry

⑨ Final report, June 1, 1961, to February 28, 1963,

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

## Personnel:

⑯ 64

Principal Investigator: John L. Margrave,Post-doctoral and Graduate Student Personnel: V. V. Dadape,  
M. A. Frisch and A. S. Kana'anUndergraduate Assistants: C. K. Barker, B. Bork, J. D. Borkowski,  
R. G. Czerepinski and D. C. Lewis

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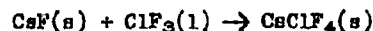
## I. Synthesis of Tetrafluorochlorates

Early work which claimed to have produced  $MF_{1+x}$  and similar compounds by reaction of  $MCl$  or  $MBr$  or  $MI$  with  $F_2$  has been shown to be in error.

Actually, with  $KCl$  one produces  $KClF_4$  and similarly with  $Rb$  and  $Cs$  halides.<sup>1</sup>

1. (a) M. Silverthorn, L. Asprey and J. Margrave, J. Am. Chem. Soc. 83, 2955 (1961).
- (b) M. Silverthorn, M. S. Thesis, University of Wisconsin (1960).

Further studies of this system were conducted by R. Czerepinski who attempted the direct reaction



A 60-70% yield was obtained but high-purity  $CsClF_4(s)$  could not be isolated.

The work has been summarized in the B. S. thesis of Mr. Czerepinski.<sup>2</sup>

2. R. G. Czerepinski, B. S. Thesis, University of Wisconsin, June, 1962.

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## II. Reactions of $\text{BrF}_3$ with Oxides and Nitrides

A nickel system for handling  $\text{BrF}_3$  and  $\text{ClF}_3$  was constructed and utilized for studies of oxides and nitrides following the method of Katz and associates at the Argonne National Laboratory. Studies of  $\text{TiO}_x$  samples were carried out which showed that the samples were essentially  $\text{TiO}_{1.00 \pm 0.01}$  but the experimental reproducibility was not better than  $\pm 1\%$ . Samples of  $\text{TiO}_x$  were examined and  $x$  was established as  $1.19 \pm 0.01$ .

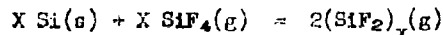
## III. The Properties of $\text{SiF}_2$ and $\text{HF}_2$

Available data on  $\text{SiF}_2$  and  $\text{HF}_2$  were reviewed and two publications resulted which established reasonable ranges for the thermodynamic stabilities of these molecules.<sup>3,4</sup> More quantitative properties of reduced fluorides

3. D. Pease, A. Kanaan and J. Margrave, J. Phys. Chem. 66, 1200 (1962).
4. J. Margrave, J. Phys. Chem. 66, 1209 (1962).

of Si were sought

- (1) through a study of the transpiration weight loss of Si when exposed to a flow of  $\text{SiF}_4$  according to the reaction



- (2) through observations of emission and absorption spectra of such systems, and

- (3) through observations of mass spectra of such systems.

The first two parts of this goal were covered by the Ph. D. thesis of A. S. Kanaan who found that there is definitely a polymeric species of  $\text{SiF}_2$  in the vapor, as well as the monomer. Pressure dependence studies support  $X \geq 3$  and, by analogy with  $\text{CF}_2$ , one predicts the existence of a

cyclic tetramer,  $\text{Si}_4\text{F}_{12}$ .<sup>5</sup> No new optical spectra were obtained.

5. (a) A. S. Kanaan, Ph. D. Thesis, University of Wisconsin (1963).  
 (b) A. S. Kanaan and J. L. Margrave, accepted for publication, Inorganic Chemistry (1964).

Mass spectrometric work concerned the products of the reaction between  $\text{CaF}_2$  and Si in a Knudsen cell at high temperatures.  $\text{SiF(g)}$  and  $\text{SiF}_2(\text{g})$  were definitely produced and their stabilities were established. For  $\text{SiF(g)}$  one finds  $\Delta H_{298}^\circ = -5 \pm 6$  Kcal/mole and for  $\text{SiF}_2(\text{g})$ , one finds  $\Delta H_{298}^\circ = -139 \pm 2$  Kcal/mole.<sup>6</sup> A similar mass spectrometric study

6. T. C. Ehlert, Ph. D. Thesis, University of Wisconsin (1963).  
 of the  $\text{Ge} + \text{CaF}_2$  reaction established  $\Delta H_{298}^\circ [\text{GeF(g)}] = -7.4 \pm 5$  Kcal/mole and  $\Delta H_{298}^\circ [\text{GeF}_2(\text{g})] = -19 \pm 20$  Kcal/mole.

Studies of  $\text{WF}_2$ ,  $\text{CrF}_2$  and  $\text{AlF}_2$  were not successful and further work is still in progress at the Rice University, Houston, Texas, under the extension of this grant.

#### IV. Thermodynamic Properties of Fluorine Compounds

A fluorine bomb calorimeter was operated in a collaborative project at the Argonne National Laboratory and the heats of formation of  $\text{BF}_3$ ,  $\text{SiF}_4$ , and  $\text{KrF}_4$  were established.<sup>7,8,9</sup> In addition, the heats of formation

7. S. Wise, H. Feder, W. Hubbard and J. Margrave, J. Phys. Chem. 65, 2157 (1961).
8. (a) S. Wise, H. Feder, W. Hubbard and J. Margrave, J. Phys. Chem. 66, 381 (1962).  
 (b) S. Wise, J. Margrave, H. Feder, W. Hubbard, J. Phys. Chem. 67, 815 (1963).
9. H. Feder, W. Hubbard, S. Wise and J. Margrave, J. Phys. Chem. 67, 1143 (1963).

of  $\text{SiO}_2^3$  and  $\text{EW}^{10}$  were determined.

10. S. E. Wise, Ph. D. Thesis, University of Wisconsin (1963).

V. Miscellaneous Work

Several efforts were made to synthesize  $\text{AlOF}$  but none were successful. High pressures were used in an effort to get crystalline  $\text{AlF}$  but no definitive material was prepared. Samples of molybdenum oxychlorides were prepared but will have to be characterized by further work since there appear to be several oxychlorides.

Fluorine compounds ( $\text{CF}_4$ ,  $\text{SiF}_4$ ,  $\text{CF}_2\text{Cl}_2$ , etc.) were passed through a plasma torch but no new compounds were synthesized. When  $\text{CCl}_4$  was passed through a plasma torch,  $\text{C}_2\text{Cl}_6$  was produced.<sup>11</sup>

11. A. S. Kanan and J. L. Margrave, Int. Sci. and Tech., No. 8, 75 (1962).