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⑬ ARD-Grants DA-AROD 314124G117 and 4384

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⑭ Research in Fluorine Chemistry

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

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R. G. Czerepinski and D. C. Lewis

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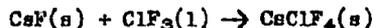
I. Synthesis of Tetrafluorochlorates

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.¹

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.²

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

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II. Reactions of BrF_3 with Oxides and Nitrides

A nickel system for handling BrF_3 and 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 IN samples were carried out which showed that the samples were essentially $\text{B}_{1.00}\text{N}_{1.00}$ but the experimental reproducibility was not better than $\pm 1\%$. Samples of TiO_x were examined and x was established as 1.19 ± 0.01 .

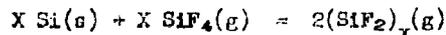
III. The Properties of SiF_2 and HF_2

Available data on SiF_2 and HF_2 were reviewed and two publications resulted which established reasonable ranges for the thermodynamic stabilities of these molecules.^{3,4} 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 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 SiF_2 in the vapor, as well as the monomer. Pressure dependence studies support $X \geq 3$ and, by analogy with CF_2 , one predicts the existence of a

cyclic tetramer, Si_4F_8 .⁵ No new optical spectra were obtained.

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

Mass spectrometric work concerned the products of the reaction between CaF_2 and Si in a Knudsen cell at high temperatures. $\text{SiF}(g)$ and $\text{SiF}_2(g)$ 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 $\text{SiF}_2(g)$, one finds $\Delta H_{298}^\circ = -139 \pm 2$ Kcal/mole.⁶ A similar mass spectrometric study

6. T. C. Ehlert, Ph. D. Thesis, University of Wisconsin (1965).

of the $\text{Ge} + \text{CaF}_2$ reaction established $\Delta H_{298}^\circ [\text{GeF}(g)] = -7.4 \pm 5$ Kcal/mole and $\Delta H_{298}^\circ [\text{GeF}_2(g)] = -19 \pm 20$ Kcal/mole.

Studies of WF_2 , CF_2 and 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 BF_3 , SiF_4 , and KF were established.^{7,8,9} 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 SiO_2^3 and EW^{10} were determined.

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

V. Miscellaneous Work

Several efforts were made to synthesize AlOF but none were successful. High pressures were used in an effort to get crystalline 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 (CF_4 , SiF_4 , CF_2Cl_2 , etc.) were passed through a plasma torch but no new compounds were synthesized. When CCl_4 was passed through a plasma torch, C_2Cl_2 was produced.¹¹

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