Results and Discussion

Oxidation of $MgU_2O_{5.84}$.—The oxidation of $MgU_2O_{5.84}$ was found to consist of two steps: (a) a low temperature oxidation at 200–300° which gave a product with oxygen composition slightly above MgU_2O_6, and (b) a second step requiring 525–550° for a conveniently measurable reaction rate. The final product of the principal oxidation step is the diuranate, with no evidence being found for the formation of an intermediate phase corresponding to $MgU_2O_{6.65}$. At these temperatures the oxidation rate was dependent upon the oxygen pressure only at very low gas pressures. Oxidation of $MgU_2O_{6.65}$ required heating at 700°, confirming the conclusion that this compound is not involved in the oxidation of MgU_2O_6 to the diuranate.

The two steps in the oxidation of $MgU_2O_{5.84}$ to MgU_2O_7 were found to follow different mechanisms. The initial step was diffusion controlled as would be expected on the basis of previous data which had shown the existence of a solid solution in this composition range ($MgU_2O_{5.84}$ to $MgU_2O_{6.04}$). The experimentally determined curve for this step is not shown on Fig. 11, but it was found to follow closely the curve shown for the strontium diuranate system. The second step followed the phase-boundary controlled reaction curve (Fig. 11, curve A) over the entire range plotted. The experimental points obtained on three separate oxidations at 550 and 575° are plotted along the theoretical curve A. The results indicate that the MgU_2O_6 to MgU_2O_7 oxidation involves little, if any, solid solution, and that the diffusion of oxygen through oxidized product is not a rate-determining factor.

Oxidation of $CaU_2O_{5.95}$.—The oxidation of $CaU_2O_{5.95}$ followed a pattern somewhat similar to that of the corresponding magnesium compound in that two steps were again evident. The low temperature oxidation process gave a product containing slightly more than six oxygen atoms per calcium atom. The second oxidation step to the diuranate took place in the same temperature range as the corresponding magnesium compound reaction.

The first portion of this second step of the oxidation curve followed the theoretical phase-boundary controlled reaction curve fairly well, but the latter portions more nearly resembled the diffusion controlled oxidation. These observations can be explained by the thermal decomposition data which show a diphasic region to ~ $CaU_2O_{6.85}$ and solid solution extending from this point to the diuranate. Oxidation to the diuranate apparently takes place by consecutive reactions, the phase-boundary reaction predominating in the initial portions, and giving way to the diffusion controlled process in the later stages.

Oxidation of $SrU_2O_{5.89}$.—Partial oxidation was observed at temperatures as low as 0°. At room temperature the oxidation rate fell essentially to zero as the composition reached $SrU_2O_{6.2}$. Heating caused further reaction, with complete oxidation requiring several hours at 550°.

As was expected from the phase diagram, the curve for the rate of oxidation of the strontium compound is much more like curve B (diffusion controlled) than like curve A (phase-boundary). The deviation between the experimental curve and curve B may be due to the formation of the intermediate oxide indicated by the thermal decomposition data.

Acknowledgment.—We are indebted to Dr. W. H. Zachariasen of the University of Chicago, to Dr. Stanley Siegel of the Chemistry Division, and to Dr. M. H. Mueller of the Metallurgy Division of Argonne National Laboratory for the X-ray data and their interpretation. We also wish to thank Dr. Norman R. Davidson of the California Institute of Technology for carefully reading the manuscript and for making a number of valuable suggestions and comments.

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[CONTRIBUTION FROM THE RADIO CORPORATION OF AMERICA, RCA LABORATORIES]

High-silica Fluosilicic Acids: Specific Reactions and the Equilibrium with Silica

BY S. MILTON THOMSEN

High-silica fluosilicic acids have escaped general recognition. They are readily prepared with any desired amount of "extra" silica up to 18% more than the composition represented by the formula H_2SiF_6. They show characteristic reactions with sodium salts and with fluorides, and these reactions are convenient for detecting and estimating the extra silica. They attack glass. They react with hydrated silica, and an equilibrium constant for this reaction has been approximately evaluated.

Introduction.—Analyses on samples of fluosilicic acid, reported[1] in 1936, showed the silica component to be present in proportions larger than required by the formula H_2SiF_6. Solutions prepared by dissolving hydrated silica in commercial fluosilicic acid have been used to produce low reflection films on glass, both by a vapor process,[2] and by a liquid bath[3] process.

This paper reports (1) preparation of high-silica fluosilicic acids (HSF acids) of predetermined compositions; (2) data on two previously reported[4] specific reactions of HSF acids; and (3) data on the equilibrium between silica and fluosilicic acid.

Terminology.—In this paper, the term fluosilicic acid is extended to apply to any homogeneous liquid reaction product of silica, hydrogen fluoride and water. All such products constitute the three-component fluosilicic acid system.

Two numbers are required to specify the composition of a fluosilicic acid. Used for this purpose are the concentration, denoted by C, and the silica number, denoted by S. Thus, C is the concentration of the hydrogen fluoride component, expressed as moles of H_2SiF_6 per liter, and S is the number of moles of silica component present for each 6 moles of hydrogen fluoride component. Both C and S are computed from data obtained by acidimetric titration.

Fluosilicic acid *of composition corresponding to the formula* H_2SiF_6, has $S = 1$. The HSF acids have $S > 1$, and the low-silica fluosilicic acids have $S < 1$. At the lower extreme is hydrofluoric acid, a degenerate fluosilicic acid with $S = 0$; at the upper extreme are the silica-saturated fluosilicic acids, having S approximately 1.18, but varying with C.

The silica component present in low-silica fluosilicic acids, and in an acid of $S = 1$, is termed primary silica. The HSF acids contain, in addition to such primary silica, a secondary silica component with its own characteristic chemical behavior.

Because the composition of silica-saturated fluosilicic acids approach closely that of $H_2SiF_6{\cdot}SiF_4$ (fluodisilicic acid) for which $S = 1.2$, the secondary silica will be considered to be present in this form. The equation for the reaction of silica to form an HSF acid is then

$$4H^+ + 5SiF_6^= + SiO_2 \longrightarrow 3[SiF_6{\cdot}SiF_4]^= + 2H_2O \quad (1)$$

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[1] Ivan Tannanaev, *J. Gen. Chem. U. S. S. R.*, **6**, 1430 (1936).

[2] F. H. Nicoll, *RCA Review*, **X**, 440 (1949).

[3] S. M. Thomsen, *ibid.*, **XII**, 143 (1951).

[4] S. M. Thomsen, THIS JOURNAL, **72**, 2798 (1950).

Appropriate modifiers are used with the term silica to distinguish several meanings. Primary and secondary silica are components of a liquid fluosilicic acid; hydrated silica is the C.P. reagent (silicic acid) as purchased; and precipitated silica is a solid phase formed and separated from a fluosilicic acid.

Preparation of High-silica Fluosilicic Acids.—Any fluosilicic acid of predetermined composition can be prepared by dissolving the required amount of assayed hydrated silica in a measured volume of standardized hydrofluoric acid. Another procedure is more convenient when many solutions, in a variety of compositions, are to be prepared. It consists in mixing the required amounts of two liquids: 15.0 N hydrofluoric acid (reagent I), and silica-saturated 2.50 M fluosilicic acid (reagent II), and diluting if necessary.

To prepare reagent II, commercial fluosilicic (2.5 to 2.7 M) is diluted to 2.50 M. Hydrated silica is added, and allowed to saturate the solution. The reaction is rapid, as indicated by a temperature rise of about 2° with a typical raw material. Saturation is complete when permanent turbidity results from the addition of a small portion of "fresh" hydrated silica, to provide some finely divided material. The saturated solution is filtered through paper.

Reagent I is made 15.0 N to have the same value of C as reagent II. A mixture made from a ml. of reagent I ($C = 2.50$, $S = 0$) and b ml. of reagent II ($C = 2.50$, $S = 1.18$), will be a fluosilicic acid with $C = 2.50$, and with S as follows

$$S = 11.8b/(a + b)$$

The 2.50 molar acid is finally diluted with water to obtain the desired C; this does not change S.

Method of Analysis.—Compositions of HSF acids were determined by an acidimetric method,[5] in which the sample is titrated in the presence of powdered sodium fluoride, to two successive end-points.

To a 5.00-ml. sample in a plastic dish are added 3 g. of powdered C.P. sodium fluoride, 0.5 ml. of 0.1% brom thymol blue and 1.0 ml. of 0.1% phenolphthalein. After being stirred, the mixture is titrated with 3 M sodium hydroxide to a greenish-blue color (pH 8). The mixture is then transferred to a borosilicate glass beaker, diluted with water to 200 ml., heated nearly to boiling, and titrated at that temperature to the phenolphthalein end-point (pH 10).

The two quantities, a, milliequivalents of sodium hydroxide in the first titration, and b, total milliequivalents for both titrations, characterize the sample. From them are computed the two quantities $C = b/6v$ (v = ml. of sample) and $S = 3(b - a)/2b$ (independent of sample volume), defined above.

Precipitation of Secondary Silica.—Sodium chloride solution is a useful reagent for distinguishing the HSF acids from the low-silica fluosilicic acids, and will give an indication of the amount of secondary silica present. The primary silica separates as a sodium fluosilicate precipitate immediately in either case, upon adding the reagent. Then follows a slow separation of the secondary silica as a silica precipitate, if present. Turbidity appears and increases for perhaps a half-hour; after several hours the precipitated silica has settled out. Two experiments will be described, illustrating the use of this reaction.

In the first experiment, enough sodium chloride solution was added to each of four different samples of fluosilicic acid to precipitate all the fluosilicate. These samples had silica numbers of 0.94, 1.00, 1.06 and 1.12; all had $C = 2.50$. To 10 ml. of each was added 15 ml. of 4.0 M sodium chloride solution. The sodium fluosilicate precipitates were allowed to settle, and the clear, supernatant liquids were decanted and allowed to stand. The last two slowly became turbid and after a few hours formed silica precipitates, the fourth having a precipitate twice as voluminous as the third. The first two remained clear. Thus, the primary and secondary silica are separately precipitated.

In the second experiment, progressively greater amounts of sodium chloride solution were added to samples of one particular 2.50 M fluosilicic acid. Into each of 13 test-tubes was put a 10-ml. sample of the acid. To each was added 4.0 M sodium chloride solution, 1 ml. to the first, 2 ml. to the second, thus up to 13 ml. to the 13th tube. The sodium fluosilicate precipitate was allowed to settle, the clear liquids were decanted into other tubes, and allowed to stand.

With silica-saturated fluosilicic acid ($S = 1.18$), all samples showed turbidity and silica precipitation. With acid of $S = 1.00$, none showed silica turbidity. With acid half-saturated with silica ($S = 1.09$), the first six samples remained clear, and the rest developed silica precipitates. In this third case, precipitation of half or less of the fluosilicic acid as sodium fluosilicate, left enough to keep all secondary silica in solution.

Progressive addition of sodium chloride solution to an HSF acid, as it removes $SiF_6^=$ from solution, enriches the solution relatively in the silica component (increases S) up to the saturation value. Thereafter a silica precipitate also forms, though with the time delay already mentioned. The equation may be written as

$$2H_2O + 3[SiF_6 \cdot SiF_4]^= + 10Na^+ \longrightarrow 5Na_2SiF_6\downarrow + SiO_2\downarrow + 4H^+ \quad (2)$$

Neutralization of an HSF acid also results in the separation of the secondary silica, and this may be represented by the pair of equations

$$4OH^- + 3SiF_6 \cdot SiF_4^= \longrightarrow 5SiF_6^= + SiO_2\downarrow + 2H_2O \quad (3)$$

$$6OH + 6H^+ \longrightarrow 6H_2O \quad (4)$$

Thermal Effects.—The following thermal data, while not obtained by accurate calorimetry, are informative and useful.

The reaction of Eq. 1, occurring as hydrated silica dissolves to form secondary silica, is exothermic. The addition of excess hydrated silica to a fluosilicic acid of initial composition $C = 2.58$, $S = 1.024$, caused a temperature rise of 2.1°. After saturation, the composition was $C = 2.58$, $S = 1.185$. Computation from these figures gives approximately 5 kcal./mole SiO_2, for the heat evolved.

Addition of excess hydrated silica to 6 N hydrofluoric acid gave a rise of 30° under the same conditions, or about 30 kcal./mole SiO_2.

Heat is also evolved when a fluoride is added to an HSF acid, thereby converting the secondary silica to primary silica, according to the equation

$$[SiF_6 \cdot SiF_4]^= + 2F^- \longrightarrow 2SiF_6^= \quad (5)$$

Addition of powdered sodium fluoride to a silica-saturated 2.50 M fluosilicic acid gave a temperature rise of 19°.

The mixing of equal volumes of 6 N hydrofluoric acid and a 2.50 M HSF acid, results in a temperature rise which is a linear function of S of the HSF acid, as shown in Fig. 1. This effect can be used to make a rapid approximate determination of S. From the data shown in Fig. 1, a figure of about 25 kcal. per mole of secondary silica is computed as the heat evolved.

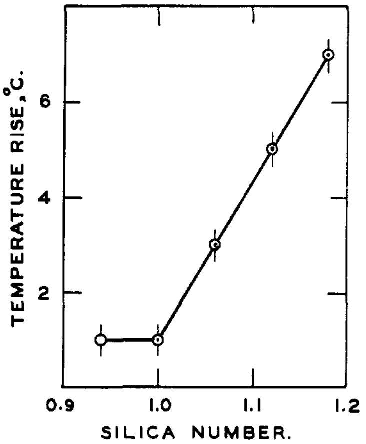

Fig. 1.—Effect of the silica number (S) of 2.50 M fluosilicic acid on the temperature rise occurring when it is mixed with an equal volume of 6 N hydrofluoric acid.

Thus, more heat per mole of silica is evolved (25 to 30 kcal.) when hydrated silica, or secondary silica of an HSF acid, reacts with hydrofluoric acid to produce primary silica (in the form of $SiF_6^=$) than when hydrated silica reacts by Eq. 1 (5 kcal.) to form secondary silica. In the latter case, Si-F bonds are presumably redistributed to in-

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[5] S. M. Thomsen, *Anal. Chem.*, **23**, 973 (1951).

volve more Si atoms, without an increase in the number of bonds.

Behavior Toward Glass.—The long-held belief[6,7] that a product corresponding to the formula H_2SiF_6 will not attack glass, is erroneous. It is apparently based upon the mistaken belief that the silica-saturated products produced by the usual laboratory methods correspond to this formula.

Fluosilicic acids not saturated with silica do attack glass. Commercially available fluosilicic acids, generally in this class, are not sold in glass containers. Six lots had silica numbers of 1.03, 1.06, 1.18, 1.04, 1.10 and 1.01. The last three were drums of acid bought some months apart from the same manufacturer.

Even the silica-saturated fluosilicic acids attack ordinary glass, such as window glass. A process for producing low-reflection films[3] on glass surfaces employs the slow, selective attack of a fluosilicic acid bath supersaturated with silica to the extent of 2 to 10 millimoles of silica per liter.

In Pyrex bottles, however, silica-saturated fluosilicic acids in concentrations from 0.5 to 2.5 M remained unchanged in composition after storage for a year, and the bottles showed no evidence of attack.

Vapor from HSF acids also attacks ordinary glass. In doing so, it produces low-reflection films[2,8] whose properties vary with the S of the acid. While the rate of attack (depth *vs.* time) is directly proportional to C, the intensity of attack, as measured by the percentage of glass removed from the filmed area (which in turn controls the index of refraction of the film) diminishes as S increases.

Evaluation of Published Data.—Data, such as that on specific gravities of fluosilicic acid solutions[9] and that on compositions of vapor in equilibrium with acid of various concentrations,[10] are ambiguous in the absence of data on the composition of the acid used. Furthermore, the common practice of specifying composition in percentage by weight introduces further ambiguity. A silica-saturated acid, computed from titration to be 30% H_2SiF_6, will actually have 31% of solute.

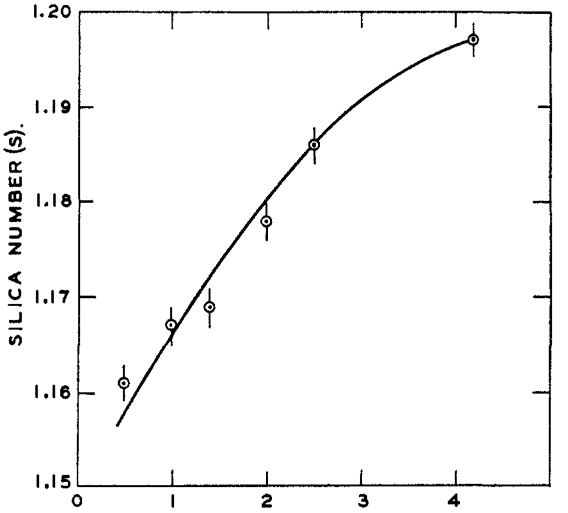

Fig. 2.—Silica number (S) at equilibrium, as a function of fluosilicic acid concentration (C).

The Equilibrium with Silica.—Fluosilicic acids of six different concentrations were saturated with silica at about 25° and the resulting products were analyzed. The results are given in Table I. Figure 2 shows that S increases slowly with increasing C.

Each entry in Table I is for a separately prepared solution. Many more were made at C = 2.50 than the typical ones listed. The variations in the figures of one column represent the uncertainty of the analytical method rather than differences in composition. This is known because (1) repeat titrations gave variations of the same magnitude, and (2) these solutions were used in the liquid-bath process[3] of making low-reflection films on glass, a process so sensitive to composition that differences of 0.5 millimole of silica per liter are easily detected.

TABLE I

THE SILICA NUMBER (S) AS A FUNCTION OF THE CONCENTRATION (C) IN SILICA-SATURATED FLUOSILICIC ACIDS

C	4.18 M	2.50 M	2.00 M	1.40 M	1.00 M	0.50 M
S	1.197	1.185	1.175	1.170	1.167	1.164
		1.190	1.181	1.167	1.167	1.158
		1.188				1.168
		1.187				
		1.185				
	1.197	1.186	1.178	1.169	1.167	1.163

Such reproducible equilibria, together with the absence of Tyndall Effect in the HSF acids, shows that the secondary silica is not present colloidally.

Assuming the reaction to be that of Eq. 1, a constant for the equilibrium with solid silica is the following, in which M' and M'' are the concentrations of $SiF_6^=$ and $SiF_6{\cdot}SiF_4^=$, respectively

$$K = \frac{M''^3}{M'^5\,(H^+)^4}$$

Table II gives the computed concentrations of the ionic species present in each of the six silica-saturated fluosilicic acids. These were computed by considering the changes occurring according to Eq. 1, as silica dissolves in fluosilicic acid of the composition corresponding to the formula H_2SiF_6, and of concentration C. Initially, $(H^+) = 2C$, $M' = C$, $M'' = 0$, and $S = 0$. After the silica is dissolved, and S has been evaluated by titration, the following relations hold: moles/liter of silica dissolved $= C(S - 1) = x$; $M'' = 3x$; $M' = C - 5x$; and $(H^+) = 2C - 4x$. No activity coefficients are used, and complete ionization of the acids is assumed.

TABLE II

COMPUTATION OF EQUILIBRIUM CONSTANT

log K (from first five values of K) = 3 ± 1

C	0.50	1.00	1.40	2.00	2.50	4.18
S	1.163	1.167	1.169	1.178	1.186	1.197
M''	0.24	0.51	0.71	1.07	1.40	2.48
M'	0.10	0.17	0.22	0.22	0.17	0.05
(H^+)	0.68	1.33	1.86	2.58	3.14	5.06
K	7000	350	6000	50	200	80,000

The first five values give an average of 3 ± 1 for log K. Using the value 10^3 for K in the equation

$$-\Delta F = RT \ln K$$

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(6) J. N. Friend and R. M. Caven, "A Textbook of Inorganic Chemistry," Charles Griffin and Co., London, 1917, p. 193.

(7) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p. 615.

(8) S. M. Thomsen, unpublished data.

(9) "Handbook of Chemistry and Physics," 32nd Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1950, p. 1646.

(10) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 6, Longmans, Green & Co., London, 1925, p. 941.

gives 4 kcal. for $-\Delta F$, which is near the 5 kcal. per mole of silica, measured for the $-\Delta H$ of reaction as silica dissolves in an HSF acid.

Princeton, N. J. Received June 27, 1951

[Contribution from the University of Colorado]

The Kinetics of the Vapor Phase Dimerization of Tetrafluoroethylene and Trifluorochloroethylene[1]

By J. R. Lacher, G. W. Tompkin and J. D. Park

Using pressures of less than one atmosphere, the rates of dimerization of tetrafluoroethylene, chlorotrifluoroethylene and their interdimerization have been studied. The reactions are second order and homogeneous. The Arrhenius equations which will reproduce the experimental data are: $16.5 \times 10^{10}\ e^{-26.299/RT}$, $3.53 \times 10^{10}\ e^{-26320/RT}$ and $8.54 \times 10^{10}\ e^{-26300/RT}$ cc./mole sec.$^{-1}$, respectively. The significance of the symmetry numbers in determining the "A-factors" is discussed in terms of the structures of the molecules involved.

Introduction

The successful dimerization at high pressures of tetrafluoroethylene and chlorotrifluoroethylene has been carried out.[2,3] The interdimerization of the two olefins has also been reported.[4] In all cases a saturated cyclobutane was obtained. A kinetic study of the reactions was undertaken at pressures of less than one atmosphere and the results are reported here,

Experimental Details

The reaction flask consisted of a one-liter Pyrex vessel fitted with a thermocouple well and capillary entrance lines. In order to test for the homogeneity of the reaction, a flask packed with Pyrex tubing was used. A Bodenstein quartz spiral served to measure pressures to about 0.1 mm. The reaction flask was placed in an electric furnace consisting of an aluminum block suitably insulated. Temperatures could be controlled to 0.2° and there were no temperature gradients present in the furnace to this accuracy. The pressure change which accompanies the reaction was used to follow its rate, and infrared analysis of the product was used to test for side reactions. In case of the interdimerization of tetrafluoroethylene and chlorotrifluoroethylene the rate was followed by infrared absorption. Samples of tetrafluoroethylene and chlorotrifluoroethylene were kindly furnished by the "Kinetic" Chemicals Division of the du Pont Company and they were purified by methods previously described.[5,6]

The rate of dimerization of chlorotrifluoroethylene was studied at temperatures between 304.5 and 509.1° and at pressures of 100 and 600 mm. roughly. The reaction was found to be second order. Second order constants were obtained from the differential equation

$$\Delta P/\Delta t = -kP^2$$

Here ΔP is the change in the pressure in mm. of the monomer which occurs in the time interval Δt seconds. For P^2 the product of the pressure at the beginning of the time interval and that at the end were used. The constants so obtained are summarized in Table I. They are independent of the initial pressure as is shown in runs 1 through 6. No significant change occurs at 394° when the pressure varies from 105 to 623 mm. Run 16 shows that a packed cell is without effect. In run 18 a thermocouple was sealed into the reaction flask so that the gases came in contact with it. A very slight cooling (0.2°) of about five seconds duration was noted when the reactor was initially filled. No significant temperature rise was observed during the reaction.

Table I

Dimerization of Chlorotrifluoroethylene

Run	T°c	Initial pressure, mm.	$k \times 10^7$, mm.$^{-1}$ sec.$^{-1}$
13	304.5	619.1	1.0
18	346.7	502.9	4.7[a]
17	347.6	525.9	5.1
6	393.4	590.3	19
5	393.6	607.0	18
4	393.6	105.0	19
3	393.6	112.0	20
1	394.5	381.8	18
2	394.9	245.8	19
16	439.1	623.2	65[b]
15	439.8	615.8	65
14	440.4	619.5	66
8	507.5	257.3	300
9	507.6	256.7	300
10	507.6	190.0	310
11	508.7	143.5	310
12	508.7	104.3	320
7	509.1	347.9	310

[a] Seated in thermocouple. [b] Packed cell.

The rate constants were also independent of the extent of the reaction. This is shown in Fig. 1. The ratio of the rate constant for each increment to the rate constant for the initial increment is plotted as an ordinate and the per cent. completion of reaction is the abscissa. The logarithms of the rate constants so obtained when graphed as a function of

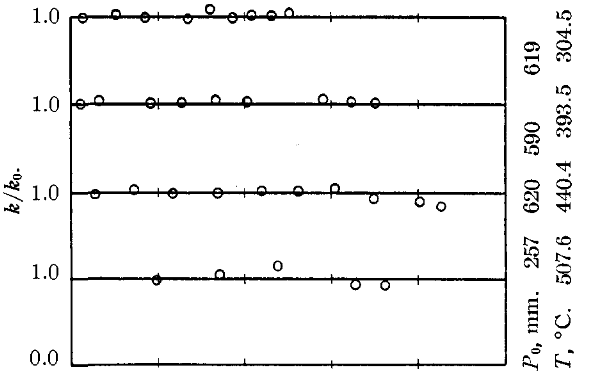

Fig. 1.—Ratio of second order rate constant at any time to initial rate constant, plotted as a function of per cent. reaction. Dimerization of chlorotrifluoroethylene.

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[1] This work was supported by Contract N6ONR-231, Task Order VI, with the Office of Naval Research, United States Navy. Presented before the Symposium on Fluorine Chemistry, 120th Meeting of the American Chemical Society, New York, N. Y., September, 1951.

[2] Jesse Harmon, U. S. Patent 2,404,374.

[3] A. L. Henne and R. P. Ruh, This Journal, **69**, 279 (1947).

[4] Paul L. Barrick, U. S. Patent 2,427,116.

[5] J. R. Lacher, J. D. Park, *et al.*, This Journal, **71**, 1330 (1949).

[6] J. R. Lacher, J. D. Park, *et al.*, *ibid.*, **71**, 1334 (1949).