NACA TN 4374 10718

TECH LIBRARY KAFB, NM
0067146

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 4374

RATE OF REACTION OF GASEOUS FLUORINE WITH WATER VAPOR AT 35° C

By Vernon A. Slabey and Edward A. Fletcher

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

Washington
September 1958

TECHNICAL LIBRARY
AFL 2811

TECH LIBRARY KAFB, NM

0067146

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 4374

RATE OF REACTION OF GASEOUS FLUORINE WITH WATER VAPOR AT 35° C

By Vernon A. Slabey and Edward A. Fletcher

5129

CN-1

SUMMARY

Fluorine and water vapor react extremely slowly or not at all in the gas phase at 35° C at partial pressures of the reactants up to 40 mm of mercury. They react at surfaces; the kinetics are first order with respect to each of the reactants. At Kel-F wax-coated surfaces, the rate of disappearance of fluorine is expressed by

$$-\frac{dF_2}{dt} = 1.6\times10^{-4}\ A_w[F_2][H_2O]$$

where $-\frac{dF_2}{dt}$ is the rate of disappearance of fluorine in moles per second, A_w is the surface area (sq cm) of the reaction vessel, and $[F_2]$ and $[H_2O]$ are the concentrations in moles per liter of the reactants. Neither ozone nor hydrogen peroxide is formed to a measurable extent in the reaction.

INTRODUCTION

One of several methods proposed for disposing of fluorine (refs. 1 and 2) under conditions where the fumes cannot be confined is the use of water sprays. It was not known, however, whether the reaction of gaseous fluorine with water vapor would be sufficiently rapid to reduce fluorine concentrations below the toxicity limits within a reasonable time. It was anticipated that the removal of small residual concentrations of fluorine vapor might be especially difficult. The present investigation was done to determine the rate of reaction of gaseous fluorine with water vapor. The reaction was studied at 35° C within the range of 20 to 40 millimeters (mercury) of fluorine pressure and 9 to 20 millimeters (mercury) of water vapor pressure.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus in which the experiments were conducted (shown in fig. 1) consisted essentially of a reactor submerged in a thermostatically controlled constant-temperature bath, a water reservoir, a fluorine reservoir, traps for collecting products, and connecting lines for the admission of reactants and the removal of products. The entire apparatus was made of Pyrex glass. In most of the experiments, the inner surface of the reactor was covered with Kel-F wax to minimize reaction with hydrogen fluoride. Stopcocks were lubricated with Kel-F stopcock grease, and the mercury in the manometers was protected from fluorine by floating a small amount of Kel-F Polymer Oil No. 3 on the mercury.

A typical experiment is described: The entire apparatus was evacuated to less than 10^{-3} millimeters of mercury, and a small quantity of water vapor, previously degassed by alternate freezing, evacuation, and melting, was admitted to the reactor by opening the appropriate stopcocks between the reactor and the water reservoir. The pressure of the water vapor admitted to the reactor was determined by measuring the temperature of a bath surrounding the water reservoir and by reading the manometer connected to the admitting line. The quantity of water vapor in the reactor was then determined by the pressure, the temperature (35° C) of the bath surrounding the reactor, and the known volume of the reactor. After the connecting lines were again evacuated, fluorine was admitted to the fluorine reservoir. About one-fifth of the fluorine in the reservoir was then permitted to bleed into the reactor. The pressure of fluorine in the reservoir was never permitted to fall below approximately five times the pressure in the reactor; this prevented back diffusion of the reactants. The quantity of fluorine introduced was determined from the change in pressure in the fluorine reservoir (indicated by the adjacent manometer), the known volume of the reservoir and connecting lines, and the ambient temperature. The reaction mixture was stirred during the course of the reaction by a magnetically driven Teflon fan.

At the end of the reaction period, the products and the unreacted fluorine and water vapor were slowly pumped out of the reactor through liquid-nitrogen-chilled traps. The reaction products that condensed in the traps were fixed by adding dilute ammonium hydroxide solution. The contents of the traps were then analyzed for fluoride ion by a method involving distillation of the sample with perchloric acid and titration with thorium nitrate solution (ref. 3).

Experiments in which the surface area was increased by the addition of Kel-F wax-coated beads to the reactor were also run.

5129

5129

CN-1 back

RESULTS AND DISCUSSION

It has been previously reported (ref. 4) that the principal reaction between fluorine and water is

$$F_2 + H_2O \rightarrow 2\ HF + \frac{1}{2}\ O_2 \tag{1}$$

Cady (ref. 5) states that hydrogen peroxide and oxygen difluoride are also formed in the reaction. Reference 4, however, indicates that oxygen difluoride is formed only in small amounts. Limited tests in the present work indicated that neither hydrogen peroxide nor ozone was a significant product, since the samples used for fluoride analyses did not contain any oxidizing materials. It was therefore concluded that the amount of hydrogen fluoride formed at any given time would be indicative of the extent of reaction between fluorine and water in accordance with equation (1).

Gross Nature of Reaction

Preliminary experiments showed that the rate of formation of hydrogen fluoride was affected by the nature of the reactor surface. For example, the rate of formation of hydrogen fluoride in a Pyrex glass reactor was about twice the rate in a reactor coated with Kel-F wax; this suggests that the reaction was heterogeneous. In subsequent studies, a Kel-F wax-coated reaction vessel was used.

With the initial reactant concentration held constant, the reactor volume and surface area were varied in a series of experiments. The data from these experiments (fig. 2) showed that the amount of fluoride ion formed in a given time was roughly proportional to the surface area of the reactor; this suggests that the gas-phase reaction was quite unimportant compared with the surface reaction.

Order of Reaction

The experimental quantity measured was the amount of fluoride actually formed in a given time in a Kel-F coated vessel having a known volume, surface area, and initial reactant concentration. These data are shown in figure 3 for a flask having a volume of 2.1 liters and a surface area of 793 square centimeters. The three curves are for the three initial conditions that were used to establish the order of the reaction. The amount of hydrogen fluoride formed after 30 minutes was determined from these three faired curves for each of three initial sets of reactant concentrations. The results are shown in table I. From curves 1 and 2, where the initial water concentration was the same, the order with respect

to fluorine was found to be about 0.88. From curves 2 and 3, where the initial fluorine concentration was held constant, the order with respect to water was found to be about 1.06. The reaction was therefore assumed to be first order with respect to each of the reactants.

Kinetics of Surface and Gas-Phase Reactions

Additional experiments were done in which the volume, surface area of the reaction vessel, and also the initial reactant concentrations were varied. The results of these experiments are tabulated in table II, which contains the results of all the experiments from which data were taken for the present analysis.

The molar rate of formation of hydrogen fluoride was assumed equal to twice the molar rate of disappearance of fluorine and of water, in accordance with equation (1). Since the relative rates of reaction at the surface and in the gas phase were not known (although the reaction was known to be heterogeneous), the reaction was assumed to follow second-order kinetics both at the surface and in the gas phase. As shown later in the report, this assumption does not affect the results.

Heterogeneous reactions are usually quite complex, and the kinetics are frequently hard to interpret. However, if the reaction products are not adsorbed on the reactor surface and the reactants only sparsely cover the surface, the reaction kinetics appear to follow the same rate law as simple gas-phase reactions except for a factor that involves the surface area (ref. 6). The rate of disappearance of fluorine in a particular reaction vessel can therefore be expressed as the sum of the rates at the wall and in the gas phase. The rate of disappearance at the wall is $k_w A_w [F_2][H_2O]$, where k_w is a rate constant per unit area of the surface, A_w is the area of the wall, and the bracketed factors are the reactant concentrations in moles per liter. The rate of disappearance in the gas phase will be $k_g V_g [F_2][H_2O]$, where k_g is the rate constant for the gas-phase reaction, and V_g is the total volume of reactants. Then,

$$-\frac{dF_2}{dt} = k_w A_w [F_2][H_2O] + k_g V_g [F_2][H_2O] \tag{2}$$

where $-dF_2/dt$ is the rate of disappearance of fluorine in moles per second in a particular reaction vessel having a surface area A_w and a volume V_g. If x is the total number of moles of fluorine used up at

time t, and a and b represent the initial concentrations in moles per liter of fluorine and water, respectively, then

$$\frac{dx}{dt} = (k_w A_w + k_g V_g)\left(a - \frac{x}{V_g}\right)\left(b - \frac{x}{V_g}\right) \tag{3}$$

$$= k_t\left(a - \frac{x}{V_g}\right)\left(b - \frac{x}{V_g}\right) \tag{4}$$

5129

where

$$\left.\begin{aligned} k_t &= k_w A_w + k_g V_g \\ \frac{k_t}{V_g} &= k_w \frac{A_w}{V_g} + k_g \end{aligned}\right\} \tag{5}$$

In these expressions, k_t is an over-all rate constant for a particular reaction vessel and, except for the dependence implied in its definition, is not of any particular significance as far as the chemical reaction is concerned. Integration of equation (4) leads to

$$k_t = \frac{V_g}{t(b - a)} \ln \frac{a\left(b - \frac{x}{V_g}\right)}{b\left(a - \frac{x}{V_g}\right)} \tag{6}$$

Values of k_t are tabulated in table II. Since k_t is related to k_w and k_g through equation (5), the determination of k_t for several vessels leads to the evaluation of k_g and k_w. From equation (5), a plot of k_t/V_g against A_w/V_g should yield a straight line, of which the slope is k_w and the intercept is k_g. The data for such a test are tabulated in table III and plotted in figure 4. The line shown in figure 4 is a plot of the equation

$$\frac{k_t}{V_g} = 1.611\times10^{-4} \frac{A_w}{V_g} + 10^{-4}$$

which was obtained by a least-squares treatment of the data. The value of k_w is therefore 1.6×10^{-4} liter^2/(mole)(sec)(cm^2), and k_g is 10^{-4} liter/(mole)(sec).

Relative Importance of Surface and Gas-Phase Reactions

The ratio of the rate of reaction at the wall to the rate within the volume of the reactants is given by

$$\frac{\text{Rate at wall}}{\text{Rate in gas phase}} = \frac{k_w A_w}{k_g V_g}$$

For a spherical vessel, this ratio is given by

$$\frac{\text{Rate at wall}}{\text{Rate in gas phase}} = \frac{4.8 \times 10^3}{r}$$

where r is the radius of the vessel in centimeters. The radius of the vessel used in most of the present studies was approximately 8 centimeters. The rate of the surface reaction was then about 600 times as great as the rate of the gas-phase reaction; that is, within experimental error, the gas-phase reaction was completely negligible.

Rate of Surface Reaction

If the gas-phase reaction is neglected, the rate constant for the surface reaction is given by

$$k_w = \frac{V_g}{A_w t(b - a)} \ln \frac{a\left(b - \frac{x}{V_g}\right)}{b\left(a - \frac{x}{V_g}\right)} = \frac{k_t}{A_w} \tag{7}$$

The values of k_w obtained from the application of equation (7) to the experimental data are given in table II and are plotted as a function of time in figure 5. Included are four data points at 3600 seconds from vessels having different surface areas. The value of k_w remains essentially constant over a wide range of time, from about 1800 to 21,600 seconds. During this time interval, the reaction had gone from about 11 to 62 percent completion. Data points obtained after shorter intervals indicated that there might be a departure from simple second-order kinetics during the early stages of the reaction, but these were the least reliable points for two reasons: (1) The time required for sampling (approx. 300 sec) was large compared with the reaction time, and (2) the amount of hydrogen fluoride formed was quite small. Thus, the effect of analytical errors was large. Correction for these errors might well put these data points on the line drawn through the other

data points. The average value of k_w, obtained from all the runs having a duration of 3600 seconds or greater, was again 1.6×10^{-4} liter^2/(mole)(sec)(cm^2). The rate of disappearance of fluorine at a Kel-F coated surface can therefore be expressed by

$$-\frac{dF_2}{dt} = 1.6 \times 10^{-4} A_w [F_2][H_2O]$$

CONCLUSIONS

A study of the rate of reaction of gaseous fluorine with water vapor at 35° C at partial pressures of the reactants up to 40 millimeters of mercury suggested the following conclusions:

1. Within the pressure range studied, the reaction of fluorine with water in the vapor phase proceeds extremely slowly or not at all.

2. A reaction between fluorine and water occurs at solid surfaces. In glass vessels the reaction is somewhat faster than in vessels coated with Kel-F wax.

3. The kinetics of the reaction can be interpreted by assuming that the simplest type of heterogeneous reaction between the two gases is occurring, that is, one in which the products of the reaction are not appreciably adsorbed on the reactor surface and the reactants only sparsely cover the reactor surface.

4. The surface reaction is first order with respect to each of the reactants. The rate of disappearance of fluorine from a mixture of water vapor and fluorine in contact with a Kel-F surface is proportional to the surface area and the concentrations of each of the reactants. It is expressed by $-\frac{dF_2}{dt} = 1.6 \times 10^{-4} A_w [F_2][H_2O]$.

5. Condensible (at -196° C) oxidizing agents such as H_2O_2 and O_3 do not appear to be formed in the reaction.

6. Water vapor probably would not be a good scavenger for fluorine.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, June 26, 1958

REFERENCES

1. Landau, Ralph, and Rosen, R.: Industrial Handling of Fluorine. Ind. and Eng. Chem., vol. 39, no. 3, Mar. 1947, pp. 281-286.

2. Turnbull, S. G., et al.: Analysis and Disposal of Fluorine. Ind. and Eng. Chem., vol. 39, no. 3, Mar. 1947, pp. 286-288.

3. Willard, H. H., and Winter, O. B.: Volumetric Method for Determination of Fluorine. Ind. and Eng. Chem., Analytical ed., vol. 5, no. 1, Jan. 15, 1933, pp. 7-10.

4. Feldmann, G. W., and Turnbull, S. G., Jr.: The Disposal of C-216, C-212, and Hydrogen Fluoride. Rep. A-2552, E. I. DuPont de Nemours & Co., Nov. 3, 1944. (Contract W-7412-ENG-151.)

5. Cady, George Hamilton: Reaction of Fluorine with Water and with Hydroxides. Jour. Am. Chem. Soc., vol. 57, no. 2, Feb. 6, 1935, pp. 246-249.

6. Glasstone, Samuel: Textbook of Physical Chemistry. Second ed., D. Van Nostrand Co., Inc., 1946, p. 1122.

TABLE I. - ORDER OF REACTION

Curve	Initial concentration of reactants, (mole/liter)X10^3		F^- formed in 30 minutes, g	Order with respect to -	
	F_2	H_2O		F_2	H_2O
1	2.19	0.911	0.0193	0.88	1.06
2	1.12	.911	.0107		
3	1.12	.463	.0052		

TABLE II. - KINETIC DATA

Run	Reaction time, sec	Initial fluorine concentration, a, mole/liter X10^3	Initial water concentration, b, mole/liter X10^3	Fluorine reacted, x, mole X10^3	Reactor volume, liters	Reactor surface area, sq cm	k_t, $\frac{\text{liters}^2}{(\text{mole})(\text{sec})}$	k_w, $\frac{\text{liters}^2}{(\text{mole})(\text{sec})(\text{cm}^2)}$ X10^4
66	120	1.089	0.9109	0.124	2.1	793	1.09	13.81
68		1.072	.9109	.108			.953	12.02
70		1.100	.9162	.118			1.05	13.27
64		2.206	.9267	.221			.979	12.34
65		2.177	.9109	.126			.554	6.98
42	600	1.125	.9057	.189			.330	4.16
37		1.123	.9162	.177			.319	4.02
48		1.109	.9109	.153			.265	3.34
38	1,200	1.002	.9319	.156			.150	1.89
41		1.154	.9109	.330			.303	3.82
47		1.103	.9109	.300			.288	3.63
94	1,800	1.123	.5414	.124			.124	1.56
39		1.116	.9319	.331			.212	2.67
43		1.110	.9214	.342			.231	2.91
46		1.147	.9109	.259			.156	1.97
61		2.234	.9109	.634			.226	2.85
55	3,600	1.100	.4425	.220			.153	1.93
96		1.074	.4633	.197			.130	1.64
50		1.101	.9109	.368			.123	1.55
54		2.150	.9005	.774			.158	1.99
58		2.142	.9109	.705			.137	1.73
62		2.240	.9109	.724			.136	1.71
99	5,400	1.069	.4738	.275			.126	1.59
59		2.219	.9109	.913			.128	1.61
60		2.199	.9109	.990			.147	1.85
101	7,200	1.129	.4633	.302			.104	1.31
102		1.123	.4633	.313			.109	1.37
103		1.121	.4581	.356			.132	1.66
104	10,800	1.156	.4633	.457			.120	1.51
52	10,800	1.096	.9109	.834			.129	1.63
53	21,600	1.103	.9109	1.18			.125	1.58
113	3,600	1.121	.474	.344	2.035	1572	.243	1.54
114		1.031	.463	.334	2.035	1572	.263	1.67
111		1.123	.463	.585	1.836	3918	.640	1.63
112		1.123	.463	.576	1.836	3918	.623	1.59

TABLE III. - OVER-ALL RATE CONSTANTS FOR

THREE DIFFERENT REACTION VESSELS

Vessel	Surface area, sq cm	Volume, liters	k_t, $\frac{\text{liters}^2}{(\text{mole})(\text{sec})}$	k_t/V_g	A_w/V_g
1	793	2.1	[a]0.130	0.062	377.6
2	1572	2.035	[b].243	.119	772.5
2	1572	2.035	[b].263	.129	772.5
3	3918	1.836	[b].640	.349	2134.0
3	3918	1.836	[b].623	.339	2134.0

[a]Average of all determinations of 3600 sec or greater duration.

[b]3600-Sec runs.

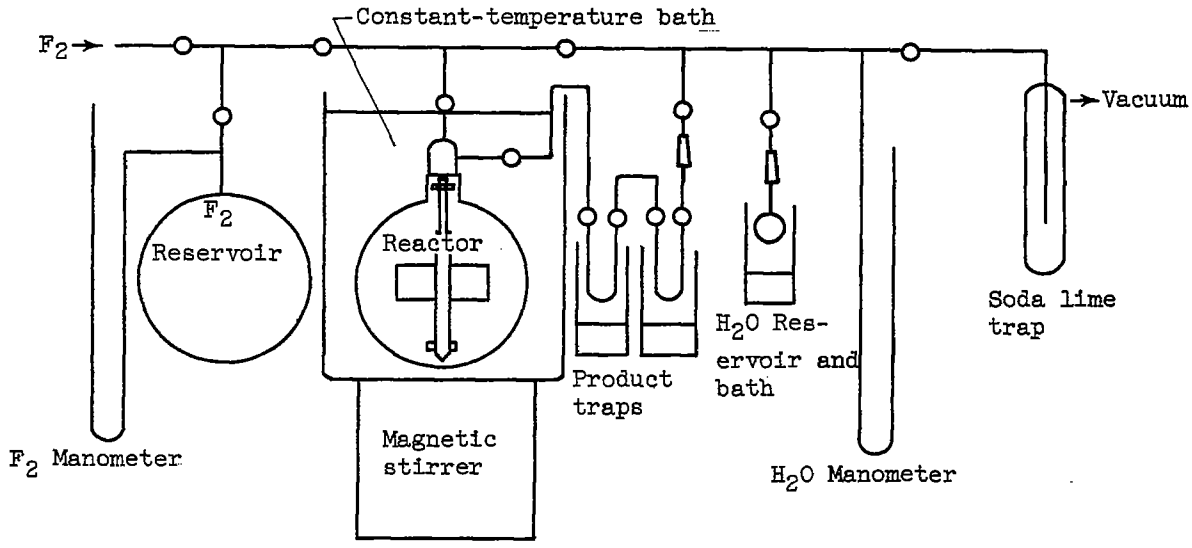

Figure 1. - Reaction system used in study of gaseous fluorine - water vapor reaction rates.

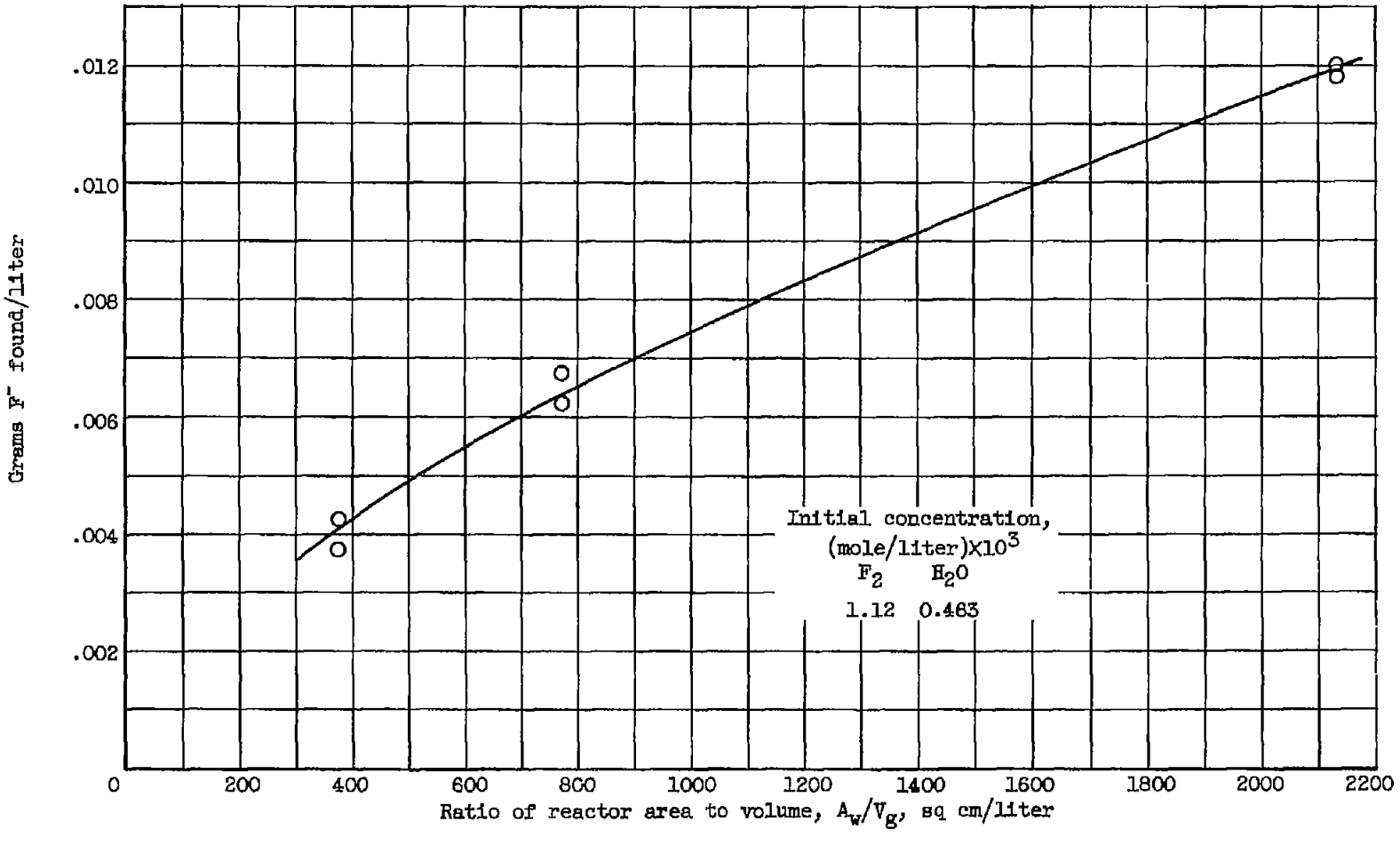

Figure 2. - Effect of reactor area-volume ratio on amount of fluoride ion formed in 1 hour at 35° C.

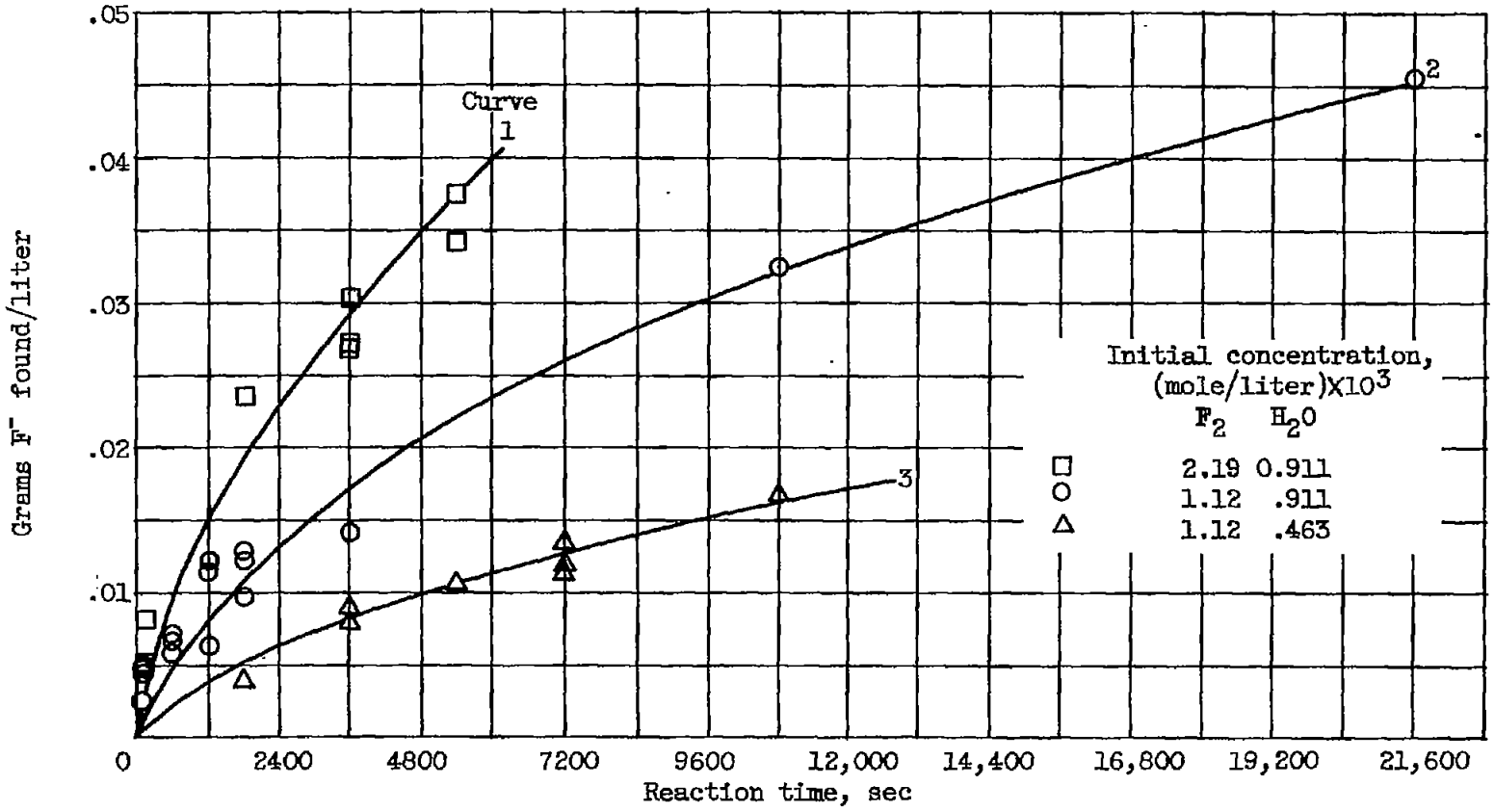

Figure 3. - Variation of fluoride ion found with reaction time and initial concentration of reactants at 35° C.

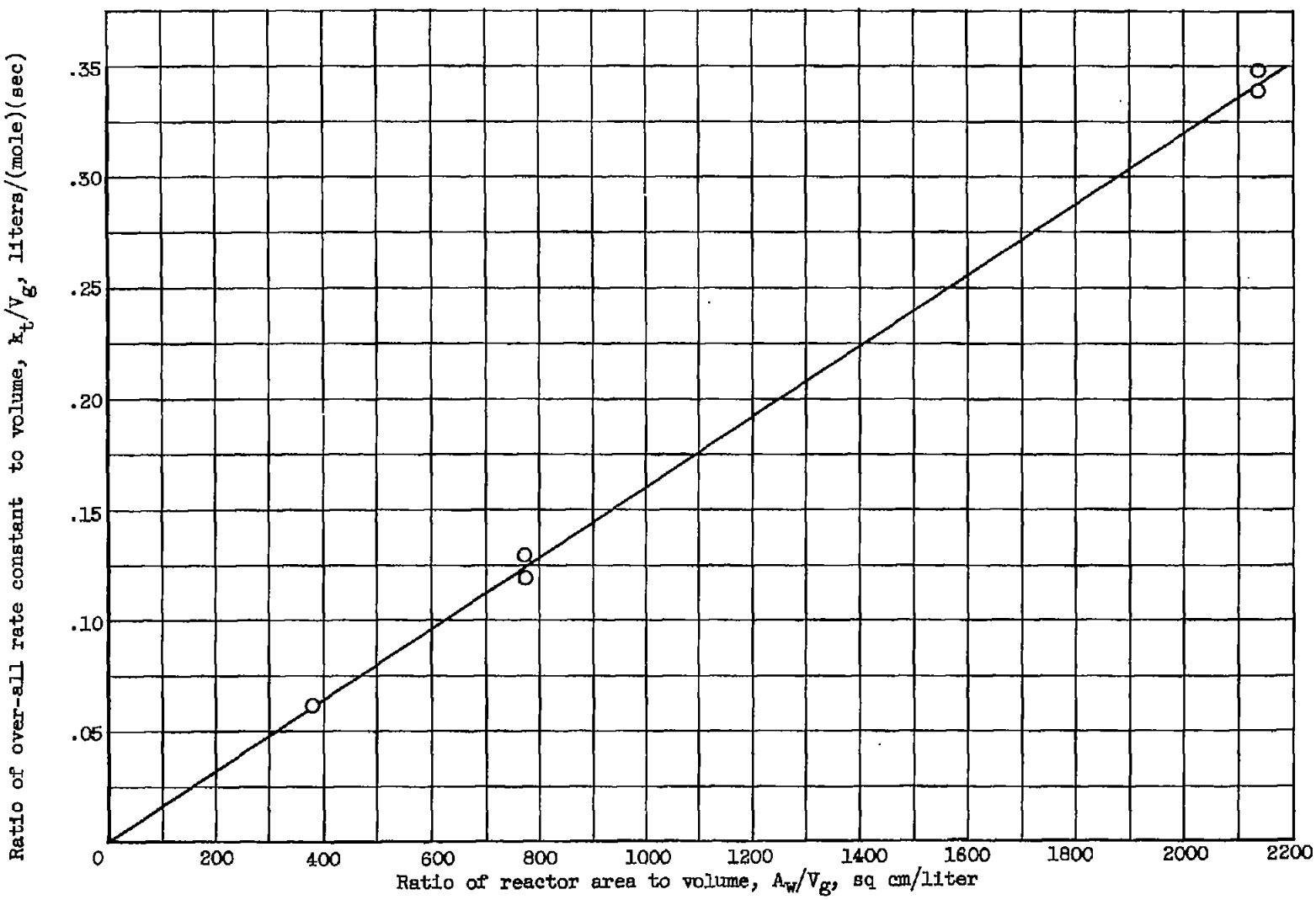

Figure 4. - Variation of over-all rate constant with reactor surface area.

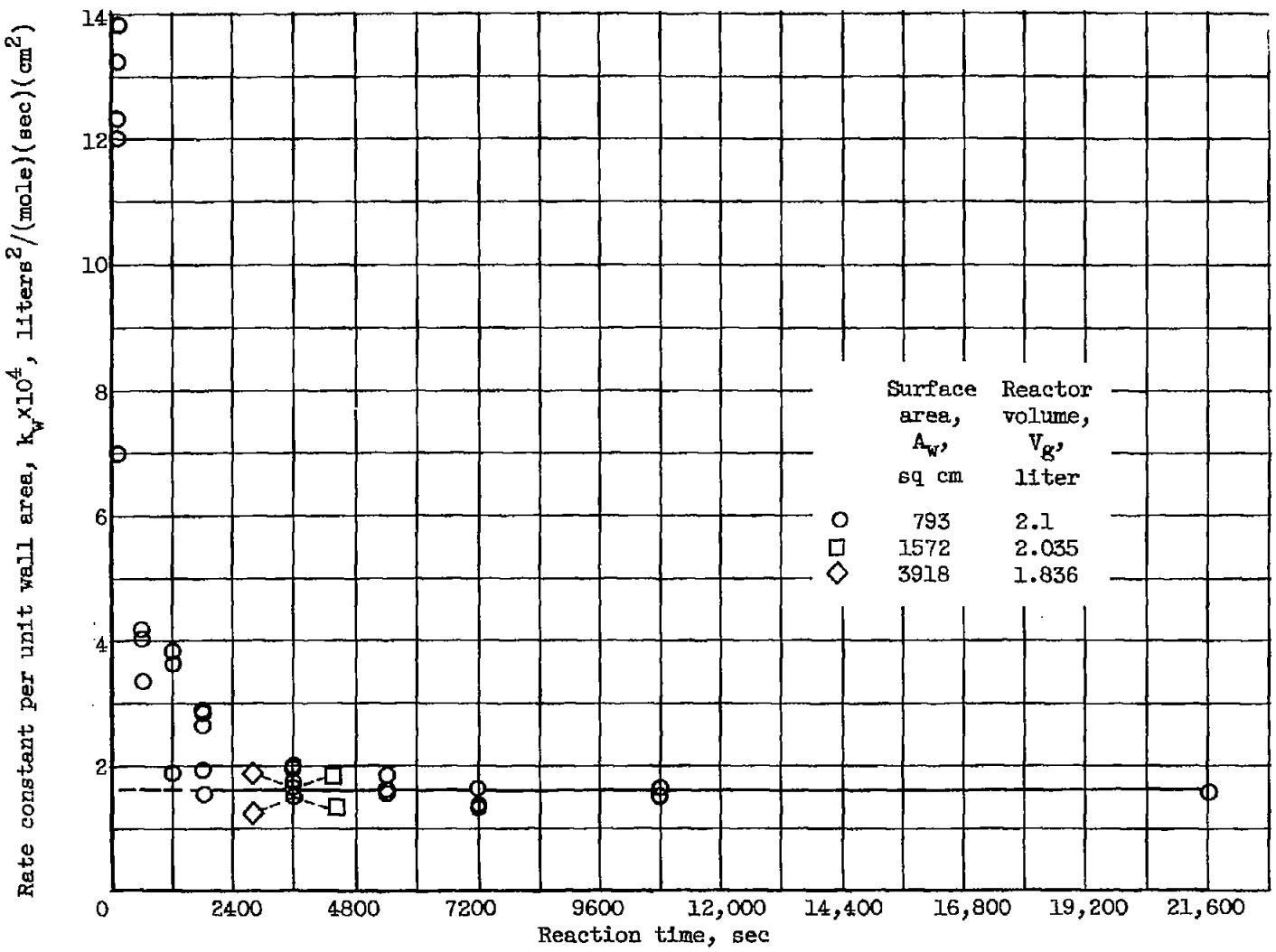

Figure 5. - Variation of rate constant per unit wall area with reaction time.