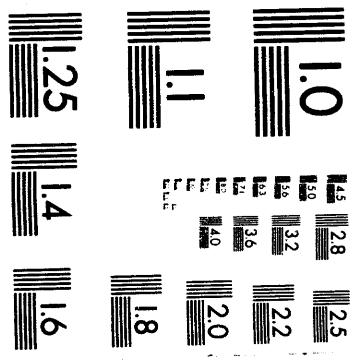
1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3

1 of 1

K/TCD-1091

Technical Division

Reinterpretation of Rate Data for the Reaction of ClF and F_2

L.D.Trowbridge

Date Published -- January 1994

Prepared by
Oak Ridge K-25 Site
Oak Ridge, Tennessee 37831-7101
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

TABLE OF CONTENTS

ABSTRACT v

INTRODUCTION 1

EXPERIMENTAL 2

RESULTS & DISCUSSION 3

CONCLUSIONS 7

ACKNOWLEDGEMENTS 10

BIBLIOGRAPHY 11

ABSTRACT

Experimental data reported by Reiner and Simmons on the rate of recombination of ClF + F_2 have been reinterpreted to yield a single rate equation. This reinterpretation assumes that the recombination reaction is surface area dependent and is first order in partial pressure of each of F_2 and ClF. The recombination rate equation used fits quite well three data sets which varied significantly in available NiF_2 surface area.

The resulting equation is:

$$dn(ClF_3)/dt = A\ S\ P(F_2)\,P(ClF)\,(1\text{-}\theta)\,e^{-E/RT}$$

where $dn(ClF_3)/dt$ is the rate of formation of ClF_3 in mol/s, S is the surface area of NiF_2 catalyst in cm^2, P(X) is the partial pressure of species X in Torr, R is the gas constant (1.987 cal/mol-K), and T is the temperature in Kelvin. The pre-exponential, A, and the activation energy, E, are given by:

$$A = 2.853 \times 10^{-8}\ \text{mole/s-cm}^2\text{-Torr}^2$$

$$E = 11665\ \text{cal/mole}$$

and the term $(1\text{-}\theta)$, a product surface-coverage related inhibition factor, is given by:

$$(1\text{-}\theta) = (1 + 0.184\,P(ClF_3))^{-1}$$

(but $(1\text{-}\theta)$ is never allowed to be less than 16%)

INTRODUCTION

Reiner and Simmons, in K/ET-776[1], reported experimental data for the reaction:

$$ClF + F_2 \longrightarrow ClF_3$$

Separate rate equations were provided, each specific to one of three sets of experiments which differed in the amount of surface area (of fluorinated nickel) in the high temperature reaction zone of the experimental apparatus. For a recent modeling project, we needed a prediction of the above reaction rate and of the corresponding ClF_3 dissociation rate. We concluded, however, that the rate equations presented by Reiner and Simmons were too specific to their experimental setup to be directly usable in our present application. Their experimental data was therefore used to derive a more general expression for the rate of combination of ClF and F_2 and this rate, combined with thermodynamic equilibrium data, can be used to calculate the dissociation rate.

EXPERIMENTAL

The experimental apparatus and methods used by Reiner and Simmons are described in detail in Reference 1. Briefly, the experimental apparatus consisted of a closed loop of nickel tubing around which the reaction gases were circulated. Gas composition was determined on initial mixing by pressure change and during the course of the experiment by infrared spectroscopy . A portion of the volume of the system was located in a tube furnace heated to the temperature of interest. The total system volume was reported to be 2.8 liters; the section of the system actually located in the hot region had an inner diameter of 2.0 inches (5.08 cm) and a length of 45 cm, so that the superficial area of the heated surface was 766 cm^2 and the volume of the heated zone was 912 cm^3.

Experiments were conducted with the reactor empty (which we will term "low area") and with the reactor packed with two quantities of fluorine-passivated sintered nickel filter. The microscopic surface areas were measured for the two sets of packing by the BET method, yielding values of 137,000 cm^2 (which will be termed "medium area" experiments) and 356,000 cm^2 (which will be termed "high area" experiments). No BET area appears to have been determined for the empty reactor. Since the reactor and the packing material all consisted of fluorinated nickel, it is reasonable to assume that the surface present in the hot region of the reactor essentially consisted of NiF_2.

Reiner reported reaction rate data in the form of rate of increase of ClF_3 pressure, extrapolated to t=0 (at which time, there would be no product present which could potentially inhibit the reaction). The data from Ref. 1 are reproduced in Table 1. All values in Table 1 are taken directly from Reference 1 except for the final column, which gives the recombination rate constant K_r derived for each particular experiment per the analysis presented here.

RESULTS AND DISCUSSION

From subsets of the Reference 1 data presented in Table 1, Reiner derived rate equations of the form

$$dP(ClF_3)/dt = A\,P(ClF)^x\,P(F_2)^y\,e^{-E/RT}$$

where the exponents x, y, and the rate constant parameters A and E were separately determined for each degree of packing. Fits were obtained which appeared to allow prediction of the reaction rate in each specific reactor configuration with reasonable accuracy. While Reiner noted that the rate appeared to correlate with surface area, he did not devise a general equation that was applicable to all experiments.

In examining the rate equations of the above form with a view to applying them to a different system, it appeared that the equations could not be directly used, as they mixed intrinsic and extrinsic properties. For example, the rate of reaction is given as a function of reactant pressure but not surface area, though the reaction, at least for the packed reactor configurations, was characterized as depending on area of catalyst. Pressure change of reactants and products depends at least partly on the volume of the system, including regions not held at high temperature, which can vary independent of the quantity of catalyst surface area present in the hot region.

In an attempt to produce a more general analysis of the experimental data, the measured rate of production of ClF_3 is converted into moles per unit time per unit area of catalyst. Pressure of ClF_3 is converted to moles using the ideal gas law applied to the volume of the hot region of the reactor at the listed experimental temperature and to the remaining volume of the system at an assumed temperature of 50°C.[A]

When applied to the high- and medium-area experiments, this treatment collapsed the two data sets into the same general region on an Arrhenius plot. While Reiner termed his empty-reactor (low-area) experiments "gas-phase", excellent agreement is obtained by assuming that even the empty-reactor data

---

[A] The external system temperature value of 50°C is a guess, as it was not clear if the external lines were heated above ambient temperature. A variation of ±30°C in this temperature would result in a variation in the predicted rate constant (at 130°C) of ±11%.

are actually surface catalyzed with an area equal to the superficial inside area of the hot tube furnace shell, times a microscopic roughness factor. Factors of two to three are commonly used microscopic "surface roughness factors" for metal piping. The predicted rate constant is fairly sensitive to the choice of a roughness factor; values of 2.5 to 4, however, result in calculated rate constants that are most consistent with the medium- and high-area data sets. In further analysis, a microscopic area for the empty reactor will be taken as three times the superficial area. In addition, for internal consistency this empty-reactor area will be added to the BET areas measured for the packing material (though this makes only about a 1% change in effective area of the system).

As previously mentioned, Reiner computed a separate power dependence of reactant partial pressure for each reactor configuration. These exponents were derived from a very limited number of experiments (three or four) in which the pressure of a single reactant was varied over a range of about a factor of 4. The exponents derived ranged from 0.15 to 1.5 and did not show a consistent pattern from one reactor configuration to the next. Considering the range of variability of results of ostensibly identical experiments, there is considerable inherent uncertainty in the pressure dependencies. Differences from one configuration to another could well be due to statistical fluctuations in the data used rather than true differences in pressure dependence. The pressure dependence exponents from Reference 1 will not be used, but rather the reaction rate will be assumed to be proportional to the first power of partial pressure of each of the reactants. This is the most obvious first approximation, though it must be confessed the reaction order is chosen partly for the sake of convenience when later the dissociation rate constant is derived from this recombination rate and the equilibrium constant.

With the above adjustments, the reported rate, in units of Torr/minute, can be converted into K_r in units of moles (ClF_3) per second per cm^2 (area of catalyst) per $Torr^2$ (of F_2 and ClF). The K_r for each experiment in Table 1 is plotted in Figure 1 along with a regression fit of K_r to the equation

$$K_r = A e^{-E/RT}$$

where $A = 2.853 \times 10^{-8}$ mole/s-cm^2-Torr^2 (with a standard deviation estimate of ±40% of that value), and E = 11665 ± 308 cal/mole. On that graph, it can be seen that the rate constants for all three sets of experiments, interpreted as described here, fall generally within a factor of two of the regression fit over a range of three orders of magnitude.

Reiner also reported a number of experiments in which he examined the effect of buildup of ClF_3 pressure upon the rate of reaction. He concluded that ClF_3 significantly inhibited the rate of reaction and calculated a product inhibition factor (1-θ), which can be considered to relate to surface coverage by reaction products. The rate equation above should be multiplied by the factor (1-θ) which was given empirically by:

$$1 - \theta \;=\; (1 + 0.184\, P(ClF_3))^{-1}$$

where $P(ClF_3)$ is in Torr. Empirically, it was observed that product inhibition reduced the reaction rate below 16% of the its initial value, so the recommended inhibition factor, (1-θ), is taken as the maximum of the above computed value and 0.16. The effect of UF_6 was also examined, and rate inhibition was also observed, but with lesser effectiveness than that of ClF_3.

Combining the product inhibition factor with the previously deduced rate equation, the recommended rate equation for ClF + F_2 recombination in the presence of NiF_2 surface is:

$$dn(ClF_3)/dt = A\ S\ P(F_2)\, P(ClF)\, (1-\theta)\, e^{-E/RT}$$

where S is the surface area of NiF_2 catalyst in cm^2, P(X) is the partial pressure of species X in Torr, R is the gas constant (1.987 cal/mol-K), and T is the temperature in Kelvin. The pre-exponential A and the activation energy E, are given by:

$$A = 2.853 \times 10^{-8}\ \text{mole/s-cm}^2\text{-Torr}^2$$

$$E = 11665\ \text{cal/mole}$$

and the term (1-θ), a product inhibition factor, is given by:

$$(1-\theta) = (1 + 0.184\, P(ClF_3))^{-1} \quad \text{(but never less than 0.16)}$$

In addition to the work of Reiner and Simmons, an unpublished local experiment done by C.F.Hale[2] also measured the reaction rate of ClF and F_2 in a nickel (or monel) reactor. That experiment was done at 114°C, at initial partial pressures of 500 Torr each of F_2 and ClF, and was carried out in a reactor that was 16 in. (40.6cm) long and 1 in (2.54 cm) in diameter. The observed rate constant, interpreted as a second order gas phase rate, was 4.2×10^{-3} l/mol/s, as derived from data taken over a four hour period. This can be converted to an initial ClF_3 production rate of 3.7×10^{-7} mol/s.

The equation presented in the current work for these conditions would predict an initial rate of 1.8×10^{-6} mol/s (using a surface roughness factor of 3 as before). This initial rate, however, is calculated without using the product inhibition factor, $(1-\theta)$. All the experimental data points in the Hale study were taken at times for which the ClF_3 partial pressure would be such as to yield the maximum degree of rate inhibition (i.e. $(1-\theta) = 0.16$). Thus the predicted rate, incorporating the product inhibition factor, is 2.9×10^{-7} mol/s. The prediction and the Hale measurement thus agree within the uncertainty of the rate equation parameters. The rate equation presented here is therefore consistent with this independent, if limited, piece of experimental information.

CONCLUSIONS

Previously reported data of Reiner and Simmons on the combination reaction of ClF and F_2 in the presence of a NiF_2 surface have been reinterpreted. The reaction rate constant is interpreted as being dependent on surface area of catalyst and partial pressure of reactants. The case for the surface area dependence is fairly strong. The reaction rate in even an empty reactor tube is adequately explained by the derived surface-dependent reaction rate without resort to a gas-phase mechanism. The case for the specific reactant partial pressure dependence used in the rate equation is, however, tentative. The rate equation derived here can likely be used with reasonable confidence for circumstances in which partial pressures of reactants do not vary a great deal from those in the present data sets.

From the observation that this reaction appears to be governed by surface reaction, one would conclude that a more thorough treatment would deduce the coverage of the surface in F_2, ClF, ClF_3, etc., as a function of pressure, and calculate the kinetics in terms of coverage rather than partial pressure. That, however, is beyond the limits of the present data, and would require further experimentation supplemented by different experimental techniques.

Table 1: Experimental conditions and data (columns 1-5) from Reference 1; K_r (column 6) is derived per analysis in this document.

T °C	Area cm^2	$dP(ClF_3)/dt$ at t=0 Torr/min	$P(F_2)$ Torr	P(ClF) Torr	K_r mole/cm^2 /$Torr^2$ s
150	766	0.01323	40	10	3.08×10^{-14}
200	766	0.08823	40	10	1.99×10^{-13}
250	766	0.16015	40	10	3.53×10^{-13}
300	766	0.67141	40	10	1.45×10^{-12}
350	766	1.0623	40	10	2.26×10^{-12}
300	766	0.4237	40	10	9.16×10^{-13}
300	766	0.5120	40	10	1.11×10^{-12}
300	766	0.1243	40	5	5.37×10^{-13}
300	766	0.5804	40	15	8.36×10^{-13}
300	766	0.8614	40	20	9.31×10^{-13}
300	766	0.2718	20	10	1.17×10^{-12}
300	766	1.0697	80	10	1.16×10^{-12}
150	137000	0.945	40	10	3.63×10^{-14}
150	137000	1.199	40	10	4.60×10^{-14}
125	137000	0.326	40	10	1.27×10^{-14}
150	137000	0.836	40	10	3.21×10^{-14}
137	137000	0.504	40	10	1.95×10^{-14}
138	137000	0.550	40	10	2.13×10^{-14}
134	137000	0.420	40	10	1.63×10^{-14}
154	137000	0.705	40	10	2.70×10^{-14}
120	137000	0.266	40	10	1.04×10^{-14}
100	137000	0.125	40	10	4.97×10^{-15}
70	137000	0.040	40	10	1.63×10^{-15}
138	137000	0.4681	40	20	9.05×10^{-15}
138	137000	0.4086	40	5	3.16×10^{-14}
138	137000	0.5762	40	15	1.49×10^{-14}
134	137000	0.1007	20	10	7.81×10^{-15}
135	137000	0.7701	80	10	1.49×10^{-14}
143	356000	1.409	40	10	2.11×10^{-14}
143	356000	1.678	40	10	2.51×10^{-14}
141	356000	1.735	40	10	2.60×10^{-14}
141	356000	1.524	40	10	2.29×10^{-14}
124	356000	0.887	40	10	1.35×10^{-14}
126	356000	0.735	40	10	1.11×10^{-14}
129	356000	0.824	40	10	1.25×10^{-14}
96	356000	0.120	40	10	1.86×10^{-15}
97	356000	0.207	40	10	3.21×10^{-15}
133	356000	1.018	40	10	1.54×10^{-14}
127	356000	0.605	40	10	9.16×10^{-15}
127	356000	1.030	40	20	7.80×10^{-15}
127	356000	1.437	40	40	5.44×10^{-15}
127	356000	0.655	20	10	1.98×10^{-14}
128	356000	1.536	80	10	1.16×10^{-14}
128	356000	1.630	80	10	1.23×10^{-14}

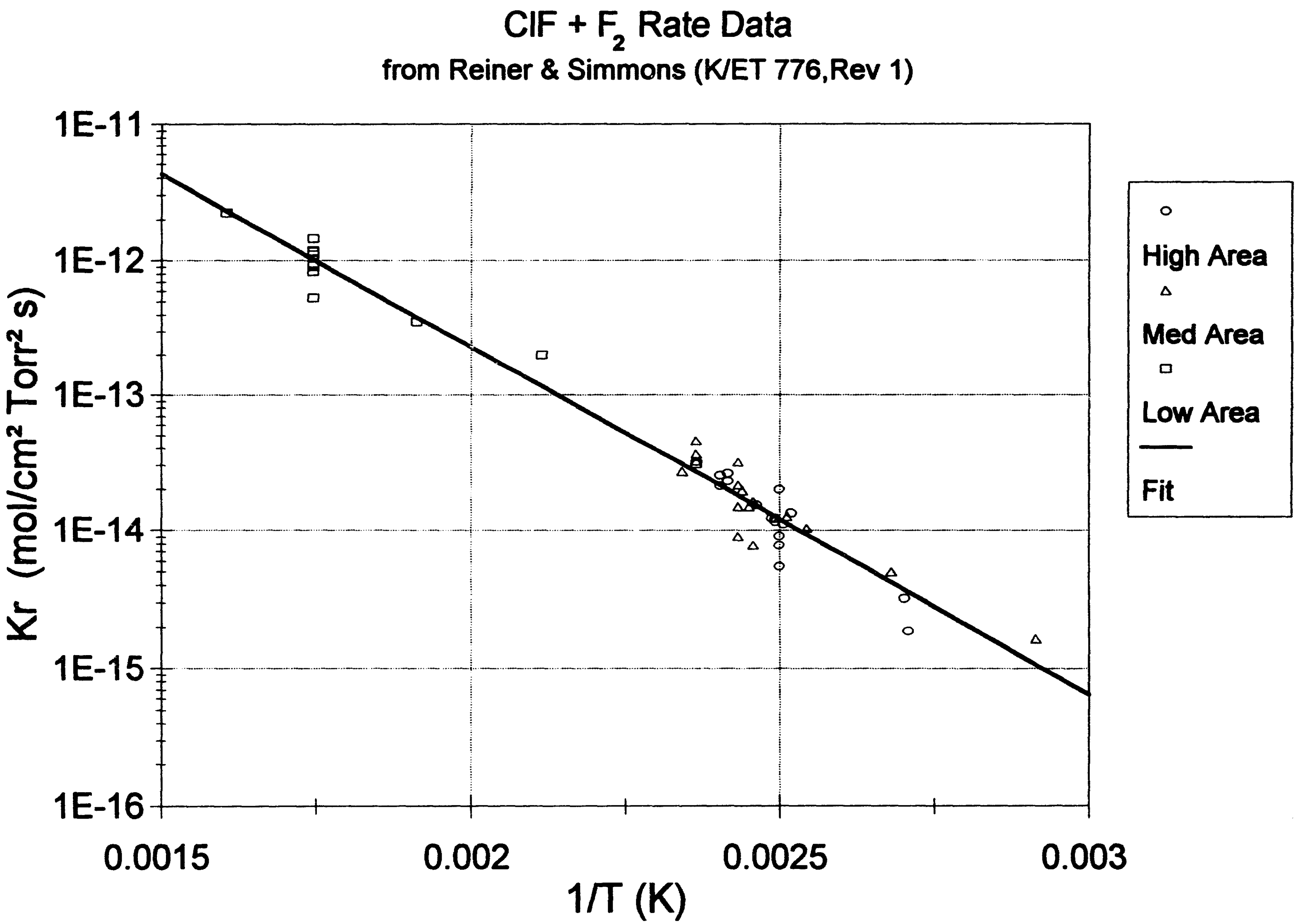

Figure 1: Experimental data on initial rate of combination of fluorine and chlorine monofluoride, interpreted as being linearly dependent on microscopic surface area and partial pressures of reactants.

ACKNOWLEDGEMENTS

The author would like to thank Drs. James Leitnaker and John Barber for their prompt review of this document. The author is also particularly grateful to Dr. Barber for pointing out the existence of the Hale experiment.

This work was done in support of the U.S. Enrichment Corporation's gaseous diffusion plants, with the financial support provided by the Process and Long Range Technical Support program.

BIBLIOGRAPHY

1 R.H.Reiner & D.W.Simmons, "Kinetics of ClF_3 Generation from ClF and F_2", K/ET-776, Rev 1, UCC-ND, Oak Ridge Gaseous Diffusion Plant, Rev 1, (UNCLASSIFIED) - (Original version 1981; revision 1 in press Dec 1993)

2 Private communication, E.J.Barber to L.D.Trowbridge, 11/7/93.

DISTRIBUTION

Oak Ridge K-25 Site

W.D.Altman
E.C.Angel
D.P.Armstrong
E.J.Barber
W.D.Bostick
D.H.Bunch
D.A.Harkins
R.L.Higgins
J.M.Leitnaker
E.B.Munday
F.W.Nehring
J.H.Pashley
J.F.Preston
A.S.Quist (3)*
R.L.Ritter
D.W.Simmons
L.D.Trowbridge (8)
D.L.Weishaar
Appl. Techn. Library
K-25 Site Records

Oak Ridge Y-12 Plant

R.H.Reiner

Paducah Gaseous Diffusion Plant

P.G.Brown
B.A.DeNeve
M.G.Otey
S.W.Poirier
R.G.Russell
S.F.Seltzer
P.D.Wooldridge
Technical Library

Portsmouth Gaseous Diffusion Plant

J.G.Crawford
W.D.Netzer
R.J.Riddle
A.J.Saraceno
R.T.Shelton
Technical Library

U.S. Enrichment Corporation

O.L.Ewing

---

* 2 copies intended for OSTI

DATE
FILMED
2/24/94

END