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THE KINETICS AND MECHANISM  
OF THE PYROLYSIS OF OXYGEN  
DIFLUORIDE AND OF THE REACTION  
OF HYDROGEN WITH OXYGEN  
DIFLUORIDE

by . . .

Thomas W. Asmus

A Dissertation  
Submitted to the  
Faculty of the Graduate  
College in partial fulfillment  
of the  
Degree of Doctor of Philosophy

Western Michigan University  
Kalamazoo, Michigan  
August 1970

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Thomas William Asmus

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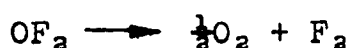
## INTRODUCTION

This work involved the study of the kinetics of the thermal decomposition of oxygen difluoride and the reaction between oxygen difluoride and hydrogen. Both reactions were carried out in the gas phase using a stirred-flow reactor, and the concentration changes were followed mass spectrometrically. The former system was studied to elucidate the mechanism of the reaction whereas the latter system was studied primarily for the purpose of determining the rate law for the reaction. All experiments were carried out at atmospheric pressure; the pyrolysis of oxygen difluoride and the reaction of hydrogen with oxygen difluoride were studied over the temperature ranges 330-431°C. and 110-220°C. respectively. Oxygen difluoride was selected for these studies because of its potential as a high energy oxidizer in propulsion systems, because its pyrolysis kinetics were not yet thoroughly understood, and because the kinetics of its reaction with hydrogen had not been investigated.

### Background

Oxygen Difluoride Pyrolysis: The first reported work on the kinetics of the pyrolysis of oxygen difluoride was carried out in a static reactor by Koblitz and Schumacher<sup>1</sup> in

1934. The products of the homogeneous decomposition at 250 and 270°C. were found to be mainly fluorine and oxygen, and the rates of the overall pressure changes were consistent with the following stoichiometry:

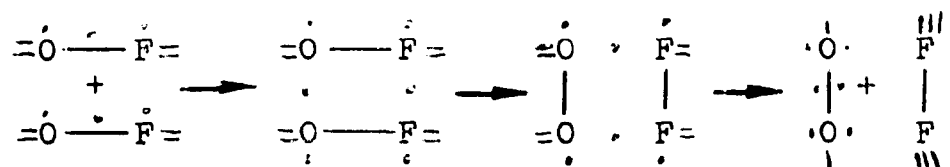


No subsequent work was reported until 1967 when Dauerman and co-workers<sup>2</sup> studied the kinetics of this reaction over the temperature range of 500-700°C. using a plug-flow reactor coupled to a mass spectrometer. The configuration of their apparatus was intended to facilitate the observation of radicals produced by the reaction, particularly the oxyfluoride (OF) radical. While operating the reactor at total pressures of 60 and 100 torr no mass spectrometric evidence for the oxyfluoride radical was found.

If the activation energy for the pyrolysis is equated with the bond dissociation energy for the first oxygen-fluorine bond as proposed by Trotman-Dickenson<sup>3</sup>, then the bond dissociation energy for the oxyfluoride radical should be about 60 kcal. mole<sup>-1</sup>. This value arises if the activation energy is taken as 40 kcal. mole<sup>-1</sup> and if the heat of atomization of oxygen difluoride is taken to be approximately 100 kcal. mole<sup>-1</sup>. These workers raised the basic question regarding the nature of the oxyfluoride radical. If the second oxygen-fluorine bond is so much stronger than the first, then why is the oxyfluoride radical not observed under the

conditions of these experiments?

Arkell and co-workers<sup>4</sup> concluded from a study in which they produced oxyfluoride radicals at 4°K. by photolysis of oxygen difluoride in nitrogen and argon matrices that the second oxygen-fluorine bond is stronger than the first. These authors suggested a value of 56 kcal. mole<sup>-1</sup> for the second oxygen-fluorine bond. Additional evidence supporting the existence of the oxyfluoride radical comes from a reaction carried out by Gatti and co-workers<sup>5</sup> whereby peroxy-sulfuryl difluoride (F-SO<sub>2</sub>-OOF) was isolated from a reaction mixture of sulfur trioxide and oxygen difluoride which was irradiated with light of 365 nm. wavelength. They concluded that this reaction must involve the oxyfluoride radical. Green and Linnett<sup>6</sup> have suggested the following bimolecular pathway which is open to oxyfluoride radicals and leads to stable products:

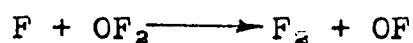


They argue that since the change in bond order in passing from oxyfluoride radicals through the transition states to products is zero, the activation energy for the process must be low. If this is the case, the reaction rate must be approaching diffusion control. Thus, it may be that the oxyfluoride radicals were not observed in Dauerman's<sup>2</sup> mass

spectrometer because of their high reactivity and not because of their instability with respect to dissociation.

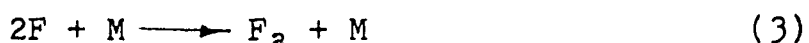
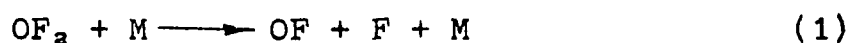
On the other hand, Dibeler and co-workers<sup>7</sup> concluded from appearance potential measurements on oxygen difluoride that the first oxygen-fluorine bond dissociation energy is approximately 60 kcal/mole. This implies that the second oxygen-fluorine bond is significantly weaker than the first. In ion impact studies the appearance potential is the measurable quantity and is the sum of several energy terms, only one of which is the bond dissociation energy. Because of this, bond dissociation energies determined in this way are subject to inordinately high uncertainties.

Troe and co-workers<sup>8</sup> studied the pyrolysis of oxygen difluoride in a shock tube over the temperature range of 600-930°C. using argon as a diluent. They concluded that the reaction is not a simple unimolecular process as had been previously stated and that the following step probably does not contribute to the rate:



Solomon and co-workers published a pair of articles in which they reported results of studies of the thermal decomposition of oxygen difluoride in incident shock waves<sup>9</sup> and in a static reactor<sup>10</sup>. The shock tube experiments were carried out over the temperature range of 587-1027°C. and over the pressure range of 10-20 atmospheres using argon

as diluent. The course of the reaction was followed by means of ultraviolet absorption spectroscopy using a light beam centered at 220 nm. Computer analysis of the data indicates that the dissociation exhibits a slow initiation phase followed by an accelerating rate. The following reaction mechanism was assumed by Solomon and co-workers in these calculations:



These investigators suggested that at high reactant concentrations such as those used in these studies, the following reaction might begin to compete with step 1:



Steps 1 through 4 constitute a chain reaction with fluorine atoms as the chain carrier. They predicted that at temperatures below the point of significant dissociation of fluorine, the addition of molecular fluorine to the reaction mixture should inhibit the reaction because of the reversible nature of step 4. These authors observed this effect and further stated that this inhibition decreases and finally vanishes at temperatures above 927°C.

The static reactor experiments of Solomon and co-workers were carried out using aluminum reactors over the tempera-

ture and pressure ranges of 290-361°C. and 10-5500 torr respectively. Concentration changes were followed by means of a mass spectrometer which was coupled to the reactor. Changes in the reactor surface to volume ratio indicated that there is no heterogeneity, and the reaction is reported to have an induction period followed by an apparent first-order decay. The presence of an induction period, which had not been observed by earlier workers<sup>1,2</sup>, is inconsistent with a mechanism involving a single elementary reaction (apparatus-induced induction periods frequently arise in static systems because of temperature and mixing effects). Moreover, it was found that the first-order rate constant increased with increasing pressure up to 5500 torr. Therefore, all of the rate measurements in this study seem to have been made in a pressure-dependent region of at least one of the elementary unimolecular steps\*. Changes in the initial pressure of oxygen difluoride at constant total pressure produced no noticeable effect on either the rate constant or on the form of the kinetics. Added oxygen had no effect on the rate and added fluorine acted moderately to retard the reaction as in the case of the shock tube work. Again, this inhibition was attributed to the reverse of

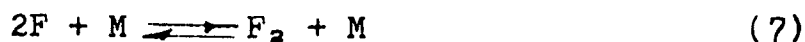
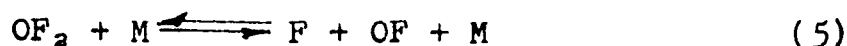
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\*Benson<sup>11</sup> has tabulated values for the pressures above which there is no total pressure dependency (activation control) for molecules of various degrees of internal freedom. For molecules such as oxygen difluoride which have 3 internal degrees of freedom, the pressure dependency limit is predicted to be  $1.9 \times 10^4$  torr.



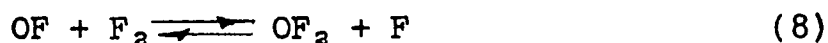
step 4 which implies that a chain reaction is possible. During the course of this study, two very small peaks at masses 70 and 51 were detected; high resolution mass spectrometry indicated that small amounts of dioxygen difluoride ( $\text{O}_2\text{F}_2$ ) and the dioxygen fluoride ( $\text{O}_2\text{F}$ ) radical were present. No analytical treatment of the data was found which quantitatively described the pressure dependence or the fluorine inhibition.

Lin and Bauer<sup>12</sup> have reported the results of studies of the thermal decomposition of oxygen difluoride in a shock tube over the temperature range of 497-1117°C. using argon as diluent; the reaction was followed mass spectrometrically. These authors state that all rates obtained by conventional techniques, either in static or in flow systems, prove to be higher than those derived from the shock tube technique. This, they claim, is attributable to surface effects which cannot be avoided in conventional systems. In part, this statement is based upon an extrapolation of an Arrhenius plot over a wide range of temperatures and for this reason may be largely invalid. The experimental results were accounted for by the following mechanism:



It is claimed that the reverse reactions (-5) and (-7) can-

not be neglected even in the early stages of the reaction. Lin and Bauer included the following additional steps in the general scheme which accounts for the decrease in oxygen yield at higher temperatures:



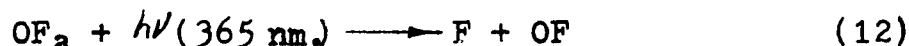
The observed rate constants at temperatures above 727°C. are lower than what would be predicted, and this is attributed to the approach to equilibrium by step 5. Based on theoretical considerations alone, these authors conclude that fluorine inhibits the oxygen difluoride decomposition by virtue of reactions 7 and 8.

The activation energy for the overall process obtained by the various methods discussed is within the range  $35^{+5}$  kcal. mole<sup>-1</sup> and is believed to be associated with the rate controlling process



Gatti and co-workers<sup>13</sup> studied the photochemical decomposition of oxygen difluoride in a quartz static reactor using monochromatic light of 365 nm. wavelength. The overall quantum yield for the reaction is reported to be 1.0 molecule photon<sup>-1</sup> and the reported mechanism for the decomposition

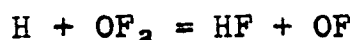
is as follows:



These workers also present evidence indicating that there is no room-temperature reaction between fluorine atoms and oxygen difluoride.

Hydrogen-Oxygen Difluoride Reaction: A thorough search of the literature has failed to reveal any activity in the area of the kinetics of the hydrogen-oxygen difluoride reaction.

The hydrogen-oxygen difluoride system has been investigated in connection with a chemical laser produced by the photolysis of the mixture<sup>14</sup>. It was reasoned that vibrationally excited hydrogen fluoride is produced by the following highly exothermic reaction:



### Kinetics in a Flow System<sup>15</sup>

Flow systems are of two general types, those in which no stirring occurs in the reactor, i.e., plug-flow, and those in which sufficient stirring occurs to effect complete mixing within the reactor.

Considering a tubular reactor of constant cross-sectional area and plug-flow conditions, the change in the number of moles of reactant with time in volume element ( $dV$ ) is given by

$$dn/dt = rdV - udc \quad (15)$$

where  $dV$  = cylindrical volume element

$r$  = rate of chemical reaction

$u$  = volume rate of flow of the  
reaction mixture

$c$  = concentration of reactant

At steady-state, Eq. 15 becomes

$$rdV = udc$$

or

$$r = (u/dV)dc$$

Under conditions of constant flow  $dV/u$  may be replaced by  $dt$  which gives the familiar closed-system kinetics equation, namely

$$r = dc/dt \quad (16)$$

If one now considers a stirred-flow reactor in which the concentrations of reactant and products are considered uniform throughout and equal to the exit stream concentration, the volume element  $dV$  may be replaced by  $V$  (the total

reactor volume), and  $dc$  may be replaced by  $(c_0 - c)$  giving

$$r = u(c_0 - c)/V \quad (17)$$

where  $c_0$  = initial concentration of reactant

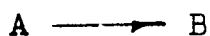
Eq. 17 is applicable to any component of the system and if flow rates are assumed constant, it may be rewritten as

$$r = (c_0 - c)/t \quad (18)$$

where  $t$  = contact time (average time in which a molecule resides in the reactor) =  $V/u$

Eq. 18 enables explicit determination of reaction rate. Alteration of initial concentrations and/or flow rates permits determination of the form of the rate equation and rate constants without integration.

The above equations are applicable to reactions of any order and any degree of complexity. As an example, consider the following simple first-order reaction:



for which  $r = \text{rate} = kc$  (19)

By combining Eqs. 16 and 19 and substituting  $dV/u$  for  $dt$ , the following differential equation applicable to tubular, plug-flow reactors is obtained:

$$- \frac{dc}{c} = \frac{k}{u} dV$$

This equation may be integrated over the reactor volume  $V_0$ ; at the entrance to the reactor  $V = 0$  and  $c = c_0$  (initial concentration of reactant), and at the exit  $V = V_0$ .

Therefore,

$$- \int_{c_0}^c \frac{dc}{c} = \frac{k}{u} \int_0^{V_0} dV$$

In this case integration gives

$$k = -(u/V_0) \ln(c/c_0) = -\frac{1}{t} \ln(c/c_0)$$

where  $c$  = concentration of A at contact time,  $t$

For a stirred-flow reactor, Eqs. 18 and 19 are combined to give:

$$r = (c_0 - c)/t = kc$$

or

$$k = (c_0 - c)/ct$$

Thus, the stirred-flow reactor offers the advantage of enabling direct determination of reaction rates from which rate constants and the order of the rate equation can be obtained without integration.

## EXPERIMENTAL

### Apparatus

A schematic representation of the flow system used for both parts of the experimental program is shown in Figure 1. The basic components of the flow system were constructed of  $\frac{1}{4}$ -inch stainless steel tubing and the reactor and downstream section were made of monel. The reactor was a modified 95 ml. Hoke model 304 monel sampling cylinder. The vacuum header and the manometers were made of Pyrex. All shut-off valves in the metal portion of the flow system were Hoke, monel, packless, diaphragm valves with cam handles. The metering of the reactant mixtures was done with Hoke monel needle valves with 1° stems. All non-threaded connections in the metal part of the system were made with silver solder. Reactant mixture flows were monitored with calibrated capillary flow meters containing Halocarbon Products Corporation's series 4-11 halocarbon oil which was inert to all oxygen difluoride mixtures subjected to it. The flow system was equipped with the means to run subatmospheric (to 10 torr) experiments, but this feature was seldom used.

Helium (distributed by Linde), without further purification, was used as the principal carrier gas in the pyrolysis reaction and in the reaction of hydrogen with oxygen difluoride.

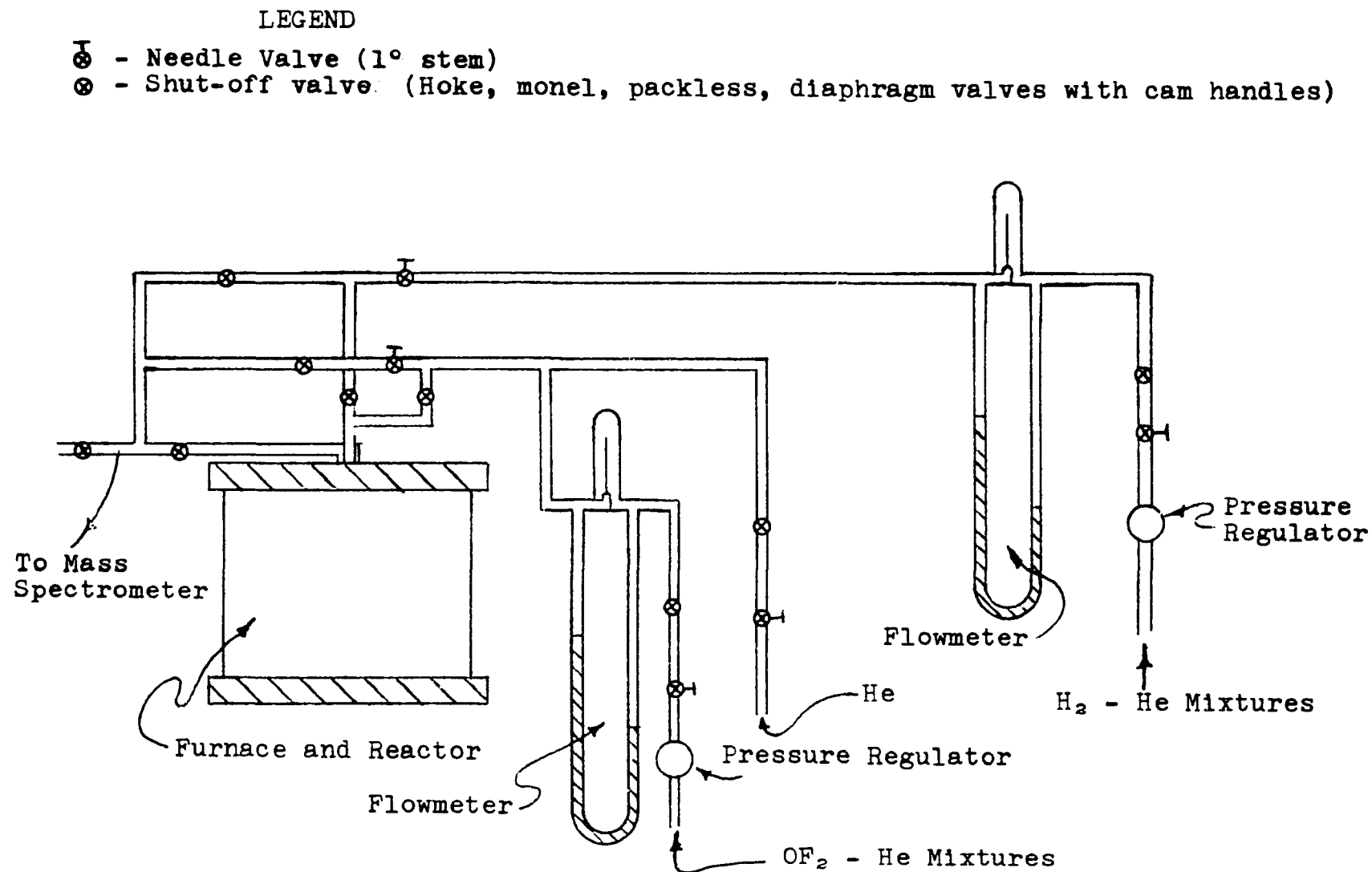


Figure 1 The Flow System



Helium-oxygen difluoride and helium-hydrogen mixtures were prepared in a separate gas handling station equipped with a vacuum system for the complete exclusion of air. Helium-oxygen difluoride mixtures were prepared in a 5 gal. Hoke stainless steel sampling cylinder and the helium-hydrogen mixtures were prepared in 10 gal. stainless steel tanks (A. C. Tank Company). All tanks were equipped with shut-off valves and Bourdon gauges. To enhance the precision of the preparation of gaseous mixtures at low reactant concentrations, i.e., up through 3 mole per cent, additional tanks containing intermediate reactant concentrations were used. The helium used as diluent in the reactant preparations served as carrier gas in the flow system. Standard pressure regulators were placed in the reactant supply lines to provide a constant pressure at the needle valves as supply tank pressures diminished during the course of a set of experiments. The supply tank capacities and the flow rates in the flow system were such that 100 psig initial pressure in the supply tanks provided sufficient sample for a day's experimentation.

As shown in Figure 1, the flow system's design provided the means to pass the gaseous stream containing reactant(s) either through or around the reactor. On the downstream side of the reactor, slightly beyond where the bypass and the reactor streams come together, a 0.015 inch (I.D.) stainless steel capillary was inserted into the exit tube. This

capillary is part of an atmospheric sampling device which continuously draws sample, at atmospheric pressure, into an AEI MS-10 mass spectrometer. Figure 2 shows the basic design of the atmospheric sampling system. The MS-10 is a low resolution (10 per cent valley at about  $m/e$  150) single focusing  $180^\circ$  sector instrument equipped with an oil diffusion pump, a liquid nitrogen cold trap, an ion gauge, and a Bristol Dynamaster series 64A high-speed recorder. This instrument, with its 1.8 kilogauss permanent magnet, has an  $m/e$  range of 2 to 200 and is equipped with a scan assembly. Thus, when the instrument is focused on the peak corresponding to one of the reactants or products of the reaction, a recorder response is registered which is proportional to the concentration. When the gaseous stream is bypassing the reactor, its concentration is known since the concentrations in the sample tanks are known. When the flow is diverted through the reactor, and if some reaction occurs in the reactor, the reactant concentrations decrease. Since the instrument has been shown to respond linearly to concentration changes, knowledge of the response at a known concentration and at zero concentration of reactant permit calculation of unknown concentrations, i.e., the concentration of reactant issuing from the reactor.

Two reactors were used in this experimentation; each had a diameter of 4 cm. and the lengths were 9 cm. and 12 cm. and the effective volumes were  $50 \pm 2$  ml. and  $86 \pm 2$  ml.

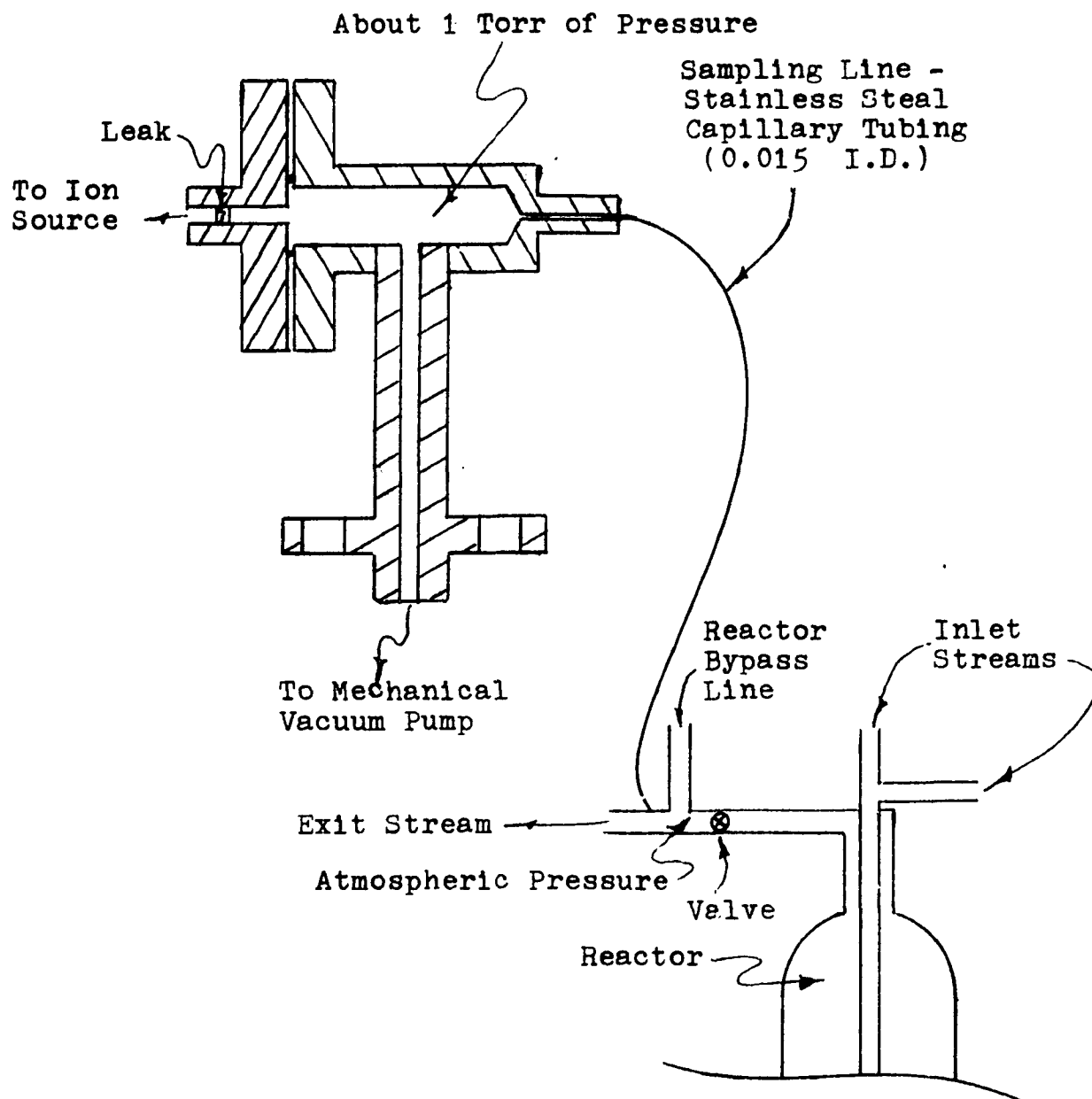


Figure 2 The Atmospheric Sampling System

respectively. The uncertainty in the reactors volumes arose from the temperature gradients established along the inlet and outlet paths. To facilitate stirring, the gaseous mixture entered the reactor through a centered  $\frac{1}{4}$ -inch tube from which it jetted through pin holes near the reactor's center. Top, middle, and bottom thermocouple wells were made by inserting closed-end sections of  $\frac{1}{4}$ -inch monel tubing through the reactors walls. These thermocouple wells were silver soldered in place and thus placed an upper temperature limit of about 650°C. on the reactors. The reactor outlet was concentric with the inlet tube. In order that explicit determination of differential rate data be attainable from this system, it was imperative that the reactor design effect relatively complete mixing of the contained gases, i.e., that the concentrations of gaseous species in the exit stream be equal to those in the reactor. Experiments conducted by Sullivan and Houser<sup>16</sup> showed that the above assumption was valid for the type of reactor described. Studies of the mixing efficiency were also made in this laboratory (see Appendix A for details).

The reactor, shown schematically in Figure 3, was heated in an electric furnace formed by wrapping a 2-inch diameter (I.D.),  $\frac{1}{8}$ -inch thick ceramic sleeve (Norton-Mullite) with two concentric sets of windings (24-gauge Nichrome resistance wire). Sheet asbestos served as insulating material to isolate the windings. The inner (controller) winding,

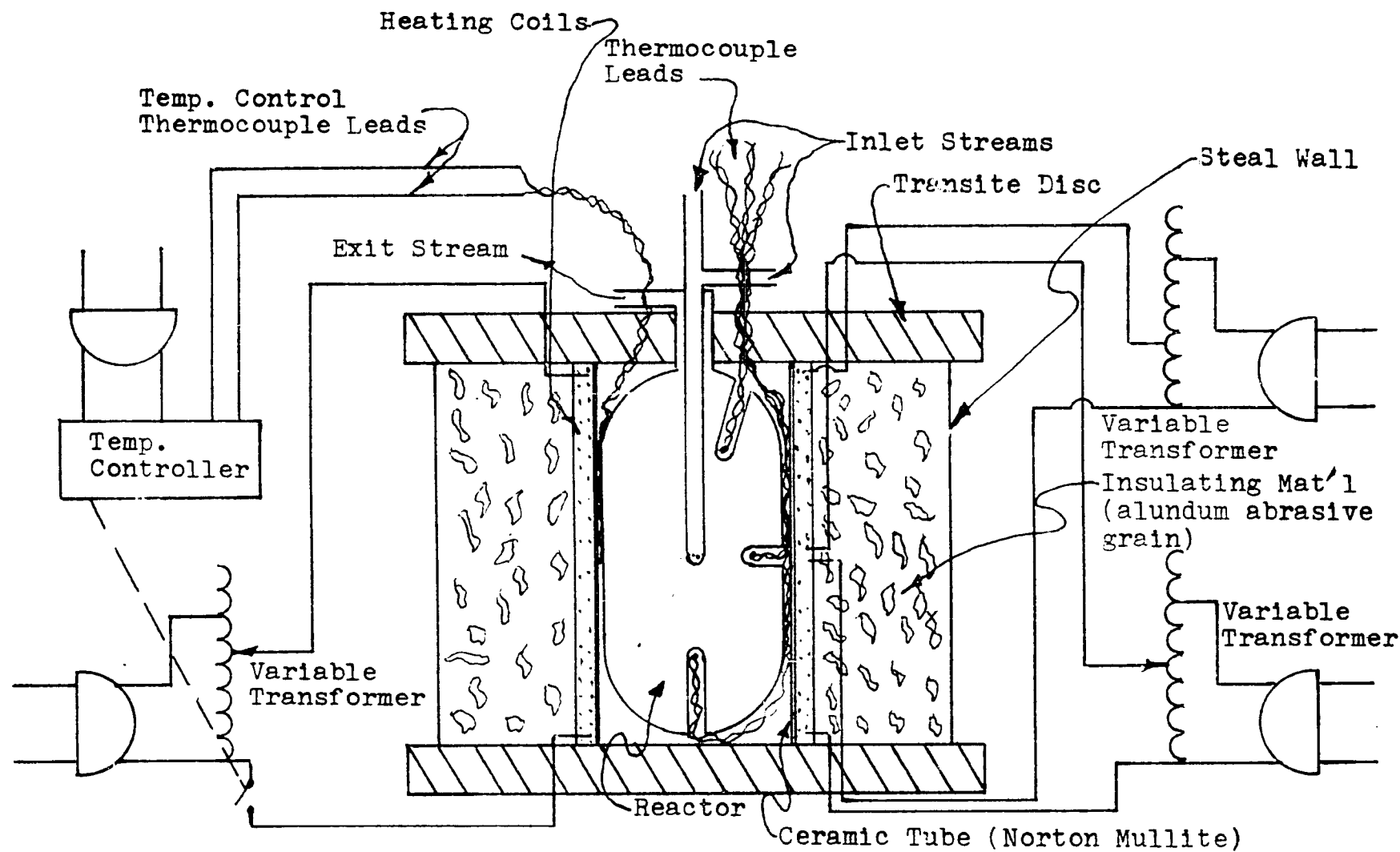


Figure 3 Reactor and Furnace Assembly

which extended the full length of the furnace, was powered by a 1 KVA variable transformer which was actuated (ON - OFF) by a Honeywell Versatronik, model R7161H, temperature controller. The outer windings, which consisted of an upper and a lower part, were powered separately by 1 KVA variable transformers and provided a constant source of heat. The independently powered outer windings facilitated uniform temperature attainment. A chromel-alumel thermocouple placed between the reactor and the furnace wall was used as a temperature sensor for the controller. Five additional standardized (NBS - Zn, Pb, Cu, Al) chromel-alumel thermocouples, which were placed in the reactors thermocouple wells, were used for temperature measurement. The thermocouples' outputs were measured with a Honeywell model 2732 portable potentiometer (0 to 150 millivolts--readable to 0.01 millivolt). The insulating portion of the furnace consisted of an 8-inch diameter by 7-inch high sheet metal housing with 1-inch thick transite discs covering each end. The heating element was concentric with the insulator housing and the resulting annular space was filled with Norton alundum abrasive grain 38X.

Since oxygen difluoride, a highly toxic substance, was used in all experiments, the flow system and the sample preparation station were constructed inside of 7- and 6-foot walk-in hoods respectively. As a further precaution against atmospheric contamination, all gases issuing from

the systems were passed through Pyrex columns ( $1\frac{1}{2}$  inch diameter by 4 feet long) packed with sodium iodide.

### Procedure

Oxygen Difluoride Pyrolysis: The cylinder of oxygen difluoride obtained for this experimental program was analyzed mass spectrometrically for impurities. The only impurity found at a measurable concentration level was oxygen and its concentration was found to be about 1 mole per cent. Since oxygen is a major product of the pyrolysis of oxygen difluoride, this impurity was thought to be insignificant compared to the concentration of oxygen produced by the reaction; thus, further purification was deemed unnecessary.

The initial concentrations of oxygen difluoride used in these experiments were 1, 3, and 10 mole per cent with helium as diluent. A 10-gal. tank of 10 mole per cent oxygen difluoride was always made for the preparation of the 1 and 3 per cent mixtures. This step-wise dilution enhanced the precision of the initial concentrations. All tanks were evacuated to about 0.07 torr prior to filling; they were then filled to 10 psig with helium prior to the addition of oxygen difluoride. Thus, the oxygen difluoride was always added over an intermediate range of pressures, the range over which the Bourdon pressure gauges were thought to be most accurate. When other components such as fluorine, oxygen, and nitrous oxide were added to the mixtures, the same

technique of addition in the intermediate pressure range was applied. The sample tank pressures never exceeded 100 psig (115 psia), the limit of the Bourdon gauges. The prepared sample tank was placed inside of the flow system's walk-in hood and was connected to the flow system by means of  $\frac{1}{4}$ -inch stainless steel tubing with fittings. The pressure regulator was set to deliver about 10 psig to the needle valve.

The capillary flowmeter was calibrated with a Precision wet testmeter in terms of pressure drop versus flow rate. The exposure of concentrations up to 10 mole per cent of oxygen difluoride to the wet testmeter caused no apparent difficulty as oxygen difluoride is only slightly soluble in water<sup>17</sup> and its hydrolysis rate in neutral water is very slow<sup>18</sup>.

Reactor temperatures were always established such that top to bottom variations never exceeded 1 C°. Since only about 50 per cent of the power was supplied by the controller heating element, temperature cycling never exceeded  $\pm 1\text{C}^\circ$ .

During the course of kinetic runs, the AEI MS-10 mass spectrometer, with its atmospheric sampling device, continuously monitored the concentration of oxygen difluoride issuing from the flow system. It was deemed impractical to operate the mass spectrometer's diffusion pump on a 24-hour-per-day basis because of its continuous demand for liquid nitrogen. When the instrument was not in use the analyzer



tube was maintained under a mechanical pump's vacuum only. Consequently, baking (200°C.) of the analyzer tube section was required prior to each use. Upon attaining a stable vacuum at about  $5 \times 10^{-6}$  torr, the electronics circuits were switched on and at least 1 hour was allowed for warm-up. When following oxygen difluoride concentration changes, which was the usual practice for kinetic runs, the accelerator voltage was tuned to the m/e 54 peak. Optimum sensitivity was obtained with an electron potential of 70 volts, an ion trap current of 100  $\mu$ amps, and a repeller potential of 1 volt. See Appendix B for special procedures.

Run No. 52, which was typical of all kinetic runs, will be used to demonstrate the method of calculation of the reaction rate. For this run the reactor temperature was 360°C., the initial concentration of oxygen difluoride was 3.0 mole per cent, and atmospheric pressure the day of the run was 742 torr. The reactant flow (3.0 per cent OF<sub>2</sub> and 97 per cent helium) was set such that a  $\Delta P$  value on the flow meter of 132 mm. resulted. From the calibration curve it was determined that this corresponded to a flow of 490 ml. min.<sup>-1</sup> at STP. This, in turn, corresponded to a flow of 1,167 ml. min.<sup>-1</sup> in the reactor. Dividing this value into the reactor volume (86 ml.) and converting to seconds gave a contact time of 4.42 sec. The per cent reaction was determined as follows: the flow was diverted through the reactor which caused a chart reading of 47 (per cent chart). The flow was

then switched to the bypass and a chart reading of 67 resulted. To obtain a chart reading corresponding to zero concentration of oxygen difluoride, the reactant flow was turned off and a pure helium stream was turned on. A value of 2 was obtained. Thus, the per cent reaction is:

$$\frac{67 - 47}{67 - 2} \times 100 = 30.8 \text{ per cent}$$

In order to determine the concentration of reactant at time,  $t$ , it is necessary to know the initial concentration,  $c_0$ , in the reactor.

$$c_0 = \frac{0.03}{.0224 \text{ l. mmole}^{-1}} \times \frac{273^\circ\text{K.}}{633^\circ\text{K.}} \times \frac{742 \text{ torr}}{760 \text{ torr}} = 0.564 \text{ mmole l.}^{-1}$$

Thus, the concentration of reactant,  $c$ , at time,  $t$ , is obtained as follows:

$$c = (0.564 \text{ mmole l.}^{-1})(1.000 - .308) = 0.390 \text{ mmole l.}^{-1}$$

The change in concentration of reactant,  $\Delta c$ , resulting from reaction was calculated in the following way:

$$\Delta c = c_0 - c = 0.564 - 0.390 = 0.174 \text{ mmole l.}^{-1}$$

Knowing  $\Delta c$  and  $t$ , the reaction rate was calculated as follows:

$$\text{rate} = r = -\frac{dc}{dt} = \frac{\Delta c}{t} = \frac{0.174}{4.42} = 0.0394 \text{ mmole l.}^{-1} \text{ sec.}^{-1}$$

There are two inherent difficulties associated with the use of stirred-flow reactors. First, at low flows there is a tendency for stirring to be inefficient, thus producing extents of reaction which are too high. Secondly, at high flows the gas temperature tends to be lower than the reactor surface temperature, thus producing extents of reaction which are too low (this problem also arises with plug-flow reactors). The study reported in Appendix A indicates that stirring, even at the lowest flows used in this experimentation, was relatively efficient; therefore, this fault is thought to have a negligible effect on the rate. A preheater was installed to heat the gaseous mixture to about 200°C. prior to entry into the reactor. It was found that this produced no noticeable effect on the rate. It was therefore concluded that the drop in the gas temperature at high flows was negligible.

The volume increase resulting from reaction had a negligible effect on the contact time and thus on the rate because the concentrations of reactant and the specific volume change were relatively low.

Hydrogen-Oxygen Difluoride Reaction: For this reaction, only those parts of this procedure will be discussed which differ from those of the pyrolysis reaction.

Both the oxygen difluoride and the hydrogen mixtures for this reaction were prepared by step-wise dilution to

enhance the degree of precision in the initial concentrations. The tanks containing hydrogen mixtures were placed outside of the walk-in hood and were connected to the flow system by means of a section of high-pressure rubber tubing. Equal flow rates of both reactants were always used so that the initial concentrations of the reactants in the reactor were one-half of those in the sample tanks. Oxygen, which was added as an inhibitor in some experiments, was added to the oxygen difluoride tank.

Generally, the changes in the concentration of oxygen difluoride were followed and the rates with respect to this reactant were calculated as in the case of the pyrolysis reaction.

The stoichiometry of this reaction was determined principally using the mass spectrometer. The principal products of the reaction were found to be water, oxygen, and hydrogen fluoride. The water was quantitatively determined mass spectrometrically by calibrating the instrument with a stream of helium saturated with water at 0°C. The ion accelerator voltage was tuned to  $m/e$  18 and about 20 minutes equilibration time was required since water has a strong tendency to become adsorbed on the walls of the analyzer tube. The results were successfully duplicated and the water peak, under these conditions, is thought to be quantitative. The oxygen produced by the reaction was also determined mass spectrometrically using known concentrations of oxygen as the cali-

brating agent. The stoichiometric coefficient for hydrogen was determined by following the hydrogen concentration changes mass spectrometrically on a series of experiments. Rates with respect to hydrogen were calculated and compared with rates with respect to oxygen difluoride. The ratios of these rates led to the stoichiometric relationship between oxygen difluoride and hydrogen. Hydrogen fluoride could not be determined mass spectrometrically probably because of the formation of the gaseous species  $(\text{HF})_n$  coupled with its strong tendency to become adsorbed. Thus, a wet technique was used. Hydrogen fluoride was trapped from the reactor's exit stream by a series of three bubblers filled with 0.1 M sodium hydroxide. Reactor conditions were set to provide a very high extent of reaction (about 90 per cent) to avoid significant fluoride ion production from the hydrolysis of unreacted oxygen difluoride. Both lead (II) nitrate and calcium chloride were used as precipitating agents. These precipitants were added in excess; the precipitates were collected, dried, and weighed. This technique indicated that about 1.6 moles of hydrogen fluoride were produced per mole of oxygen difluoride consumed. Since there was ample opportunity for the hydrogen fluoride to react with the glass bubble traps, the reported stoichiometric ratio is considered to be a lower limit.

## Materials

Oxygen difluoride was obtained from Allied Chemical Company and was used without further purification. Helium, the principal carrier gas, hydrogen, oxygen (medical), and nitrogen (dry) were supplied by Linde and were used without additional purification.

## RESULTS AND DISCUSSION

### Oxygen Difluoride Pyrolysis

Reaction products: The products of the thermal decomposition of oxygen difluoride as found mass spectrometrically in this study are consistent with those previously reported<sup>1</sup> and are oxygen and fluorine. In addition to these products, Solomon and co-workers<sup>10</sup> reported mass spectrometric evidence for small quantities of dioxygen difluoride ( $O_2F_2$ ) and the dioxygen fluoride radical ( $O_2F$ ) among the reaction products. Failure to observe these relatively unstable products in the present study may be due to the higher temperatures at which the reaction was studied and/or the lower sensitivity of the instrument used.

Kinetic results: The basic kinetic data obtained in this investigation are presented in Appendix C. Figures 4 through 8 are plots of  $\log r$  (rate) versus  $\log (OF_2)$  which give rise to straight lines if the rate law is of the following form:

$$r = kc^n$$

Only 1 of the 3 available sets of kinetic data are presented graphically in Figures 4 through 8 though all 3 sets show the same trends. Here,  $n$  is the physical slope of the straight line resulting from log-log plots. The straight lines which

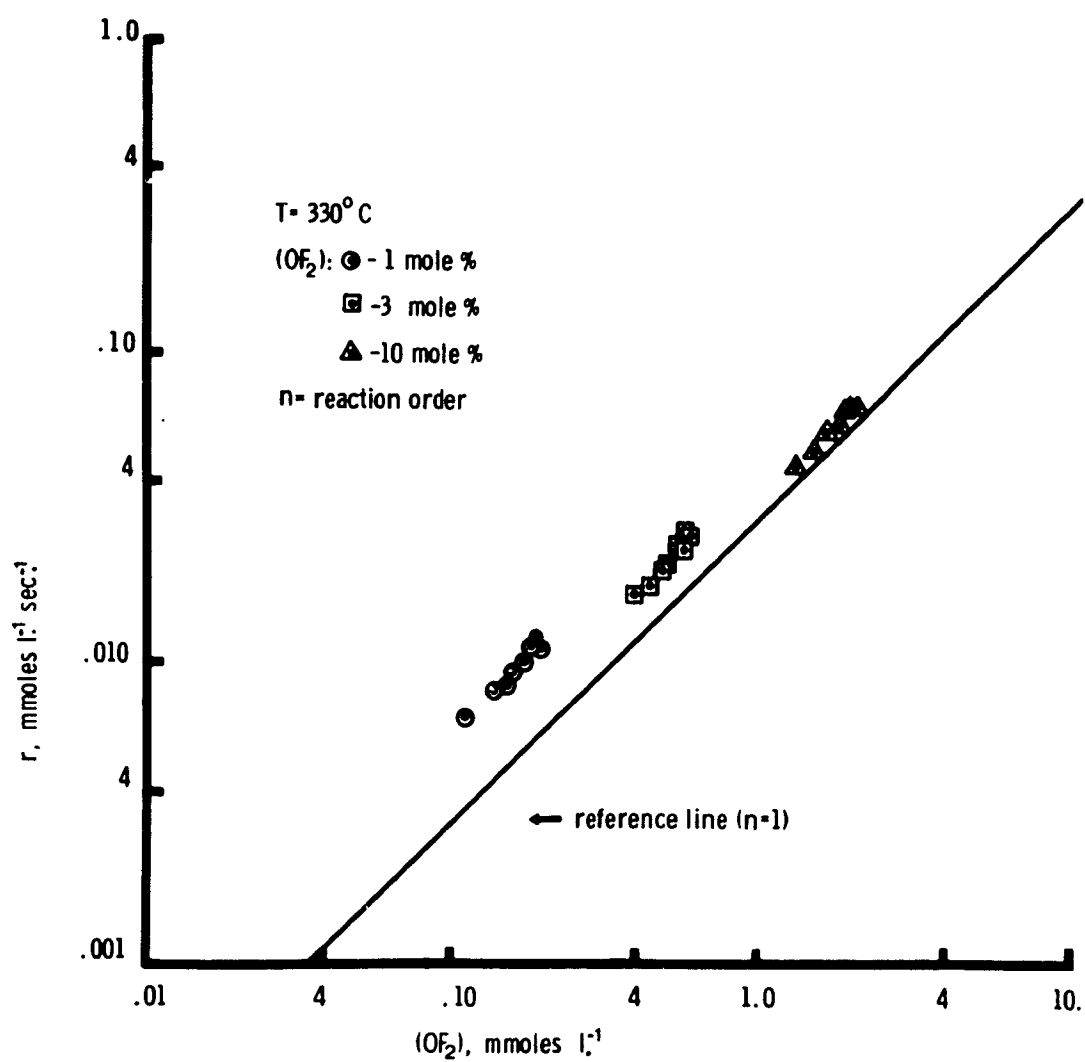


Figure 4. Log  $r$  versus log  $(\text{OF}_2)$  at  $330^{\circ}\text{C}$ .



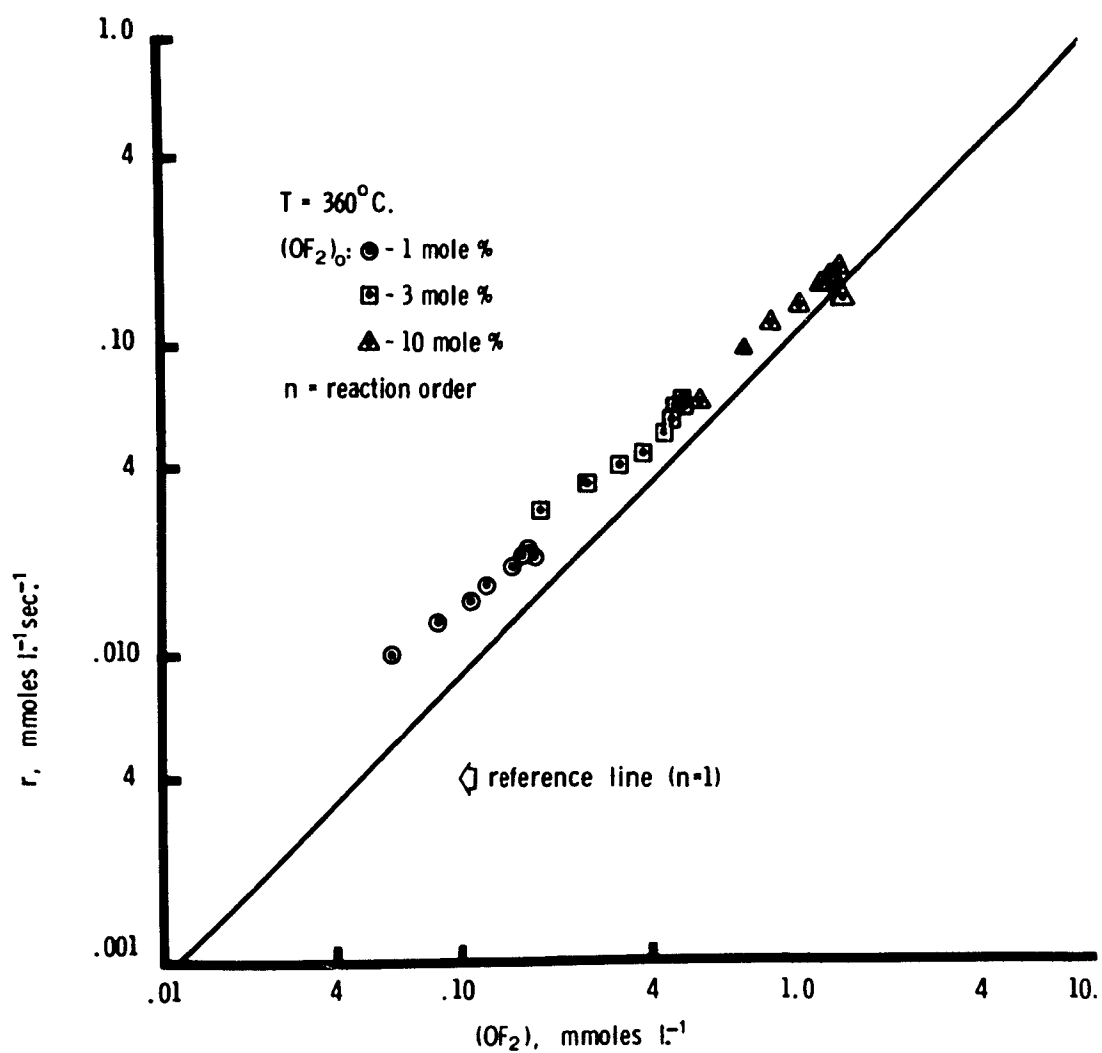


Figure 5. Log  $r$  versus log  $(\text{OF}_2)$  at  $360^{\circ}\text{C}.$

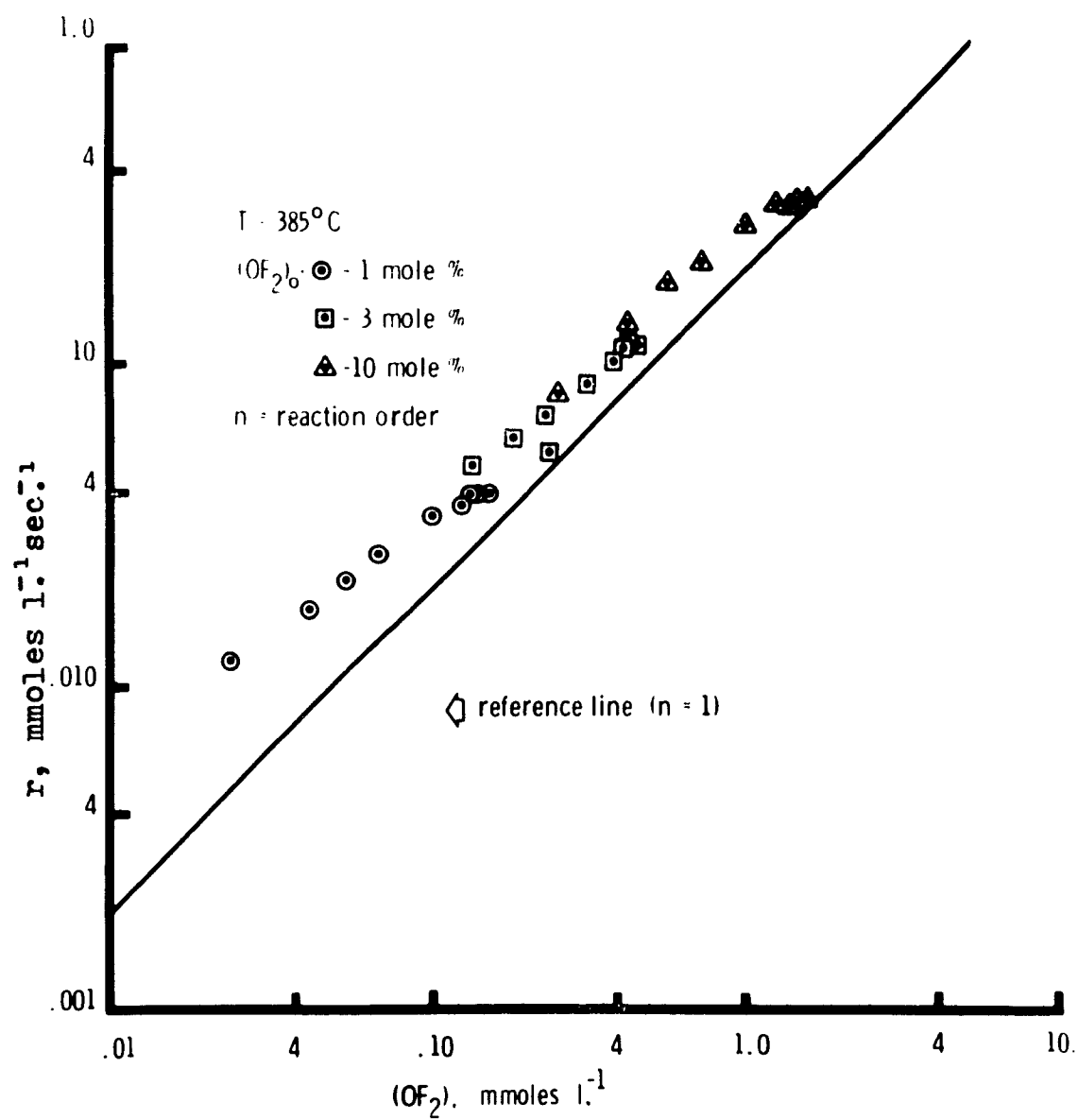


Figure 6. Log  $r$  versus log  $(\text{OF}_2)$  at  $385^{\circ}\text{C}$ .

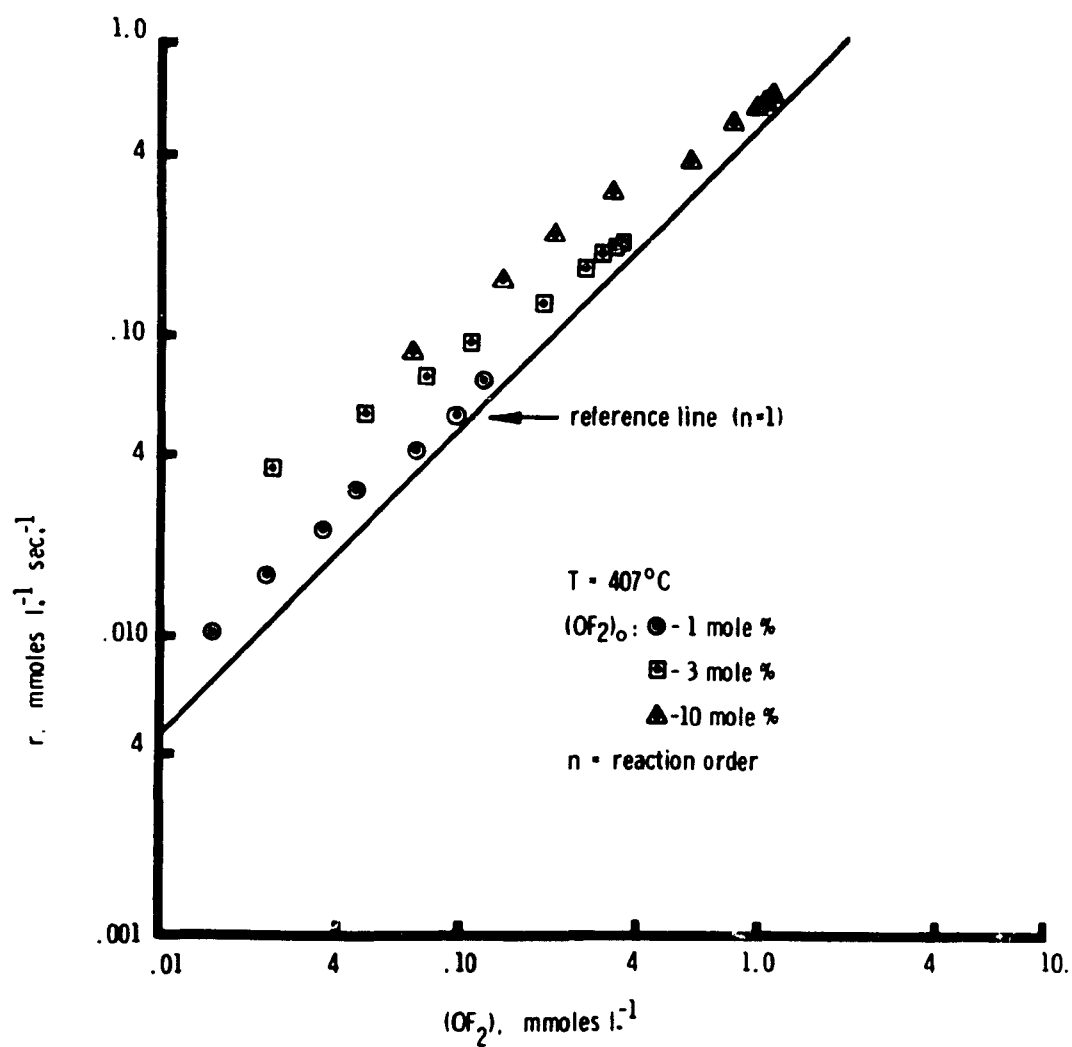


Figure 7. Log  $r$  versus log  $(OF_2)_0$  at  $407^\circ C$ .

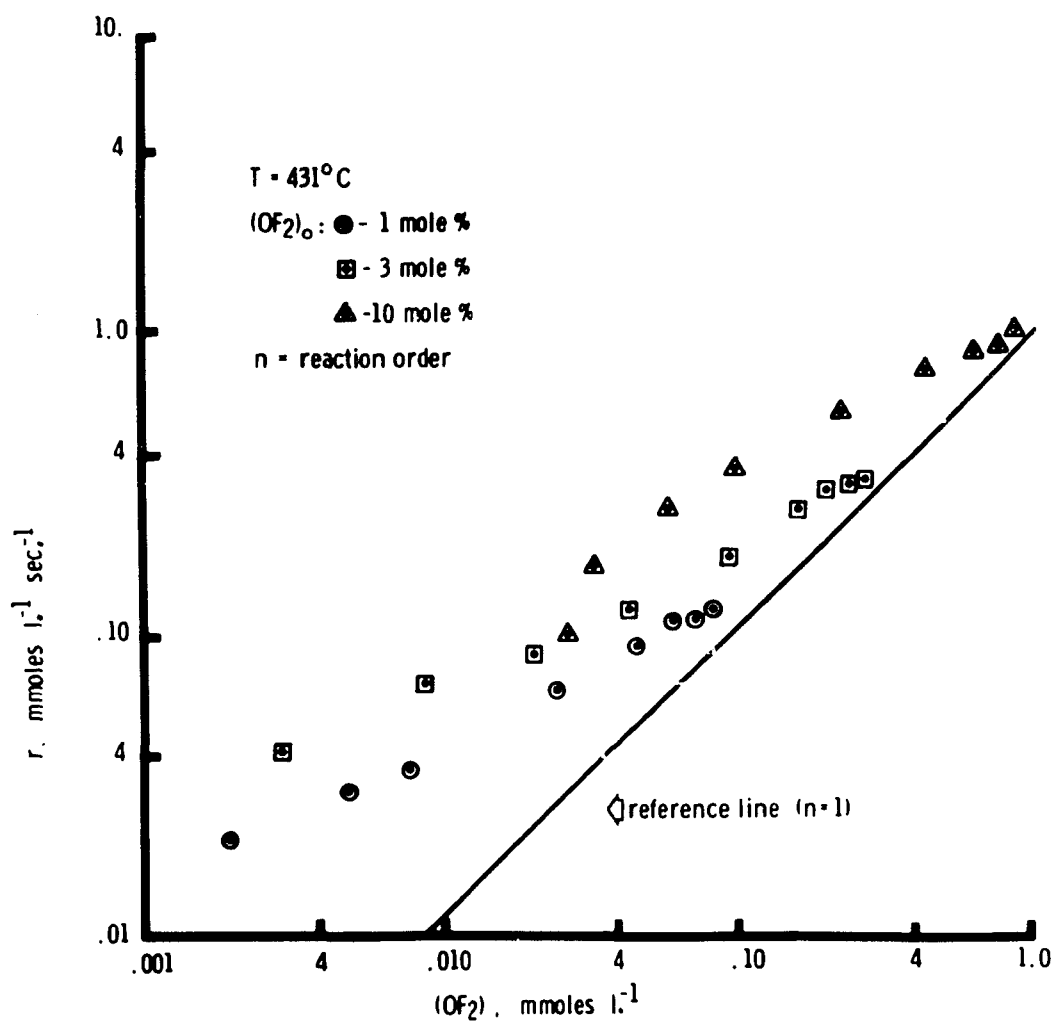
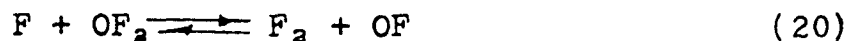


Figure 8. Log  $r$  versus log  $(\text{OF}_2)$  at  $431^{\circ}\text{C}$ .

have been drawn represent the situation where  $n = 1$ . It is to be noted that if all of the points, irrespective of initial concentration, are considered the slope of a straight line corresponding to a best fit would be slightly less than 1. This result is consistent with recent findings of Schumacher<sup>19</sup>. This trend is observed at all of the reaction temperatures here studied. It is also to be noted that at the lower temperatures, i.e., 330 and 360°C., the series of points for a single initial reactant concentration have slopes slightly greater than that corresponding to the mass of points. At the higher temperatures, i.e., 385, 407, and 431°C., the slopes for a series of points for a given initial reactant concentration tend to be lower than those for the mass of points. In short, the order with respect to concentration,  $n_c$ , is less than 1 at all temperatures. The order with respect to time,  $n_t$ , is slightly greater than  $n_c$  at the lower temperatures and lower than  $n_c$  at the higher temperatures. When  $n_t$  is greater than  $n_c$ , inhibition by products is indicated whereas  $n_t$  less than  $n_c$  indicates acceleration (when reaction products do not alter the rate  $n_c = n_t$ ). The observed inhibition which diminishes with increasing temperature is consistent with the findings of Blauer and Solomon<sup>9</sup> and may be attributable to the reversible nature of the following step:



The data resulting from product addition studies are shown in Appendix D. Initial concentrations of  $\frac{1}{3}$ , 1, and 3 mole per cent fluorine were added to the reaction mixture and a small but significant amount of inhibition resulted as may be seen from the data in Appendix D. When compared with standard data taken at about the same time, the lowering of the rate ranged from about 15 per cent at 330°C. to about 5 per cent at 431°C.

A more definitive conclusion regarding the significance of Eq. 20 (forward direction) is expected from an experimental program proposed by Houser<sup>20</sup> whereby fluorine atoms will be generated in a flow system via r-f discharge at about 1 torr pressure and then reacted with oxygen difluoride at temperatures below those at which significant pyrolysis occurs. Decreases in the oxygen difluoride concentration will indicate that reaction is occurring via Eq. 20 (forward direction).

No quantitative explanation for the apparent acceneration (increase in  $r/(OF_2)$  with time) at 407 and 431°C. is available at this point. However, a qualitative explanation may be that  $r/(OF_2)$  increases as the concentration of radicals increases with reaction time in an approach to steady-state. Houser<sup>20</sup> has shown that for reactions producing a radical (fluorine atom) which may in turn react with reactant (consecutive-parallel mechanism), the relative time to reach steady-state increases as temperature increases.

Thus, the above observed increase in  $r/(OF_2)$  is not unexpected if the rate of radical production exceeds the rate of consumption in the initial stages of the reaction. Since the pyrolysis mechanism appears to involve more steps than a simple consecutive-parallel mechanism (as will be discussed in the next section), it is not possible to use a more quantitative approach to resolve this apparent acceleration.

Initial concentration of  $\frac{1}{2}$ , 1, and 3 mole per cent oxygen were also added to the reaction mixture and produced no effect on the rate.

To investigate the possibility of the existence of heterogeneous components of this reaction the reactor was stuffed with helices ( $\frac{1}{4}$  inch I.D.) of 16 gauge monel wire. This increased the surface area by 2.5 times while only slightly reducing the reactor's volume. Data resulting from experiments carried out at 385°C. are presented in Appendix E. Figure 9 shows that stuffing the reactor produced about a 10 per cent increase in the rate. From this it may be concluded that the reaction is primarily homogeneous with a relatively small heterogeneous component.

To account for the observed order being slightly less than 1\*, rate expressions of the following form are reasonable:

---

\*Since helium is only about 40 per cent as effective as oxygen difluoride with respect to activation of reactant during collision, the  $r/(OF_2)$  ratios for the 10 mole per cent concentrations should be about 10 per cent higher than those for the 3 mole per cent concentrations for a unimolecular reaction in the second-order region. Only about 2 per cent difference is expected between the 3 and 1 mole per cent concentrations. Thus, it may be concluded that the true order is somewhat lower than the data indicate.

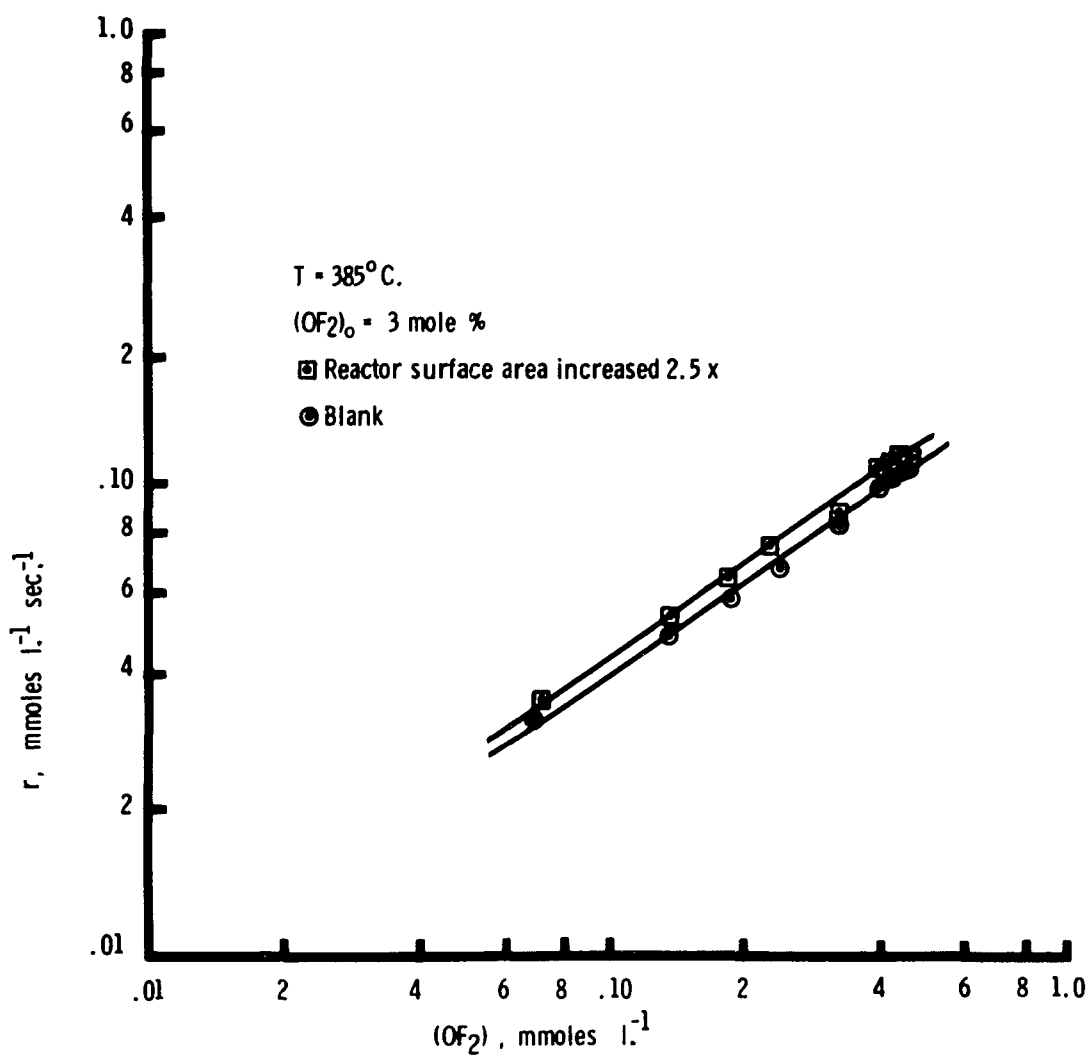


Figure 9 Log  $r$  versus log  $(\text{OF}_2)$  - heterogeneous effects



$$r = k(\text{OF}_2) + k' \quad (21)$$

and

$$r = k(\text{OF}_2) + k'' (\text{OF}_2)^{\frac{1}{2}} \quad (22)$$

A rate law of the form of Eq. 21 would be expected if there existed a small zero-order component of the reaction. The zero-order term could be explained by the presence of a zero-order heterogeneous component. Such a situation could result if the surface's reaction sites were saturated with reactant. If the zero-order term in Eq. 21 is attributed to heterogeneity, then a reduction in observed order upon increasing the surface area is predicted since the zero-order term is a greater contributor to the rate. The data, as presented in Figure 9, do not bear this out since the slopes of the lines corresponding to different surface areas are about the same. Therefore, Eq. 21 does not represent a valid form of the rate law. Failure to observe order change on increasing the surface area implies that the heterogeneous component is close to first-order, i.e., the surface is sparsely covered with reactant.

Assuming that Eq. 22 represents a valid form of the rate law, plots of  $r/(\text{OF}_2)$  versus  $(\text{OF}_2)^{-\frac{1}{2}}$  would be expected to give rise to straight lines and unify the data at the 3 different initial reactant concentrations. It was found that this treatment did not adequately unify the data. To cir-

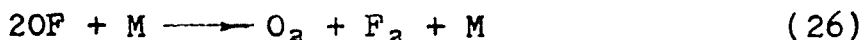
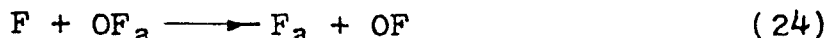
cumvent some of the complexities of this reaction resulting from product effects, plots of  $r/(OF_2)$  versus time were extrapolated to time zero (Figures 10 through 14). Initial values of  $r/(OF_2)$  or  $[r/(OF_2)]_0$  versus  $(OF_2)_0^{-\frac{1}{2}}$  for the 3 initial concentrations were plotted and gave rise to reasonably straight lines at all of the temperatures studied as can be seen in Figures 15 through 17.

Abnormally large scatter in  $r/(OF_2)$  values are predicted especially at the extremes in the extent of reaction because of the nature of the components of the quotient. For example, if the extent of reaction, as measured, is too high then the rate will be too high but  $(OF_2)$  will be too low. Thus, errors present in the rate are magnified when  $r/(OF_2)$  is calculated.

Reaction mechanism: An acceptable mechanism for this reaction must be able to account for the origin of all observed products and the observed initial rate law, i.e.,

$$r_0 = k(OF_2)_0 + k''(OF_2)_0^{\frac{1}{2}}$$

A chain mechanism which leads to an order of less than 1 is as follows:



$T = 330^{\circ}\text{C.}$

( $\odot$ ,  $\square$ , and  $\triangle$  represent equivalent sets of experiments)

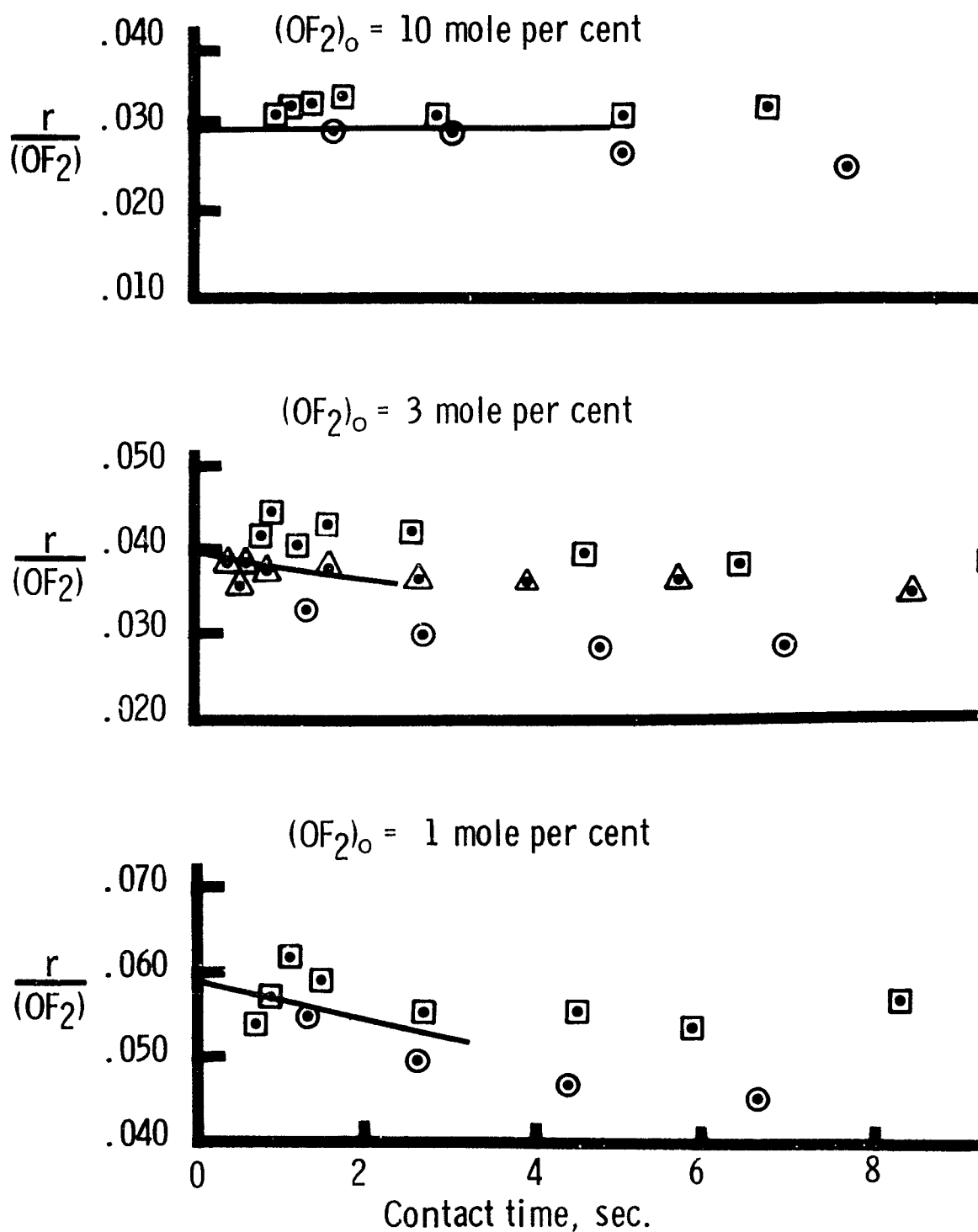


Figure 10  $r/(\text{OF}_2)$  versus contact time at  $330^{\circ}\text{C.}$

$T = 360^{\circ} \text{C.}$

( $\odot$ ,  $\square$ , and  $\triangle$  represent equivalent sets of experiments)

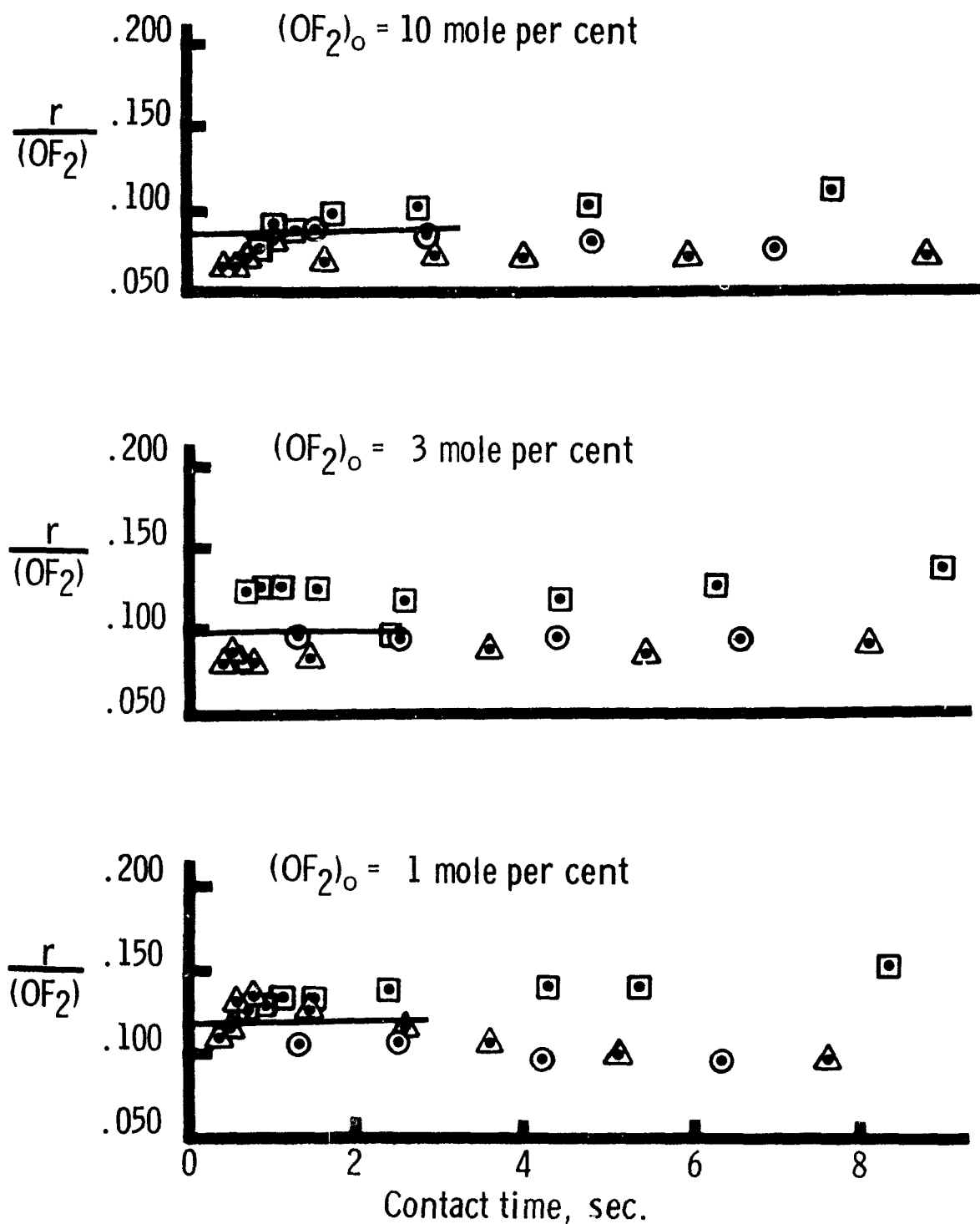


Figure 11.  $r/(\text{OF}_2)$  versus contact time at  $360^{\circ} \text{C.}$

$T = 385^{\circ}\text{C}.$

( $\odot$ ,  $\square$ , and  $\triangle$  represent equivalent sets of experiments)

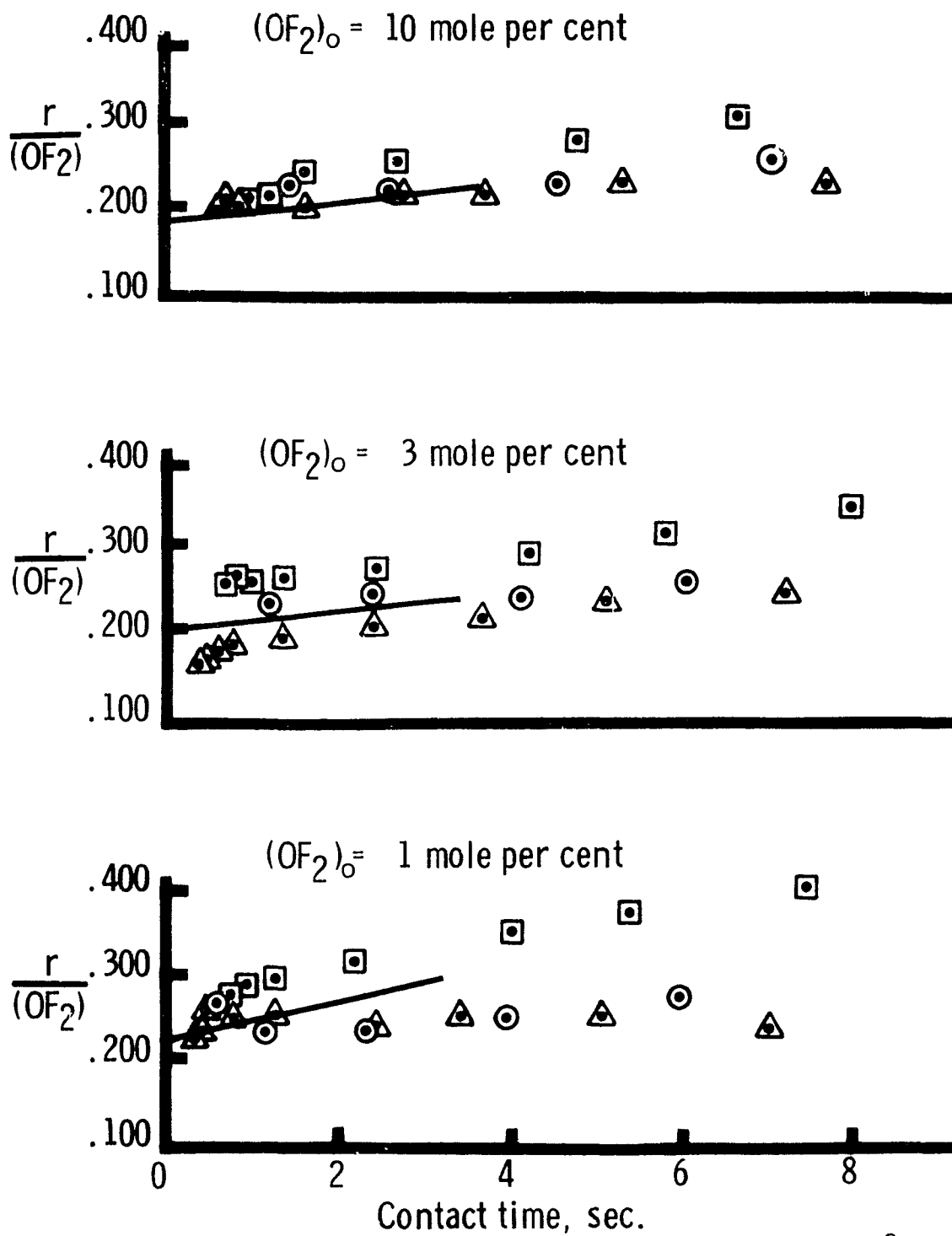


Figure 12  $r/(\text{OF}_2)$  versus contact time at  $385^{\circ}\text{C}.$

$T = 407^{\circ} \text{C.}$

( $\odot$ ,  $\square$ , and  $\triangle$  represents equivalent sets of experiments)

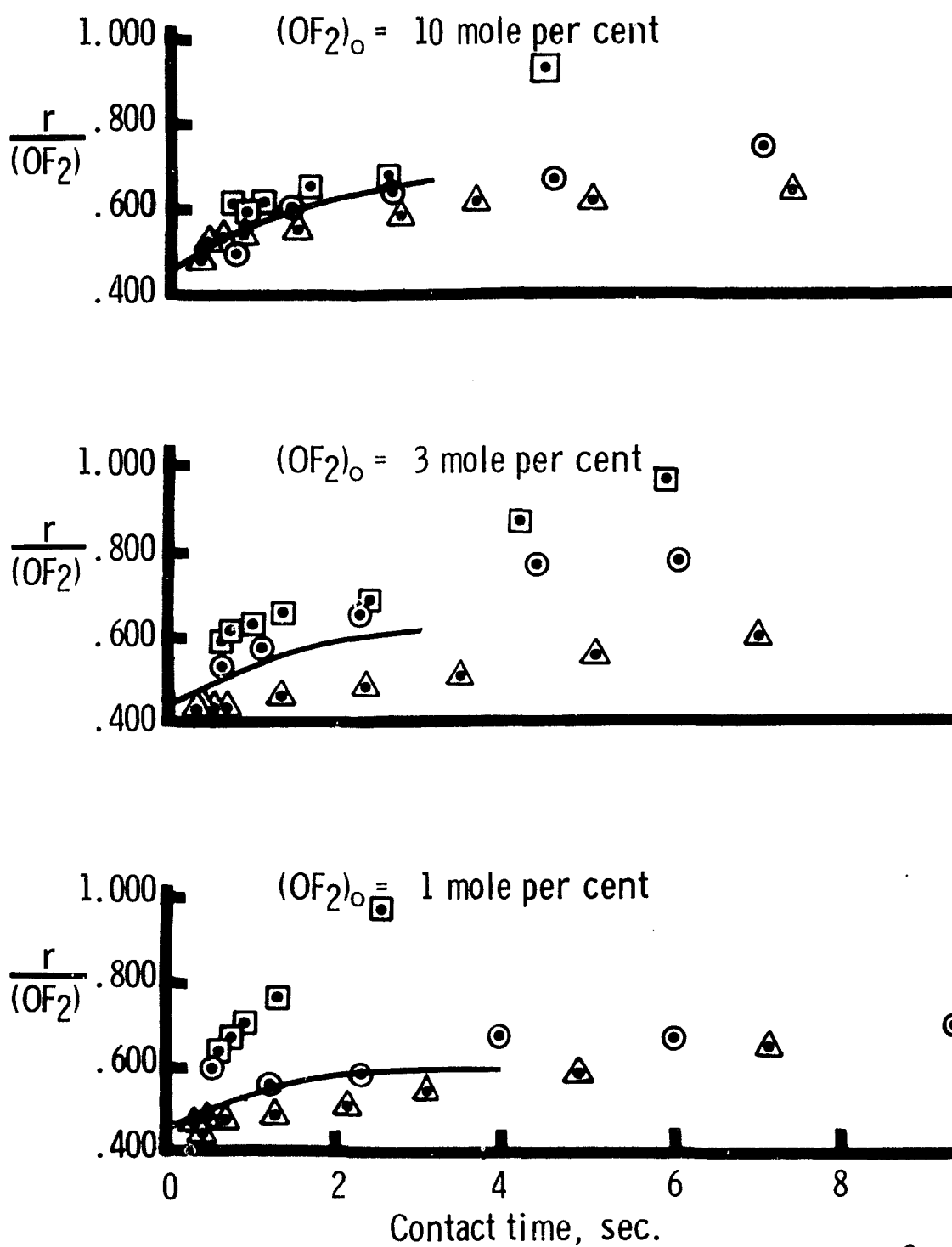


Figure 13  $r/(\text{OF}_2)$  versus contact time at  $407^{\circ} \text{C.}$

$T = 407^{\circ}\text{C.}$

( $\odot$ ,  $\square$ , and  $\triangle$  represents equivalent sets of experiments)

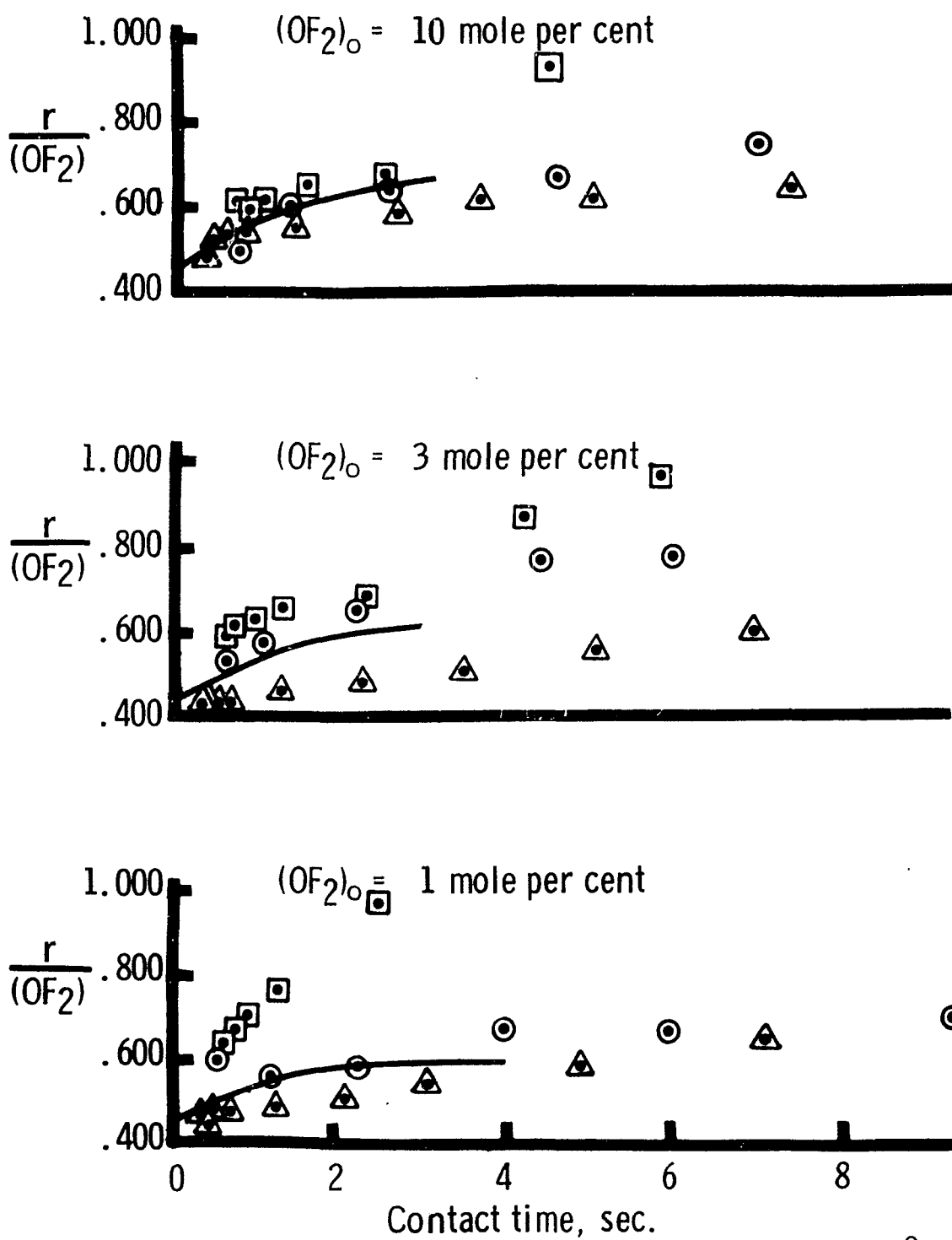


Figure 13  $r/(\text{OF}_2)$  versus contact time at  $407^{\circ}\text{C.}$

$T = 431^{\circ} \text{C.}$

( $\odot$ ,  $\square$ , and  $\triangle$  represent equivalent sets of experiments)

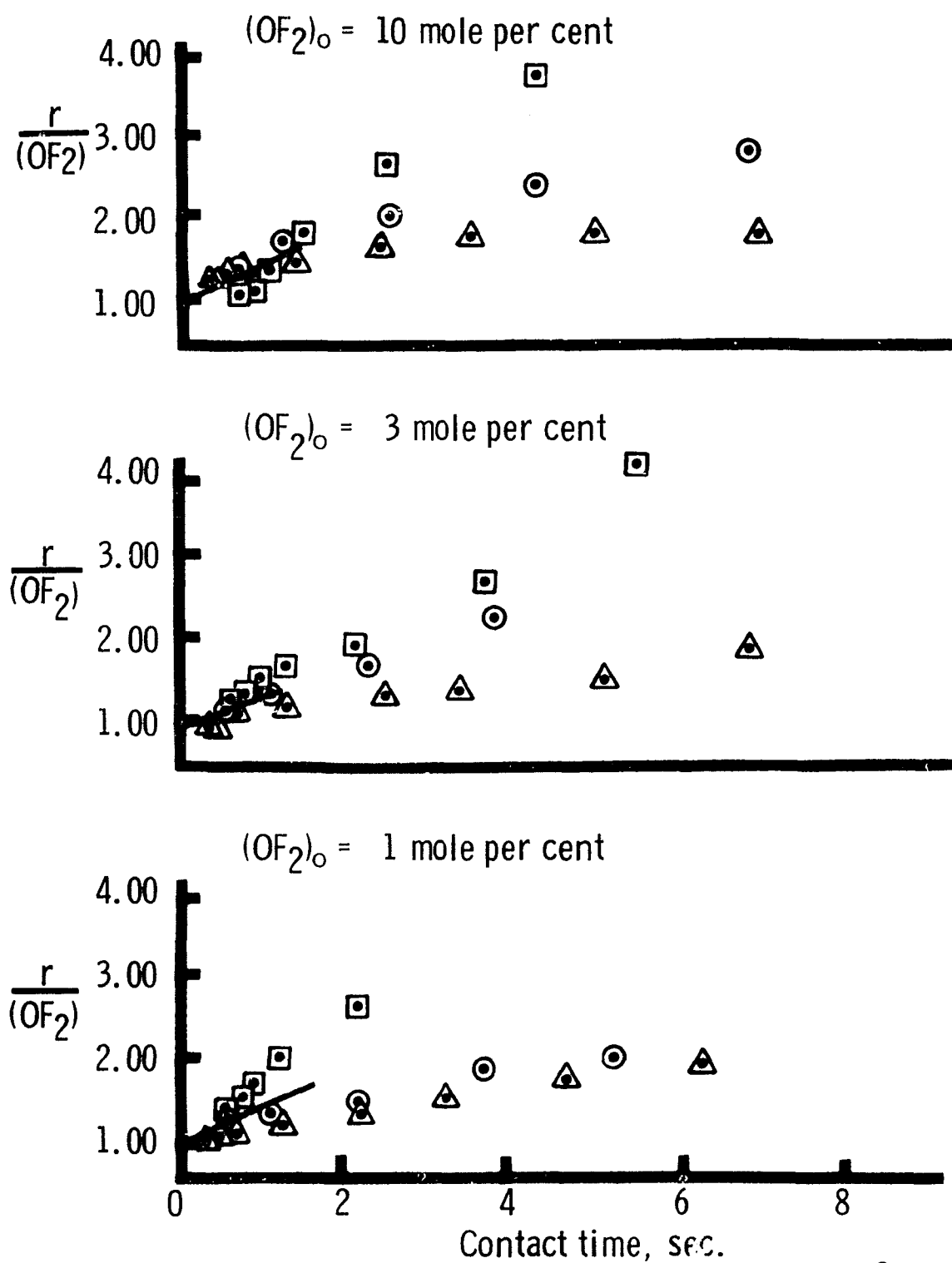


Figure 14  $r/(\text{OF}_2)$  versus contact time at  $431^{\circ} \text{C.}$



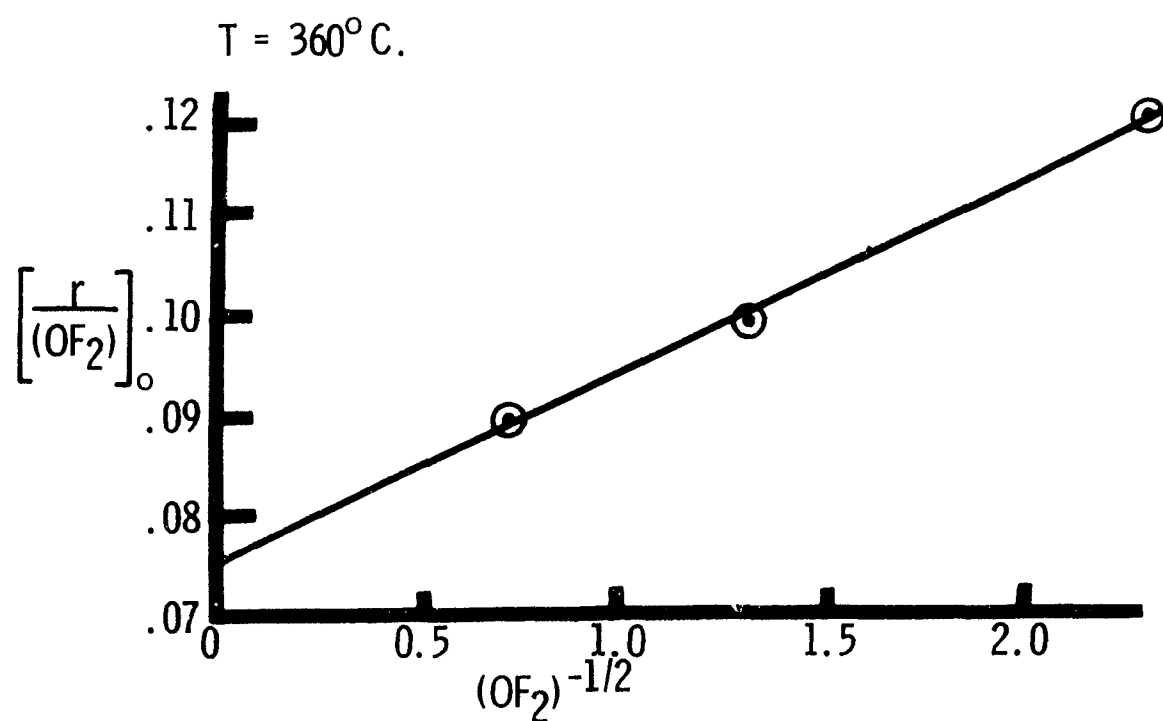
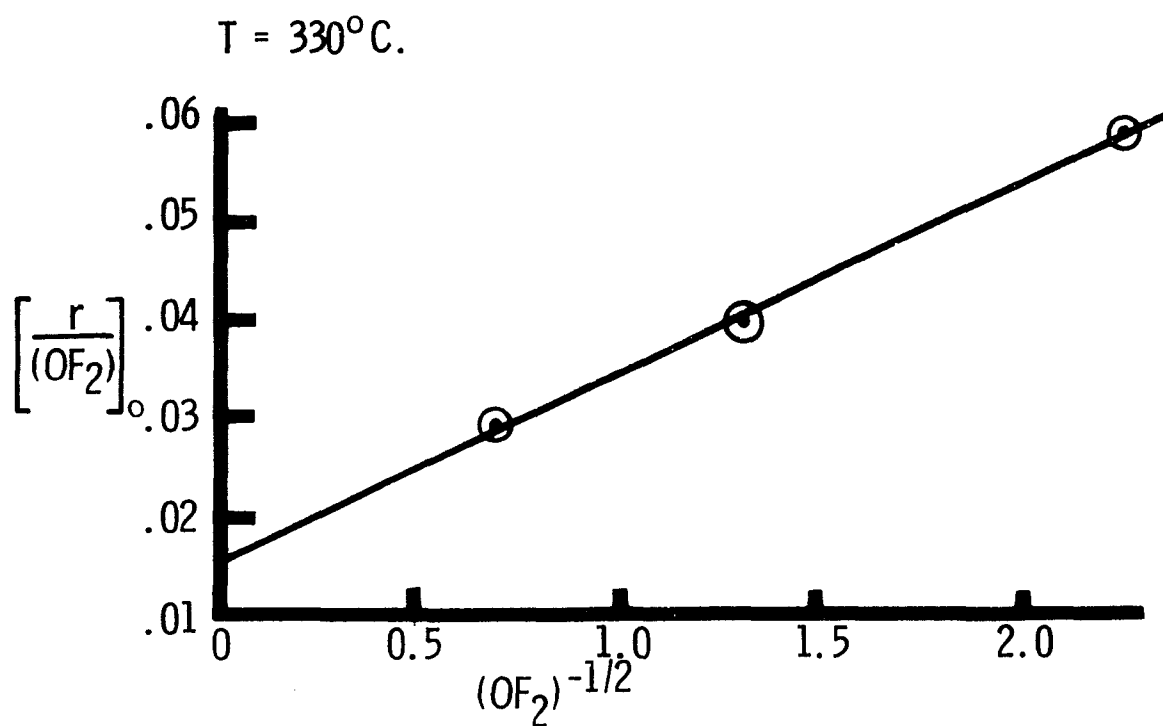


Figure 15  $\left[\frac{r}{(\text{OF}_2)}\right]_0$  versus  $(\text{OF}_2)^{-1/2}$

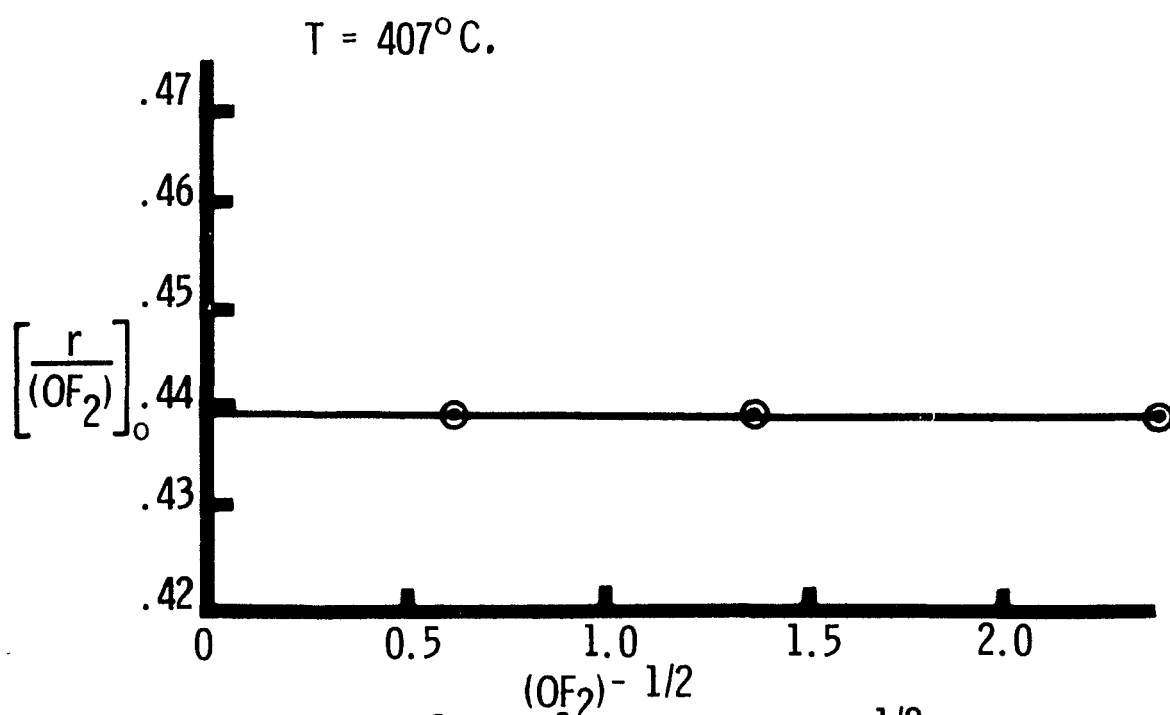
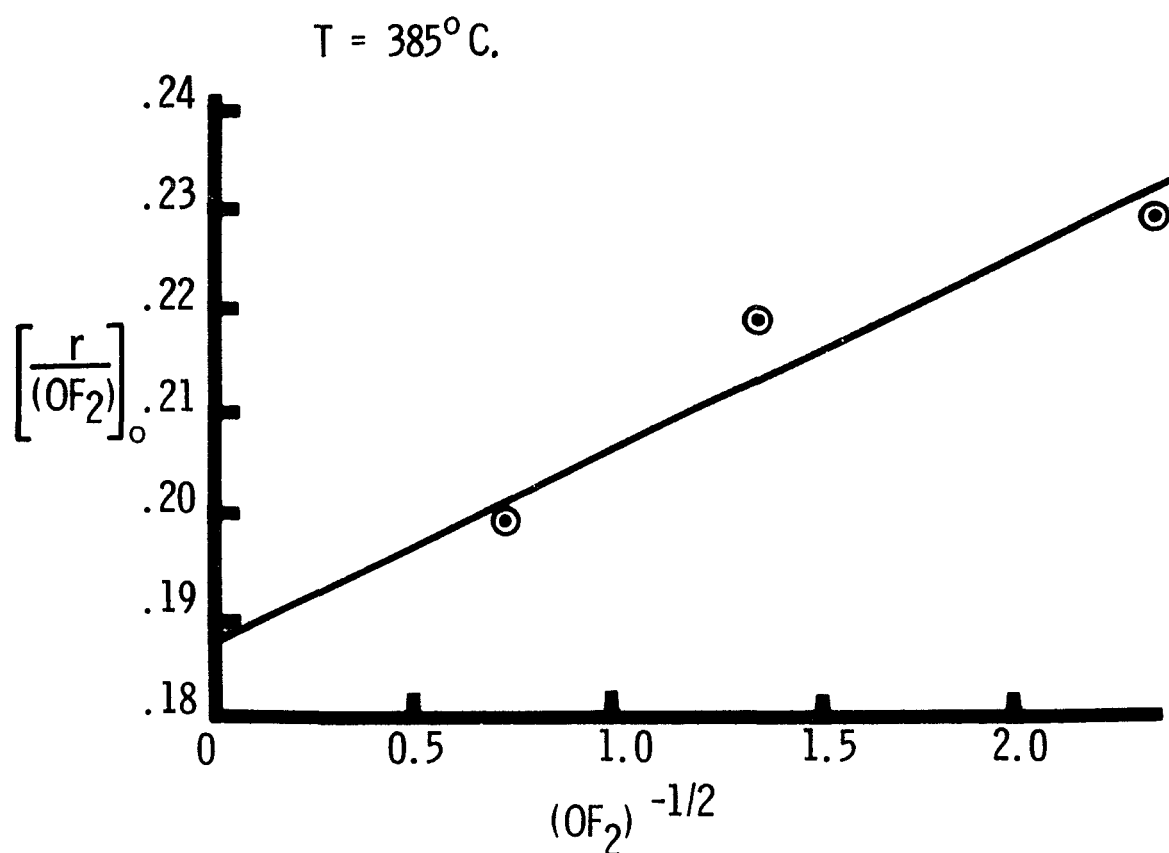


Figure 16.  $\left[\frac{r}{(\text{OF}_2)}\right]_0$  versus  $(\text{OF}_2)^{-1/2}$

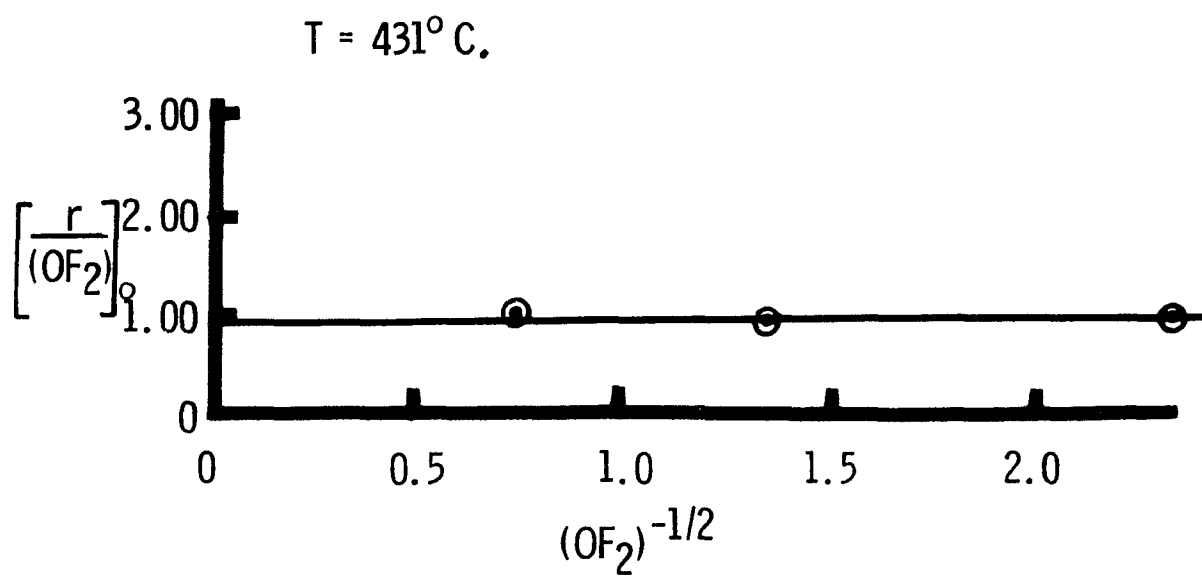


Figure 17.  $\left[\frac{r}{(\text{OF}_2)}\right]_0$  versus  $(\text{OF}_2)^{-1/2}$

Thus

$$r = k_{23}(M)(OF_2) + k_{24}(F)(OF_2) \quad (28)$$

A steady-state treatment of the radicals leads to

$$(F) = \frac{k_{23}(M)}{k_{24}} + \frac{k_{25}}{k_{24}} \left( \frac{k_{23}}{k_{26}} \right)^{\frac{1}{2}} \frac{M}{(OF_2)^{\frac{1}{2}}}$$

which on substitution into Eq. 28 gives

$$r = 2k_{23}(M)(OF_2) + k_{25} \left( \frac{k_{23}}{k_{26}} \right)^{\frac{1}{2}} (M)(OF_2)^{\frac{1}{2}} \quad (29)$$

Since (He) is very large compared to  $(OF_2)$ , the (M) value in Eq. 29 remains virtually constant. Eq. 29 is of the same form as Eq. 22, thus, the above mechanism accounts for the observed initial rate law. The third body, M, in Eq. 26 is required in order that the derived rate law, Eq. 29, be consistent with Schumacher's<sup>19</sup> observation that the total order (with respect to M and  $OF_2$ ) be less than 2. Note that the total order in the second term of Eq. 29 is  $\frac{3}{2}$ . Had M been excluded from Eq. 26 the order with respect to M in the second term of Eq. 29 would have been  $\frac{3}{2}$ , thus giving a total order of 2 for the second term.

Termination of the type shown in Eq. 26 of the above mechanism coupled with the propagation step in Eq. 25 is necessary to lead to an order less than 1. A commonly invoked propagation-termination sequence which always leads to orders of 1 or greater is as follows:



In summary, based on the current data, Eqs. 30 and 31 cannot be excluded from the overall reaction mechanism, and indeed it would be expected that they do contribute. However, the observation that the reaction is definitely less than first-order is a very strong indication that the contributions of Eqs. 25 and 26 are significant. A simple steady-state treatment involving all of the possible reaction steps, including fluorine inhibition (reverse of step 24), will not yield a rate equation that can be tested quantitatively, and as stated earlier, steady-state may not apply at the higher temperatures.

Temperature dependence: The rate constants for the first- and one-half-order terms were determined from the intercepts and slopes respectively of the  $[\text{r}/(\text{OF}_2)]_0$  versus  $(\text{OF}_2)_0^{-\frac{1}{2}}$  plots (Figures 15 through 17). These values are presented in Table I.

TABLE I  
Rate Constants

<u>T, °C.</u>	<u>k(first-order)</u> <u>sec.<sup>-1</sup></u>	<u>k''(one-half-order)</u> <u>mmoles<sup>-1/2</sup> l.<sup>-1/2</sup> sec.<sup>-1</sup></u>
330	0.016	0.019
360	0.075	0.019
385	0.188	0.019
407	0.440	0
431	1.000	0

Analysis of the Arrhenius plot for the first-order rate constant (Figure 18) gives the following expression:

$$k = 10^{10.5} \exp(-34,000 \pm 300^*) / RT(\text{sec}^{-1})$$

The apparent negative activation energy associated with the one-half-order rate constant may be the result of a shift in the reaction mechanism in which the relative importance of Eqs. 30 and 31 versus Eqs. 25 and 26 changes.

Uncertainties in the individual measurements and their effect on end results are given in Appendix F.

Nitrogen as carrier gas: Several series of experiments were carried out using nitrogen instead of helium as carrier gas. The rates determined under these conditions were indistinguishable from those which resulted from using helium. Thus, it may be concluded that the activating efficiencies of nitrogen and helium are about the same. This conclusion is in conflict with early results of Koblitz and Schumacher<sup>1</sup> where helium is reported to be only 40 per cent as efficient as nitrogen. Recent findings of Schumacher<sup>19</sup> indicate other inconsistencies in the previously reported activation efficiencies; it may therefore be reasonable to assume that the early results are unreliable.

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\*See Appendix F.

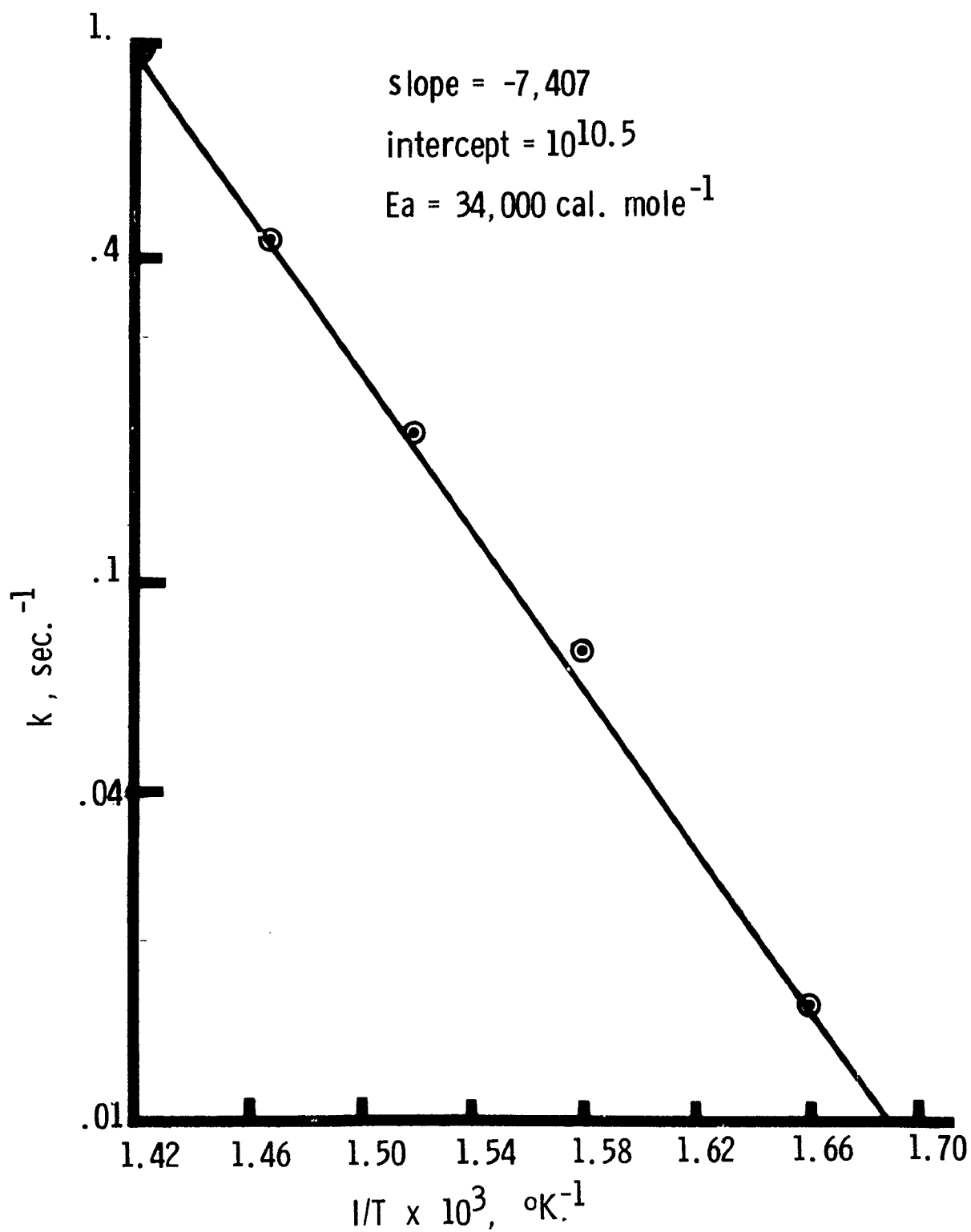


Figure 18. Arrhenius plot (first-order rate constants)

## Hydrogen-Oxygen Difluoride Reaction

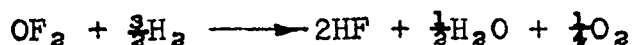
Reaction products and stoichiometry: The products of the hydrogen-oxygen difluoride reaction as found in this study are hydrogen fluoride, water, and oxygen. As previously stated in the experimental section, water and oxygen were detected and quantitatively determined mass spectrometrically. Hydrogen fluoride, which was expected as a product based on results of thermochemical studies<sup>22</sup>, was confirmed and determined using a wet technique\*. Previous non-kinetic studies<sup>14,22</sup> of this reaction indicate that hydrogen fluoride and water are the only major products. This discrepancy is probably due to the extreme differences in conditions (temperature and concentration) under which the reaction was previously studied. No mass spectrometric evidence for fluorine, hydrogen peroxide or other oxygen fluorides was found.

Quantitative mass spectrometric measurements of the concentrations of oxygen difluoride, hydrogen, water, and oxygen plus semi-quantitative measurements of the hydrogen fluoride concentration (by wet technique) plus determination of rates with respect to hydrogen provide ample support for the following stoichiometry for this reaction:

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\*Hydrogen fluoride could not be determined mass spectrometrically probably because of the formation of the gaseous species (HF)<sub>g</sub> coupled with its strong tendency to be adsorbed.





Pertinent details of the techniques used are reported in the experimental section, and the data which support the above conclusion are shown in Appendix G.

Kinetic results: Initial experiments were carried out at 110, 130, 150, 170, and 190°C. and at the following concentrations of reactants:

<u>mole % OF<sub>2</sub></u>	<u>mole % H<sub>2</sub></u>
1	5
0.5	5
0.5	1
1	2
1	1

The data obtained from experiments carried out at 110°C. were not used in the analytical treatments since the extents of reaction were so low that abnormally large uncertainties would have resulted. Attempts were made to employ higher concentrations, i.e., 2 mole per cent oxygen difluoride and 4 mole per cent hydrogen; however, the reaction went to completion under these conditions probably because of thermal acceleration which resulted from the reaction's high exothermicity, i.e., non-isothermal conditions prevailed. The data resulting from these experiments are shown in Appendix O. Figure 19 shows the relationships between per cent reaction and time. The general shape of the curve is typical of those resulting from all of the experiments described above.

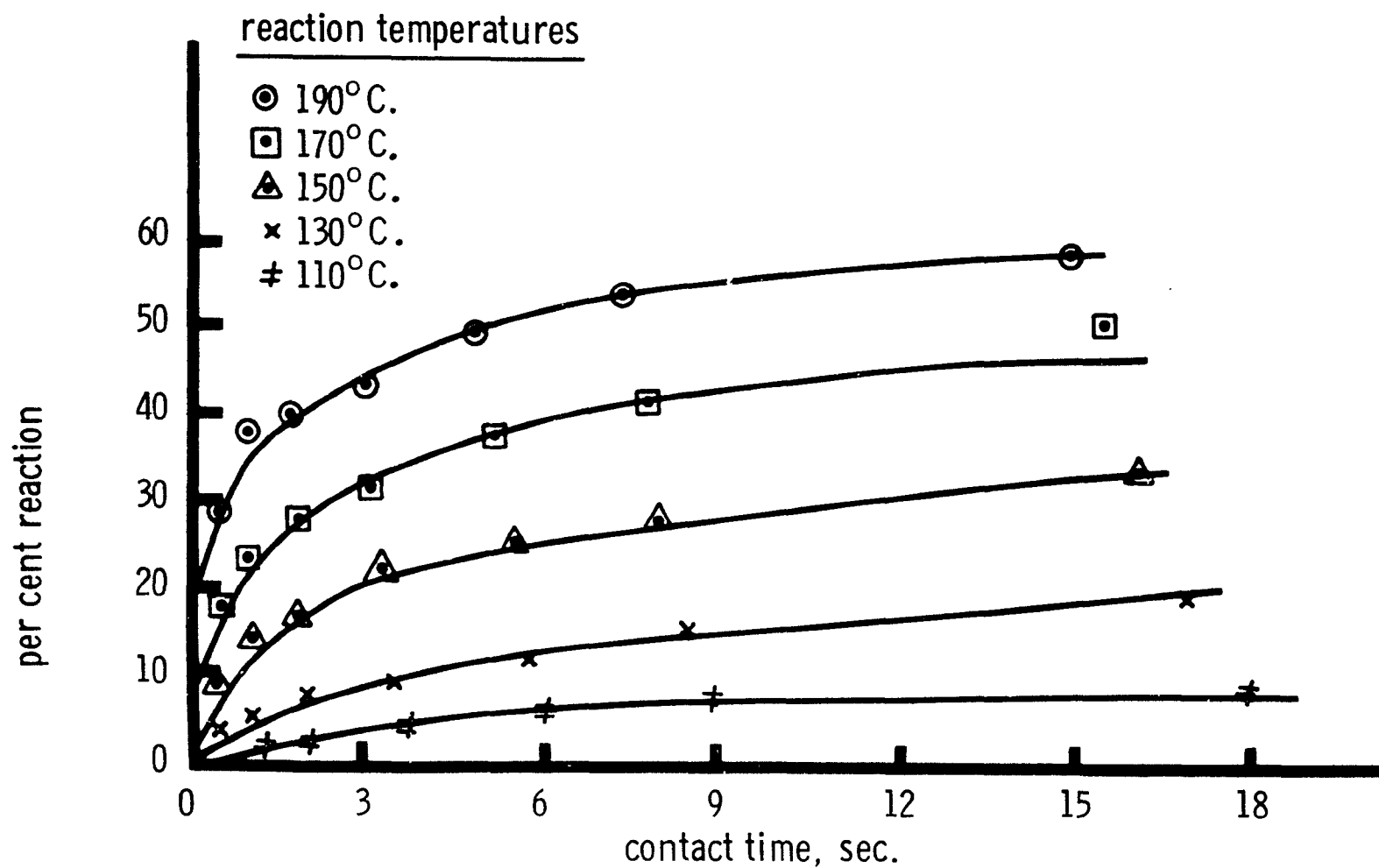


Figure 19. Per cent reaction versus contact time at 110, 130, 150, 170, and 190°C. -runs 90 through 123

The rapidity with which the per cent reaction levels off with time is indicative of inhibition by product(s).

Initial concentrations of the 3 major products of this reaction were added to the reaction mixture to test their effect on the rate. Water was added by passing the hydrogen-helium stream over a crushed ice bath which gave a concentration of 0.3 mole per cent water in the reactor (saturation assumed). The added water had no apparent effect on the rate. Hydrogen fluoride was added to the oxygen difluoride storage tank to give an initial concentration of 0.8 mole per cent in the reactor. Again this product had no observable effect on the rate. Oxygen was added to the oxygen difluoride storage tank to give an initial concentration of 0.8 mole per cent in the reactor. This product acted strongly to inhibit the reaction. The data obtained from the product addition studies are shown in Appendix H.

Several experiments were performed to test for reaction of hydrogen with the added oxygen. At 190°C. no hydrogen-oxygen reaction was found.

To explore the oxygen concentration dependence of this reaction, 2 and 5 mole per cent oxygen was added to reaction mixtures consisting of 1 mole per cent oxygen difluoride and 5 mole per cent hydrogen. It was discovered that 5 per cent oxygen inhibited the reaction only slightly more than did

the 2 per cent concentration of oxygen. Therefore, it was concluded that oxygen concentrations greater than 5 per cent would not significantly further inhibit the reaction; thus, 5 per cent oxygen may be considered to effect full or limiting inhibition. Data supporting this conclusion are shown in Appendix I.

Under conditions of full inhibition and with the hydrogen concentration such that its concentration did not significantly change over the course of the reaction (1%  $\text{OF}_2$  - 5%  $\text{H}_2$  - 5%  $\text{O}_2$  and 0.5%  $\text{OF}_2$  - 5%  $\text{H}_2$  - 5%  $\text{O}_2$ ) the order with respect to oxygen difluoride was determined at 190 and 220°C. The results of these experiments are shown in Figure 20 and in Appendix J. From the slope of the log-log plot it is obvious that under full inhibition the order with respect to oxygen difluoride is approximately 1.

The order with respect to hydrogen under conditions of full inhibition was elucidated by varying the hydrogen concentration while leaving the oxygen difluoride and oxygen initial concentrations unchanged (1%  $\text{OF}_2$  - 5%  $\text{H}_2$  - 5%  $\text{O}_2$  and 1%  $\text{OF}_2$  - 2%  $\text{H}_2$  - 5%  $\text{O}_2$ ). Experiments were run at 190 and 220°C., and  $r^*/(\text{OF}_2)$  values were calculated and are presented in Appendix K. The ratios of the  $r/(\text{OF}_2)$  values

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\*This rate is with respect to oxygen difluoride.

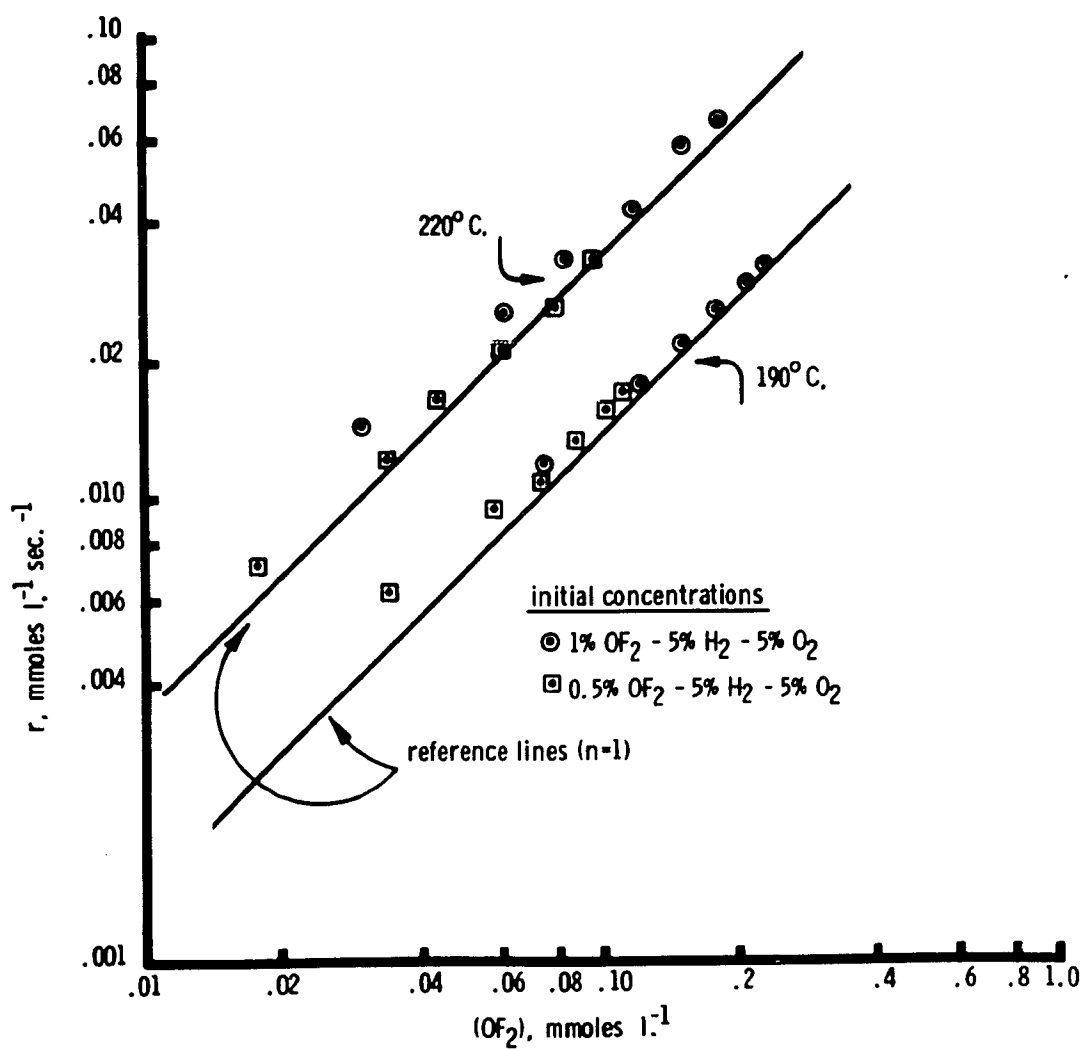


Figure 20.  $\log r$  versus  $\log (\text{OF}_2)$  at 190 and 220°C. for the fully inhibited reaction

at 5 per cent hydrogen to those at 2 per cent hydrogen averaged about 1.32 at both temperatures (this ratio would have been 1.58 for one-half-order hydrogen dependence). Therefore, the fully inhibited reaction has an apparent hydrogen dependence of about 0.3 order. The hydrogen dependency with respect to time appears to be zero-order, i.e., the  $r/(OF_2)$  values show no consistent trends with time.

This reaction was tested for heterogeneity by stuffing the reactor with helices formed from monel wire as described in the previous section. The result was to increase the reactor's surface area by 2.5 times while only slightly reducing its volume. Several series of experiments were performed with and without the reactor stuffing and with and without a 5 per cent initial concentration of oxygen. The results are shown in Figures 21 and 22 and the supporting data are reported in Appendix L. It can be seen that this reaction has a significant heterogeneous component and that this constitutes a greater proportion of the rate when the oxygen concentration is high. Thus, it appears that the component of the rate which does not strongly depend on the oxygen concentration does contain the heterogeneous part of the rate. Or, in other words, the oxygen dependent part of the rate appears to be homogeneous.

The hydrogen dependence of the rate of the fully inhibited reaction was further studied with the reactor stuffed so as to determine the effect of increased heterogeneity on

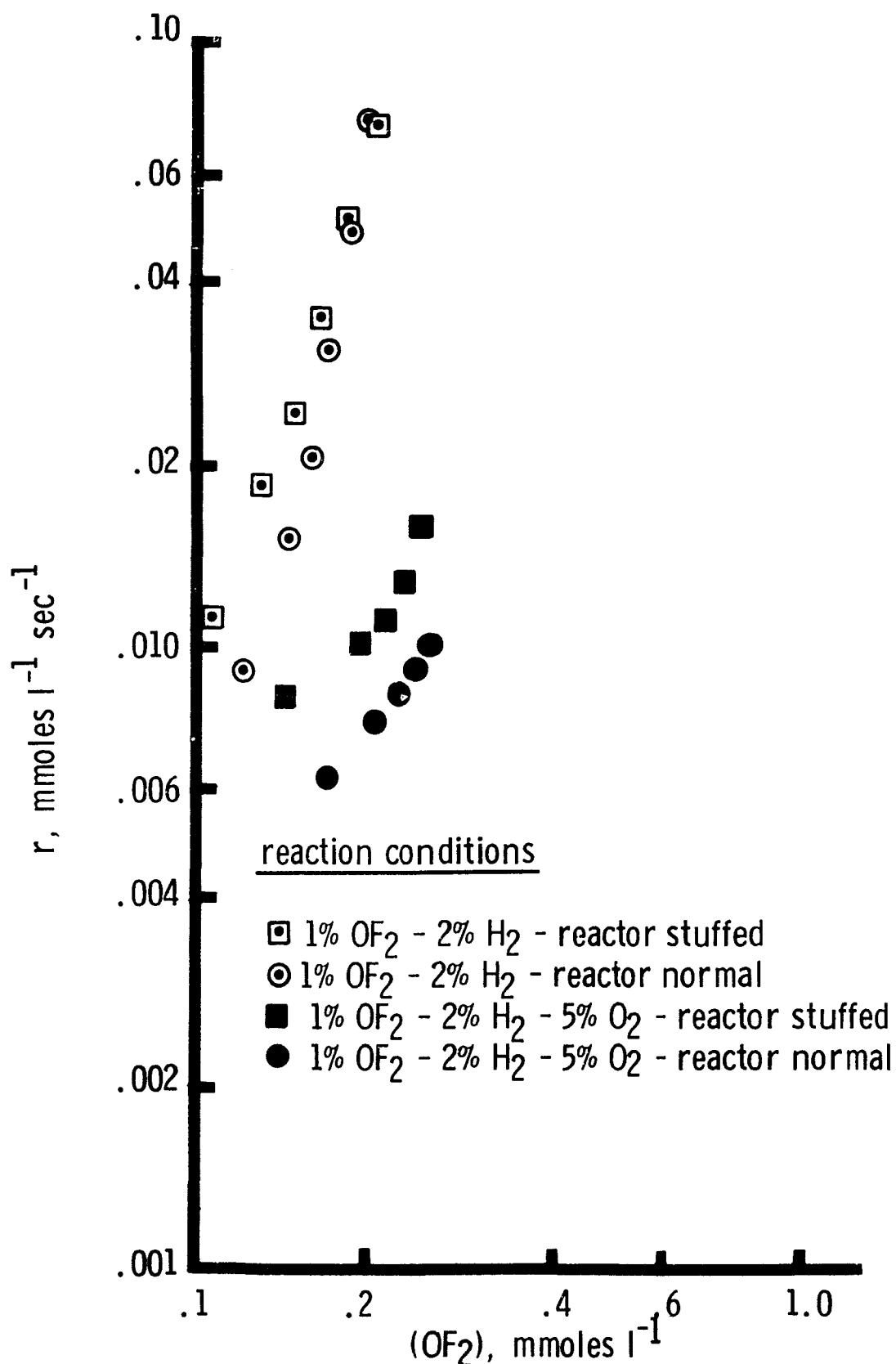


Figure 21. Log  $r$  versus log (OF<sub>2</sub>) at 170°C.  
showing heterogeneous effects

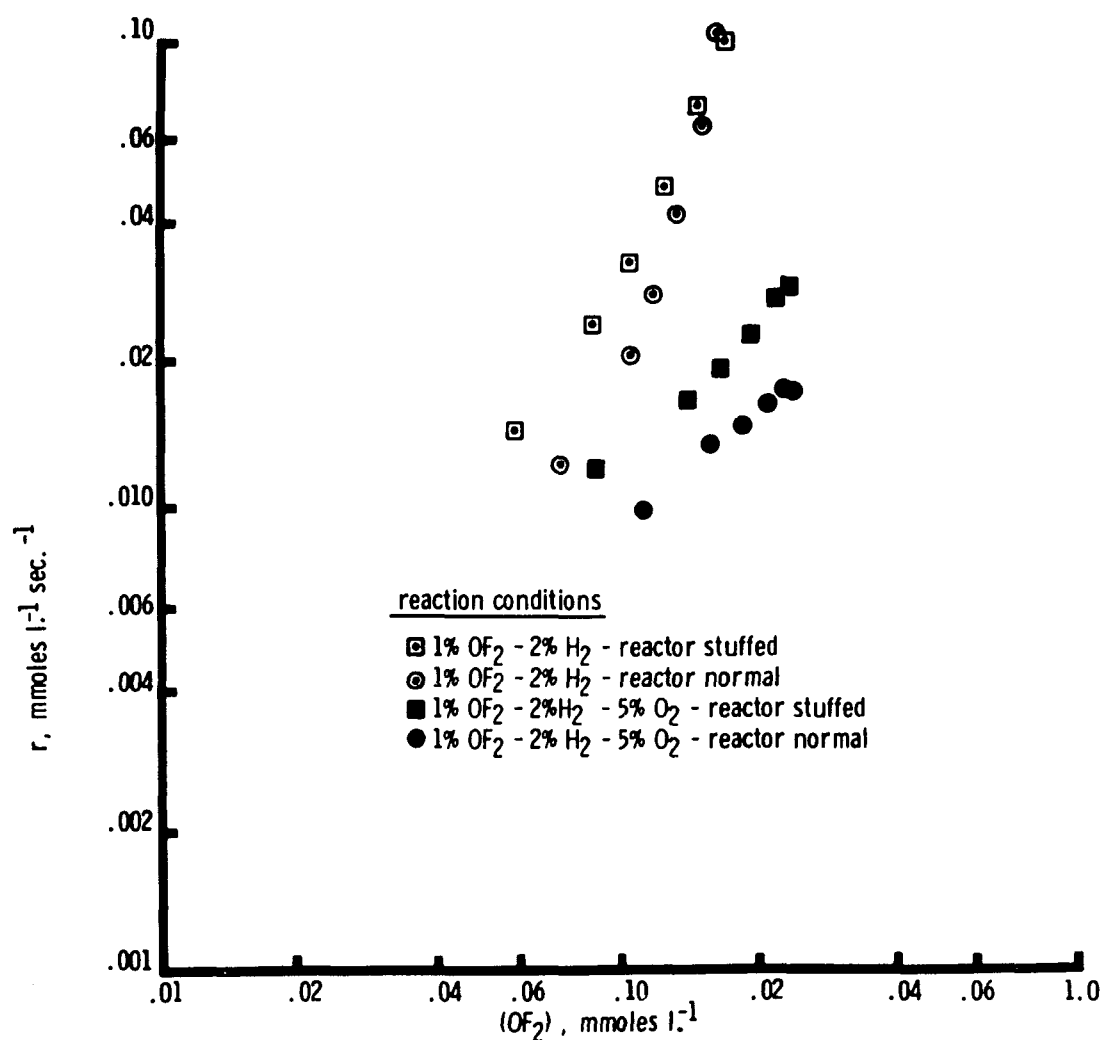


Figure 22. Log  $r$  versus log  $(\text{OF}_2)$  at  $190^\circ\text{C}$ , showing heterogeneous effects



the order with respect to hydrogen. The initial concentration of hydrogen was varied as before (1%  $\text{OF}_2$  - 5%  $\text{H}_2$  - 5%  $\text{O}_2$  and 1%  $\text{OF}_2$  - 2%  $\text{H}_2$  - 5%  $\text{O}_2$ ), and experiments were carried out at 190 and 220°C. The average value of the ratio of  $r/(\text{OF}_2)$  at 5 per cent to that at 2 per cent hydrogen was 1.17 which corresponds to a hydrogen order of 0.17 for the fully inhibited reaction (this is to be compared with a hydrogen order of 0.3 for the unstuffed reactor). From these experiments it may be concluded that the order with respect to hydrogen of the fully inhibited reaction decreases with increasing heterogeneity. Data arising from the above described experiments are reported in Appendix M.

The above observation suggests the possibility that there are two terms in the rate law for the fully inhibited reaction. One term may correspond to the heterogeneous component and be zero-order in hydrogen while the other term, the homogeneous one, may have significant hydrogen dependence, i.e., one-half or first-order. A heterogeneous term which is zero-order in hydrogen would be expected to arise if the surface reaction sites were saturated with hydrogen. Since the oxygen difluoride dependence for the stuffed and unstuffed reactor appears to be first-order as seen in Figures 21 and 22 it is suggested that both terms for the fully inhibited reaction are first-order in oxygen difluoride. Thus, for the fully inhibited reaction, a rate law of the following form is proposed:

$$r = k_a(\text{OF}_2) + k_b(\text{OF}_2)(\text{H}_2)^m \quad (32)$$

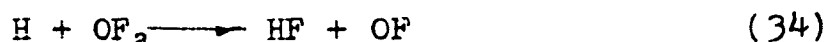
where  $m = \frac{1}{2}$  or 1

To elucidate the portion of the rate law which is highly oxygen dependent, experiments were conducted with intermediate concentrations of oxygen to produce corresponding levels of inhibition. To mixtures of 1 per cent oxygen difluoride and 2 and 5 per cent hydrogen, 0, .05, 0.1, and 0.2 per cent oxygen concentrations were added. The resulting data are reported in Appendix N.

It is believed that the oxygen dependent part of the rate law is of the following form:

$$\frac{k_c(\text{OF}_2)^p(\text{H}_2)^s}{1 + b(\text{O}_2)^q/(\text{OF}_2)}$$

A term of the above form with the oxygen concentration in the denominator qualitatively accounts for the observed inhibition. The ratio of  $(\text{O}_2)/(\text{OF}_2)$  arises because of the competition which is believed to occur between oxygen and oxygen difluoride for hydrogen atoms in the following steps:



The reaction depicted in Eq. 33, which has been previously invoked for the hydrogen-fluorine reaction<sup>23</sup>, probably accounts for the inhibition. Hydrogen atoms consumed in this

way cannot contribute to the rate by reacting with oxygen difluoride in the highly exothermic reaction represented by Eq. 34. Thus, the following seems to be a reasonable form for the total rate law:

$$r = k_a(\text{OF}_2) + k_b(\text{OF}_2)(\text{H}_2)^m + \frac{k_c(\text{OF}_2)^p(\text{H}_2)^s}{1 + b(\text{O}_2)^q/(\text{OF}_2)} \quad (35)$$

If the second term is small compared to the other terms and if the 1 in the denominator of the third term is assumed small compared to  $b(\text{O}_2)^q/(\text{OF}_2)$ , then Eq. 35 can be tested analytically with the experimental data. Dividing both sides of Eq. 35 by  $(\text{OF}_2)$ ,  $r/(\text{OF}_2)$  may be plotted versus various forms of  $\frac{k_c(\text{OF}_2)^p(\text{H}_2)^s}{b(\text{O}_2)^q}$ , i.e., with various combinations of values of  $q$ ,  $p$ , and  $s$ .

The following variations of the proposed rate law, Eq. 35, were tested analytically with the basic kinetic data found in Appendix O at 170 and 190°C.:

<u>form:</u>	<u>q</u>	<u>p</u>	<u>s</u>
a)	1	1	1
b)	1	1	$\frac{1}{2}$
c)	2	1	$\frac{1}{2}$
d)	2	1	1
e)	2	2	$\frac{1}{2}$
f)	2	2	1

It was graphically shown that forms a) and b) unified the data with respect to differences in initial concentrations of oxygen difluoride and hydrogen significantly better than forms c) through f). Plots corresponding to forms a) and b) at

130, 150, 170, and 190°C. are shown in Figures 23 through 26 and 27 through 30 respectively. From these plots it is to be noted that form a) generally resulted in less curvature than form b); however, form b) unified the data with respect to changes in initial concentrations of hydrogen better than did form a). Unification of the data was relatively poor at 190°C. for both forms a) and b). Values of  $q$  and  $p$  other than 1 resulted in significant disunification of the data; therefore,  $q = p = 1$  is fairly well established. The curvature in these plots may have arisen from variations in the oxygen production rate.

Figures 31 and 32 show analytical treatments corresponding to forms a) and b) respectively for experiments carried out with intermediate initial concentrations of oxygen at 170°C. These data are reported in Appendix N. It is to be noted that form a) resulted in a greater amount of scatter than form b); however, form b), as before, produced more curvature than form a). The slopes of these plots were comparable to those at 170°C. for which there was no initial concentration of oxygen.

At this point it does not seem feasible to assign a unique rate law to this reaction, and therefore forms a) and b) must be considered equally satisfactory.

The intercepts from Figures 23 through 32 in theory correspond to the sum  $[k_a + k_b(H_2)^m]$  which, to a first approximation, is a constant. Thus, the values of these intercepts

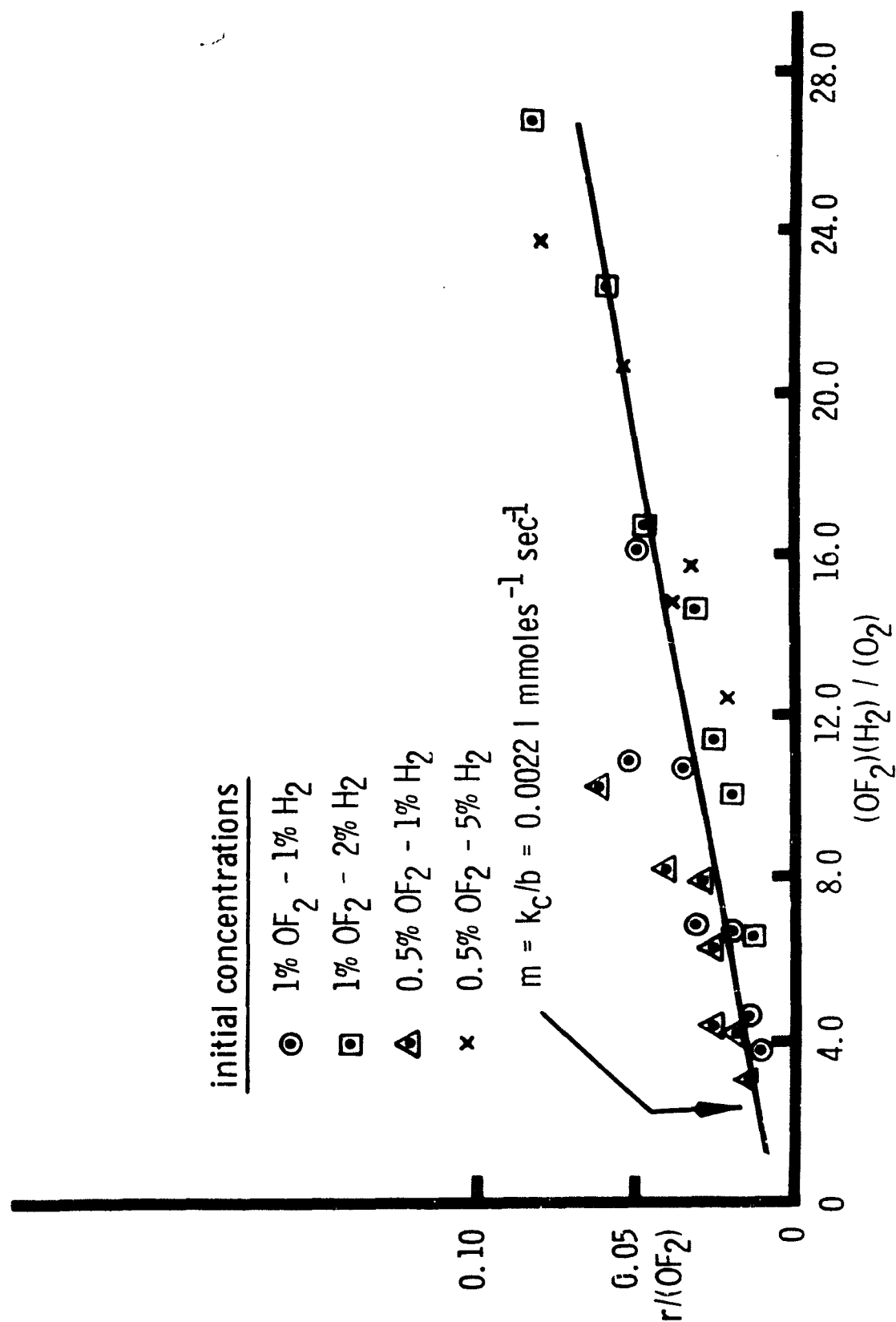


Figure 23  $r/(OF_2)$  versus  $(OF_2)(H_2) / (O_2)$  at 130°C.

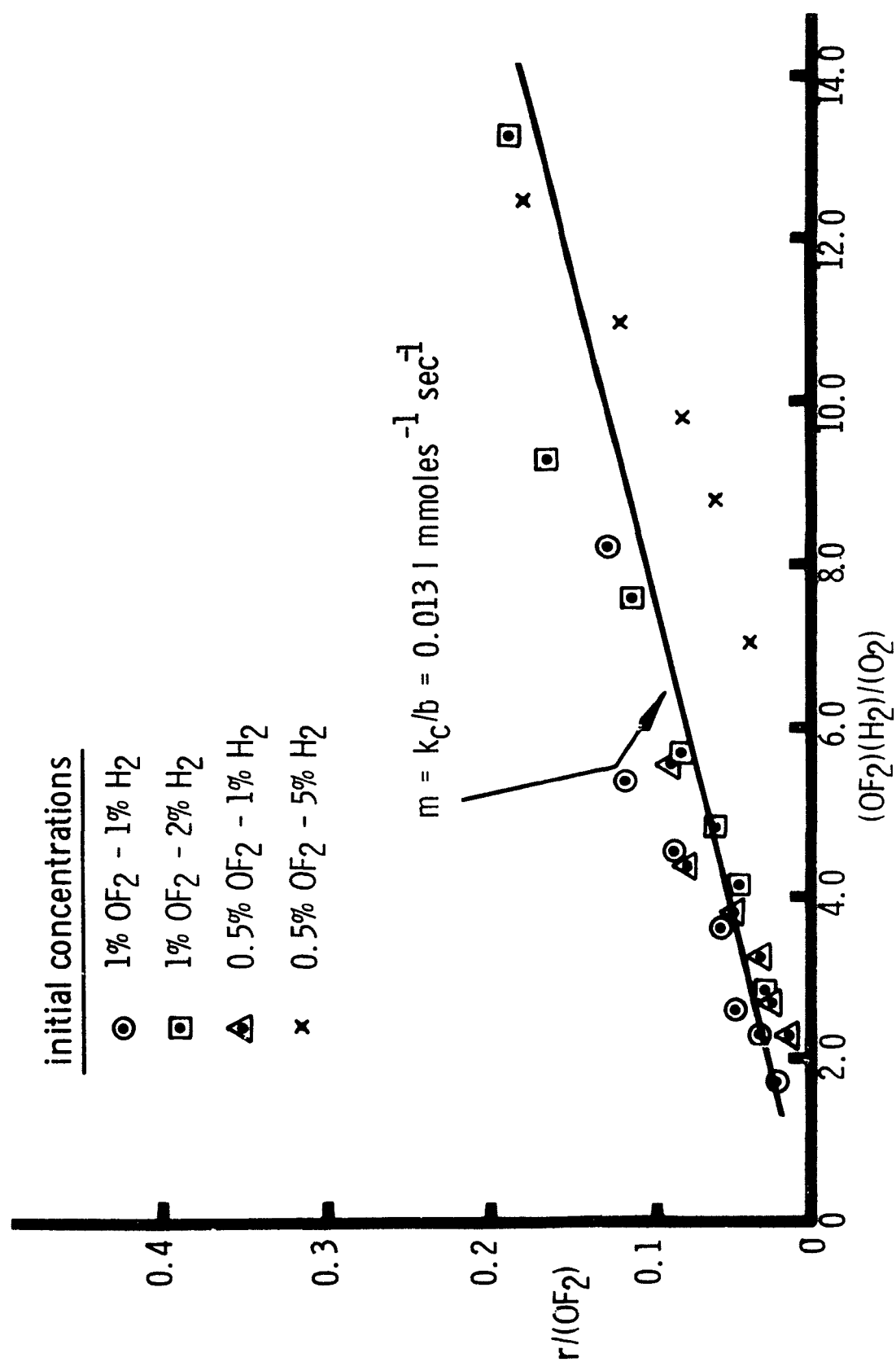


Figure 24  $r/(OF_2)$  versus  $(OF_2)(H_2)/(O_2)$  at 150°C.

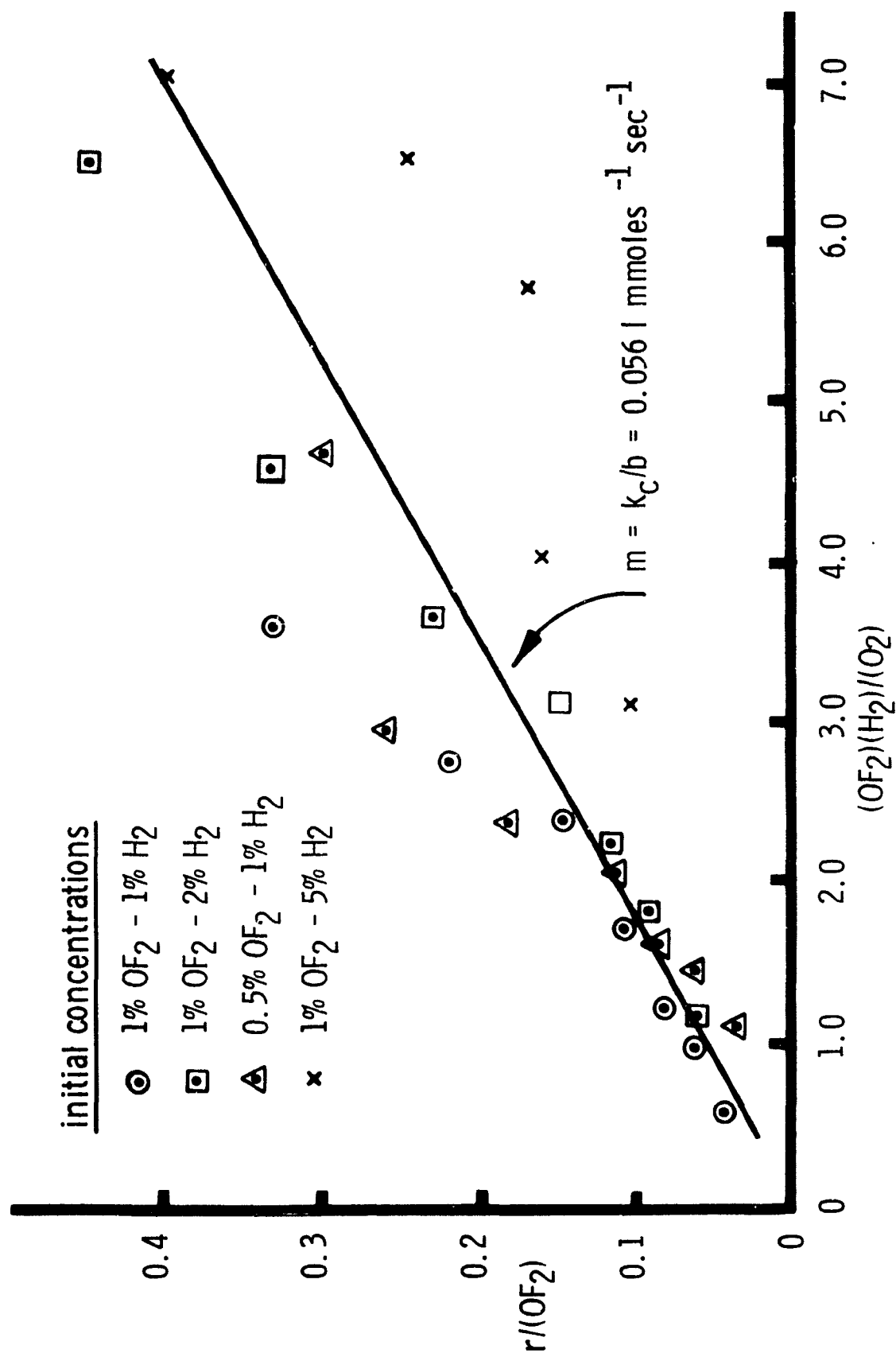


Figure 25.  $r/(OF_2)$  versus  $(OF_2)(H_2)/(O_2)$  at 170°C.

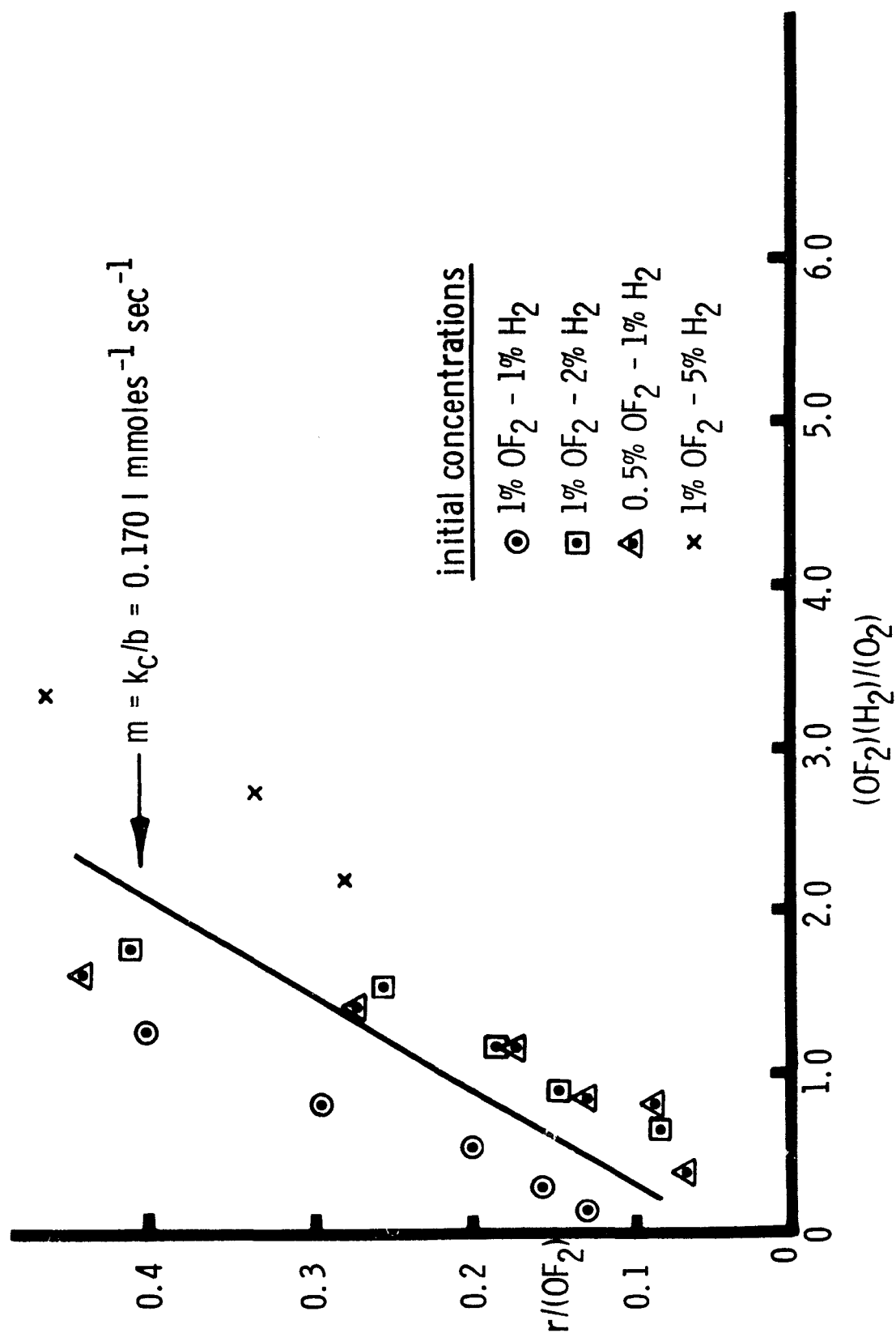


Figure 26  $r/(OF_2)$  versus  $(OF_2)(H_2)/(O_2)$  at 190°C.



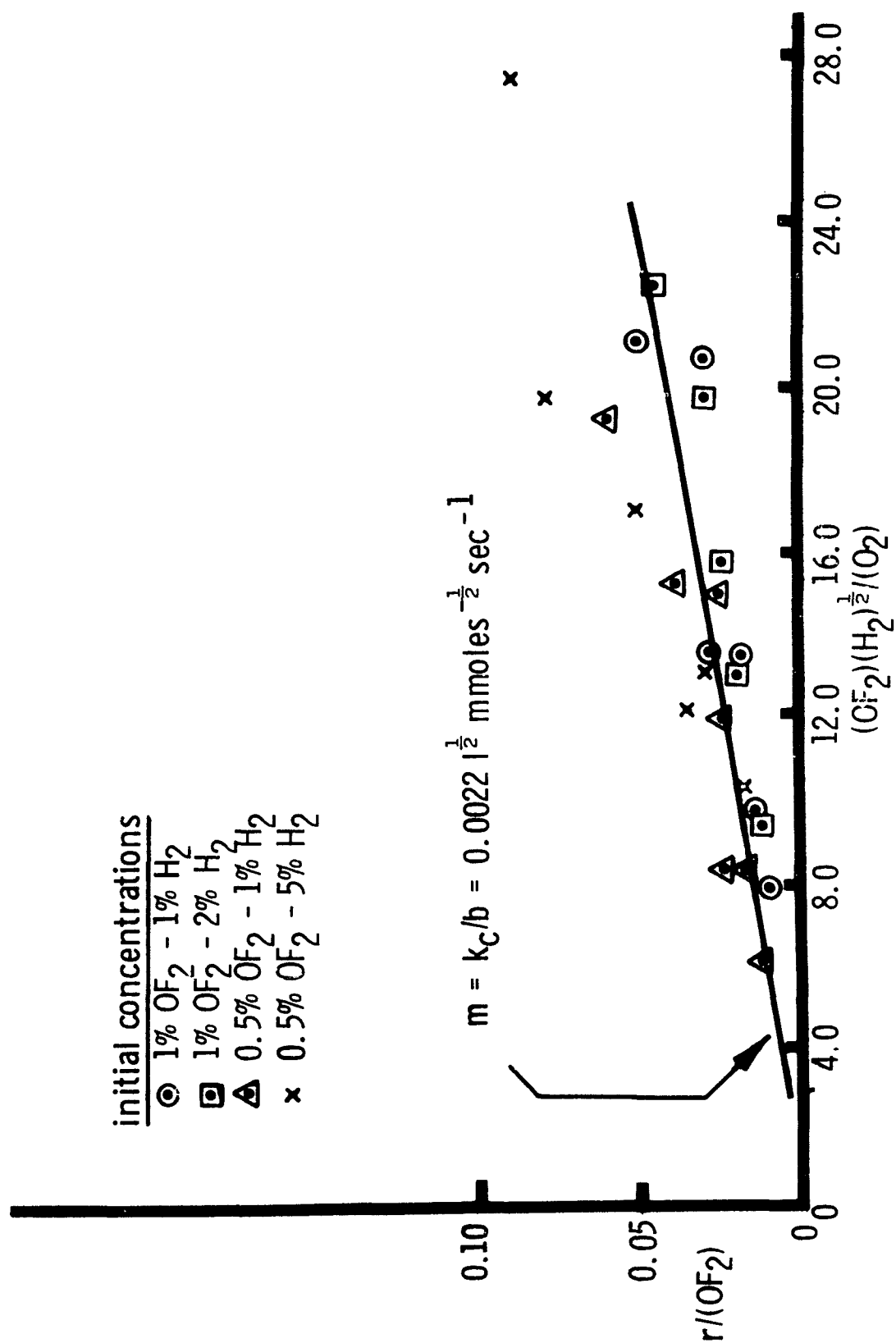


Figure 27  $r/(OF_2)$  versus  $(OF_2)(H_2)^{\frac{1}{2}}/(O_2)^{\frac{1}{2}}$  at 130°C.

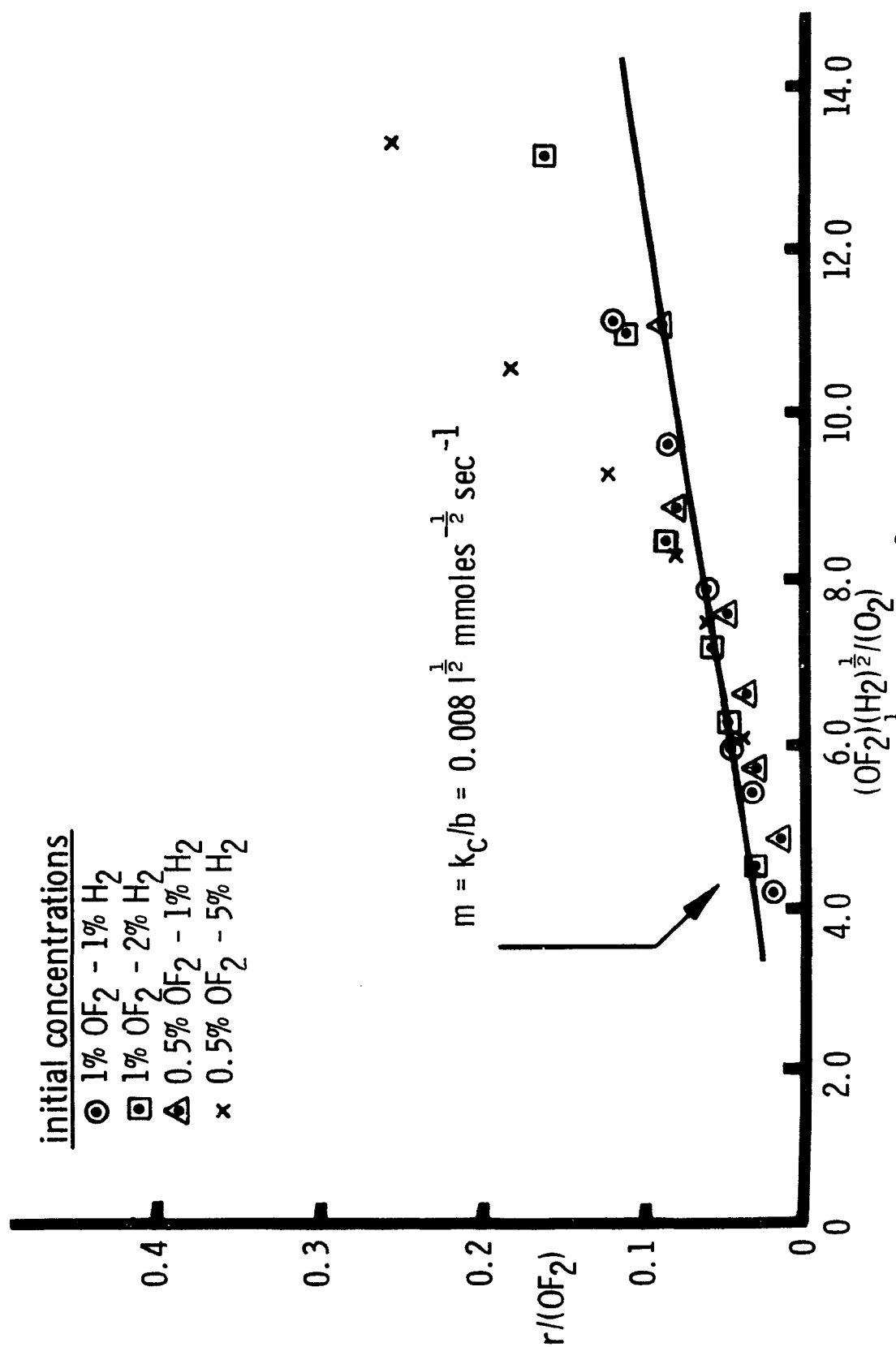


Figure 28  $r/(\text{OF}_2)$  versus  $(\text{OF}_2)(\text{H}_2)^{\frac{1}{2}}/(\text{O}_2)^{\frac{1}{2}}$  at 150°C.

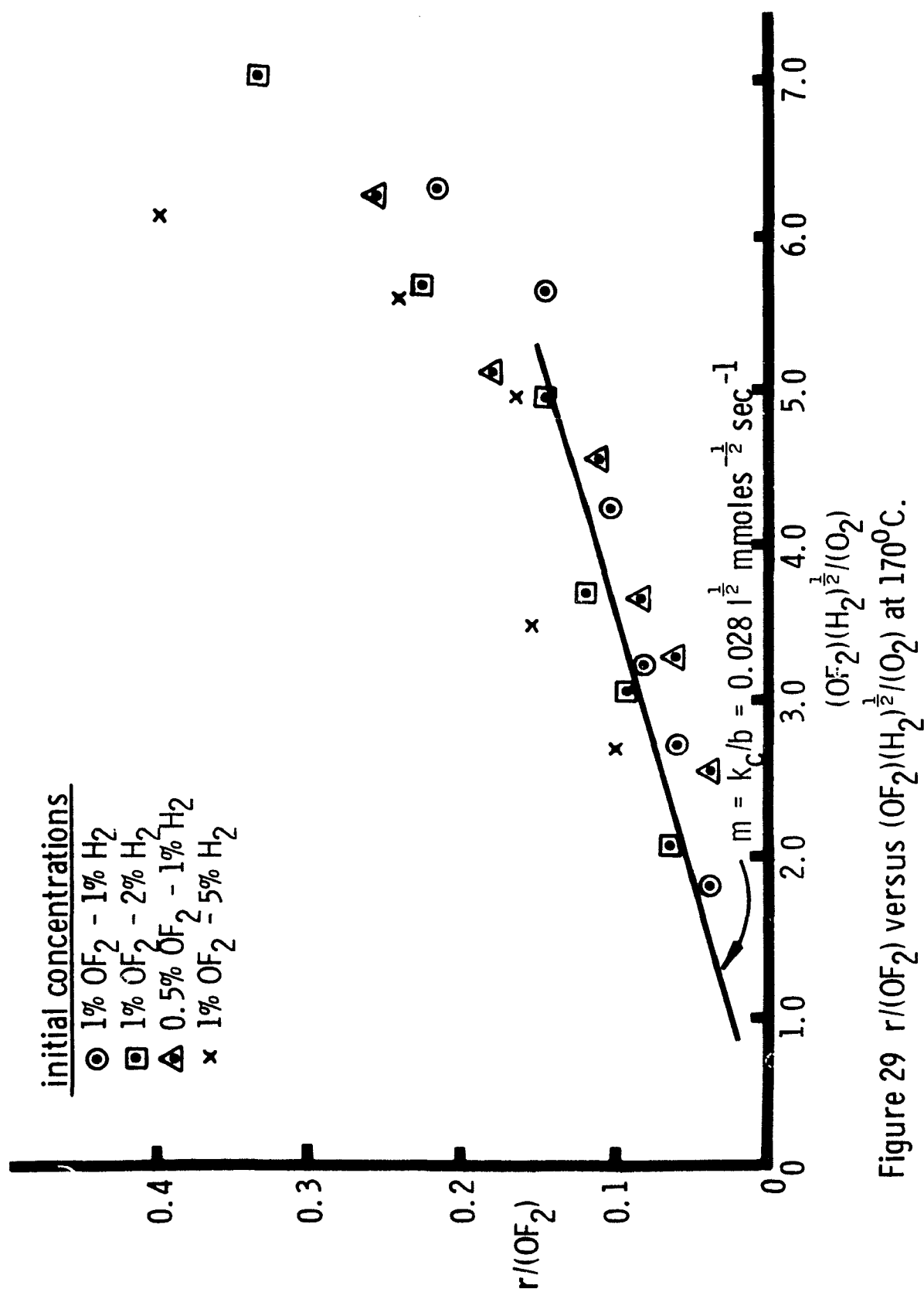


Figure 29  $r/(\text{OF}_2)$  versus  $(\text{OF}_2)(\text{H}_2)^{\frac{1}{2}}/(\text{O}_2)^{\frac{1}{2}}$  at 170°C.

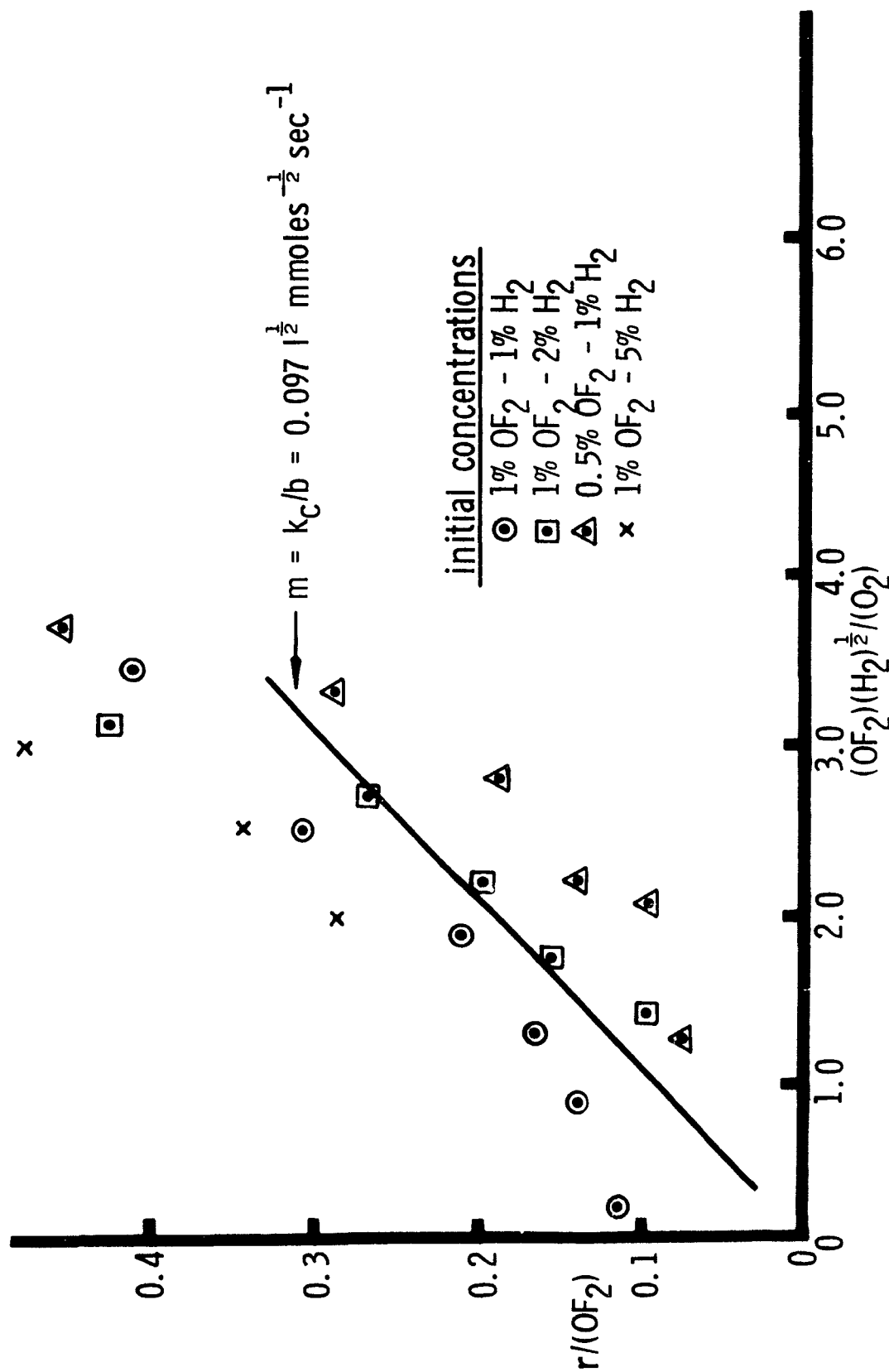


Figure 30  $r/(OF_2)$  versus  $(OF_2)(H_2)^{\frac{1}{2}}/(O_2)^{\frac{1}{2}}$  at 190°C.

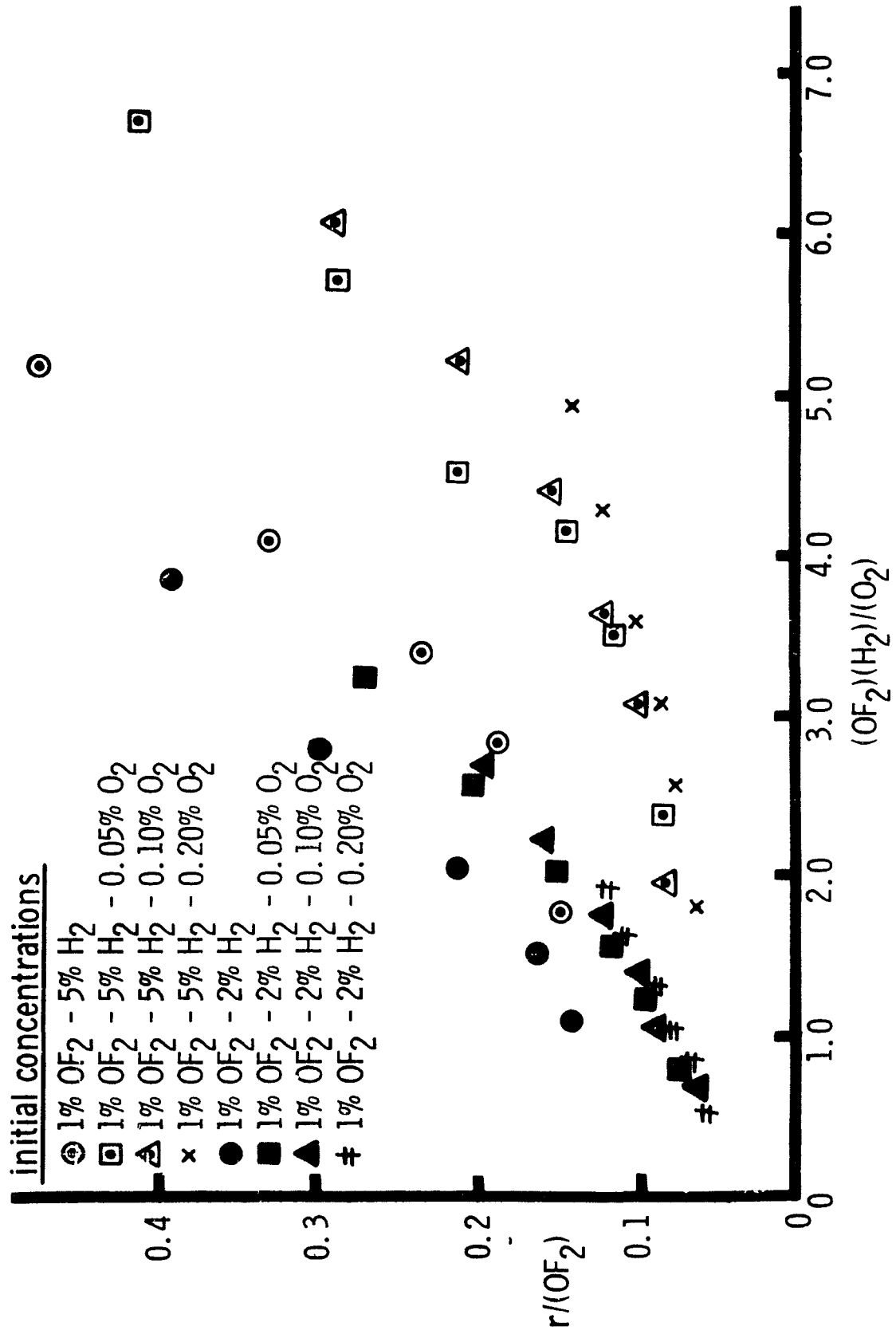
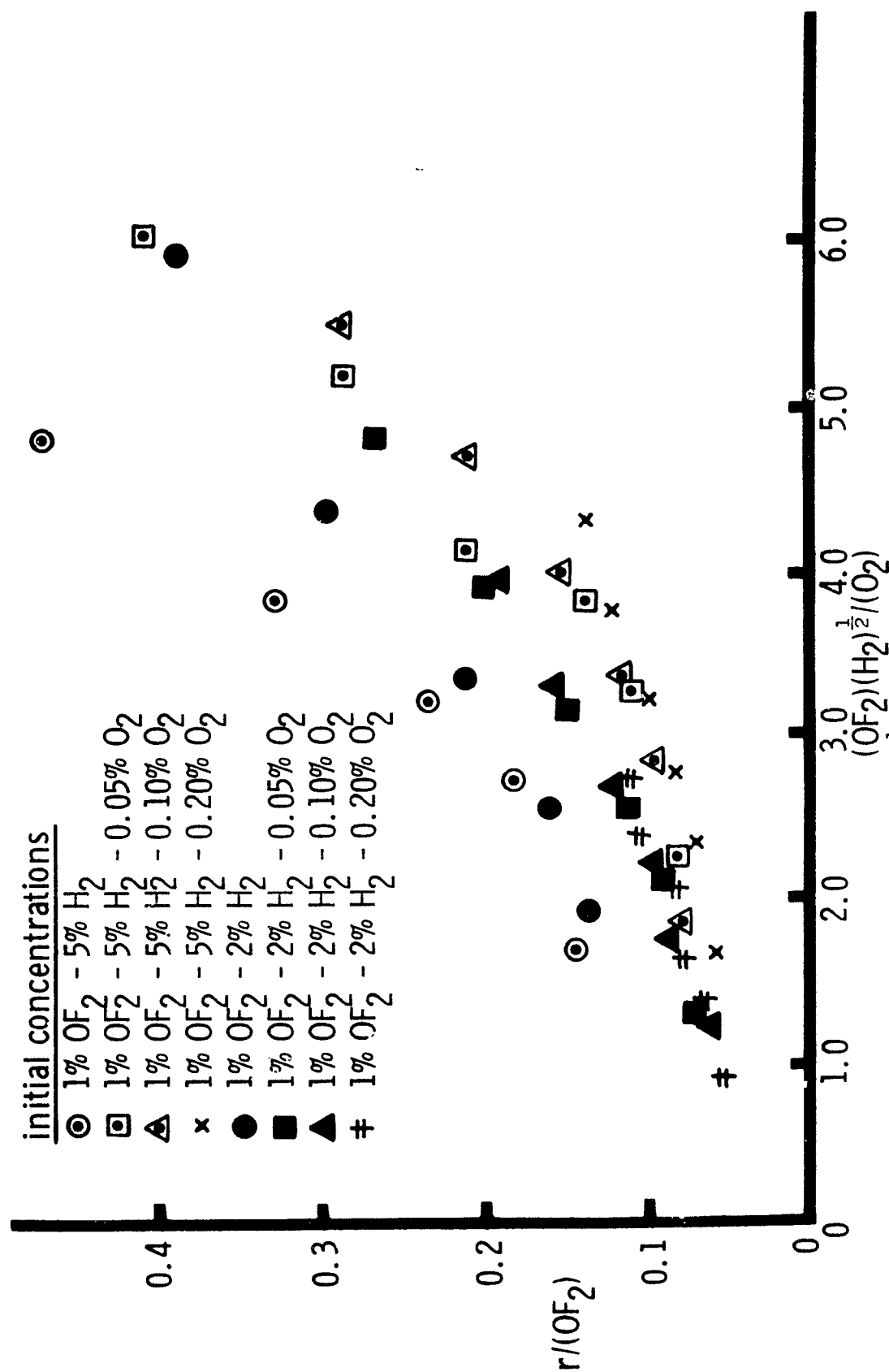


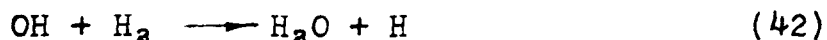
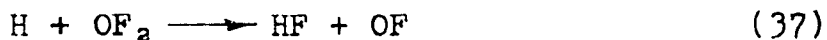
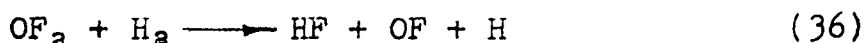
Figure 31  $r/(OF_2)$  versus  $(OF_2)(H_2)/(O_2)$  at 170°C.



should be equal to the  $r/(OF_2)$  values found in Appendix I for the fully inhibited reaction at corresponding temperatures. In all cases the values of the intercepts are significantly lower than the corresponding  $r/(OF_2)$ . No explanation for this lack of agreement is immediately apparent.

Reaction mechanism: Since a unique rate law for this reaction is not known and since this reaction has a significant heterogeneous component, it is not feasible at this point to assign a mechanism to this reaction which is totally satisfactory.

A mechanism which accounts for the observed products, the observed inhibition by oxygen, and which leads to one of the approximations to the observed rate law, i.e., the homogeneous part of form a) of Eq. 35 is as follows:



Thus

$$r = k_{36}(OF_2)(H_2) + k_{37}(H)(OF_2) \quad (43)$$

A steady-state treatment of the F, H, OF, and OH radicals leads to

$$(H) = \frac{2k_{36}(OF_2)(H_2)}{k_{38}(M)(O_2)}$$

which, on substitution into Eq. 43, gives

$$r = k_{36}(OF_2)(H_2) + \frac{2k_{36}k_{37}(OF_2)^2(H_2)}{k_{38}(M)(O_2)}$$

which may be written as

$$r = k_{36}(OF_2)(H_2) + \frac{2k_{36}k_{37}(OF_2)(H_2)}{k_{38}(M)(O_2)/(OF_2)} \quad (44)$$

to be consistent with the form of Eq. 35. The mechanism which has been presented contains no termination steps; therefore, the derived rate law, Eq. 44, implies that the rate is infinite initially when the oxygen concentration is close to zero. The inclusion of termination steps leads to complexities which cannot be dealt with using ordinary techniques. This mechanism does not account for the heterogeneous component of the reaction; however, it is felt that there may be some radical termination at the walls.

The initiation step, Eq. 36, seems valid since neither oxygen difluoride nor hydrogen undergo significant thermal dissociation in the temperature range over which this reaction was studied. As mentioned earlier, the combination of the reactions represented by Eqs. 37 and 38 account for the



observed inhibition by oxygen. With the exception of the initiation step, Eq. 36, all of the steps in the suggested mechanism are substantially exothermic.

Temperature dependence: The slopes of the points in Figures 23 through 26 and 27 through 30 were determined<sup>\*</sup>; these values correspond to  $k_c/b$  and are presented in Table II.

TABLE II

Rate Constants for the Stoichiometric Reaction

form a):

<u>T, °C.</u>	<u><math>k_c/b</math>, l. mmoles<sup>-1</sup> sec.<sup>-1</sup></u>
130	0.0022
150	0.013
170	0.056
190	0.170

form b):

<u>T, °C.</u>	<u><math>k_c/b</math>, l.<sup>1/2</sup> mmoles<sup>-1/2</sup> sec.<sup>-1</sup></u>
130	0.0022
150	0.008
170	0.028
190	0.097

Figures 33 and 34 are Arrhenius plots of  $k_c/b$  for forms a) and b) of the rate law respectively. Expressions for the combined rate constants,  $k_c/b$ , are as follows:

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<sup>\*</sup>In some cases it was necessary to heavily weight the point (0,0) to avoid having negative intercepts.

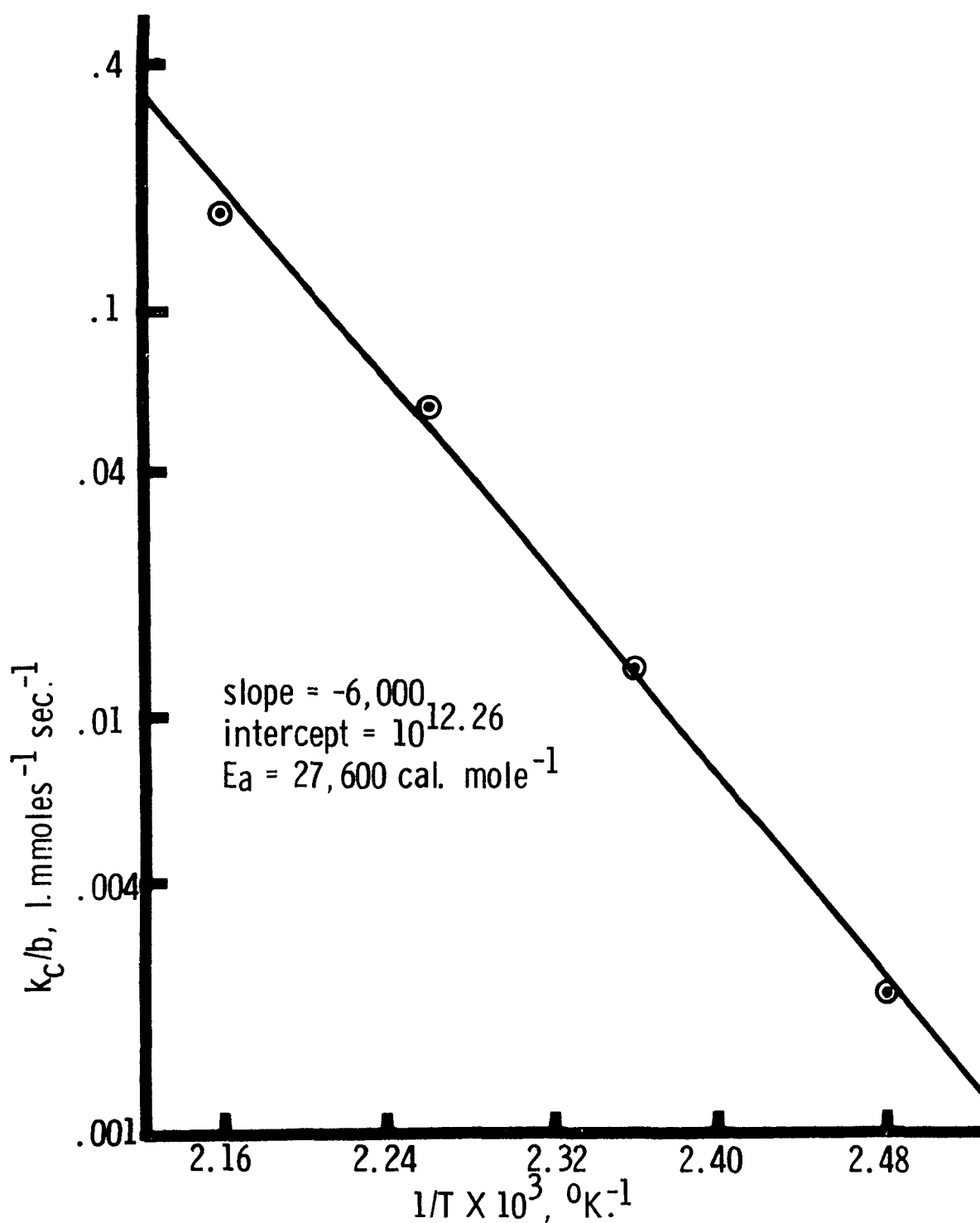


Figure 33 Arrhenius plot for  $(\text{OF}_2)(\text{H}_2)/(\text{O}_2)$  treatment - see figures 23 through 26

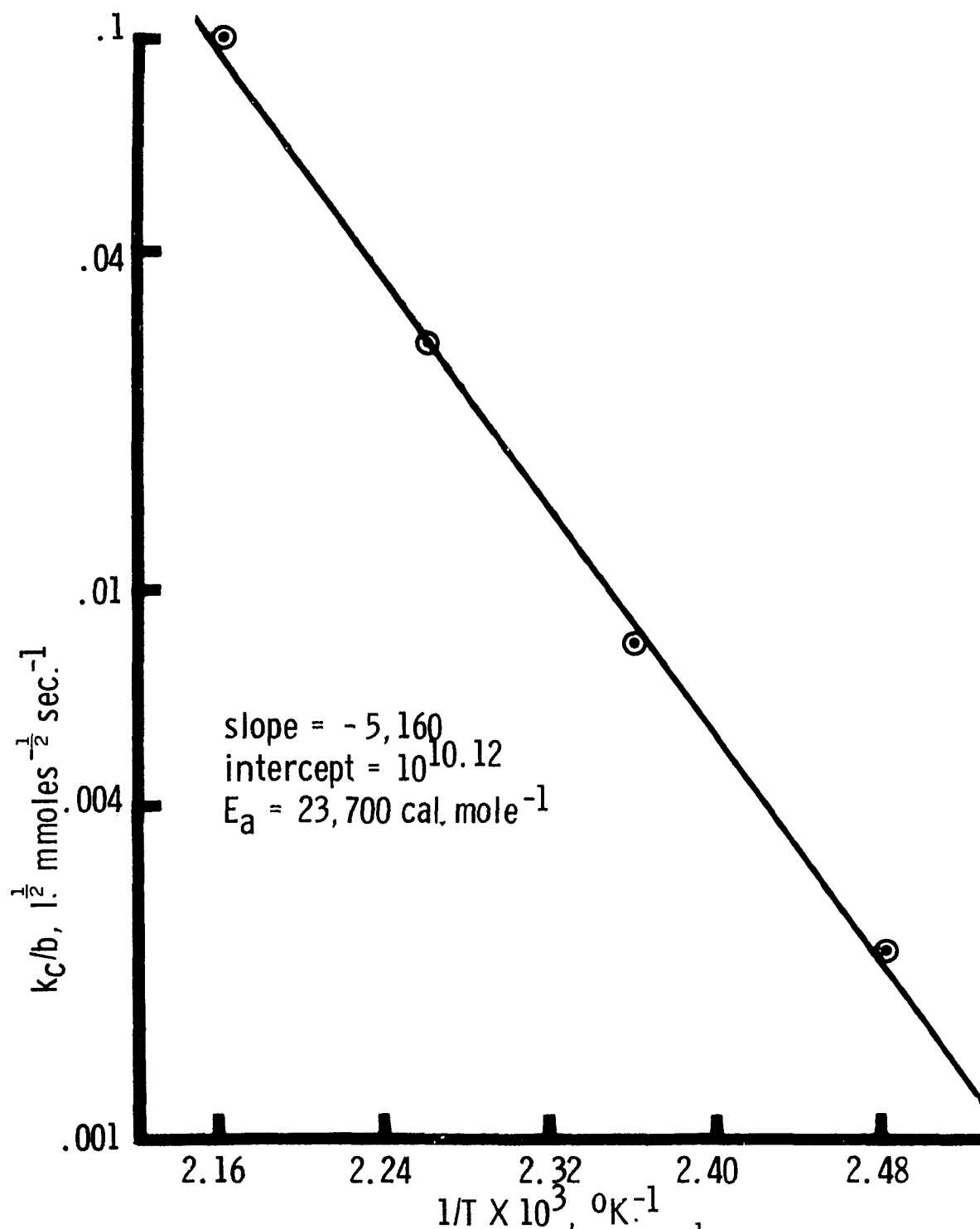


Figure 34 Arrhenius plot for  $(\text{OF}_2)(\text{H}_2)^{\frac{1}{2}}/(\text{O}_2)$  treatment - see figures 27 through 30

form a)

$$k_c/b = 10^{12.28} \exp(-27,600)/RT(1. \text{ mmoles}^{-1} \text{ sec}^{-1})$$

form b)

$$k_c/b = 10^{10.12} \exp(-23,700)/RT(1. \frac{1}{2} \text{ mmoles}^{-\frac{1}{2}} \text{ sec}^{-1})$$

These activation energies are the differences between those of  $k_c$  and  $b$ .

The  $r/(OF_2)$  values for the fully inhibited reaction correspond to the composite 'rate constant'  $[k_a + k_b(H_2)^m]$  for the first 2 terms of Eq. 35. These values are presented in Table III.

TABLE III

Rate Constants for the Fully Inhibited Reaction

<u>T, °C.</u>	<u>(H<sub>2</sub>)<sub>0</sub></u>	<u>[k<sub>a</sub> + k<sub>b</sub>(H<sub>2</sub>)<sup>m</sup>], sec<sup>-1</sup></u>
170	2	0.040
190	2	0.113
190	5	0.145
220	2	0.305
220	5	0.407

Though there is some hydrogen dependence in this rate constant, it is shown to have little effect on the slope of the Arrhenius plot, Figure 35, and thus the activation energy. An expression for this composite rate constant at the initial hydrogen concentration of 2 per cent is as follows:

$$[k_a + k_b(H_2)^m] = 10^{7.22} \exp(17,400)/RT(\text{sec}^{-1})$$

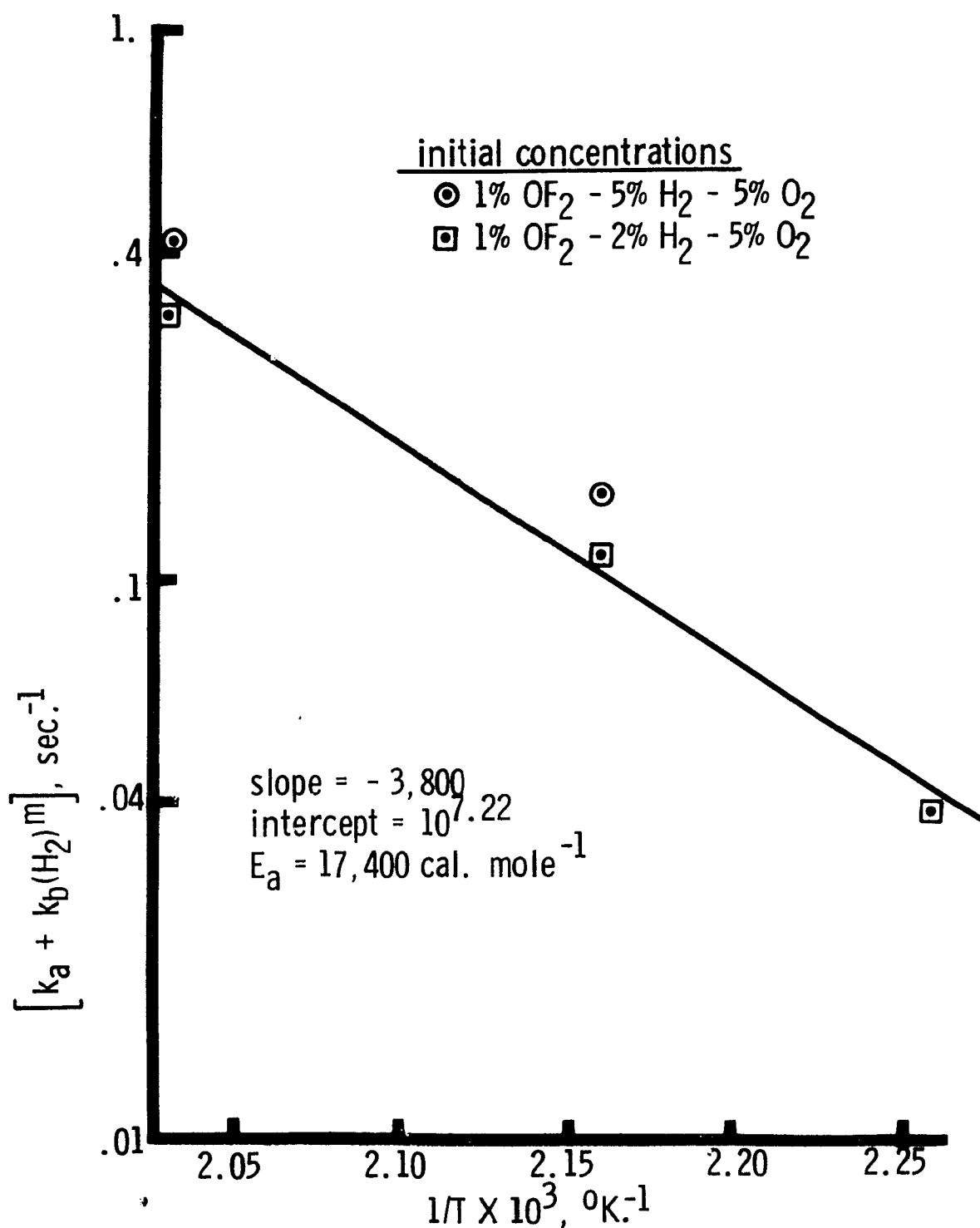


Figure 35 Arrhenius plot for the composite "rate constant" for the fully inhibited reaction

The relatively low activation energy associated with the first 2 terms of Eq. 35 is consistent with the presence of a significant heterogeneous component.

Future work: It is obvious from the work done to date on this reaction that an extremely complex mechanism is operating. To simplify the process of elucidating the mechanism it is suggested that some reactor material be used which promotes homogeneity. Aluminum has been found to be effective in promoting homogeneity in other reaction systems involving oxygen difluoride<sup>19</sup>. To more conclusively establish the rate law, additional studies of the hydrogen concentration dependence of the rate and the oxygen production rate are recommended.

## APPENDIX A

### An Investigation of Stirring Efficiency

The stirring efficiency for this system was determined by providing a concentration jump at the reactor's entrance. The non-steady state concentration change was then observed mass spectrometrically at the reactor's exit. Ideally, the concentration would change with time according to the following equation:

$$\frac{dc}{dt} = \frac{u}{V}(c_0 - c)$$

Integration gives

$$c = c_0 \exp(-ut/V)$$

The results for two extremes in contact times are shown in Figure 36. It should be noted that at the low contact time the observed result was indistinguishable from that predicted theoretically. At the high contact time, some deviation from ideality was observed; however, this is to be compared to a step-function which would have resulted had there been no mixing.

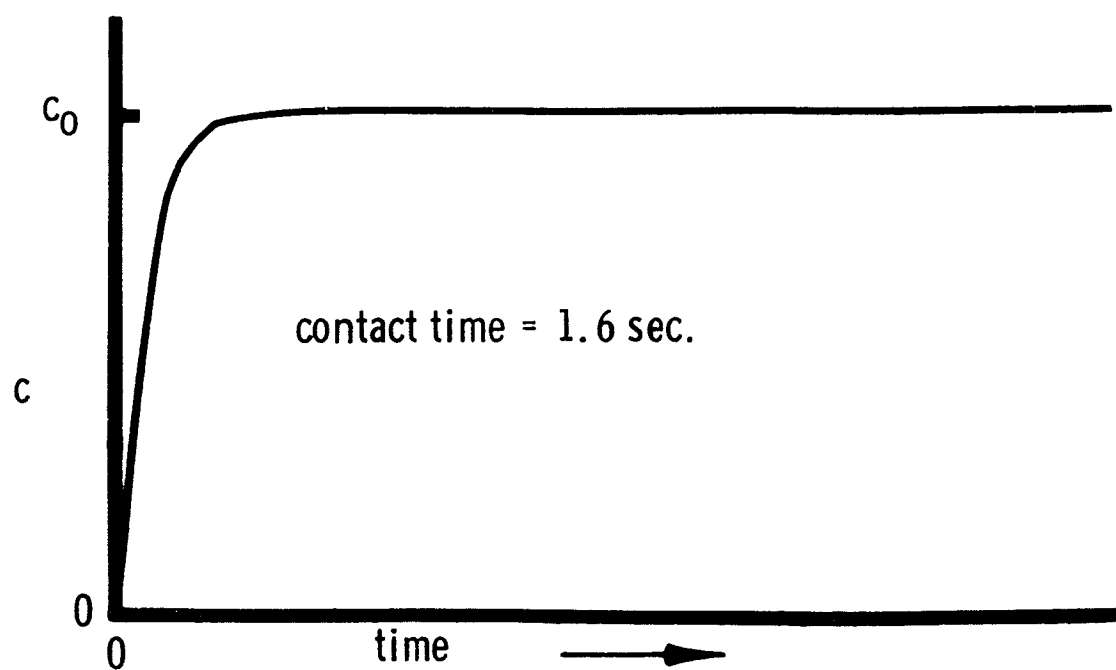
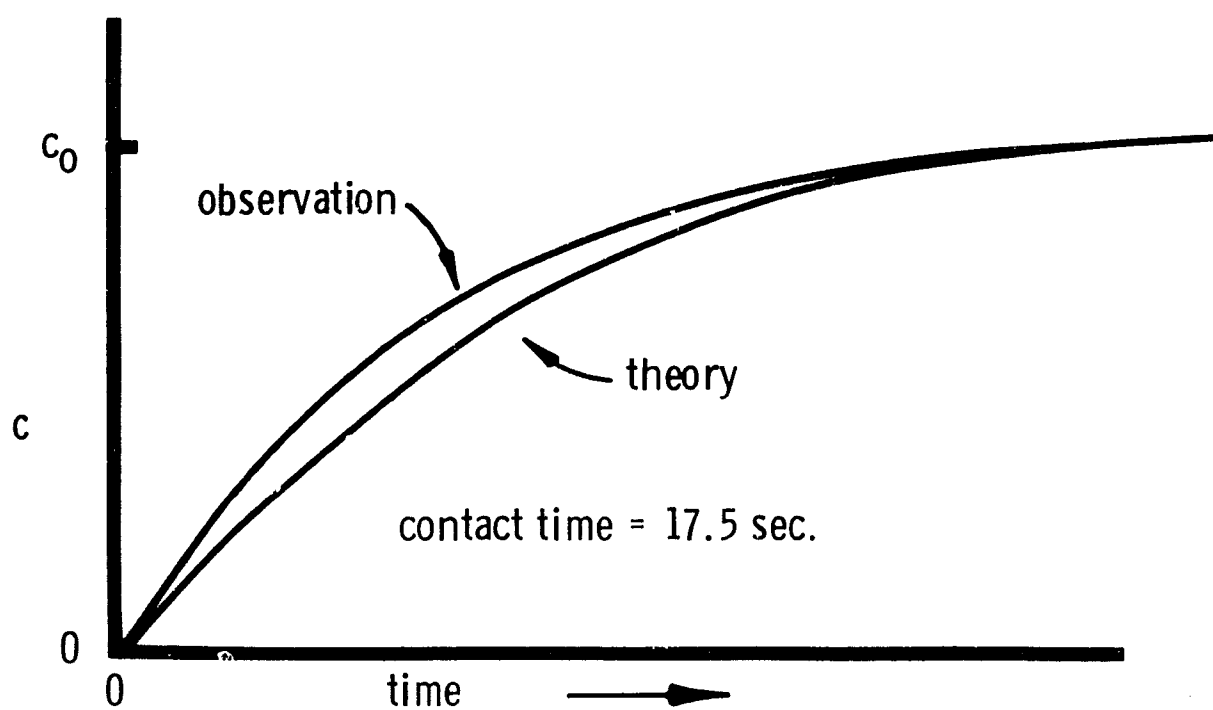


Figure 36 A study of stirring efficiency



## APPENDIX B

### Special Procedures for the AEI MS-10 Mass Spectrometer

Since the analyzer tube portion of the AEI MS-10 mass spectrometer was exposed to a corrosive environment created by the oxygen difluoride, some special attention was required. To maintain a high level of stability in the instrument, the ion source required cleaning about once a month under normal conditions of use, i.e., about 20 hours per week. Upon removing and dismantling the ion source, the ion burns were cleaned off with a fine grade emery paper. Before reassembling the ion source, the components were further cleaned by following the procedure outlined in the instruction manual (AEI publication 2032-69 Ed. B). That is, the quartz components were washed in a warm 10% nitric acid-10% sulphuric acid solution for 1 minute and all of the parts were washed in a detergent solution of 1 part to 200 parts water at 60°C. for 5 minutes. All parts were then rinsed in boiling distilled water 3 times prior to reassembly.

Following about 6 months of normal use, an inlet leak disintegrated and thus required replacement. The replacement inlet leak has been in operation for about 1 year and appears to be still in satisfactory condition.

The sample inlet capillary of the atmospheric sampling

device, which is a 4-foot-long section of .015 inch I.D. stainless steel capillary tubing, required replacement about once every 2 months. This capillary tended to plug-up with scale material which originated presumably from oxygen difluoride of the capillary's inner surface.

After 1½ years of use with oxygen difluoride, there was no evidence of corrosion in the analyzer tube or vacuum system.

## APPENDIX C

### Basic Kinetic Data -- Pyrolysis Reaction

#### Symbols:

$t$  = contact time, sec.

$X/(OF_2)_0$  = fraction of oxygen difluoride reacted

$(OF_2)$  = concentration of oxygen difluoride, mmoles  $l^{-1}$

$r$  = rate, mmoles  $l^{-1} \text{ sec}^{-1}$

$$T = 330^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 1 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
129	19.80	.461	.106	.0047	.044 *
130	11.10	.330	.133	.0059	.044 *
131	6.69	.233	.152	.0069	.045
132	4.45	.170	.164	.0076	.047
133	2.65	.116	.175	.0087	.050
134	1.37	.073	.184	.0102	.056
325	14.50	.451	.107	.0061	.057 *
326	8.34	.321	.132	.0076	.048
327	5.92	.242	.148	.0079	.053
328	4.56	.202	.156	.0086	.055
329	2.76	.135	.169	.0094	.056
330	1.49	.082	.179	.0107	.060
331	1.15	.065	.182	.0113	.062
332	.93	.052	.185	.0107	.058
333	.79	.043	.187	.0102	.055
(50 ml. reactor)					
433	8.57	.243	.150	.0056	.037 *
434	5.66	.197	.159	.0069	.043 *
435	4.03	.163	.166	.0079	.048 *
436	2.77	.140	.170	.0101	.059 *
437	1.48	.108	.177	.0142	.080 *
438	.88	.079	.183	.0170	.093 *
439	.68	.056	.187	.0162	.087 *
440	.55	.043	.190	.0146	.077 *
441	.47	.034	.191	.0151	.079 *

\*These points were not used in the  $r/(\text{OF}_2)$  versus  $t$  since they were either grossly out of line or  $t$  was too large to significantly affect  $[r/(\text{OF}_2)]_0$ .

$$T = 330^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 3 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
72	23.20	.370	.372	.0094	.025 *
73	11.40	.227	.457	.0118	.026 *
74	7.03	.166	.493	.0139	.028
75	4.82	.121	.519	.0150	.029
76	2.73	.076	.546	.0165	.030
77	1.39	.045	.565	.0187	.033
370	13.30	.346	.385	.0153	.040 *
371	9.45	.267	.432	.0166	.038
372	6.48	.198	.472	.0181	.038
373	4.67	.156	.497	.0197	.040
374	2.63	.100	.530	.0224	.042
375	1.60	.064	.551	.0238	.043
376	1.23	.047	.561	.0228	.041
377	.99	.041	.564	.0252	.045
378	.84	.034	.569	.0238	.042
(50 ml. reactor)					
388	8.57	.235	.455	.0162	.036
389	5.79	.177	.490	.0180	.037
390	3.97	.129	.519	.0189	.037
391	2.74	.092	.540	.0197	.037
392	1.61	.059	.560	.0211	.038
393	.92	.035	.574	.0217	.038
394	.72	.029	.578	.0222	.038
395	.58	.020	.582	.0206	.035
396	.45	.018	.584	.0223	.038

$$T = 330^{\circ}\text{C}.$$

$$(\text{OF}_2)_0 = 10 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
135	19.80	.350	1.290	.0349	.027 *
136	12.60	.244	1.500	.0381	.025 *
137	7.66	.162	1.660	.0418	.025
138	5.06	.120	1.740	.0474	.027
139	3.02	.079	1.820	.0530	.029
140	1.59	.047	1.890	.0565	.030
379	16.40	.326	1.320	.0390	.030 *
380	10.20	.231	1.508	.0444	.029 *
381	6.77	.179	1.610	.0517	.032
382	5.04	.138	1.690	.0536	.032
383	2.84	.083	1.800	.0558	.031
384	1.79	.055	1.850	.0614	.033
385	1.40	.044	1.874	.0615	.033
386	1.14	.035	1.890	.0615	.033
387	.99	.030	1.900	.0607	.032
(50 ml. reactor)					
478	8.60	.149	1.693	.0345	.070 *
479	6.36	.110	1.773	.0342	.019 *
480	4.38	.081	1.830	.0366	.020 *
481	3.08	.058	1.875	.0376	.020 *
482	1.74	.034	1.923	.0385	.020 *
483	1.05	.022	1.946	.0419	.022 *
484	.82	.017	1.958	.0389	.020 *
485	.67	.010	1.970	.0297	.015 *
486	.58	.009	1.973	.0293	.015 *

$$T = 360^{\circ}\text{C}.$$

$$(\text{OF}_2)_0 = 1 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X'/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
123	1.30	.125	.165	.0181	.110
124	2.49	.200	.150	.0151	.110
125	4.25	.290	.133	.0129	.097
126	6.37	.389	.115	.0114	.099
127	10.30	.500	.092	.0093	.101 *
128	17.20	.641	.068	.0070	.104 *
334	13.10	.691	.057	.0098	.172 *
335	8.39	.564	.081	.0124	.153
336	5.42	.434	.105	.0148	.141
337	4.33	.380	.115	.0162	.141
338	2.41	.250	.139	.0191	.137
339	1.50	.169	.154	.0207	.134
340	1.11	.129	.161	.0216	.134
341	.89	.102	.166	.0215	.130
342	.75	.088	.169	.0214	.127
(50 ml. reactor)					
442	7.69	.431	.108	.0105	.098
443	5.17	.354	.122	.0130	.107
444	3.67	.287	.135	.0147	.109
445	2.59	.232	.145	.0170	.117
446	1.45	.159	.159	.0207	.130
447	.84	.103	.170	.0226	.133
448	.66	.079	.174	.0228	.131
449	.53	.060	.178	.0209	.117
450	.44	.049	.180	.0203	.113

$$T = 360^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 3 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
49	24.90	.694	.173	.0157	.091 *
50	10.70	.506	.278	.0268	.096 *
51	6.62	.393	.342	.0336	.098
52	4.42	.308	.390	.0394	.101
53	2.47	.198	.452	.0454	.100
54	1.31	.117	.498	.0504	.101
289	13.50	.688	.175	.0287	.164 *
290	9.04	.555	.250	.0346	.139
291	6.30	.450	.309	.0401	.130
292	4.52	.355	.362	.0442	.122
293	2.59	.244	.425	.0529	.124
294	1.57	.167	.468	.0598	.128
295	1.18	.130	.489	.0619	.127
296	.92	.105	.503	.0641	.128
297	.78	.090	.511	.0652	.128
(50 ml. reactor)					
397	8.18	.437	.319	.0302	.095
398	5.52	.335	.376	.0344	.092
399	3.62	.245	.427	.0384	.090
400	2.45	.180	.464	.0416	.090
401	1.44	.113	.502	.0444	.088
402	.88	.069	.527	.0443	.084
403	.69	.055	.535	.0452	.085
404	.55	.047	.539	.0489	.091
405	.47	.039	.544	.0467	.086



$T = 360^{\circ}\text{C.}$

$(\text{OF}_2)_0 = 10 \text{ mole per cent}$

<u>run no.</u>	<u>t</u>	<u><math>X/(\text{OF}_2)_0</math></u>	<u><math>(\text{OF}_2)</math></u>	<u>r</u>	<u><math>r/(\text{OF}_2)</math></u>
(86 ml. reactor)					
78	25.50	.692	.579	.0510	.088 *
79	11.40	.490	.958	.0810	.085 *
80	7.00	.358	1.210	.0960	.079
81	4.82	.284	1.350	.1100	.082
82	2.88	.204	1.500	.1320	.088
83	1.53	.121	1.650	.1500	.091
235	19.60	.679	.596	.0645	.108 *
236	10.80	.552	.832	.0952	.114 *
237	7.70	.471	.984	.1140	.116
238	4.85	.339	1.230	.1300	.106
239	2.77	.223	1.445	.1500	.104
240	1.75	.151	1.580	.1600	.101
241	1.29	.110	1.660	.1550	.093
242	1.06	.089	1.695	.1650	.097
243	.91	.070	1.730	.1440	.083
(50 ml. reactor)					
487	8.89	.404	1.127	.0859	.076
488	5.97	.314	1.300	.0988	.076
489	4.05	.236	1.444	.1100	.076
490	2.96	.188	1.535	.1200	.078
491	1.65	.107	1.690	.1210	.072
492	1.03	.073	1.751	.1540	.088
493	.79	.058	1.780	.1400	.079
494	.64	.045	1.805	.1330	.074
495	.55	.037	1.820	.1310	.072

$$T = 385^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 1 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
115	16.70	.835	.0298	.0091	.305 *
116	9.95	.753	.0447	.0137	.306 *
117	6.14	.637	.0657	.0188	.286
118	4.09	.516	.0875	.0229	.262
119	2.43	.372	.1137	.0277	.244
120	1.27	.239	.1380	.0339	.245
121	.68	.159	.1525	.0419	.275
343	12.66	.867	.024	.0122	.508 *
344	7.64	.761	.043	.0177	.412
345	5.50	.680	.057	.0220	.386
346	4.16	.601	.071	.0258	.364
347	2.31	.434	.101	.0334	.330
348	1.38	.296	.125	.0384	.307
349	1.07	.243	.135	.0403	.298
350	.85	.196	.143	.0411	.288
351	.72	.165	.149	.0402	.270
(50 ml. reactor)					
451	7.18	.645	.065	.0163	.251
452	5.23	.577	.077	.0201	.261
453	3.53	.434	.094	.0249	.265
454	2.56	.398	.110	.0281	.255
455	1.38	.268	.133	.0355	.267
456	.82	.179	.150	.0393	.262
457	.63	.141	.156	.0411	.264
458	.51	.111	.162	.0395	.244
459	.43	.092	.165	.0398	.241

$$T = 385^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 3 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
55	17.80	.831	.092	.0252	.274 *
56	10.30	.742	.140	.0390	.278 *
57	6.19	.629	.201	.0552	.275
58	4.25	.524	.258	.0669	.259
59	2.48	.385	.333	.0843	.253
60	1.27	.236	.414	.1010	.244
298	14.30	.873	.069	.0330	.479 *
299	8.16	.249	.136	.0496	.365
300	5.95	.666	.181	.0605	.334
301	4.34	.576	.230	.0717	.312
302	2.49	.414	.317	.0900	.284
303	1.45	.289	.385	.1076	.280
304	1.11	.238	.412	.1162	.282
305	.89	.203	.431	.1242	.288
306	.75	.172	.449	.1225	.273
(50 ml. reactor)					
406	7.39	.665	.183	.0490	.268
407	5.75	.573	.233	.0594	.255
408	3.75	.467	.290	.0680	.234
409	2.52	.362	.348	.0781	.225
410	1.44	.238	.415	.0902	.217
411	.56	.150	.463	.0959	.207
412	.66	.115	.482	.0955	.198
413	.53	.094	.494	.0955	.194
414	.45	.077	.503	.0926	.184

$$T = 385^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 10 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
84	19.04	.850	.271	.0810	.299 *
85	11.33	.750	.452	.1200	.266 *
86	7.20	.625	.678	.1570	.272
87	4.65	.530	.850	.2070	.244
88	2.65	.385	1.113	.2630	.236
89	1.46	.261	1.337	.3240	.242
244	18.40	.858	.254	.0835	.329 *
245	9.88	.761	.427	.1380	.323 *
246	6.70	.683	.567	.1830	.323
247	4.88	.586	.740	.2150	.291
248	2.69	.417	1.044	.2790	.267
249	1.67	.299	1.257	.3190	.254
250	1.23	.219	1.400	.3170	.226
251	1.02	.184	1.460	.3240	.222
252	.88	.159	1.508	.3220	.214
(50 ml. reactor)					
496	7.84	.658	.622	.1530	.246
497	5.40	.568	.786	.1920	.244
498	3.74	.471	.963	.2290	.238
499	2.72	.387	1.116	.2590	.232
500	1.66	.263	1.341	.2880	.215
501	.99	.179	1.495	.3290	.220
502	.75	.145	1.559	.3460	.220
503	.61	.114	1.612	.3390	.216
504	.53	.100	1.640	.3410	.208

$$T = 407^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 1 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
108	14.90	.912	.015	.0107	.695 *
109	9.34	.867	.023	.0163	.700
110	5.96	.797	.036	.0234	.660
111	4.05	.730	.047	.0315	.665
112	2.34	.573	.075	.0428	.572
113	1.27	.412	.103	.0567	.550
114	.66	.282	.126	.0747	.594
352	11.76	.966	.006	.0144	2.400 *
353	7.55	.921	.014	.0214	1.530 *
354	5.06	.868	.023	.0300	1.300 *
355	3.82	.810	.033	.0372	1.130 *
356	2.28	.678	.056	.0522	.970
357	1.34	.505	.087	.0657	.755
358	1.03	.419	.102	.0709	.694
359	.84	.357	.113	.0742	.657
360	.71	.308	.121	.0760	.628
(50 ml. reactor)					
460	7.16	.820	.032	.0201	.628
461	4.92	.742	.045	.0266	.591
462	3.14	.633	.065	.0354	.544
463	2.27	.537	.082	.0414	.504
464	1.33	.394	.107	.0519	.484
465	.79	.272	.128	.0607	.474
466	.61	.226	.136	.0656	.482
467	.49	.181	.144	.0653	.454
468	.41	.154	.149	.0653	.438

$$T = 407^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 3 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
62	10.20	.886	.060	.0456	.760 *
63	6.05	.826	.091	.0717	.787
64	4.41	.771	.120	.0919	.765
65	2.32	.601	.210	.1359	.647
66	1.22	.406	.312	.1746	.560
67	.70	.266	.385	.2000	.520
307	13.40	.954	.024	.0372	1.550 *
308	8.40	.905	.050	.0564	1.130 *
309	5.84	.850	.079	.0761	.964
310	4.20	.784	.113	.0977	.865
311	2.41	.622	.198	.1350	.682
312	1.38	.471	.277	.1780	.643
313	1.07	.394	.317	.1930	.610
314	.85	.338	.346	.2085	.603
315	.73	.295	.369	.2115	.573
(50 ml. reactor)					
415	6.96	.808	.101	.0612	.605
416	5.14	.743	.136	.0761	.560
417	3.53	.646	.187	.0962	.514
418	2.41	.539	.243	.1180	.486
419	1.39	.391	.320	.1490	.466
420	.82	.265	.387	.1700	.440
421	.64	.219	.412	.1790	.435
422	.52	.186	.428	.1910	.446
423	.44	.160	.443	.1910	.431

$$T = 407^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 10 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
90	11.00	.900	.175	.1430	.818 *
91	6.97	.841	.278	.2110	.759
92	4.52	.751	.435	.2910	.669
93	2.66	.526	.654	.4110	.629
94	1.42	.460	.944	.5670	.601
95	.79	.292	1.238	.6450	.521
253	18.30	.958	.073	.0910	1.250 *
254	10.00	.918	.143	.1600	1.120 *
255	6.70	.878	.212	.2280	1.070 *
256	4.46	.805	.339	.3140	.930
257	2.57	.653	.604	.4030	.668
258	1.63	.511	.850	.5460	.643
259	1.18	.416	1.015	.6140	.605
260	.98	.368	1.100	.6520	.593
261	.85	.336	1.155	.6930	.600
(50 ml. reactor)					
505	7.34	.827	.306	.1980	.646
506	5.06	.762	.419	.2650	.633
507	3.68	.695	.537	.3330	.620
508	2.69	.613	.681	.4010	.589
509	1.51	.453	.963	.5280	.549
510	.95	.333	1.174	.6180	.526
511	.72	.280	1.267	.6820	.539
512	.59	.238	1.340	.7140	.533
513	.51	.203	1.402	.7020	.500

$$T = 431^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 1 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
102	9.36	.944	.010	.0170	1.790 *
103	5.29	.914	.015	.0290	2.000
104	3.79	.877	.021	.0390	1.880
105	2.22	.777	.038	.0590	1.510
106	1.21	.620	.064	.0870	1.350
107	.64	.461	.091	.1230	1.350
361	12.61	.994	.001	.0130	1.330 *
362	8.14	.988	.002	.0210	1.030 *
363	5.51	.970	.005	.0300	5.960 *
364	2.20	.854	.025	.0660	2.630
365	1.30	.720	.047	.0940	2.000
366	1.00	.633	.062	.1070	1.760
367	.82	.560	.074	.1160	1.570
368	.69	.500	.085	.1230	1.440
369	4.47	.950	.008	.0360	4.500 *
(50 ml. reactor)					
469	6.33	.925	.013	.0250	1.910
470	4.76	.896	.018	.0320	1.770
471	3.31	.840	.027	.0430	1.600
472	2.24	.757	.041	.0580	1.410
473	1.29	.614	.066	.0810	1.220
474	.76	.465	.091	.1040	1.140
475	.59	.398	.102	.1160	1.130
476	.48	.340	.112	.1220	1.090
477	.40	.300	.119	.1280	1.070



$$T = 431^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 3 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
68	.68	.444	.282	.3330	1.180
69	1.18	.616	.195	.2680	1.350
70	2.28	.800	.102	.1780	1.740
71	3.84	.897	.052	.1180	2.270
316	12.20	.994	.003	.0410	13.800 *
317	7.12	.982	.009	.0700	7.760 *
318	5.56	.958	.021	.0870	4.150
319	3.78	.914	.044	.1220	2.780
320	2.18	.810	.096	.1880	1.960
321	1.33	.689	.157	.2620	1.670
322	1.04	.614	.195	.3040	1.560
323	.83	.535	.236	.3250	1.380
324	.70	.472	.267	.3400	1.270
(50 ml. reactor)					
424	6.92	.930	.036	.0680	1.900
425	5.19	.890	.056	.0870	1.560
426	3.41	.832	.086	.1240	1.440
427	2.48	.775	.115	.1590	1.380
428	1.35	.618	.194	.2330	1.200
429	.80	.468	.271	.2990	1.100
430	.62	.405	.303	.3320	1.090
431	.50	.352	.330	.3590	1.090
432	.42	.389	.352	.3700	1.050

$$T = 431^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 10 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
96	10.55	.964	.061	.1540	2.520 *
97	6.84	.954	.078	.2220	2.850
98	4.34	.914	.145	.3560	2.450
99	2.58	.840	.270	.5500	2.040
100	1.37	.707	.495	.8720	1.760
101	.77	.533	.790	1.1730	1.490
262	16.40	.984	.027	.1010	3.740 *
263	9.70	.980	.034	.1700	5.000 *
264	6.06	.965	.059	.2680	4.540 *
265	4.30	.941	.099	.3680	3.720 *
266	2.50	.868	.222	.5830	2.630
267	1.57	.742	.434	.7930	1.830
268	1.16	.621	.636	.9000	1.410
269	.95	.538	.776	.9560	1.230
270	.81	.490	.856	1.0130	1.180
(50 ml. reactor)					
514	7.02	.930	.119	.2250	1.890
515	4.96	.907	.158	.3110	1.970
516	3.53	.865	.230	.4160	1.810
517	2.49	.808	.326	.5520	1.700
518	1.44	.690	.527	.8150	1.550
519	.88	.561	.746	1.0900	1.460
520	.69	.496	.856	1.2190	1.420
521	.56	.433	.965	1.3040	1.350
522	.49	.393	1.032	1.3660	1.320

# APPENDIX D

## Product Addition Studies

T = 330°C.

(OF<sub>2</sub>)<sub>0</sub> = 3 mole per cent

(F<sub>2</sub>)<sub>0</sub> = 3 mole per cent

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
141	19.70	.299	.413	.0089	.022
142	11.80	.205	.468	.0103	.022
143	7.10	.139	.507	.0115	.023
144	4.65	.099	.530	.0127	.024
145	2.74	.064	.551	.0139	.025

T = 360°C.

(OF<sub>2</sub>)<sub>0</sub> = 3 mole per cent

(F<sub>2</sub>)<sub>0</sub> = 3 mole per cent

(86 ml. reactor)					
147	18.80	.603	.223	.0180	.081
148	11.20	.464	.301	.2320	.077
149	6.74	.347	.367	.0288	.079
150	4.43	.261	.415	.0330	.080
151	2.61	.175	.463	.0375	.081
152	1.45	.109	.500	.0420	.084

T = 360°C.

(OF<sub>2</sub>)<sub>0</sub> = 3 mole per cent

(F<sub>2</sub>)<sub>0</sub> = 0.5 mole per cent

(86 ml. reactor)					
608	1.29	.110	.497	.0470	.095
609	1.69	.141	.479	.0470	.098
610	2.30	.175	.460	.0430	.093
611	3.36	.246	.421	.0410	.098
612	7.95	.437	.314	.0310	.099
613	17.90	.662	.189	.0210	.111

$T = 360^{\circ}\text{C}.$

$(\text{OF}_2)_0 = 3 \text{ mole per cent}$

$(\text{F}_2)_0 = 1 \text{ mole per cent}$

<u>run no.</u>	<u>t</u>	<u><math>X/(\text{OF}_2)_0</math></u>	<u><math>(\text{OF}_2)</math></u>	<u>r</u>	<u><math>r/(\text{OF}_2)</math></u>
(86 ml. reactor)					
620	22.60	.686	.175	.0170	.097
621	6.60	.380	.345	.0320	.073
622	3.32	.231	.428	.0390	.091
623	2.35	.177	.458	.0420	.092
624	1.92	.149	.474	.0430	.091
625	1.36	.109	.496	.0440	.089
626	11.10	.507	.274	.0250	.091

$T = 360^{\circ}\text{C}.$

$(\text{OF}_2)_0 = 3 \text{ mole per cent}$

$(\text{O}_2)_0 = 0.5 \text{ mole per cent}$

(86 ml. reactor)					
669	1.34	.135	.484	.0550	.114
670	1.91	.182	.457	.0530	.116
671	4.48	.320	.380	.0400	.105
672	7.17	.410	.330	.0320	.097
673	10.76	.532	.262	.0270	.103
674	19.55	.668	.185	.0190	.103

$T = 360^{\circ}\text{C}.$

$(\text{OF}_2)_0 = 3 \text{ mole per cent}$

$(\text{O}_2)_0 = 1 \text{ mole per cent}$

(86 ml. reactor)					
651	1.31	.151	.474	.0640	.135
652	1.93	.186	.456	.0530	.116
653	4.47	.329	.375	.0410	.109
654	6.98	.417	.326	.0330	.101
655	10.36	.514	.272	.0280	.103
656	19.55	.662	.189	.0190	.101

$T = 360^{\circ}\text{C.}$

$(\text{OF}_2)_0 = 3 \text{ mole per cent}$   
 $(\text{O}_2)_0 = 3 \text{ mole per cent}$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
645	1.32	.151	.474	.0635	.134
646	1.91	.198	.447	.0580	.130
647	4.26	.332	.373	.0430	.115
648	6.88	.425	.321	.0340	.106
649	10.25	.523	.266	.0290	.109
650	19.55	.676	.181	.0190	.105

$T = 385^{\circ}\text{C.}$

$(\text{OF}_2)_0 = 3 \text{ mole per cent}$   
 $(\text{F}_2)_0 = 3 \text{ mole per cent}$

(86 ml. reactor)					
600	4.03	.528	.254	.0710	.280
601	2.51	.400	.323	.0860	.266
602	1.98	.328	.362	.0890	.246
603	1.66	.293	.380	.0950	.250
604	1.43	.258	.400	.0970	.242
605	1.25	.233	.408	.1040	.255
606	.89	.183	.440	.1100	.250
607	.70	.144	.461	.1100	.238

$T = 385^{\circ}\text{C.}$

$(\text{OF}_2)_0 = 3 \text{ mole per cent}$   
 $(\text{F}_2)_0 = 1 \text{ mole per cent}$

(86 ml. reactor)					
614	.90	.177	.439	.105	.240
615	.72	.137	.460	.102	.222
616	1.29	.224	.414	.092	.222
617	1.59	.266	.391	.089	.228
618	3.14	.423	.308	.072	.234
619	11.47	.767	.124	.036	.290

$$T = 385^{\circ}\text{C.}$$

$$\begin{aligned}(\text{OF}_2)_0 &= 3 \text{ mole per cent} \\ (\text{O}_2)_0 &= 0.5 \text{ mole per cent}\end{aligned}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor)					
663	.71	.175	.442	.1320	.298
664	1.30	.273	.390	.1120	.287
665	2.51	.424	.309	.0910	.295
666	4.53	.556	.238	.0660	.277
667	7.80	.691	.166	.0470	.283
668	10.29	.746	.136	.0390	.287

$$T = 385^{\circ}\text{C.}$$

$$\begin{aligned}(\text{OF}_2)_0 &= 3 \text{ mole per cent} \\ (\text{O}_2)_0 &= 1 \text{ mole per cent}\end{aligned}$$

(86 ml. reactor)					
657	9.77	.734	.143	.0400	.279
658	7.12	.672	.176	.0510	.290
659	4.51	.571	.230	.0680	.295
660	2.47	.426	.308	.0920	.299
661	1.27	.273	.390	.1150	.295
662	.71	.179	.440	.1350	.307

$$T = 385^{\circ}\text{C.}$$

$$\begin{aligned}(\text{OF}_2)_0 &= 3 \text{ mole per cent} \\ (\text{O}_2)_0 &= 3 \text{ mole per cent}\end{aligned}$$

(86 ml. reactor)					
639	10.15	.740	.139	.0390	.280
640	7.64	.677	.173	.0480	.278
641	4.64	.570	.230	.0660	.287
642	2.43	.427	.307	.0920	.300
643	1.27	.267	.393	.1130	.288
644	.71	.177	.441	.1330	.302

$T = 385^{\circ}\text{C}.$

$(\text{OF}_2)_0 = 3$  mole per cent

$(\text{F}_2)_0 = 3$  mole per cent

<u>run no.</u>	<u>t</u>	<u><math>X/(\text{OF}_2)_0</math></u>	<u><math>(\text{OF}_2)</math></u>	<u>r</u>	<u><math>r/(\text{OF}_2)</math></u>
(86 ml. reactor)					
633	10.79	.724	.150	.0370	.247
634	7.75	.646	.193	.0450	.233
635	4.64	.522	.260	.0610	.235
636	2.53	.361	.349	.0770	.220
637	1.38	.230	.420	.0900	.214
638	.78	.142	.467	.0990	.212

$T = 385^{\circ}\text{C}.$

$(\text{OF}_2)_0 = 3$  mole per cent

$(\text{F}_2)_0 = 3$  mole per cent

(86 ml. reactor)					
153	18.10	.817	.099	.0243	.246
154	10.80	.730	.146	.0364	.249
155	6.49	.604	.214	.0501	.234
156	4.26	.476	.282	.0603	.214
157	2.52	.342	.355	.0730	.206
158	1.40	.216	.422	.0835	.198

$T = 407^{\circ}\text{C}.$

$(\text{OF}_2)_0 = 3$  mole per cent

$(\text{F}_2)_0 = 3$  mole per cent

(86 ml. reactor)					
159	17.60	.920	.041	.0073	.666
160	10.45	.899	.053	.0448	.845
161	6.30	.808	.100	.0669	.669
162	4.13	.711	.151	.0895	.592
163	2.43	.569	.225	.1220	.542
164	1.36	.405	.310	.1550	.500

$$T = 431^{\circ}\text{C.}$$

$$(\text{OF}_2)_0 = 3 \text{ mole per cent}$$

$$(\text{F}_2)_0 = 3 \text{ mole per cent}$$

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
		(86 ml. reactor)			
165	16.90	.953	.024	.0285	1.190
166	10.00	.940	.030	.0475	1.580
167	6.08	.916	.042	.0762	1.820
168	4.00	.874	.066	.1104	1.730
169	2.36	.784	.109	.1679	1.540
170	1.31	.632	.186	.2440	1.310



# APPENDIX E

## Heterogeneous Effects

T = 385°C.

(OF<sub>2</sub>)<sub>0</sub> = 3 mole per cent

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
(86 ml. reactor - blank)					
531	14.30	.873	.069	.0330	.479
532	8.16	.748	.136	.0496	.365
533	5.95	.655	.187	.0595	.318
534	4.34	.559	.239	.0696	.291
535	2.49	.401	.324	.0872	.269
536	1.45	.278	.391	.1035	.265
537	1.11	.223	.421	.1080	.257
538	.89	.183	.442	.1120	.254
539	.75	.159	.456	.1131	.248
(86 ml. reactor - surface area increased 2.5 times)					
540	13.20	.867	.072	.0355	.493
541	7.50	.746	.137	.0539	.393
542	5.47	.659	.184	.0653	.355
543	4.00	.572	.232	.0773	.333
544	2.29	.405	.322	.0907	.282
545	1.33	.280	.390	.1137	.291
546	1.02	.222	.421	.1175	.279
547	.81	.185	.441	.1230	.279
548	.69	.150	.460	.1175	.256

## APPENDIX F

### Analysis of Uncertainties

Uncertainties for individual measurements and their influence on the final results were estimated in the following manner:

1) The uncertainty in the helium-reactant flow rate depended upon the magnitude of the pressure drop in the manometer flow meters which could be read to  $\pm 0.1$  cm. The lowest and highest readings were 2.5 cm. and 50 cm. respectively. Thus the uncertainties for a single flow meter were  $0.1/2.5 = 4.0\%$  and  $0.1/50 = 0.2\%$ . Maximum uncertainty therefore occurred at high contact times. The uncertainties stated above are applicable to the pyrolysis reaction since only 1 flow meter was used. The hydrogen-oxygen difluoride reaction required 2 flow meters; therefore, the uncertainty in the flow to the reactor would be multiplied by about  $(2)^{\frac{1}{2}}$ , i.e., 5.7% and 0.3%.

2) Uncertainty in the initial concentration of reactant(s) was determined solely by the technique used in preparing the gaseous samples. Since step-wise dilution was used for preparing samples of low reactant concentrations, the uncertainty is probably about the same for high and low concentrations. Based on the precision with which the Bour-

don gauges could be read and the reproducibility of the readings, an uncertainty of 2 per cent in the initial concentrations was estimated.

3) The volume of the reactor was measured to about  $\pm 2$  ml., and the total volume was 86 ml. Hence, the uncertainty in the effective reactor volume was  $2/86 = 2.3$  per cent. This source of uncertainty arose from the temperature gradient established along the inlet and outlet paths of the reactor and did not contribute to the random behavior of the individual values. Rather, it was added to the final uncertainty in the rate constants. Changes in the reactor's volume resulting from the temperature coefficient of thermal expansion were considered negligible.

4) The uncertainty in the mass spectrometric determination of the concentration changes in oxygen difluoride arose principally from random instrumental factors which resulted in irreproducibility. This source of uncertainty was felt to be of the order of 3 per cent.

5) Uncertainty in the final concentration arose from uncertainties in the initial concentration (2) and instrumental uncertainties (4). Hence, the total uncertainty in the final concentration was  $[(2)^2 + (3)^2]^{\frac{1}{2}}$  about 3.6 per cent.

6) Uncertainties in the contact time resulted principally from (1), (3) and the volume change which accompanied

reaction. This latter source of uncertainty contributed primarily when the reactant concentration was high, i.e., 10 per cent and when the extent of reaction was high, i.e., when the contact time and the temperature were high. The maximum contribution from this source was about 4 per cent. Thus, there was a compounding effect, i.e., uncertainty which arose from (1) and from volume change occurred under the same conditions. Hence, the uncertainty in contact time ranged from  $[(5.7)^2 + (4)^2 + (2.3)^2]^{\frac{1}{2}}$  or 7.3 per cent to  $[(0.3)^2 + (2.3)^2]^{\frac{1}{2}}$  or 2.3 per cent.

7) For the pyrolysis reaction, the following examples, which represent moderate extremes in reaction conditions, are illustrative:

a) For run no. 339 of the pyrolysis experiments, the initial concentration,  $c_0 = 0.185 \text{ mmoles l}^{-1}$  (1%), the final concentration,  $c = 0.154 \text{ mmoles l}^{-1}$ , the contact time  $t = 1.50 \text{ sec.}$ , and the temperature  $T = 360^\circ\text{C.}$

$$\Delta c = c_0 - c = 0.185 \pm 0.185 \times 2\% - 0.154 \pm 0.154 \times 3.6\% = (0.185 \pm 0.004) - (0.154 \pm 0.005) = 0.031 \pm 0.009 \text{ mmoles l}^{-1}$$

Therefore, the total uncertainty in  $\Delta c$  is  $\pm 0.009/0.031 = \pm 29\%$ . Hence, the uncertainty in the calculated rate,  $\Delta c/t$ , for a low concentration and an intermediate extent of reaction and contact time is  $[(29)^2 + (2.3)^2]^{\frac{1}{2}} = 29\%$ .

b) For run no. 255 of the pyrolysis experiments, the initial concentration  $c_0 = 1.740 \text{ mmoles l}^{-1}$  (10%), the final concentration,  $c = 0.212 \text{ mmoles l}^{-1}$ , the contact time  $t = 6.70 \text{ sec.}$  and the temperature  $T = 407^\circ\text{C.}$

$$c = c_0 - c = 1.740 \pm 1.740 \times 2\% - 0.212 \pm 0.212 \times 3.6\% = \\ (1.740 \pm 0.035) - (0.212 \pm 0.008) = 1.528 \pm 0.043$$

Therefore, the total uncertainty in  $c$  is  $\pm 0.043/1.528 = \pm 2.8\%$ . Hence, the uncertainty in the calculated rate,  $\Delta c/t$ , for a high concentration and a high extent of reaction and contact time is  $[(2.8)^2 + (7.3)^2]^{\frac{1}{2}} = \pm 8\%$ . Thus, from these examples it may be noted that there is a leveling effect, i.e., conditions which produce high uncertainties in  $\Delta c$  produce low uncertainties in the contact time and vice versa. However, as seen in the above examples, the uncertainty in  $\Delta c$  overpowers that of the contact time.

Thus, rate values calculated from low temperature experiments with low reactant concentrations would have probable uncertainties of about 29 per cent where those resulting from high temperature experiments where high reactant concentrations were involved would have probable uncertainties of about 8 per cent.

8) The rate constants for the pyrolysis reaction were determined from the intercepts of the plot shown in Figures 15 through 17 and are equal to  $r/(OF_2)$  at the intercepts,

i.e., when  $(OF_2)^{-\frac{1}{2}}$  is zero. Thus, the uncertainty in the rate constants may be considered to be about equal to the uncertainty in the rates. Since the value of each rate constant is derived from many rates, the reported uncertainties for the rates are considered to be an outer limit for the uncertainty in the rate constants. The uncertainty in the activation energy arises from the uncertainties in the rate constants and in the reaction temperatures ( $\pm 2^\circ\text{C}.$ ) and are related through the Arrhenius equation

$$k = A \exp(-E_a/RT)$$

The effect of the above uncertainties on the activation was derived as follows:

$$K_k = (\partial E_a / \partial k)(D_k)$$

where  $K_k$  is the contribution to the uncertainty in the activation energy,  $E_a$ , by  $k$ , and  $D_k$  is the average uncertainty in  $k$ . Thus, for an intermediate temperature and rate constant, i.e.,  $385^\circ\text{C}.$  and  $0.2 \text{ sec}^{-1}$

$$K_k = -RTD_k/k = -(1.99)(658)(0.2 \times 19\%)/(0.2) = -250 \text{ cal.}$$

similarly

$$K_T = (\partial E_a / \partial T)(D_T)$$

where  $K_T$  is the contribution to the uncertainty in the activation by the temperature, i.e.,  $385^\circ\text{C}.$   $\pm 2^\circ\text{C}.$  or  $2/658 = 0.3\%$ .

Thus

$$K_T = 2.303RD_T(\log A - \log k) = \\ (2.303)(1.99)(658 \pm 0.3\%)[10.5 - (-0.7)] = 103 \text{ cal.}$$

and the total uncertainty, K, in the activation energy is

$$K = (K_K^2 + K_T^2)^{\frac{1}{2}} = [(-250)^2 + (103)^2]^{\frac{1}{2}} = 270 \text{ cal.}$$

Hence

$$E_a = 34,000 \pm K \text{ cal.} = 34,000 \pm 270 \text{ cal.}$$

For the above calculations the limits of uncertainty were selected so as to include about 75 per cent of all of the pyrolysis data, i.e., moderately extreme conditions were chosen so as to exclude about 12 per cent of the reaction conditions at each extreme. Hence, the uncertainty reported for the activation energy, i.e., about 300 cal. is believed to correspond roughly to the 75 per cent confidence level.

9) The uncertainties associated with hydrogen-oxygen difluoride experiments will not be rigorously treated here since the analysis of uncertainties for the pyrolysis reaction adequately illustrate the sources of error which are inherent in flow system kinetic studies.

Briefly, the data resulting from hydrogen-oxygen difluoride experiments were subject to higher uncertainties than

those resulting from the pyrolysis reaction because of the generally lower reactant concentration used and because 2 flows were measured instead of 1. The former point led to high uncertainties in  $(c_0 - c)$  and the latter point contributed additional uncertainty to the contact time. Based roughly on a 75 per cent confidence level, the uncertainty in the rates ranged from about 41 per cent at low temperatures and low concentrations to about 11 per cent at high temperatures and high concentrations.

Uncertainty values for the various activation energies are not reported because it is felt that they would have little meaning since the state of the understanding of the hydrogen-oxygen difluoride reaction is relatively low.

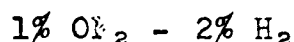


## APPENDIX G

### The Stoichiometry of the Hydrogen-Oxygen Difluoride Reaction

#### The stoichiometric relationship between hydrogen and oxygen difluoride:

$$T = 190^{\circ}\text{C}.$$



<u>run no.</u>	<u>X/(H<sub>2</sub>)<sub>o</sub></u>	<u>X/(OF<sub>2</sub>)<sub>o</sub></u>	<u>r<sub>H<sub>2</sub></sub></u>	<u>r<sub>OF<sub>2</sub></sub></u>	<u>r<sub>H<sub>2</sub></sub>/r<sub>OF<sub>2</sub></sub></u>
272	.571	.824	.0199	.0143	1.39
273	.466	.688	.0325	.0239	1.36
274	.438	.596	.0456	.0310	1.47
275	.444	.696	.0154	.0121	1.27
276	.411	.600	.0285	.0208	1.37
277	.390	.542	.0405	.0282	1.44
278	.369	.475	.0636	.0411	1.55
279	.327	.420	.1024	.0659	1.56

#### The stoichiometric relationship between oxygen and oxygen difluoride:

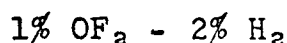
$$T = 170^{\circ}\text{C}.$$



A 0.5 per cent mixture of oxygen in helium gave a mass spectrometer response of 50 units ( $m/e = 32$ ). At 50 per cent reaction, a response of 12 units resulted; this corresponded to 0.12 per cent oxygen in the stream. Thus, the stoichiometric ratio  $\text{O}_2/\text{OF}_2$  is about 1/4.

The stoichiometric relationship between water and oxygen difluoride:

$$T = 190^{\circ}\text{C}.$$



A helium stream saturated with water at  $0^{\circ}\text{C}$ . gave a mixture containing 0.31 per cent water which resulted in a 28.5 unit ( $m/e = 18$ ) mass spectrometer response. At 63 per cent reaction a 30.5 unit response resulted which corresponded to 0.33 per cent water in the stream. Thus, the stoichiometric ratio  $\text{H}_2\text{O}/\text{OF}_2$  is about  $1/2$ .

The stoichiometric relationship between hydrogen fluoride and oxygen difluoride:

$$T = 220^{\circ}\text{C}.$$



The flows were adjusted so as to give about 90 per cent reaction. The exit stream was scrubbed with 0.1M NaOH in a series of 3 bubblers. Calcium chloride (0.1M) was used as a precipitating agent. In 30 minutes 4.50 mmoles of oxygen difluoride reacted and 0.286 gm. or 3.67 mmoles of calcium fluoride were collected. Since there are 2 moles of fluoride ion per mole of calcium fluoride, 7.34 mmoles of fluoride ion were produced by the reaction. Thus, the stoichiometric ratio,  $\text{HF}/\text{OF}_2$ , is  $7.34/4.50$  or about 1.6. This value is regarded as a lower limit since there was ample

opportunity for hydrogen fluoride to be lost through reaction with the Pyrex in the system.

0

# APPENDIX H

## Product Addition Studies Hydrogen-Oxygen Difluoride Reaction

The effect of added water on the rate:

T = 170°C.

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>
	1% OF <sub>2</sub> - 2% H <sub>2</sub> - 0.3% H <sub>2</sub> O			
165	15.50	.446	.149	.0078
166	7.75	.380	.167	.0132
167	5.16	.348	.175	.0182
168	3.09	.311	.185	.0272
169	1.72	.272	.196	.0425
170	.97	.231	.207	.0640
171	.52	.174	.222	.0910
	1% OF <sub>2</sub> - 2% H <sub>2</sub>			
165a	15.50	.455	.147	.0079
166a	7.75	.398	.162	.0138
167a	5.16	.374	.168	.0196
168a	3.09	.333	.179	.0292
169a	1.72	.285	.192	.0448
170a	.97	.250	.202	.0692
171a	.52	.197	.216	.1027

The effect of added oxygen on the rate:

	1% OF <sub>2</sub> - 2% H <sub>2</sub> - 0.8% O <sub>2</sub>			
178	15.50	.366	.171	.0063
179	7.75	.241	.204	.0084
180	5.16	.172	.223	.0089
181	3.09	.116	.238	.0100
182	1.72	.070	.250	.0111
183	.97	.046	.256	.0134 *

---

\*Runs 165a through 171a may be used as reference.

The effect of added hydrogen fluoride on the rate:

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>
	1% OF <sub>2</sub> - 2% H <sub>2</sub> - 0.8% HF			
190	15.50	.464	.144	.0081
191	7.75	.401	.161	.0139 *

---

\*Runs 165a and 166a may be used as reference.

# APPENDIX I

## Preliminary Studies of the Oxygen Dependence of the Rate of the Hydrogen-Oxygen Difluoride Reaction

T = 190°C.

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 2% O <sub>2</sub>					
233	14.80	.737	.068	.0128	.188
234	7.40	.548	.116	.0191	.164
235	4.94	.425	.148	.0221	.149
236	2.97	.301	.179	.0262	.146
237	1.64	.201	.205	.0317	.155
238	.93	.124	.225	.0345	.153
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub>					
227	14.80	.710	.075	.0123	.164
228	7.40	.522	.123	.0181	.147
229	4.94	.420	.149	.0219	.147
230	2.97	.300	.180	.0259	.144
231	1.64	.185	.209	.0292	.140
232	.93	.116	.227	.0324	.143

T = 220°C.

1% OF <sub>2</sub> - 5% H <sub>2</sub> - 2% O <sub>2</sub>					
239	13.90	.918	.020	.0158	.790
240	6.94	.800	.048	.0277	.577
241	4.62	.693	.074	.0359	.485
242	2.77	.547	.109	.0473	.434
243	1.54	.386	.147	.0605	.411
244	.87	.271	.175	.0750	.429
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub>					
221	13.90	.876	.030	.0151	.504
222	6.94	.745	.061	.0258	.423
223	4.62	.655	.083	.0340	.410
224	2.77	.504	.119	.0437	.367
225	1.54	.378	.149	.0591	.397
226	.87	.240	.182	.0668	.367

# APPENDIX J

## Studies to Establish the Order with Respect to Oxygen Difluoride for the Fully Inhibited Hydrogen- Oxygen Difluoride Reaction

T = 190°C.

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
0.5% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub>					
251	14.80	.735	.034	.0064	.188
252	7.40	.544	.059	.0095	.161
253	4.94	.430	.074	.0111	.150
254	2.97	.320	.088	.0138	.157
255	1.64	.203	.103	.0159	.154
256	.93	.123	.113	.0173	.153
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub>					
227	14.80	.710	.075	.0123	.164
228	7.40	.522	.123	.0181	.147
229	4.94	.420	.149	.0219	.147
230	2.97	.300	.180	.0259	.144
231	1.64	.185	.209	.0292	.140
232	.93	.116	.227	.0324	.143

T = 220°C.

0.5% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub>					
245	13.90	.850	.018	.0073	.405
246	6.94	.715	.034	.0124	.365
247	4.62	.633	.044	.0169	.384
248	2.77	.495	.061	.0213	.349
249	1.54	.343	.079	.0266	.337
250	.87	.232	.092	.0323	.351
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub>					
221	13.90	.876	.030	.0151	.504
222	6.94	.745	.061	.0258	.423
223	4.62	.655	.083	.0340	.410
224	2.77	.504	.119	.0437	.367
225	1.54	.378	.149	.0591	.397
226	.87	.240	.182	.0668	.367

# APPENDIX K

## Studies to Establish the Order with Respect to Hydrogen of the Fully Inhibited Hydrogen-Oxygen Difluoride Reaction

T = 190°C.

run no.	t	X/(OF <sub>2</sub> ) <sub>0</sub>	(OF <sub>2</sub> )	r	r/(OF <sub>2</sub> )	$\frac{[r/(OF_2)]_5}{[r/(OF_2)]_2}$
		1% OF <sub>2</sub>	2% H <sub>2</sub>	5% O <sub>2</sub>		
257	14.80	.630	.095	.0110	.116	
258	7.40	.458	.139	.0160	.115	
259	4.94	.358	.165	.0186	.113	
260	2.97	.248	.193	.0215	.112	
261	1.64	.151	.218	.0238	.109	
262	.93	.096	.232	.0270	.116	
		1% OF <sub>2</sub>	5% H <sub>2</sub>	5% O <sub>2</sub>		
227	14.80	.710	.075	.0123	.164	1.41
228	7.40	.522	.123	.0181	.147	1.28
229	4.94	.420	.149	.0219	.147	1.30
230	2.97	.300	.180	.0259	.144	1.28
231	1.64	.185	.209	.0292	.140	1.28
232	.93	.116	.227	.0324	.143	1.23

T = 220°C.

		1% OF <sub>2</sub>	2% H <sub>2</sub>	5% O <sub>2</sub>		
263	13.90	.819	.043	.0142	.330	
264	6.94	.690	.074	.0240	.324	
265	4.62	.584	.100	.0303	.303	
266	2.77	.451	.132	.0390	.295	
267	1.54	.298	.168	.0467	.278	
268	.67	.193	.193	.0541	.281	
		1% OF <sub>2</sub>	5% H <sub>2</sub>	5% O <sub>2</sub>		
221	13.90	.867	.030	.0151	.504	1.53
222	6.94	.745	.061	.0258	.423	1.31
223	4.62	.655	.083	.0340	.410	1.35
224	2.77	.504	.119	.0437	.367	1.24
225	1.54	.378	.149	.0591	.397	1.33
226	.67	.240	.182	.0668	.367	1.31



# APPENDIX L

## Studies to Elucidate the Effect of Surface Area on the Rate of the Hydrogen-Oxygen Difluoride Reaction

T = 170°C.

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>
1% OF <sub>2</sub> - 2% H <sub>2</sub> (reactor stuffed)				
369	14.20	.625	.101	.0118
370	7.10	.504	.133	.0192
371	4.74	.435	.152	.0247
372	2.84	.375	.168	.0356
373	1.58	.303	.187	.0519
374	.89	.241	.204	.0731
1% OF <sub>2</sub> - 2% H <sub>2</sub> (reactor normal)				
387	15.10	.539	.124	.0096
388	7.56	.447	.149	.0159
389	5.04	.401	.161	.0214
390	3.02	.358	.173	.0318
391	1.68	.307	.186	.0494
392	.95	.262	.199	.0741
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 5% O <sub>2</sub> (reactor stuffed)				
375	14.20	.455	.147	.0086
376	7.10	.280	.194	.0106
377	4.74	.205	.214	.0116
378	2.84	.142	.231	.0134
379	1.58	.095	.243	.0165
380	.89	.049	.256	.0146
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 5% O <sub>2</sub> (reactor normal)				
381	15.10	.363	.171	.0065
382	7.56	.223	.209	.0079
383	5.04	.161	.225	.0087
384	3.02	.110	.240	.0096
385	1.68	.067	.251	.0107
386	.95	.037	.259	.0106

T = 190°C.

<u>run no.</u>	<u>t</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>r</u>
1% OF <sub>2</sub> - 2% H <sub>2</sub> (reactor stuffed)				
363	13.60	.768	.060	.0145
364	6.80	.656	.088	.0248
365	4.53	.584	.107	.0331
366	2.72	.508	.126	.0481
367	1.51	.427	.147	.0728
368	.85	.336	.171	.1010
1% OF <sub>2</sub> - 2% H <sub>2</sub> (reactor normal)				
345	14.50	.709	.075	.0125
346	7.23	.592	.105	.0120
347	4.83	.538	.119	.0286
348	2.90	.478	.134	.0424
349	1.61	.421	.149	.0670
350	.91	.364	.163	.1040
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 5% O <sub>2</sub> (reactor stuffed)				
357	13.60	.650	.090	.0123
358	6.80	.453	.141	.0170
359	4.53	.348	.168	.0196
360	2.72	.249	.193	.0235
361	1.51	.164	.215	.0278
362	.85	.096	.232	.0295
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 5% O <sub>2</sub> (reactor normal)				
351	14.50	.557	.114	.0099
352	7.23	.385	.158	.0137
353	4.83	.282	.185	.0149
354	2.90	.186	.209	.0166
355	1.61	.112	.228	.0180
356	.91	.062	.241	.0176

# APPENDIX M

## The Order with Respect to Hydrogen for the Fully Inhibited Hydrogen-Oxygen Difluoride Reaction Reactor Stuffed

T = 190°C.

run no.	t	X/(OF <sub>2</sub> ) <sub>0</sub>	(OF <sub>2</sub> )	r	r/(OF <sub>2</sub> )	$\frac{[r/(OF_2)]_5}{[r/(OF_2)]_2}$
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub> (reactor stuffed)						
471	13.60	.680	.082	.0129	.157	
472	6.80	.520	.123	.0182	.148	
473	4.54	.430	.146	.0245	.168	
474	2.72	.301	.180	.0283	.157	
475	1.51	.200	.206	.0338	.164	
476	.85	.130	.224	.0388	.173	
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 5% O <sub>2</sub> (reactor stuffed)						
465	13.60	.672	.084	.0127	.151	1.04
466	6.80	.485	.132	.0184	.140	1.06
467	4.54	.377	.160	.0214	.134	1.25
468	2.72	.261	.190	.0246	.130	1.21
469	1.51	.162	.215	.0278	.129	1.27
470	.85	.099	.232	.0294	.127	1.36

T = 210°C.

1% OF <sub>2</sub> - 5% H <sub>2</sub> - 5% O <sub>2</sub> (reactor stuffed)						
453	13.10	.820	.044	.0154	.350	
454	6.53	.665	.082	.0251	.306	
455	4.35	.558	.109	.0315	.289	
456	2.62	.433	.140	.0405	.289	
457	1.45	.307	.171	.0517	.302	
458	.82	.203	.196	.0614	.313	
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 5% O <sub>2</sub> (reactor stuffed)						
459	13.10	.818	.045	.0153	.340	1.03
460	6.53	.617	.094	.0233	.248	1.23
461	4.35	.533	.115	.0301	.262	1.10
462	2.62	.400	.148	.0374	.253	1.14
463	1.45	.276	.178	.0469	.263	1.15
464	.82	.174	.203	.0527	.260	1.20

# APPENDIX N

## Studies of the Hydrogen-Oxygen Difluoride Reaction with Intermediate Initial Concentrations of Oxygen

T = 170°C.

<u>run no.</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>(H<sub>2</sub>)</u>	<u>(O<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
1% OF <sub>2</sub> - 2% H <sub>2</sub>						
483	.710	.078	.252	.0508	.0123	.158
484	.522	.129	.329	.0380	.0181	.140
485	.458	.146	.355	.0338	.0238	.163
486	.397	.162	.279	.0298	.0347	.214
487	.340	.178	.402	.0258	.0530	.298
488	.276	.195	.428	.0215	.0765	.392
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 0.05% O <sub>2</sub>						
489	.526	.127	.327	.0514	.0092	.073
490	.428	.154	.367	.0446	.0148	.096
491	.367	.168	.388	.0412	.0195	.116
492	.315	.184	.412	.0372	.0275	.149
493	.262	.199	.434	.0334	.0407	.204
494	.207	.213	.456	.0299	.0580	.272
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 0.1% O <sub>2</sub>						
507	.506	.133	.335	.0627	.0088	.066
508	.406	.160	.376	.0560	.0141	.088
509	.334	.179	.405	.0512	.0174	.097
510	.275	.195	.429	.0472	.0240	.123
511	.210	.212	.455	.0430	.0332	.157
512	.160	.226	.475	.0394	.0444	.196
1% OF <sub>2</sub> - 2% H <sub>2</sub> - 0.2% O <sub>2</sub>						
513	.475	.141	.348	.0896	.0083	.059
514	.351	.174	.398	.0782	.0123	.071
515	.293	.190	.421	.0741	.0153	.081
516	.222	.209	.450	.0694	.0194	.093
517	.160	.226	.475	.0651	.0250	.111
518	.102	.241	.499	.0614	.0289	.120

$T = 170^{\circ}\text{C}.$

<u>run no.</u>	<u>X/(OF<sub>2</sub>)</u>	<u>(OF<sub>2</sub>)</u>	<u>(H<sub>2</sub>)</u>	<u>(O<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
1% OF <sub>2</sub> - 5% H <sub>2</sub>						
477	.694	.082	1.069	.0499	.0121	.148
478	.592	.110	1.110	.0428	.0205	.186
479	.550	.121	1.127	.0400	.0287	.237
480	.504	.133	1.146	.0370	.0440	.331
481	.451	.148	1.167	.0332	.0704	.476
482	.410	.159	1.184	.0305	.1140	.718
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 0.05% O <sub>2</sub>						
495	.568	.116	1.120	.0540	.0099	.085
496	.465	.144	1.162	.0471	.0161	.112
497	.420	.156	1.180	.0442	.0219	.140
498	.396	.162	1.190	.0426	.0346	.214
499	.332	.180	1.215	.0382	.0517	.287
500	.287	.192	1.234	.0352	.0795	.414
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 0.1% O <sub>2</sub>						
501	.562	.118	1.122	.0665	.0097	.082
502	.436	.152	1.174	.0580	.0151	.099
503	.380	.167	1.196	.0542	.0198	.118
504	.323	.182	1.219	.0505	.0281	.155
505	.268	.197	1.241	.0467	.0418	.212
506	.216	.210	1.262	.0435	.0610	.290
1% OF <sub>2</sub> - 5% H <sub>2</sub> - 0.2% O <sub>2</sub>						
519	.488	.137	1.153	.0874	.0085	.062
520	.368	.170	1.201	.0792	.0128	.075
521	.302	.188	1.228	.0747	.0157	.084
522	.240	.204	1.253	.0707	.0210	.103
523	.173	.222	1.280	.0662	.0273	.123
524	.119	.237	1.302	.0624	.0331	.140

# APPENDIX O

## Stoichiometric Experiments--the Hydrogen-Oxygen Difluoride Reaction

T = 130°C.

<u>run no.</u>	<u>X/(OF<sub>2</sub>)</u>	<u>(OF<sub>2</sub>)</u>	<u>(H<sub>2</sub>)</u>	<u>(O<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
1% OF <sub>2</sub> - 1% H <sub>2</sub>						
130	.160	.248	.224	.015	.0028	.011
131	.133	.256	.236	.013	.0046	.018
132	.098	.266	.252	.010	.0051	.019
133	.090	.268	.255	.010	.0080	.030
134	.059	.278	.269	.007	.0090	.032
135	.051	.280	.272	.007	.0142	.051
136	.028	.287	.282	.005	.0136	.047
1% OF <sub>2</sub> - 2% H <sub>2</sub>						
111	.197	.237	.503	.018	.0034	.014
112	.151	.250	.524	.014	.0053	.021
113	.126	.258	.536	.012	.0065	.025
114	.095	.267	.548	.010	.0083	.031
115	.080	.271	.555	.009	.0127	.047
116	.056	.278	.566	.007	.0160	.058
117	.042	.282	.571	.006	.0229	.081
0.5% OF <sub>2</sub> - 1% H <sub>2</sub>						
63	.196	.119	.253	.010	.0017	.014
64	.139	.128	.266	.008	.0024	.019
65	.129	.129	.267	.008	.0033	.026
66	.081	.136	.278	.006	.0035	.026
67	.050	.141	.285	.005	.0038	.027
68	.043	.142	.287	.005	.0056	.040
69	.035	.143	.288	.004	.0086	.060

<u>run no.</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>(H<sub>2</sub>)</u>	<u>(O<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
		0.5% OF <sub>2</sub> - 5% H <sub>2</sub>				
36	.266	.109	1.480	.013	.0023	.021
37	.210	.117	1.480	.011	.0036	.031
38	.175	.122	1.480	.010	.0046	.038
39	.149	.126	1.480	.009	.0064	.051
40	.128	.129	1.480	.008	.0100	.077
41	.088	.135	1.480	.006	.0121	.090 *
42	.040	.142	1.480	.005	.0108	.076 *

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\*This point was not used in the treatments since it was significantly out of line.

T = 150°C.

<u>run no.</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>(H<sub>2</sub>)</u>	<u>(O<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
1% OF <sub>2</sub> - 1% H <sub>2</sub>						
137	.255	.209	.174	.021	.0044	.021
138	.212	.221	.192	.018	.0074	.034
139	.198	.225	.198	.017	.0104	.046
140	.157	.237	.215	.014	.0136	.058
141	.134	.244	.224	.012	.0206	.085
142	.106	.251	.237	.011	.0295	.118
143	.068	.262	.252	.008	.0337	.129 *
1% OF <sub>2</sub> - 2% H <sub>2</sub>						
104	.340	.186	.419	.027	.0059	.032
105	.237	.204	.446	.022	.0095	.047
106	.247	.212	.458	.020	.0128	.060
107	.219	.220	.470	.018	.0188	.085
108	.168	.234	.491	.015	.0261	.112
109	.142	.241	.502	.013	.0394	.164
110	.095	.255	.522	.010	.0478	.188 *
0.5% OF <sub>2</sub> - 1% H <sub>2</sub>						
70	.228	.109	.234	.011	.0020	.018
71	.182	.115	.241	.010	.0032	.031
72	.161	.118	.248	.009	.0042	.036
73	.141	.121	.252	.008	.0062	.051
74	.127	.123	.255	.007	.0100	.081
75	.087	.129	.264	.006	.0118	.091
0.5% OF <sub>2</sub> - 5% H <sub>2</sub>						
43	.390	.086	1.410	.017	.0034	.040
44	.333	.094	1.410	.015	.0058	.062
45	.308	.098	1.410	.014	.0081	.083
46	.279	.102	1.410	.013	.0122	.120
47	.247	.106	1.410	.012	.0194	.183
48	.207	.112	1.410	.010	.0287	.256
49	.157	.119	1.410	.009	.0417	.350 *



T = 170°C.

<u>run no.</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>(H<sub>2</sub>)</u>	<u>(O<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
1% OF <sub>2</sub> - 1% H <sub>2</sub>						
144	.395	.163	.110	.0295	.0068	.042
145	.324	.182	.138	.0247	.0112	.062
146	.293	.190	.151	.0227	.0153	.081
147	.247	.203	.169	.0195	.0214	.105
148	.200	.215	.188	.0165	.0314	.146
149	.176	.222	.198	.0157	.0486	.219
150	.150	.229	.208	.0130	.0747	.326 *
1% OF <sub>2</sub> - 2% H <sub>2</sub>						
97	.506	.133	.334	.0370	.0088	.066
98	.416	.157	.370	.0310	.0144	.092
99	.376	.168	.386	.0282	.0196	.117
100	.311	.185	.413	.0240	.0272	.147
101	.281	.193	.424	.0220	.0442	.229
102	.242	.204	.440	.0192	.0671	.329
103	.185	.219	.464	.0155	.0970	.443 *
0.5% OF <sub>2</sub> - 1% H <sub>2</sub>						
76	.375	.084	.194	.0143	.0033	.039
77	.327	.091	.204	.0125	.0057	.062
78	.300	.094	.210	.0117	.0079	.084
79	.258	.100	.218	.0103	.0113	.113
80	.234	.103	.223	.0095	.0185	.180
81	.200	.108	.230	.0083	.0278	.257
82	.132	.117	.243	.0060	.0342	.292 *
1% OF <sub>2</sub> - 5% H <sub>2</sub>						
18	.613	.104	1.345	.0442	.0106	.102
19	.551	.121	1.345	.0400	.0191	.158
20	.462	.145	1.345	.0340	.0240	.166
21	.428	.154	1.345	.0317	.0372	.242
22	.404	.160	1.345	.0303	.0634	.396
23	.387	.165	1.345	.0290	.1070	.648 *

T = 190°C.

<u>run no.</u>	<u>X/(OF<sub>2</sub>)<sub>0</sub></u>	<u>(OF<sub>2</sub>)</u>	<u>(H<sub>2</sub>)</u>	<u>(O<sub>2</sub>)</u>	<u>r</u>	<u>r/(OF<sub>2</sub>)</u>
1% OF <sub>2</sub> - 1% H <sub>2</sub>						
151	.633	.094	.013	.0437	.0110	.117
152	.513	.125	.059	.0360	.0178	.142
153	.451	.141	.083	.0320	.0235	.167
154	.386	.158	.108	.0277	.0334	.211
155	.333	.171	.128	.0245	.0524	.306
156	.277	.186	.150	.0208	.0767	.412
157	.222	.200	.171	.0173	.1110	.555 *
1% OF <sub>2</sub> - 2% H <sub>2</sub>						
90	.588	.106	.287	.0407	.0102	.096
91	.540	.118	.306	.0377	.0188	.159
92	.490	.131	.325	.0345	.0255	.195
93	.439	.144	.345	.0312	.0380	.264
94	.408	.152	.357	.0292	.0640	.421
95	.381	.159	.367	.0275	.1060	.666 *
96	.291	.182	.402	.0218	.1510	.830 *
0.5% OF <sub>2</sub> - 1% H <sub>2</sub>						
83	.532	.060	.155	.0188	.0046	.078
84	.428	.074	.175	.0152	.0074	.100
85	.414	.076	.178	.0147	.0107	.141
86	.355	.083	.189	.0130	.0155	.187
87	.315	.088	.197	.0117	.0250	.284
88	.298	.091	.201	.0110	.0410	.451
89	.218	.101	.216	.0085	.0556	.550 *
1% OF <sub>2</sub> - 5% H <sub>2</sub>						
24	.854	.039	1.285	.0576	.0147	.377 *
25	.693	.082	1.285	.0467	.0237	.289
26	.644	.095	1.285	.0435	.0328	.345
27	.583	.107	1.285	.0405	.0505	.472
28	.570	.110	1.285	.0398	.0896	.815 *
29	.544	.117	1.285	.0380	.1510	1.290 *

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