A STUDY OF THE KINETICS OF SOME FORMATION AND ISOTOPE EXCHANGE REACTIONS INVOLVING THE CHLORINE FLUORIDES

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By

James Parkhurst Phelps

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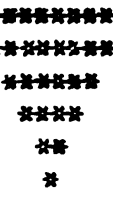

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I. INTRODUCTION

The study of reaction kinetics is one method of obtaining information about the structure of molecules. Whether the study is concerned with rates, mechanisms, and energetics of chemical reactions in the classical sense, that is, reactions in which products are different chemical species from reactants, or with rates, mechanisms, and energetics of isotope exchange reactions in which products are chemically equivalent to reactants is important only from the viewpoint of specific information desired. Both methods of attack yield data important in determining the structural nature of reactants and products.

Although some work dealing with isotope exchange in the halogen fluorides has been reported, there are almost no classical reaction-kinetic data for these compounds.

The present work deals with both isotope exchange kinetics and reaction kinetics, with, perhaps, the emphasis on the former. The systems chlorine trifluoride and chlorine, chlorine trifluoride and chlorine monofluoride, and chlorine monofluoride and chlorine have been studied to determine isotopic chlorine exchange in the gas phase. In addition, the chemical reaction kinetics of the system chlorine trifluoride and chlorine have been studied.

Special equipment suitable for studying gaseous reactions of halogen fluorides has been designed and constructed, including equipment for the study of isotope exchange in which a radioactive isotope is utilized.

II. HISTORICAL SURVEY OF HALOGEN FLUORIDES

The known stable halogen fluorides are chlorine monofluoride, chlorine trifluoride, bromine monofluoride, bromine trifluoride, bromine pentafluoride, iodine pentafluoride, and iodine heptafluoride. Excellent general reviews of the chemical and physical properties of these compounds have been given by Thompson (1), Sharpe (2), Greenwood (3), and Booth and Pinkston (4,5). Specific information on conductivities, magnetic susceptibilities, and vapor pressure studies is given by Panish (6), and on electric moments by Pruett(7).

Because the present work is concerned almost exclusively with the chlorine fluorides, attention will be focused upon chlorine monofluoride and chlorine trifluoride. These compounds, in common with all of the halogen fluorides, are extremely reactive, chlorine trifluoride being one of the most reactive materials known. This fact necessitates special techniques and equipment, the details of which are discussed later, for their study.

Production of the Chlorine Fluorides

There are almost no kinetic data available concerned solely with the formation of halogen fluorides, nor is there extensive information on the yields of chlorine monofluoride or trifluoride under varying conditions. Ruff and his associates (8,9) first made chlorine monofluoride by the action of slightly moist hydrogen chloride on fluorine

at room temperature; if the gases were dry there was no reaction below 250° C. On the other hand, Domange and Neudorffer (10) reported that the reaction between fluorine and chlorine in one-to-one ratio to form chlorine monofluoride proceeds readily at 220° C. to 230° C. A further method was found by Schmitz and Schumacher (11), who prepared the monofluoride by allowing chlorine and chlorine trifluoride to react at 250° C.

Chlorine trifluoride was first made by Ruff and Krug (12) by passing a mixture of chlorine and excess fluorine through a tube heated to 250° C., a process which produced very small amounts of product. At -170° C., a three-to-two mixture of chlorine to fluorine yielded a ratio of one to four of chlorine trifluoride to chlorine monofluoride. Ruff and Krug concluded that the better yields of the trifluoride were obtained at lower temperatures. However, Swinehart (13) reported that the direct union of chlorine and fluorine in a copper reaction vessel at 200° C. proceeds immediately to chlorine trifluoride. Schmitz and Schumacher (11) found that the reaction

$$ClF + F_2 = ClF_3$$

is reversible, and obtained the values shown in Table I for the equilibrium constant

$$K_p = \frac{P\ ClF \cdot P\ F_2}{P\ ClF_3}$$

TABLE I

EQUILIBRIUM CONSTANTS FOR THE FORMATION OF CHLORINE TRIFLUORIDE

T	°C.	180	200	220	250	300	350
K_p	atm. x 10^4	0.069	0.212	0.63	2.98	24	143

Isotope Exchange Reactions

The radioactive nuclide F^{18} has been used for several investigations of isotope exchange between halogen fluorides and other fluorine-containing compounds. Rogers and Katz (14) studied the exchange between hydrogen fluoride and some interhalogens. Exchange in the liquid phase at room temperature was found to be practically instantaneous in the following systems: HF and BrF_3 ; HF and ClF_3 ; HF and BrF_5 ; HF and IF_5 ; ClF_3 and BrF_3. These exchanges were postulated to occur through ionic equilibria. In the gas phase, exchange in the following systems: HF and ClF_3 ; HF and ClF ; HF and BrF_3 ; HF and BrF_5 ; and HF and IF_7 was also instantaneous at room temperature. The formation of intermediate complexes was postulated to account for these exchanges. Bernstein and Katz (15) found no exchange between elemental fluorine and halogen fluorides at temperatures below 100°C., but measurable exchange rates above 200° C. Adams, Bernstein and Katz (16) studied the kinetics of isotope exchange between elemental fluorine and the interhalogens chlorine trifluoride, bromine pentafluoride, and iodine heptafluoride. Gas phase exchange in the temperature range 181° C. to 257° C. was found to occur by either a heterogeneous mechanism, or a combination of heterogeneous and homogeneous mechanisms.

Other exchange reactions, while not strictly halogen fluoride reactions, are pertinent. Dodgen and Libby (17) found no exchange between hydrogen fluoride and fluorine at room temperature, but a measurable rate at 210° C. in a copper reaction vessel. Adams,

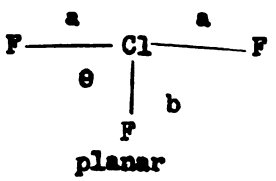
Bernstein and Katz (18) studied the kinetics of the hydrogen fluoride-fluorine system in nickel apparatus between 194° C. and 257° C., and found that exchange occurred by a heterogeneous mechanism. On the other hand, chlorine exchange between gaseous hydrogen chloride and chlorine is rapid at room temperature but was shown by Libby and Johnson (19) to be surface catalyzed, or heterogeneous. The hydrogen bromide-bromine system undergoes rapid exchange in the gas phase at room temperature (20), as does the system hydrogen iodide-iodine (21), but the mechanism of exchange is not known (21,22).

Summary of Properties of the Chlorine Fluorides

Because many of the experimental procedures as well as the treatment of results involved in the work to be described are closely connected with physical properties, some of the properties of the chlorine fluorides are listed in Tables II, III and IV. Some properties of certain halogens have been listed for later reference.

TABLE II

PROPERTIES OF THE CHLORINE FLUORIDES AND CHLORINE

	ClF	ClF_3	Cl_2
Boiling Point, °C.	-100.8 (4)*	11.3 (4)	-34.6 (26)
Melting Point, °C.	-154 (4)	-83 (4)	-101.6 (27)
Dipole Moment, D	0.88(23)	0.554 (24)	--
Density, g/ml. at 0°C.	--	1.891 (4)	0.003214 (26)
Dielectric Constant at 20°C.	--	4.28 (1)	1.98 (28)
Configuration	--	 planar	--
Bond Length, Å.	1.628 (23)	θ= 87°29' a= 1.698 (25) b= 1.598	1.984 (29)
Bond Strength,** kcal/mole at 25°C.	60.6	40.3***	58.0

* References are given in parentheses.
** Calculated from thermochemical data in Table III.
*** Average bond energy.

TABLE III

SOME THERMOCHEMICAL VALUES FOR THE HALOGENS AND THE CHLORINE FLUORIDES IN THE GAS PHASE AT 1 ATMOSPHERE PRESSURE (30)

Symbol	ΔH_f, kcal/mole		ΔF_f, kcal/mole (*)				S° cal/deg. mole
	298.16°K	500°K	298.16°K	476.56°K	497.46°K	518.56°K	298.16
F	18.903	19.19	14.820	12.30	12.00	11.69	37.9173
F_2	0	0	0	0	0	0	48.447
Cl	28.942	29.17	25.122				39.4569
Cl_2	0	0	0	0	0	0	53,291
ClF	-11.923	-11.94	-12.279	-12.483	-12.507	-12.532	52.062
ClF_3	-37.29	-37.10	-27.96	-22.42	-21.77	-21.13	68.04

* ΔF_f values at 476.56°K, 497.46°K, and 518.56°K obtained graphically from literature values at 400°K., 500°K, and 600°K.

TABLE IV

Kp VALUES* FOR THE EQUILIBRIUM $(ClF_3)_2 \rightleftharpoons 2ClF_3$

T in °C.	Kp in Atm.
9.5	26.9
20.0	32.1
24.2	35.4

* Reference (4).

III. GAS-HANDLING, REACTION, AND COUNTING APPARATUS

Because of the high reactivity of all of the halogen fluoride compounds, particularly chlorine trifluoride, a special system was constructed. This system was housed in a hood equipped with sliding safety-glass doors, the frames of which were asbestos covered. Nickel, Monel,[1] and fluorothene were used extensively. One reaction chamber was constructed of copper, and copper tubing was used for several non-permanent connections.

The Gas-Handling System

A schematic diagram of the apparatus is shown in Figure 1, and a photograph in Figure 2. Pressures of the gases were read from a Helicoid[2] Bourdon gauge and were considered accurate to within one millimeter of mercury. Low pressures were obtained from a McLeod Gauge mercury manometer. Temperatures were obtained from thermometers calibrated against a secondary standard which in turn was calibrated against a platinum resistance thermometer.[3] Various traps for measuring portions of chlorine trifluoride, chlorine monofluoride, and chlorine were included, as well as a system designed for trap-to-trap distillation. A copper expansion or reaction vessel was constructed and placed

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[1] Monel is the trade mark name of the International Nickel Company for a high nickel-content alloy.

[2] Manufactured by American Chain and Cable Company.

[3] A Mueller Bridge was used.

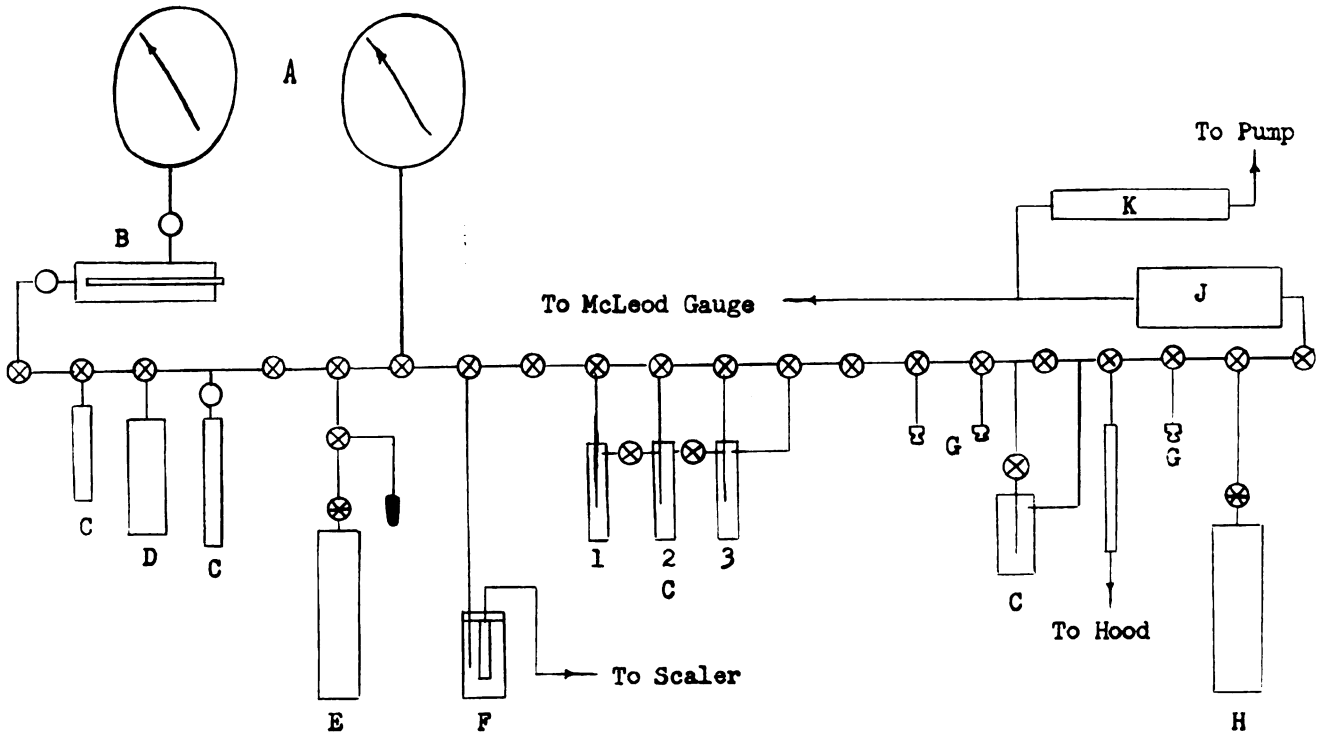

Figure 1. Schematic diagram of the exchange and gas-handling apparatus for halogen fluorides: A, Helicoid pressure gauges, 0-1500 mm. Hg absolute; B, nickel reaction chamber; C, Monel or nickel traps for handling and distilling materials; D, copper expansion vessel; E, radioactive chlorine storage tank; F, nickel gas-counting chamber; G, connections for cells or traps; H, chlorine trifluoride storage tank; J, soda lime tower; K, drying tower; ⊗ , straight-through or T-valves with phosphor-bronze bellows; ⊗ , valves supplied on gas cylinders; ○ , valves with Inconel diaphragm.

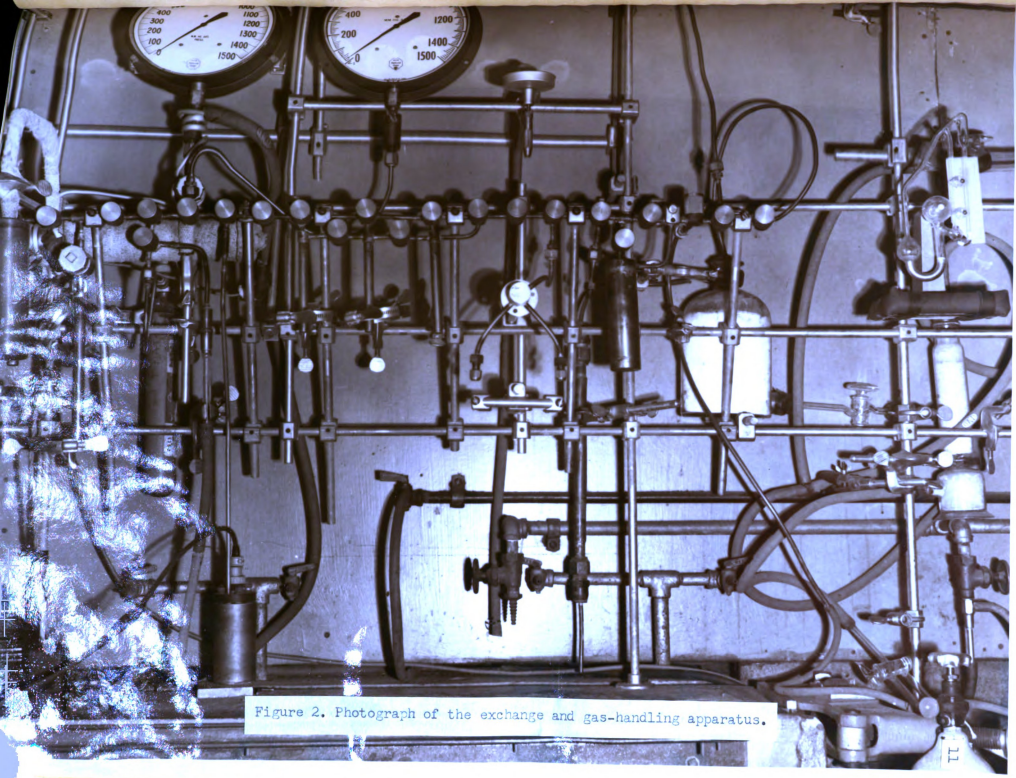

Figure 2. Photograph of the exchange and gas-handling apparatus.

in a position such that it could be surrounded with a hot bath for experiments above room temperature. A steel cylinder was used for the storage of radioactive chlorine gas; another steel cylinder contained chlorine trifluoride. A nickel reaction chamber and a counting chamber for radioactive gases were connected to the gas-handling system; details of these devices will be given later. The system was evacuated by means of a Cenco Hyvac vacuum pump which was protected from halogen fluoride gas by a large bottle of soda-lime, and from water by a drying tower filled with anhydrous calcium sulfate. Several take-off connections with flare fittings were made. The main manifold line of the system and the individual connections to traps, storage and reaction chambers, gauges, and so forth were one-quarter inch outside diameter nickel or Monel tubing. All permanent connections were silver-soldered, as were the various end-caps used in constructing traps, reaction chambers, and counting chamber. Valves were either phosphor-bronze bellows valves with nickel or nickel alloy bases, or Inconel[1] diaphragm valves.

The Gas Reaction Chamber

A schematic diagram of the nickel reaction chamber is given in Figure 3. The chamber was about 24 cm. long and about 4.15 cm. in diameter, and had an inside volume of 311.9 ml. A thermometer well was silver soldered into the center of the chamber, extending back about three-quarters of the total length. The outside of the chamber

[1] Inconel is the trade mark name of the International Nickel Company for a high nickel-content alloy.

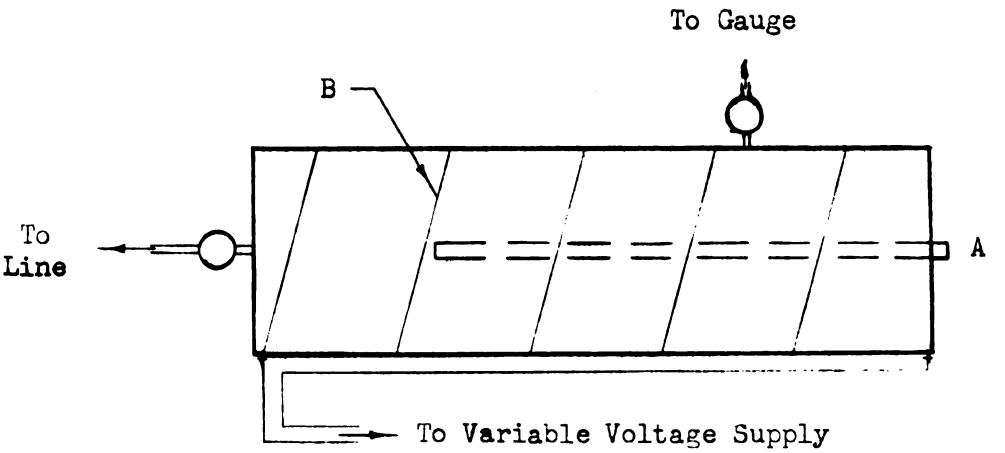

Figure 3. Schematic diagram of the nickel reaction chamber: A, thermometer well; B, nichrome resistance wire; ◯, Inconel diaphragm valves.

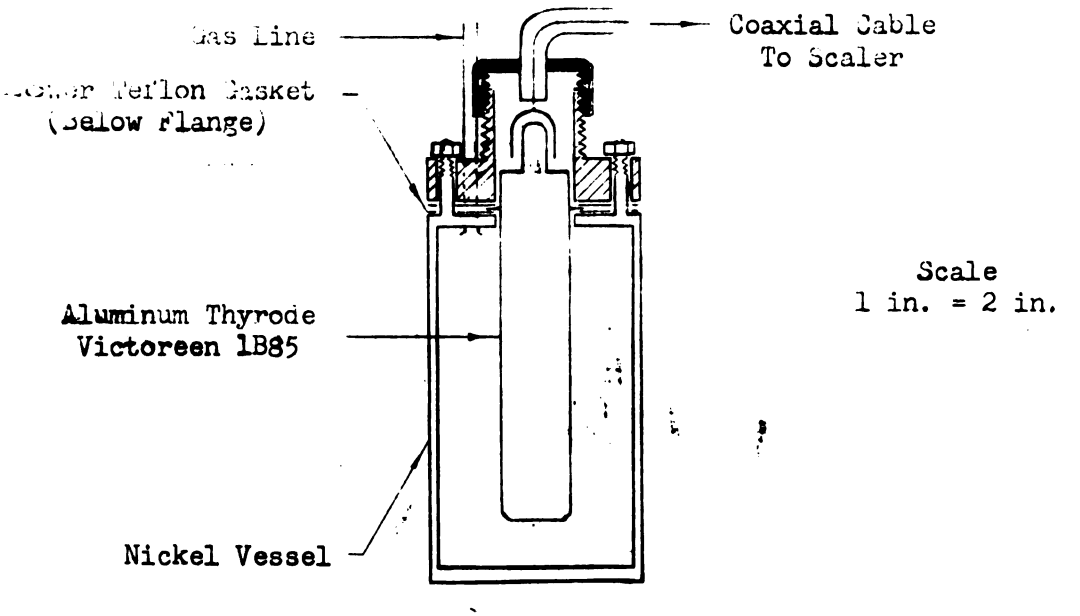

Figure 4. Cross-section of the gas-counting chamber.

was covered with a thin fiber-glass net over which was wrapped nichrome resistance wire. This wire wrapping was covered with several layers of asbestos tape to minimize heat loss to the surroundings. Ends of the nichrome wire were connected to a variable-voltage or auto-transformer, so that the temperature attained in the chamber, which was a function of the voltage applied across the wire, was adjustable. In order to decrease fluctuations in temperature caused by fluctuations in line voltage, a constant voltage transformer was placed between line voltage and auto-transformer. In this way it was possible to maintain the reaction chamber temperature at a reasonably constant value ($\pm 0.5^{\circ}C.$) throughout a given experiment, even though the reaction temperature was considerably higher than room temperature. Aluminum tubing was coiled about the valve between the hot chamber and the main line as well as the valve between the hot chamber and the Helicoid gauge. During experiments in which the reaction chamber was heated, tap water was circulated in the tubing. The reason for this cooling was two-fold. First, both valves involved depend on a flexible nickel alloy (Inconel) diaphragm, which is tough, but nonetheless thin, and consequently a critical weakness of the system if allowed to be in contact with halogen fluorides at high temperatures. Second, the valve between chamber and gauge was closed during certain experiments, and the temperature of the gas enclosed in the gauge as well as that of the gas enclosed in the hot chamber was required for calculation of results. It was thus necessary to have, in addition to the volumes involved, some sharp defining point in the connection such that gas

below that point could be said to be at hot chamber temperature, and gas above that point at another temperature. The valve was ideal for this juncture.

The Gas-Counting Chamber

A cross-section of the gas-counting chamber is given to scale in Figure 4. The main body of the chamber was prepared to house a Victoreen 1B85 Aluminum Thyrode. This counting tube is especially designed to replace thin-walled glass tubes. It has a greater shock and vibration resistance than glass tubes, and the inertness of aluminum to halogen fluorides makes the tube valuable for the present application. In addition, although thin enough to detect 0.16 mev. beta particles, the aluminum shell is constructed to resist implosion, and therefore is suitable for gas-counting application. Near the top, the tube is flanged; this flange was sandwiched with Teflon* gaskets which served to make a vacuum-tight seal between chamber and tube when the specially constructed cap was placed over the tube and bolted in place. A coaxial cable connected the counting tube to a Radioactive Products Incorporated Raychronix Model A-4 scaler.

Because radioactive material was being used in the experiments, certain precautions were necessary. Radioactive materials were stored in a specific area. The nature of the investigations carried out made it necessary to produce radioactive chlorine gas from radioactive hydrogen chloride (the details of this procedure are given in a later

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*Teflon is the trade mark name for E. I. DuPont de Nemours Company's tetrafluoroethylene polymer.

section); chlorine gas could then be stored for use as required. It did not leave the metal handling system until pumped through the soda-lime bottle. Any gas passing through the system plus pump escaped by way of a hood. Therefore, the time of greatest danger of contamination was during radioactive chlorine production and the subsequent disposal of waste materials. Careful monitoring of activity was done with a Nuclear Instrument and Chemical Corporation Survey Meter, Model 2610A, before, during and after these productions; residues and wastes were discarded through a University disposal system. Monitoring was periodically and independently done by a representative of the University Radioactive Isotopes Committee.

Absorption Cells

A 10 cm. infrared absorption cell suitable for use with halogen fluoride gases was constructed. This is drawn to scale in Figure 5 and photographed in Figure 7. The body of the cell was nickel; windows were rolled sheet silver chloride; the cell end-plate and adapter (for Perkin Elmer Model 21) was brass. This cell was used for experiments discussed in Appendix I.

A 10 cm. gas absorption cell suitable for investigation of the ultra-violet absorption spectrum of halogen fluoride materials is shown in Figures 6 and 7. The cell body was nickel; fluorothene-sheet windows were held in position by brass end-caps. In the lower region of the ultra-violet spectrum, fluorothene itself absorbs some light. The absorption spectrum, balanced against air, of fluorothene about

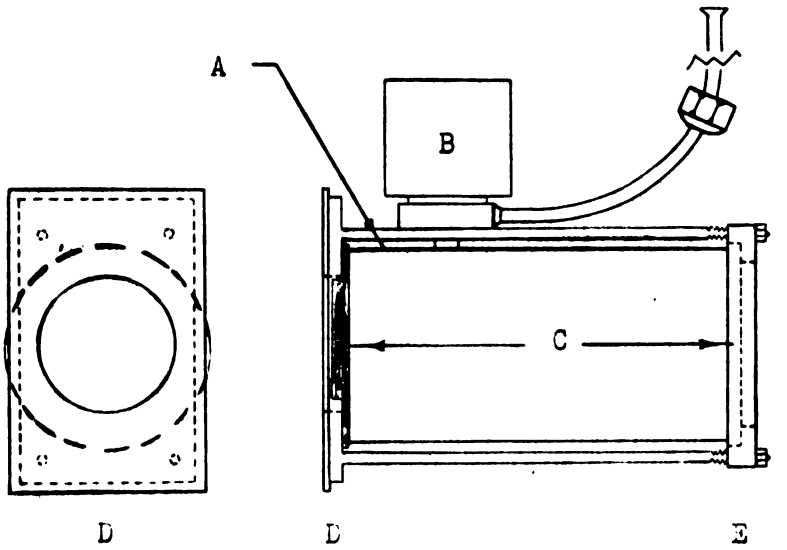

Figure 5. Infrared absorption cell: A, nickel cylinder; B, phosphor-bronze bellows valve; C, silver chloride windows; D, brass end plate machined to fit Perkin Elmer (model number 21) adapter; E, brass end cap.

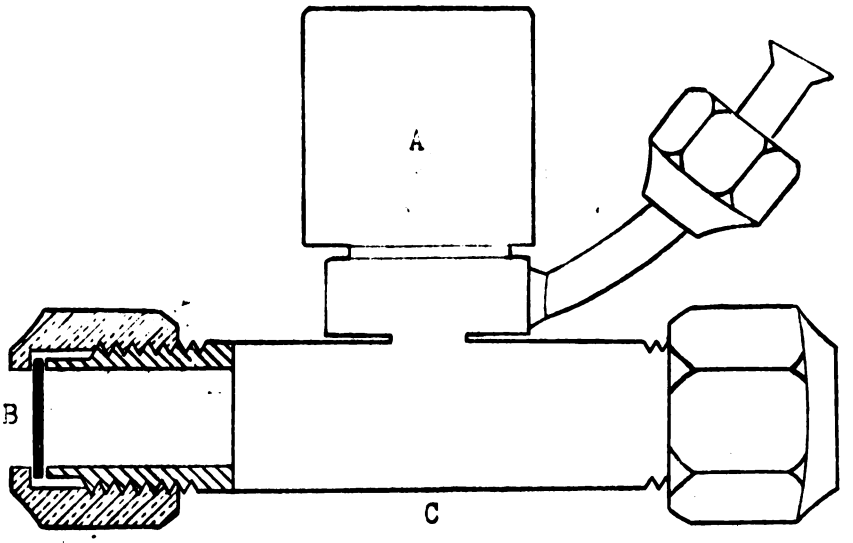

Figure 6. Ultra-violet 10 cm. absorption cell. A, phosphor-bronze bellows valve; B, fluorothene window; C, nickel cylinder.

Figure 7. Photograph of two indicator cells and two microwindow cells.

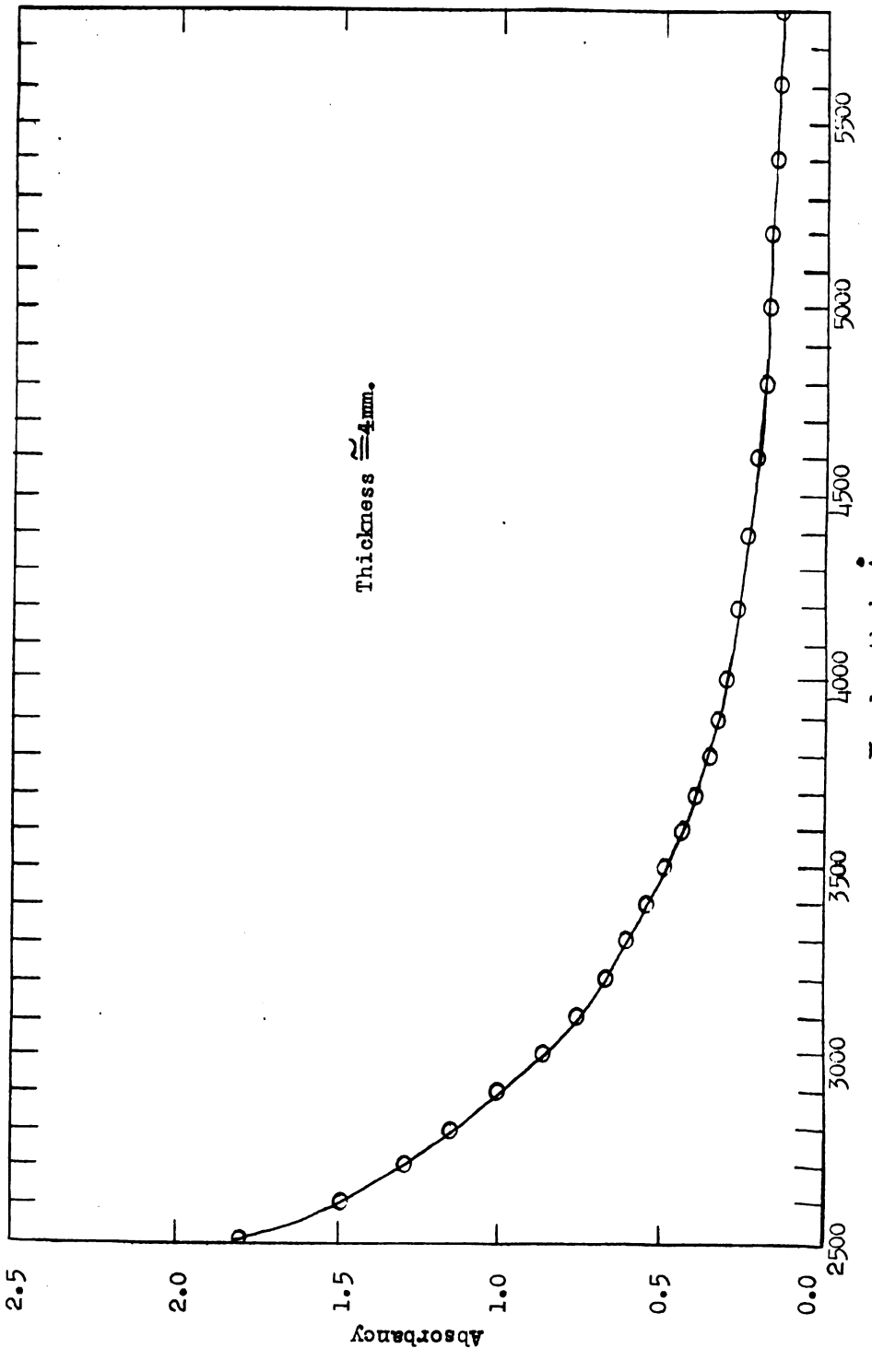

Figure 8. Ultra-violet absorption of fluorothene.

four times as thick as that used in cell windows is shown in Figure 8. Because of this absorption, a matched pair of cells was made. One evacuated cell was used as a reference, while the other, containing gas to be investigated, was balanced against the reference cell. These cells are suitable for use with the Beckman Model DU Spectrophotometer.

IV. THEORETICAL ASPECTS OF KINETICS AND EXCHANGE REACTIONS

Kinetics

Study of the rates at which reactions occur and the influence of conditions on these rates is called chemical kinetics (31). In most cases, the rate of a chemical change is proportional to the concentrations of reacting substances; consequently, the speed of the process must decrease as the reactants are being consumed. The curve of reaction rate versus time approaches the time axis asymptotically with very large time values. In practice, because the continuous rate is normally difficult to ascertain, the reaction rate or speed is determined at a particular instant; valuable results can be obtained from these data.

Reactions are divided into classes which are based on the experimentally determined order of the reaction, that is, the number of atoms or molecules whose concentrations determine the speed, or kinetics of the process. Often, results thus obtained are interpreted in terms of the molecularity of the reaction, or the number of atoms or molecules taking part in each elementary step leading to chemical reaction. Although the order and the molecularity of a reaction are not necessarily identical, the determination of the molecularity usually requires much more information than the relatively simple, kinetically-obtainable, order. Because of this, and because one aim of kinetics is to determine the elementary steps of a process, the experimental order is frequently taken to be the same as the molecularity. Fortunately, this is often the case.

Chemical reactions are not always simple; complications may arise as a result of side reactions, reversible reactions, heterogeneous (surface catalyzed) processes and other causes. For purposes of defining classes of reactions, only isolated reactions free from secondary effects will be considered.

As a representative class, consider a second-order reaction, that is, one in which the rate at any instant is directly proportional to the concentrations of the reactants, or mathematically

$$1) \quad \frac{dx}{dt} = k\,(a-x)\,(b-x) \qquad ; \qquad a \neq b$$

where $\frac{dx}{dt}$ = the rate of reaction

k = specific reaction rate constant

a = initial concentration of reactant A

b = initial concentration of reactant B

x = the decrease of A after time t = decrease of B after time t.

If equation (1) is integrated, taking into consideration that $x = o$ when $t = o$, and $x = x$ when $t = t$, then

$$2) \quad kt = \frac{2.303}{(a-b)} \log \left[\frac{b(a-x)}{a(b-x)} \right] \qquad ; \; a \neq b$$

$$3) \quad kt \,/\, \frac{2.303}{(a-b)} = \log \left(\frac{a-x}{b-x}\right) + \log \frac{b}{a} \; ; \; a \neq b$$

Therefore, if a reaction is second order, a plot of the experimentally determined $\log \left(\frac{a-x}{b-x}\right)$ values versus t should yield a straight line. The slope of the line affords a means of evaluating k. For the case $a = b$, equation (1) simplifies to

4) $\frac{dx}{dt} = k\,(a-x)^2$

which yields, on integration

5) $kt = \frac{1}{a}\left(\frac{x}{a-x}\right)$

Here, a plot of $\left(\frac{x}{a-x}\right)$ versus t should result in a straight line for a second-order reaction.

Classes of zero, first, and third, as well as fractional order reactions may be treated in a manner entirely analogous to that used for the second-order case above.

In addition to strict classes of reactions, it is often possible to deduce mechanisms by postulating a reasonable series of steps leading ultimately from reactants to products, setting up the differential equations indicated by these steps, performing the necessary calculations, and comparing the final rate equation with that determined experimentally. In this process, the intermediate steps are not particularly limited; they may involve radicals, ions, molecular complexes, and so forth, even combinations of the above.

Heterogeneous processes are brought about by surface adsorption of reactant or reactants. Following adsorption, reaction occurs at the surface, after which products are desorbed. Of interest in this connection is the Langmuir isotherm for two adsorbates (36).

6) $\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}$; $\theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B}$

Where θ_A and θ_B = fractions of surface area covered by A and B at partial pressures P_A and P_B

b_A and b_B = adsorption coefficients

Because b_A and b_B are determined empirically, (6) may also be written

$$\theta_A = \frac{b'_A C_A}{1 + b'_A C_A + b'_E C_B} \quad ; \quad \theta_B = \frac{b'_B C_B}{1 + b'_A C_A + b'_E C_B}$$

Where C_A and C_B = concentrations of A and B.

Three cases are of interest

First: two reactants, both weakly adsorbed.

7) $$\text{rate} = -\frac{dP}{dt} = k\,\theta_A\theta_B = k'\,P_A P_B$$

Second: two reactants, A weakly and B moderately adsorbed.

8) $$\text{rate} = -\frac{dP}{dt} = k\,\theta_A\theta_B = \frac{k\,b_A b_B P_A P_B}{(1 + b_B P_B)^2} = k'\,\frac{P_A P_B}{(1 + b_B P_B)^2}$$

Third: two reactants, A weakly and B strongly adsorbed.

9) $$\text{rate} = -\frac{dP}{dt} = k\theta_A\theta_B = \frac{k\,b_A b_B P_A P_B}{b_B^2 P_B^2} = k'\,\frac{P_A}{P_B}$$

Temperature Dependence and Energy of Activation

In most cases, the dependence of reaction rate on temperature may be expressed by the Arrhenius Equation

10) $$k = A \exp\left(-\frac{\Delta Ea}{RT}\right)$$

where k = specific reaction rate constant

A = frequency factor

ΔEa = energy of activation

R = molar gas constant = 1.986 cal./mole deg.

T = temperature in degrees K.

The energy of activation for a reaction can be calculated from specific reaction rate values at two temperatures.

Entropy of Activation

For any elementary reaction, the specific reaction rate constant, k, may be defined as a constant, $K^{\ddagger}$, multiplied by a universal frequency factor (32) $\frac{K_B T}{h}$

Where K_B = Boltzmann constant = 1.3803×10^{-16} $\frac{\text{erg}}{\text{molecule degree}}$

T = temperature in degrees K.

h = Planck's constant = 6.623×10^{-27} erg second

Thus

11) $$k = \frac{K_B T}{h} K^{\ddagger}$$

Although $K^{\ddagger}$ is not strictly an equilibrium constant, it is similar to one. Therefore, it is possible to define the free energy of activation, $\Delta F^{\ddagger}$, by

12) $$\Delta F^{\ddagger} = -RT \ln K^{\ddagger} = -RT \ln \left(\frac{hk}{K_B T}\right)$$

and the heat of activation, $\Delta H^{\ddagger}$ by

13) $$\Delta H^{\ddagger} = RT^2 \frac{d \ln Kp^{\ddagger}}{dT} = RT^2 \frac{d \ln K_c^{\ddagger}}{dT} - (n-1) RT$$

where $Kp^{\ddagger}$ is $K^{\ddagger}$ in pressure units

$K_c^{\ddagger}$ is $K^{\ddagger}$ in concentration units

n is the molecularity (and order) of the reaction

then

$$14) \quad \Delta H^{\ddagger} = RT^2 \frac{d \ln \left[k \left(\frac{h}{K_B T} \right) \right]}{dT} - (n-1)\, RT$$

or

$$15) \quad \Delta H^{\ddagger} = RT^2 \frac{d \ln k}{dT} - RT - (n-1)\, RT$$

$$16) \quad \Delta H^{\ddagger} = RT^2 \frac{d \ln k}{dT} - n\, RT$$

But from the Arrhenius equation,

$$17) \quad \ln k = -\frac{\Delta Ea}{RT} + \ln A$$

$$\frac{d \ln k}{dT} = \frac{\Delta Ea}{RT^2}$$

$$18) \quad RT^2 \frac{d \ln k}{dT} = \Delta Ea$$

Therefore

$$19) \quad \Delta H^{\ddagger} = \Delta Ea - n\, RT$$

Once $\Delta F^{\ddagger}$ and $\Delta H^{\ddagger}$ are obtained, then the entropy of activation, $\Delta S^{\ddagger}$, can be determined from the relationship

$$20) \quad \Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T}$$

Exchange Reactions

Exchange reactions are somewhat different from usual reactions, because the original concentrations of reactants do not change during the course of reaction. Often exchange is followed by means of

radioactive isotopes, although isotopic mass differences are utilizable with the aid of a mass spectrograph. In order to derive a quantitative exchange law, consider the schematic reaction (33).

21) $AX + BX^* = AX^* + BX$

Where A and B represent different atoms or radical groups; X^* represents a radioactive atom of X.

Define, in mole/liter concentrations

$AX + AX^* = a$

$BX + BX^* = b$

$AX^* = x$

$BX^* = y$

$x + y = z$

Neglecting radioactive decay, and any isotope effects, the rate of increase $\frac{dx}{dt}$ of AX^* is given by

22) $$\frac{dx}{dt} = R\frac{y}{b}\left(\frac{a-x}{a}\right) - R\frac{x}{a}\left(\frac{b-y}{b}\right) = \frac{a+b}{ab} R x + \frac{z}{b} R$$

Where R = the rate of the reaction between AX and BX in the dynamic equilibrium.

Integration of 22) under the conditions, $t = \infty$, $x = x_\infty$; $t = o$, $x = o$, that is, AX is initially inactive, yields

23) $$2.303 \log \left[\frac{1}{1 - \frac{x}{x_\infty}}\right] = \frac{a + b}{ab} Rt$$

Here $\frac{x}{x_\infty}$ is seen to be identical with f, the fraction of exchange after time t.

The derivation holds equally well for the case of molecules containing more than one atom of the species studied, for example, AX_n instead of AX, but here concentration must be expressed in terms of equivalents of exchanging atom per liter instead of moles per liter.

An isotope effect, that is, a difference in exchange rate between isotopes, is noted where the relative mass difference of the isotopes involved is large (34, 35). For heavier atoms, as the relative mass difference becomes negligible, the isotope effect becomes negligible.

V. THE CHLORINE TRIFLUORIDE-CHLORINE SYSTEM

Introduction

The combination heterogeneous-homogeneous mechanism found (15) for the exchange of fluorine between chlorine trifluoride and elemental fluorine has been mentioned previously. The exchange reaction

24) $ClF_3 + Cl_2^* \rightleftharpoons Cl^*F_3 + Cl_2$

(where an asterisk denotes a tagged atom) is similar to the exchange reaction

25) $ClF_3^* + F_2 \rightleftharpoons ClF_3 + F_2^*$

studied by Adams et al., and consequently was investigated for exchange. Qualitatively, exchange was found to occur in the gas phase at temperatures above 180°C. However, because the reaction

26) $ClF_3 + Cl_2 \longrightarrow 3ClF$

also occurs above 180° C., thus clouding the exchange interpretations, a study of the kinetics of formation of chlorine monofluoride was made.

Materials

Anhydrous chlorine trifluoride, technical grade, was obtained from the Harshaw Chemical Company. Before use, this material was purified by successive condensation-vaporization processes; the gases non-condensible by an isopropanol-Dry Ice bath were discarded by removal through the system pump. Each condensate was degassed for several minutes by leaving the trap open to the pump. Purity of the chlorine

trifluoride was determined by means of the ultra-violet spectrum obtained by use of the cells described in Section III. Three or four purifications yielded material nearly free from chlorine (Figure 9). Fluorine (16) and chlorine monofluoride (Section VI) are quantitatively separated from chlorine trifluoride by the above procedure. Traces of hydrogen fluoride may have been present, but overall impurities after trap-to-trap distillation have been estimated to be less than one mole per cent (6,7).

Chlorine^{36} was selected as the tracer. The disturbingly long half-life of four hundred thousand years is partially compensated, from a safety point of view, by the weakness of the negative beta emission (0.72 mev.). The Cl^{36} was obtained from Oak Ridge National Laboratory in the form of aqueous hydrogen chloride which contained four microcuries of activity per milliliter. Tagged elemental chlorine was made according to the reaction (37).

$$27)\quad MnO_2 + 2HCl + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + Cl_2$$

The system used for chlorine production is shown in Figure 10. For one batch of chlorine, the following were placed in the reaction flask and heated to about 80° C.: 17.55 grams sodium chloride, 13.17 grams manganese dioxide pretreated with concentrated nitric acid to remove manganous carbonate, 12.375 ml. distilled water, 12.375 ml. sulfuric acid and 0.825 ml. of the tagged hydrogen chloride solution. The gas produced was washed with a saturated solution of copper sulfate to remove hydrogen chloride, then dried with concentrated sulfuric acid and anhydrous calcium sulfate. The sodium chloride was Mallinckrodt

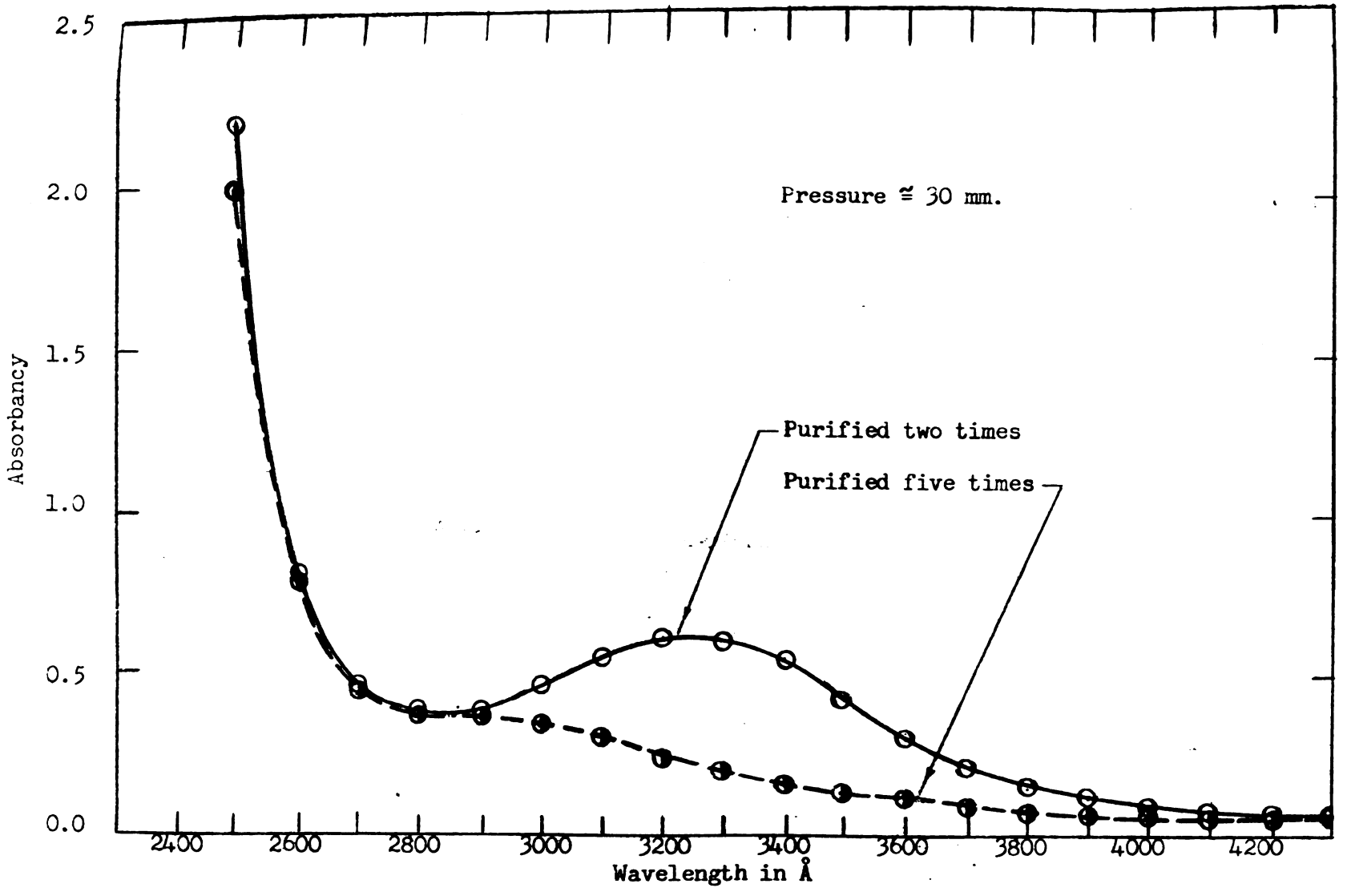

Figure 9. Chlorine trifluoride spectrum.

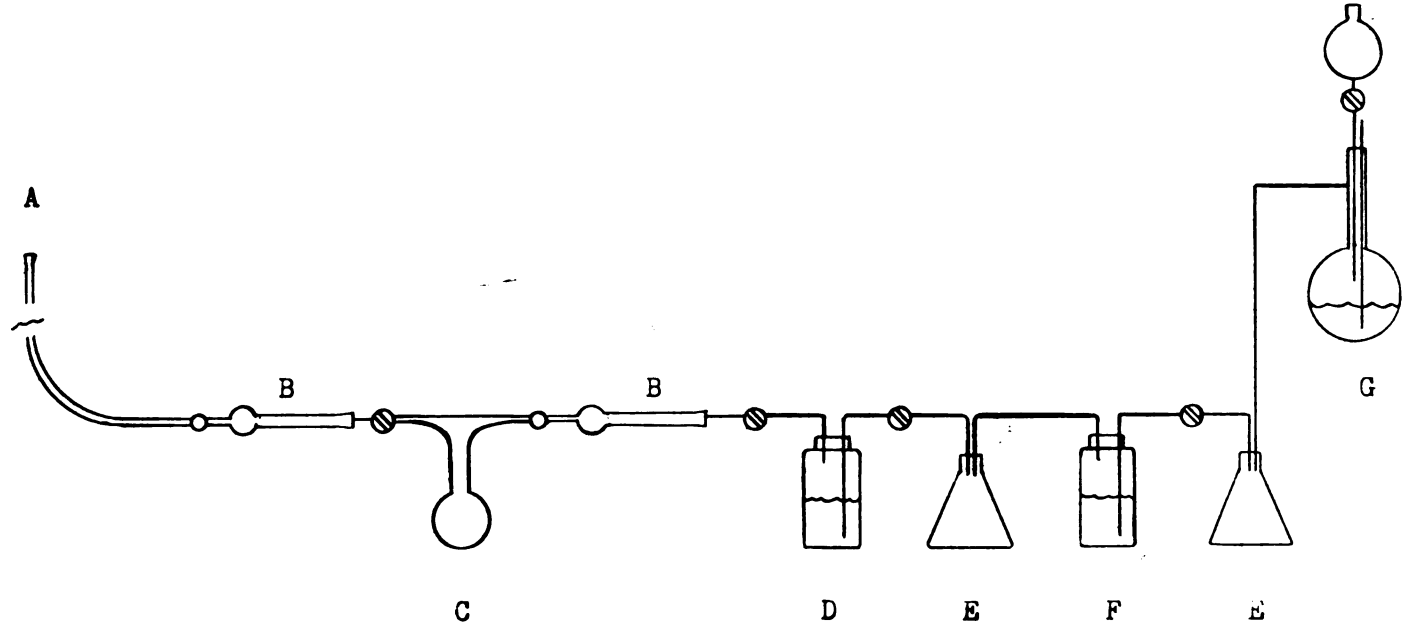

Figure 10. Glass system for chlorine production: A, tapered fitting leading to metal system; B, drying tubes filled with Drierite; C, trap for condensation of chlorine before removal to metal system; D, sulfuric acid washing bottle; E, safety traps; F, saturated copper sulfate washing bottle; G, reaction flask fitted with dropping funnel and thermometer.

Analytical Reagent; the manganese dioxide was Central Scientific Company technical grade; the sulfuric acid was DuPont C.P. of specific gravity 1.84; the nitric acid was DuPont C.P.; the copper sulfate was Baker C.P. pentahydrate; and the anhydrous calcium sulfate was W. A. Hammond Drierite. After production, the tagged chlorine was purified by successive condensation-degassing-vaporization treatments, after which an ultra-violet spectrum of the gas was taken (Figure 11). The activity at various pressures was determined in the gas counting vessel (Figure 12). The gas was stored in a steel cylinder.

Non-radioactive chlorine of technical grade was obtained from the Ohio Chemical and Surgical Company and was used where applicable after being dried by anhydrous calcium sulfate and purified by the condensation procedure.

Exchange Procedure

Study of the exchange reaction between chlorine and chlorine trifluoride was carried out in the nickel system described in Section III. Equal amounts (as determined by gas pressures) of chlorine and chlorine trifluoride* were mixed under the varying conditions of the particular experiments. Each constituent was kept out of contact with the other until actual mixing. For example, chlorine was expanded into the pre-evacuated reaction vessel to a pressure of about three hundred millimeters of mercury, then condensed into the chlorine trap by liquid nitrogen and the valve closed. Similarly, chlorine trifluoride was

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*A correction was applied where necessary for chlorine trifluoride dimerization (4).

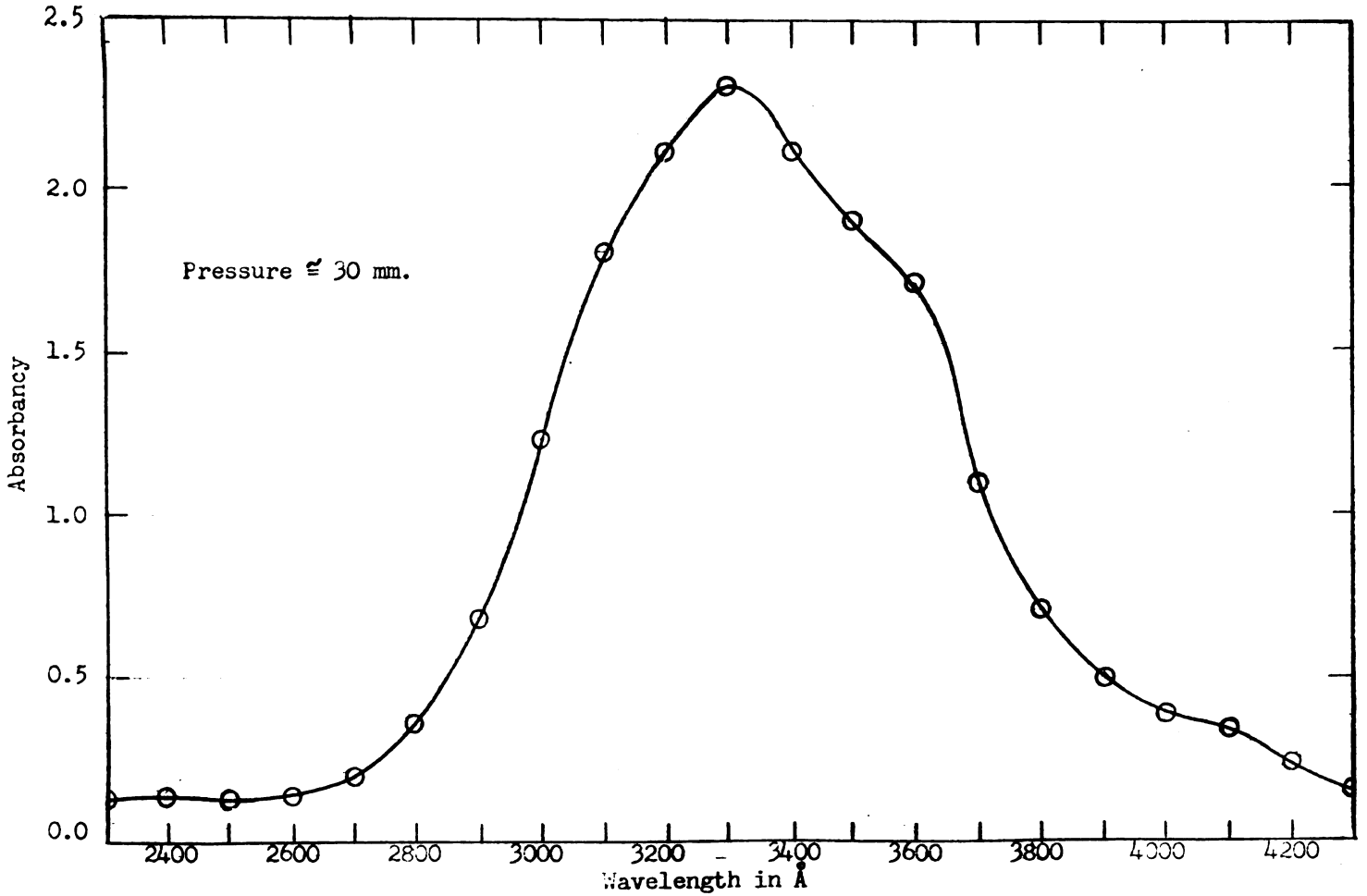

Figure 11. Radioactive chlorine spectrum.

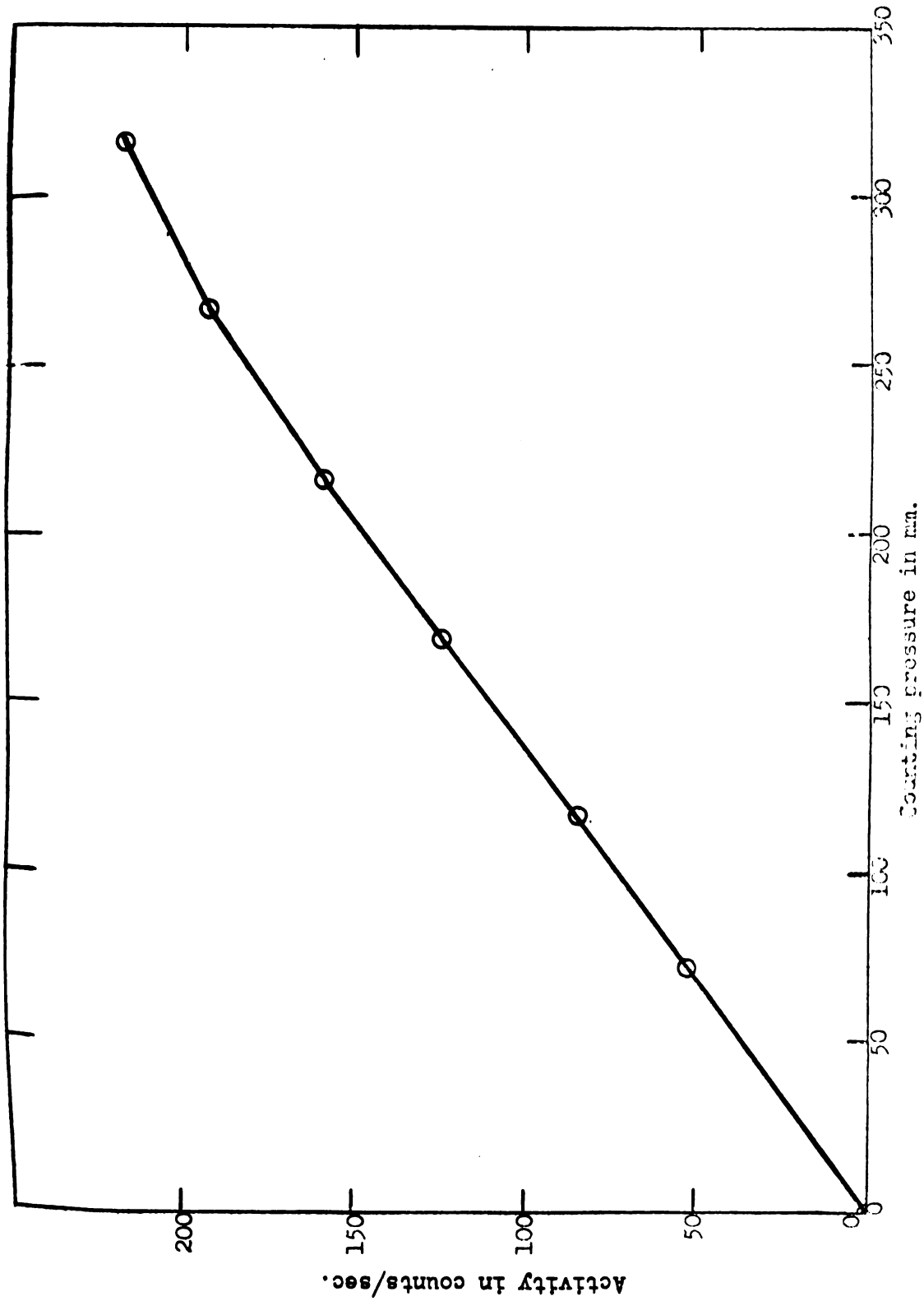

Figure 14. Activity of radioactive chlorine at various pressures.

measured and condensed into the chlorine trifluoride trap and the valve closed. The cold baths were then removed from both traps, and the traps warmed to room temperature, after which both valves were opened simultaneously and the gases allowed to mix during expansion.

Reactants were quenched by condensing the mixture into the first trap of the distillation system with a liquid nitrogen bath and were subsequently separated by distillation. The distillation process consisted of placing a liquid nitrogen bath around trap number two (Figure 1), replacing the liquid nitrogen bath around trap number one with an isopropanol-Dry Ice bath, and opening the valve between trap one and trap two for five minutes. This allowed the more volatile chlorine to be separated from the chlorine trifluoride. Then the valve was closed and the procedure repeated from trap two to trap three for three minutes. Trap one was immersed in a cold bath even when not concerned directly with the distillation to insure a low pressure inside the trap. The final chlorine fraction in trap three was warmed, expanded into the gas-counting chamber at a pressure shown by the Helicoid gauge, and counted. A sample of the gas was taken for spectral analysis, (see Figure 13 for a typical spectrum). After counting, this gas fraction was discarded by pumping through the soda-lime bottle. The chlorine trifluoride fraction remaining in traps one and two was purified several times by the condensation-degassing method, then expanded into the counting chamber and counted at a known pressure. A sample of this gas fraction also was taken for spectral analysis, (see Figure 14 for a typical spectrum).

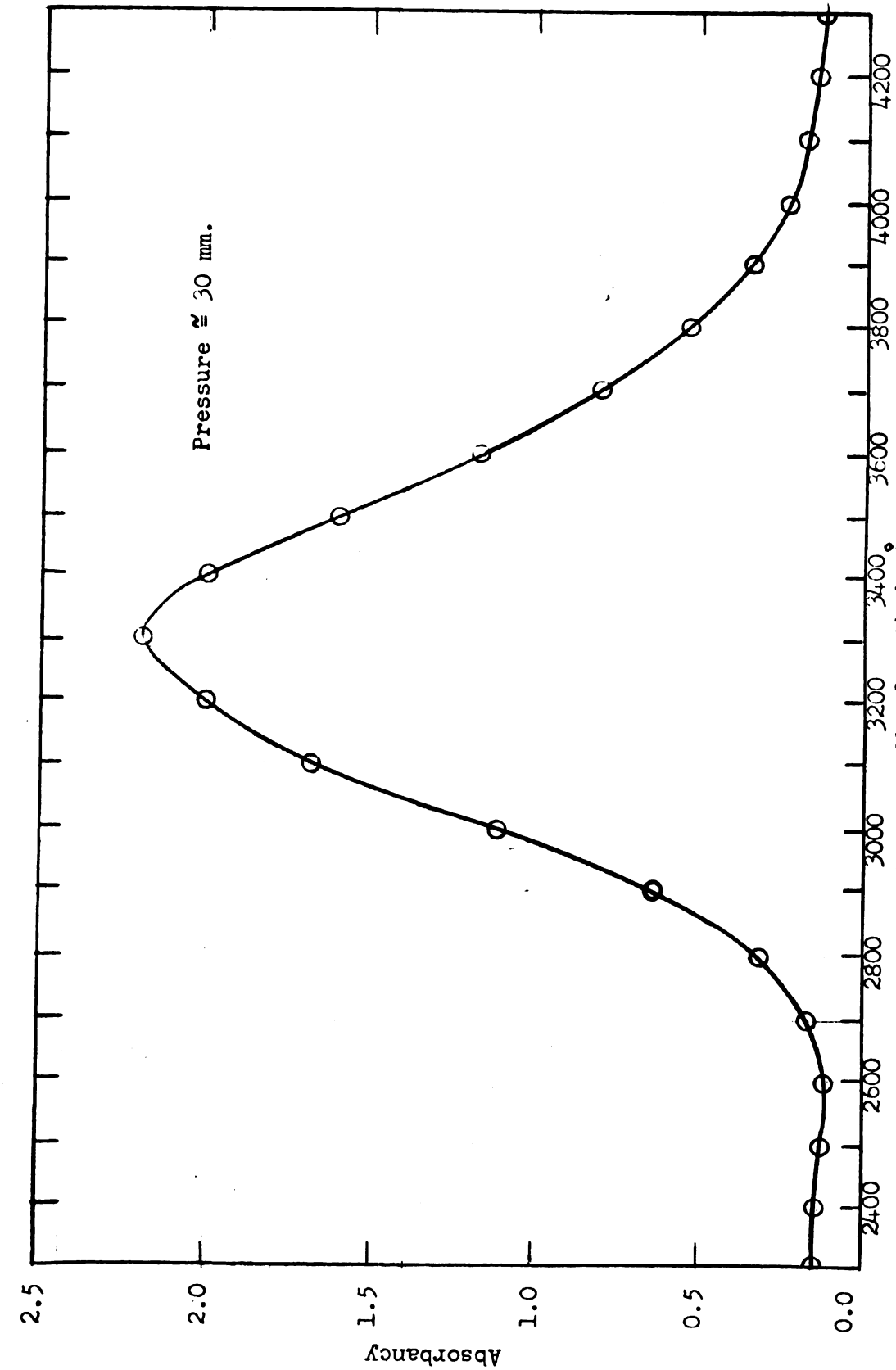

Figure 13. Spectrum of chlorine fraction after distillation.

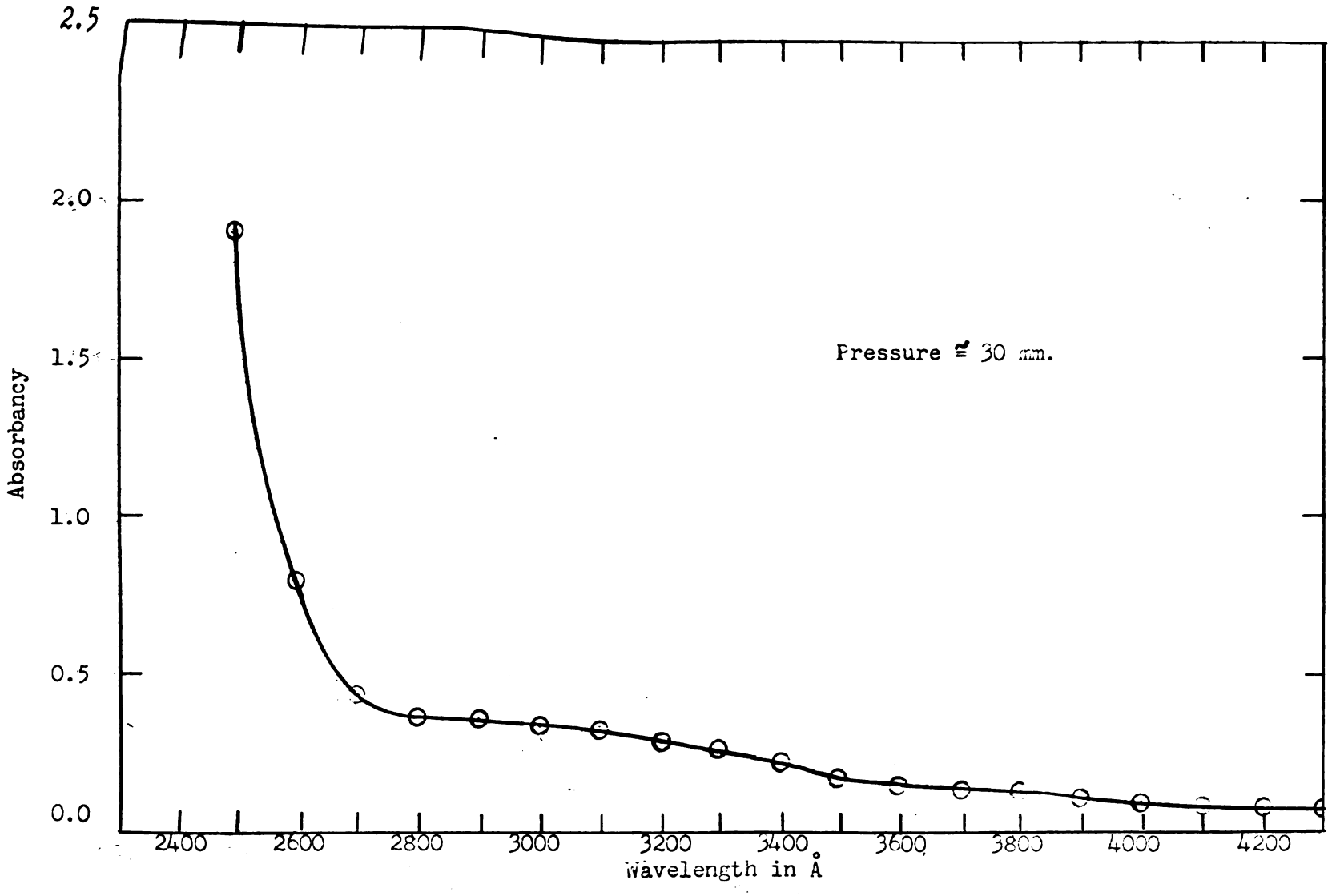

Figure 14. Spectrum of chlorine trifluoride fraction after distillation.

For exchange experiments at temperatures up to 170° C., the copper reaction vessel was used immersed in an Aroclor* bath, the temperature of which was measured with a thermometer. Experiments at higher temperatures were done in the nickel reaction vessel heated by nichrome resistance wire.

Exchange Results

No exchange was found after one-half hour contact time between a mixture of equal parts of the immiscible liquid chlorine and liquid chlorine trifluoride. The reactants were condensed with liquid nitrogen into a fluorothene trap the valve of which was then closed, and they were maintained as liquids by replacing the liquid nitrogen bath with an isopropanol-Dry Ice bath. The trap, which had an outside diameter of about six millimeters and an inside diameter of about three millimeters, was somewhat limber; it was flexed to agitate the liquids inside. Trap length was about fifteen centimeters. The liquids were qualitatively immiscible since a line of demarcation appeared roughly at the center of the liquid column in the trap.

After a contact time of two hours, exchange between a mixture of equal parts of gaseous chlorine and gaseous chlorine trifluoride did not take place in the copper reaction chamber at temperatures up to 165° C. The pressure in the reaction vessel at each temperature was calculated from the measured gas pressure in the reaction vessel at room temperature.

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* Monsanto Chemical Company's Aroclor-1248, a chlorinated biphenyl.

Qualitatively, chlorine exchanged between chlorine trifluoride and elemental chlorine after a reaction time of fifteen to thirty minutes under a pressure of six hundred millimeters of mercury and a temperature of 255° C. Quantitative data were not obtainable because of the complicating reaction

$$26) \quad ClF_3 + Cl_2 \longrightarrow 3ClF$$

which was found to occur in the temperature range necessary for positive exchange results.

Procedure for the Study of the Kinetics of Formation of Chlorine Monofluoride

Initial amounts of reactants were measured in the gas-handling system and mixed in the copper vessel. This vessel served as an expansion chamber throughout the experiments. Chlorine trifluoride and untagged chlorine were purified according to the method already described. After mixing, the reactants were expanded into the pre-evacuated nickel reaction chamber which was kept at the desired temperature. The expansion process consisted of complete opening of the entrance valve to the nickel chamber at time zero, followed immediately by closing of the valve. As soon as the valve was closed, reaction chamber pressure was recorded. This entire process required approximately ten to fifteen seconds; the pressure recorded was assumed to be the equilibrium initial pressure of reactants at time zero. Subsequently, pressure was recorded as a function of time.

Kinetics Results

Recorded pressure data were first corrected for gauge deviations by means of a calibration curve (Figure 15) for the gauge involved. Since the pressure gauge was at room temperature where no reaction occurs and the reaction chamber at a much higher temperature, a second correction was applied for the gas volume moving from the hot chamber into the gauge. Because the change in pressure was initially large, there was a large positive pressure on the gas in the gauge; it was assumed that for the first part of the reaction no back-diffusion of unreacted gases from the gauge to the hot chamber occurred. In addition, it was assumed that all of the gas displaced into the gauge chamber was chlorine monofluoride, or conversely, that none of the original reactants were lost. This is reasonable since in the beginning, displacement was small; by the time the correction became relatively large the reaction had proceeded some distance, and hence the displaced gas was largely the product, chlorine monofluoride. Consider the reaction

$$26) \quad Cl_2 + ClF_3 \longrightarrow 3ClF$$

A pressure increase will be caused by the formation of chlorine monofluoride. If the entire system were maintained at constant temperature, then the pressure read would be the pressure of the reactants plus products. Gas in the gauge at room temperature will not react. Gas in the reaction vessel at a higher temperature will react producing an increase in pressure; in order to cause an increase in observed gauge pressure some of the gas must move from reaction chamber to gauge.

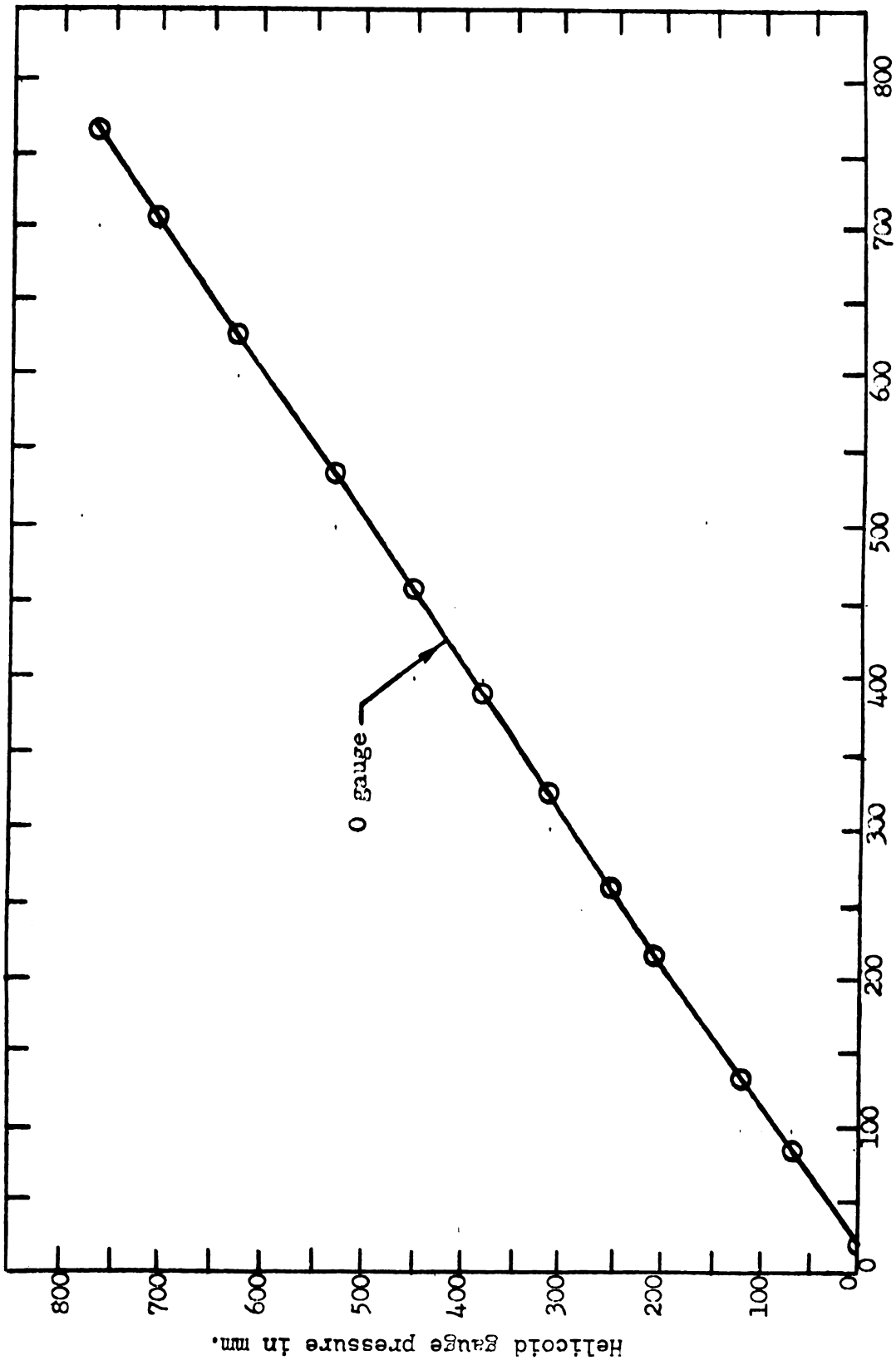


Figure 15. Calibration curve for helicoid gauge.

The effective gauge volume relative to the reaction chamber volume is given by

$$28) \quad V'g = Vg \left(\frac{Tr}{Tg} \right)$$

where $V'g$ = effective gauge volume at temperature of reaction vessel

Vg = actual gauge volume = 19.6 ml.

Tr = temperature of the reaction vessel in degrees Kelvin

Tg = temperature of the gauge in degrees Kelvin

The total effective volume of the system is

$$Vg' + V_R$$

where V_R = volume of the reaction chamber = 311.9 ml. Gas will be distributed equivalently throughout the entire volume. The fractional effective volume of the gauge is

$$\frac{Vg'}{Vg' + V_R}$$

Therefore, the amount of gas (in terms of pressure) being displaced into the gauge is

$$(Pt - Po) \left(\frac{V'g}{Vg' + V_R} \right)$$

Where Pt = total pressure at time t

Po = initial total pressure

or the change in pressure times the fractional effective volume of the gauge. Consequently, the corrected pressure, that is, the pressure that would appear in the reaction chamber if no gas were lost is

$$29)\quad Pc = Pt + (Pt - Po)\left(\frac{V_g'}{V_g' + V_R}\right)$$

where Pc = corrected total pressure at time t.

This correction is initially small, for example under conditions of Po = 400 mm., Tr = 200° C., Tg = 30° C. and Pt = 410 mm.

$$Pc = 410 + (410 - 400)\ \frac{19.6\left(\frac{473}{300}\right)}{19.6\left(\frac{473}{300}\right) + 311.9} = 410.90$$

Pressures of chlorine, chlorine trifluoride and chlorine monofluoride were calculated from the corrected pressure values. Consider a reactant mixture of equal amounts of chlorine and chlorine trifluoride at an initial pressure, Po, of 400 mm. Then

$$P(ClF_3)_o = P(Cl_2)_o = \frac{Po}{2} = 200 \text{ mm.}$$

$$P(ClF)_o = 0$$

At time t with a total pressure P_c

$$30)\quad P(ClF_3)_t = P(Cl_2)_t = \frac{Po}{2} - (P_c - P_o) = \frac{Po}{2} + P_o - P_c = \frac{3P_o}{2} - P_c$$

$$31)\quad P(ClF)_t = 3(P_c - P_o)$$

Plots of

$$P\left(\frac{ClF}{3}\right)_t / P(ClF_3)_t \quad \text{vs. time}$$

for a 1:1 mix of reactants, and

$$\log \frac{P(ClF_3)_t}{P(Cl_2)_t} \quad \text{vs. time;} \quad P(ClF_3)_t > P(Cl_2)_t$$

or

$$\log \frac{P(Cl_2)_t}{P(ClF_3)_t} \quad \text{vs. time;} \quad P(Cl_2)_t > P(ClF_3)_t$$

for cases where initial pressures were not equal indicate the reaction proceeds according to a second order rate law. The data deviate from straight line relationships as reaction time grows large. For the case of equal proportions of the reactants the deviation is always such that the ratio $P(\underline{ClF}_3)/P(ClF_3)_t$ is too large. This can be explained by the back diffusion of unreacted gas from the cold gauge. Toward the latter part of the reaction, the expansion positive pressure decreases because the rate of reaction decreases, hence some back diffusion should occur. This tends to increase the relative amount of reactants in the reaction chamber. However, the ratio $P(\underline{ClF}_3)/P(ClF_3)_t$ was obtained using $P(ClF_3)_t$ calculated assuming no back diffusion, and therefore, since $P(ClF_3)_t$ is actually larger than that plotted, then the ratio $P(\underline{ClF}_3)/P(ClF_3)_t$ is actually smaller than that plotted. The case of the non-equal starting amounts of reactants can be explained by entirely analogous reasoning.

Plots of the experimental data treated as discussed above are given in Figures 16 through 36. The lines drawn to calculate slopes of the curves are reproduced as precisely as possible. Values of the specific reaction rate constant, k, were calculated in the following manner. For a 1:1 mixture of reactants

$$32) \quad k = \frac{\text{slope}}{c}$$

where $c = [ClF_3]_o$, the initial concentration of chlorine trifluoride

or $c = [Cl_2]_o$, the initial concentration of chlorine.

For a non-1:1 mixture

$$33) \quad k = \frac{2.303 \text{ slope}}{a - b}$$

when $a = [Cl_2]_o$; $[Cl_2]_o > [ClF_3]_o$ and $b = [ClF_3]_o$

or $a = [ClF_3]_o$; $[ClF_3]_o > [Cl_2]_o$ and $b = [Cl_2]_o$

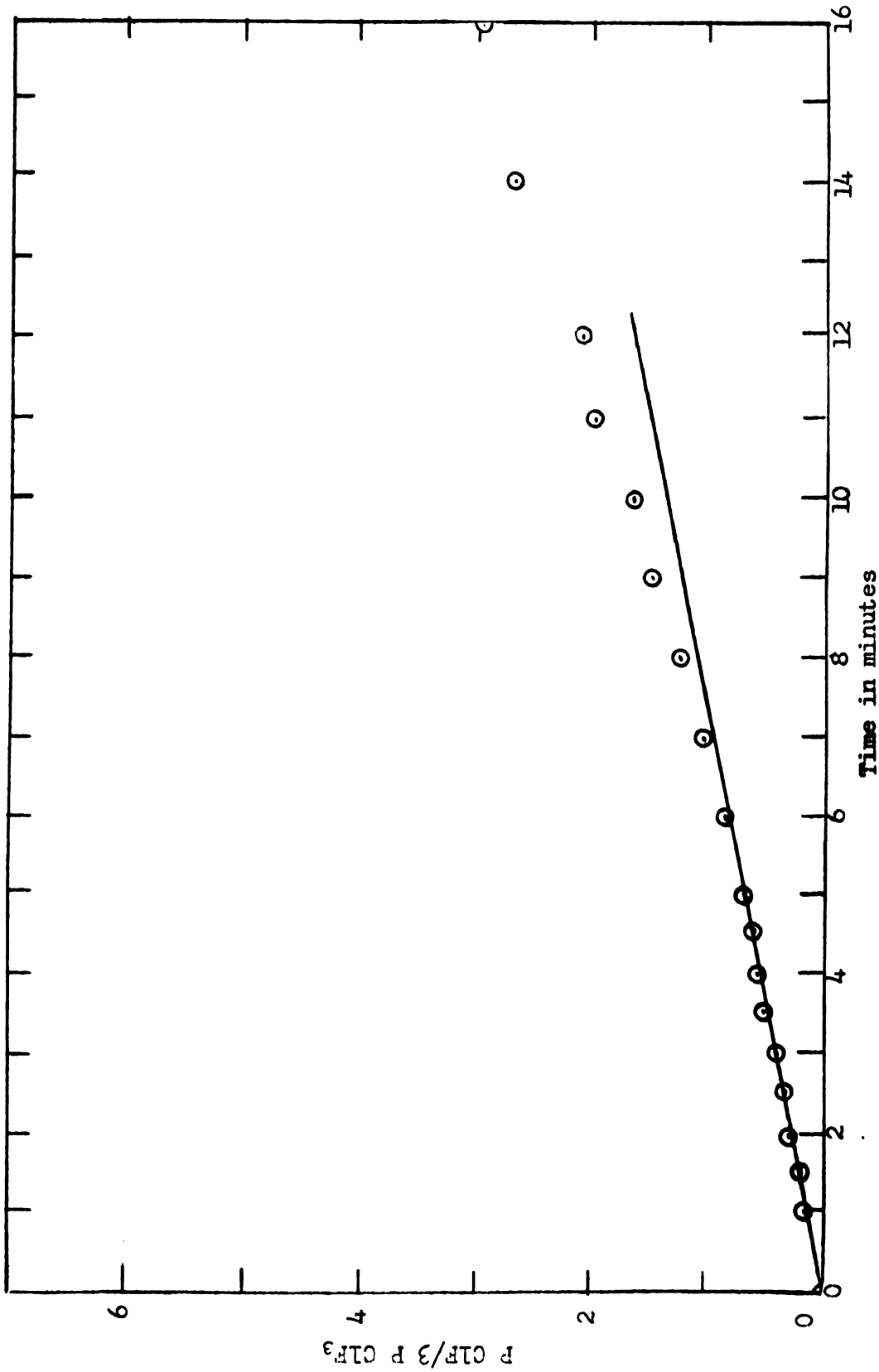


Figure 16. Chlorine monofluoride formation at 240°C.

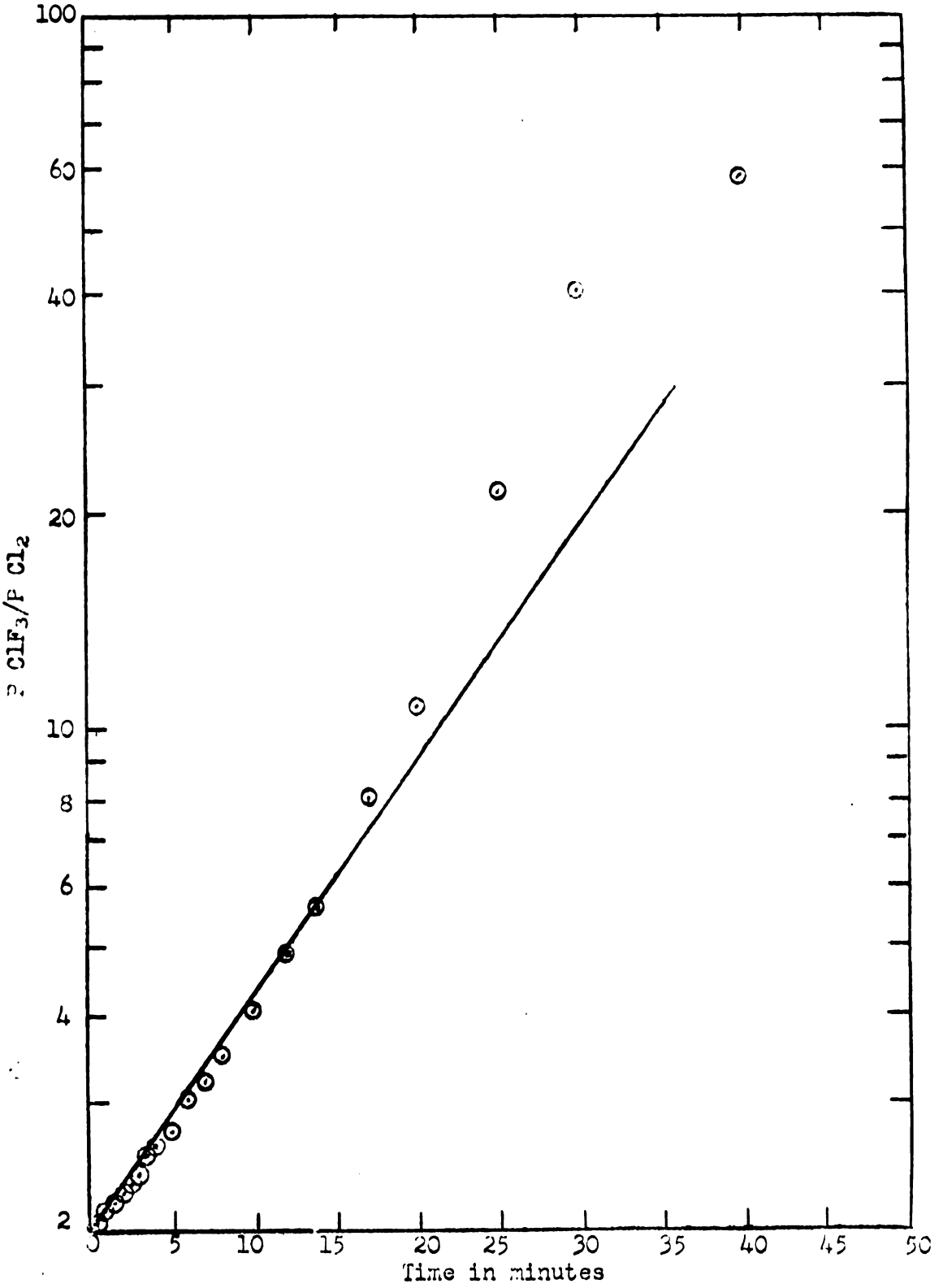


Figure 17. Chlorine monofluoride formation at 240°C.

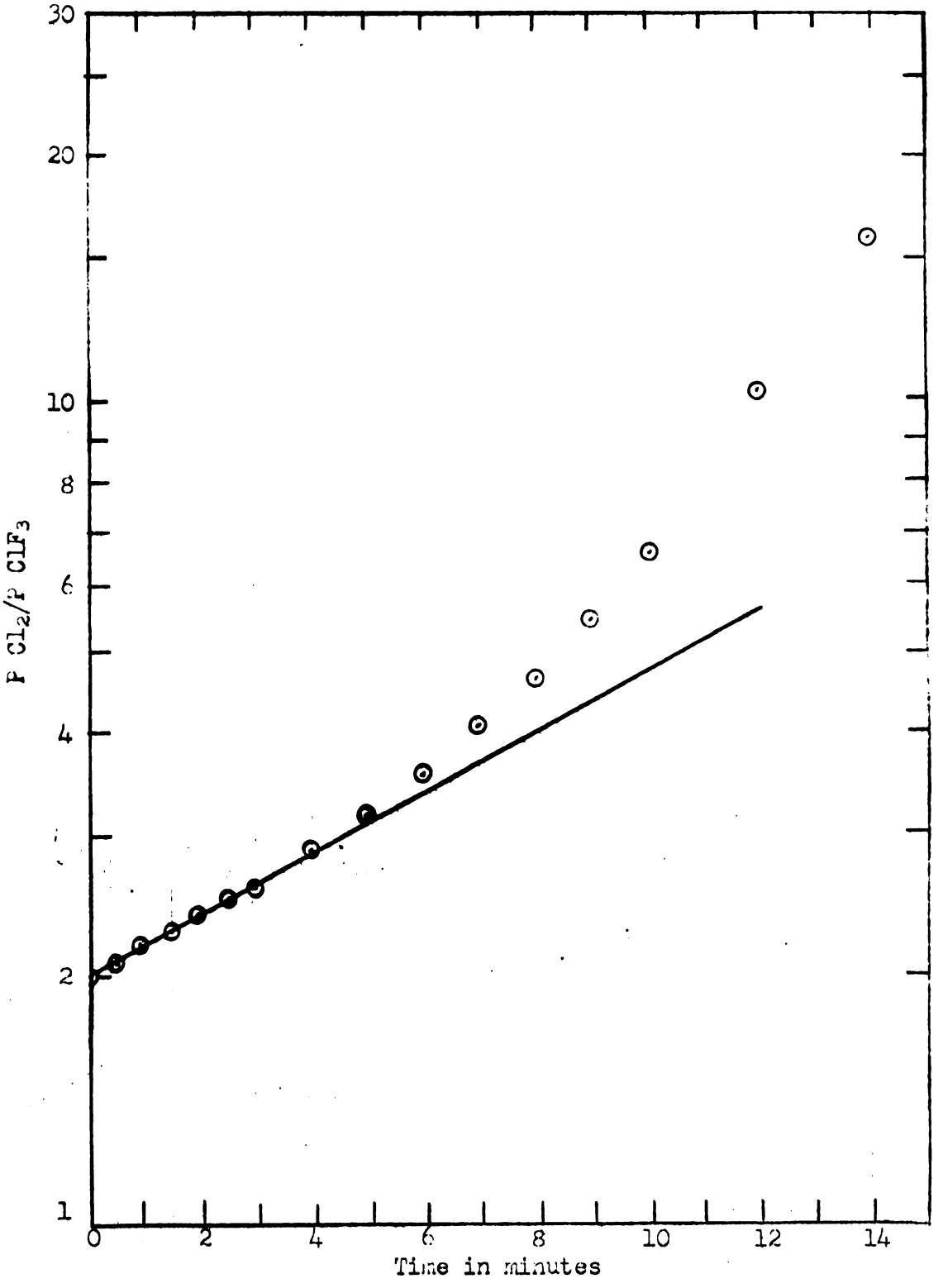


Figure 18. Chlorine monofluoride formation at 240°C.

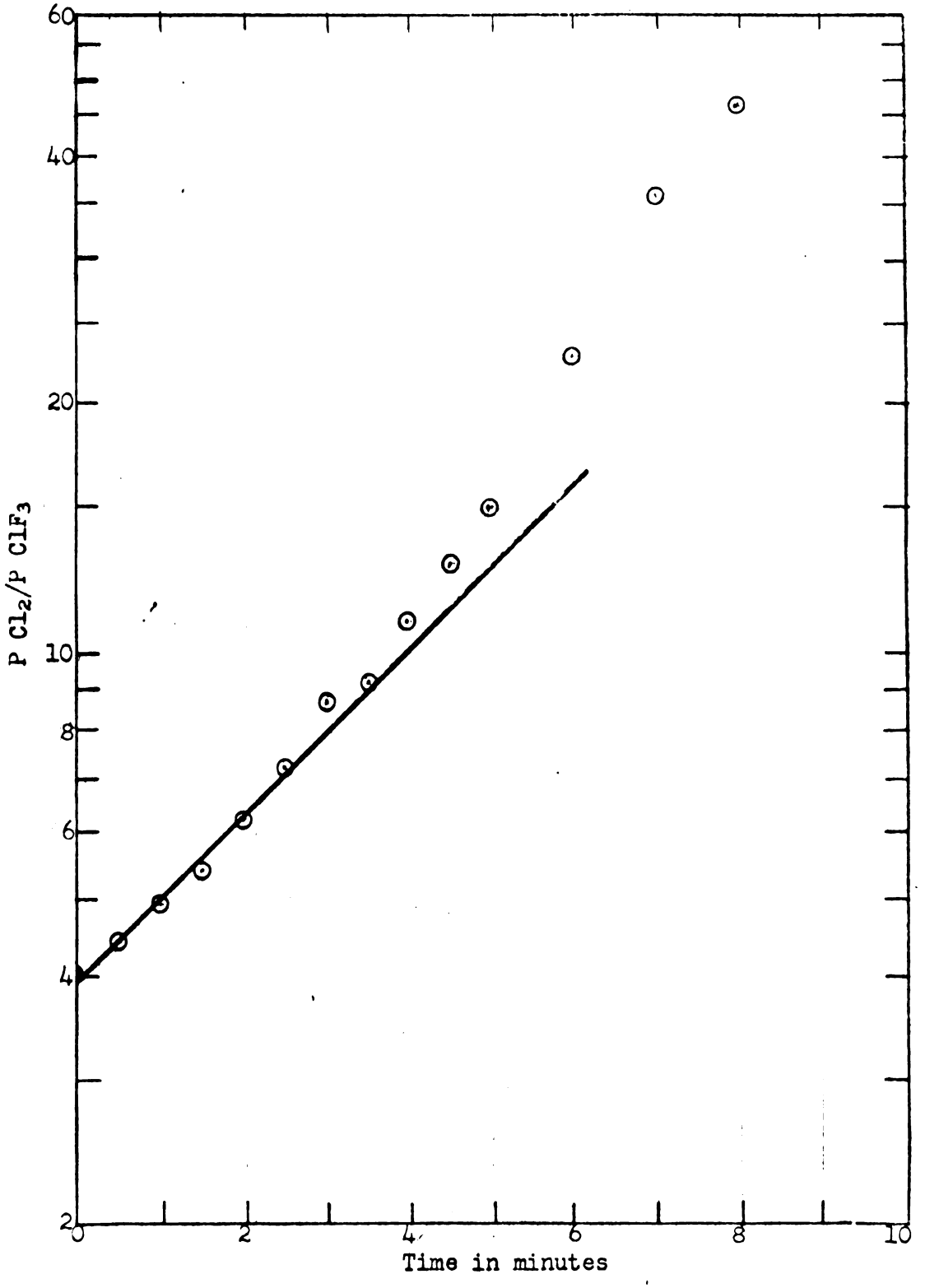


Figure 19. Chlorine monofluoride formation at 240°C.

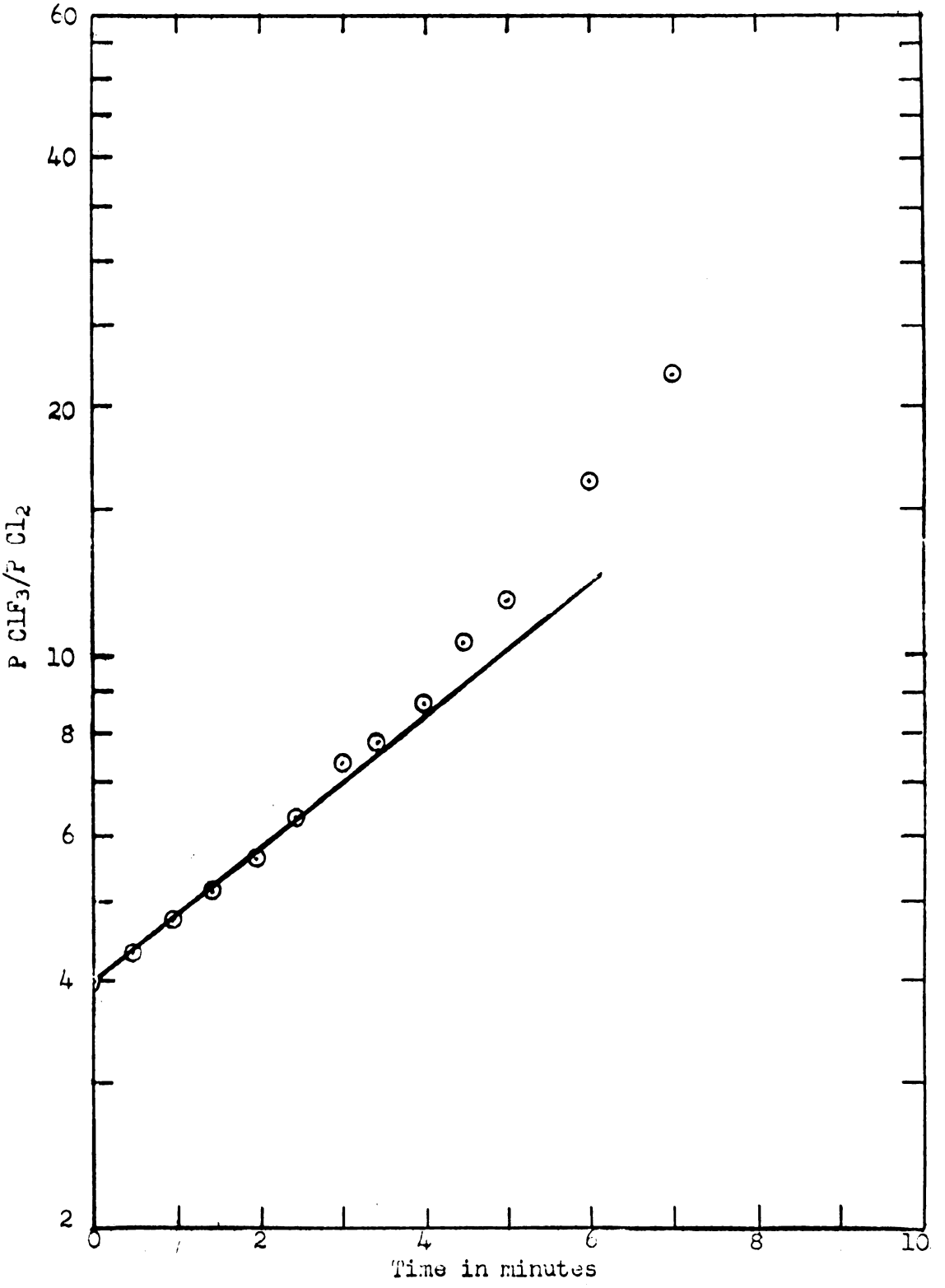


Figure 20. Chlorine monofluoride formation at 240°C.

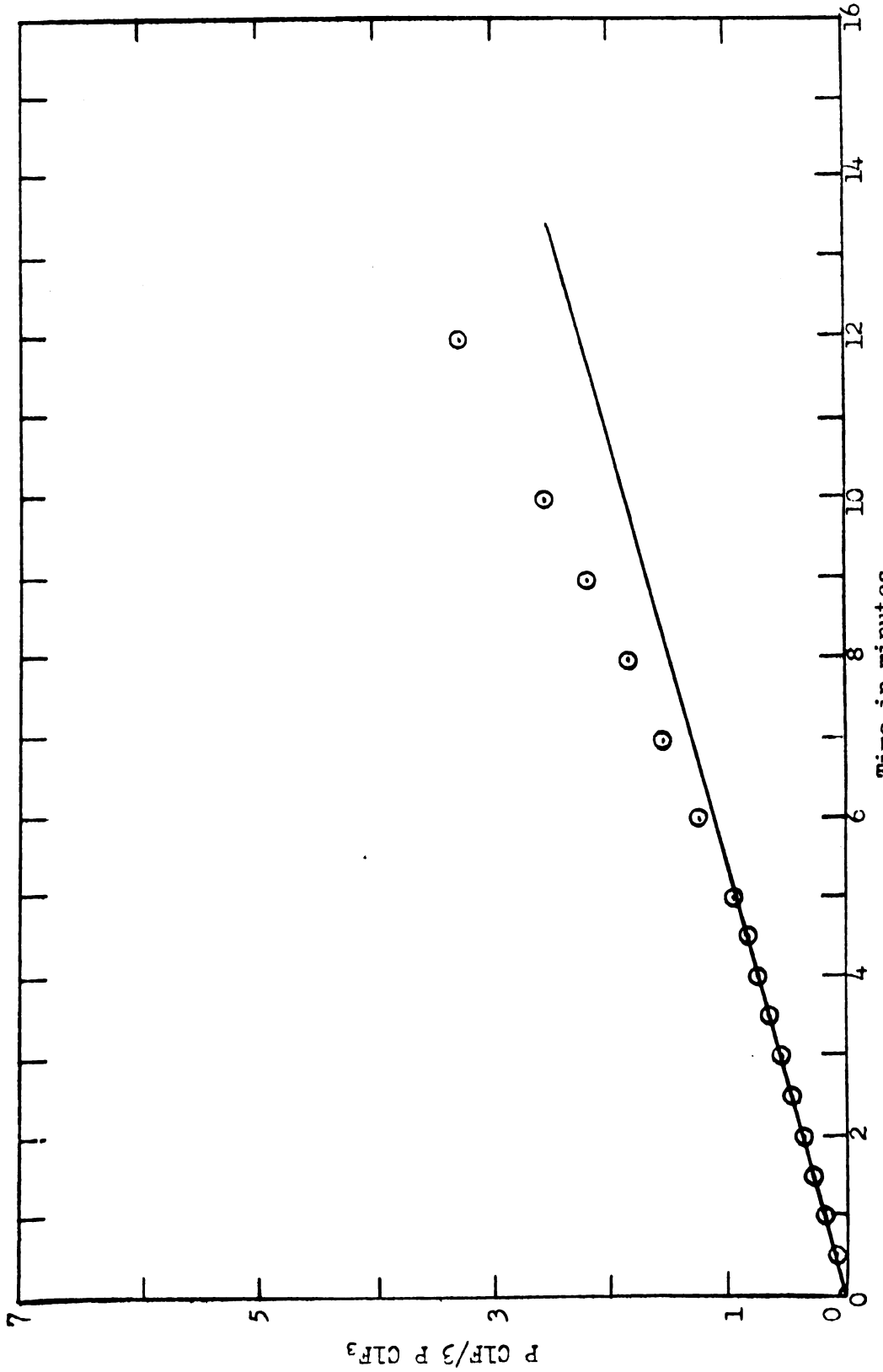


Figure 21. Chlorine monofluoride formation at 240°C.

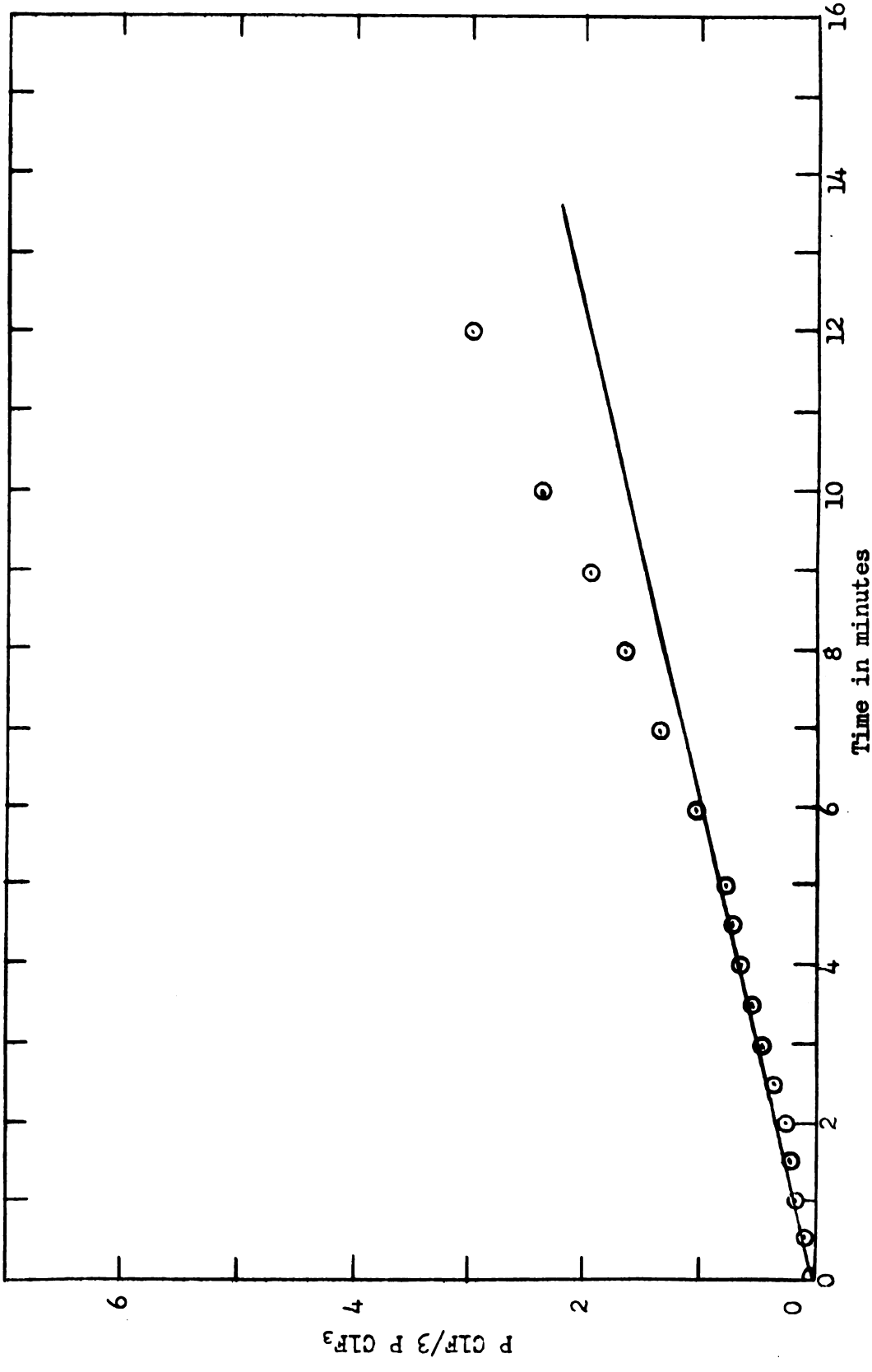


Figure 22. Chlorine monofluoride formation at 240°C.

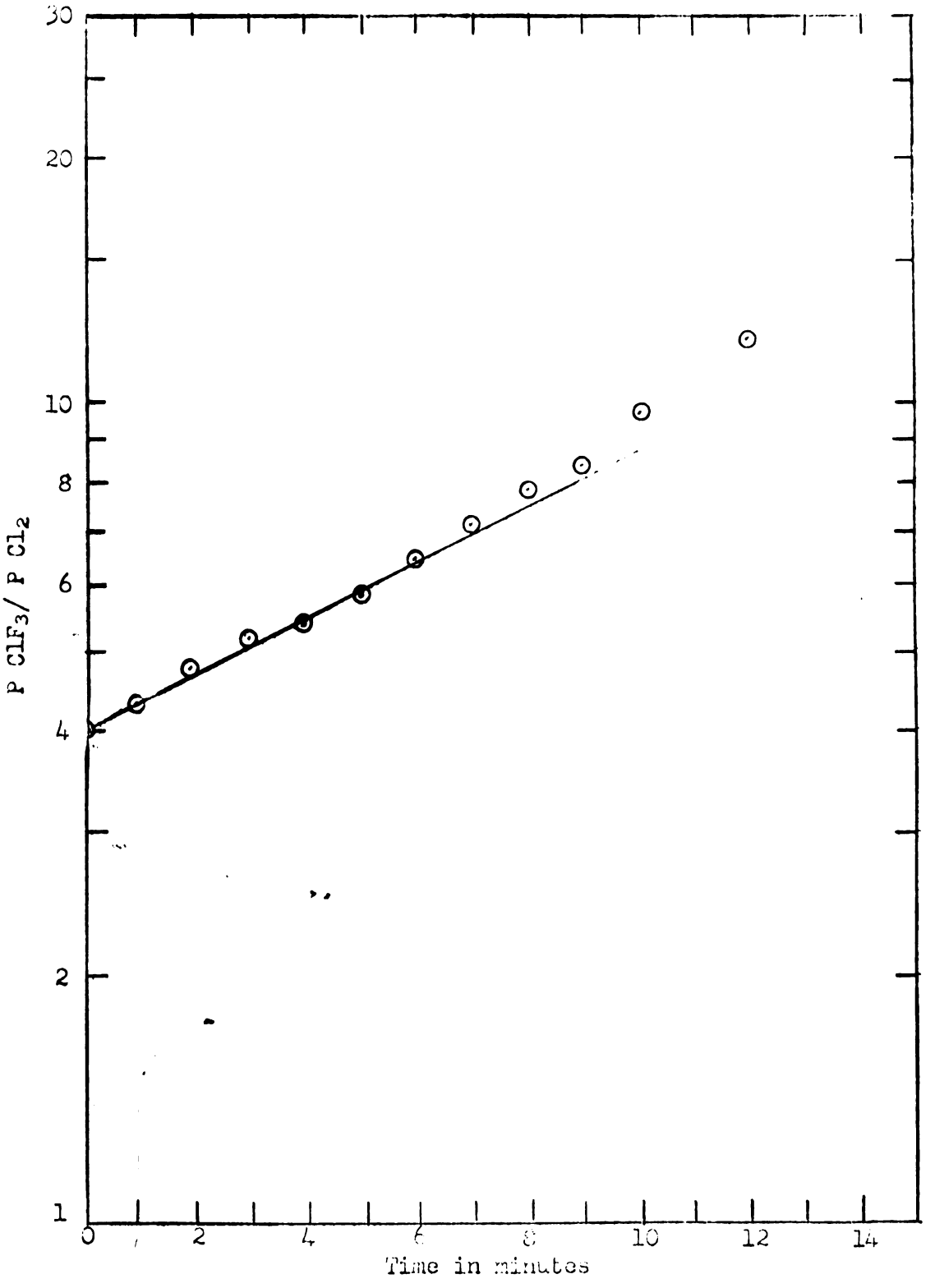


Figure 23. Chlorine monofluoride formation at 220°C.

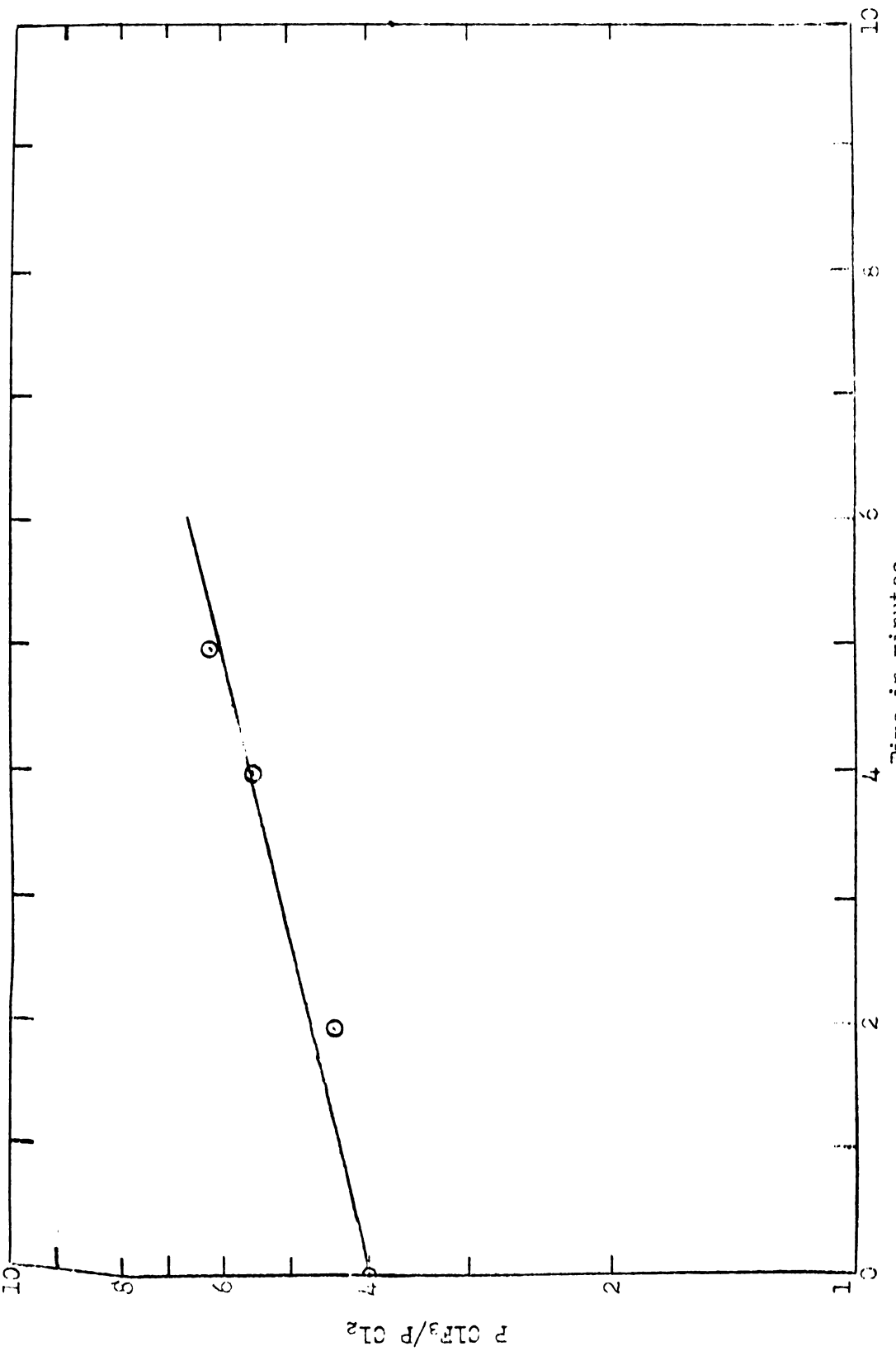


Figure 24. Chlorine monofluoride formation at 220°.

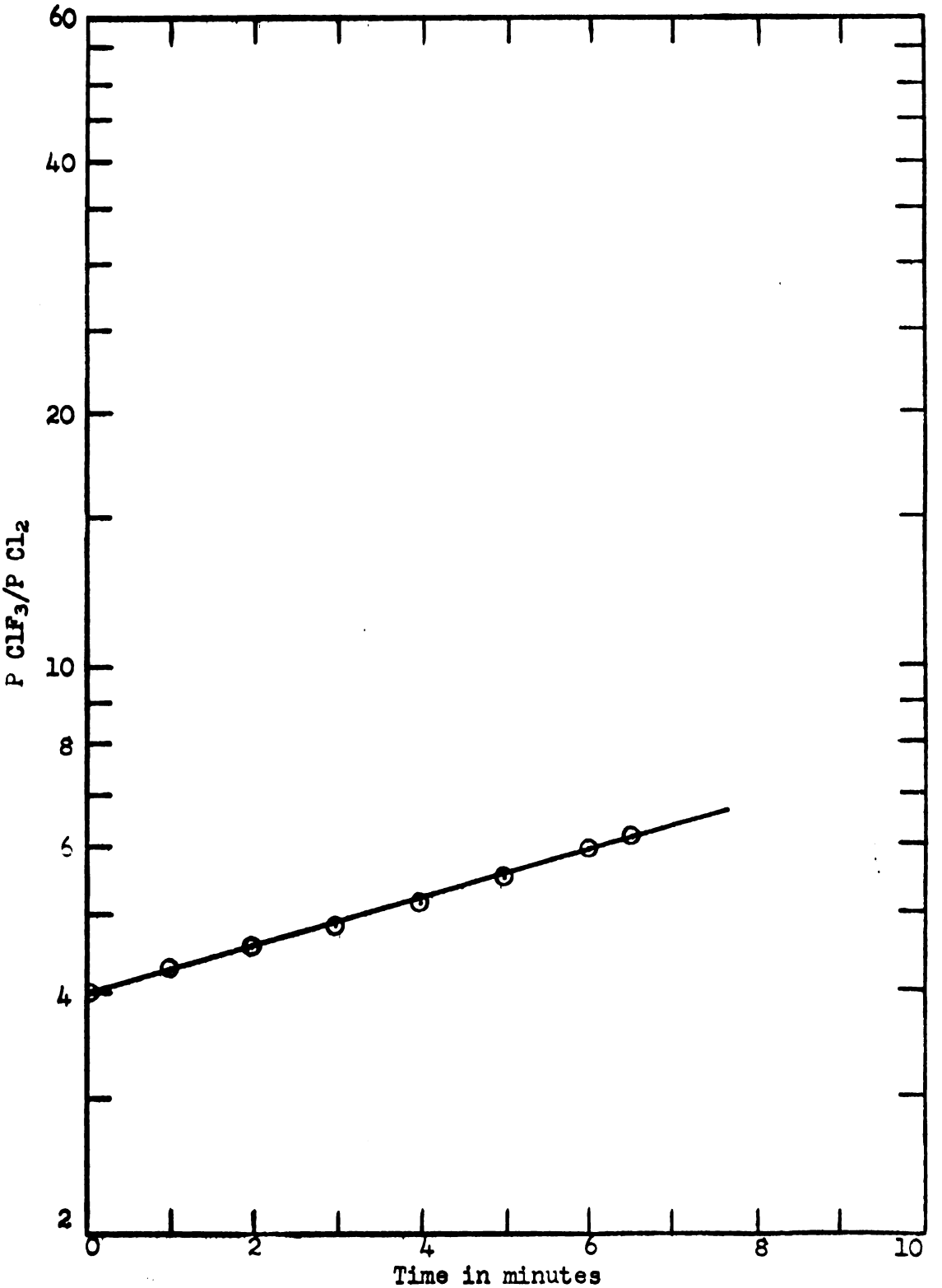


Figure 25. Chlorine monofluoride formation at 220°C.

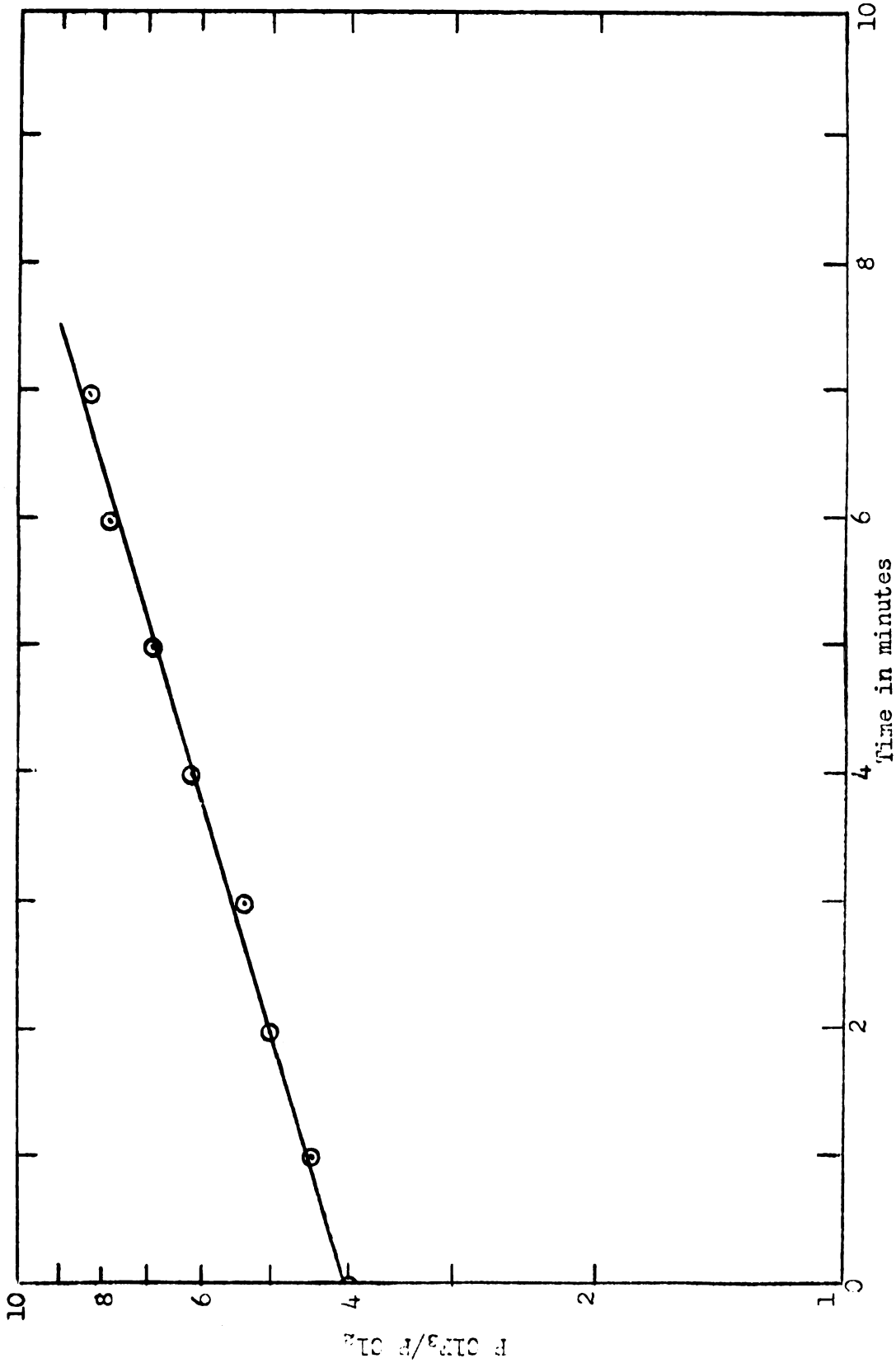


Figure 26. Chlorine monofluoride formation at 220°C.

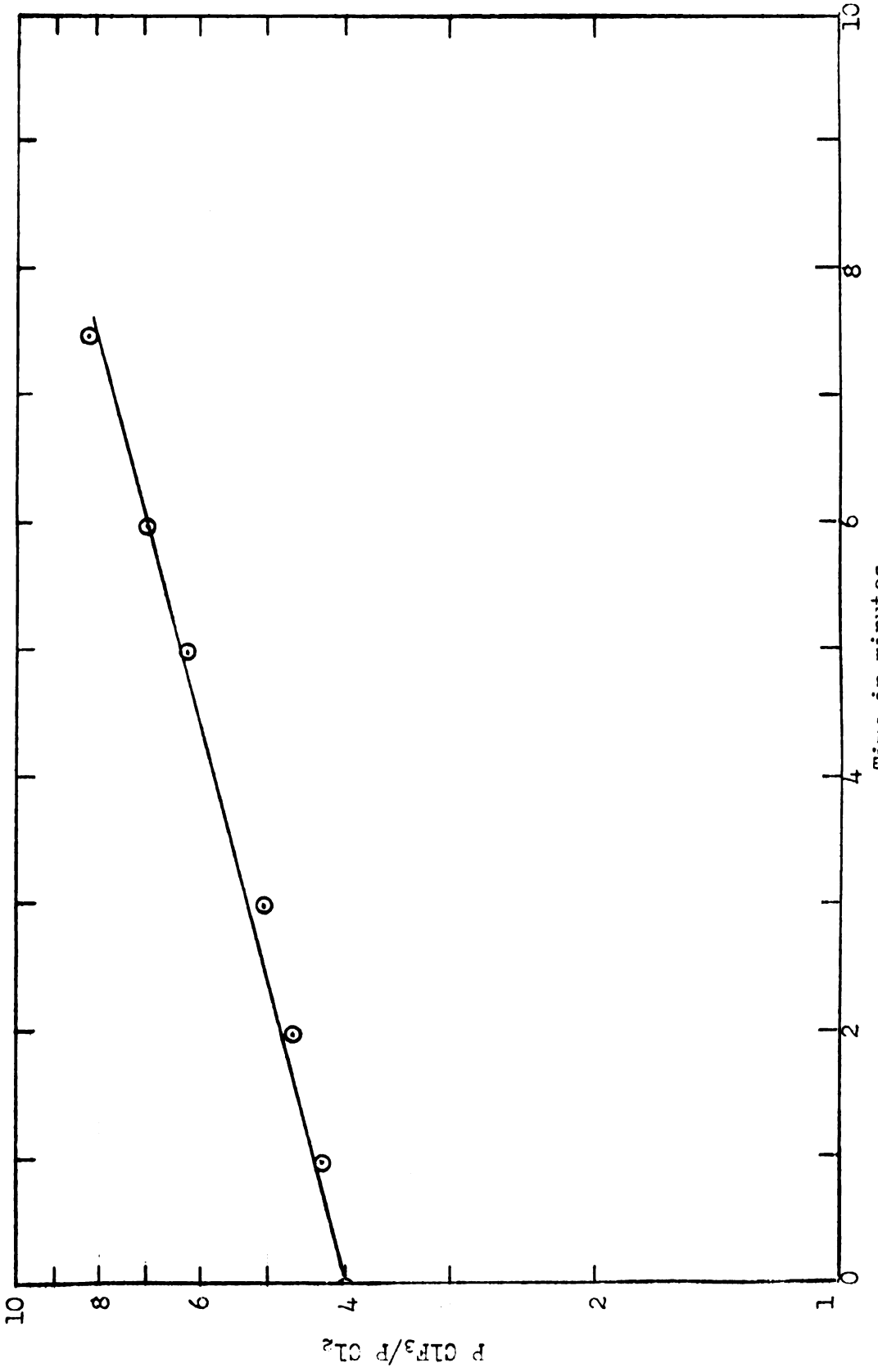


Figure 27. Chlorine monofluoride formation at 220°C.

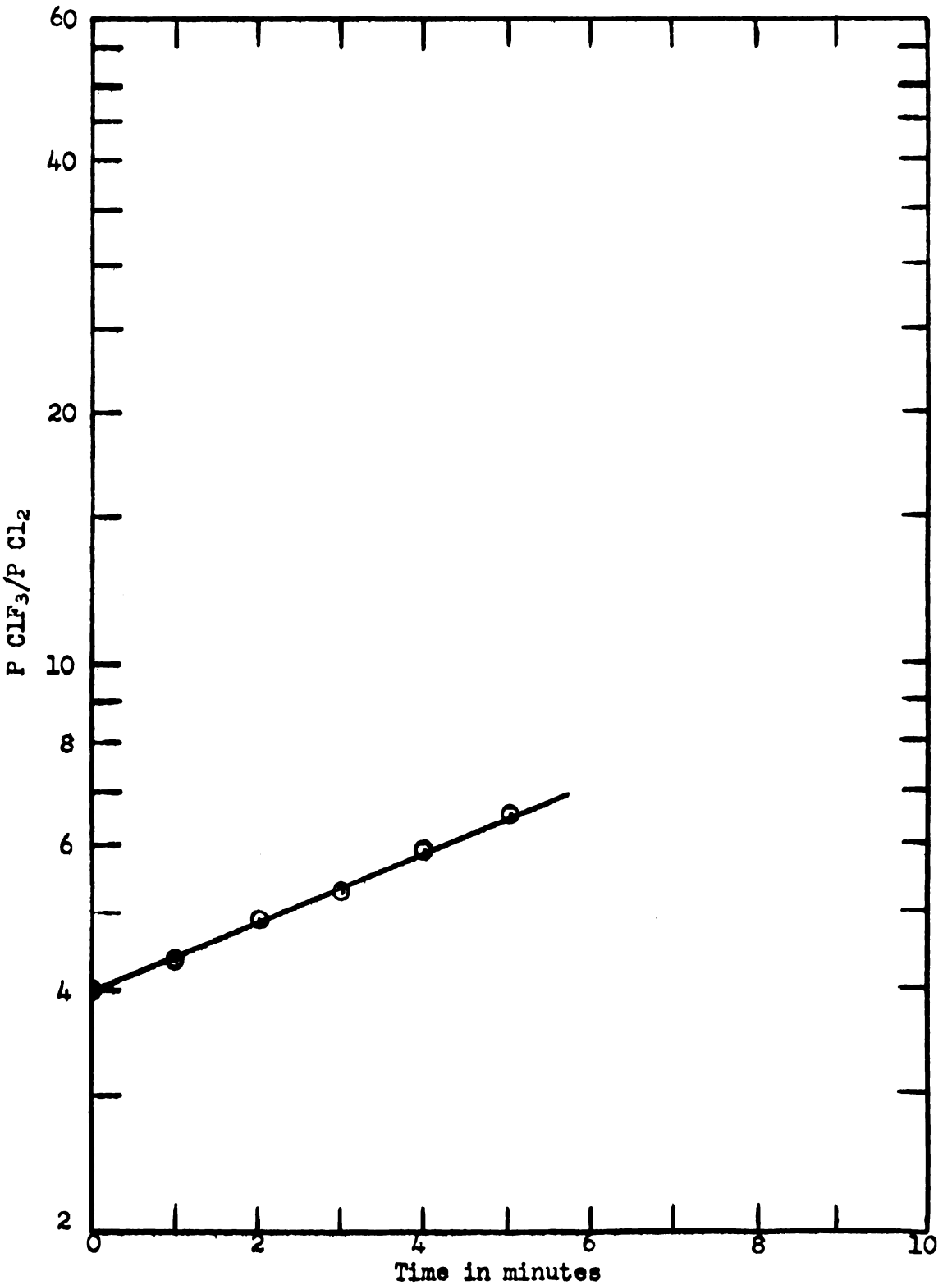


Figure 28. Chlorine monofluoride formation at 220°C.

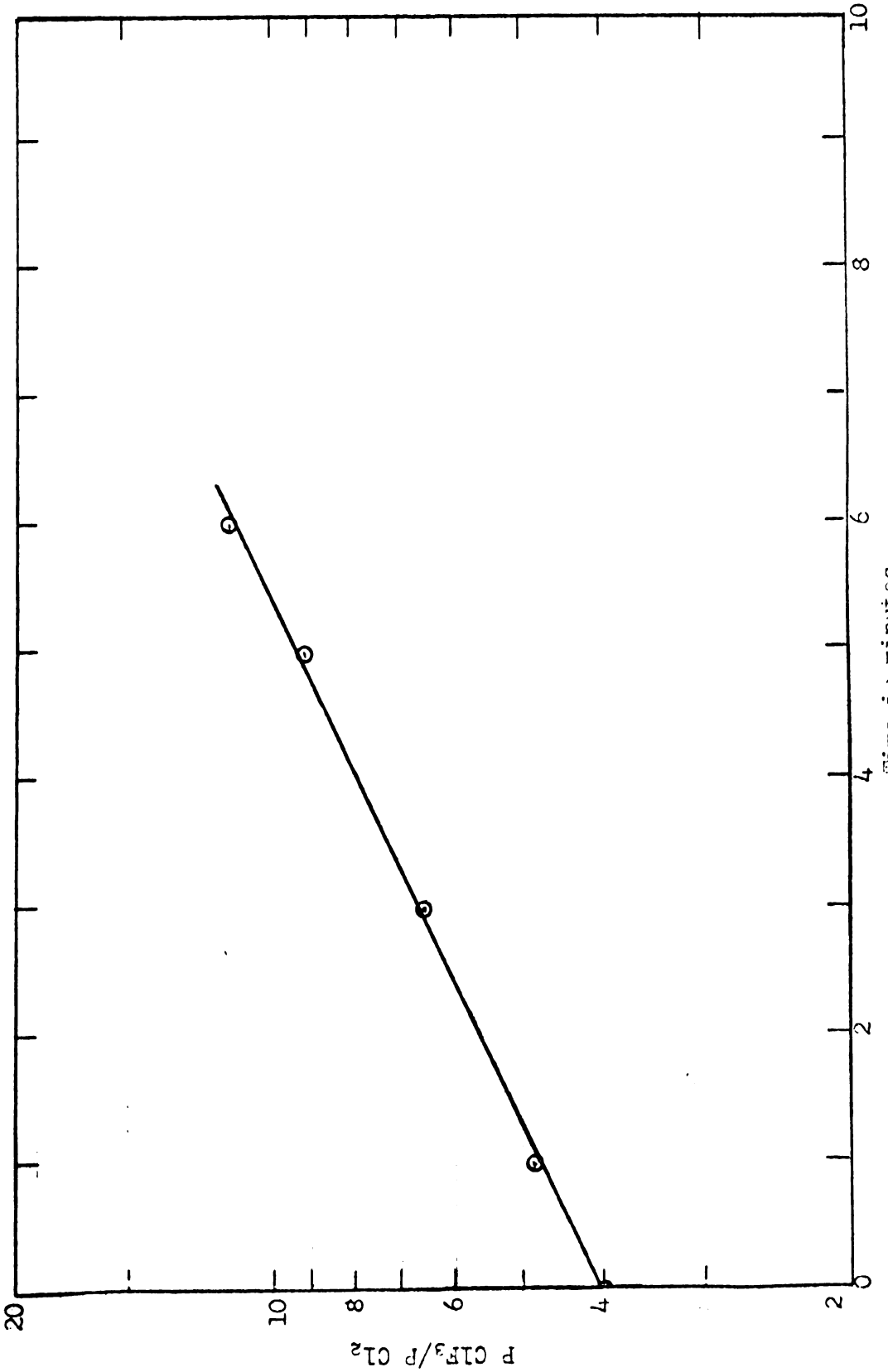


Figure 29. Chlorine monofluoride formation at 220°C.

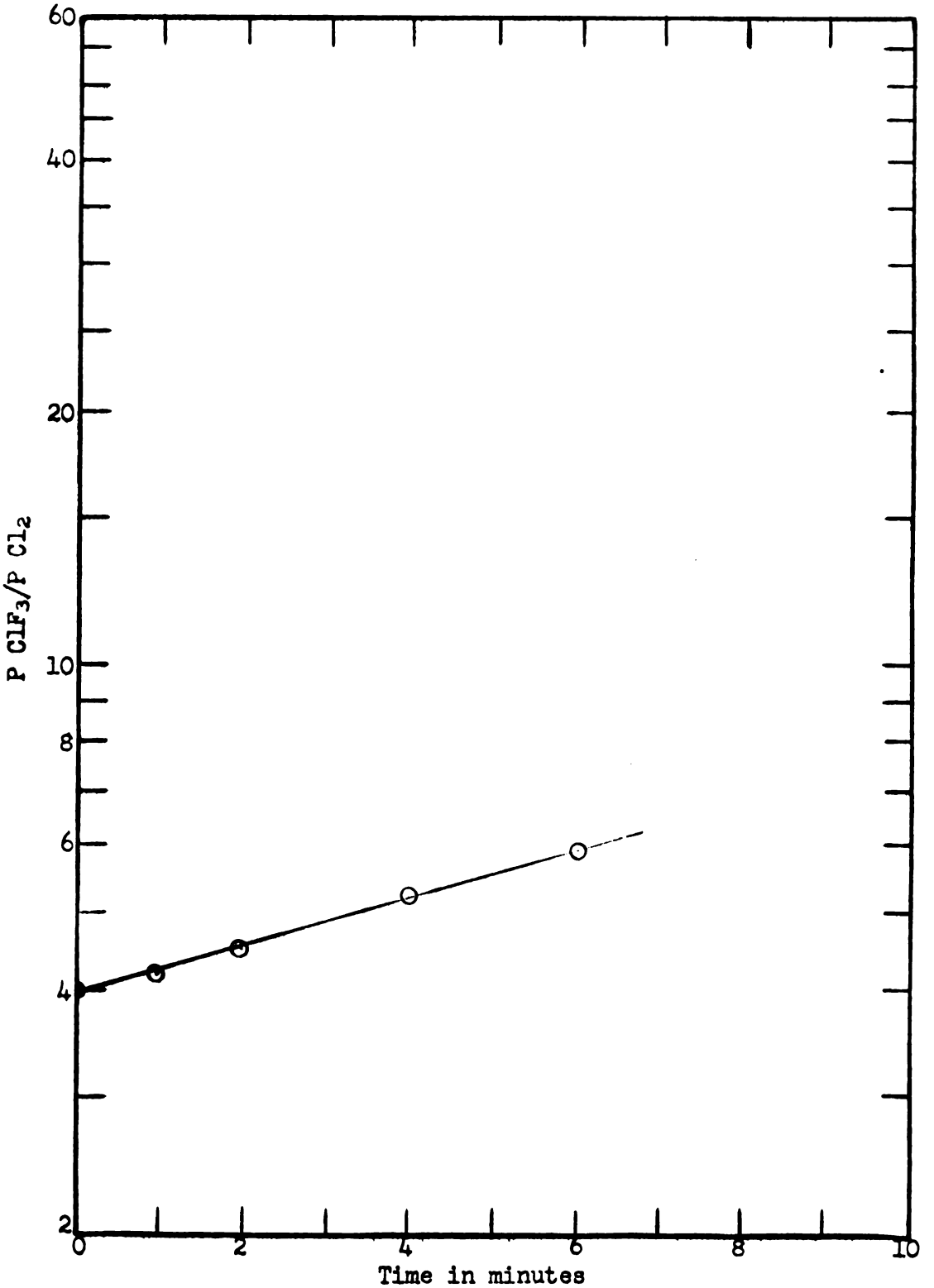


Figure 30. Chlorine monofluoride formation at 220°C.

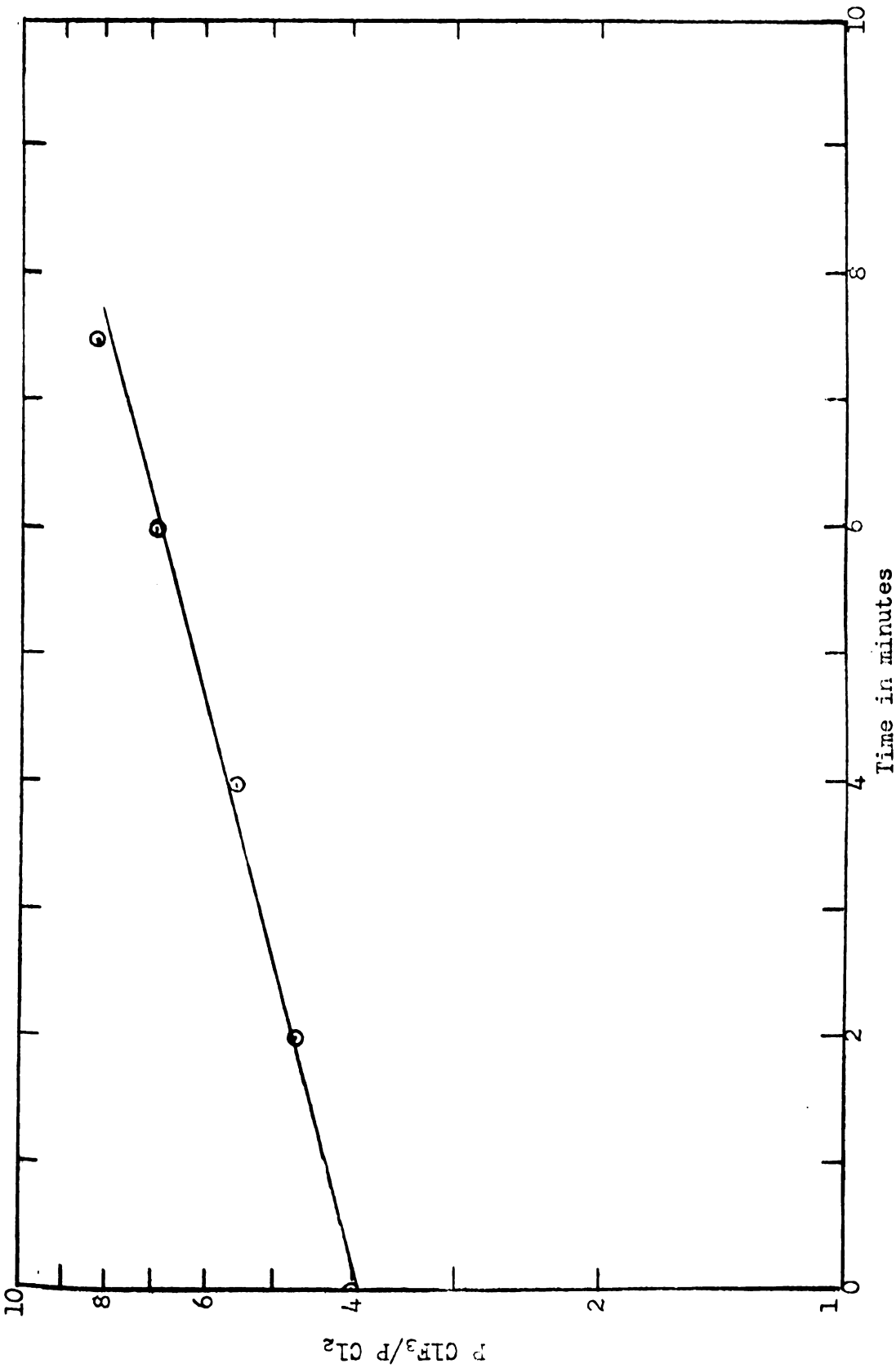


Figure 31. Chlorine monofluoride formation at 220°C.

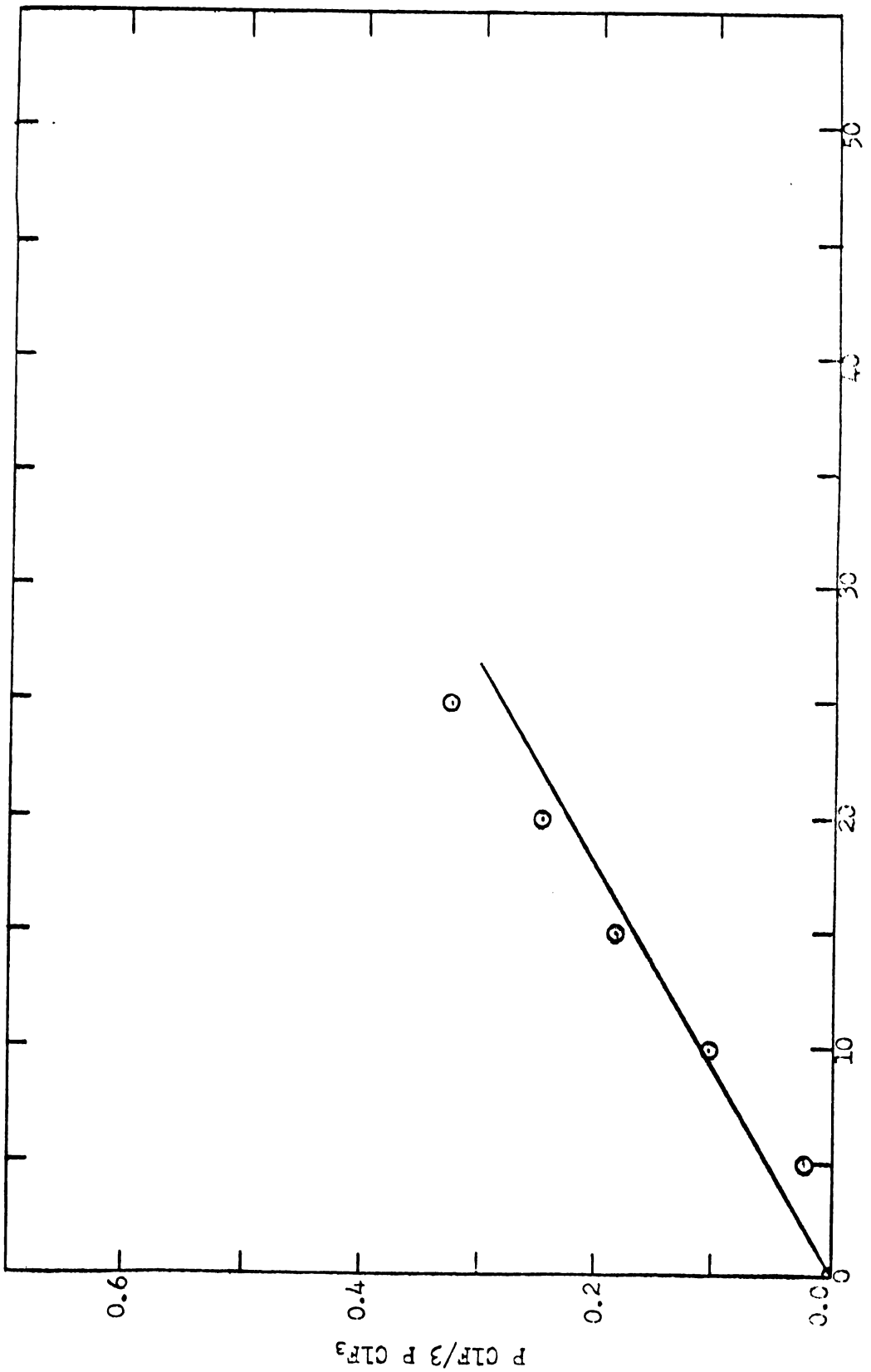


Figure 32. Chlorine monofluoride formation at 130°C.

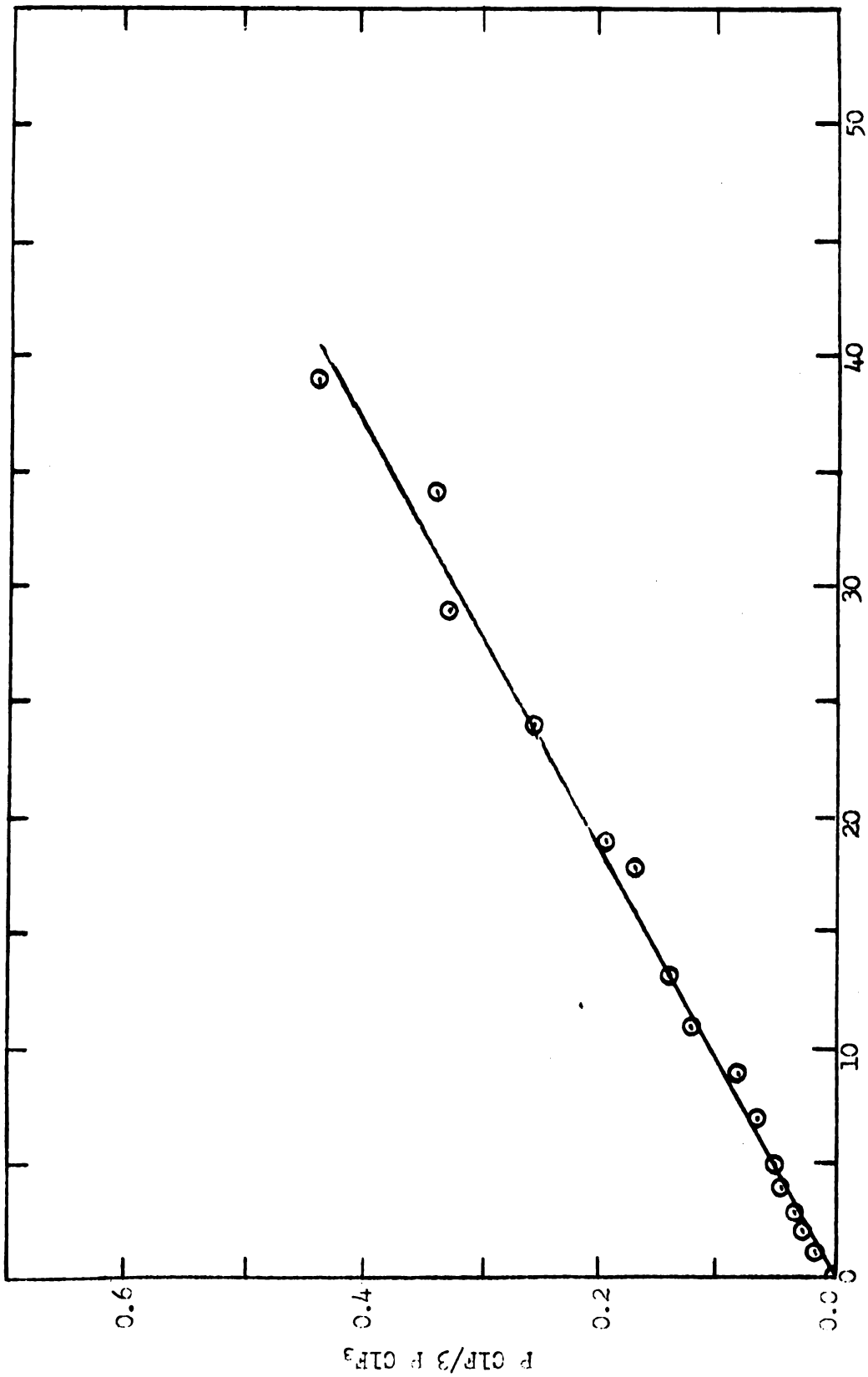


Figure 33. Chlorine monofluoride formation at 180°C.

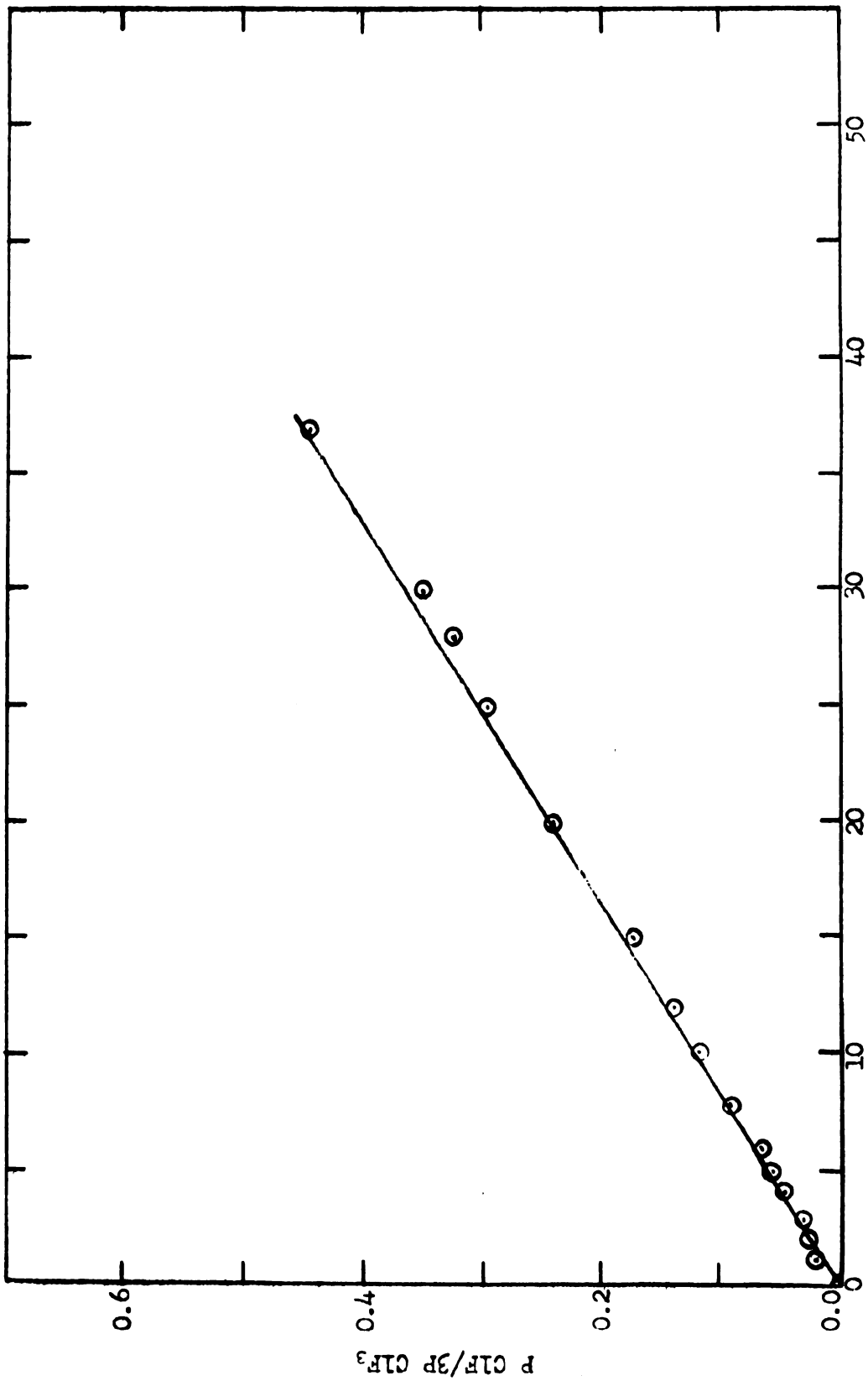


Figure 34. Chlorine monofluoride formation at 180°C.

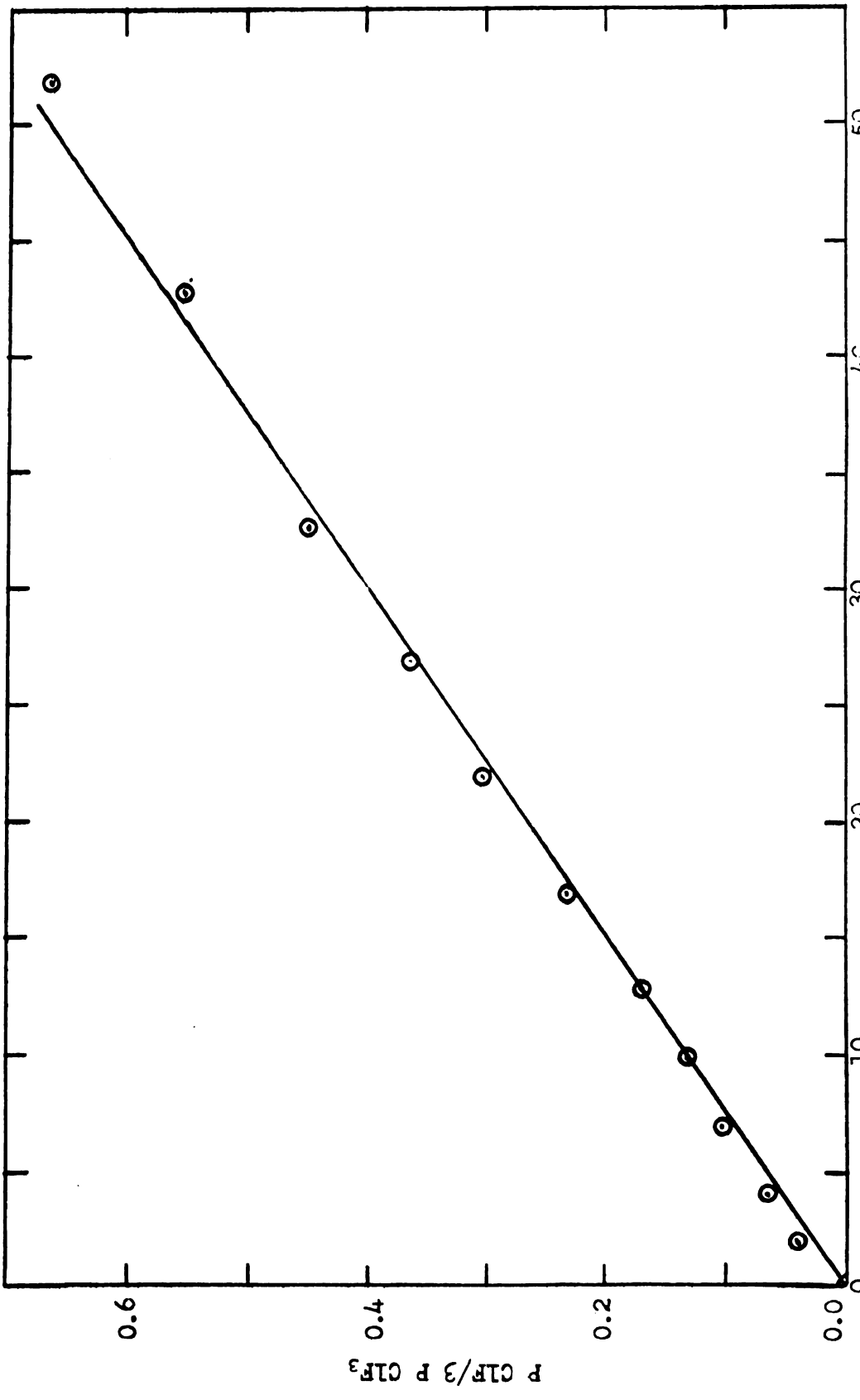


Figure 35. Chlorine monofluoride formation at 180°C.

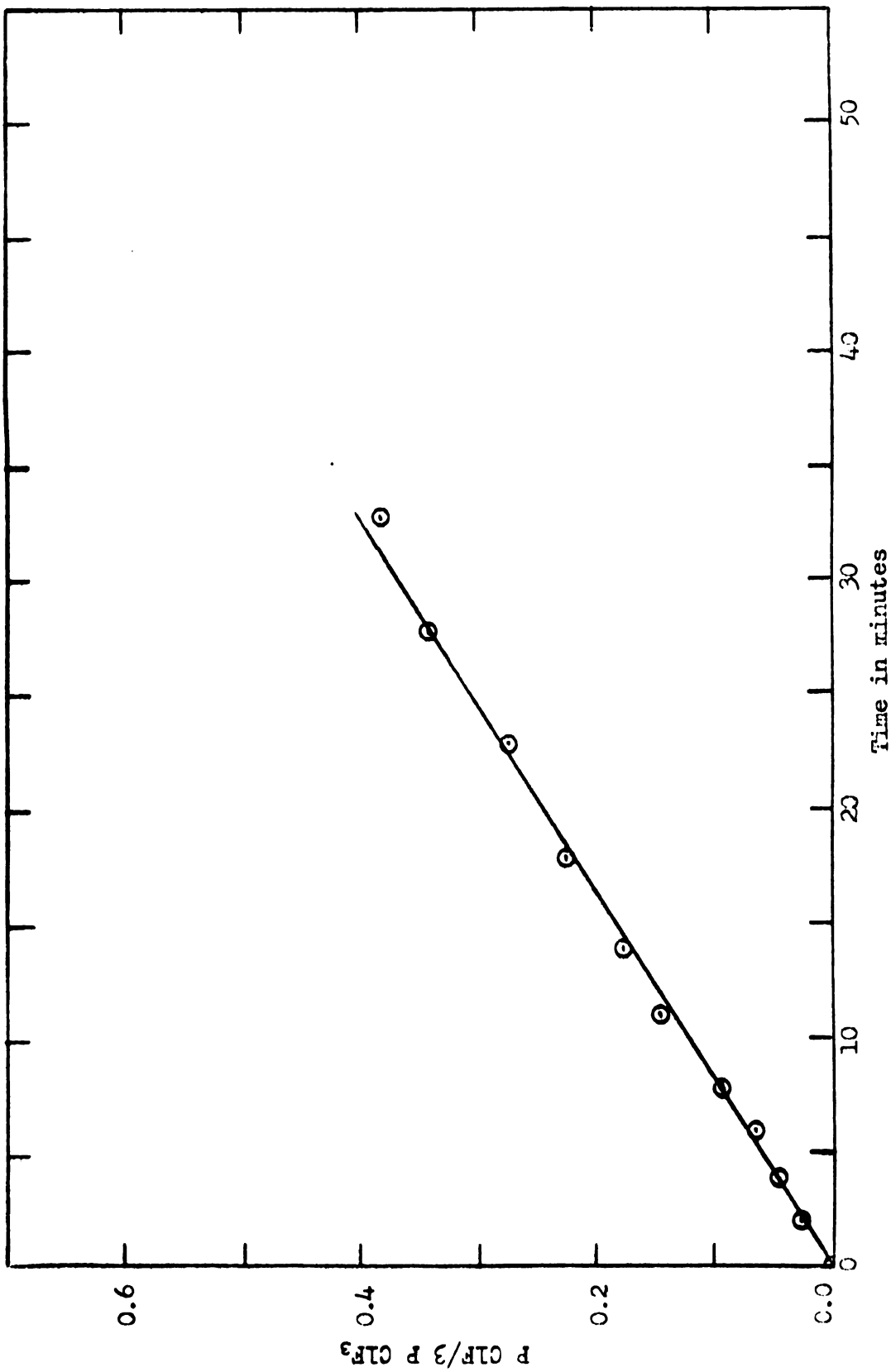


Figure 36. Chlorine monofluoride formation at 150°C.

Concentration values were calculated from pressure values by use of the ideal gas law.

34) $PV = nRT$

where P = pressure in atmospheres

V = volume in liters

n = number of moles of gas

R = molar gas constant = .08205 $\frac{\text{l-atm.}}{\text{mole degree}}$

T = temperature in degrees Kelvin.

The results for three different temperatures are summarized in Tables V, VI and VII.

Assuming an Arrhenius equation relationship between specific reaction rate constants

10) $k = A \exp\left(-\frac{\Delta Ea}{RT}\right)$

Then

17) $\ln k = -\frac{\Delta Ea}{RT} + \ln A$

35) $\log k = \frac{-\Delta Ea}{2.303\,RT} + \frac{1}{2.303} \log A$

If $\log k$ vs. $\frac{1}{T}$ is plotted, then

$$-\frac{\Delta Ea}{2.303\,R} = \text{slope}$$

36) $\Delta Ea = -\text{slope}\ 2.303R$

Average specific reaction rate constants were plotted vs. $\frac{1}{T}$ in Figure 37. From the slope of the experimental curve, ΔEa was calculated to be 21.8 kcal/mole.

TABLE V

KINETICS OF CHLORINE MONOFLUORIDE FORMATION† AT 240° C.

Figure	$P(ClF_3)_o$ mm.	$P(Cl_2)_o$ mm.	c mole/l. (x10³)	a-b mole/l. (x10³)	Slope $sec.^{-1}$ (x10³)	k $l.mole^{-1}sec.^{-1}$
16	217.0	217.0	6.78	0	2.262	0.3320
17	285.3	142.7	-	4.46	0.553	0.2858
18	142.7	285.3	-	4.46	0.617	0.3190
19	85.8	343.2	-	8.04	1.681	0.4818
20	345.6	86.4	-	8.10	1.324	0.3761
21	111.0	111.0	3.47	0	3.125	0.9015
22	160.5	160.5	5.02	0	2.679	0.5340
--	57.5	57.5	1.80	0	4.239	2.379*
					k average	0.461

† See Appendix II for original data

* Discarded on the basis of statistical deviation from the mean.

The equilibrium constant for the reaction

$$ClF_3 + Cl_2 = 3ClF$$

at 240°C. was calculated from thermochemical values (30) to be

$$K_p = \frac{P(ClF)^3}{P(ClF_3)\,P(Cl_2)} = 8.7 \times 10^6 \text{ atm.}$$

TABLE VI

KINETICS OF CHLORINE MONOFLUORIDE FORMATION† AT 220° C.

Figure	$P(ClF_3)_o$ mm.	$P(Cl_2)_o$ mm.	c mole/l. ($\times 10^3$)	a-b mole/l. ($\times 10^3$)	Slope $sec.^{-1}$ ($\times 10^3$)	k $l.mole^{-1}sec.^{-1}$
23	344.0	86.0	-	8.39	0.5620	0.1544
24	344.8	86.2	-	8.41	0.6064	0.1661
25	343.2	85.8	-	8.375	0.4955	0.1364
26	345.6	86.4	-	8.435	0.7826	0.2138
27	340.0	85.0	-	8.295	0.6578	0.1827
28	308.8	77.2	-	7.532	0.7112	0.2176
29	348.0	87.0	-	8.485	0.1228	0.3336
30	343.2	85.8	-	8.375	0.4682	0.1288
31	348.0	87.0	-	8.485	0.6522	0.1772
					k average	0.190

† See Appendix II for original data

The equilibrium constant for the reaction

$$ClF_3 + Cl_2 = 3ClF$$

at 220°C. was calculated from thermochemical values (30) to be

$$K_p = \frac{P(ClF)^3}{P(ClF_3)\,P(Cl_2)} = 8.3 \times 10^6 \text{ atm.}$$

TABLE VII

KINETICS OF CHLORINE MONOFLUORIDE FORMATION† AT 180° C.

Figure	$P(ClF_3)_o$ mm.	$P(Cl_2)_o$ mm.	c mole/l. ($\times 10^3$)	a-b mole/l. ($\times 10^3$)	Slope $sec.^{-1}$ ($\times 10^3$)	k $l.mole^{-1}sec.^{-1}$
32	208.0	208.0	7.36	0	0.18870	0.02562
33	213.5	213.5	7.55	0	0.18055	0.02390
34	215.0	215.0	7.60	0	0.19907	0.02620
35	196.5	196.5	6.95	0	0.22222	0.03196
36	201.5	201.5	7.12	0	0.20408	0.02866
					k average	0.0273

† See Appendix II for original data

The equilibrium constant for the reaction

$$ClF_3 + Cl_2 = 3ClF$$

at 180°C. was calculated from thermochemical values (30) to be

$$K_p = \frac{P(ClF)^3}{P(ClF_3)\,P(Cl_2)} = 7.6 \times 10^6 \text{ atm.}$$

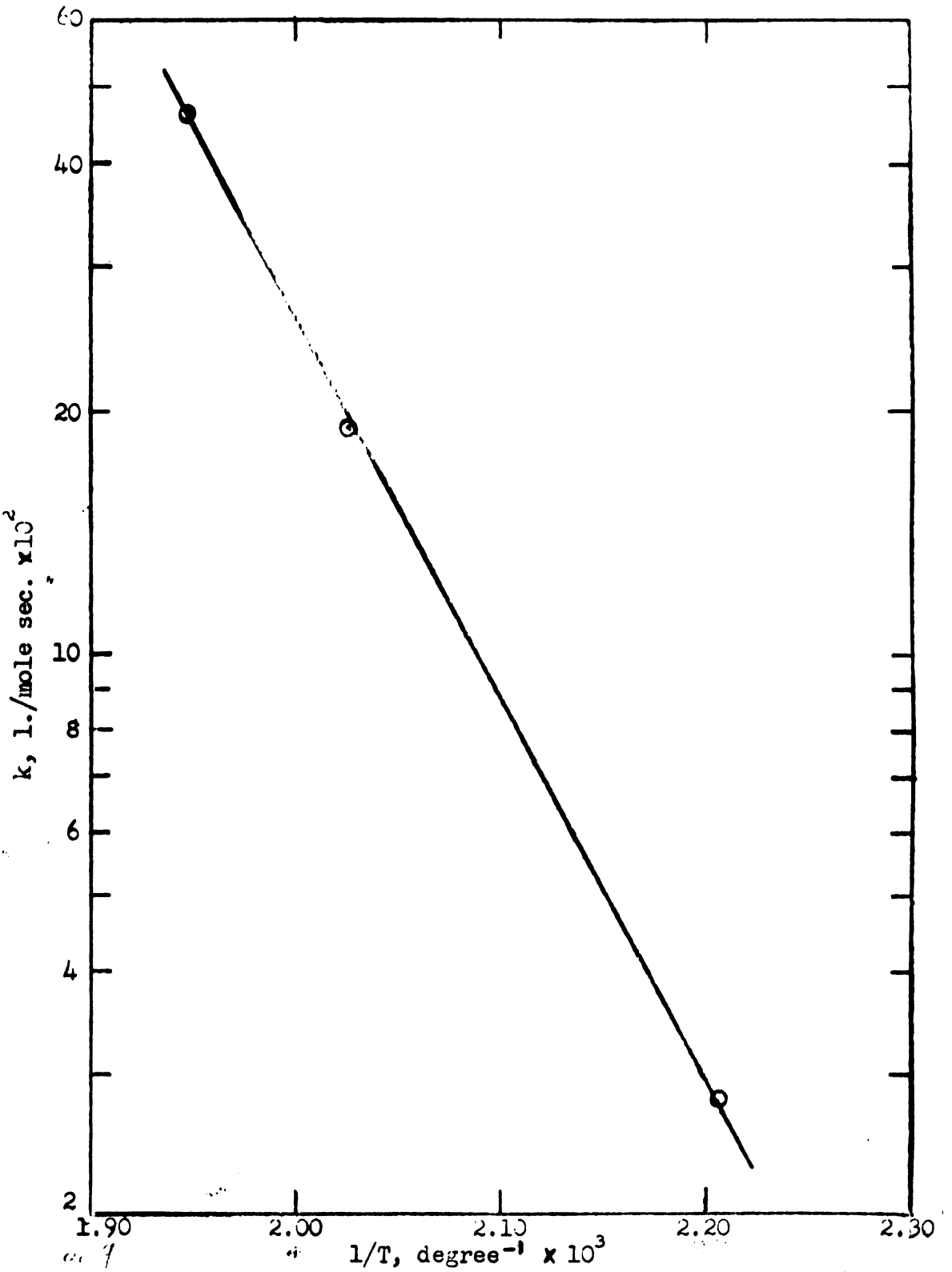


Figure 37. Arrhenius plot for chlorine monofluoride formation.

Using the equations given in Section IV, the entropy of activation for the formation of chlorine monofluoride was calculated.

12) $\Delta F^{\ddagger} = -RT \ln \left(\frac{h\,k}{k_B T} \right) = - (1.986)\ (493)\ (2.303) \log$

$$\frac{(1.901 \times 10^{2})(6.624 \times 10^{-27})}{(1.3803 \times 10^{-16})\ (493)}$$

$\Delta F^{\ddagger} = 24{,}213$ cal./mole

19) $\Delta H^{\ddagger} = \Delta Ea - nRT \qquad 21829 - 2(1.986)(493)$

$\Delta H^{\ddagger} = 19{,}871$ cal./mole

20) $\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta F^{\ddagger}}{T} = \frac{19871 - 24213}{493} = -8.81$ e.u.

For the calculation, the standard state for $\Delta S^{\ddagger}$ was taken as one mole per cubic centimeter; consequently, the units of k were cubic centimeters per mole second. For a bimolecular reaction between polyatomic molecules $\Delta S^{\ddagger}$, with one mole per cubic centimeter taken as the standard state, is expected to be negative, because of the decreased probability of activated complex formation associated with the necessary changing of rotational degrees of freedom into vibrational degrees of freedom.

Discussion

There were three main sources of error in this experiment, namely:

1. Uncertainty in the initial time and pressure (P_o) readings on expansion of gas into hot chamber.
2. Assumptions necessary in correcting for unreacted gas in the pressure gauge chamber.
3. Possible errors in measuring temperature and pressure.

The overall error was estimated to be between five and ten per cent. The activation energy is probably accurate to ± 1 kcal, and the activation entropy to ± 0.5 e.u.

The bond energy[†] of chlorine trifluoride may be calculated from heat of formation data (Table III, Section II).

37)	$ClF_3 = 3/2\ F_2 + 1/2\ Cl_2$	$\Delta H_f = 37.3$ kcal/mole
38)	$1/2\ Cl_2 = Cl$	$\Delta H_f = 28.9$ kcal/mole
39)	$3/2\ F_2 = 3F$	$\Delta H_f = 56.7$ kcal/mole
40)	$ClF_3 = 3F + Cl$	$\Delta H = 122.9$ kcal/mole

hence

$$D = 122.9 / 3 = 41.0 \text{ kcal/mole}$$

Assuming D is a fair approximation to the actual ΔH of one chlorine-fluorine bond, the heat of formation of ClF_2 may be estimated.

41) $ClF_3 = ClF_2 + F \qquad \Delta H \simeq D \simeq 41.0$ kcal/mole

Then $\Delta H_f(ClF_2) \simeq \Delta H_f(ClF_3) - \Delta H_f(F) + 41.0$

$\Delta H_f(ClF_2) \simeq -37.3 - 18.9 + 41.0 = -15.2$ kcal/mole

An upper limit for the chlorine-fluorine bond energy could be taken as the bond energy in chlorine monofluoride

42)	$ClF = 1/2\ Cl_2 + 1/2\ F_2$	$\Delta H_f = 11.9$ kcal/mole
38)	$1/2\ Cl_2 = Cl$	$\Delta H_f = 28.9$ kcal/mole
43)	$1/2\ F_2 = F$	$\Delta H_f = 18.9$ kcal/mole
44)	$ClF = Cl + F$	$\Delta H = 59.7$ kcal/mole

[†] III ΔH values used in this discussion were those at 298.16° K. Table III shows that this is a good approximation.

In this case

$$\Delta H_f(ClF_2) = \Delta H_f(ClF_3) - \Delta H_f(F) + 59.7 = 3.5 \text{ kcal/mole}$$

Consider possible steps leading to a second-order rate law for the formation of chlorine monofluoride. A free-radical mechanism such as

45) $ClF_3 + Cl_2 \xrightarrow{K_1} ClF + Cl + ClF_2$

46) $Cl + ClF_2 \xrightarrow{K_2} 2ClF$

yields the rate law

47) $$-\frac{d(ClF_2)}{dt} = K_1(ClF_3)(Cl_2)$$

which satisfies the second-order requirement. However, this rate process would require two radicals to react with each other in preference to reaction with the higher population of chlorine or chlorine trifluoride, which seems unlikely. In addition, the experimental activation energy should be at least equal to the enthalpy change in reaction 45). But for 45)

$$\Delta H = -\Delta H_f(ClF_3) - \Delta H_f(CL_2) + \Delta H_f(ClF) + \Delta H_f(Cl) + \Delta H_f(ClF_2)$$

$$\Delta H = 37.3 + 0 - 11.9 + 28.9 - 15.2$$

$$\Delta H = 39.1 \text{ kcal/mole}$$

which is substantially larger than the 21.8 kcal/mole activation energy. If the upper limit value for $\Delta H_f(ClF_2)$ is used, the enthalpy change in 44) is 37.3 + 0 - 11.9 + 28.9 + 3.5 = 57.8 kcal/mole, which is higher than the value obtained previously. Finally, suppose the bond energy of the first chlorine-fluorine rupture in chlorine trifluoride is

arbitrarily taken about equal to 22 kcal/mole ($\triangle$ Ea). The total energy of bonding in chlorine trifluoride is about 123 kcal/mole, from 40). This indicates that each remaining bond would have an energy of about (123-22)/2 = 50.5 kcal/mole or, by 44) within about 9 kcal/mole of the energy of the bond in the monofluoride, which seems somewhat unlikely. It is no doubt possible to approximate both experimental activation energy and order by a free-radical chain mechanism assigning suitable steps and stepwise activation energies. However, such approximations might be considered rather arbitrary, because there is not enough information about the system to allow selection of stepwise activation energies, for example, which could be verified for self-consistency with other work.

An alternative mechanism is

48) $ClF_3 + Cl_2 \xrightarrow{K_1} ClF + Cl_2 + F_2$

49) $F_2 + Cl_2 \xrightarrow{K_2} 2ClF$

which again yields the proper rate law. The enthalpy change in 48) is

$$\triangle H = \triangle H_f(ClF) + \triangle H_f(Cl_2) + \triangle H_f(F_2) - \triangle H_f(Cl_2) - \triangle H_f(ClF_3)$$

$$\triangle H = -11.9 + 0 + 0 - 0 + 37.3 = 25.4 \text{ kcal/mole}$$

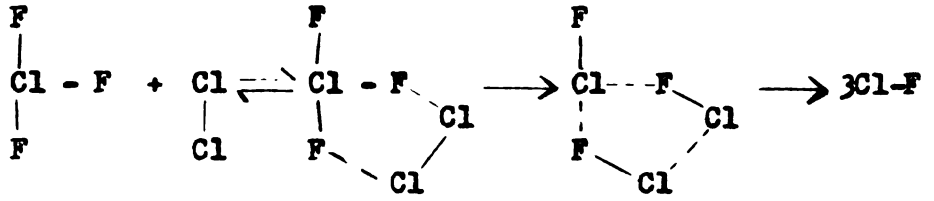
The energy requirement is thus reasonably close to that found experimentally. However, chlorine trifluoride is known to disproportionate (Table I) in the temperature range studied. It therefore seems that no bimolecular collision between chlorine and chlorine trifluoride would be necessary to obtain the products indicated by step 48).

A third alternative is to postulate the existence of a complex intermediate. For example

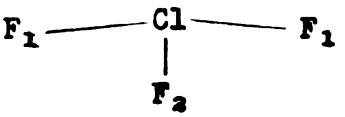
50) $ClF_3 + Cl_2 \xrightarrow{K_1} ClF_3 \cdot Cl_2$

51) $ClF_3 \cdot Cl_2 \xrightarrow{K_2} 3ClF$

This mechanism would yield a second-order rate law provided the rate determining step is assumed to be 50); a second-order rate law is also found if 50) is written as a reversible reaction, thus implying a transition-state-complex, which may be preferable. This process is certainly energetically possible. Supporting evidence can be obtained from the large negative value for the entropy of activation. For a given case the more negative the value of $\Delta S^{\dagger}$, the smaller the steric factor hindering the formation of the activated complex. For the present case it is possible to postulate a complex which might be expected to form with little steric hindrance. Chlorine may join the chlorine trifluoride molecule at either wing of the planar tee, and then break apart to yield chlorine monofluoride as schematically shown below.

52) 

From the planar tee structure for chlorine trifluoride



the $F_1 - F_2$ distance is 2.280 A°. Since the Cl - Cl distance is 1.984 A° in the Cl_2 molecule, the complex pictured in equation 48) is plausible.

A number of possible mechanisms other than second order were tested with the experimental data, without finding a rate law which adhered

to the data. Some mechanisms tested were

A. A first order rate law

B. mechanism

$$ClF_3 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} ClF + F_2$$

$$F_2 + Cl_2 \xrightarrow{K_3} 2ClF$$

rate law*

$$\frac{P_{ClF_3}}{\frac{dP_{total}}{dt}} = K \frac{P_{ClF}}{P_{Cl_2}} + K'$$

C. mechanism

$$Cl_2 \xrightarrow{K_1} 2Cl$$

$$Cl + ClF_3 \xrightarrow{K_2} ClF_2 + ClF$$

$$ClF_2 + Cl_2 \xrightarrow{K_3} 2ClF + Cl$$

$$M + Cl + Cl \xrightarrow{K_4} Cl_2 + M$$

(M = wall)

rate law*

$$\frac{dP_{total}}{dt} = \frac{K (P_{ClF_3})^{3/2}}{(P_{total})^{1/2}}$$

D. mechanism

$$ClF_3 \xrightarrow{K_1} ClF_2 + F$$

$$F + Cl_2 \xrightarrow{K_2} ClF + Cl$$

$$Cl + ClF_3 \xrightarrow{K_3} ClF + ClF_2$$

$$ClF_2 + Cl_2 \xrightarrow{K_4} 2ClF + Cl$$

$$M + Cl + Cl \xrightarrow{K_5} Cl_2 + M$$

rate law*

$$\frac{\frac{dP_{total}}{dt}}{P_{ClF_3}} = \frac{K (P_{ClF_3})^{1/2}}{(P_{total})^{1/2}} - K'$$

---

* $\frac{dP_{total}}{dt}$ values obtained graphically from pressure and time data.

E. mechanism

$Cl_2 \xrightarrow{K_1} 2Cl$

$Cl + ClF_3 \xrightarrow{K_2} ClF_2 + ClF$

$ClF + ClF_2 \xrightarrow{K_3} Cl + ClF_3$

$ClF_2 + Cl_2 \xrightarrow{K_4} 2ClF + Cl$

$Cl + 2ClF \xrightarrow{K_5} ClF_2 + Cl_2$

$Cl + Cl \xrightarrow{K_6} Cl_2$

rate law

$$\frac{\dfrac{(P_{Cl_2})^{3/2} P_{ClF_3}}{P_{ClF}}}{\dfrac{dP_{total}}{dt}} = K \frac{P_{Cl_2}}{P_{ClF}}$$

and

$$\frac{\dfrac{(P_{ClF})^2}{P_{ClF}}}{\dfrac{dP_{total}}{dt}} = K' \frac{P_{Cl_2}}{P_{ClF}}$$

The first expression applying in the early stages of reaction, the second near the end of reaction.

VI. THE CHLORINE TRIFLUORIDE AND CHLORINE MONOFLUORIDE SYSTEM

Introduction

Only qualitative data were obtained in the study of chlorine exchange in the chlorine trifluoride-chlorine system because the reaction to give chlorine monofluoride interfered. However, this circumstance was fortuitous in that it indicated the feasibility of production of chlorine monofluoride for experimentation purposes. Moreover, tagged chlorine monofluoride production required only one additional operation beyond those needed for the chlorine-chlorine trifluoride exchange; namely, the application of the formation reaction studied in the preceding section using tagged chlorine. Furthermore, an exchange study of the chlorine monofluoride-chlorine trifluoride system was expected to yield quantitative data since no side reaction was predicted.

Materials

All materials except chlorine monofluoride were produced in the manner described in Section V. Chlorine monofluoride was produced according to the reaction

$$53) \quad ClF_3 + Cl_2^* \longrightarrow 3Cl^*F$$

in the nickel reaction chamber at a temperature of 240° C. Because of the low boiling point (-100.8° C.), and consequent high vapor pressure at room temperature, of chlorine monofluoride, this material was made in small lots as needed rather than attempt storage of a large amount.

Each lot was purified before use by trapping (liquid nitrogen bath), degassing, then vaporization from an isopropanol-Dry Ice bath and discard of any residue. Purity of the first one or two lots was established by the ultra-violet spectrum (Figure 38). Since chlorine monofluoride is quantitatively separable from chlorine trifluoride by means of an isopropanol-Dry Ice bath, the only probable impurity was chlorine; the fact that mixtures of the monofluoride with the trifluoride underwent little pressure change with time when expanded into the hot reaction chamber was subsequently taken as positive evidence of purity.

Exchange Procedure

Tagged chlorine monofluoride was made as described above, then expanded into the gas-counting chamber and counted at various pressures. The activity was found to be essentially linear with gas pressure in the regions investigated (Figure 39). Since initial experiments showed that exchange did not occur at room temperature, chlorine monofluoride was mixed in various ratios with chlorine trifluoride in the copper expansion chamber of the gas-handling system. As in the kinetics experiments, after mixing the reactants were expanded into the pre-evacuated nickel reaction chamber which was kept at the desired temperature. The expansion process was exactly the same as described in Section V with one exception; immediately after reading the initial pressure, the valve from hot chamber to pressure gauge was closed. This valve was kept closed until just before quenching, at which time the valve was opened and the pressure again recorded. All the gas in hot chamber plus gauge

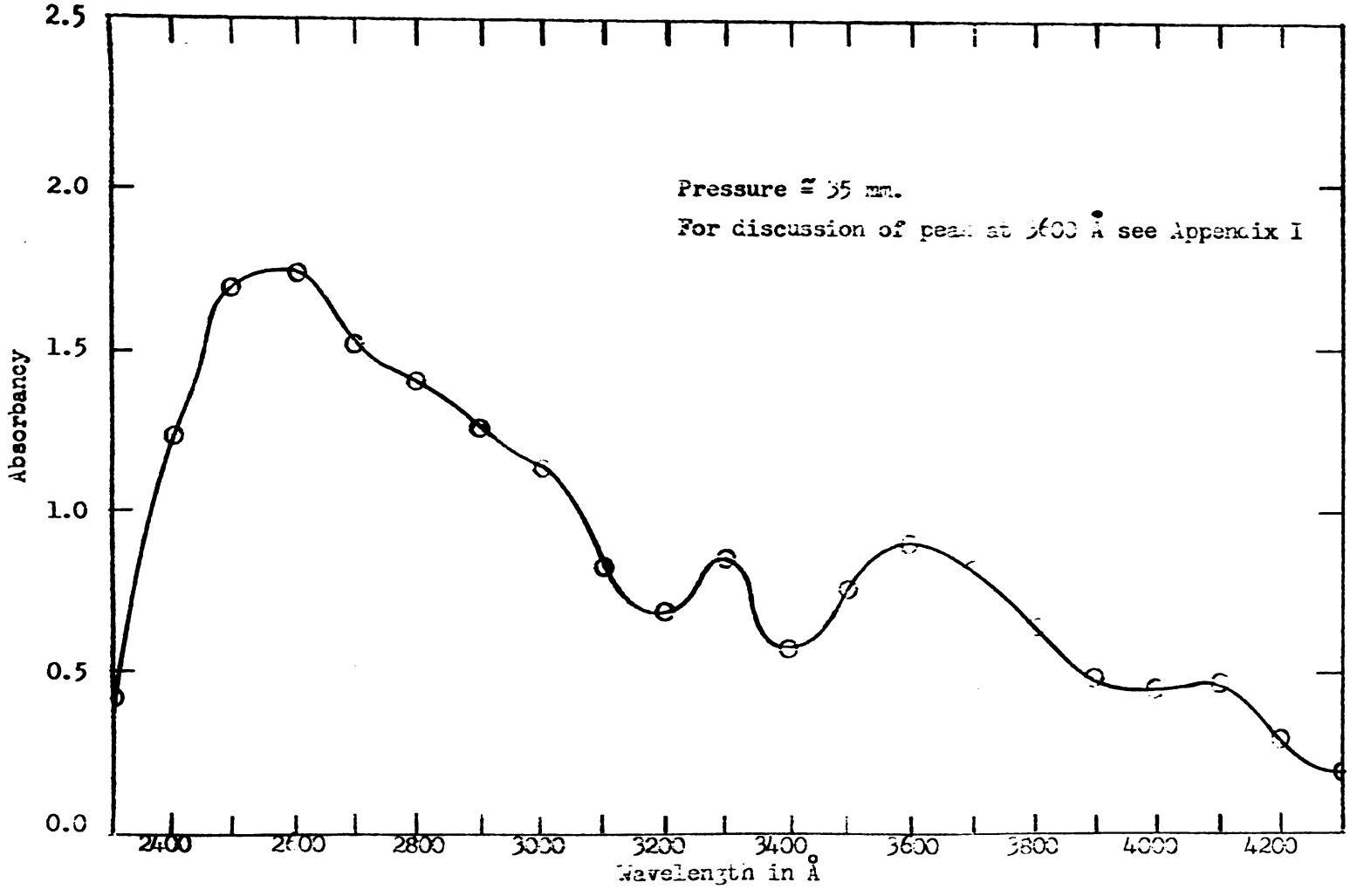


Figure 33. Chlorine monofluoride spectrum.

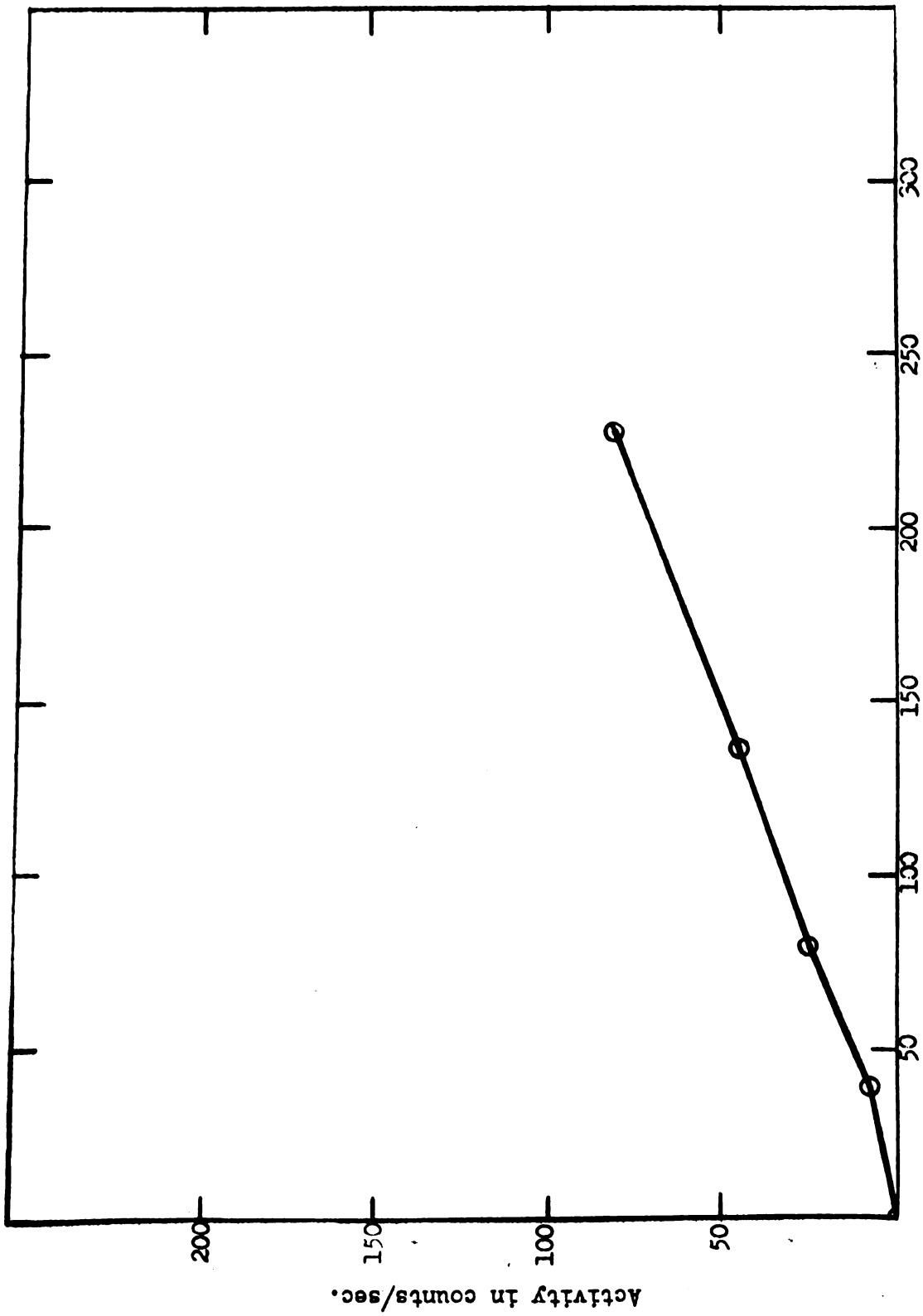


Figure 39. Activity of radioactive chlorine monofluoride at various pressures.

was removed in the quenching process which consisted of condensing the gases into a trap surrounded with a liquid nitrogen bath. Quantitative separation of reactants was effected by distilling chlorine monofluoride from the mixture of monofluoride and trifluoride at isopropanol-Dry Ice bath temperature (Figures 40 and 41). Chlorine monofluoride was expanded into the gas counting chamber and counted at a known pressure. After counting, the monofluoride was removed through the soda-lime bottle. Next, the residue from the distillation was purified by one or more vaporization-condensation-degassing cycles to remove traces of the monofluoride, then expanded into the counting chamber and counted at a known pressure. Because the pressure of the gas counted in some instances was low (< 50 mm.), and because the gauge calibration over a period of several months fluctuated by as much as three millimeters (Figures 42 and 43, and Appendix II) causing a relatively large error at very low pressures, the chlorine monofluoride fraction was counted at the same pressure as the chlorine trifluoride fraction, with few exceptions. In this way, possible error caused by gauge fluctuation was eliminated, for the fraction of exchange was calculated from the activities of each gas after reaction. Retention of total activity was, in most cases, ninety per cent or better. Activities of the separated reactants varied from about one to twenty counts per second above background; individual background counts were taken before each sample was counted to eliminate error due to adsorption.

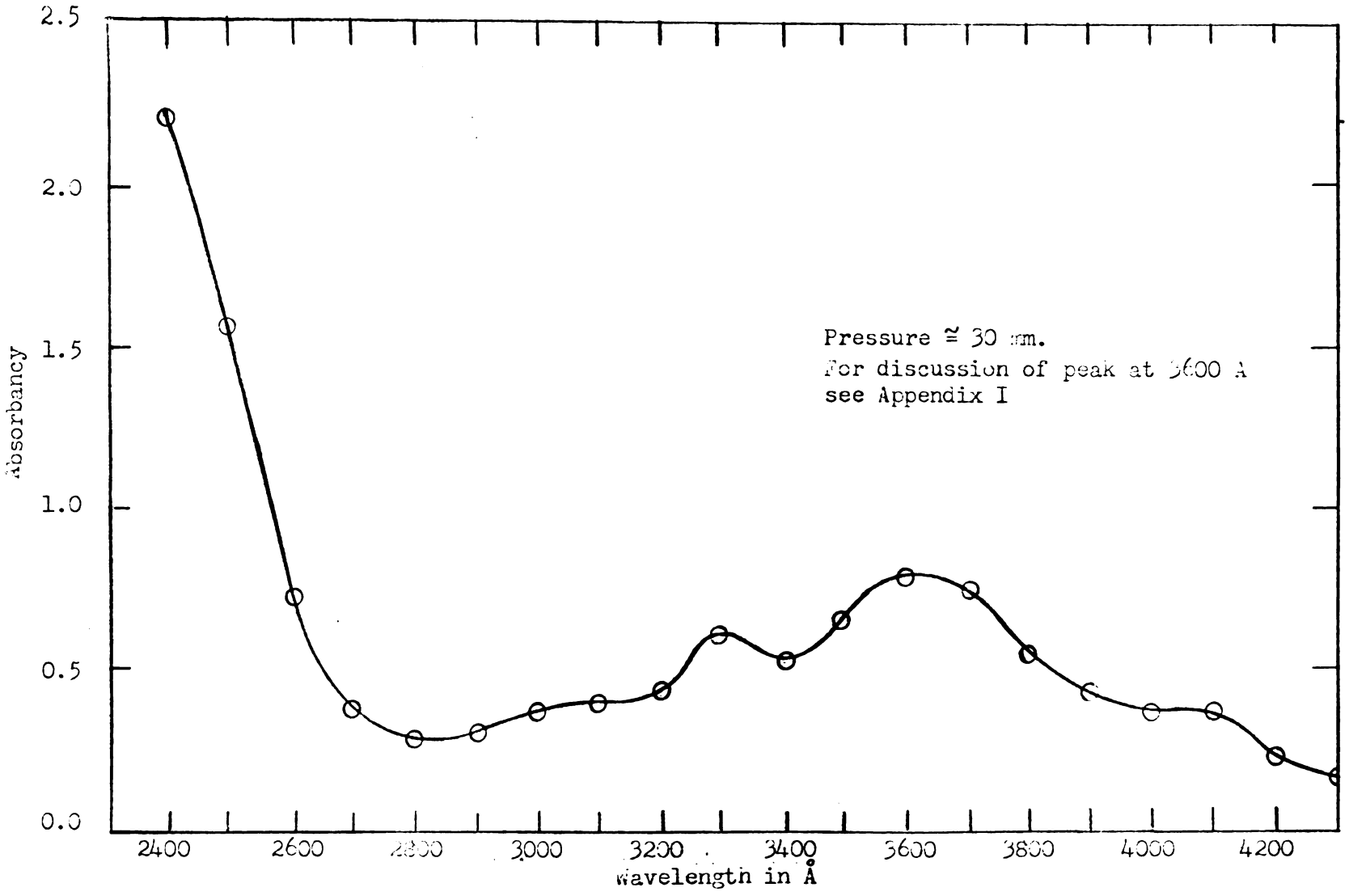


Figure 40. Spectrum of chlorine trifluoride separated from chlorine monofluoride.

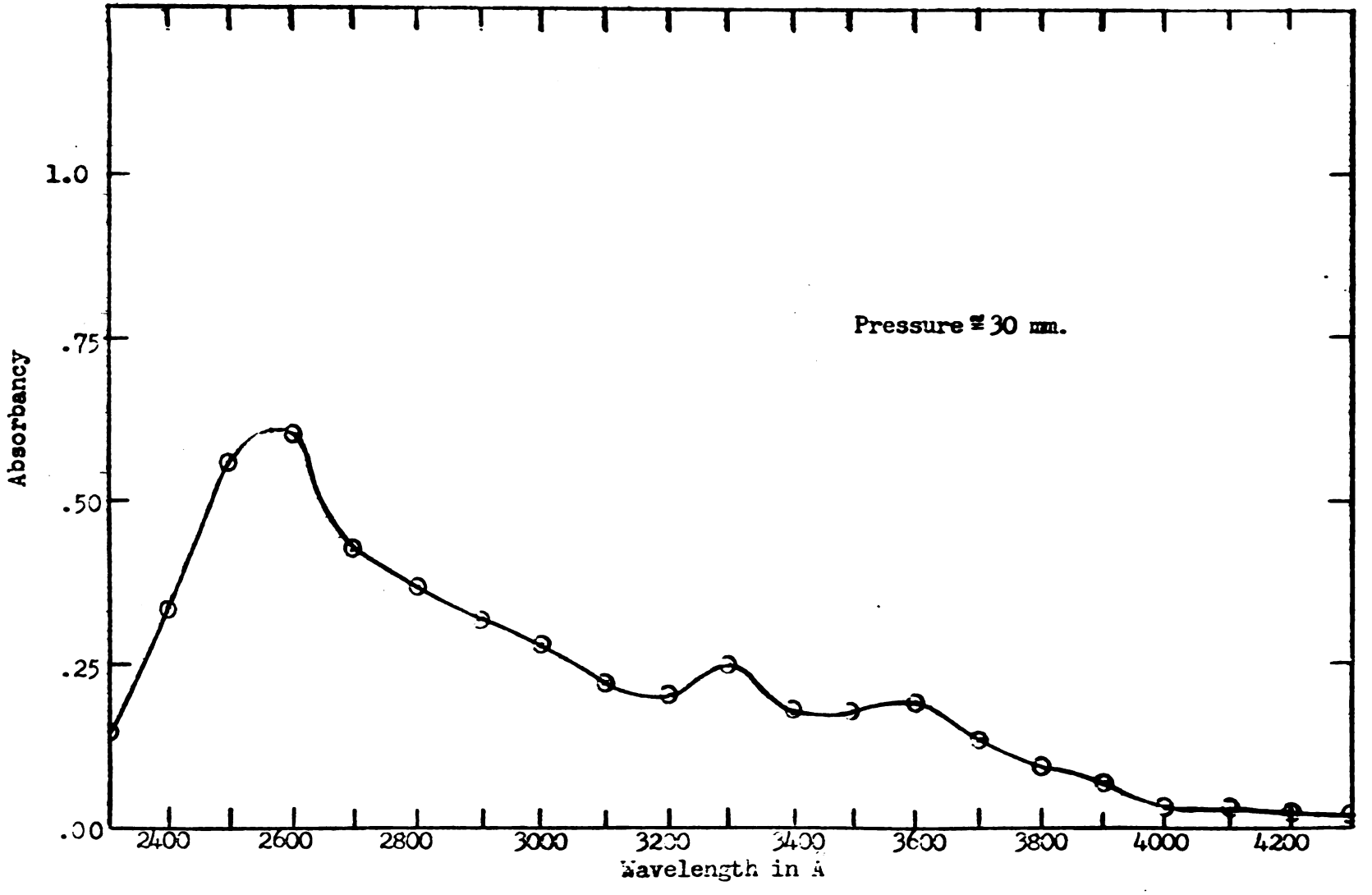


Figure 41. Spectrum of chlorine monofluoride separated from chlorine trifluoride.

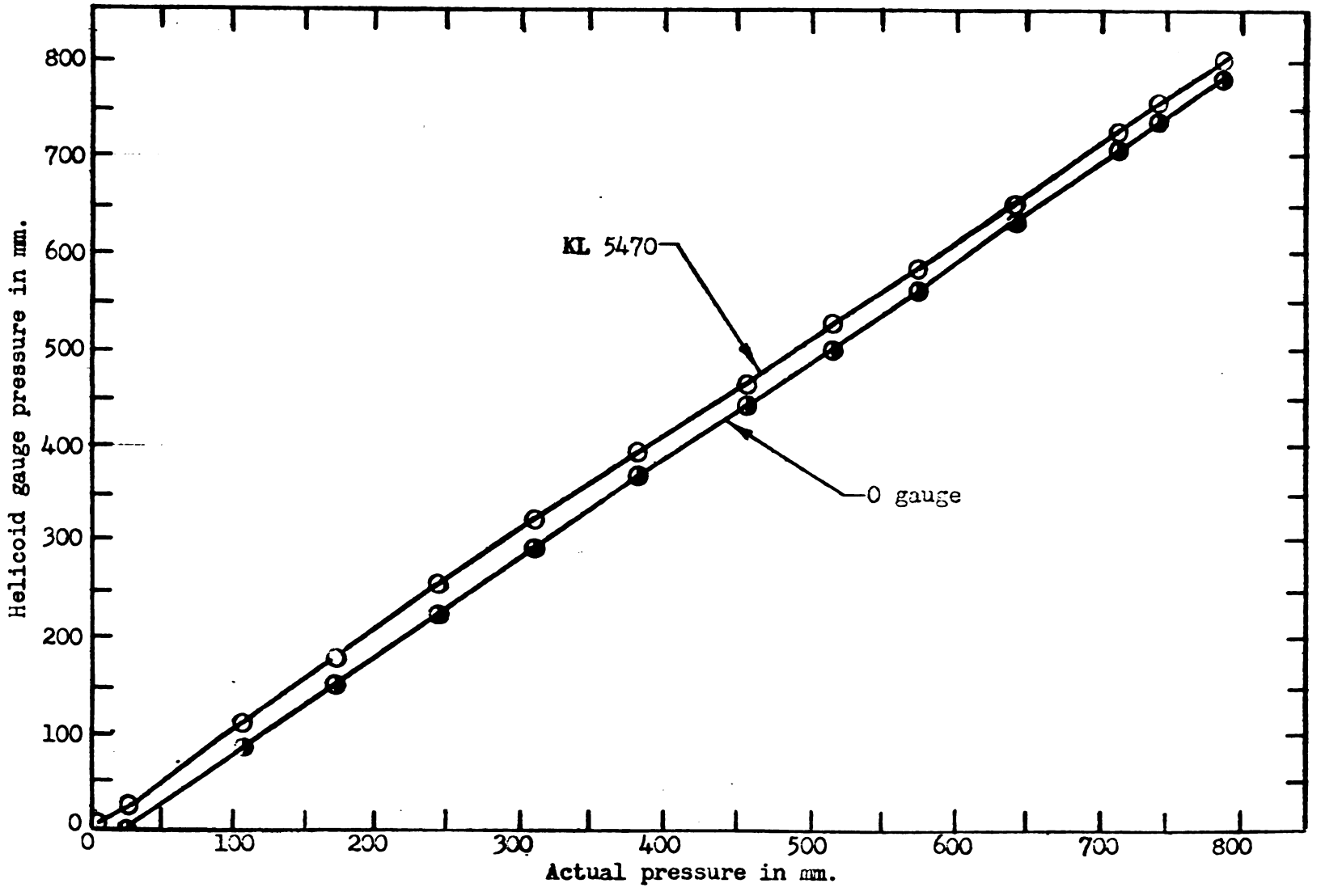


Figure 42. Second calibration curve for Helicoid gauges.

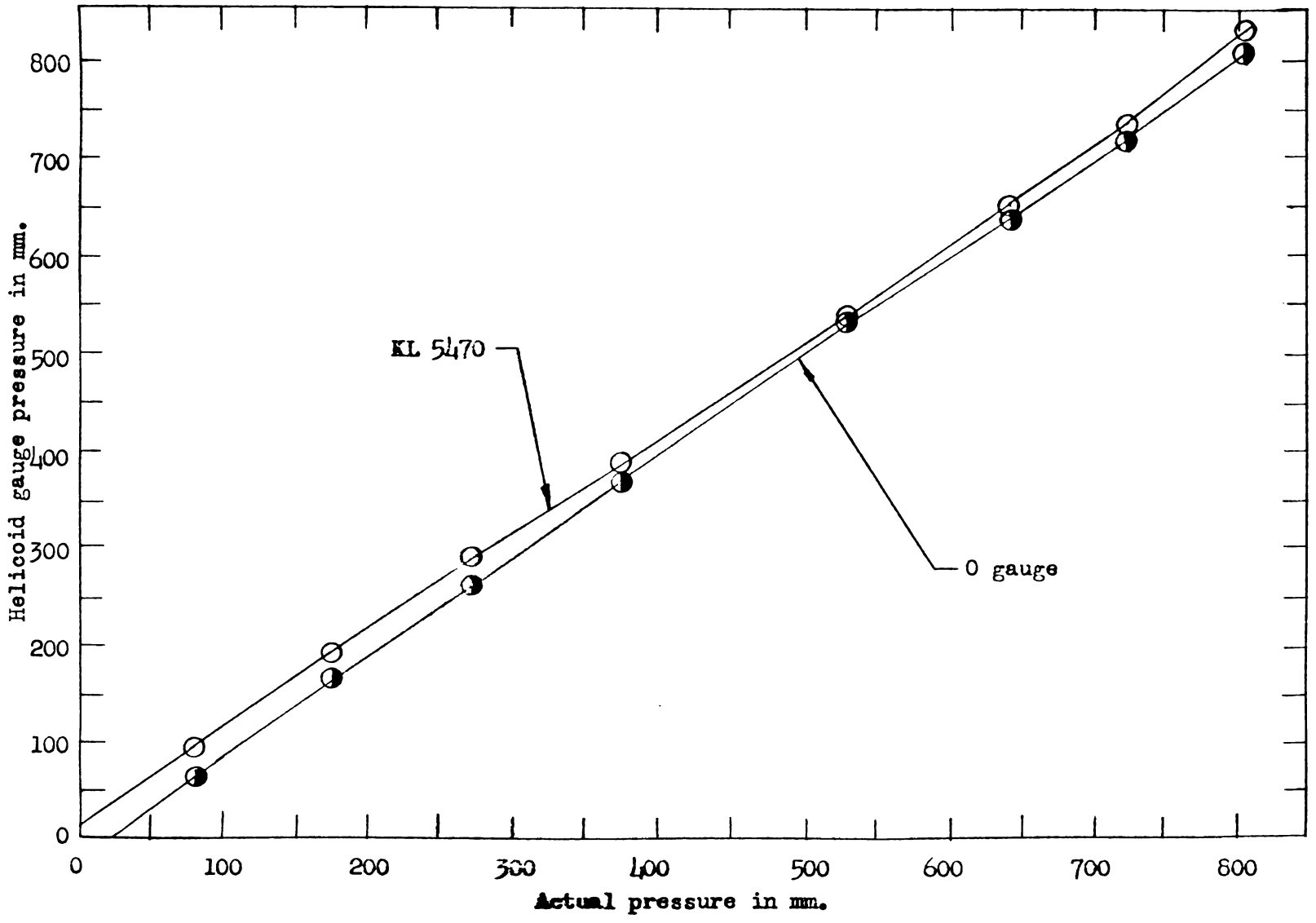


Figure 13. Third calibration curve for Helicoid gauges.

Results

Chlorine exchange did not occur between gaseous chlorine trifluoride and gaseous chlorine monofluoride in the copper vessel at pressures of about six hundred millimeters of mercury and temperatures up to 165° C. Exchange did occur when the temperature was maintained at 200° C. for one hour.

Quantitative results were obtained from experiments carried out in the nickel chamber. Exchange was studied at about 203° C., 224° C., and 245° C., as a function of the concentration of each constituent. The rate of exchange, R, was calculated for each individual experiment by the following method (See Section IV).

$$54)\quad R = \frac{2.303}{t}\,\frac{[ClF]\,[ClF_3]}{[ClF] + [ClF_3]}\,\log\frac{1}{1-f}$$

where t = time in minutes and brackets denote concentrations, calculated by the ideal gas law. The fraction exchanged, f, at time t, was calculated from the relationship

$$55)\quad f = \frac{\text{(experimental fractional activity in } ClF_3)}{\text{(theoretical fractional activity in } ClF_3\text{, at equilibrium)}\ (F)}$$

where F = fraction of gas in hot chamber (exchanging) = $\dfrac{V_R}{V_R + V_g\left(\frac{T_R}{T_g}\right)}$

V_R = volume of the reaction chamber = 311.9 ml.

V_g = volume of gauge = 19.6 ml.

T_R = temperature of the reaction chamber in °K

T_g = temperature of the gauge in °K.

For examples of this calculation, consider the cases:

1. Exchange between a mixture for which $ClF + Cl^*F : ClF_3 = 2:1$ at 473° K where $T_g = 301^\circ$ K ; equal amounts of each gas counted after separation; activity of Cl^*F = 6 counts/sec.; activity of Cl^*F_3 = 2.5 counts/sec.

   then $$F = \frac{311.9}{311.9 + 19.6\left(\frac{473}{301}\right)} = \frac{311.9}{342.7}$$

   and $$f = \frac{\frac{2.5}{2.5 + (2 \times 6)}}{\left(\frac{1}{3}\right)\left(\frac{311.9}{342.7}\right)}$$

2. Exchange between a mixture for which $ClF + Cl^*F : ClF_3 = 1:2$ at 473° K where $T_g = 301^\circ$ K ; equal amounts of each gas counted after separation; activity of Cl^*F = 10 counts/sec.; activity of Cl^*F_3 = 2.5 counts/sec.

$$f = \frac{\frac{2.5 \times 2}{2.5 \times 2 + 10}}{\left(\frac{2}{3}\right)\left(\frac{311.9}{342.7}\right)}$$

The rate of exchange, R, at constant temperature was plotted as a function of the concentration of chlorine trifluoride, with chlorine monofluoride being held constant, and also as a function of the monofluoride with the trifluoride being held constant (Figures 44 through 51). These graphs indicated the rate of exchange might be proportional to the square root of the concentration of each constituent. Although a second possibility will be discussed later, consider first the functional dependence

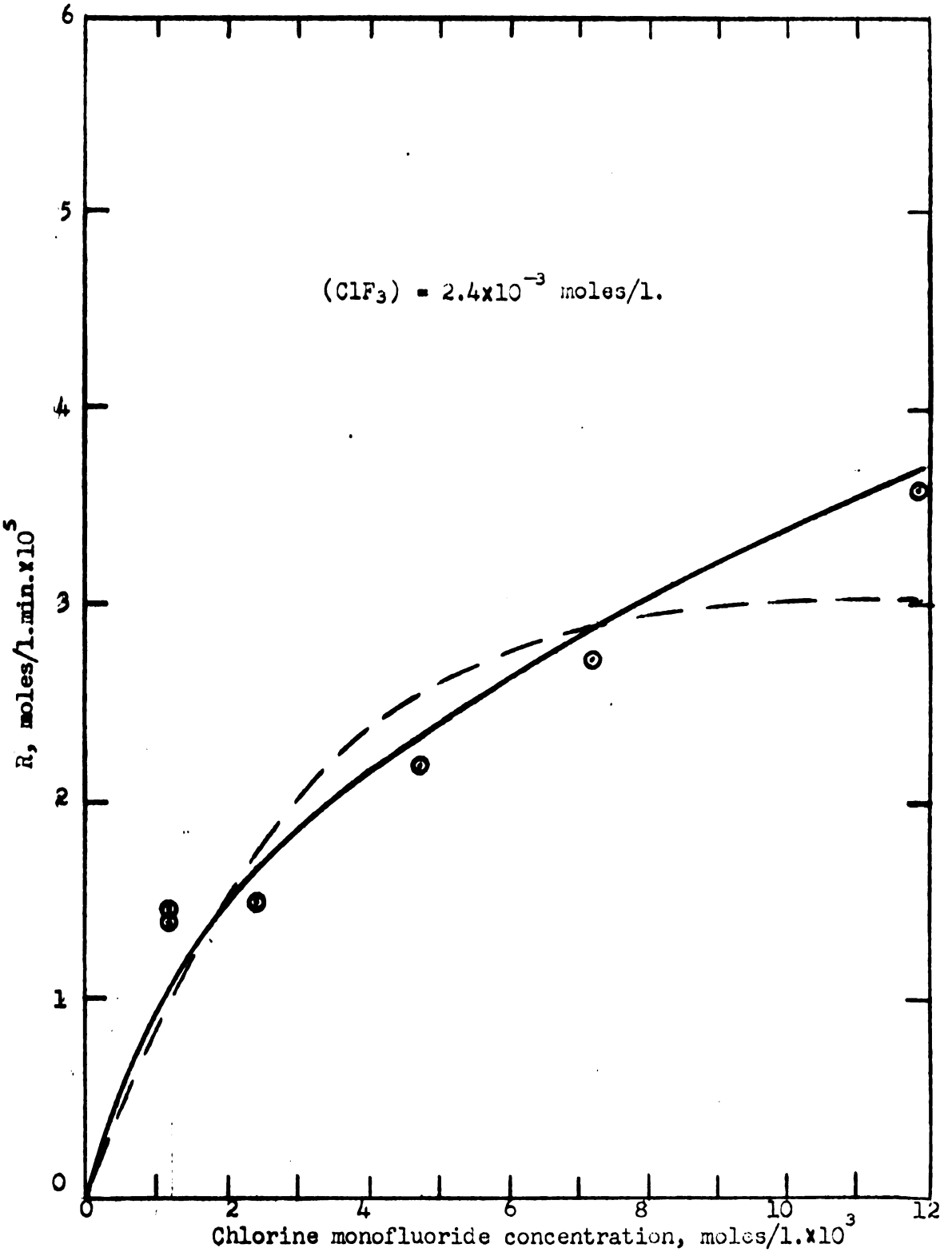


Figure 44. Chlorine trifluoride-chlorine monofluoride exchange at 203°C.

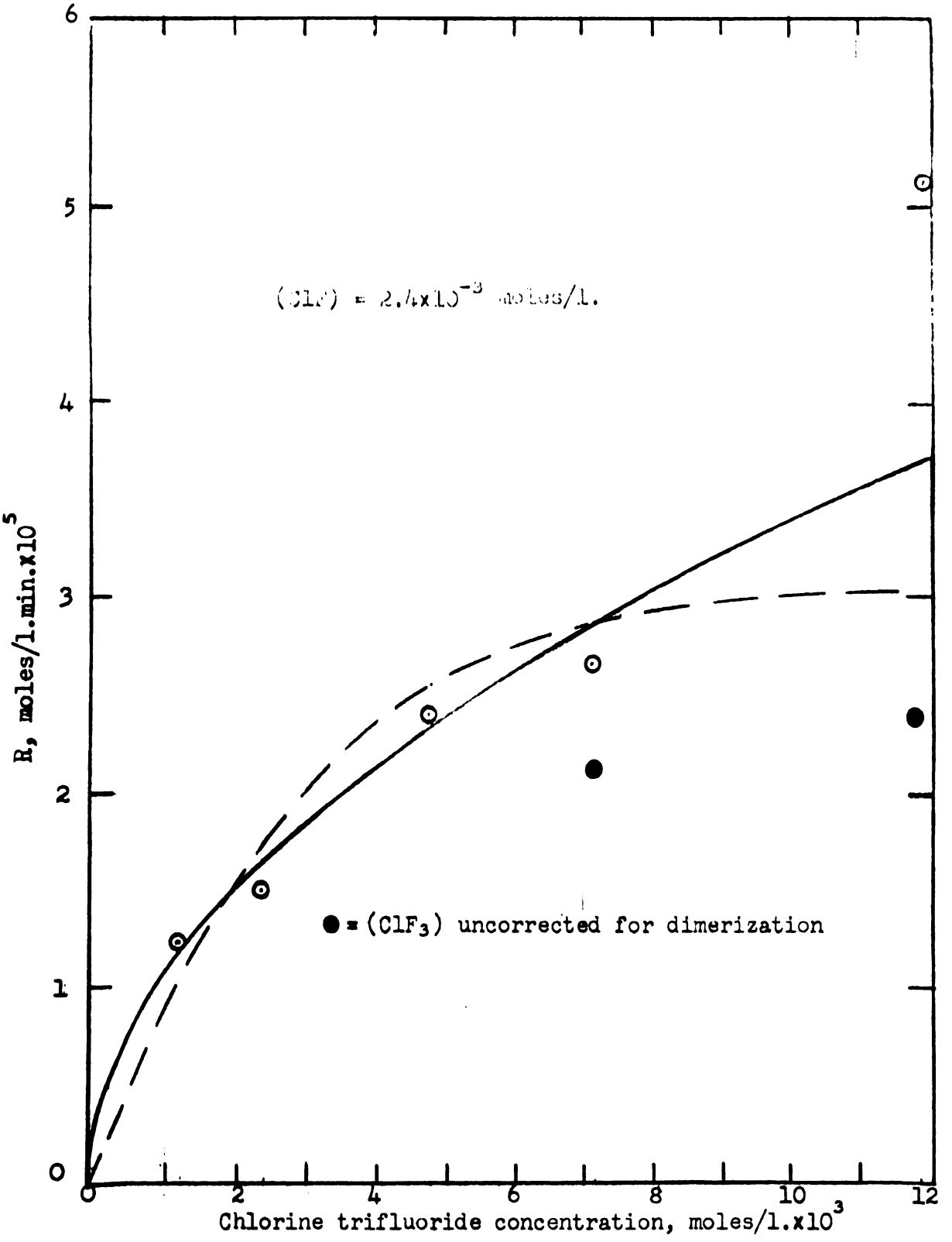


Figure 45. Chlorine trifluoride-chlorine monofluoride exchange at 203°C.

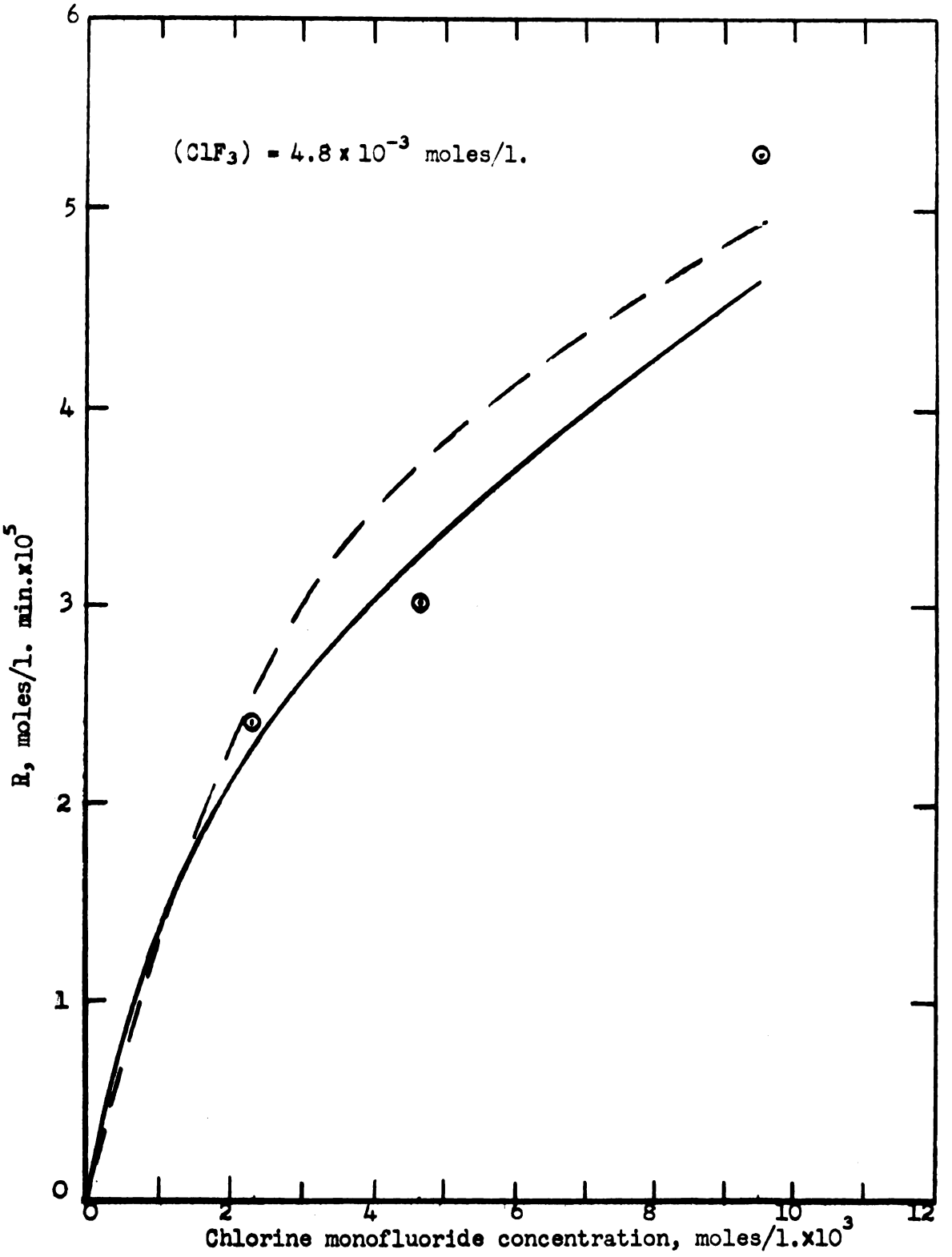


Figure 46. Chlorine trifluoride-chlorine monofluoride exchange at 20.3°C.

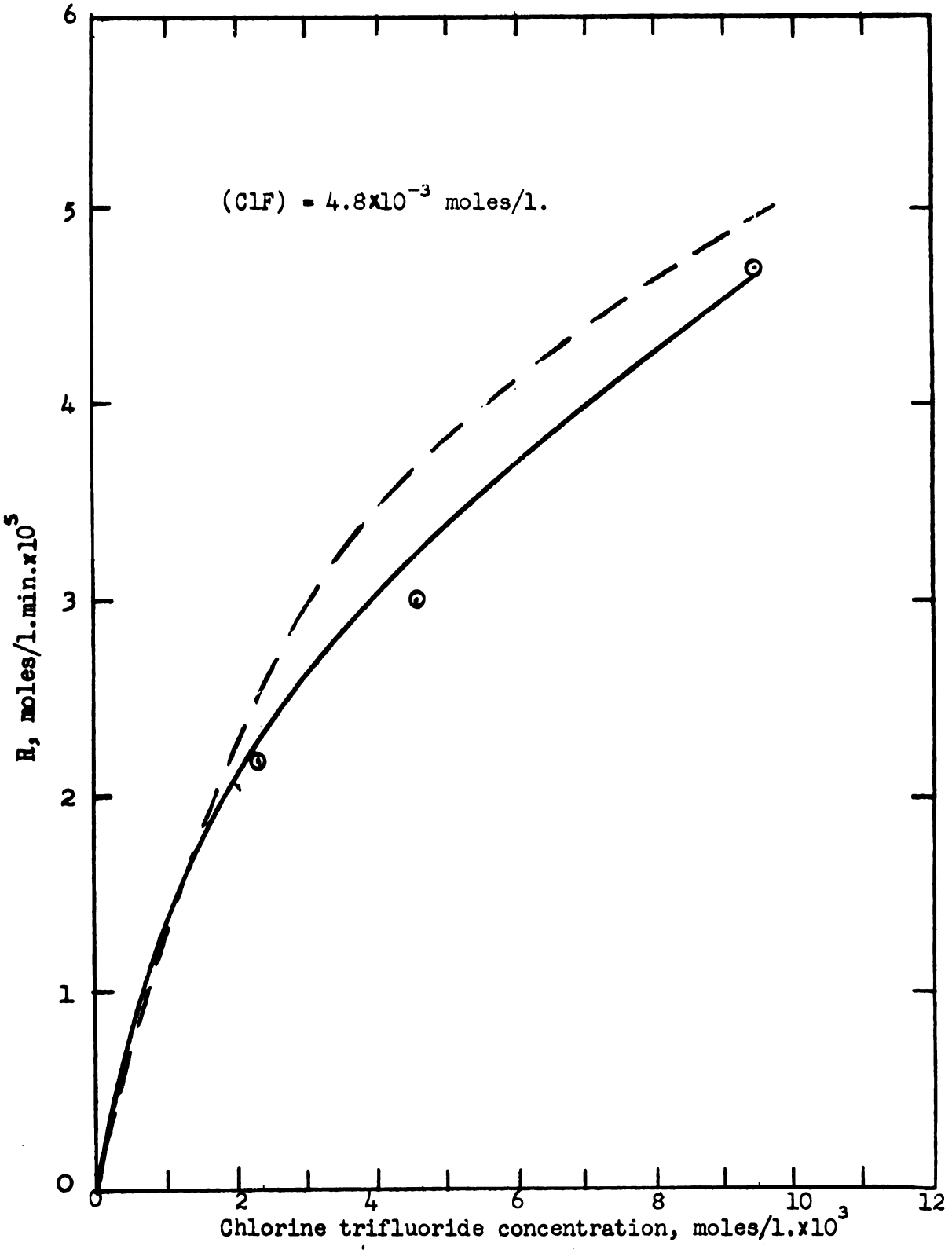


Figure 47. Chlorine trifluoride-chlorine monofluoride exchange at 203°C.

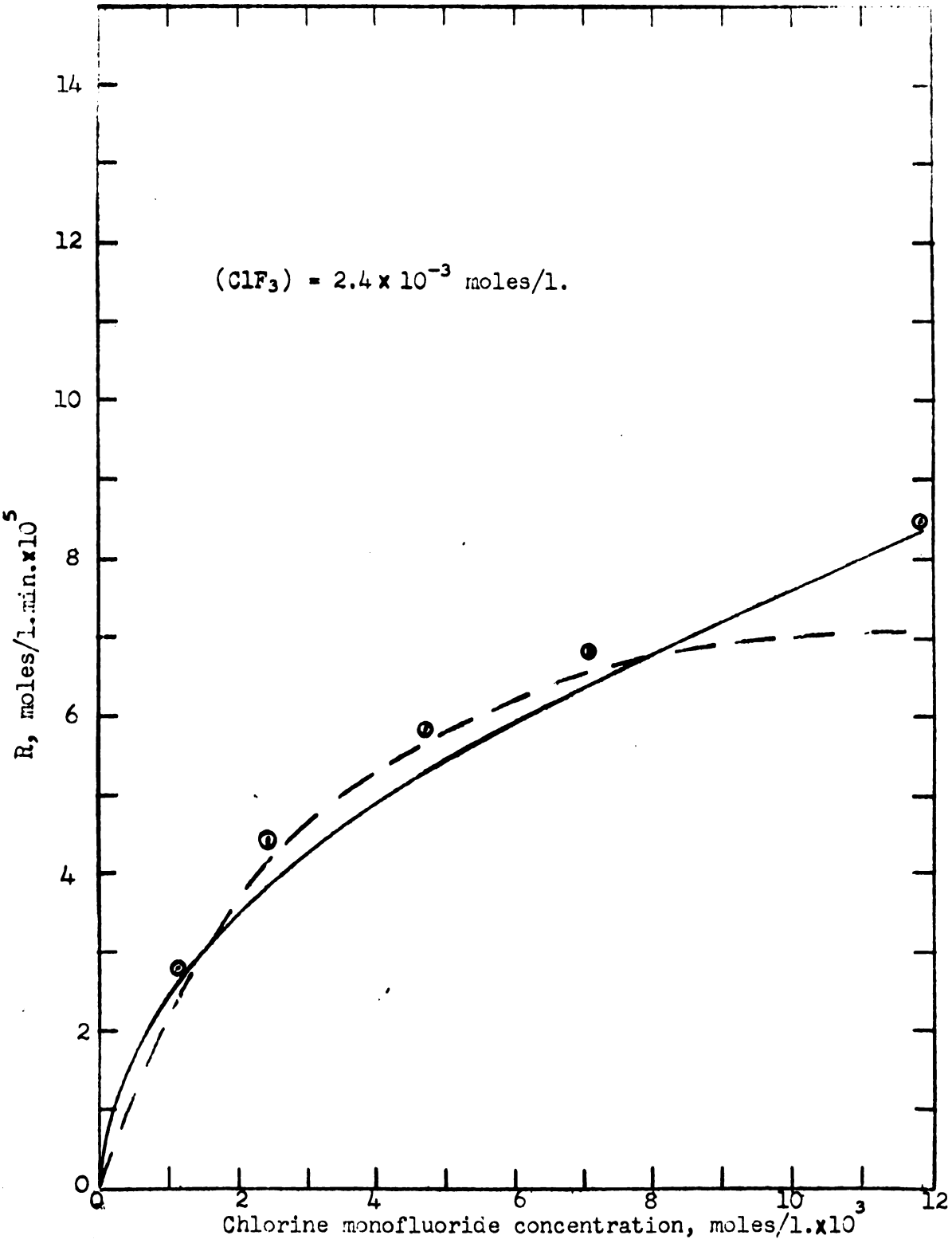


Figure 46. Chlorine trifluorice-chlorine monofluoride exchange at 24.4°C.

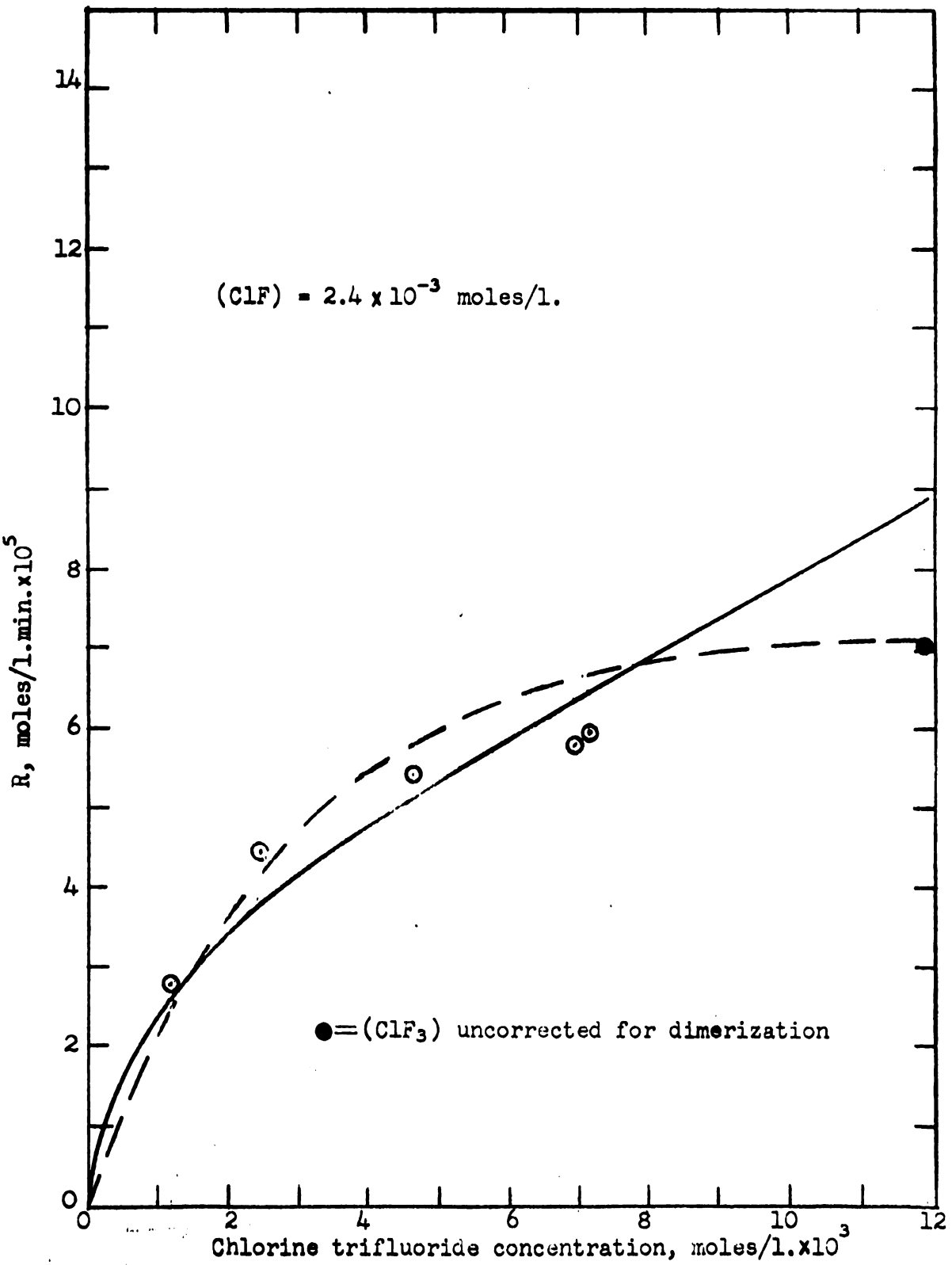


Figure 49. Chlorine trifluoride-chlorine monofluoride exchange at 224°C.

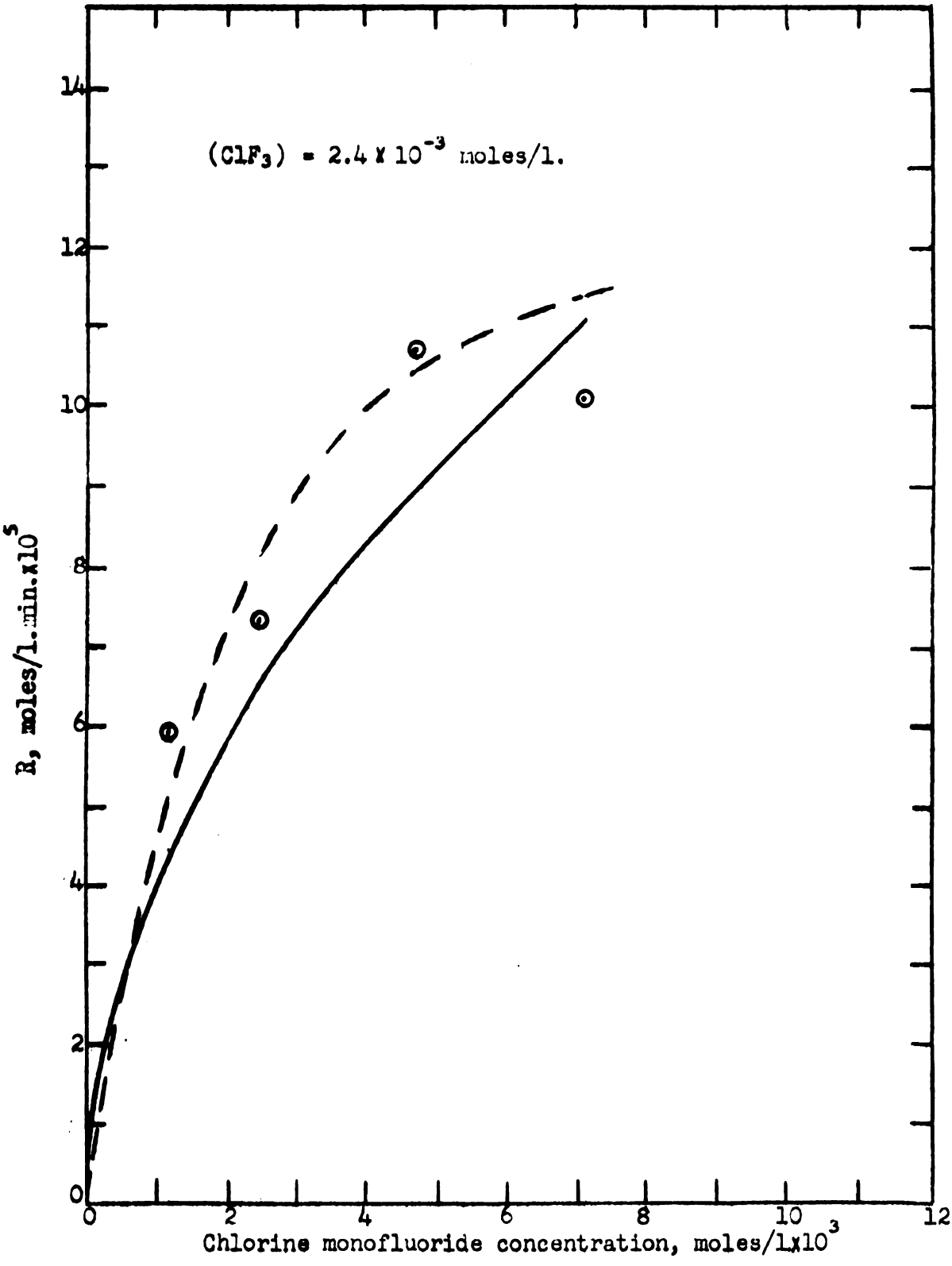


Figure 50. Chlorine trifluoride-chlorine monofluoride exchange at 245°C.

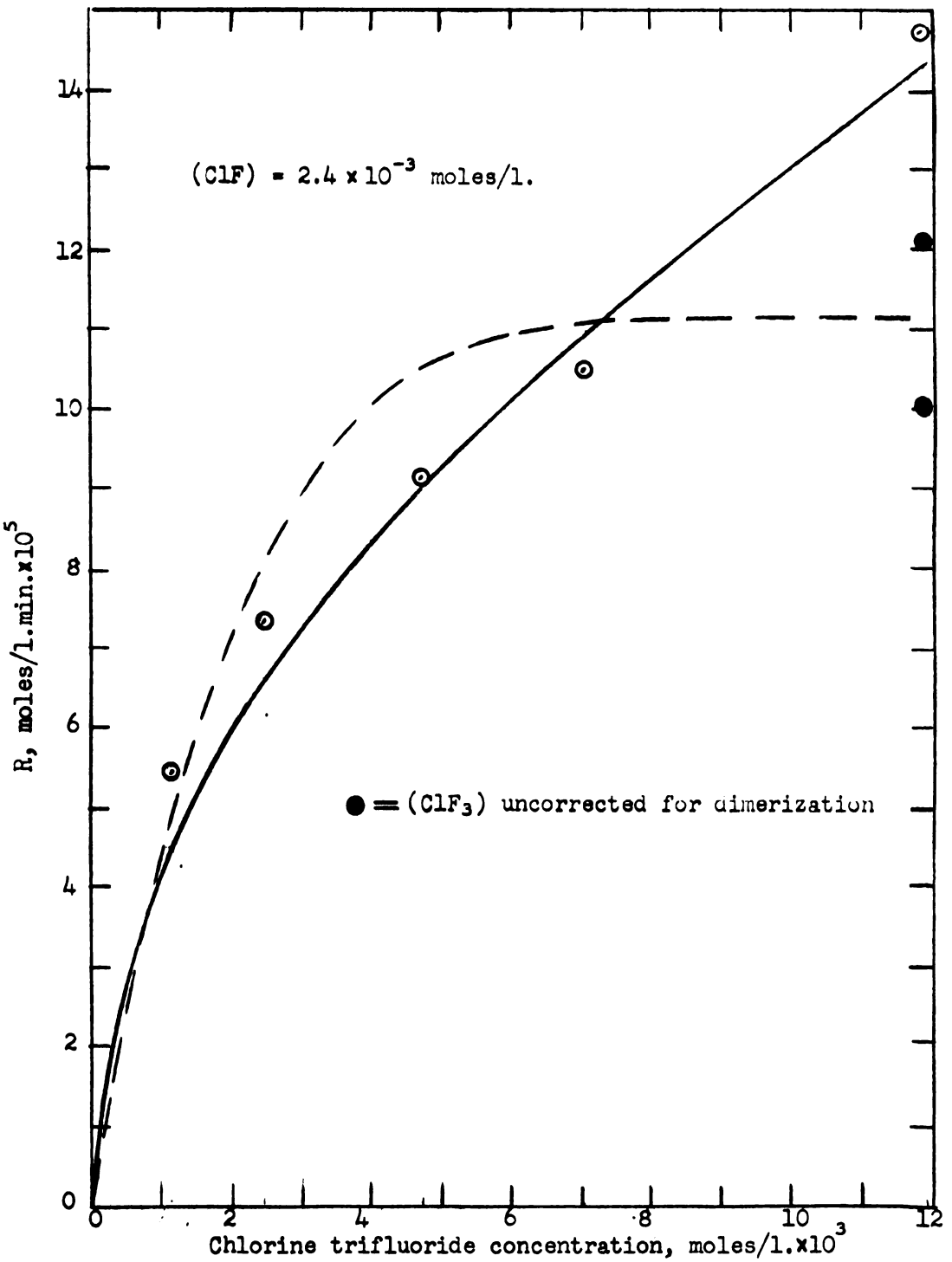


Figure 51. Chlorine trifluoride-chlorine monofluoride exchange at 245°C.

56) $R = K \sqrt{[ClF_3][ClF]}$

where K = some constant

$[ClF_3]$ = concentration of chlorine trifluoride in moles/l.

$[ClF]$ = concentration of chlorine monofluoride in moles/l.

Consequently, $R/\sqrt{[ClF_3][ClF]}$ should be constant at constant temperature if the postulated relationship is correct. That this relationship is indeed followed rather well is shown in Tables VIII, IX and X, in which values for $R/\sqrt{[ClF_3][ClF]}$ at 203.4° C., at 224.3° C., and at 245.4° C. are tabulated along with other pertinent data. Assuming that 56) is followed, then

57) $K_{av.} = (R/\sqrt{[ClF_3][ClF]})_{av.}$; T = constant

It is therefore possible to calculate the theoretical value of the rate, R calc., at the measured concentration (and temperature) of each experiment, thus

57a) $R_{calc.} = K_{av.} \sqrt{[ClF_3][ClF]}$

The values of Rcalc. are given in Tables VIII, IX and X. In addition, Rcalc. values were plotted on the graphs containing the experimentally determined points for R vs. concentration of one constituent (Figures 44 through 51), and a smooth curve drawn representing the theoretical curve obtained from Rcalc. Rather good agreement between theoretical curve and experimental points was found.

From a plot (Figure 52) of $K_{av.}$ versus $\frac{1}{T}$, the energy of activation for the exchange was calculated to be 15.9 kcal/mole.

TABLE VIII

HOMOGENEOUS EXCHANGE* IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 203.4° C.

Reaction Number	Exchange Time (min.)	[ClF] mole/l. ($\times 10^2$)	[ClF_3] mole/l. ($\times 10^2$)	f	R mole/l. min ($\times 10^6$)	$R/\sqrt{[ClF_3][ClF]}$ $min.^{-1}$ ($\times 10^2$)	Rcalc. mole/l. min. ($\times 10^6$)
1	60	11.89	2.378	0.6613	3.576	6.726	3.684
2	60	7.219	2.406	0.5949	2.718	6.522	2.888
3	60	2.389	2.389	0.5266	1.489	6.232	1.655
4	60	2.381	7.143	0.5113	2.131	5.168	2.857
5	60	2.370	11.85	0.5260	2.382	4.495	3.672
6	60	4.767	2.383	0.5628	2.191	6.500	2.335
7	60	2.372	4.744	0.5971	2.396	7.142	2.324
8	60	4.677	4.677	0.5381	3.010	6.436	3.240
9	60	9.509	4.755	0.6336	5.305	7.889	4.659
10	60	4.744	9.489	0.5882	4.678	6.972	4.649
11	60	2.406	1.203	0.5995	1.223	7.189	1.179
12	60	1.203	2.406	0.6432	1.378	8.098	1.179
13	30	1.197	2.394	0.4190	1.445	8.533	1.173
14	60	2.395	11.97	0.7861	5.129	9.579	3.710
15	60	2.381	7.142	0.5907	2.659	6.447	2.857
					Average	6.929	

* See Appendix II for original data.

TABLE IX

HOMOGENEOUS EXCHANGE* IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 224.3° C.

Reaction Number	Exchange Time (min.)	[ClF] moles/l. ($\times 10^3$)	[ClF_3] moles/l. ($\times 10^3$)	f	R moles/l. min.($\times 10^6$)	$R/\sqrt{[ClF_3][ClF]}$ min.$^{-1}$($\times 10^2$)	Rcalc. moles/l. min($\times 10^6$)
16	25	11.87	2.374	0.6580	8.463	1.594	8.361
17	25	7.121	2.374	0.6170	6.836	1.662	6.477
18	25	2.430	2.430	0.6012	4.470	1.839	3.828
19	25	2.325	6.975	0.5676	5.850	1.453	6.344
20	25	2.379	11.90	0.5899	7.069	1.329	8.382
21	25	4.769	2.384	0.6043	5.871	1.741	5.312
22	25	2.320	4.639	0.5841	5.427	1.654	5.167
23	25	2.406	1.203	0.5763	2.748	1.615	2.680
24	25	1.189	2.378	0.5746	2.788	1.658	2.649
25	25	2.374	7.121	0.5686	5.987	1.456	6.476
26	30	1.756	5.268	0.6009	4.033	1.326	4.791
					Average	1.575	

* See Appendix II for original data

TABLE X

HOMOGENEOUS EXCHANGE* IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 245.4° C.

Reaction Number	Exchange Time (min.)	[ClF] moles/l. ($\times 10^3$)	[ClF_3] moles/l. ($\times 10^3$)	f	R moles/l. min.($\times 10^5$)	$R/\sqrt{[ClF_3][ClF]}$ $min.^{-1}$($\times 10^2$)	Rcalc. moles/l. min.($\times 10^5$)
27	15	3.571	10.71	0.5442	14.03	2.268	16.65
28	15	2.376	11.88	0.5312	10.00	1.883	14.30
29	15	7.127	2.376	0.5732	10.11	2.457	11.08
30	15	2.470	2.470	0.5910	7.361	2.980	6.649
31	15	2.353	7.059	0.5902	10.50	2.576	10.97
32	15	2.381	11.90	0.6016	12.17	2.287	14.33
33	15	2.376	11.88	0.6736	14.77	2.780	14.30
34	15	4.731	2.365	0.6385	10.70	3.199	9.004
35	15	2.355	1.177	0.6460	5.434	3.264	4.482
36	15	1.177	2.355	0.6789	5.946	3.571	4.482
37	15	2.365	4.731	0.5697	9.115	2.725	9.004
					Average	2.692	

* See Appendix II for original data

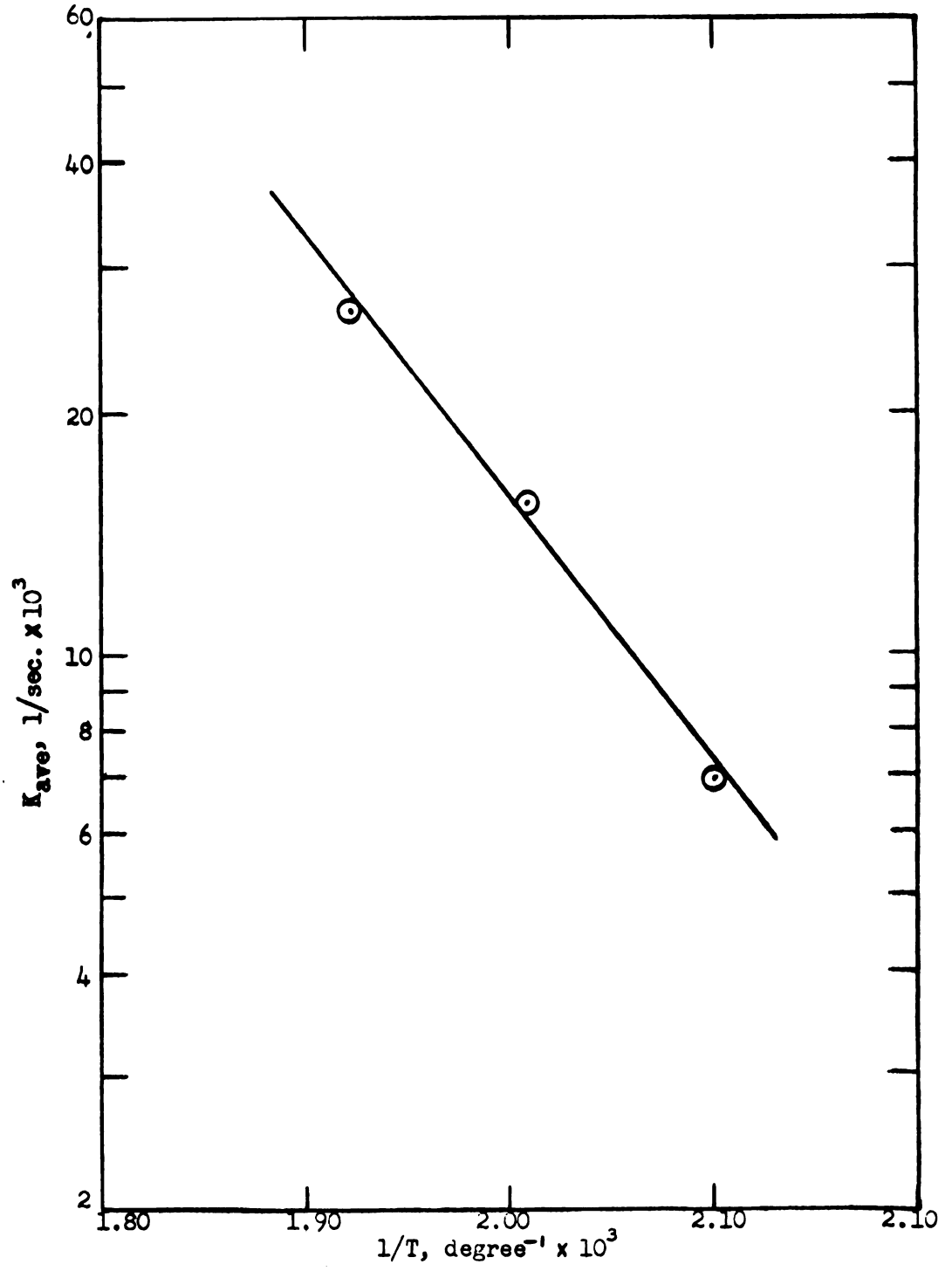


Figure 52. Arrhenius plot for chlorine monofluoride- chlorine trifluoride exchange: homogeneous mechanism.

The activation entropy for the exchange was calculated to be -46.0 e.u., assuming the order of the reaction (n) is one.

There is a second possible functional dependence of R on the concentration of constituents. Recall the Langmuir adsorption isotherm (equation 6, Section IV). If R were proportional to the fraction of surface covered by both chlorine trifluoride and chlorine monofluoride, then

58) $$R = K\theta_{ClF_3}\theta_{ClF} = \frac{K_1 b_{ClF_3} b_{ClF} [ClF_3]\,[ClF]}{[1 + b_{ClF_3}[ClF_3] + b_{ClF}[ClF]\,]^2}$$

where K_1 = specific reaction rate constant in moles/l.sec.

$b_{ClF_3} = b_{ClF} = b$, some constant (assumed equal for both reactants because of the similarity of rate dependence on each constituent.)

or

59) $$R = K_1 \frac{b^2 [ClF_3]\,[ClF]}{[\,1 + b\,([ClF_3] + [ClF])\,]^2}$$

60) $$\sqrt{\frac{R}{[ClF_3]\,[ClF]}} = \sqrt{\frac{K_1 b^2}{[1 + b\,([ClF_3] + [ClF])]^2}}$$

61) $$\sqrt{\frac{[ClF_3]\,[ClF]}{R}} = \frac{1 + b([ClF_3] + [ClF])}{\sqrt{K_1}\ b} = \frac{[ClF_3]+[ClF]}{\sqrt{K_1}} + \frac{1}{b\sqrt{K_1}}$$

Equation 61) is a linear equation; experimental data were plotted and a line drawn by the method of least squares, from which K_1 and b were obtained by the relationships

62) $$\text{slope} = \frac{1}{\sqrt{K_1}}$$

63) $$\text{y-intercept} = \frac{1}{b\sqrt{K_1}}$$

The values of K_A and b at the temperatures of the experiments are given in Table XI. These K_A and b values, as well as equation 59) were used to calculate the theoretical rate, R_A, for various experimental values of reactant concentration. The R_A values obtained are listed in Tables XII and XIII; these same values were used to graph the theoretical curves, assuming heterogeneous catalysis, in Figures 44 through 51.

From a plot (Figure 53) of K_A versus $1/T$, the energy of activation for the exchange was calculated to be 14.3 kcal/mole. The activation entropy in this case was calculated to be -67.9 e.u., arbitrarily taking the order of the reaction (n) to be one.

Discussion

The main sources of error in the exchange experiments were

1. Possible errors in measuring temperature and pressure.
2. Possible incomplete separation of reactants, because of, for example, surface adsorption.
3. Statistical errors inherent in radioactive counting.

In some instances, the net counts per second were only one count per second above background activity; it is therefore of interest to exemplify the magnitude of the statistical error. Consider the case of a background count of 600 counts in 15 minutes, and, with a sample in place, a total counting rate of 1000 counts in 10 minutes. Then (33)

$$R_{background} = \frac{600 \pm \sqrt{600}}{15} = 40 \pm 1.6 \text{ counts/min} = 0.66 \pm 0.021 \text{ counts/sec.}$$

$$R_{total} = \frac{1000 \pm \sqrt{1000}}{10} = 100 \pm 3.2 \text{ counts/min.} = 1.66 \pm 0.053 \text{ counts/sec.}$$

$$R_{net} = 100 - 40 \pm \sqrt{1.6^2 + 3.2^2} = 60 \pm 3.6 \text{ counts/min.} = 1 \pm 0.06 \text{ counts/sec.}$$

TABLE XI

CONSTANTS ARISING FROM THE APPLICATION OF THE LANGMUIR ADSORPTION ISOTHERM

Temperature °C.	b l./mole	K_1 † mole/l. min. $\times 10^3$
203.4	103.6	0.6238
224.27	110.6	1.361
245.38	165.3	1.627

† Equation 58

TABLE XII

HETEROGENEOUS EXCHANGE IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 203.4° C.

Reaction Number	$[ClF_3]$ moles/l.x 10^3	$[ClF]$ moles/l.x 10^3	R_A moles/l. min. x10^6
1	2.378	11.89	3.080
2	2.406	7.219	2.915
3	2.389	2.389	1.709
4	7.143	2.381	2.884
5	11.85	2.370	3.073
6	2.383	4.767	2.550
7	4.744	2.372	2.496
8	4.677	4.677	3.776
9	4.755	9.509	4.930
10	9.489	4.744	4.921
11	1.203	2.406	1.026
12	2.406	1.203	1.026
14	11.97	2.395	3.098
15	7.142	2.381	2.884

TABLE XIII

HETEROGENEOUS EXCHANGE IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 224.3° C. AND 245° C.

Reaction Number	Temperature °C.	$[ClF_3]$ moles/l. $\times 10^3$	$[ClF]$ moles/l. $\times 10^3$	R_A moles/l.min. $\times 10^5$
16	224.3	2.374	11.87	7.063
17	224.3	2.374	7.121	6.691
18	224.3	2.430	2.430	4.170
20	224.3	11.90	2.379	7.079
22	224.3	4.639	2.320	5.717
23	224.3	1.203	2.406	2.460
24	224.3	2.378	1.189	2.419
25	224.3	7.121	2.374	6.691
28	245.4	11.88	2.376	11.14
29	245.4	2.376	7.127	11.39
30	245.4	2.470	2.470	8.217
31	245.4	7.059	2.353	11.30
32	245.4	11.90	2.381	11.15
34	245.4	2.365	4.731	10.53
35	245.4	1.177	2.355	4.913
37	245.4	4.731	2.365	10.53

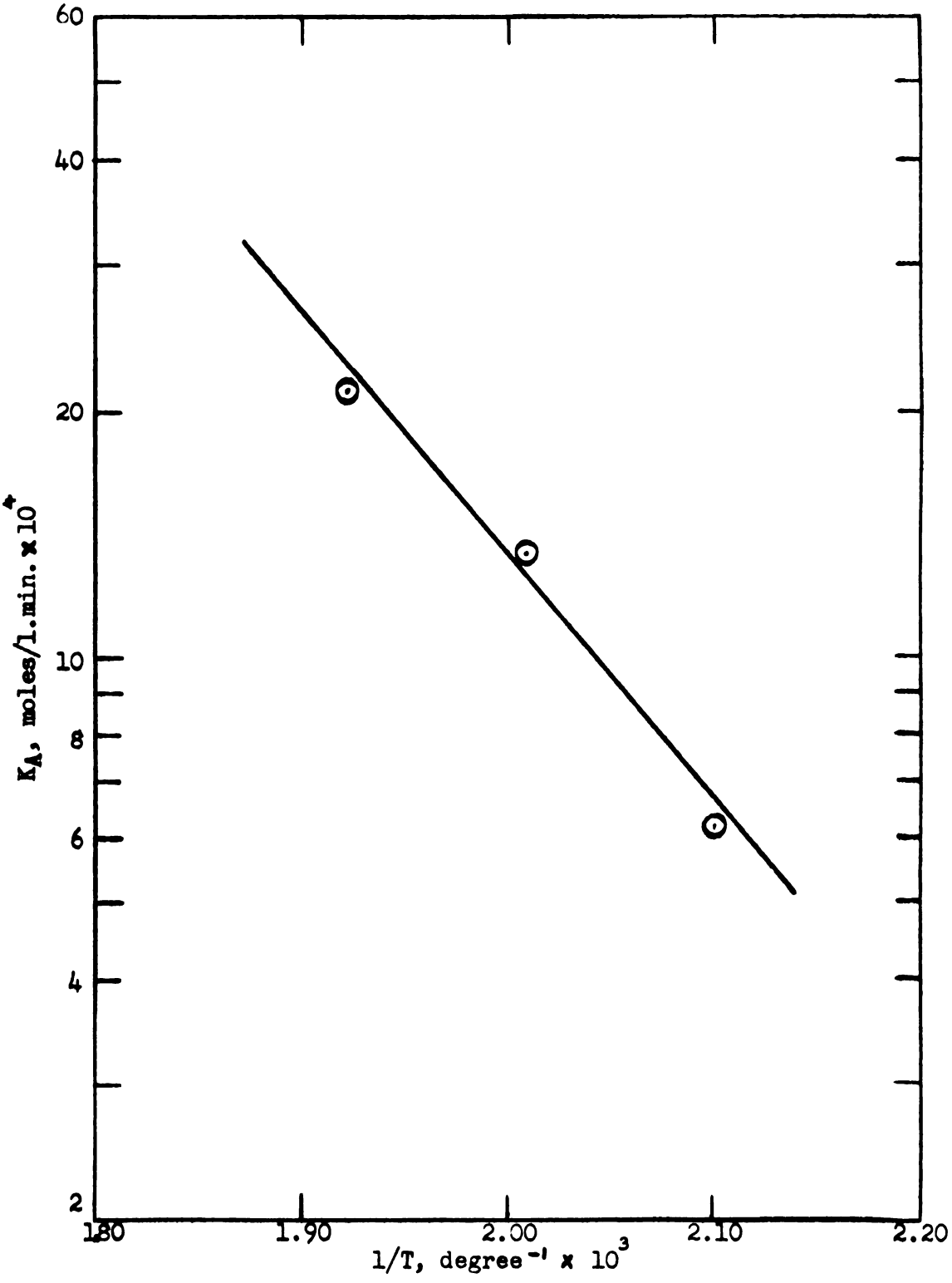


Figure 53. Arrhenius plot for chlorine monofluoride-chlorine trifluoride exchange: heterogeneous mechanism.

Because the example chosen is essentially the lower limit in net counting rate above background, and is much less than the total counting time used in these experiments, the error shown should be the maximum error caused by low activities. Overall error was estimated to be within ten to fifteen per cent. The activation energy is probably accurate to $\pm$ 1 kcal/mole and the activation entropy to $\pm$ 1 e.u.

The behavior of the rate of exchange, R, with the change in concentration of constituents can be interpreted in terms of either a homogeneous mechanism, or heterogeneous catalysis. Both arguments will be presented.

The case for a homogeneous mechanism. A homogeneous mechanism for exchange would have to predict the dependence of R on the square root of the product of reactant concentrations. The calculations determining the dependence of R upon reactant concentration for a particular mechanism are difficult in exchange reactions because some reactants and intermediates are tagged, and hence different (although chemically equivalent) from the corresponding untagged species. For simple mechanisms, it is possible to express the rate, $\frac{dx}{dt}$, (cf. equation 22) of increase of tagged atoms in species AX, in terms of the rate constants and constituent concentrations appropriate for the equations of the proposed mechanism, equate this $\frac{dx}{dt}$ to the equivalent $\frac{dx}{dt}$ used in deriving equation 22), and find R in terms of reactant concentrations and rate constants of the mechanism. An example of this treatment is (A) in the list of mechanisms (see page 109). Somewhat more complex mechanisms can be treated by the method of Marcus (38), which is

related to the process outlined above but involves simplifying assumptions. Thus Marcus lets BX^* be the concentration of those BX-type molecules which are tagged at time t, and defines the label* such that it vanishes when the specified atom enters a position in an AX-type molecule, but not when the specified atom enters a position in one of the intermediates. BX^* decreases steadily with time from its value at $t = o$ to zero at $t = \infty$. Assuming no reaction between two tagged molecules, Marcus derives

64) $$R = -\left(\frac{b}{BX^*}\right)\cdot\left(\frac{d\,BX^*}{dt}\right)$$

where b = total concentration of BX-type molecules in atoms/unit volume.

An example of Marcus' method is (B) in the list of Mechanisms tested.

Some mechanisms† tested were the following:

(A) Standard method, reproduced in detail.

$$ClF_3 \xrightarrow{K_1} ClF + F_2$$

$$Cl^*F_3 \xrightarrow{K_1} Cl^*F + F_2$$

$$ClF + F_2 \xrightarrow{K_2} ClF_3$$

$$Cl^*F + F_2 \xrightarrow{K_2} Cl^*F_3$$

$$\frac{d(ClF_3^*)}{dt} = \frac{dx}{dt} = K_2\,(Cl^*F)\,(F_2) - K_1(Cl^*F_3) = K_2y(F_2) - K_1\,x$$

$$d(F_2) = 0 = K_1[(ClF_3)+(Cl^*F_3)] - K_2[(ClF)+(Cl^*F)](F_2) = K_1a - K_2b(F_2)$$

$$(F_2) = \frac{K_1a}{K_2b}$$

$$\frac{dx}{dt} = K_1\frac{ay}{b} - K_1x = K_1\frac{(ay-bx)}{b} = R\,\frac{ay-bx}{ab} \quad \text{(by equation 22)}$$

$$\frac{K_1}{b} = \frac{R}{ab}$$

$$R = K_1a$$

or the rate is proportional to (ClF_3) total.

† The notation of equation 22) is frequently used for simplification.

(B) Marcus' method, reproduced in detail.

$$\dagger \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2ClF_2 \qquad \text{where } \dagger = FClF_2ClF \text{ complex}$$

$$ClF_2 + Cl^*F \xrightarrow{K_2} Cl^*F_2 + ClF$$

$$Cl^*F_2 + ClF_3 \xrightarrow{K_3} ClF_2 + ClF_3$$

$$-\frac{d(Cl^*F)}{dt} = K_2 (ClF_2)(Cl^*F)$$

$$-\frac{1}{Cl^*F}\frac{d(Cl^*F)}{dt} = K_2 (ClF_2)$$

$$\frac{d(ClF_2)}{dt} = 0 = 2K_1(\dagger) - K_{-1}(ClF_2)^2 - K_2(ClF_2)(Cl^*F) + K_3(Cl^*F_2)(ClF_3)$$

$$\text{subtract } \frac{d(Cl^*F_2)}{dt} = 0 = K_2(ClF_2)(Cl^*F) - K_3(Cl^*F_2)(ClF_3)$$

$$2K_1(\dagger) = K_{-1}(ClF_2)^2$$

$$(ClF_2) = \sqrt{\frac{2K_1}{K_{-1}}}\sqrt{(\dagger)}$$

$$-\frac{1}{Cl^*F}\frac{d(Cl^*F)}{dt} = K_2\sqrt{\frac{2K_1}{K_{-1}}}\sqrt{(\dagger)} = \frac{R}{b}$$

$$R = K_2\sqrt{\frac{2K_1}{K_{-1}}}\, b\sqrt{(\dagger)}$$

or the rate is proportional to $(ClF)_{total}\sqrt{\text{concentration of complex}}$

(C) Reaction sequence

α) $Cl^*F + ClF_3 \longrightarrow Cl^*F_2 + ClF_2$

β) $\begin{cases} Cl^*F_2 + ClF_2 \longrightarrow Cl^*F + ClF_3 \\ Cl^*F_2 + ClF_2 \longrightarrow ClF + ClF_3 \end{cases}$

γ) $Cl^*F_2 + ClF_3 \longrightarrow ClF_2 + ClF_3$

δ) $ClF_2 + Cl^*F \rightleftharpoons ClF + Cl^*F_2$

Final expression

assuming

$$\frac{d(Cl^*F_2)}{dt} = 0 = \frac{d(ClF_2)}{dt}$$

$$R = K\,(ClF)_{total}(ClF_3)$$

$$= K\,b\,(a-x)$$

(D) If for α) in (C) above

$ClF + ClF_3 \rightleftharpoons 2ClF_2$ is substituted,

the final expression is essentially the same.

(E) If α), γ), and ζ) are used, in conjunction with

$ClF_3 \rightleftharpoons ClF_2 + F$

$Cl^*F + F \longrightarrow Cl^*F_2$

$Cl^*F_2 + F \longrightarrow ClF_3$

assuming

$$\frac{d(ClF_2)}{dt} = \frac{d(F)}{dt} = \frac{d(Cl^*F_2)}{dt} = 0$$

$$R = K\,(ClF_3)(ClF)_{total}\left[1 - \frac{K(ClF_2)^2}{(ClF)^2 + (ClF_3)}\right]$$

No method of eliminating the term (ClF_2) was found.

Very complex mechanisms can be treated by the equilibrium method of Sternberg (39). This method is based upon the fact that exchange reactions are assumed to occur in a system at dynamic equilibrium, in which R is constant throughout a given experiment. This condition necessarily implies the presence of equilibrium concentrations (independent of labelling) of reactive intermediates as well as of stable reactants. Equilibrium concentrations can be evaluated with the assumption that the concentrations of reactive intermediates are negligible relative to the concentrations of stable species. With the additional assumption that the concentrations of tagged and untagged intermediates at time t are those obtained by the instantaneous equilibration of a mixture of the tagged and untagged reactants having the composition existing at time t, the individual concentrations of each of the tagged and untagged intermediates can be calculated. Using the concentrations of

intermediates thus found, an expression for the rate of increase of tagged atoms $(\frac{dx}{dt})$ in molecular species AX, or the equivalent rate of decrease of tagged atoms $(-\frac{dy}{dt})$ in molecular species BX, is written for the postulated mechanism. This expression can be reduced to the form

65) $$\frac{dx}{dt} = -\frac{dy}{dt} = N\frac{z}{b} - N\frac{a+b}{ab}x$$

where $\frac{dx}{dt}$ = rate of increase of tagged atoms in species AX.

N = function of the concentration of the molecular species AX and BX, and of the rate constants for the individual steps of the postulated mechanism

a, b, x, z have the same meaning as in 22), Section IV.

However, this dx/dt is the same dx/dt used in the original derivation of the exchange rate, R, where (cf. Section IV)

22) $$\frac{dx}{dt} = R\frac{y}{b}\left(\frac{a-x}{a}\right) - R\frac{x}{a}\left(\frac{b-y}{b}\right) = R\left(\frac{ay - bx}{ab}\right)$$

or

66) $$\frac{dx}{dt} = R\frac{z}{b} - R\frac{a+b}{ab}x$$

By equating coefficients of either z/b or (a+b/ab)x in equations 65) and 66), R is found in terms of a, b and the rate constants for the steps of the postulated mechanism.

For a possible mechanism in the chlorine trifluoride-chlorine monofluoride exchange, consider the following application of Sternberg's method.

If pertinent equilibria in the system are taken to be

67) $$\underset{b}{ClF} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \underset{c}{Cl} + \underset{d}{F}$$

68) $\underset{a}{ClF_3} \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \underset{f}{ClF_2} + \underset{d}{F}$

69) $\underset{b}{ClF} + \underset{d}{F} \underset{K_6}{\overset{K_5}{\rightleftharpoons}} \underset{f}{ClF_2}$

70) $\underset{d}{F} + \underset{d}{F} \underset{K_8}{\overset{K_7}{\rightleftharpoons}} \underset{g}{F_2}$

where a b c d f g are equilibrium concentrations, then on the basis of the equations

$K_1 b = K_2 c d$ $\qquad$ $K_5 b d = K_6 f$

$K_3 a = K_4 f d$ $\qquad$ $K_7 d^2 = K_8 g$

explicit solutions for c, d, g, and f may be obtained in terms of a, b, and the rate constants. If, now, the molar contributions of equations 67) 68) 69) and 70) are considered to be l, m, n, and p respectively, that is, equation 67) contributes l moles of Cl and l moles of F, et cetera, then the total moles of each constituent are

$Cl = c = l$

$F = d = l + m - n - 2p$

$ClF_2 = f = m + n$

$F_2 = g = p$

Since c, d, f and g are known, l, m, n and p may now be related to a, b, and the rate constants. For example, 71) $m = g + \frac{d - c + f}{2} =$

$$\frac{K_3K_6K_7}{K_4K_5K_8}\frac{a}{b} + \frac{1}{2}\sqrt{\frac{K_3K_6\,a}{K_4K_5\,b}} - \frac{K_1}{2K_2}\sqrt{\frac{K_4K_5b^3}{K_3K_6a}} + \frac{1}{2}\sqrt{\frac{K_3K_5ab}{K_4K_6}}$$

72) $d = \sqrt{\frac{K_3K_6b}{K_4K_8a}}$ and so forth.

A particular mechanism leading to exchange may now be selected.

Consider the following steps

73) $ClF_3 \xrightarrow{K_3} ClF_2 + F$

74) $ClF_2 + Cl^*F \xrightarrow{K_4} Cl^*F_2 + ClF$ and /or 79) $F + Cl^*F \xrightarrow{K_5} Cl^*F_2$

75) $Cl^*F_2 + ClF \xrightarrow{K_9} ClF_2 + Cl^*F$ 80) $Cl^*F_2 \xrightarrow{K_6} Cl^*F + F$

76) $Cl^*F_2 + ClF_3 \xrightarrow{K_{10}} Cl^*F_3 + ClF_2$

77) $ClF_2 + Cl^*F_3 \xrightarrow{K_{10}} ClF_3 + Cl^*F_2$

78) $ClF_2 + F \xrightarrow{K_4} ClF_3$

For this mechanism

81) $-\frac{d(Cl^*F)}{dt} = K_9(ClF_2)(Cl^*F) - K_9(Cl^*F_2)(ClF) + K_5(F)(Cl^*F) - K_6(Cl^*F_2)$

82) $-\frac{d(Cl^*F)}{dt} = K_9(ClF_2)(Cl^*F) - K_9(Cl^*F_2)(ClF) + \frac{K_6(Cl^*F)(ClF_2)_{eq}}{(ClF)_{eq}} - K_6(Cl^*F_2)$ by equation 69)

but

83) $(ClF_2) = \frac{(ClF)}{(ClF)_{total}} \cdot n + \frac{ClF_3}{(ClF_3)_{total}} \cdot m = f - \frac{mx}{a} - \frac{ny}{b}$

84) $(Cl^*F_2) = \frac{(Cl^*F)}{(ClF)_{total}} \cdot n + \frac{(Cl^*F_3)}{(ClF_3)_{total}} \cdot m = \frac{ny}{b} + \frac{mx}{a}$

85) $(F) = 1 + n - m - 2P = d$

86) $(ClF) = b$

87) $(Cl^*F) = z - x$

hence

88) $-\frac{d(Cl^*F)}{dt} = K_9 f [z - x] - K_9 [ny + \frac{bmx}{a}] + K_6 \frac{(z-x)f}{b} - K_6[\frac{ny}{b} + \frac{mx}{a}]$

neglecting products of those constituents present in small quantity, for example, xy. Making use of the relationship $f = m + n$,

89) $-\frac{d(Cl^*F)}{dt} = K_9 m b \frac{z}{b} - K_9 m b \frac{a+b}{ab} x + K_6 m \frac{z}{b} - K_6 m \frac{a+b}{ab} x$

Therefore,

R = K_9 m b from equations 74), 75) and/or K_6m from equations 79) and 80).

Using 71), terms resulting from 74) and 75) are

$$90)\quad R = \frac{K_9 K_3 K_6 K_7}{K_4 K_5 K_8}\, a + \frac{K_9}{2}\sqrt{\frac{K_3 K_6\, ab}{K_4 K_5}} - \frac{K_1 K_9}{2K_2}\sqrt{\frac{K_4 K_5 b^5}{K_3 K_6 a}} + \frac{K_9}{2}\sqrt{\frac{K_3 K_6 ab^3}{K_4 K_6}}\,.$$

Terms resulting from 79) and 80) which may be added, used alone, or discarded, depending on apparent validity, are

$$91)\quad R = \frac{K_3 K_6 K_7}{K_4 K_5 K_8}\,\frac{a}{b} + \frac{K_6}{2}\sqrt{\frac{K_3 K_6 a}{K_4 K_5 b}} - \frac{K_1 K_6}{2K_2}\sqrt{\frac{K_4 K_5 b^3}{K_3 K_6 a}} + \frac{K_8}{2}\sqrt{\frac{K_3 K_6 ab}{K_4 K_5}}$$

Although it might seem that some rationale could be advanced for the contributive importance of those terms involving the square root of the concentration product, examination reveals that the important terms are not those which are desired. Each term involving the square root of the concentration product also involves

$$\sqrt{\frac{K_3 K_6}{K_4 K_5}}$$

which is found to be about $\sqrt{7.6 \times 10^{-4}}$ at 203.4° C. by using the thermodynamic data in Table III, Section II, in conjunction with the relationships

$$92)\quad \frac{K_3 K_6}{K_4 K_5} = \frac{[ClF][F][F]}{[ClF_3]} \quad \text{from 68) and 69)}$$

and

93) $\Delta F = 0 = \Delta F^{\circ} + RT \ln K_p$

where $\Delta F^{\circ} = \Delta F_f(ClF) + 2\,\Delta F_f(F) - \Delta F_f(ClF_3)$

K_p = pressure quotient (at deviations from the standard state of 1 atm.)

$$= \frac{K_3 K_6}{K_4 K_5} .$$

Similarly,

$$\frac{K_7}{K_8} \simeq 1.2 \times 10^{12}$$

The values given above have been converted to concentration units to facilitate comparison with experimental data (calculated in terms of concentrations). From these facts, it is seen that the terms in 90) and 91) involving the square root of the concentration product are completely overwhelmed by the first terms. There is no possibility that K_9 in term two of equation 90), for example, is large enough to overcome the K_7/K_8 ratio in term one of 90). This follows because K_9 is calculable. Consider the case of term two in 90) alone being important. Then

94) $$R = \frac{K_9}{2} \sqrt{\frac{K_3 K_6}{K_4 K_5}} \sqrt{ab} \simeq \frac{K_9}{2} \sqrt{7.6 \times 10^{-4}} \sqrt{ab}$$

and experimentally

56) $$R = K \sqrt{ab}$$

which indicates

95) $$K^{\dagger} \simeq \frac{K_9}{2} \sqrt{7.6 \times 10^{-4}}$$

---

† See Table VIII.

or at 203.4°C

$$K_g \simeq \frac{2(6.93 \times 10^{-3})}{\sqrt{7.6 \times 10^{-4}}} = 0.502$$

Although other reaction mechanisms were considered, no combination was found which escaped the above dilemma.

There have been few homogeneous exchange reactions reported in which R was not proportional to the first power of reactant concentrations. However, Gryder and Dodson (40) found the rate of exchange of Ce III to Ce IV in aqueous media varied as $(Ce\ III)^1\ (Ce\ IV)^n$, where n varied from 0 to 1 depending on the medium. Also, Boggs and Brockway (41) found that the rate of chlorine exchange between gaseous CHF_2Cl and HCl at 360° C. to 465° C. was proportional to the square root of each constituent concentration. Unfortunately, no mechanism, or explanation, for this behavior was offered, but it was shown that the reaction was homogeneous.

The case for a heterogeneous mechanism. Unless a large amount of information about the system has been obtained and correlated, mechanisms for heterogeneous reactions are seldom offered. Usually a low activation energy and a large negative activation entropy, along with difficulty in predicting the rate dependence on constituent concentration by a homogeneous mechanism are taken as good evidence of heterogeneity. Differences in rate with variation in surface area are usually indicative, but in the very analogous chlorine trifluoride and fluorine system, Adams, Bernstein and Katz (16) were not able to find any such correlation, even though the exchange reaction appeared to be heterogeneous.

Farrar and Smith (42) have shown that chlorine trifluoride is adsorbed strongly by nickel fluoride; the adsorption is Langmuir-type adsorption. Chlorine monofluoride might be expected to adsorb on nickel fluoride strongly because of its relation to the trifluoride; it has been shown (43), however, that chlorine, which is also somewhat similar to chlorine monofluoride, does not adsorb strongly on nickel fluoride.

Final considerations. Although the data do not uniquely determine the dependence of R on reactant concentration, they do strongly suggest that R is proportional to the square root of the product of reactant concentrations. It seems important that those experimental points in Figures 44 through 51 which indicate that the adsorption curves are obeyed are, in general, points which were obtained without correcting the pre-reaction-chlorine trifluoride concentrations for dimerization. If the chlorine trifluoride portions were corrected for dimerization using the data in Table IV, the rate, R, increased somewhat, and showed approximately square-root dependence on the reactant concentrations (see Figures 45 and 51, for example). It also seems important that in Tables VIII, IX and X, the column listing $R/\sqrt{[ClF_3][ClF]}$ values (in reality the specific reaction rate constant, K, assuming square-root dependence as in equation 56)) shows rather good constancy. This criterion is perhaps more reliable than Figures 44 through 51, since in the tables, all data obtained at a given temperature may be represented, whereas the graphs in Figures 44 through 51, by their very nature, are limited to some part of the data at one temperature.

If R is dependent on the square-root of reactant concentration, then it seems reasonable to suppose that exchange is taking place by a homogeneous mechanism. There are other supporting factors. First, if the mechanism were not homogeneous, then results should be dependent on the history of the reaction chamber. The data were obtained from experiments between which, in most cases, the chamber history varied. For example, only a few data were obtained with any one lot of chlorine monofluoride. Each new lot of the monofluoride was made in the same chamber used for rate measurements; this would be expected to alter the chamber surface. Then again, all experiments at one temperature were not done consecutively, nor were the concentrations altered by periodic dilutions; rather, variations were somewhat at random. A second factor is that the system under discussion, chlorine trifluoride-chlorine monofluoride is very similar to the system discussed in Section V, chlorine trifluoride-chlorine. Initial pressures of reactants were comparable, and the same temperature range was covered, all in the identical reaction chamber. These facts, although not absolute evidence, do indicate a high probability of similar mechanisms in the two systems, and it is difficult to explain the data of Section V in terms of anything but a homogeneous mechanism. Attempts to explain the second order rate dependence of chlorine monofluoride formation from chlorine trifluoride and chlorine in terms of a heterogeneous mechanism meet with a contradiction. The observed rate dependence would be expected to arise through a heterogeneous mechanism only if both reactants were weakly adsorbed (equation 7), but it is known (43) that chlorine is adsorbed much less strongly than chlorine trifluoride.

All considerations, then, seem to indicate that chlorine exchange between chlorine trifluoride and chlorine monofluoride occurs by a homogeneous mechanism, with the rate of exchange proportional to the square root of reactant concentrations. No mechanism consistent with such a dependence was found.

VII. THE CHLORINE MONOFLUORIDE-CHLORINE SYSTEM

Introduction

In the previous sections, chlorine atom exchange between chlorine trifluoride and chlorine as well as between chlorine trifluoride and chlorine monefluoride was studied. In order to include all possible combinations, exchange between chlorine monefluoride and chlorine was studied.

Materials

All materials used in this investigation were produced and purified in the manner discussed in Sections V and VI.

Exchange Procedure

Initial amounts of reactant were measured in the gas-handling system and condensed into separate traps by means of liquid nitrogen baths. Care was taken to prevent contact of the gases in this measuring stage. Because of the high vapor pressure of chlorine monofluoride at room temperature, special techniques were necessary. The monofluoride could not be warmed to room temperature in the measuring trap; consequently this material was expanded into the volume enclosed by the nickel reaction chamber, Helicoid gauge, measuring trap, and gas-handling line involved, all being at room temperature. The chlorine, which was measured and condensed into a second trap before measurement

of the monofluoride, was heated to room temperature in the closed trap which was then opened to the gas-handling system, and the chlorine allowed to expand into the system containing monofluoride. The assumption was made that mixing was instantaneous.

After suitable time, the gas mixture was condensed into the chlorine measuring trap by a liquid nitrogen bath. Both chlorine trifluoride and chlorine have a substantial vapor pressure at isopropanol-Dry Ice bath temperatures; therefore, separation was effected in the following manner. A copper bar one inch in diameter and ten inches long was bored, with a drill just slightly larger than the chlorine trap diameter, to a depth of about six inches. This bar was used as a heat conducter. It was placed around the trap; the temperature of the trap was controlled by the depth of immersion of the copper bar in a liquid nitrogen bath. By suitable adjustment, a slow distillation was effected. Only a small fraction of the total gas involved was needed to obtain the activity, so that only the initial material distilled was considered to be chlorine monofluoride and counted. For the same reason, only the last fraction was counted as chlorine. That this procedure resulted in reasonable separation was shown by the results of the first experiment.

Exchange Results

Chlorine exchange between chlorine monofluoride and elemental chlorine occurred at room temperature. The first experiment consisted of mixing the reactants in equal amounts in the system at room

temperature, or about 29° C. Separation and counting of the reactants was done after three different contact times. The same material was used throughout. For example, after the first quenching, separation, and counting, the reactants were expanded back into the original part of the system involved in the exchange. This procedure, of necessity, made some uncertainty in the exact reaction times, as well as some deviation from the original temperature. However, the results show that exchange does take place at room temperature, as well as showing that separation of chlorine and chlorine monofluoride was attained by the distillation procedure used, since the fraction exchanged varied from 0.655 to 0.849 to 1.0 for reaction times of 60, 160, and 1080 minutes, respectively. The second experiment was performed carefully and was considered to be quantitatively correct.

Calculations were made in a manner similar to that noted in Section VI, taking into account that elemental chlorine has two atoms of the species tagged. Since exchange occurred at room temperature, no correction for unreacted gas in the pressure gauge was necessary. Thus

$$96) \quad R = \frac{2.303}{t} \frac{[ClF][2Cl_2]}{[ClF] + [2Cl_2]} \log \frac{1}{1 - f}$$

and for the case

a 1:1 mixture of $Cl_2 + Cl_2^*$:ClF at room temperature; equal amounts of each gas counted after separation; activity of Cl^*F = 22.10 counts/sec.; activity of Cl_2^* = 85.73 counts/sec.

then the fraction exchanged

$$f = \frac{22.10}{\frac{22.10 + 85.73}{(1/3)}} .$$

Results of both experiments are summarized in Table XIV.

TABLE XIV

EXCHANGE* IN THE CHLORINE MONOFLUORIDE-CHLORINE SYSTEM

Temperature °K	Exchange Time (min.)	[ClF] moles/l. ($x10^3$)	[Cl_2] moles/l. ($x10^3$)	f	R moles/l. min.($x10^5$)	t 1/2 min.
~ 29	~ 60	6.24	6.24	0.655	7.38	39.1
~29	~160	6.24	6.24	0.849	4.91	58.7
~ 29	~1080	6.24	6.24	1.0	--	--
27	150	4.57	4.57	0.6149	1.938	109

* See Appendix II for original data

Discussion

The main source of error in the experiments was the possible incomplete separation of reactants, although errors inherent in radioactive counting as well as errors in measuring temperature and pressure were possible. The overall maximum error was estimated to be ten per cent.

The results of some exchange experiments involving interhalogens or other compounds of interest are shown in Table XV, as reported by various authors. It is pertinent to note that many of these exchanges taking place readily at room temperature have been postulated to occur through molecular complexes.

In the present case, it seems reasonable to expect exchange between chlorine and chlorine monofluoride to occur through a molecular complex. It is known (Table I) that chlorine trifluoride dissociates at elevated temperatures to form chlorine monofluoride and fluorine; as the temperature is dropped, the re-formation of the trifluoride is favored. This means that the bonding orbitals in the central atom, chlorine, change in a way to accommodate the extra fluorine atoms. Elemental chlorine has essentially the same outer electronic configuration as elemental fluorine, but each atom of the chlorine molecule has unfilled 3d orbitals, and therefore more potentialities for hybridization than fluorine. In a mixture of chlorine monofluoride and chlorine, it might be expected that some intermediate complex could form, then break down, in the process shifting the fluorine atom to another chlorine atom, or, in effect, causing chlorine atom exchange. It would be most interesting

TABLE XV

SOME EXCHANGE RESULTS

Reactants 1 and 2		Phase 1 and 2		Temperature °C.	Exchange*	Probable Mechanism	Reference
HF	ClF_3	g	g	Room	+ +	Intermediate complexes	14
HF	BrF_5	g	g	Room	+ +	Intermediate complexes	14
HF	IF_7	g	g	Room	+ +	Intermediate complexes	14
HF	BrF_3	g	g	Room	+ +	Intermediate complexes	14
HF	ClF	g	g	Room	+ +	Intermediate complexes	14
HF	SF_6	g	g	Room	--	--	14
HF	CCl_2F_2	g	g	Room	--	--	14
HF	F_2	g	g	Room	--	--	14
BrF_3	ClF_3	g	g	Room	+ +	Intermediate complexes	14
F_2	ClF_3	g	g	Room	--	--	14
HF	BrF_3	l	l	Room	+ +	Ionic equilibria	14
HF	ClF_3	l	l	Room	+ +	Ionic equilibria	14
HF	BrF_5	l	l	Room	+ +	Ionic equilibria	14
HF	IF_5	l	l	Room	+ +	Ionic equilibria	14
HF	SbF_5	l	l	Room	+ +	Ionic equilibria	14
ClF_3	BrF_3	l	l	Room	+ +	Ionic equilibria	14
HF	NaF	g	s	Room	+ +	--	14
ClF_3	$NaHF_2$	g	s	Room	+	--	14
ClF_3	NaF	g	s	Room	+	--	14
BrF_5	$NaHF_2$	g	s	Room	+	--	14

* ++ represents rapid exchange; + represents slow exchange; -- represents no (or slight) exchange.

(Continued next page)

TABLE XV - Continued

Reactants 1 and 2		Phase 1 and 2		Temperature °C.	Exchange*	Probable Mechanism	Reference
F_2	NaF	g	s	Room	--	--	14
F_2	ClF_3	g	g	181-257	+	Heterogeneous	16
F_2	IF_7	g	g	181-257	+	Heterogeneous	16
F_2	BrF_5	g	g	181-257	+	Heterogeneous	16
F_2	HF	g	g	194-257	+	Heterogeneous	18
HCl	Cl_2	g	g	Room	+	Heterogeneous	19
HBr	Br_2	g	g	Room	+	?	20
HI	I_2	g	g	Room	+	?	21
ClF_3	Cl_2	g	g	180-255	+	Probably homogeneous	present work
ClF_3	ClF	g	g	200-245	+	Probably homogeneous $R=K(ClF_3)^{1/2}(ClF)^{1/2}$	present work
ClF	Cl_2	g	g	Room	+	Intermediate complexes	present work
† CH_3Cl	HCl	g	g	375-420	+	$R=K(CH_3Cl)$ Heterogeneous	41
† CH_2FCl	HCl	g	g	420-510	+	$R=K(CH_2FCl)$ Heterogeneous	41
† CHF_2Cl	HCl	g	g	360-465	+	$R=K(CHF_2Cl)^{1/2}(HCl)^{1/2}$ Homogeneous	41
† CH_3Cl	HCl	g	g	400	--	--	41
CH_3F	HF	g	g	400-500	--	--	47
CH_2F_2	HF	g	g	400-500	--	--	47
CHF_3	HF	g	g	400-500	--	--	47
CF_4	HF	g	g	400-500	--	--	47
CF_2Cl_2	HF	g	g	400-500	--	--	47

† Pyrex system used.

te study fluorine atom exchange between chlorine monofluoride and elemental fluorine, in view of the results found in the system studied.

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APPENDICES

APPENDIX I

SOME COMMENTS ON AN UNKNOWN MATERIAL ENCOUNTERED DURING THE COURSE OF THE PRECEDING WORK

Introduction

The history of interhalogen and fluorine chemistry is dotted with examples of unidentified colored materials. Ruff and Ascher (9) reported that when hydrogen chloride gas came in contact with fluorine gas above liquid fluorine, a greenish light was seen and a white floc settled in the liquid fluorine. Fractionation yielded an orange colored liquid which boiled between -100° C. and -80° C., but quantity limitations prevented identification of the material.

Ruff and Ascher (9) passed a 2:1 mixture of fluorine to chlorine at 400° C. through a quartz tube containing a fluorite boat filled with rhodium catalyst. The condensate of this process contained an orange-red liquid which etched the quartz, accompanied by the formation of silicon tetrafluoride. The liquid was not identified.

Fredenhagen and Krefft (44) sparked a mixture of fluorine and chlorine at room temperature and observed that a yellow flame spread throughout the mixture accompanied by either a detonation or a "puff", depending on reacting mixture. In the absence of water, there was no explosion.

Ruff and Laass (45) reported that in fused quartz, gaseous chlorine trifluoride (normally colorless) exhibits an orange cast,

possibly due to traces of chlorine oxide from a reaction with silicon dioxide.

While making successive purification distillations of hydrogen fluoride, Dutton (46) noticed that the first condensate from the shipping cylinder occasionally was a brick red solid.

In the present case, during the separation of chlorine and chlorine trifluoride by distillation, samples of gas were analyzed by determining their ultra-violet spectrum. In this investigation, a green color was occasionally noted in the chlorine trifluoride fraction. This gas had an absorption maximum in the region of 3700 Å, a slightly higher wavelength than the region of the maximum in the chlorine spectrum. Little importance was initially attached to the green material, because it was necessary to uncouple and recouple the spectral cell to the gas-handling system for each sample. Although a metal cap was placed on the system take-off connection, and a cork inserted in the flared tubing of the cell, traces of water undoubtedly reached the inside of the tubing. Water would be expected to react with chlorine trifluoride to form traces of one of the fluorine or chlorine oxides. Chlorine dioxide, which has about the same visible color properties, has no ultra-violet absorption peaks at 3600 Å, 3700 Å or 3800 Å, the region of maximum absorption found (Figure 54). Woolf (47) has recently reported the formation of chloryl fluoride by the reaction $20\ BrF_3 + 12KClO_3 = 12ClO_2F + 6O_2 + 4Br_2 + 12\ KBrF_4$. No visible or ultra-violet spectrum is reported, although Woolf notes that chloryl fluoride may have been produced by Ruff and Krug (12) by the hydrolysis of chlorine trifluoride.

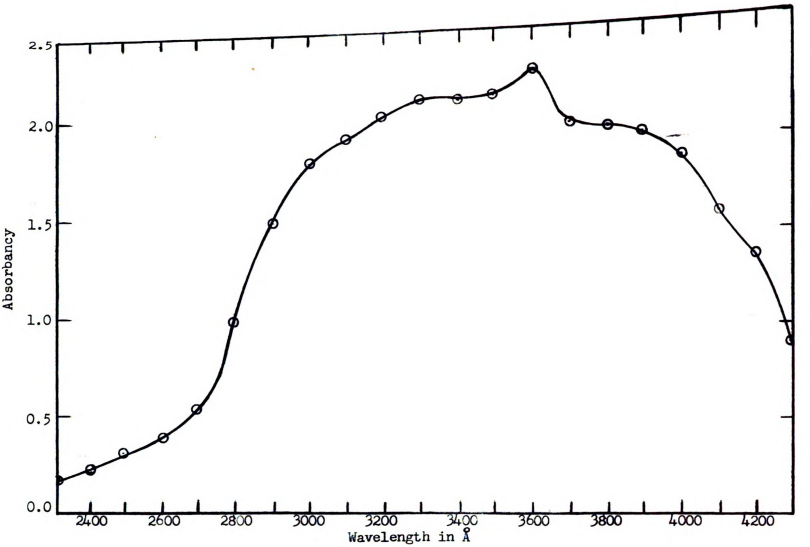

Figure 54. Spectrum of unknown material.

However, Schmeisser and Ehenhoch (48) have reported chloryl fluoride to be colorless in the gaseous state.

Occurrence

Production of the unknown material was not predictable. Small bits of silver solder, silver solder and flux, nickel screening, and pieces of copper had no observable effect on the gas production.

It seemed possible that chlorine trifluoride contaminated with chlorine (or amounting to the same thing, a catalytic effect from surfaces resulting from exposure to such a mixture) was responsible for the phenomenon. Consequently, a pair of 10 cm. viewing cells (Figure 55) were made and evacuated for 24 hours without contact with chlorine trifluoride or chlorine. The cells were then treated with chlorine trifluoride (about 100 mm. gas pressure) and re-evacuated. Next, 100 mm. of chlorine trifluoride was placed in one cell, and 100 mm. of chlorine in the other. No visible green gas formed in either of these cells over a two week period. The cells were then evacuated after which 100 mm. of chlorine trifluoride was placed in each cell without visible green material formation.

Generally, exposure of the opened coupling between cell and take-off to moist air, then recoupling and treatment with chlorine trifluoride produced the material. However, there were instances when this procedure failed to produce any coloration. Under conditions favorable for formation, the recoupled cell was treated with 50 mm. to 200 mm. of chlorine trifluoride. The green gas was visibly formed at a rapid rate,

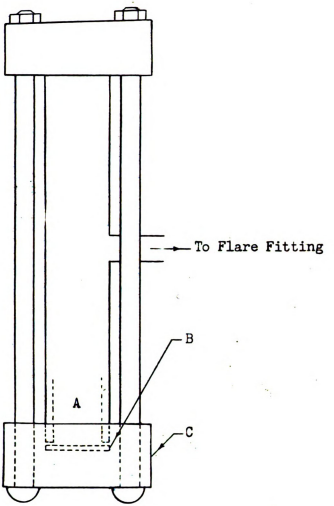

Figure 55. Viewing cell: A, nickel cylinder; B, fluorothene window; C, aluminum end cap.

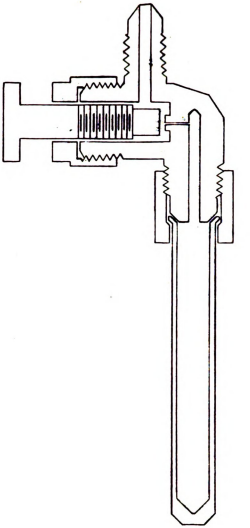

Figure 56. Fluorothene weighing cell

turning quite intensely green in a matter of ten or fifteen seconds. This gas could be pumped out, the cell evacuated, then more chlorine trifluoride expanded into the cell accompanied by more green material formation. This cycle could be repeated several times; after a number of cycles, formation was slower, sometimes allowing time for rapid, semi-quantitative scanning of the absorption spectrum. As green material formed, chlorine trifluoride disappeared. For the most intensely green samples, chlorine trifluoride was absent.

Purity and Physical Properties

Purity of the green gas was in doubt because the gas was either unstable or very reactive with some constituent of the system. The process of successively condensing and distilling to purify was not feasible because the amount of green material decreased with each distillation. Furthermore, a sample was condensed once, and expanded into the system consisting of cell, line, and Heliceid gauge. Valves were then closed isolating the cell and the Heliceid gauge. Spectral curves of the material in the cell after time t, along with notations of pressure in the Heliceid gauge at time t are shown in Figure 57.

A fluorothene weighing vessel (total weight about 55 grams, see Figure 56) was made for vapor-density molecular weight measurements, but use of the apparatus was not warranted because sufficiently pure material could not be obtained.

In appearance, the material was an intensely green gas which condensed to a dark cherry-red liquid and solidified as a brick-red solid.

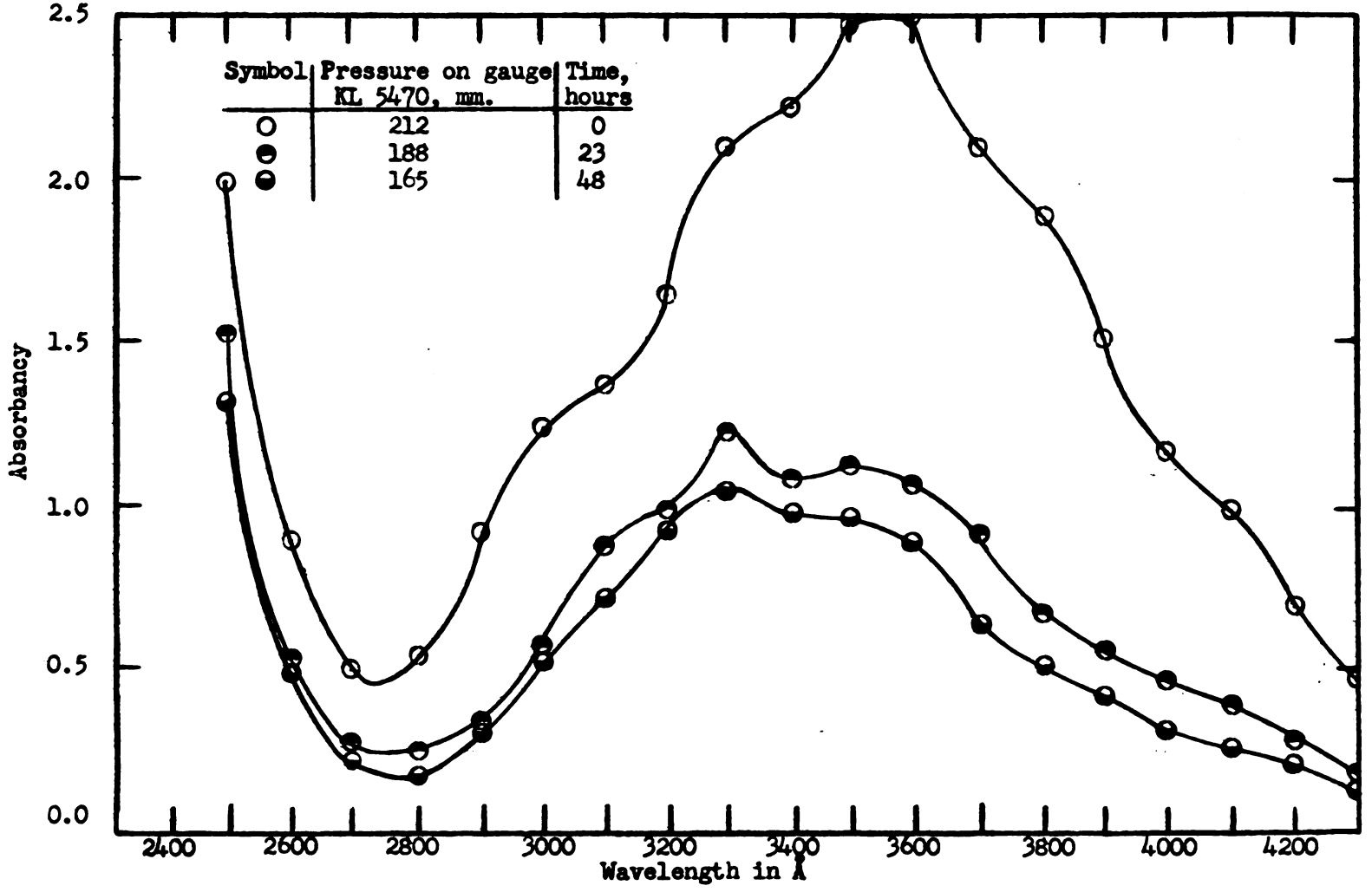

Figure 57. Spectrum of unknown material as a function of time.

Usually the red condensed material was mottled with a slightly yellowish colored solid, which, by comparison with pure chlorine trifluoride, was taken to be the trifluoride. This was reasonable because the condensed material came from the spectral cell, plus system connections, plus weighing cell itself; the total volume was thus several times the volume of the spectral cell. By assuming this yellowish colored material to be chlorine trifluoride, and by qualitative comparison, the melting point of the red solid was estimated to be between -100° C. and -80° C. Similarly, the boiling point was estimated to be between -20°C and +5° C.

Other Work

Using the infrared cell described in Section IV, and a Perkin-Elmer Model 21 Spectrophotometer, numberous attempts were made to obtain the infrared spectrum of the material. No evidence of the presence of materials other than chlorine trifluoride or chlorine monofluoride was obtained.

APPENDIX II

ORIGINAL DATA

Chlorine monofluoride formation data

Chlorine trifluoride and chlorine exchange data

Chlorine trifluoride-chlorine monofluoride exchange data

Chlorine monofluoride-chlorine exchange data

Helicoid gauge calibration data

CHLORINE MONOFLUORIDE FORMATION DATA

Time Min.	Pressure Observed on "0" Gauge (mm.) at 180° C.				
Figure No.	32	33	34	35*	36*
0	402	414	416	405	414
1		416	434		
2		418	435	411	419
3		420	436		
4		421.5	439	415	422
5	407	423	441		
6			443		426
7		425		421	
8			447		430
9		430			
10	421		451	425	
11		434			436
12			454		
13		437		430	
14					441
15	431		459		
17		442		437	
18					447
19		445			
20	440		468		
22				445	
23			472		453
24		453			
25	449		475		
27				451	
28			465		459
29		461			
30			468		
33				458	464
34		467.5			
37			479		
38					
39		473			
41			484		
43				467	474
44		480			
45			488		
48			491		
50		485.5	493		
52				475	
54		489	497		
57			499		
59		493		480	
60			502		
66				485	
71	506				

* Pressure observed on KL 5470 gauge.

CHLORINE MONOFLUORIDE FORMATION DATA

Time Min.	Pressure Observed on "0" Gauge (mm.) at 220° C.								
Figure No.	23	24	25	26	27	28	29	30	31
0	416	417	415	419	412	375	421	415	421
1	425		421	429	419	381	438	421	
2	432	433	427	438	426	387		426	437
3	437		433	444	432	394	457		
4	442	443	437.5	452		400		437	461
5	447	449.5	442	457	444	404.5	472		
6	451.5		446	463	449		478	445	
6.5			448						
7	456			467					
7.5				470	456		485		468
8	460.5							454	
9	464								
10	467.5								
12	473								
15	479								
18	483								
22	486								

CHLORINE MONOFLUORIDE FORMATION DATA

Time	Pressure Observed on "O" Gauge (mm.) at 240° C.						
Min.	Figure No. 16	17	18	19	20	21	22
0	420	428	414	415	419	205	307
.5		434	424	425	427	213	318
1	442	440	432	434	434	221	326
1.5	451	447	441	441	440	227.5	333
2	461	453	449	448	446	232	340
2.5	469	459	456	455	452.5	238	347
3	477	465	462	460.5	458	242	353
3.5	483	471		465	463	246	358
4	490	475	475	470	467	250	364
4.5	496			474	472	253	369
5	502	484	485	477	475	256	374
6	513	493	495	482.5	482	261	383
7	523	500	503	487	486	267	391
8	531	505	510	489	491	271	398
9	539	515	516			275	404
10	546	524	522	492	496	278	410
11	551						
12	557		531			283	417
13				493	499		
14	566	530	536				
15						290	426
16	571		541				
17		539					
18				494	500		
19			543				
20		544				295	435
22	586						
25		551	545				
27	593						
30		554					441
32						300	442
35			546				
38		555					443
40							
42	601						
45							
50		556					
52				496.5			

CHLORINE MONOFLUORINE FORMATION DATA*

Time Min.	Pressure Observed in "0" Gauge (mm.)		
Temperature, °C.	240	245	203
0	96	365	322
.5	103		330
1	107	392	333
1.5	110		
2	113	408	338
2.5	116		
3	119	422	343
3.5	121		
4		434	348
5	126	445	352
6	129	453	
7		461.5	359
8	135	470	
9		476	366
10	139	482	
12		491	375
14		500	
18	147		
20		513	395
25		519	406
30		522	

* Data at 240° C. were not included in rate constant determination on the basis of statistics; data at 245° C. and 203° C. were not included because of deviation from 240° C. and 200° C.

DATA FOR EXCHANGE IN CHLORINE-CHLORINE TRIFLUORIDE SYSTEM

Temperature °C.	Time of Contact Hours	Cl_2/ ClF_3	Counting Pressure, Corrected Cl_2 mm.	Activity Cl_2 c/sec.	Counting Pressure, Corrected ClF_3 mm.	Activity ClF_3 c/sec.
-50, liquid phase	1/2	1	307	216.26	395	.31
30, gas phase	1	1	313	209.7	323	.64
75	1/2	1	97	66.36	212	.10
75	2	1	254	159.53	85	.12
120	1/2	1	167	120.24	210	.25
120	2	1	237	162.20	200	.22
165	1/2	1	110	76.37	251	.32
165	2	1	216	139.62	40	.19
220	1/12	1/4	108	54.5	128	.75
220	1/8	1/4	128	48.63	78	.89
255	1/3	1/2	264	93.86	25	2.07

DATA FOR EXCHANGE IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 224.3° C.

Reaction Number	ClF/ ClF_3	Total Pressure, Corrected mm.	Gauge Temp. °C.	Counting Pressure, Corrected ClF mm.	Activity ClF c/sec.	Counting Pressure, Corrected ClF_3 mm.	Activity ClF_3 c/sec.	Percent Activity Retention	t 1/2 min.	R x 10^6 mole/ l.min.
16	5	438	35	36	7.79	36	4.31	93.7	16.20	8.463
17	3	292	33	36	8.39	36	4.10	99.3	18.05	6.836
21	2	220	29	31	5.89	31	2.63	86.1	18.77	5.871
23	2	111	28	27	4.86	27	2.05	98.3	20.23	2.748
18	1	149.5	28	36	8.94	36	3.35	99.7	18.84	4.470
20	1/5	439	30	36	5.82	36	.93	98.6	19.44	7.069
22	1/2	214	27	56	10.01	56	2.73	87.3	19.75	5.427
24	1/2	110	28	41	5.45	41	1.45	93.2	20.28	2.788
19	1/3	286	27	36	7.40	36	1.55	99.2	20.66	5.850
25	1/3	292	30	66	15.93	66	3.33	100+	20.61	5.987
26	1/3	216	30	47	8.60	47	1.97	85.3	22.64	4.033

DATA FOR EXCHANGE IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 245.4° C.

Reaction Number	ClF/ClF_3	Total Pressure, Corrected mm.	Gauge Temp. °C.	Counting Pressure, Corrected ClF mm.	Activity ClF c/sec.	Counting Pressure, Corrected ClF_3 mm.	Activity ClF_3 c/sec.	Percent Activity Retention	t 1/2 min.	R x 10^5 mole/l.min.
29	3	304	30	36	11.0	36	4.91	100+	12.22	10.11
34	2	227	30	41	7.64	41	3.74	99.8	10.22	10.70
35	2	113	30	28	4.91	28	2.37	99.3	10.01	5.434
30	1	158	30	46	12.35	46	4.50	99.7	11.63	7.361
36	1/2	113	30	35	5.47	35	1.89	91.2	9.15	5.946
37	1/2	227	30	56	9.35	56	2.44	100+	11.99	9.115
31	1/3	301	30	57	12.46	57	2.77	95.7	11.65	10.50
27	1/3	457	30	67	12.06	67	2.35	78.0	13.23	14.03
28	1/5	456	30	66	12.07	66	1.61	83.8	18.02	10.00
32	1/5	457	30	46	7.61	46	1.26	87.2	11.30	12.17
33	1/5	456	28	36	5.79	36	1.19	99.8	9.28	14.77
	5	450	31	40	12.24	40	3.77	94.2	21.40	6.330*
	1	236	28	88	23.62	71	4.74	95.5	17.77	7.192*
	1	454	30	86	25.70	86	6.60	100	17.28	14.24*
	1/3	232	30	57	10.37	57	1.94	92.5	13.76	1.360*

* Not used in text because the valve between reaction chamber and gauge was not closed.

DATA FOR EXCHANGE IN THE CHLORINE TRIFLUORIDE-CHLORINE MONOFLUORIDE SYSTEM AT 203.4° C.

Reaction Number	ClF/ClF_3	Total Pressure, Corrected mm.	Gauge Temp. °C.	Counting Pressure, Corrected ClF mm.	Activity ClF c/sec.	Counting Pressure, Corrected ClF_3 mm.	Activity ClF_3 c/sec.	Percent Activity Retention	t 1/2 min.	R x 10^5 mole/ l.min.
1	5	421	29	27	7.89	27	4.40	99.5	38.40	3.576
2	3	284	29	27	8.45	27	3.97	100.	46.02	2.718
6	2	211	26	27	6.61	27	2.72	98.3	50.27	2.191
9	2	421	27	56	12.78	56	6.08	100+	41.42	5.305
11	2	106.5	28	31	5.78	31	2.57	100+	45.45	1.223
8	1	276	25	56	15.50	56	5.02	99.7	53.85	3.010
3	1	141	30	36	11.09	36	3.49	99.4	55.61	1.489
7	1/2	210	28	56	9.54	56	2.71	87.2	45.75	2.396
10	1/2	420	28	66	13.34	66	3.70	95.1	46.86	4.678
12	1/2	106.5	27	41	6.44	41	2.06	89.9	40.35	1.378
13	1/2	106	30	40	7.91	40	1.35	90.0	38.29	1.445
4	1/3	281	30	46	11.40	46	2.04	99.3	58.08	2.131
15	1/3	281	30	56	11.75	56	2.65	98.8	46.55	2.659
5	1/5	420	30	46	9.78	46	1.30	98.7	57.47	2.382
14	1/5	424	27	36	2.75	36	0.81	87.3	26.97	5.129

DATA FOR EXCHANGE IN THE CHLORINE-CHLORINE MONOFLUORIDE SYSTEM AT ROOM TEMPERATURE

ClF/Cl_2	Total Pressure, Corrected mm.	Gauge Temp. °C.	Counting Pressure, Corrected ClF mm.	Activity ClF c/sec.	Counting Pressure, Corrected Cl_2 mm.	Activity Cl_2 c/sec.	Percent Activity Retention	t 1/2 min.	R x 10^5 mole/ l. min.
1	235	29	86	24.35	86	87.22	100	39.10	7.375
1	235	29	86	28.45	86	72.11	81.6	58.7	4.913
1	235	29	96	35.04	96	64.16	83.3	--	--
1	171	27	86	22.10	86	85.73	97.2	109.0	1.938

HELICOID GAUGE CALIBRATION

Date	8/10/54		8/31/54			8/1/55		
	Actual "0" Pressure, mm.	Helicoid Gauge Reading	Actual "0" Pressure, mm.	Helicoid Gauge Reading	KL547C Helicoid Gauge Reading	Actual "0" Pressure, mm.	Helicoid Gauge Reading	KL547C Helicoid Gauge Reading
	1	0	2	0	5	9.5	0	24
	19	0.0	25	5	27	28	5	42
	86	70	106	87	116	82	62	93
	135	120	170	154	182	177.5	159	191
	217	204	244	228	254	274.5	258	289
	259.5	250	309	295	321	376	362	389
	323	310	382	370	395	530	523	538
	389.5	381	456	442	466	642	632	655
	454	451	513	501	522	723	713	735
	537	530	574	564	584	805	804	828
	628	623	641	632	650			
	709.5	703	714	705	723			
	767.5	762	741	736	755			
			790	782	800			

May Circulate
after MAR 31 '58

Thesis
c.2 Phelps, J.P.
Study of the kinetics of some formation and isotope exchange reactions involving the chlorine flourides.
Ph.D. 1956