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F^{18} EXCHANGE BETWEEN FLUOROCARBONS
AND SOME FLUORINE-CONTAINING COMPOUNDS

T. A. Gens

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CHEMISTRY DIVISION

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T. A. Gens

DATE ISSUED

AUG 22 1957

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F^{18} EXCHANGE BETWEEN FLUOROCARBONS AND
SOME FLUORINE-CONTAINING COMPOUNDS

T. A. Gens

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CHAPTER I

INTRODUCTION

The existence of the 112 minute fluorine eighteen isotope was reported by Snell in 1937.¹ Several studies have been made using this radioactive isotope to follow exchange reactions. Since F^{18} is a positron emitter, the 0.511-Mev. annihilation gamma radiation provides an excellent means of detecting this isotope. Practically all work up to the present has been in homogeneous, usually gas phase, systems. Dodgen and Libby made an early study of rates of exchange in the gas phase between F_2 and HF. They found that little exchange occurred below $200^\circ C$.² Above this temperature exchange occurred, but this exchange was probably catalyzed by metal fluorides on the wall of the vessel. Nonexchange was explained by the absence of unfilled electron levels in the higher shells of fluorine. Such unfilled levels were thought to allow formation of intermediates of the general formula HX_3 with other halogens and the corresponding hydrogen halides. Rapid exchange has been observed in these systems.

Katz and co-workers have made several studies using F^{18} . Rogers and Katz studied exchange between HF and several interhalogen compounds.³ They found that the room temperature exchange reactions between liquid HF and several liquid interhalogen compounds were

essentially complete in ten minutes while the same reactions in the gas phase were essentially complete in three minutes. These results made it appear feasible that an ionic mechanism could be operative in the liquid phase and that a mechanism postulating an intermediate complex could explain the gas phase reactions. Essentially zero exchange was observed between HF and SF₆ or CCl₂F₂ and between ClF₃ and F₂.

Bernstein and Katz studied the gas phase exchange between interhalogen compounds and fluorine and found essentially no exchange below 100°.⁴ Above 100° a measurable rate of exchange was observed, from which it was possible to propose mechanisms for the exchange reaction. Small but observable exchange between interhalogen compounds and several metallic fluorides was reported.

Boggs, Van Artsdalen, and Brosi found no exchange in the gas phase between HF and fluorinated methanes at 500° over one hour.⁵

Although no systematic studies have been made of heterogeneous exchange between HF and metallic fluorides, such exchange has been observed in several cases.^{2,33}

Consideration of other systems in which similar exchange studies could be performed points out the wide applicability and the advantages of the fluorocarbon-inorganic fluoride system. Exchange studies between hydrocarbons and inorganic hydrides, using deuterium and tritium, are feasible but limited to the few stable inorganic hydrides. Many exchange studies between deuterium and hydrocarbons on the surface of various catalysts, such as the cracking catalysts, have

been made by Taylor and co-workers and others.^{6,7} These studies, which were designed primarily to look into surface effects, did not involve investigation of isotopic distribution within the crystal. Thus, they differed fundamentally from the studies reported in this manuscript. However, a series of papers by Wright and Weller describe a more analogous system.⁸ Wright and Weller studied isomerization and hydrogenation of unsaturated hydrocarbons over BaH_2 and CaH_2 . They attributed the catalytic activity to production of dual metal-metal hydride sites by removal of hydrogen during evacuation at 200 to 300°. Exchange between hydrogen and deuterium was also found to be catalyzed by BaH_2 and CaH_2 . Deuterium over CaH_2 , carefully evacuated at 200°, approached isotopic equilibrium with the hydride within a few hours. Diffusion of hydride ions between the interior and the surface was advanced as the explanation of these results. If any reaction mechanism as rapid as the one which will be discussed with the fluorocarbon-alkali fluoride system was operative here, its effect was not apparent at 200° with the technique used.

Several heterogeneous exchange reactions between completely⁹ and partially^{9,10,11} halogenated hydrocarbons and inorganic halides have been studied. Blau and Willard observed rapid exchange of chlorine atoms at room temperature between CCl_4 or partially chlorinated hydrocarbons and $AlCl_3$.⁹ Observations made by Kistiakowsky and Van Wazer¹⁰ in the exchange of CH_3Br with $BaBr_2$ and $AlBr_3$ may have resulted from mechanisms similar to those apparently operative in the

fluorocarbon-alkali fluoride system. They observed activation energies of 12 kcal mole⁻¹ with BaBr₂ and 4.6 kcal mole⁻¹ with AlBr₃. While there are innumerable inorganic chlorides, bromides, and iodides which may be used in exchange studies, fluorocarbons are the only fully halogenated hydrocarbons in which such great numbers of compounds are stable. A great many partially chlorinated, brominated, or iodinated hydrocarbons, while stable, do not have the high vapor pressure of fluorocarbons and cannot be conveniently studied in the gas phase. Many such systems have been studied in the liquid phase.^{11,12,13,14} In none of these studies have observations resembling those discussed in this manuscript been made.

Winter found that exchange of oxygen gas with some inorganic oxides involved subsurface lattice ions, and he was able to correlate his exchange results with the semiconducting properties of the oxide.¹⁵ Kolthoff and O'Brien found that quite rapid exchange occurred between Br₂ gas and solid AgBr.¹⁶ The mechanisms involved in such inorganic systems may resemble those involved in exchange between fluorocarbons and alkali fluorides.

Fluorocarbons have great thermal stability and resistance to chemical reaction.¹⁷ The dissociation energy of CF₄ is reported as 130 kcal mole⁻¹¹⁸ compared with 102 kcal mole⁻¹ for CH₄.¹⁹ These properties make fluorocarbons valuable in many unique applications, but also make it impossible to apply synthesis or degradation reactions similar to those normally applied in organic chemistry. To

obtain significant reaction with fluorocarbons, hot tube reactions, often under high pressure, are frequently resorted to. In hot tube reactions the nature of the surface usually affects the reaction. It is common practice to pack the hot tube with an inert material which supplies a surface for reaction and possibly produces other unknown effects.

Many reactions with fluorocarbons which are very feasible thermodynamically cannot be carried out, even at high temperatures. There exists great need for catalysts capable of lowering the activation energy sufficiently to allow smooth low temperature reactions producing few products in high yield, both for research use and for successful commercial application of the unique properties of fluorocarbons. Most of the science and technology of fluorocarbons has developed over the last few years. Starting with a small sample of fluorocarbon supplied by J. H. Simons in 1941, a group at Columbia University developed the solid and liquid fluorocarbons needed in the Manhattan project.^{20,21} At the same time a different method of fluorocarbon production was being developed at Johns Hopkins University.²² Since the field is so new, there is very little published work to serve as a guide in searching for materials to catalyze fluorocarbon reactions. A study of the exchange of fluorine between fluorocarbons and inorganic fluorides using F^{18} offered the possibility of gathering much information concerning the effect of various salts in exchange reactions. It was thought that if salts were found which exchanged

with fluorocarbons, information thus gathered would be helpful in the search for catalysts for use in other fluorocarbon reactions.

CHAPTER II

APPARATUS

Photographs are used to show the instruments and the two vacuum racks containing the apparatus used in this work. In addition, sketches are included to aid in interpreting the photographs.

Figure 1 is a sketch showing the essential parts of the system used to study the exchange of fluorocarbons, SiF_4 , and SF_6 with alkali fluorides. Figure 2 is a photograph of this apparatus. The multiple unit clam-type furnace has been removed to show the Inconel reactor tube. Dimensions of the Inconel portion of the reaction tube were: length, 13.0"; O.D., 0.375"; thickness, 0.025". A Chromel-Alumel thermocouple was soldered to the middle of the reactor tube with high melting silver solder. Copper cooling coils through which water was circulated were soft soldered on the portions of the reactor tube which extended out of each end of the furnace. These cooling coils prevented the melting of the soft solder seal on the sleeves directly beneath the coils. The sleeves connected the Inconel tube to Housekeeper seals, and thus to the rest of the system, which was made of Pyrex. Inconel metal was most satisfactory as a reactor tube material because of its resistance to reaction at high temperature and its unusually poor conductance properties, which made it simpler to protect the Housekeeper seals. Fans, one of which is visible in Fig. 2, were also used in

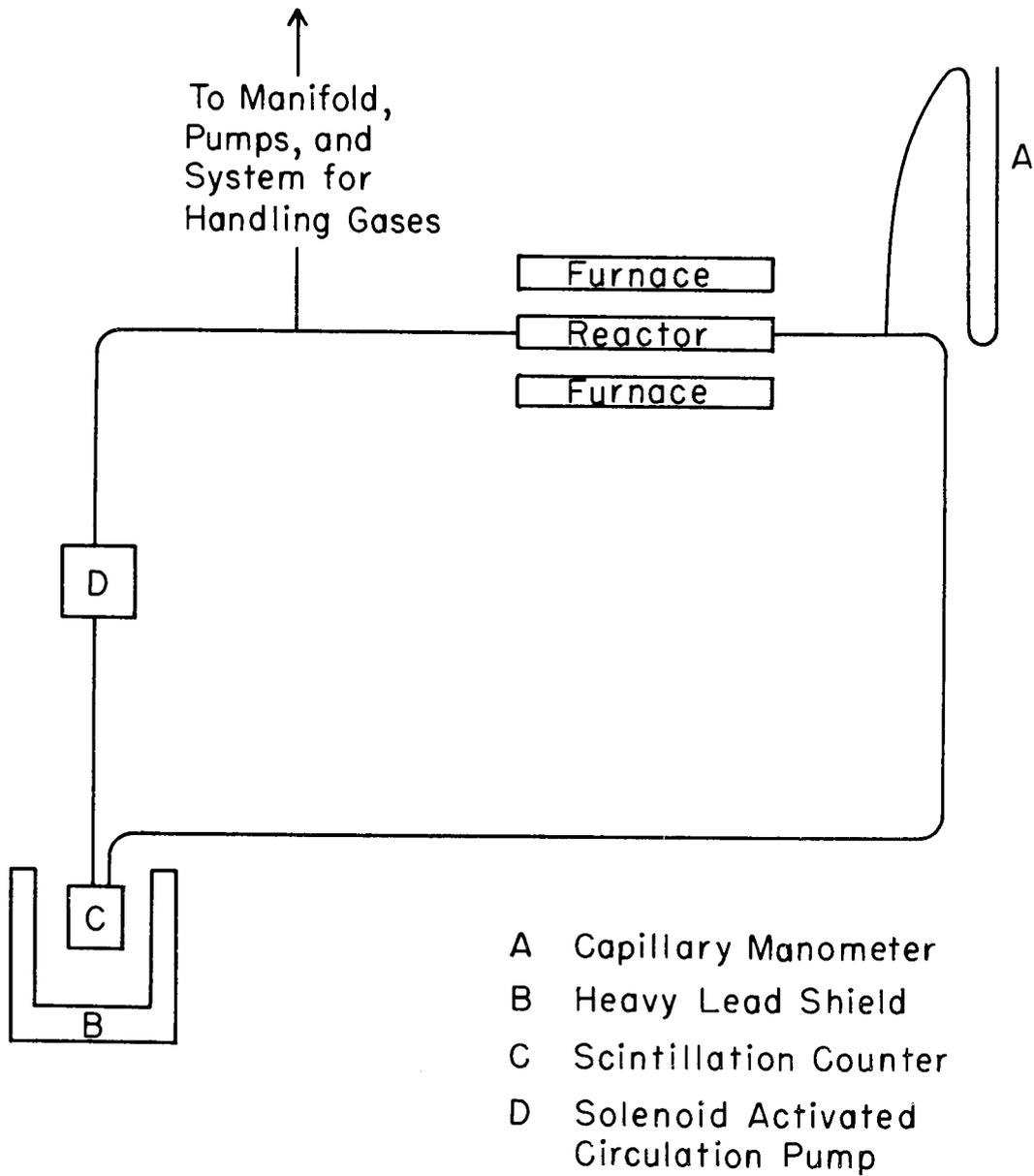


Fig.1. EXCHANGE SYSTEM, SKETCH

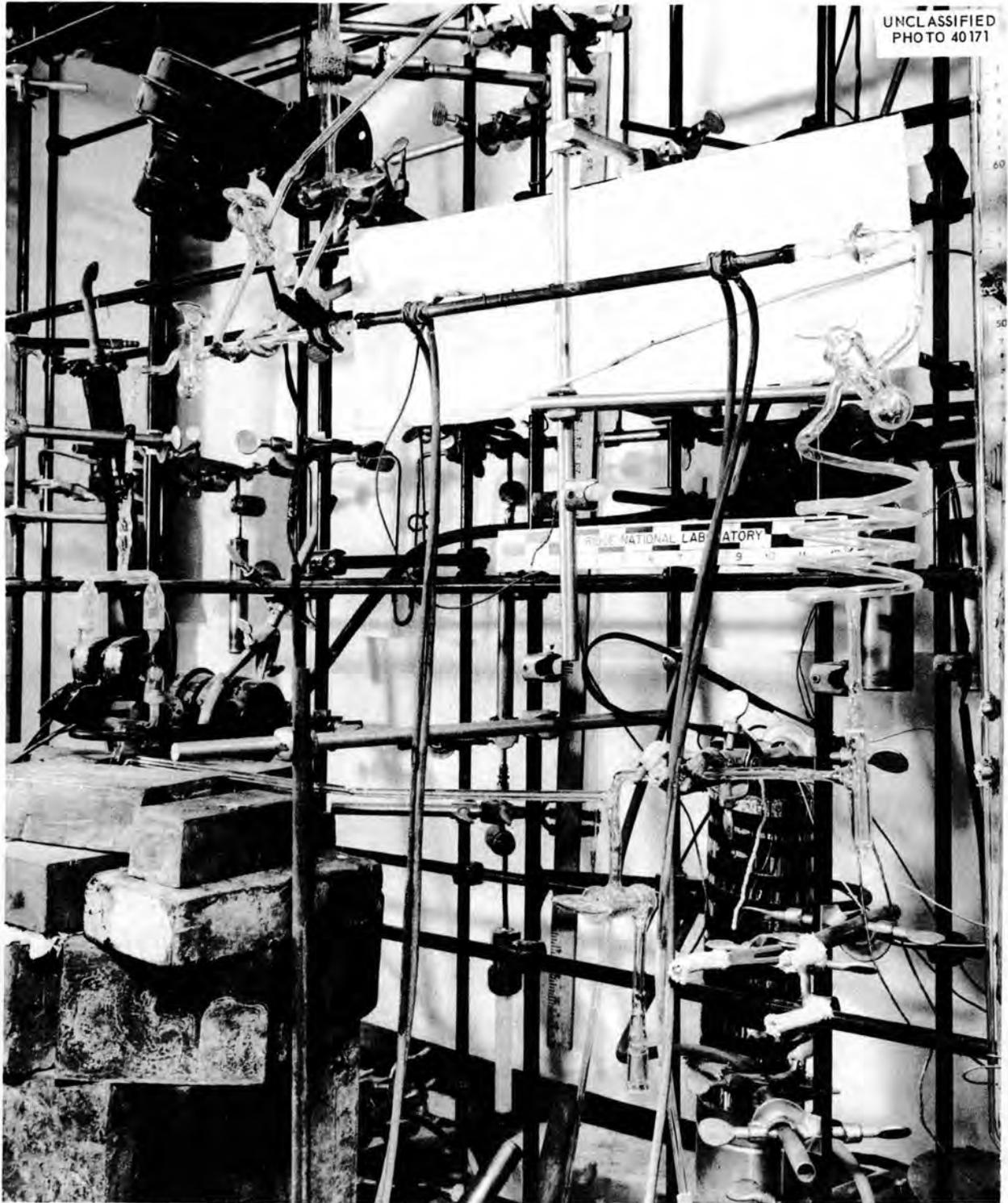


Fig. 2. Exchange System with Inconel Reactor Tube.

cooling the exit and entrance. A split stainless steel sleeve of 1.250" O.D., 0.250" thickness, and 7.0" length surrounded the Inconel reactor tube inside the 8.0" long heating coils in the furnace. The large heat capacity of this steel sleeve prevented rapid temperature fluctuations. The Chromel-Alumel thermocouple seen in Fig. 2 below the Inconel tube was inserted into a hole drilled half-way through the length of the stainless steel sleeve. This thermocouple activated the temperature controller, as outlined in Fig. 10. This system was built to be used at temperatures as high as 1000^o, and at times was actually used at temperatures of nearly 700^o.

The spiral in Fig. 2 was of 4 mm. O.D. Pyrex. It provided the flexibility needed to open the system at the reactor tube. The stop-cock just above the spiral was added before the kinetic studies were made. A cold finger was located beneath the spiral. As the gas entered the cold finger it was filtered through a type D sintered Pyrex frit. This frit and a similar frit above the pump on the left side of Fig. 2 isolated the counter from the reactor tube. A well type NaI scintillation counter beneath the lead shield counted the circulating gas. The solenoid-activated pump just above the counter, and the flowmeter above the pump, are described below. The capillary mercury manometer, part of which is visible on the right of Fig. 2, was connected to the gas system by a capillary Pyrex line which entered above the flowmeter. Beside this manometer line was the exit to the auxiliary system. At the bottom of the exchange system was the tap through which radioactive

gas was withdrawn and returned in the counter calibration procedure which is described under Calculations.

Figure 3 shows a drawing of the Pyrex constant temperature exchanger used in the kinetic studies. This exchanger was placed in the position occupied by the Inconel reactor tube in Fig. 2. Figure 4 shows the exchanger in position. The vapor bath and furnace have been lowered to show the coil in which the entering gas was preheated. This 4 mm. O.D. preheater coil was about one yard in length and held 10 cc., nearly one-tenth of the volume of the system. A Pt, Pt-10% Rh thermocouple, which was withdrawn for photographing in Fig. 4, was inserted through the condenser for the experiments, as shown in Fig. 3. The temperature of the vapor or ice bath was measured from the thermocouple by a Rubicon slide-wire potentiometer with which the E.M.F. was estimated to the nearest 0.0001 mv. A 10-inch Pyrex tube with a 50/50 ground glass joint (the same size tube and joint as in the vapor bath in Fig. 3), wound with sheet asbestos and Nichrome wire, served as a furnace when it replaced the vapor bath. The temperature controller was connected to this furnace.

The circulation pump and flowmeter are shown in Fig. 5. Similar pumps are described in the literature.^{23,24} Other satisfactory solutions to the problem of obtaining circulation in similar systems have been reported.^{25,26} This pump circulated the gas with very small hold-up through a complete cycle in about a minute. A small fan behind the pump kept the solenoids cool. A ground glass piston filled with soft

Legend for Fig. 3

- A. Gas Exit
- B. Gas Entrance
- C. CsF Salt
- D. Porous "D" Pyrex Frit
- E. 12/30 Ground Glass Joint
- F. Thermocouple
- G. Water Cooled Condenser
- H. 50/50 Ground Glass Joints
- I. Vapor Bath
- J. Liquid Used for Vapor Bath
- K. Furnace

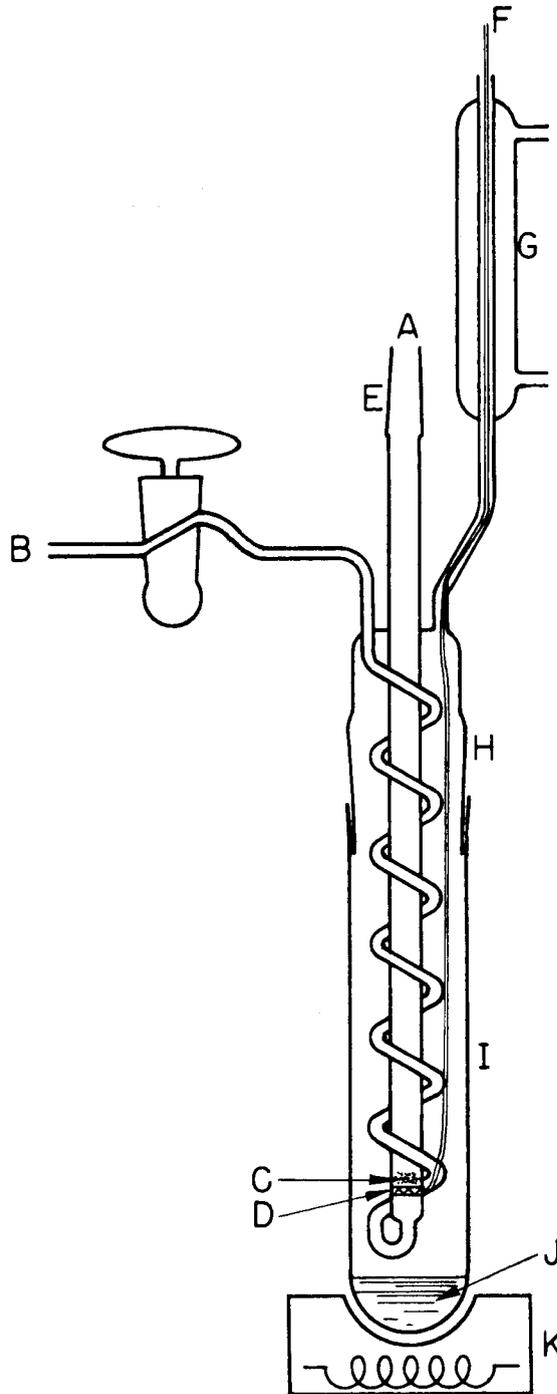


Fig. 3. CONSTANT TEMPERATURE EXCHANGER

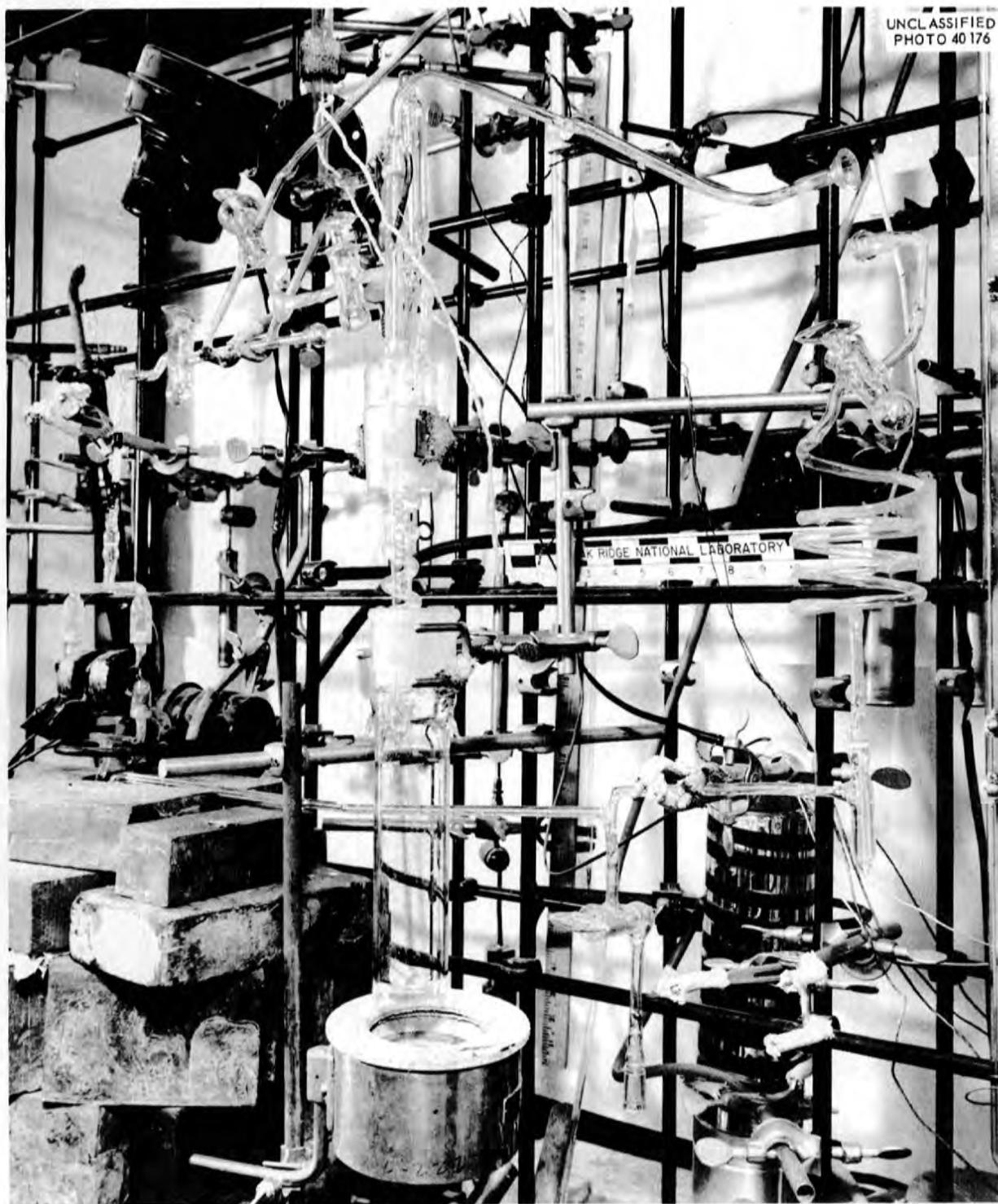


Fig. 4. Exchange System with Pyrex Constant Temperature Exchanger.

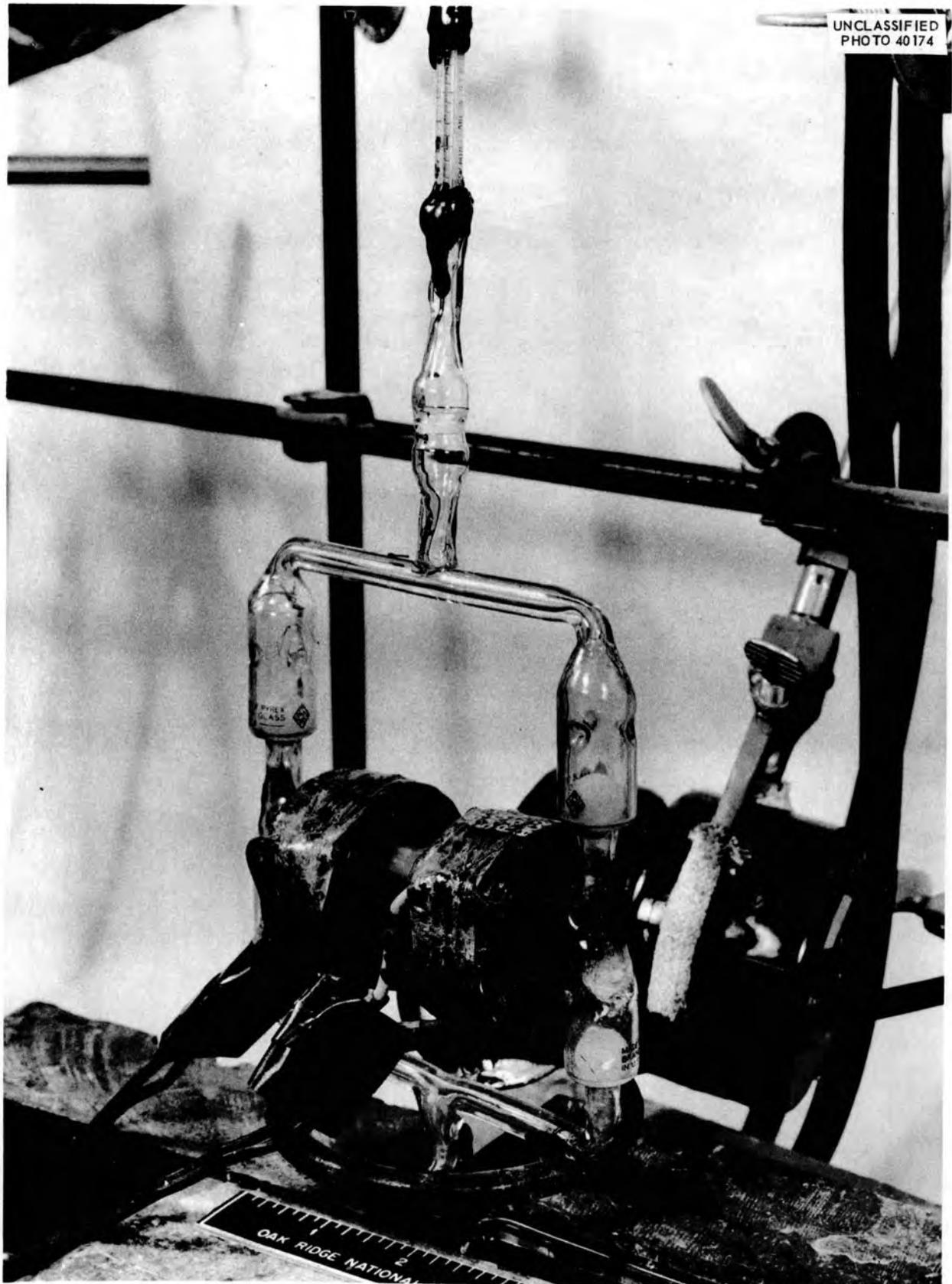


Fig. 5. Solenoid-Activated Circulation Pump.

iron operated inside the solenoids. Current to the solenoids was turned on and off at the desired rate by an ordinary laboratory stirring motor equipped with a small cam which operated a microswitch. Several of these pieces of equipment were operated from a small control box behind the lead shield in Fig. 6. Above the pump a Fisher-Porter variable-area flowmeter was mounted with Apiezon W wax. Between the flowmeter and pump was a type D sintered Pyrex frit.

Figure 6 covers the same area seen in Fig. 4 and also shows some of the manifold and gas handling system. A gas storage bulb was attached to the manifold. On the right was the mercury diffusion pump and the vacuum line leading to the Welch pump beneath the vacuum rack.

In Fig. 7 are sketched the essential parts of the system which was used to produce salts containing F^{18} by exchange with HF. This same system was used for exchange studies between gaseous fluorine compounds and HF, and between gaseous fluorine compounds and NiF_2 , CuF_2 , PdF_2 , and CsF . Figure 8 shows a photograph of the same area. The soda lime trap to prevent HF from entering the pump is also visible on the right. The fluorothene tube, in which the products from the LITR bombardment were placed for exchange with liquid HF, is attached below the filter in Fig. 8. The Booth-Cromer pressure gage²⁷ allowed measurement of the vapor pressure of the HF. The diffusion pump, which is on the left side of Fig. 8, was not used when HF vapor was present.

The nickel tube in which the inorganic fluorides were exchanged with HF and the nut by which it was attached are shown in Fig. 9. A

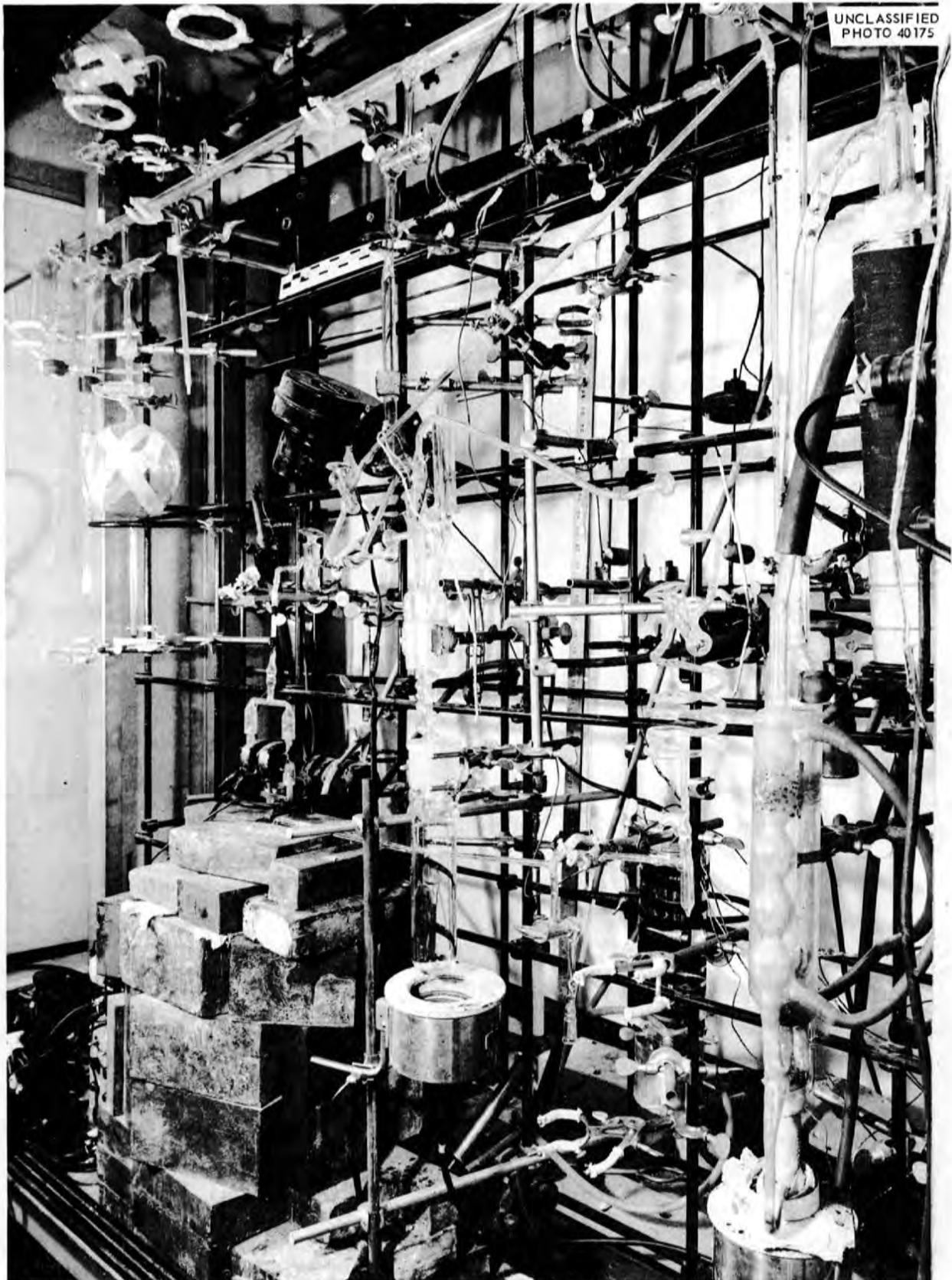


Fig. 6. Exchange System Plus Auxiliary Glass System.

Legend for Fig. 7

- A. HF Container
- B. Threaded Nut for Attaching Inorganic Fluoride Exchange Tube
- C. Thermocouple and Potentiometer
- D. Furnace
- E. Filter
- F. Threaded Nut for Attaching Tube Containing Reactor Products
(Including F¹⁸)
- G. Booth-Cromer Pressure Gage

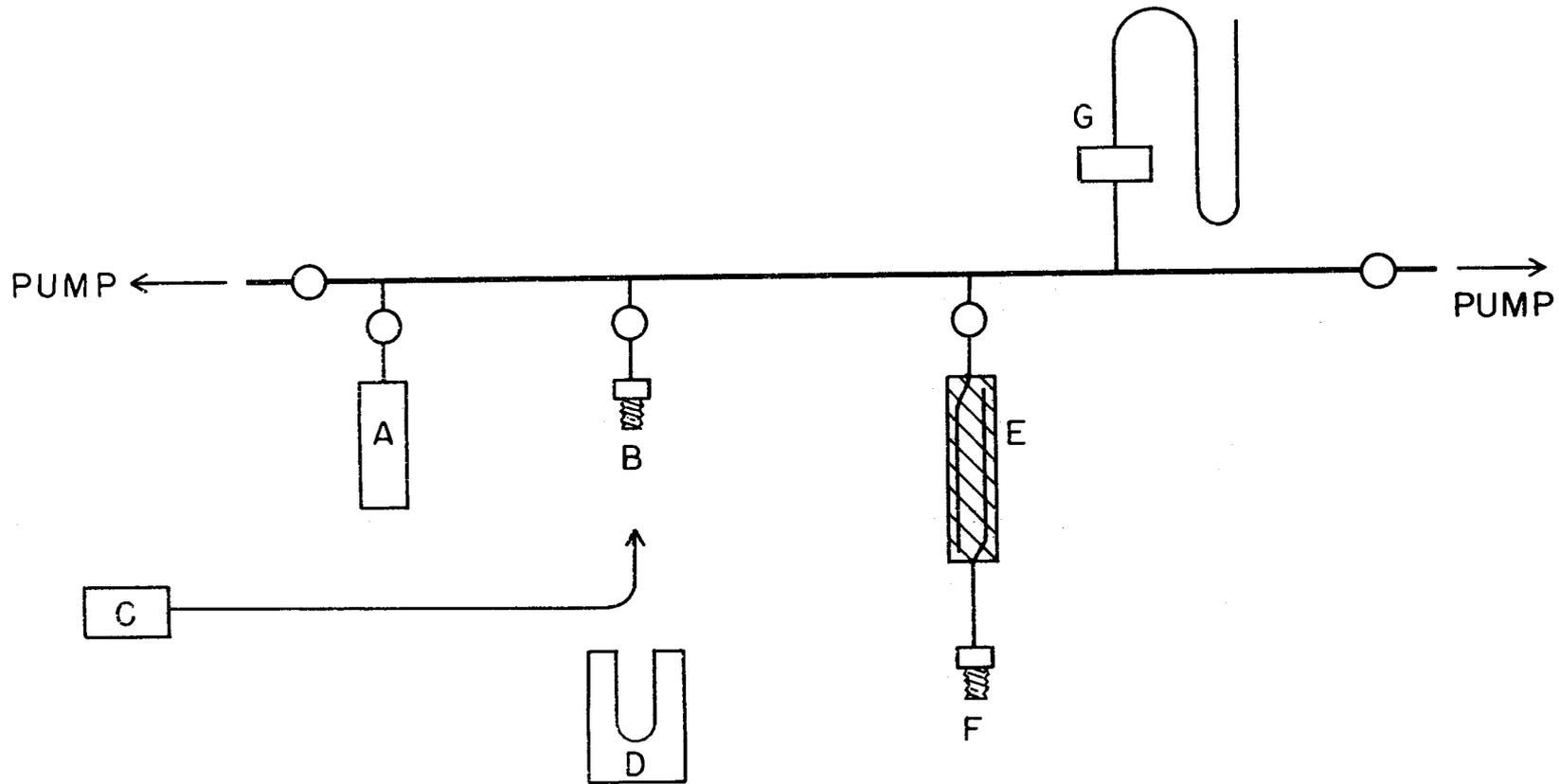


Fig.7. ALL NICKEL SYSTEM FOR PREPARING INORGANIC FLUORIDES, SKETCH

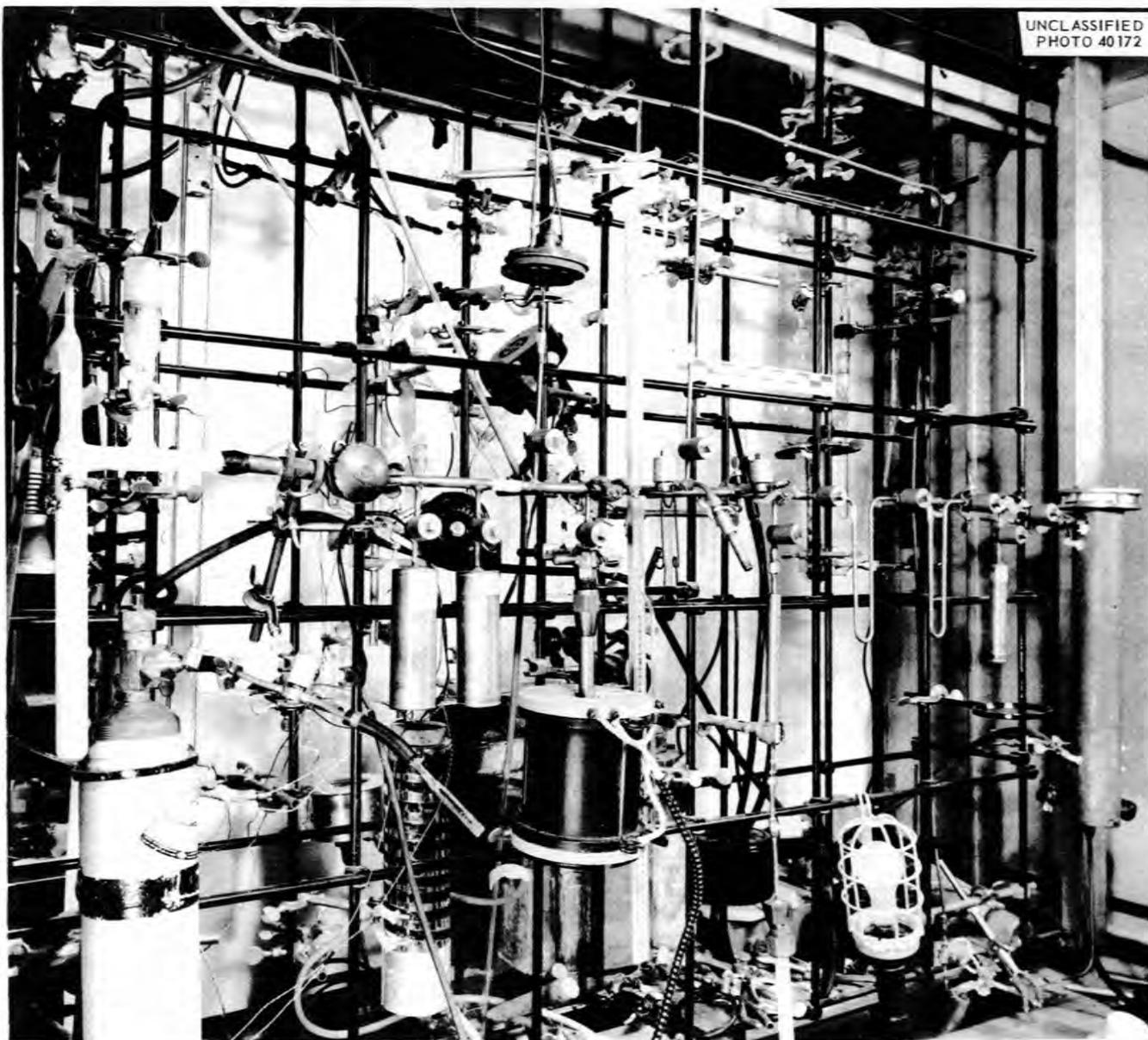


Fig. 8. All Nickel System for Preparing Inorganic Fluorides.

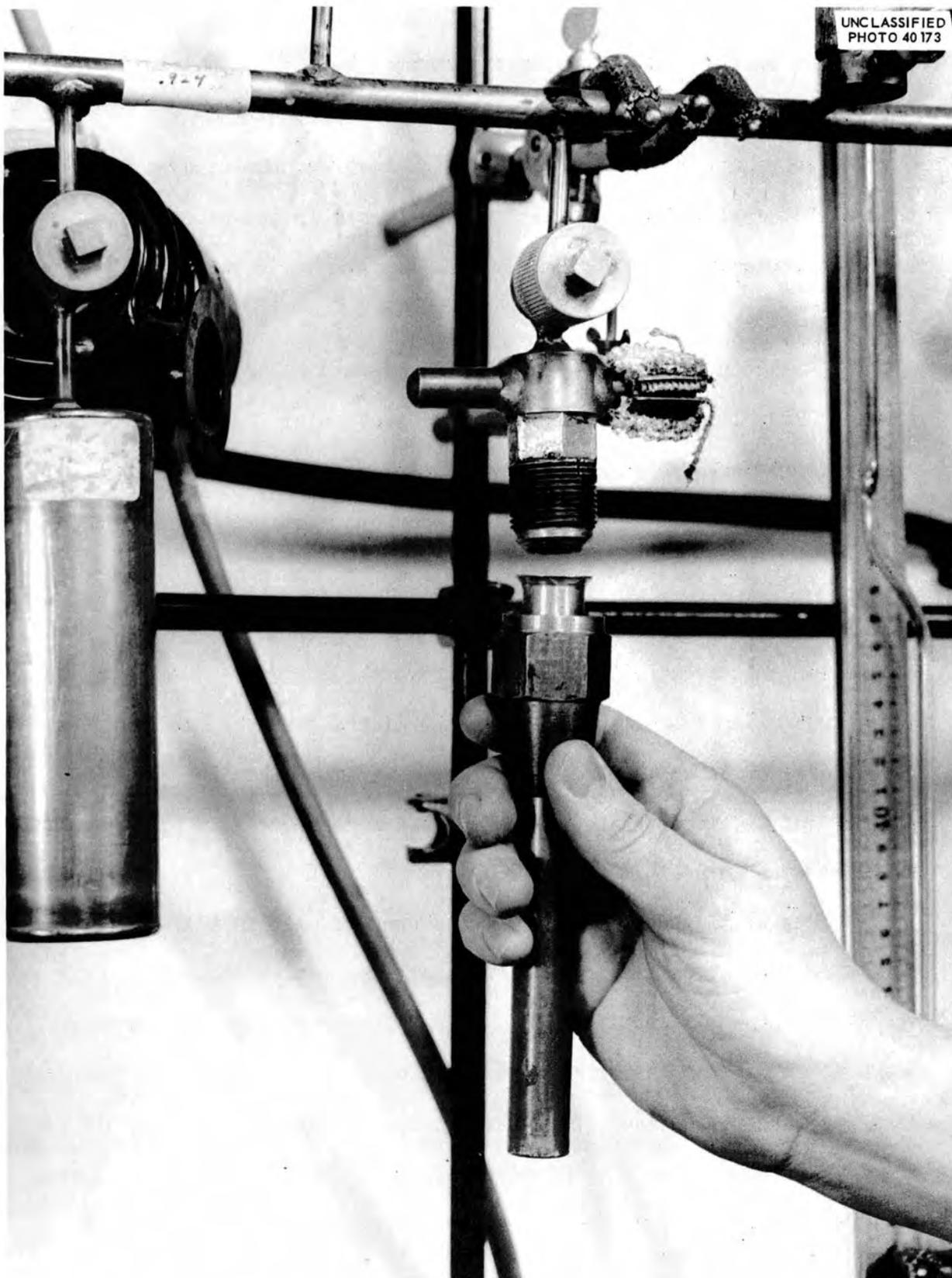


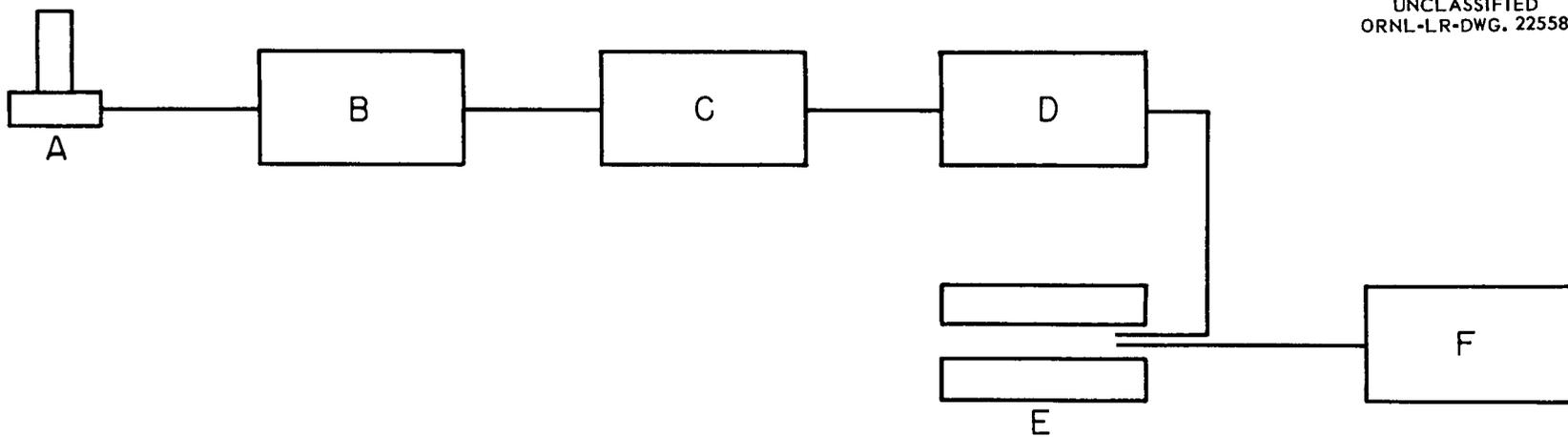
Fig. 9. Inorganic Fluoride Exchange Tube.

copper washer was used to insure a vacuum tight seal. An inch deep thermocouple well in the bottom of the tube is not visible.

No reaction of HF was observed to occur on the exposed parts of this nickel system, except that NiF_2 was formed in the exchange tube at elevated temperatures. The Fulton bellows type valve had inert Teflon liners.

A sketch of the counting and temperature control apparatus is shown in Fig. 10. The impulses from the photomultiplier tube and small preamplifier were fed into the linear count rate meter. The counting rate was recorded on the Brown chart recorder, along with the temperature, which was measured by the Chromel-Alumel thermocouple on the Inconel reactor tube. A similar thermocouple activated the temperature controller which controlled the current to the furnace. The temperature controller was not used during the kinetic studies, nor was temperature recorded on the Brown recorder. For these studies the temperature of the vapor baths was determined more accurately with the Rubicon potentiometer.

Figure 11 shows some of the instruments used in this work. The bottom instrument on the left is an Atomic Instruments Model 312 high voltage supply. It supplied high voltage to the photomultiplier tube. The ORNL Counter Amplifier is directly above. The dial on this instrument gave the percentage of input impulses that were amplified. At the counting rates used in this work, this percentage remained at essentially 100. The output from the amplifier went to the ORNL Linear Count



- A NaI Scintillation Counter with Photomultiplier and Preamplifier
- B Amplifier and High Voltage Supply
- C Linear Counting Meter
- D Chart Recorder
- E Furnace
- F Temperature Control

Fig. 10. COUNTING AND TEMPERATURE CONTROL, SKETCH

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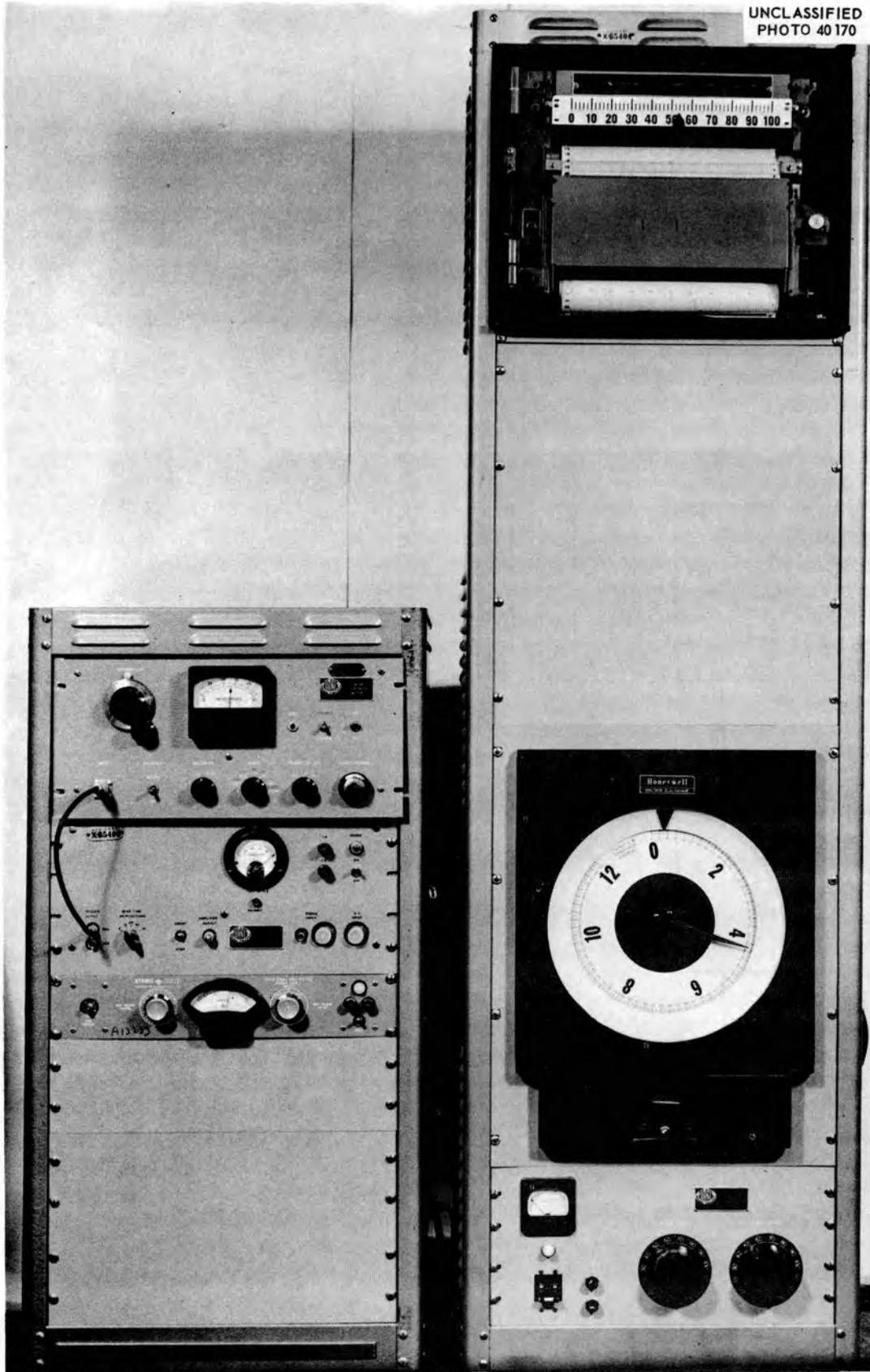


Fig. 11. Instruments.

Rate Meter, which is the top instrument on the left. This instrument was designed and built for this work by Edward Fairstein and co-workers. The ORNL Specification No. is 136, and the Drawing No. is Q-1511. Various multiplier and range settings allowed measurement of counting rates up to 2×10^6 cpm. The counting rate was read from the face of the instrument and also recorded on the two point, 10 mv. Brown Chart Recorder. Temperature of the reactor tube in the survey experiments was simultaneously printed on the recorder. The temperature range which the recorder could follow was from 0° to approximately 1000° .

At the lower right of Fig. 11 is the Minneapolis Honeywell Electroline Temperature Controller, which was capable of seeking and holding any temperature up to 1200° . The pointer at the top of the controller face reads the actual temperature at the Chromel-Alumel thermocouple. In this photograph, it is reading room temperature, about 30° .

The Harshaw standard NaI scintillation counter crystal was not visible because of the lead shielding. This crystal was of the well type and was mounted in a moisture proof can. The crystal was $1\text{-}3/4$ " in diameter and 2" in depth and had a well of $3/4$ " in diameter and $1\text{-}1/2$ " in depth. When the crystal was canned, this well was large enough to hold the Pyrex bulb of 5 cc. volume. An RCA-5819 photomultiplier tube was attached to the NaI crystal.

Another instrument not shown was the General Electric ionization vacuum gage used to measure pressure between 10^{-6} and 10^{-3} mm. of Hg.

CHAPTER III

PREPARATION OF FLUORIDE SALTS CONTAINING F^{18}

Fluorine eighteen can be prepared by using slow neutrons in the reactions $Li^6 (n,t) He^4$; $O^{16} (t,n) F^{18}$. Because this is a two step reaction in which F^{18} is produced from tritons which in turn are produced from slow neutrons, high levels of F^{18} activity cannot be made by this method. The most readily available source of slow neutrons was the ORNL Graphite Reactor,²⁸ which produced a slow neutron flux of about 10^{12} neutrons $cm^{-2} sec^{-1}$.²⁹ The Low Intensity Test Reactor (LITR)³⁰ with a slow neutron flux of above 10^{13} neutrons $cm^{-2} sec^{-1}$ was more frequently used in this work. Alkali fluoride salts could be prepared by using LITR bombardments with between 10^5 and 10^6 counts per minute (cpm) of F^{18} at the beginning of the exchange experiment. Salts with about 10^4 times as much F^{18} activity were prepared by the reaction $F^{19} (p,pn) F^{18}$ in the ORNL 86-inch cyclotron.

The advantage of the higher F^{18} activity levels produced by the cyclotron bombardments was counterbalanced by the disadvantage of a more uncertain cyclotron operating schedule. Therefore, early exchange work was all based on the LITR and was of necessity carried out at higher temperature to obtain easily measurable exchange.

The LITR was chosen over the slightly more convenient Graphite

Reactor because of its higher slow neutron flux. In addition, experimental results indicated that the distribution of neutron energies was more favorable in the LITR. An experiment was performed to test this possibility. Some cobalt-aluminum alloy was included as a slow neutron monitor³¹ in the capsules along with the charges in which F^{18} was to be produced. After neutron bombardment, counting rate measurements were made of both the F^{18} present and the amount of Co^{60} produced in the monitor. This same procedure was followed in both reactors, keeping all concentrations, bombardment times, and F^{18} isolation steps (described below) as identical as possible. It was found that 43.5 times as much F^{18} was produced in the LITR as in the Graphite Reactor, but that the slow neutron flux was only 10.5 times as great in the LITR. The fast neutron reaction $F^{19} (n,2n) F^{18}$ in the LITR was found experimentally to produce very little F^{18} and could not account for the advantage observed for the LITR over the Graphite Reactor. This conclusion agrees in general with similar experimental results of Boggs.⁵ All the work in the high temperature exchange studies used the LITR as a source of F^{18} . The main disadvantage of this method, besides the fact that the F^{18} activity produced was low, was that nuclei such as Na^{23} , which are activated by thermal neutrons, were always present in small concentrations. This presented problems both in purification and in shielding.

It was found in attempts to prepare PdF_2 containing F^{18} directly in the LITR by the reaction $F^{19} (n,2n) F^{18}$ that large thermal neutron

cross sections of trace impurities and of palladium made this method impractical. Volatile radioactive trace impurities were found to contaminate the fluorocarbon gas stream during experiments. These impurities could not be removed easily before the experiments. Radiation originating from palladium created problems in shielding and handling. This method of preparing salts was abandoned.

Table 1 lists some of the methods that have been used to prepare F^{18} . The two nuclear reactions used in this work are included with references to work in which others have used the same reactions. This table is not a complete summary. The selections were made from considerations of variety or practicality. References 32 and 33 give a more complete survey of the many methods by which F^{18} has been produced.

In the last reaction listed in Table 1, it can be seen that different techniques have been used to mix the necessary nuclei, Li^6 and O^{16} , in the charge which was bombarded by slow neutrons. Consideration must be given to the short range of the triton particle.⁴¹ It is preferable to have the oxygen and lithium in the same molecule, but the formation of gaseous products or water interfered with the use of such salts in the present work.

To remove the F^{18} after neutron bombardment, HF was condensed on the products, mixed thoroughly, and distilled off through the filter (Figs. 7 and 8). Lithium salts which contain oxygen react with HF to produce gases or water, or both. Hydrogen fluoride has a higher vapor

TABLE 1
SIX METHODS OF PREPARING RADIOACTIVE F¹⁸

Nuclear Reaction	Target	Radiation Source	Comments
F ¹⁹ (n, 2n) F ¹⁸	10-40 mg. NH ₄ F; ⁵ liquid HF; ² HF, KHF ₂ ³⁴	LITR Neutrons from the cyclotron reaction Li ⁶ (d, n) Be ⁷	LRP ^a
F ¹⁹ (γ, n) F ¹⁸	KHF ₂ ³⁴	Betatron 48 or 84- Mev X-rays	HRP ^b
F ¹⁹ (p, pn) F ¹⁸	10 mg NaF; ⁵ AlF ₃ ³⁵	ORNL 86-inch cyclotron	HRP, great quantities
O ¹⁶ (α, pn) F ¹⁸	H ₂ O; ³⁶ PbO ³⁷	UCRL 60-inch cyclotron	Erratic yield
F ¹⁹ (d, t) F ¹⁸	NaF ³⁸	Cavendish cyclotron	Threshold at 6 Mev.
Li ⁶ (n, t) He ⁴ ; O ¹⁶ (t, n) F ¹⁸	LiF and Al ₂ O ₃ ^{5,34} LiCO ₃ ; ³⁹ LiNO ₃ ^{39,40}	Slow Neutrons	LRP

- a. Low radiochemical purity
b. High radiochemical purity

pressure than water and slow distillation leaves the water behind. However, to avoid the possibility of entrainment of water it was preferable not to use the salts which reacted to give water. Experimental procedure was also simpler if there were no gaseous products to remove. Because of the small particle size of less than one micron, it was found that Linde B Alumina worked satisfactorily when mixed with LiF. High purity of this alumina was also a very desirable property. Analysis of a sample of this alumina put through a dry run with HF showed some fluoride ion to be present. It was thought that this result was caused by strongly adsorbed HF rather than by reaction. Nevertheless, some HF residue was always discarded in the distillation procedure to insure that no moisture was distilled off.

At least a 2:1 molar excess of this HF was condensed onto the fluoride salt in the fluoride exchange tube in Fig. 9 and the tube was warmed slowly to 70°, with the exit valve closed. After allowing about fifteen minutes for achievement of isotopic equilibrium, the HF was pumped off through the soda-lime trap. Pumping was continued while the fluoride salt was heated, usually at 400°. With the alkali fluorides, increasing difficulty in decomposing the bifluorides was encountered in progressing through the group from LiF to CsF. With CsF a temperature between 550° and 600° was maintained over at least one-half hour, after which the CsF was found to have sublimed to the cooler part of the reactor tube near the top. Previous work has indicated that even after this procedure some HF may have been present in the CsF.⁴² Flushing

with argon at high temperature was required to remove the last of the HF.

Alkali fluoride salts were prepared by cyclotron bombardment for the low temperature exchange studies and the kinetic studies. Between 0.3 and 0.5 gram of dry alkali fluoride was packed into cylindrical tubes made of 2S aluminum. These tubes were of 0.250" O.D., 0.0045" thickness, and 2.75" length. The ends of the tube were flattened, folded over once, and crimped tightly shut in a vise. The tubes were flattened and placed in the cyclotron target head behind a 2S aluminum window of 0.012" thickness. Cooling water was circulated at 40 pounds per square inch gage pressure at a sufficient rate to allow only a one degree temperature rise in the cooling water during bombardment. The protons at the target had an energy of 21 Mev. The beam current was approximately 80 microamperes. It was possible by this method to prepare one curie of F^{18} in 15 min. A general description of the cyclotron is available,⁴³ as is a discussion of radioisotope production rates⁴⁴ and a description of target heads⁴⁵ quite similar to those used in producing F^{18} .

The aluminum tubes were opened behind a lead barricade by quickly ripping them into two pieces with long handled pliers. The alkali fluorides were washed from the two pieces into a beaker of water. Alkali fluoride carrier was added, and the solutions were filtered through Whatman No. 50 filter paper. The water was removed by evaporation on a hot plate. The hot, dry alkali fluorides were placed in hot weighing bottles to prevent adsorption of atmospheric moisture.

This precaution was not required for LiF and NaF. The weighing bottles were stored in a desiccator. The weight of a portion of alkali fluoride removed for an experiment was determined by difference. The portion removed was quickly placed in the exchange system and evacuated.

From this point on the fluoride salts prepared by either method were handled in the same manner. Evacuation was continued as the salts were heated. For the survey experiments the salts were heated to approximately two-thirds of their melting points. The CsF was heated to 400° for the kinetic studies. These temperatures were maintained until the pressure as read on the ionization vacuum gage was reduced to 10^{-4} mm. Dry argon was circulated while the alkali fluoride was kept at high temperature. If any radioactivity was observed in the argon, it was pumped out and the process was repeated until no more activity was detected. The system was then thoroughly evacuated and brought to the temperature desired for the start of the exchange study. In the kinetic studies, the argon was not monitored by circulation through the counter, but was admitted and pumped off the CsF three times to insure a clean surface.

Besides the alkali fluorides, CdF_2 , CrF_2 , PdF_2 , MgF_2 , NiF_2 and CuF_2 were prepared by exchange with HF. Palladium difluoride showed very little tendency to exchange with HF. By use of the HF with high specific activity described in the survey with HF, it was possible to prepare a gram of PdF_2 with over 10^8 cpm of F^{18} . Many fluorides have been found to be quite soluble in HF.⁴⁶ This technique probably can be

used successfully with a great many inorganic fluorides to incorporate F^{18} . The technique of direct bombardment by protons also appears to be applicable to many inorganic fluorides.

CHAPTER IV

CALCULATIONS

The amount of exchange in all experiments described as survey or kinetic studies was calculated by the following equation:⁴⁷

$$N = \text{Net fraction exchanged} = \frac{F_{\text{gas}}^{18}/F_{\text{total}}^{18}}{F_{\text{gas}}/F_{\text{total}}}, \quad (1)$$

where F_{gas}^{18} = F^{18} counting rate, gas phase,

F_{total}^{18} = sum of F^{18} counting rates, gas and solid phases,

F_{gas} = weight of fluorine, gas phase,

F_{total} = sum of weights of fluorine, gas and solid phases.

When N equaled one, the F^{18} atoms were randomly distributed among all fluorine atoms in the two phases.

The following experimental values, which varied, were used to solve this equation:

Temperature of the Inconel reaction tube, °C	= T_1 ,
Pressure of fluorocarbon, mm. of Hg	= P_1 ,
Initial counting rate of the alkali fluoride, cpm	= $(\text{AFCR})_0$,
Counting rate of the background, cpm	= $(\text{Bgd})_1$,
Recorded counting rate of fluorocarbon in the counting chamber, including $(\text{Bgd})_1$, cpm	= $(\text{RCR})_1$,
Counting rate of total gas when counted at the same geometry as the salt, cpm	= $(\text{CRIG})_1$,

Factor to correct $(RCR)_i - (Bgd)_i$ to $(CRTG)_i = (CF)_i$.

All counting rates $(RCR)_i$, $(AFCR)_o$ and $(CRTG)_i$ were corrected for decay of F^{18} by the exponential law $R/R_o = e^{-\lambda t}$ where $\lambda = 0.693/t_{1/2}$ and $t_{1/2} = 112$ minutes.

Other values, constant within a particular run, needed to solve Equation 1 were:

Pressure of gas in the exchange system at 298° K,
 mm. of Hg = P_{298} ,
 Volume of the exchange system, cc. = V_s ,
 Volume of the counting chamber, cc. = V_{cc} ,
 Weight of fluorine in one mole of gas, g. = WF_{gas} ,
 Weight of fluorine in the salt, g. = F_{salt} ,
 298° K = T .

The terms in Equation 1 became:

F_{gas} , g. = $(WF_{gas})(\text{moles of gas})$
= $(WF_{gas})(P_{298}V_s/RT)$, by the ideal gas law.
 F_{total} , g. = $F_{gas} + F_{salt}$
= $(WF_{gas})(P_{298}V_s/RT) + F_{salt}$.
 F_{gas}^{18} , cpm. = $(CRTG)_i = (CF)_i \left[(RCR)_i - (Bgd)_i \right]$.
 F_{total}^{18} , cpm. = $F_{gas}^{18} + F_{alkali\ fluoride}^{18}$
= $(AFCR)_o$, corrected for decay, since all F^{18}
was initially in the alkali fluoride.

Substitution yielded:

$$N = \frac{(CF)_i \left[(RCR)_i - (Bgd)_i \right] / (AFCR)_o}{(WF_{gas})(P_{298}V_s/RT) / (WF_{gas})(P_{298}V_s/RT) + F_{salt}} \quad (2)$$

Radioactive C_3F_6 was counted as a liquid in an external well type scintillation counter very similar to the one in the gas line to give the quantity $(CRTG)_i$. This radioactive C_3F_6 was placed in the exchange system and $(CF)_i$ was determined from the observed values of $(RCR)_i - (Bgd)_i$. For correct evaluation of N, it was necessary that $(CF)_i$ be determined very similarly to $(AFCR)_o$. Therefore, $(AFCR)_o$ was determined by counting aqueous solutions of the alkali fluoride in the same external counter at the same geometry, at approximately the same counting rates, and applying counting loss corrections. The empty reactor tube of Fig. 2, or the empty exchanger of Figs. 3 and 4, was at room temperature when $(CF)_i$ was determined. When the reactor tube or exchanger was warmed, $(CF)_i$ decreased and P_i increased.

Consideration of $(CF)_i$ shows that it is a function of the ratio of the total number of moles of gas present in the system to the number of moles of gas in the counting chamber. While the reactor tube or exchanger was at room temperature, this ratio, which will be called n_s/n_{cc} , was equal to the ratio V_s/V_{cc} , by the ideal gas law. Thus the following evaluation of $(CF)_i$, as a function of P_i as T_i changed, could be made:

$$(CF)_{298} = k (n_s/n_{cc}) = k (V_s/V_{cc}) \quad (3)$$

$$\text{where } k = \frac{(F_{cr}^{18}/F_{dr}^{18})_{EC}}{(F_{cr}^{18}/F_{dr}^{18})_{GLC}}$$

and $(F_{cr}^{18}/F_{dr}^{18})_{EC}$ = the ratio of counting rate to disintegration rate
in the external counter,

and $(F_{cr}^{18}/F_{dr}^{18})_{GLC}$ = the same ratio in the gas line counter.

$$(CF)_i = k(n_s/n_{cc})_{T_i} = k(n_s/k' P_i), \quad (4)$$

$$\text{where } n_s = P_{298} V_s/RT \quad (5)$$

$$\text{and } k' = V_{cc}/RT, \quad (6)$$

since the counter chamber temperature stayed approximately at T, and the only systems considered were those in which n_s stayed constant. Dividing 5 by 6 gave

$$n_s/k' = V_s P_{298}/V_{cc}. \quad (7)$$

Substituting (7) in (4) gave

$$(CF)_i = (k \cdot V_s/V_{cc})(P_{298}/P_i). \quad (8)$$

Substituting (3) in (8) gave

$$(CF)_i = (CF)_{298} \times (P_{298}/P_i). \quad (9)$$

Thus, $(CF)_i$ could be calculated very simply from the experimentally determined $(CF)_{298}$. From known values of V_{cc} and V_s , Equation 3 gave k from the experimental value of $(CF)_{298}$. The first calibration gave a value of 25.27 for $(CF)_{298}$ and k was calculated to be 1.38. In a similar calibration in the kinetics chapter, where V_s and $(CF)_{298}$ were both different and small adjustments had been made in the count rate meter, k was calculated to be 1.31. The term k did not enter directly into calculations, but this agreement showed that the values for k, V_s , V_{cc} and $(CF)_{298}$ were all approximately correct.

For the high temperature experiments, the volume of the system, 86.3 cc., was less than in the calibration experiment where a cold finger had been added. By Equation 3, where $V_{cc} = 5$,

$$(CF)_{298} = 1.38 \times \frac{86.3}{5} = 23.82.$$

This value of $(CF)_{298}$ was used for the high temperature studies and the first few low temperature studies.

It was not necessary to have $(CF)_{298}$ in Equation 9 if it was known at some other temperature, since:

$$\begin{aligned} (CF)_2 &= (CF)_{298} (P_{298}/P_2), \\ (CF)_1 &= (CF)_{298} (P_{298}/P_1), \\ (CF_2/CF_1) &= (P_1/P_2), \\ (CF)_2 &= (CF)_1 (P_1/P_2). \end{aligned} \tag{10}$$

Equation 10 was applied in the kinetic studies.

Usually the background $(Bgd)_1$ was subtracted from the recorded counting rate $(RCR)_1$ directly as these values were obtained from the recorder chart paper. Therefore, this new quantity, the net recorded counting rate, $(NRCR)_1$, and also the value for $(CF)_1$ from Equation 9 were introduced into Equation 2. Rearrangement yielded:

$$N = \frac{C(NRCR)_1}{P_1(AFCR)} \tag{11}$$

$$\text{where } C = \frac{(CF)_{298} \left[(WF_{\text{gas}}) P_{298} V_s + RTF_{\text{salt}} \right]}{(WF_{\text{gas}}) V_s}.$$

Figure 12 shows an example of the experimental data to which

Equation 11 was applied. The heavy dark line on the left in Fig. 12 shows the temperature of the reaction zone. Times were written on the left margin with temperature in the adjacent column. For the first 55 minutes a constant temperature of about 48° was maintained. For the next 40 minutes the temperature was raised at about 5° per minute. The temperature was then again held constant for 40 minutes at about 256° . The counting rate record starts on the right of the chart. A full scale value of 10,000 cpm (10 K in Fig. 12) was sufficient for 62 minutes; 20,000, 67 minutes; 100,000, 98 minutes; 200,000, the remainder. A straight line was drawn for the slightly changing background. Data for two crude constant temperature studies and one survey run were obtained from this chart. The survey run is discussed in connection with Fig. 19 as Run C14a. The constant temperature results are tabulated as RbF, C_3F_6 in Table 6. For the kinetic studies, no temperature data were recorded as in Fig. 12, and the speed of the recorder was increased so that the distance covered in 10 minutes in Fig. 12 was covered in one minute.

As an example of actual calculations as they were made from chart data, the $(NRCR)_1$ of 7050 at 81° and 59 minutes from Fig. 12 is substituted along with other experimental data in Equation 11 to give the following value for N:

$$N = \frac{(7983)(7050)}{(287)(2.259 \times 10^8)} = 8.686 \times 10^{-4} .$$

The experimental values used in calculating C were as follows:

$$c = \frac{(25.27) \left[(114)(283)(91.3) + (1.86 \times 10^7)(.0184) \right]}{(114)(91.3)} = 7983 .$$

The particular value calculated above appears in Fig. 19 at a value of 2.825 for $1000/T$, °K.

By use of Equation 11, only the exchange visible to the counter could be evaluated. Exchange which is invisible to the counter also occurs. Once an F^{18} atom enters the gas phase, the probability that it will re-exchange with a fluorine atom in the alkali fluoride is as great as is the probability that any other fluorine atom in the gas phase will exchange with a fluorine atom in the alkali fluoride. The results obtained by Equation 11 had to be correlated with the mechanistic picture which developed during this work. The following paragraphs discuss this correlation and its effect.

As will be seen in the discussion of results, all the evidence indicated that both a fast and slow exchange reaction occurred. The fast reaction soon led to a pseudo-equilibrium between the gas phase and a portion of the alkali fluoride. The calculated magnitude of N was not an actual measure of the amount of exchange, since exchange continued after random distribution by the fast reaction without changing the F^{18} concentration in the gas. Thus, N should be considered as the fraction of the alkali fluoride which was in equilibrium with the gas phase when the fast reaction is being considered. No corrections for exchange invisible to the counter needed to be made on the results of Equation 11 as long as the fast reaction was being considered, since

equilibrium concentration of F^{18} was being measured. Results of the survey studies will be shown to represent almost entirely the fast exchange equilibrium.

Therefore, N , which could only be defined as net fraction exchanged early in this work, was redefined after analysis of all observations as fraction of alkali fluoride in exchange equilibrium with the gas phase. Use of N was continued with its original meaning because the necessity of the second definition did not become apparent until after the kinetic studies were made.

The same treatment of the data was applied with SiF_4 and SF_6 because of its convenience and because of the desirability of comparing these results with those of the fluorocarbons.

In the kinetic studies, the determination of the rate of the slow reaction required a different treatment of the exchange results calculated by Equation 11. To calculate the rate of exchange, a correction had to be added to the slow increase in counting rate observed in the gas to account for the exchange which removed F^{18} from the gas phase. This same problem is always faced in kinetic studies involving isotopic exchange, and the standard treatment of McKay⁴⁹ was used. At first consideration, it appeared that McKay's treatment, which was worked out for systems in which the tracer was distributed homogeneously throughout the different phases, could not be applied to gas-solid exchange experiments. The reason that it could be used in this work is explained in connection with proposed mechanisms in the discussion of results.

CHAPTER V

CHEMICAL AND RADIOCHEMICAL PURITY AND ERROR

Chemical Purity of Gases and Salts

All fluorocarbons were treated as follows to remove air, moisture and other impurities. The gases were distilled from storage bulbs into a liquid nitrogen-cooled trap. This trap was open to the mechanical and diffusion pumps to remove any traces of air. After the fluorocarbons passed twice through a tube filled with P_2O_5 , a Regnault molecular weight determination⁵⁰ was made. This procedure established that all molecular weights were within 1% of the theoretical value.

Perfluoropropene was purchased from Peninsular Chem-Research, Inc. The only suspected impurity was C_3F_7H . Mass spectrographic analysis of this C_3F_6 and also of C_3F_6 prepared by a similar process in the laboratory showed an estimated 0.3 mole percent of C_xF_xH . No other impurities were detected. It seemed unlikely that this concentration of C_xF_xH could have any serious effect on fluorine exchange, at least at the lower temperatures used. No attempt was made to remove this impurity.

Perfluorobutane was prepared in the laboratory by the Electrochemical Process⁵¹ starting with C_4H_9COOH . Acidic products were removed by passage through cold aqueous base. Preliminary single plate distillation was performed in an open system, and material boiling near

0° was removed. After removing air and drying with P_2O_5 this fraction was carefully distilled through a column of approximately 30 plates. The material used in these studies boiled between -2.25° and -1.60° . Infrared analysis of C_4F_{10} prepared by a similar procedure indicated a mixture of the isomers perfluoroisobutane and perfluoro-n-butane.

Perfluorodiethylether, CF_4 , CF_3H , and C_2F_6 were all prepared by a procedure similar to that described for C_4F_{10} , except that only a single plate distillation was required to isolate a pure sample of the low boiling CF_4 . Oxygen difluoride was removed from these gases by passage through a buffered KI solution. Infrared analyses indicated no impurities in these materials. No impurities were detected in a mass-spectrographic analysis of the C_2F_6 .

The compounds SiF_4 of 99.5% purity and SF_6 of 99.0% purity were used as purchased from the Matheson Company, except that air and other low boiling materials were removed by the same process described above, and SF_6 was dried by passage through a tube packed with P_2O_5 . Since SiF_4 reacts on contact with moisture, the drying step was not required. A single plate vacuum distillation was performed in the vacuum system with both SF_6 and SiF_4 , and the first and last portions of the distillates were discarded.

Baker Analyzed LiF and Fisher Certified Reagent NaF were used as purchased. Spectrographic analysis indicated that the LiF contained as much as 1% calcium. Baker and Adamson ACS Reagent Grade KF was first dried and then sublimed before use. Rubidium fluoride was obtained

from General Chemical Company. The reported impurities were about 1% K and traces of the other alkali metals. Cesium fluoride was obtained from the A. D. Mackay Company. The reported impurities included 0.12% Rb and traces of the other alkali metals. Spectrographic analysis of this CsF also showed as much as 0.1% Al and traces of Si. A sample of the very pure CsF used by Bredig, Bronstein, and Smith⁴² was obtained for the last kinetic study. This CsF also showed traces of Al by spectrographic analysis. Similarity of experimental results in the last kinetic study to all previous results indicated that impurities were not the cause of the unique observations in this work. Upon heating at 400° under vacuum, RbF and CsF changed color from pure white to grey. This discoloration appeared to be as intense when the very pure CsF was used as when the CsF purchased from the A. D. Mackay Company was used. Support for a defect-caused mechanism was found in this discoloration. Analysis of samples of all the alkali fluorides by the spectrophotometric method⁵² both before and after exchange with fluorocarbons showed no change in composition from the theoretical values. The standard pyrohydrolysis method⁵³ of analysis for fluoride was found to be unsatisfactory for all the more volatile fluorides (KF, RbF, and CsF).

Anhydrous nickel fluoride was prepared by hydrofluorination of Special Reagent Grade Baker and Adamson $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 400 to 500°. Anhydrous cupric fluoride was prepared by hydrofluorination at 250 to 300° of the Baker and Adamson ACS Reagent Grade, partially hydrated

product. Hydrofluorination produced salts which were spectroscopically pure in any materials which formed volatile fluorides. Anhydrous chromous fluoride was prepared by the thermal decomposition of $(\text{NH}_4)_3\text{CrF}_6$ in a stream of hydrogen at 700° . The $(\text{NH}_4)_3\text{CrF}_6$ was prepared by the reaction of Fisher Scientific $\text{CrF}_3 \cdot 3\text{-}1/2 \text{H}_2\text{O}$ with NH_4F at 100° . A mixture of PdF_2 and PdF_3 was prepared by direct fluorination of spectroscopically pure PdCl_2 at 400° . An attempt was made to convert the mixture completely into the trifluoride by dissolving in excess BrF_3 and distilling off the Br_2 and BrF_3 . The resulting addition compound $\text{PdF}_3 \cdot \text{BrF}_3$ was found to decompose at 200° under vacuum to yield PdF_3 , but X-ray analysis showed that the decomposition was incomplete. Heating the impure PdF_3 to 400° in the presence of HF , followed by an additional hour of heating at 400° under vacuum, yielded a product which gave the theoretical fluoride analysis for PdF_2 by the pyrohydrolysis method.⁵³

Radiochemical Purity

In early attempts to prepare alkali fluorides by using LITR bombardments as a source of F^{18} , it was found that other radiations besides those of F^{18} were present in the alkali fluorides. The filter shown in Figs. 7 and 8 was added to the apparatus. This filter was packed with a matting made of fine nickel wire which effectively stopped radioactive materials from contaminating the product. Investigations of purity were made with the ORNL 60-channel gamma spectrometer.⁵⁴ Figure 13 shows a typical plot of counting rate against channel number for pure

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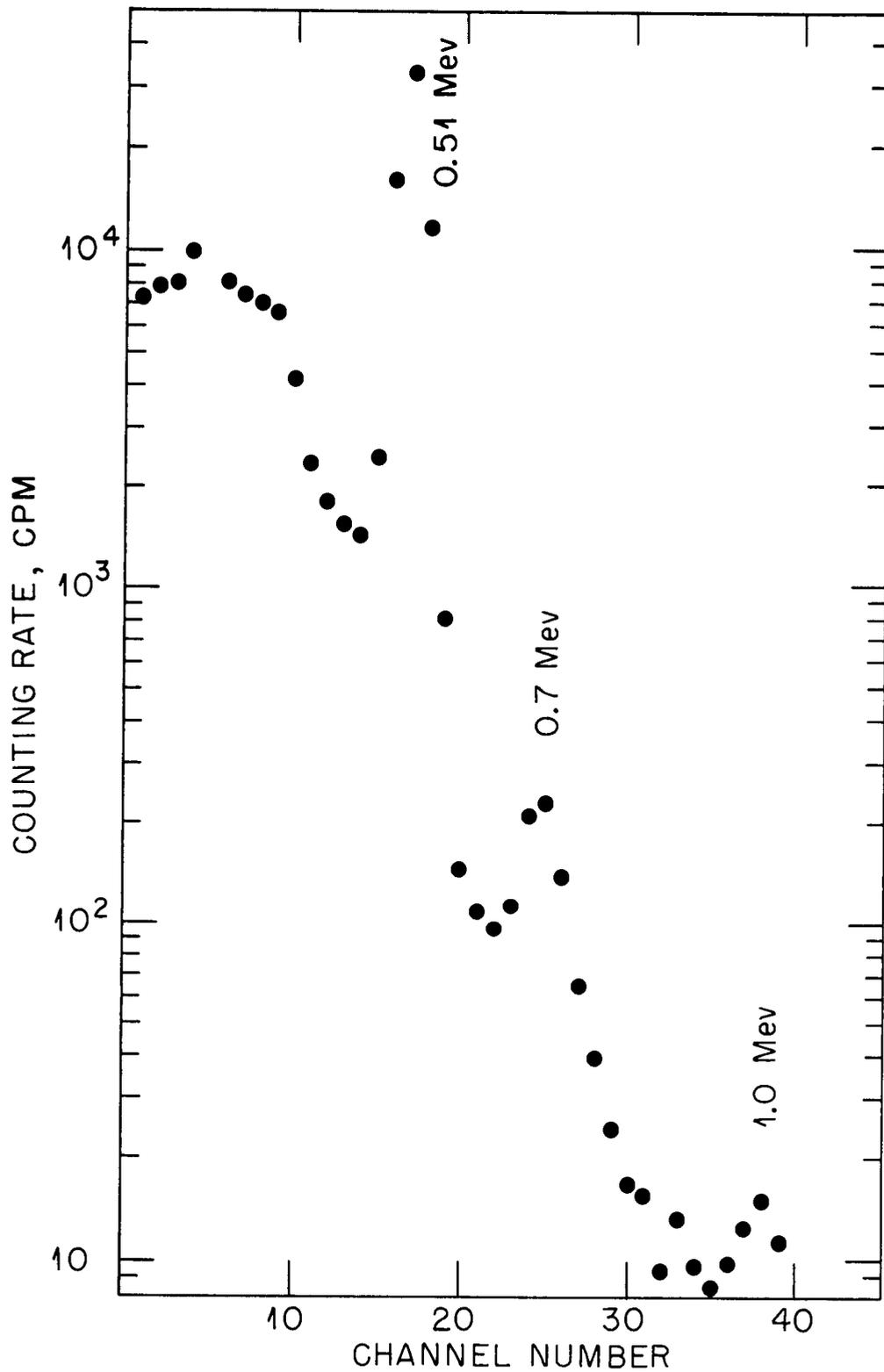


Fig.13. GAMMA SPECTROMETER PLOT OF F^{18} RADIATIONS

F^{18} radiations. It was deduced from such a plot and the known amount of Na^{24} radiation in the reactor irradiated sample that there was less than one ppm contamination of the product by material from the original sample after installation of the filter. Background variations did not allow any closer evaluation of contamination. Many plots similar to Fig. 13 were made after installation of the filter, and no evidence of radiochemical contamination appeared.

In Fig. 13 the very small peak at 1.0 Mev was caused by the occurrence of two gamma rays of 0.51 Mev being registered by the spectrometer simultaneously as a single radiation. At first, the peak at 0.7 Mev was not understood. To insure that this peak was not the result of radiochemical impurity, further studies were made. It was found to have a 112 minute half life and therefore was almost certainly associated with F^{18} . Since the 180° backscattered Compton radiation from a 0.511-Mev gamma ray would have an energy of about 0.20 Mev and would be in coincidence with the primary forward gamma of the annihilation pair, the 0.7-Mev peak could result from this scattering process. In the case of LITR-produced F^{18} the activity was always associated with approximately a gram of salt which could act as a back-scatterer. When measurements were made with high specific activity F^{18} produced on the cyclotron, the 0.7-Mev peak was absent. It was possible to produce a 0.7-Mev peak by placing the high specific activity source between a scatterer and the scintillation spectrometer detector. It was concluded that the fluoride salts containing F^{18} prepared with this

system were of high radiochemical purity.

Less danger of radiochemical contamination existed in the production of F^{18} with the cyclotron, since the impurities have cross sections comparable with the cross section of F^{19} under proton bombardment.⁵⁵ Thus, radiochemical contamination was approximately proportional to the concentration of the bombarded nuclei, and by using moderately pure salts, the specific activity of F^{18} for a few hours after bombardment was such that other radiations could not be detected. This technique also produced radioactive isotopes from the cations, but the half lives were such that their radiations caused no difficulty in the case of the alkali fluorides. For example, with a sample of LiF in which the total F^{18} activity was over 10^{10} cpm after bombardment, a counting rate of about 10^5 cpm from the 53 day Be^7 isotope was detected after the F^{18} had decayed. Several half-life studies on the radioactive gas, after exchange with these alkali fluorides, indicated that only F^{18} radiations were present. Half-life determinations were also made on the gases after exchange with salts prepared by the technique based on the LITR, and only F^{18} radiations were observed.

Error

The following table presents the most important sources of error which entered into the terms in Equation 11. These estimates were made on the typical example of calculations, which accompanied Fig. 12. The first error in Table 2 has the greatest effect on N. This error has a small effect on the precision within a particular run.

TABLE 2
ERROR

Term	Estimated Limits of Error	Source
$(AFCR)_o$	$\pm 2\%$	$t_{1/2}$, over 4 hr.
$(NRCR)_i$	$\pm 1\%$	Statistical fluctuation of count rate meter
P_{298}, P_i	$\pm 1\%$	Isochore plots obtained with capillary Hg manometer
	$\pm 1\%$	Temperature uncertainty
V_s	$\pm 2\%$	Estimation for loss of calibrating water
F_{salt}	$\pm 1\%$	Weighing
C	$\pm 1\%$	P_{298}, V_s, F_{salt}
N	$\pm 3\%$	Accumulated error

Most systematic errors were kept small by the technique of comparing counting rates of salts and gases on the same external counter. Other potential sources of error, not considered significant in any of the data presented, are discussed below.

The higher boiling materials C_4F_{10} and $(C_2F_5)_2O$ adsorbed sufficiently on the counting chamber walls to cause experimental difficulty. However, a very slight increase in the counting chamber temperature, with increasing T_1 , completely removed this effect with both materials. Figure 14 demonstrates that much adsorption occurred on the system walls

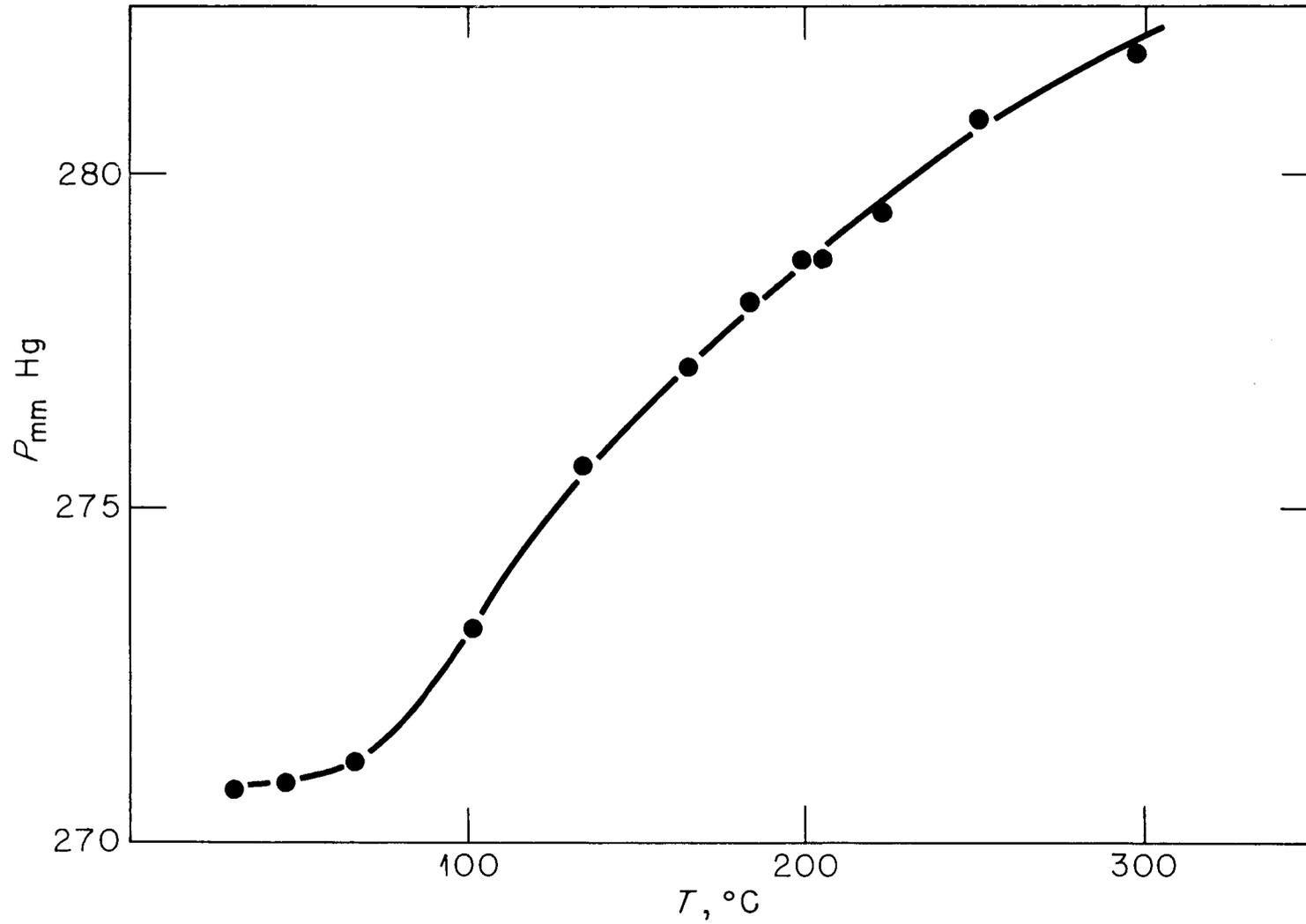


Fig. 14. PRESSURE-TEMPERATURE BEHAVIOR OF C_4F_{10} ABOVE CsF

and on the salt with C_4F_{10} at low reactor chamber temperatures. Therefore, no data is presented for C_4F_{10} and $(C_2F_5)_2O$ below a reactor chamber temperature of 270° , although these materials exchanged readily at 0° , the lowest temperature used.

Heating rate was approximately $5^\circ \text{ min.}^{-1}$. Deliberate variation of this rate indicated that results were not appreciably affected.

Some background variation almost always occurred during low temperature runs. Figure 12 presents a typical example. This variation was not significant.

There was some possibility that all HF was not removed, especially with CsF, in the high temperature survey work. Agreement in results from the same systems between low and high temperature surveys indicates that there was no error from this source.

The rate of gas flow was constant at about one cycle per minute. Determination of the rate of the slow exchange process was not hindered by this rate of flow. The fast exchange process was probably delayed in its approach to equilibrium. No error was introduced in the kinetic studies, since only equilibrium data for the fast reaction were reported. A small delay must have been involved in following N during survey runs, but this small delay was common to all runs.

In the kinetic studies, the temperature of the constant temperature bath was determined with a precision of $\pm 0.1^\circ$ by a Pt, 10% Pt-Rh thermocouple. Calibration by ice baths and steam baths showed this thermocouple to be within $\pm 0.1^\circ$ of the true temperature

at these two points. The most favorable conditions were chosen and the best techniques developed in the survey studies were used to keep all errors at a minimum.

CHAPTER VI

GENERAL EXCHANGE STUDIES

High Temperature Survey

At first these studies were performed on various fluoride salts in order to find fluorides capable of exchanging with fluorocarbons at moderate temperatures. In exchange studies with C_3F_6 up to 500° and 340° over CrF_2 and CuF_2 , respectively, these fluorides produced few counts in the gas phase beyond what might be attributed to statistical variation in background. Sodium fluoride produced easily detectable counts with C_3F_6 at 400° . Further experiments in both the high and low temperature surveys were confined to the alkali fluorides.

Both C_3F_6 and C_4F_{10} were passed over CsF , KF , NaF and LiF in the apparatus shown in Figs. 1 and 2. Temperature was increased at the rate of 5° per minute. With C_4F_{10} , the counting rate was found to be sufficient for accurate calculations only with CsF and KF and at high temperatures.

The results were always found to be almost linear up to large values of N when the logarithm of N was plotted against reciprocal temperature. Figure 15 shows such plots for C_3F_6 on each of the four fluorides studied. Curvature started between N values of 0.2 and 0.4

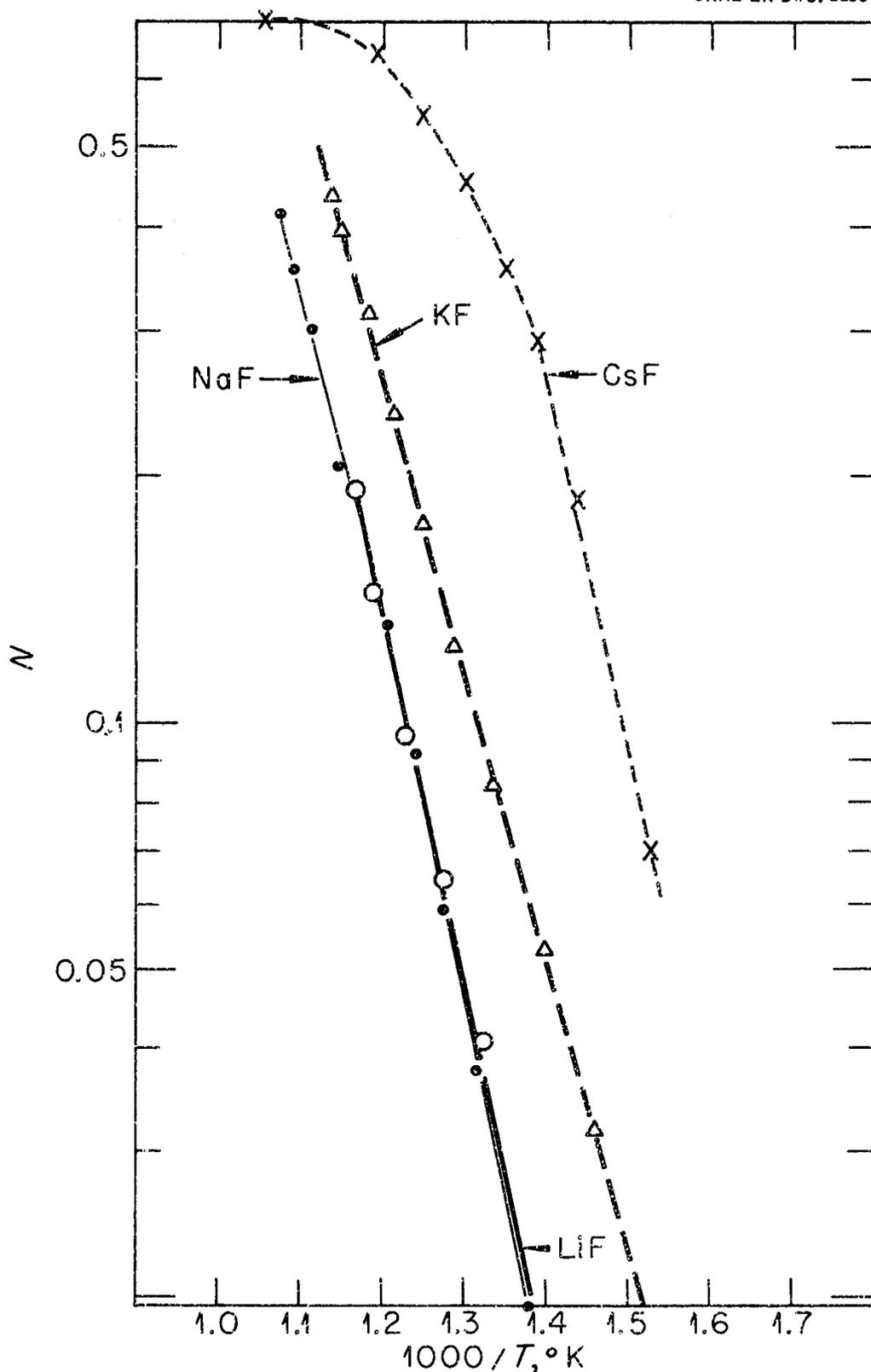


Fig.15. FRACTION OF EXCHANGE OCCURRING WITH C_3F_6 OVER THE ALKALI FLUORIDES

with CsF and increased as the run was continued. Some curvature was observed with NaF at about the same values of N as with CsF. In Fig. 16, three runs with C_3F_6 and NaF were compared. The fact that the lowest points fell below the line on all three runs is significant for reasons which become apparent when results are discussed in connection with Fig. 36.

Figure 17 shows the behavior of C_4F_{10} . Low temperature survey plots included on the same graph showed general reproducibility. The CsF curve was to the right of the KF curve, as it was in Fig. 15. In Fig. 17 the CsF plot continued to be linear past the temperature where curvature started with C_3F_6 . Values of N were lower at comparative temperatures with C_4F_{10} than with C_3F_6 , as Fig. 18 illustrates. Curvature appeared to accompany large values of N and was not affected by the temperature.

Wide variations in concentration of either phase did not produce any noticeable change in results. This is shown by Fig. 16, where approximately the same weight of NaF was used in all three runs, but C_3F_6 pressures at room temperature varied from about 200 to 600 mm.

Runs which yielded fragmentary information, because of low counting rate or counter chamber contamination, were summarized in Table 3.

Low Temperature Survey

Four fluorocarbon gases, C_3F_6 , C_4F_{10} , $(C_2F_5)_2O$, and CF_4 were

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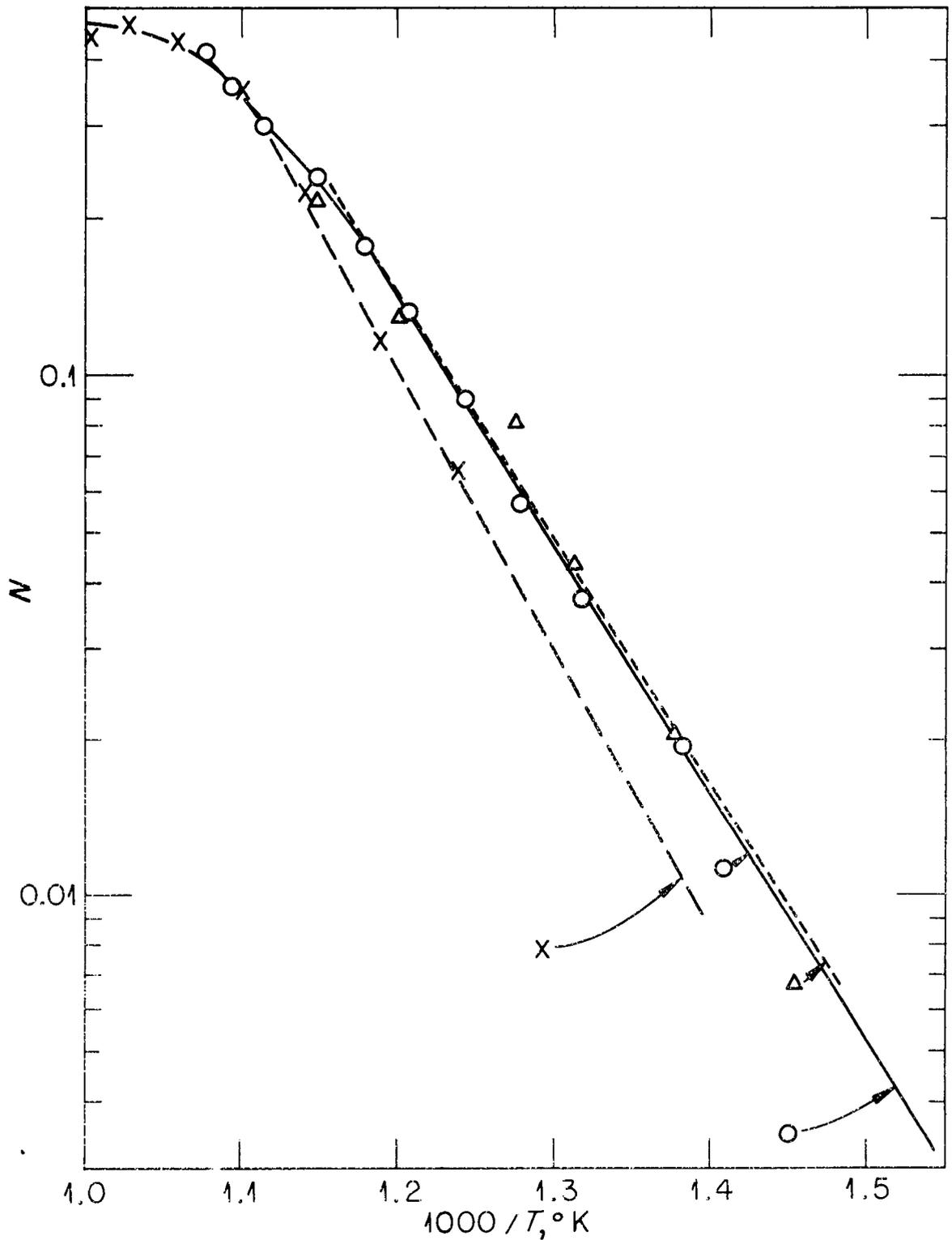


Fig.16. FRACTION OF EXCHANGE OCCURRING WITH C_3F_6 OVER NaF; THREE RUNS

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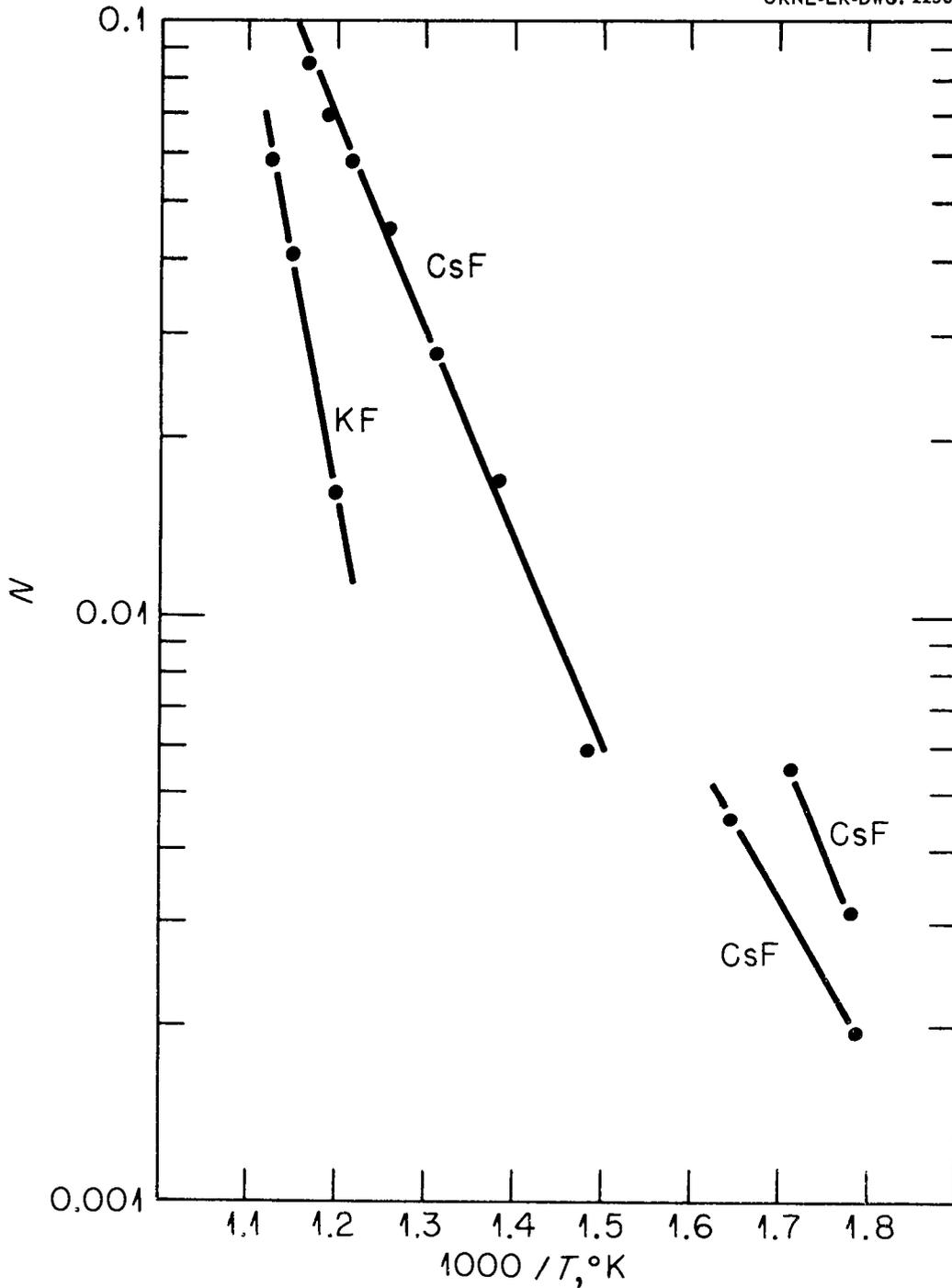


Fig.17. FRACTION OF EXCHANGE OCCURRING WITH C_4F_{10} OVER CsF AND KF

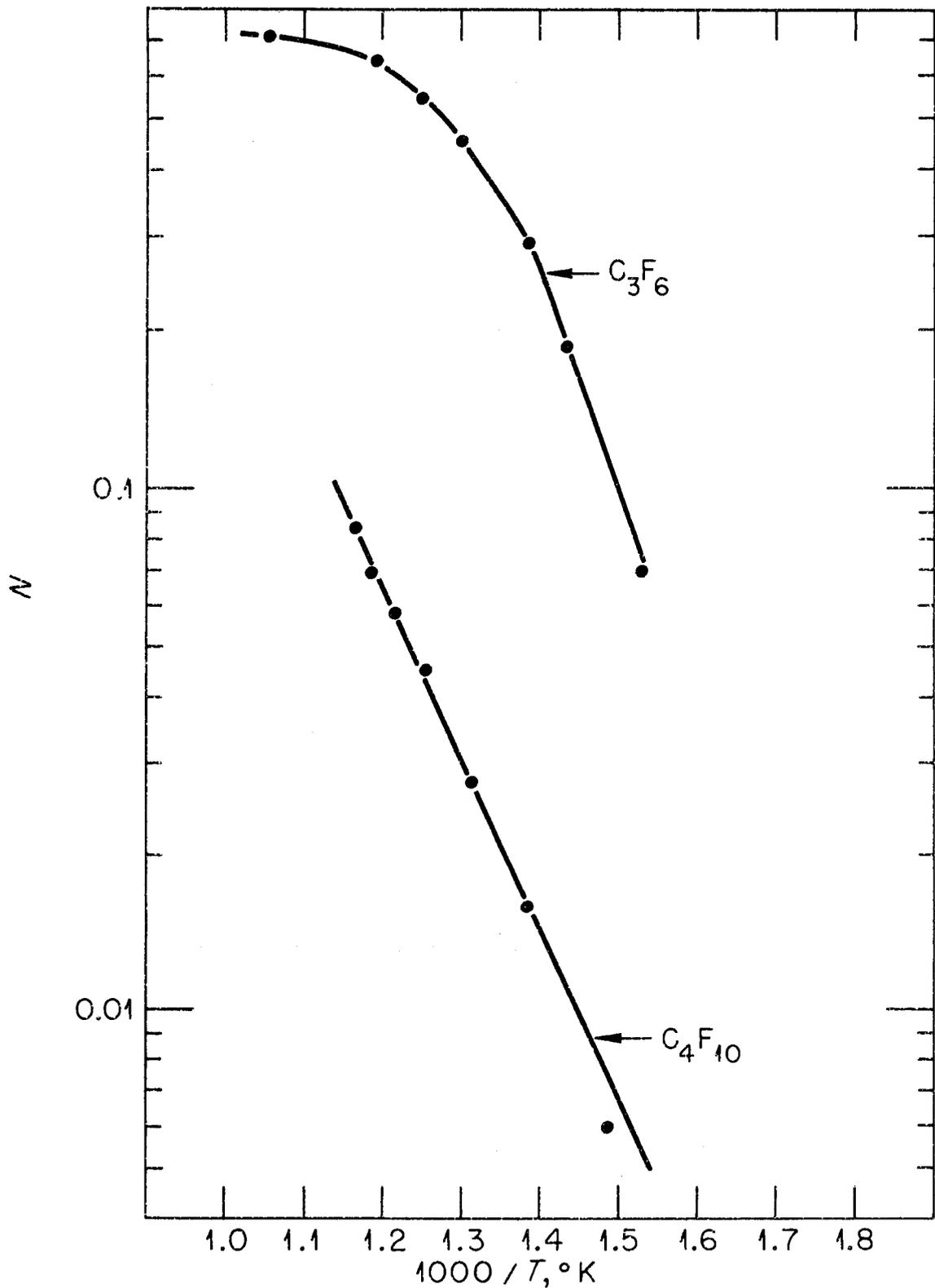


Fig.18. FRACTION OF EXCHANGE OCCURRING WITH
WITH C₃F₆ AND C₄F₁₀ OVER CsF

TABLE 3

DATA FROM STUDIES HAVING EXPERIMENTAL
DIFFICULTIES OR NEGATIVE RESULTS

Run No. and Materials	Temperature at Which Exchange Was First Observed	Results
14 $\text{CuF}_2\text{-C}_3\text{F}_6$		No exchange up to 325° . Activity in CuF_2 was such that less than 10% exchange could not be detected.
19 $\text{CrF}_2\text{-C}_3\text{F}_6$	300°	Less than 8% exchange at 425° .
C3c $\text{KF-(C}_2\text{F}_5)_2\text{O}$		About 0.05% exchange at 600° .
C4a $\text{KF-(C}_2\text{F}_5)_2\text{O}$		Less than 5% exchange at 625° . Background would not return to normal. No evidence of decomposition.
C8a $\text{CsF-(C}_2\text{F}_5)_2\text{O}$		0.4% exchange at 450° . No decomposition. Background would not return to normal.
C5a LiF-SF_6	325°	Background would not return to normal.
C6a LiF-SF_6	310°	0.5% exchange at 447° . Background would not return to normal.
C7c KF-SF_6	350°	Less than 0.2% exchange at 450° . Background would not return to normal.
C10c CsF-SF_6	400°	Background would not return to normal.
C12d RbF-SF_6		No exchange up to 350° .

TABLE 3 - Continued

Run No. and Materials	Temperature at Which Exchange Was First Observed	Results
C13b NaF-SF ₆		No exchange up to 280°.
C4b KF-C ₄ F ₁₀	600°	Less than 5% exchange at 650°. Decomposition started at 600°.
C13a NaF-C ₄ F ₁₀		0.04% exchange at 300°. Background would not return to normal.
C15b NaF-C ₄ F ₁₀		Less than 0.2% exchange at 300°.
C16d CsF-CF ₃ H	290°	Decomposition started at 290°.
C18a CsF-C ₂ F ₆	250-300°	Less than 0.03% exchange at 400°.
C19a KF-C ₂ F ₆		No exchange up to 500°.
C12b RbF-(CF ₃) ₃ N	Room temperature	Physical adsorption interfered with calculations.
44-111 KF-C1CF=CF ₂	500°	Pressure dropped throughout the experiment.
39-107 LiF-CF ₃ SF ₅	475°	Pressure increase occurred before counts were detected.
40-106 LiF-CF ₃ N=CF ₂	400°	Pressure increased slowly throughout the experiment.

passed over the five alkali fluorides in the same apparatus used in the high temperature survey. Figures 19 through 22 show the results, which were very similar to those of the high temperature survey. In Fig. 19 the same relationship between different fluorides observed in Fig. 15 occurred again. Two runs with RbF showed good reproducibility. The LiF prepared with the cyclotron contained some volatile material, possibly a complex fluoride. By preparing the LiF very carefully, results obtained with C_4F_{10} and $(C_2F_5)_2O$ are regarded as dependable.

In Fig. 20, the general conclusion can be drawn that CsF and RbF exchange better with C_4F_{10} than does KF or LiF. With $(C_2F_5)_2O$, in Fig. 21, CsF is indicated as being superior to RbF, which in turn is superior to LiF.

Few points were obtained with CF_4 , since high temperatures were avoided and detectable exchange did not occur until at about 300° with CsF and at nearly 400° with RbF. Figure 22 shows similar slopes with these two salts, but CsF appears to exchange better than RbF. The slopes of Fig. 22 are greater than with the other fluorocarbons.

Figure 23 compares high and low temperature CsF- C_3F_6 runs (AC I and AC II are discussed in the kinetics studies). This figure, plus a further comparison between high and low temperature runs, discussed below in connection with Fig. 36, indicates that similar processes take place and that the different methods of preparing fluorides yield similar results.

The curve for CF_3H in Fig. 24 shows an inflection just under

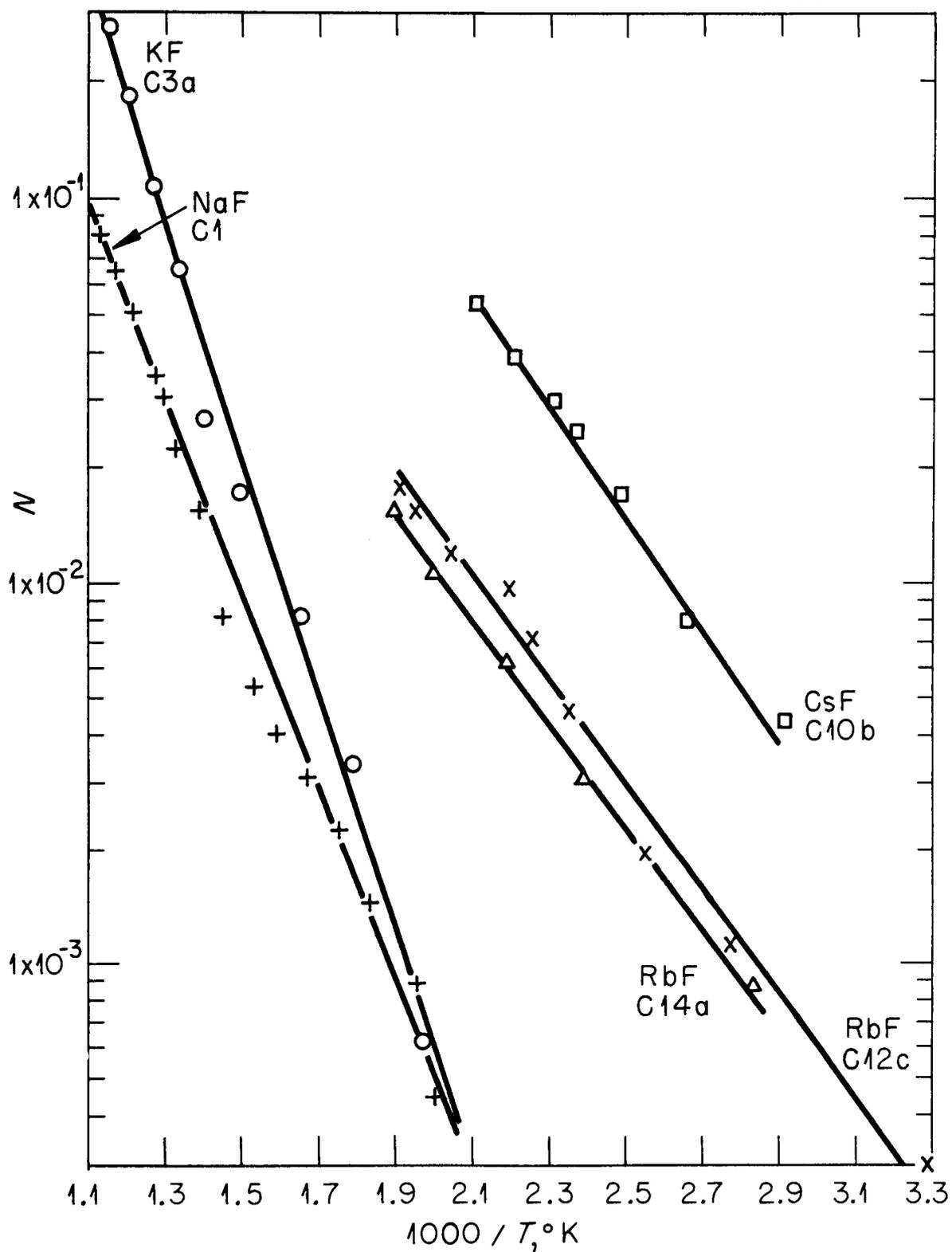


Fig.19. FRACTION OF EXCHANGE OCCURRING WITH C₃F₆ OVER THE ALKALI FLUORIDES AT LOWER TEMPERATURE

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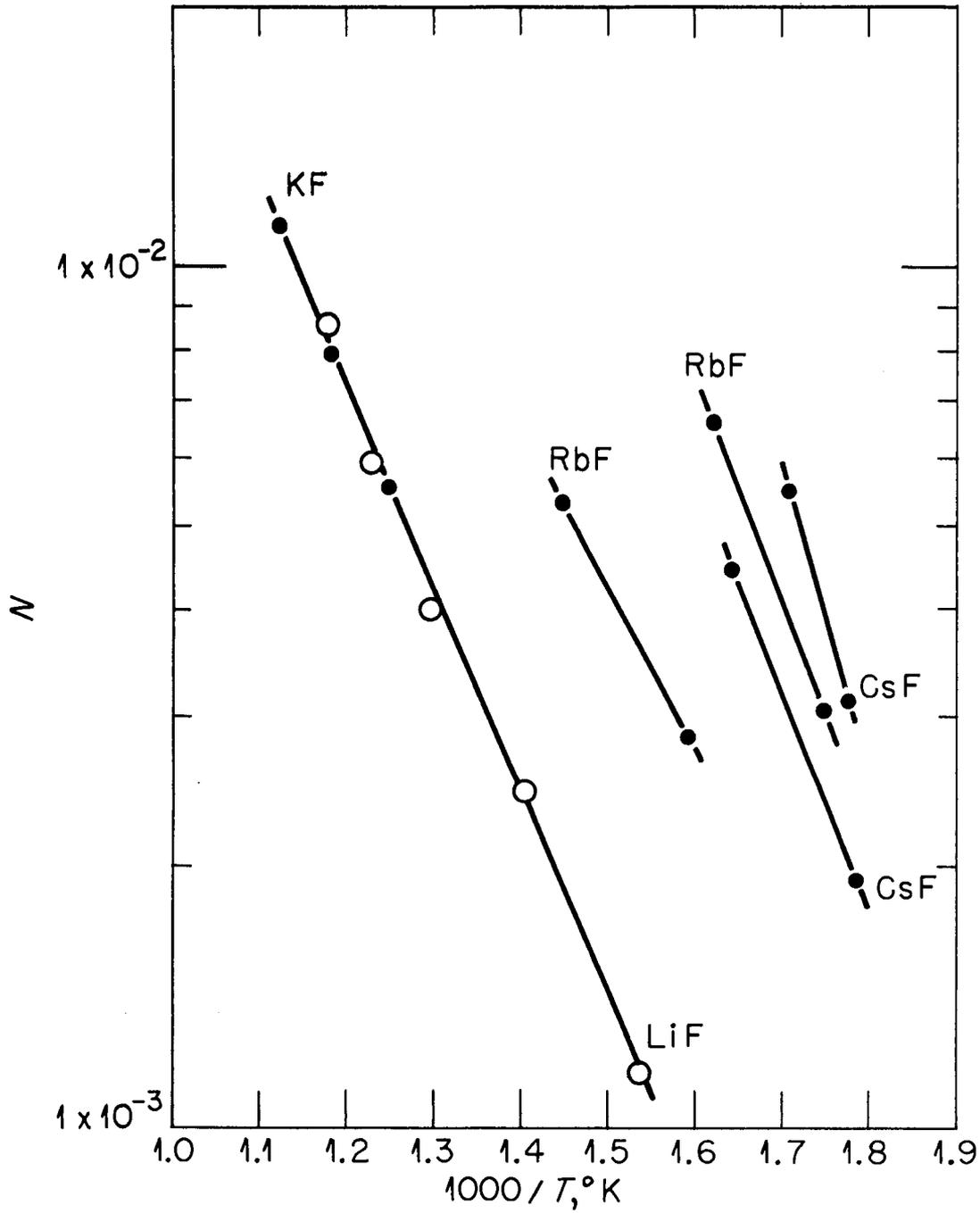


Fig. 20. FRACTION OF EXCHANGE OCCURRING WITH C_4F_{10} OVER THE ALKALI FLUORIDES AT LOWER TEMPERATURE

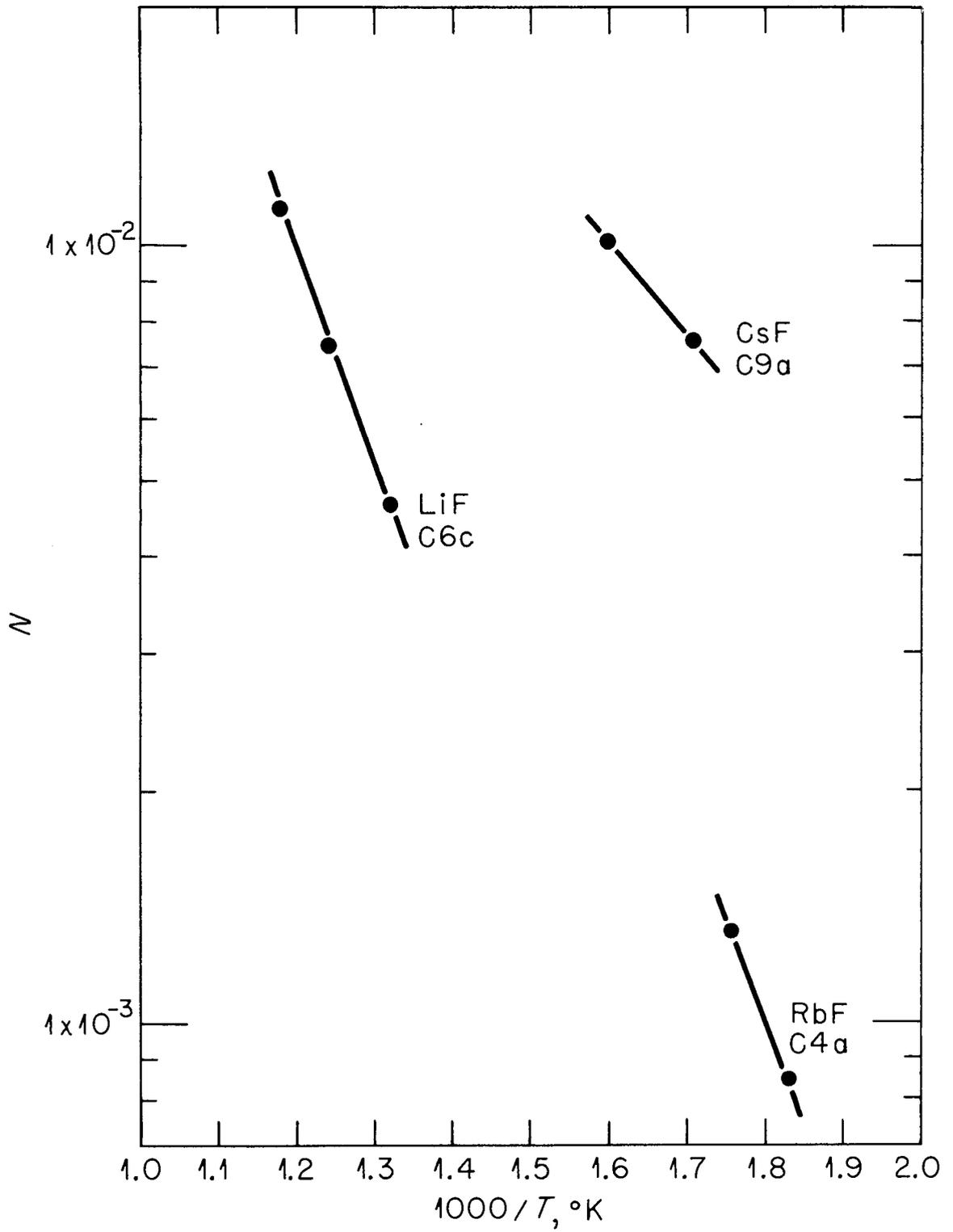


Fig. 21. FRACTION OF EXCHANGE OCCURRING WITH $(C_2F_5)_2O$ OVER THE ALKALI FLUORIDES

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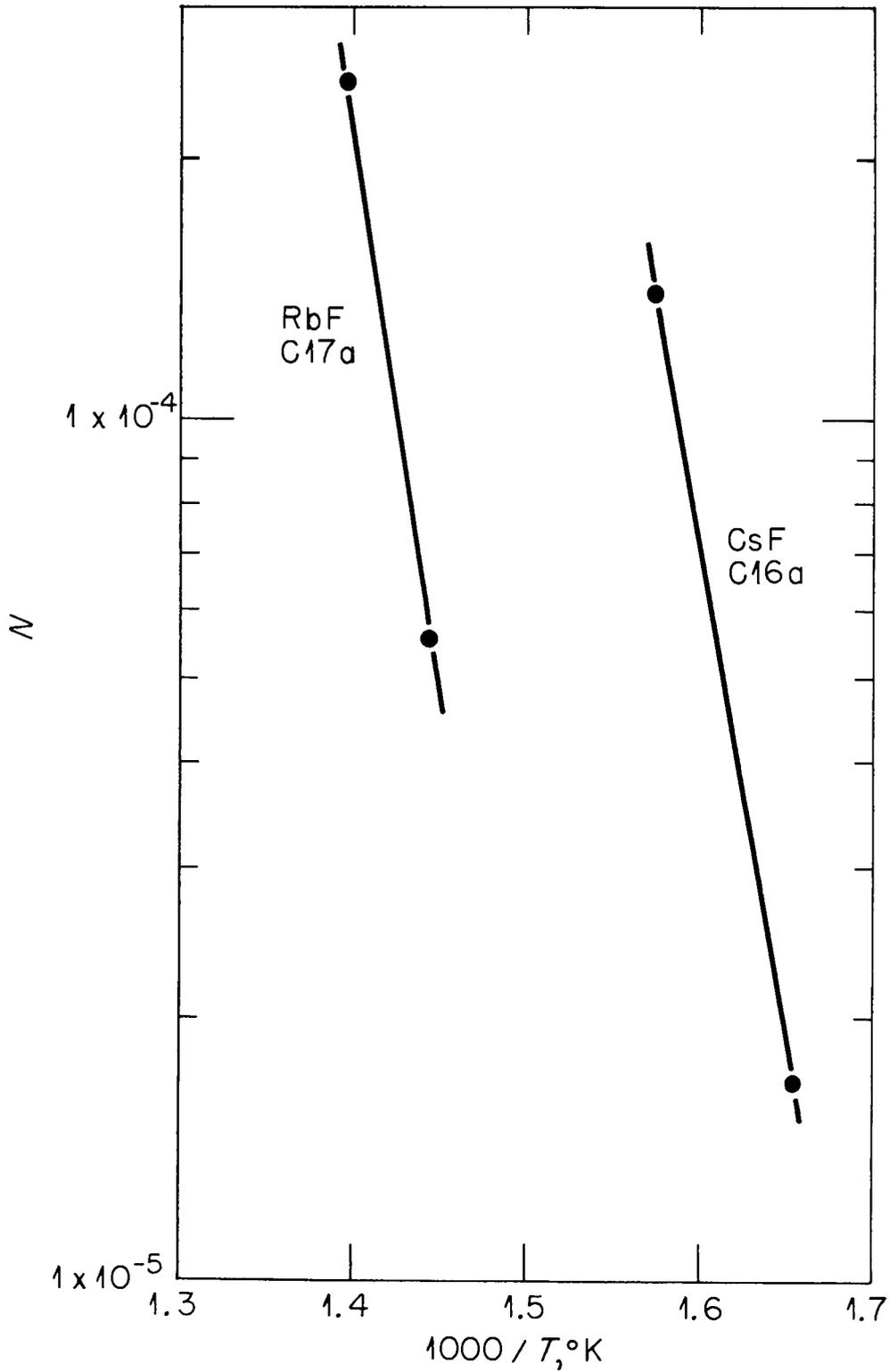


Fig. 22. FRACTION OF EXCHANGE OCCURRING WITH CF_4 OVER RbF AND CsF

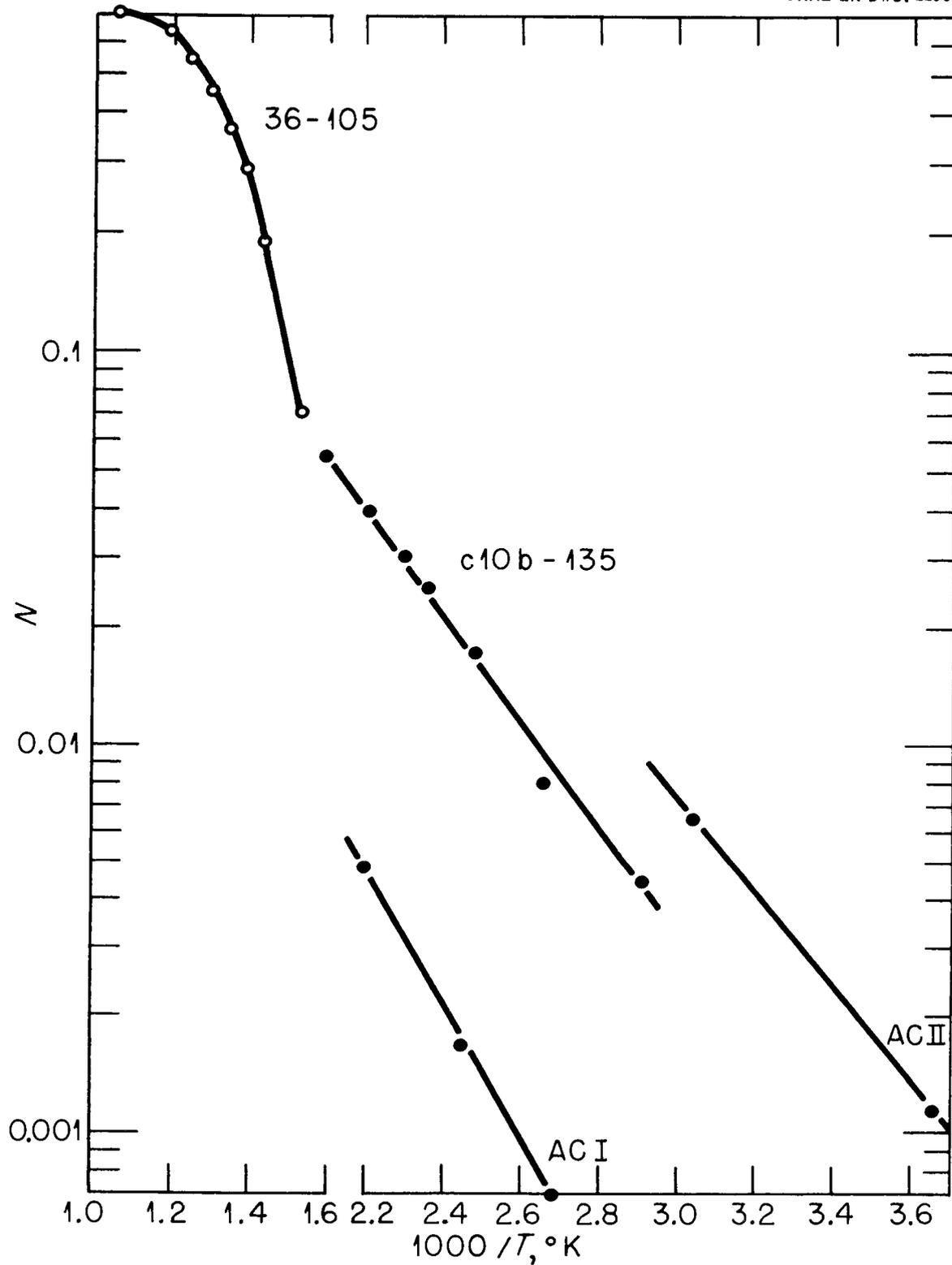


Fig. 23. FRACTION OF EXCHANGE OCCURRING WITH C_3F_6 OVER CsF BY THREE TECHNIQUES

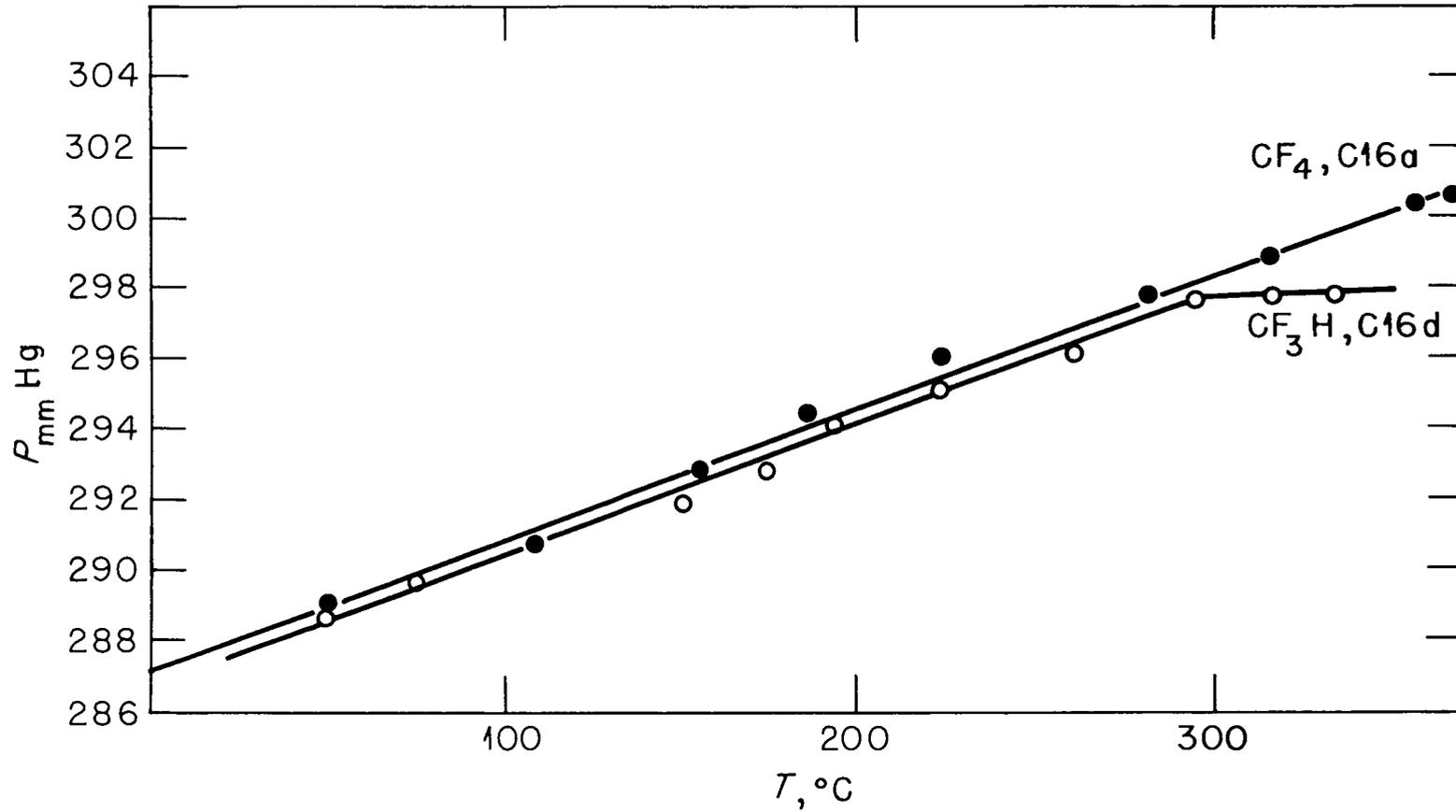


Fig. 24. PRESSURE-TEMPERATURE BEHAVIOR OF CF_4 AND CF_3H OVER CsF

300°. As listed in Table 3, radioactivity was first observed in the gas phase at about this temperature with the $\text{CF}_3\text{H-CsF}$ system. Tri-fluoromethane is known to have thermal and chemical stability approaching that of CF_4 .⁵⁶ The $\text{CF}_4\text{-CsF}$ system also produced detectable radioactivity in the gas phase at 300°. It therefore appears possible that a similar process was involved in both cases. With CF_3H , decomposition must have occurred to yield fewer molecules in the gaseous state, while CF_4 was not transformed into new materials.

When SiF_4 was passed over the alkali fluorides, decreasing slopes of the isochores were observed. Figure 25 shows that with LiF this slope did not differ appreciably from that of SiF_4 alone, but the slope decreased at higher temperatures with KF , RbF , and CsF . One run with KF was followed beyond the inflection point, and the pressure continued to decrease. The quantity N could no longer be easily determined after a significant quantity of SiF_4 was removed from the gas phase. Therefore, in Fig. 26, the values of N go only up to the temperatures where deviations in the pressure-temperature curves were observed. In Fig. 25, it can be seen that various starting pressures were used. The two runs with KF had nearly equimolar quantities of SiF_4 but Run C4c had nearly twenty times as much KF as did Run C7b. This variation of concentration appears to have separated the curves from these runs in Fig. 26. The run with LiF had molar concentrations of SiF_4 and salt similar to those of Run C4c with KF , and the results of these two runs in Fig. 26 are quite similar. A fluorocarbon run was included for comparison in

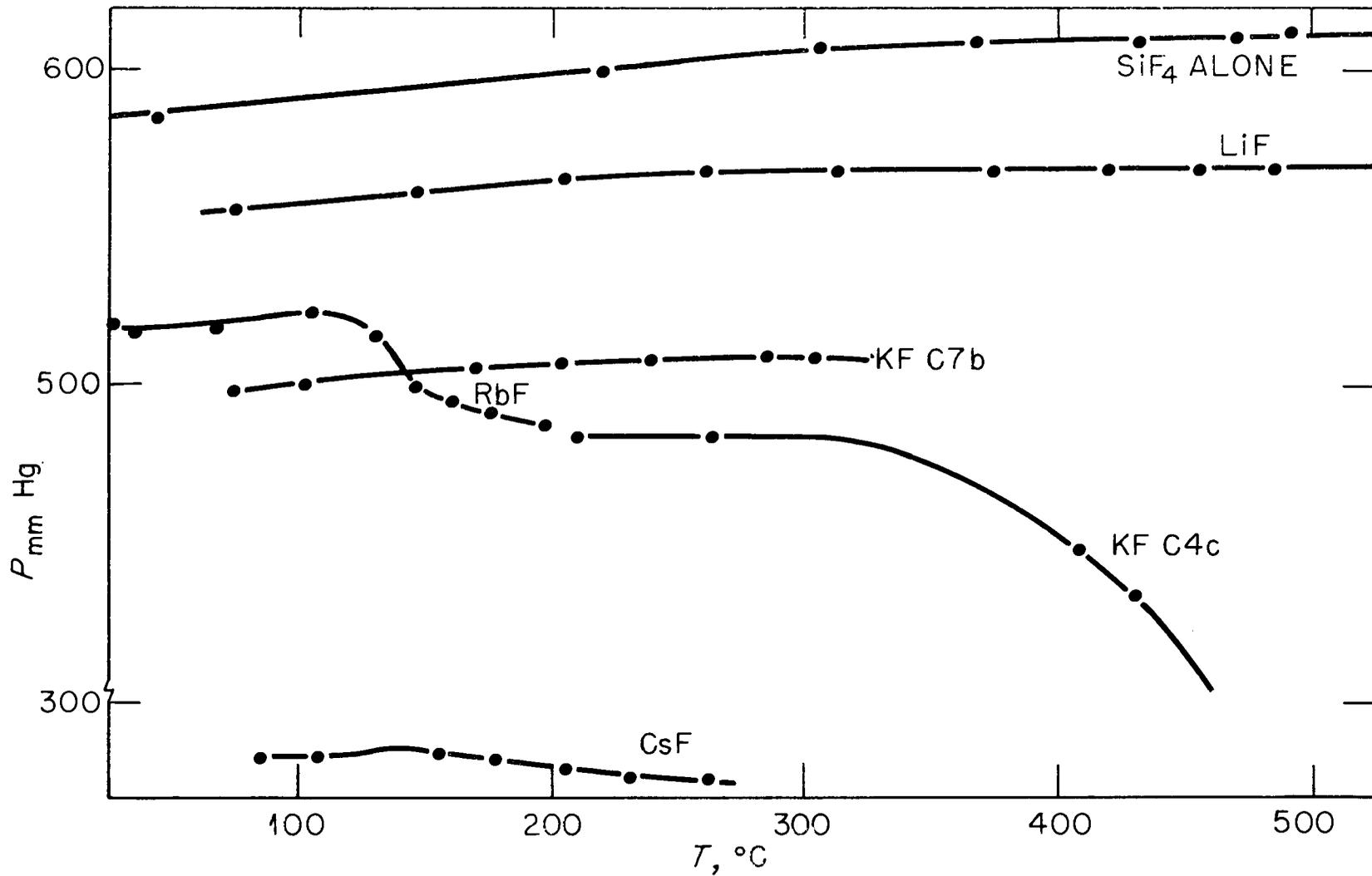


Fig. 25. PRESSURE-TEMPERATURE BEHAVIOR OF SiF₄ ALONE AND ABOVE ALKALI FLUORIDES

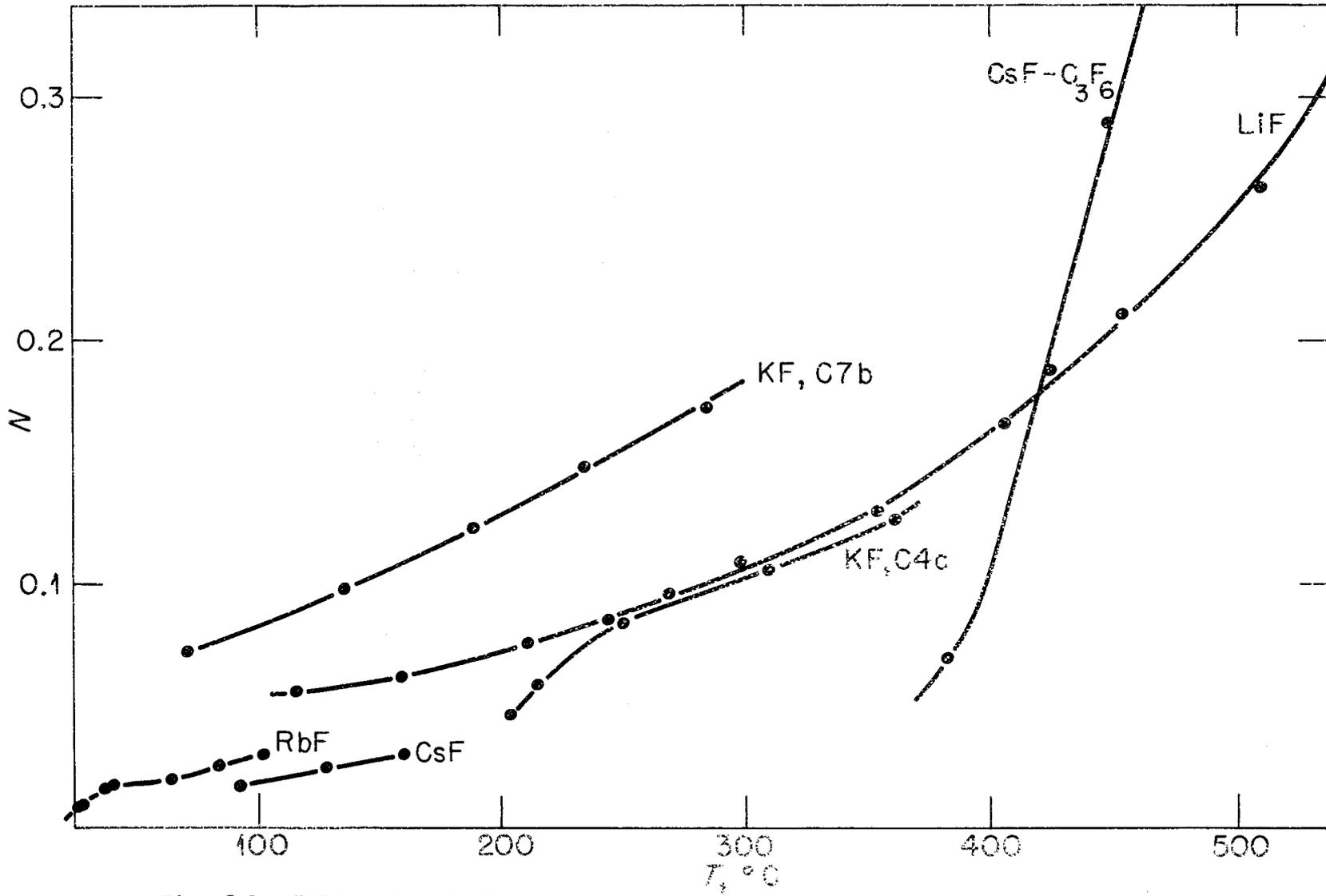


Fig. 26. RESULTS OBTAINED BY PASSING SiF_4 OVER ALKALI FLUORIDES

Fig. 26. Logarithms of the results with SiF_4 plotted against reciprocal temperature, as shown in Fig. 28, were not linear. No traces of Li_2SiF_6 could be found by spectroscopic analysis for silicon in the LiF after the experiment, while KF , RbF , and CsF all showed large amounts of silicon.

Exchange studies with SF_6 were also carried out in the same manner. Table 3 shows that radioactivity was detected at temperatures above 300° with different alkali fluorides. In this respect, SF_6 resembled CF_4 and CF_3H . Comparison of temperatures at which counts were detected with SF_6 to the isochores in Fig. 27 shows that a pressure decreasing reaction accompanied the radioactivity. Pumping failed to remove up to as much as three-fourths of the radioactivity present at the end of these experiments. The pressure reducing reaction might be $2\text{SF}_6 \longrightarrow \text{S}_2\text{F}_{10} + \text{F}_2$. The compound S_2F_{10} has a normal boiling point of 29° and would be adsorbed by the cool counter chamber surface.

The surface areas of representative samples of alkali fluorides used in the low temperature survey, as measured by the BET method using krypton gas, were found to be:

$$\text{CsF} = 0.11 \text{ m.}^2 \text{ g.}^{-1}$$

$$\text{RbF} = 0.08 \text{ m.}^2 \text{ g.}^{-1}$$

$$\text{KF} = 0.08 \text{ m.}^2 \text{ g.}^{-1}$$

$$\text{NaF} = 0.22 \text{ m.}^2 \text{ g.}^{-1}$$

$$\text{LiF} = 1.1 \text{ m.}^2 \text{ g.}^{-1}$$

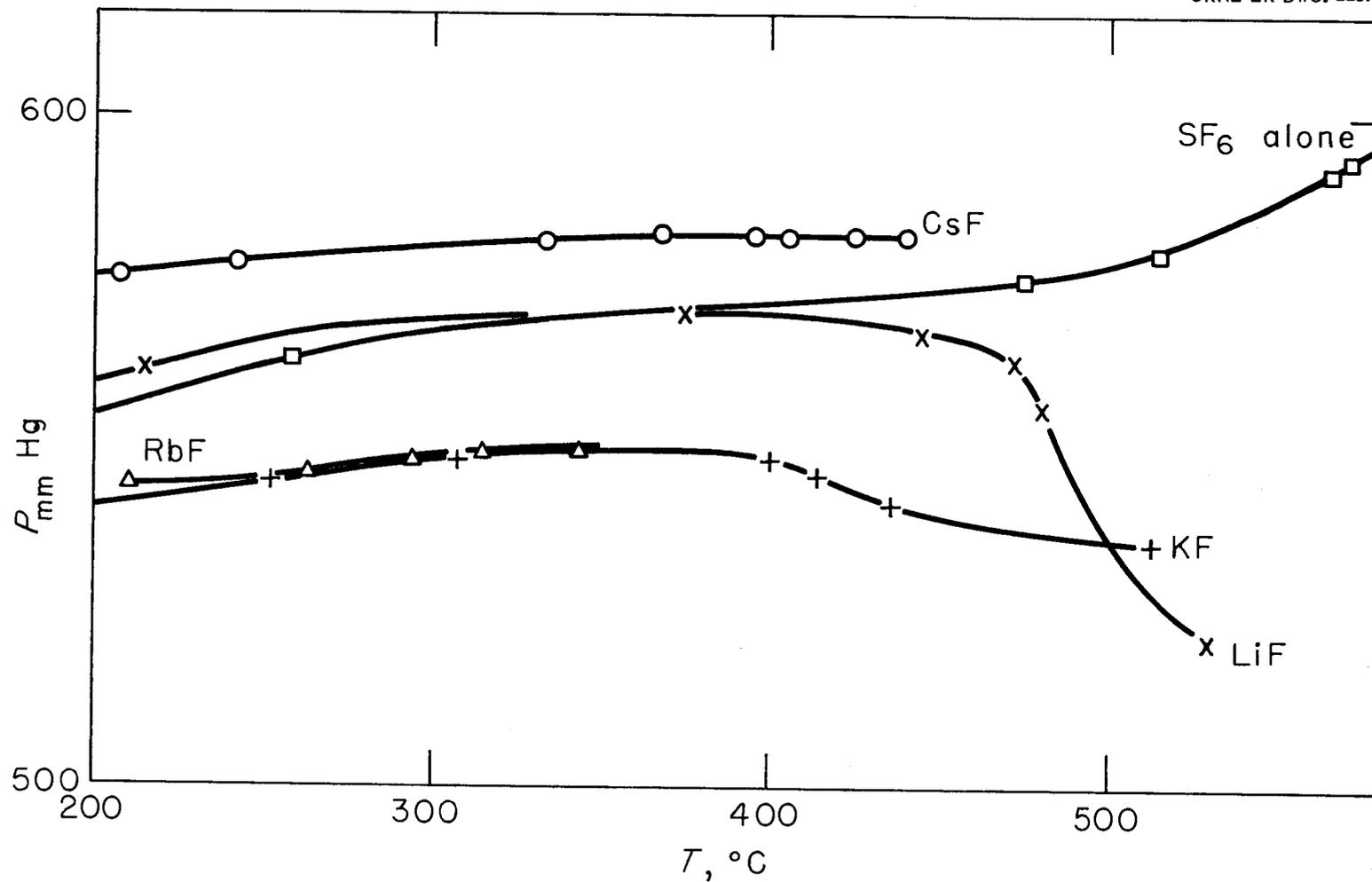


Fig. 27. PRESSURE-TEMPERATURE BEHAVIOR OF SF_6 ALONE AND OVER THE ALKALI FLUORIDES

Figure 28 is a collection of examples of all the low temperature exchange studies.

Figure 29 shows examples of isochores from five gases. None of these gases which produced curves varying significantly from that of argon were used in further exchange studies, with the exception of SiF_4 .

Survey of Hydrogen Fluoride and Various Inorganic Fluorides
for Indications of Exchange with SF_6 and Fluorocarbons

Nonexchange of F^{18} between HF and fluorinated methanes has been reported.⁵ This work used HF of low specific activity; consequently values of N below about 0.10 could not be detected. Since hydrogen may be considered the first member of the alkali group, this work was repeated with HF of high specific activity.

The cyclotron was used to prepare KF containing F^{18} . The aluminum tubes containing KF were broken open and dropped into the fluorothene tube shown in Fig. 8. This tube was attached to the vacuum line and evacuated. One to two cc of HF was condensed from the HF storage vessel into the fluorothene tube by cooling with liquid nitrogen. The fluorothene tube was warmed to room temperature to allow the HF to exchange with the KF and pick up F^{18} . Potassium fluoride was chosen because it goes into solution with a rapid exothermic reaction, thus causing random distribution of the F^{18} .

A molar excess of HF was used, so that most of the F^{18} was removed with the HF when it was distilled away. This HF usually had

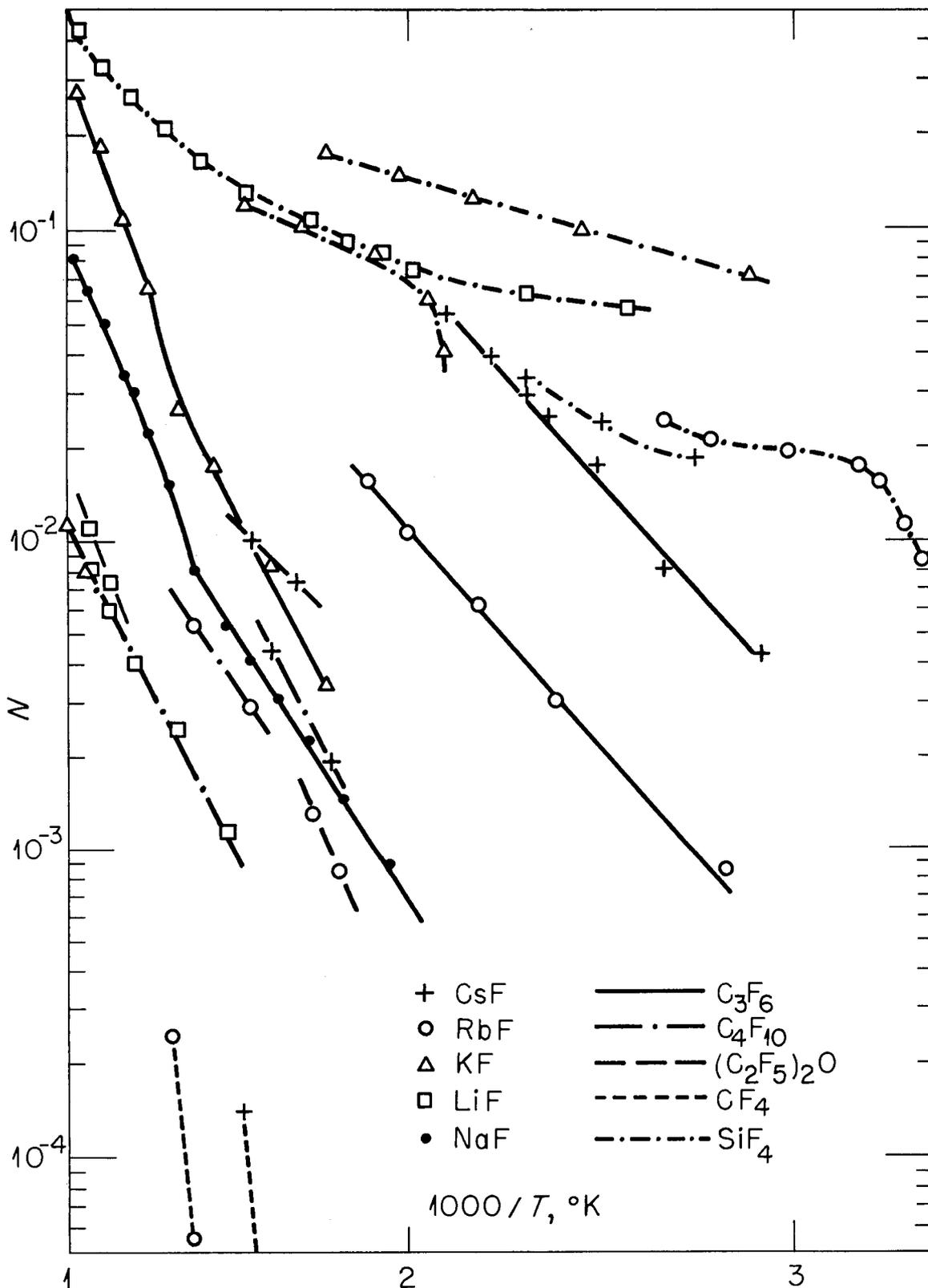


Fig. 28. LOW TEMPERATURE SUMMARY PLOT

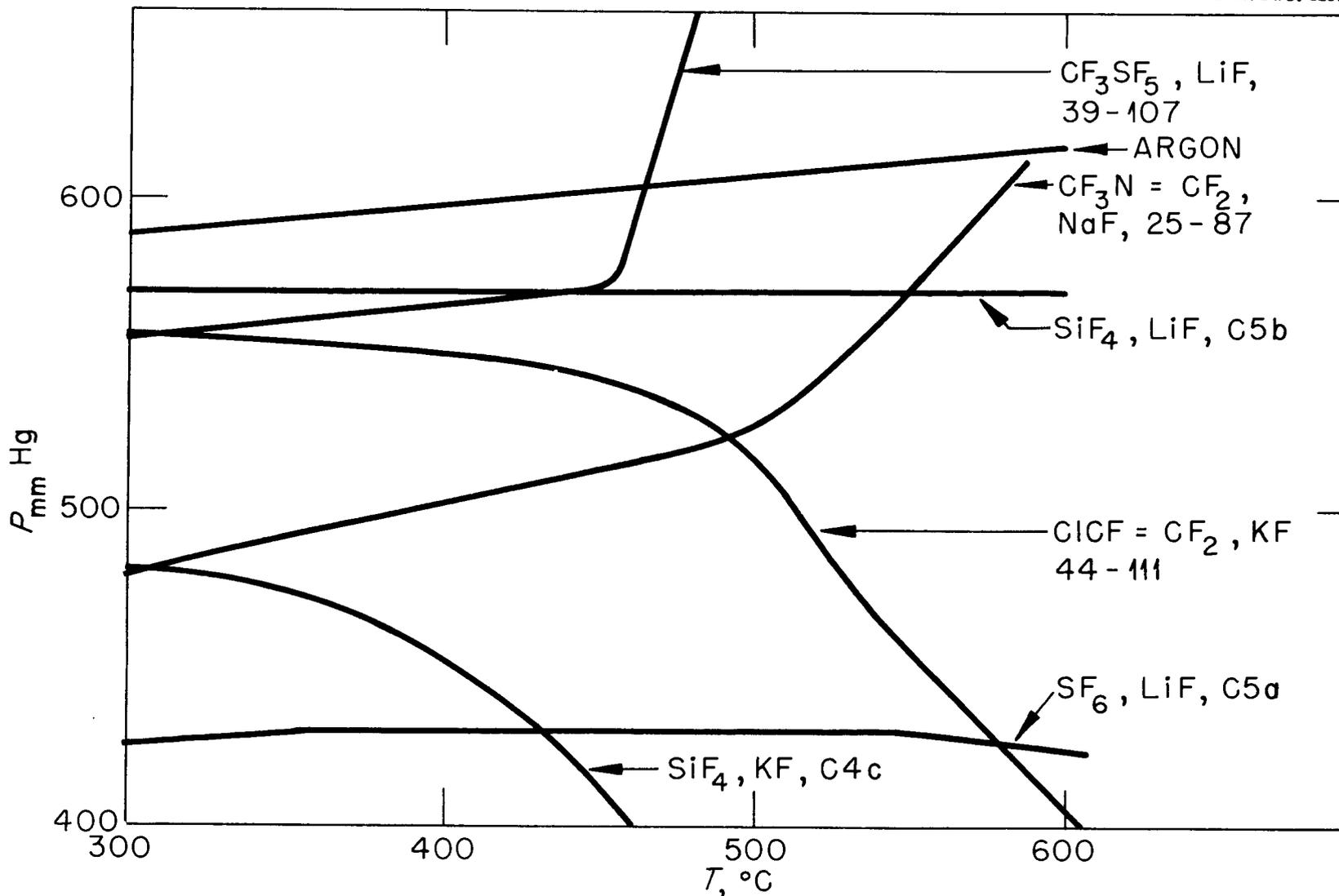


Fig. 29. PRESSURE-TEMPERATURE BEHAVIOR OF ARGON AND FIVE GASEOUS FLUORINE COMPOUNDS OVER THE ALKALI FLUORIDES

sufficient F^{18} activity to read one roentgen per hour at contact with a laboratory monitor on the outside of a 20 cc nickel storage vessel.

A portion of this HF was admitted to the manifold at a pressure of 200 to 400 mm and condensed into the nickel exchange tube shown in Fig. 9. A sample of the gas to be studied, also at a pressure of 200 to 400 mm, was admitted to the manifold and then condensed into the exchange tube with the HF. The exchange tube was quickly warmed to $500 \pm 10^\circ$ with a small furnace. This temperature was maintained for one hour.

The furnace was removed and the reactor tube was cooled with liquid nitrogen. The exchange tube was opened to the manifold and the pressure measured. A small residual pressure was often noted, and with C_3F_6 considerable pressure was observed. Therefore the two U tubes on the exit side of the manifold were cooled with liquid nitrogen and the reaction products were distilled into these U tubes while the noncondensable gases were pumped off.

Any F^{18} removed in this manner introduced error into the determination. Since the residual pressure was small above the products cooled with liquid nitrogen, this error was small, except for the experiment with C_3F_6 . The reaction products were condensed into a fluorothene tube packed with moist NaOH pellets. This fluorothene tube was warmed to room temperature to cause reaction of the HF with the NaOH pellets. Unreacted gas was distilled off through the filter, condensed into a small nickel counting vessel, and its counting rate was determined. The NaOH pellets and the newly formed NaF were washed from

the fluorothene tube and diluted to 100 ml in a volumetric flask. Aliquots were removed and counted. Precautions very similar to those described under the survey calculations were taken during counting to reduce error.

No evidence of HF was observed in any of the gases counted when they were bubbled slowly through an indicator solution. The gas from Run VII had an unmistakable odor of H₂S.

Table 4 demonstrates the stepwise development of the calculations of the exchange experiments with HF. From the pressure of HF (column 2) and of the gaseous fluorine-containing compound (column 3), the fraction of total fluorine atoms (column 7) in the fluorocarbon or SF₆ was calculated from the ideal gas law as follows:

$$P = \frac{nRT}{V},$$

and $P = kn,$

since $V =$ volume of manifold,

and $T =$ room temperature;

$$\begin{aligned} \text{Column 7} &= \frac{(P_{FC}) (Fs/\text{mole FC})}{(P_{FC})(Fs/\text{mole FC}) + (P_{HF})(Fs/\text{mole HF})} \\ &= \frac{(P_{FC}) (Fs/\text{mole FC})}{(P_{FC})(Fs/\text{mole FC}) + (P_{HF})}, \end{aligned}$$

where P_{FC} = pressure of gaseous fluorine-containing compound,
Fs/mole FC = fluorine atoms per mole of gaseous fluorine-containing compound,

P_{HF} = pressure of HF

TABLE 4
EXCHANGE STUDIES BETWEEN HF AND
SOME FLUORINE-CONTAINING COMPOUNDS

Run, Page and Compound	Pressure of HF, mm.	Pressure of Fluorine- Containing Compound	Residual Pressure	Counting Rates	
				NaF	Gaseous Compound
(1)	(2)	(3)	(4)	(5)	(6)
I, B15, C ₃ F ₆	143	380	50	3.437x10 ⁵	2.212x10 ⁵
IIa, B16, SF ₆	367	379	—	2.064x10 ⁷	1.485x10 ⁵
IIIa, B26, CF ₄	368	370	—	3.950x10 ⁶	1.317x10 ⁵
IIIb, B30, CF ₄	300	387	3	4.811x10 ⁶	4.255x10 ⁴
IV, C3, CF ₃ H	350	230	9	9.952x10 ⁷	7.691x10 ⁵
V, C5, CF ₃ H	280	247	8	4.237x10 ⁷	1.002x10 ⁵
VI, C7, CF ₃ H	276	237	3	6.105x10 ⁷	7.236x10 ⁵
VII, C9, SF ₆	310	281	0	1.368x10 ⁸	8.310x10 ⁵
VIII, C10, SF ₆	297	245	9	1.609x10 ⁸	2.114x10 ⁶
IX, C12, C ₄ F ₁₀	302	270	3	8.038x10 ⁷	2.006x10 ⁶
X, C14, C ₄ F ₁₀	302	261	0	7.665x10 ⁶	2.356x10 ⁵

TABLE 4 - Continued

Fraction F in Gaseous Compound	Counting Rates		T° C	Percent Exchange	Remarks
	Sum of (5) and (6)	At 100% Exchange			
(7)	(8)	(9)	(10)	(11)	(12)
0.941	5.649×10^5	5.316×10^5	500	41.6	PON ^a
0.861	2.079×10^7	1.790×10^7	500	0.83	PON
0.801	4.082×10^6	3.270×10^6	500	4.0	VLR ^b
0.834	4.854×10^6	4.048×10^6	400	1.1	VLR
0.397	1.003×10^8	3.982×10^7	400	1.9	VLR
0.726	4.247×10^7	3.083×10^7	500	0.33	VLR
0.721	6.173×10^7	4.451×10^7	250	1.6	VLR
0.845	1.376×10^8	1.163×10^8	500	0.72	VLR, H ₂ S
0.832	1.630×10^8	1.356×10^8	250	1.6	VLR, no H ₂ S
0.899	8.239×10^7	7.407×10^7	500	2.7	VLR
0.896	7.901×10^6	7.079×10^6	250	3.3	VLR

- a. Pumped off noncondensibles
- b. Very little residual pressure

Fs/mole HF = 1 = fluorine atoms per mole of HF.

The fraction of total fluorine atoms in the fluorocarbon or SF₆ was multiplied by the total F¹⁸ counting rate (column 8), which was the sum of the counting rates of the HF (column 5) and of the gaseous fluorine-containing compound (column 6), to give the counting rate possible at random distribution, or 100% exchange. The product of observed counting rate of the gaseous fluorine-containing compound in column 6 multiplied by 100 and divided by the counting rate corresponding to 100% exchange in column 9, yielded percent exchange (column 11). Column 10 gives the temperature which was held for one hour in the reaction tube. The remark PON in column 12 stands for pumped off non-condensibles. The amount of F¹⁸ pumped off was significant only where PON was noted. VLR means that the residual pressure over the reaction products at liquid nitrogen temperature was so small that no significant amount of F¹⁸ was pumped off with the noncondensable materials.

After Run X of Table 4, the nickel reactor tube was removed. The tube was coated with NiF₂ with a sufficient counting rate to possibly account for the small percentages of exchange listed in Table 4. Studies were then performed by heating C₄F₁₀ over NiF₂ and CF₄ over CuF₂, PdF₂ and CsF for one hour. The results are summarized in Table 5. Calculations were of the type discussed above with HF. The four inorganic fluorides were prepared by exchange with HF. Surface areas of these fluorides were measured by the BET method using Kr. As has been discussed above, CsF is very difficult to prepare free of

HF by this method without loss by sublimation. Because of such loss, not enough CsF remained to allow surface area measurement. The number 0.01 m^2 is a reasonable maximum estimate.

TABLE 5
EXCHANGE STUDIES BETWEEN SOME INORGANIC FLUORIDES
AND FLUOROCARBONS AT 500°

Run, Page	Materials	Surface Area	% Exchange
XI, C16	C_4F_{10} , NiF_2	4.7 m^2	19.5
XII, C19	CF_4 , CuF_2	2.3 m^2	11.8
XIII, C22	CF_4 , PdF_2	1.2 m^2	29.1
XIV, C24	CF_4 , CsF	$<0.01 \text{ m}^2$	2.8

CHAPTER VII

KINETICS OF THE EXCHANGE REACTIONS

The results of the rate studies performed in combination with the survey studies are listed in Table 6. Figure 30 shows the graphs from which these data were obtained.

TABLE 6
KINETICS OF EXCHANGE AT CONSTANT TEMPERATURE

Materials	T, °C	Rate, N, min ⁻¹
NaF, C ₃ F ₆	22 ± 2	5.14 x 10 ⁻⁶
NaF, C ₃ F ₆	260 ± 4	6.18 x 10 ⁻⁵
RbF, C ₃ F ₆	46 ± 2	6.53 x 10 ⁻⁶
RbF, C ₃ F ₆	256 ± 3	8.49 x 10 ⁻⁵
CsF, C ₃ F ₆	203 ± 3	8.25 x 10 ⁻⁵
RbF, (C ₂ F ₅) ₂ O	300 ± 5	3.49 x 10 ⁻⁶
CsF, CF ₄	368 ± 3	3.16 x 10 ⁻⁵

In the two systems, NaF, C₃F₆ and RbF, C₃F₆, lower and higher constant-temperature data were taken from the beginning and end, respectively, of the same survey experiment. Considerable increase in rate with temperature was evident in these four studies. Table 6 shows quite similar rates with C₃F₆ above NaF, RbF, and CsF when the temperatures were approximately equal. Both (C₂F₅)₂O and CF₄ appeared to produce

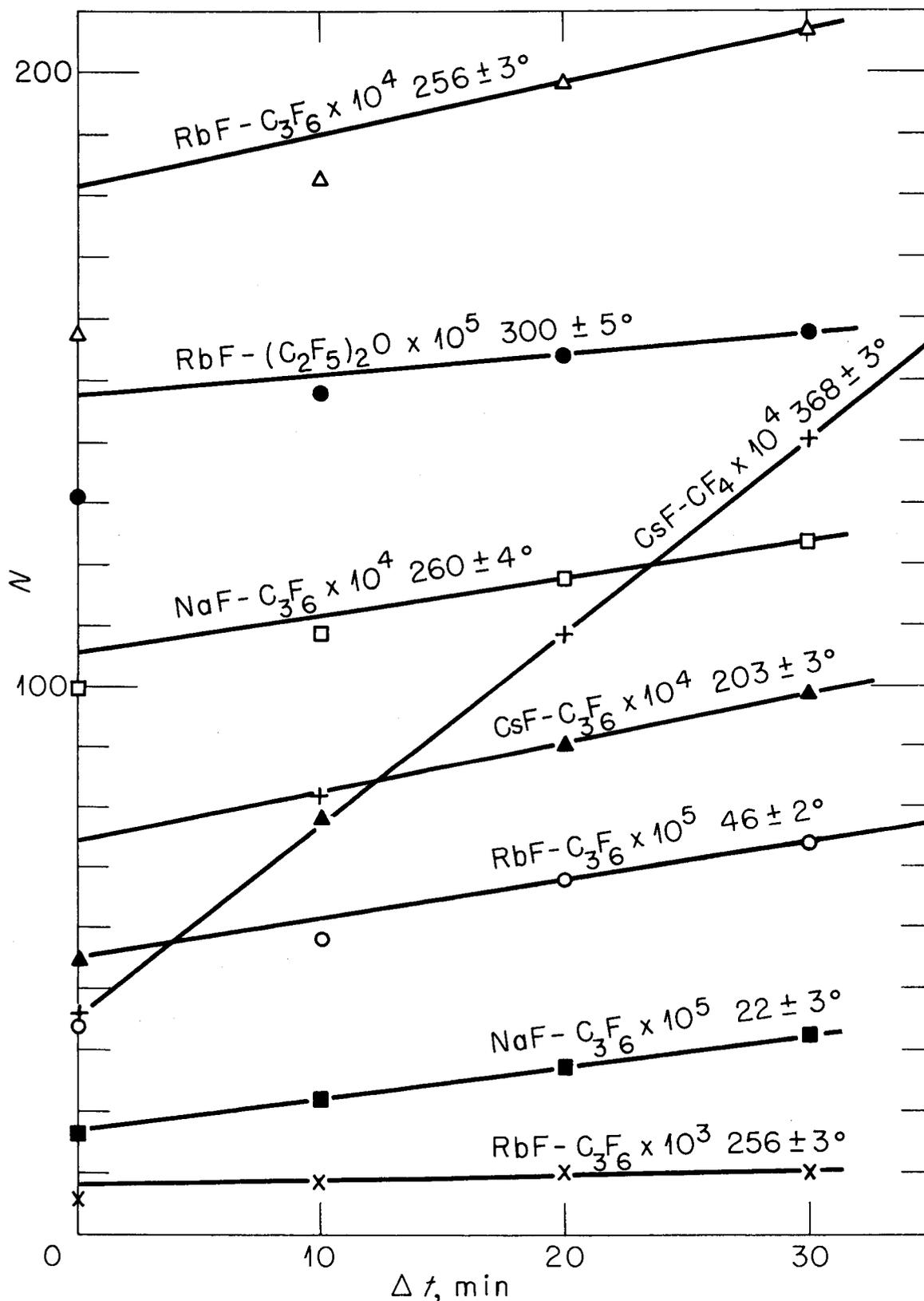


Fig. 30. KINETIC STUDIES

slower rates than did C_3F_6 on the same salts at comparable temperatures. Figure 30 indicates that after a few minutes at constant temperature the rates became constant.

Careful rate studies were made in the exchange apparatus shown in Figs. 3 and 4. The procedure was modified slightly from that used in survey studies. To prevent physical adsorption difficulties, the C_3F_6 or CF_4 was admitted to all of the system except the exchanger. When the gas was admitted to the exchanger, by opening the stopcocks which isolated this part of the system, the pressure decreased in the counter chamber and no adsorption of radioactive fluorocarbon gas occurred. Simultaneously, a timer was turned on and times were recorded to the nearest second.

After collecting data for one-half hour or longer, the gas was condensed in the cold-finger with liquid nitrogen. A vapor bath containing a higher boiling liquid was installed, and the entire procedure was repeated using the same gas and salt. For Study AC I, the procedure was repeated for a third time at a still higher temperature. Figure 31 shows the results for the Run AC Ia at 98.9° , AC Ib at 130.5° and AC Ic at 182.5° and for Run AC IIa at 0.0° and AC IIb at 55.4° . AC Ic was continued for 90 minutes with no deviation from linearity becoming apparent. In AC I, 5.518×10^{-3} mole of CsF was used; in AC II, 1.007×10^{-2} mole. Equal amounts of C_3F_6 were used in the two studies.

The rates obtained from the slopes in Fig. 31 are shown in

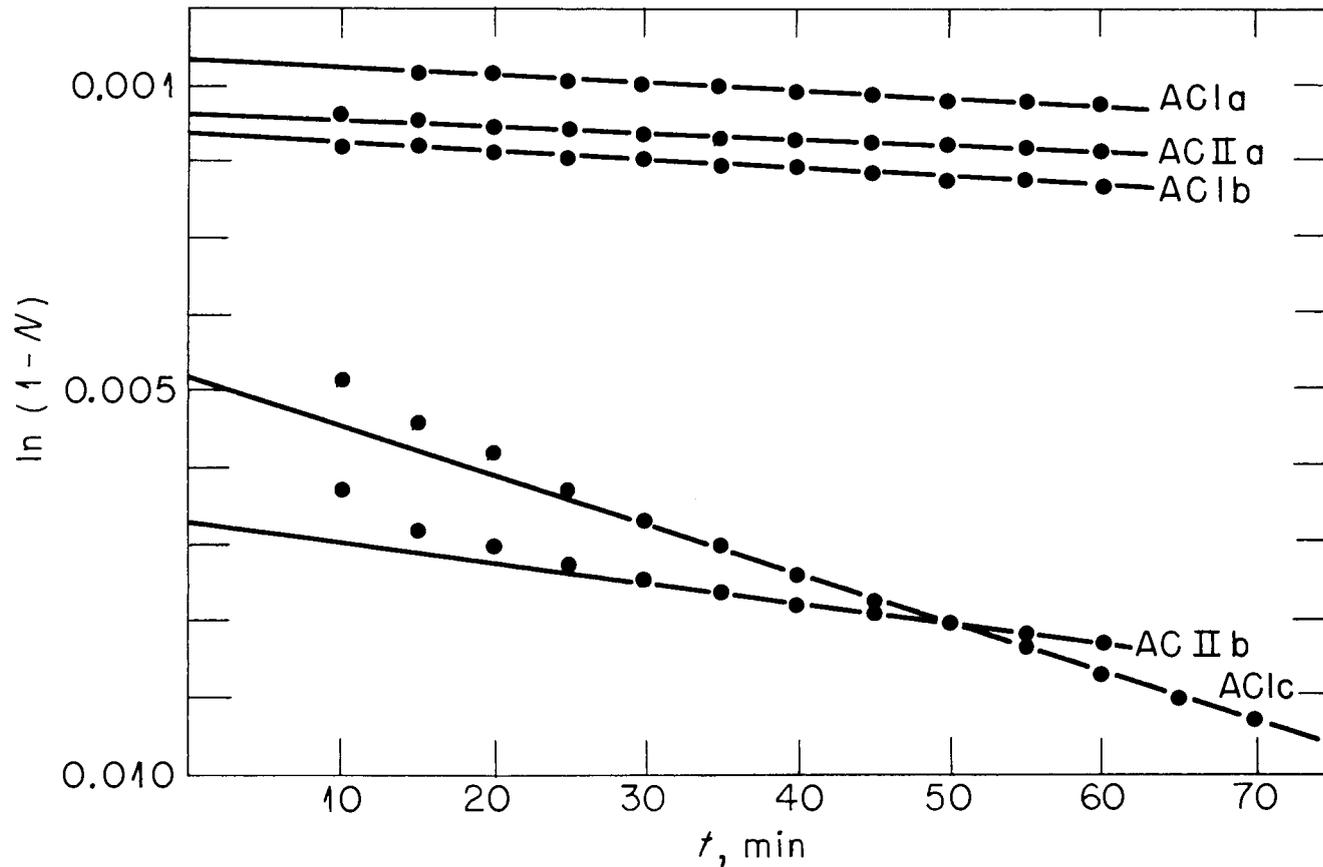


Fig.31. KINETIC STUDIES OF EXCHANGE OCCURRING WITH C_3F_6 OVER CsF

Arrhenius Plots in Fig. 32. The inflection in AC I at a temperature of about 425° K corresponds to the expected Tammann temperature⁵⁷ at about one-half the melting point. Activation energies calculated from the slopes of Fig. 32 are $4.0 \text{ kcal mole}^{-1}$ for AC II and $0.8 \text{ kcal mole}^{-1}$ for AC I below the Tammann temperature. Above the Tammann temperature, the activation energy in AC I was estimated as $17 \text{ kcal mole}^{-1}$.

In Fig. 31, extrapolations of the linear plots back to zero time did not intercept the ordinate at zero. Logarithms of the values of N at the ordinate intercepts are plotted against $1000/T^{\circ}\text{K}$ in Fig. 23. This combination plot shows that the survey results were caused almost entirely by the fast reaction.

One study, AC III, was attempted with CF_4 over CsF at 99° and 209° . At 99° an immediate exchange occurred which gave an N value of 2.1×10^{-5} . No change in this value was observed over one-half hour. At 209° no change in N could be detected. The counting rate was then too close to the natural background to follow the exchange further. The measured BET surface area on this salt was $0.11 \text{ m}^2 \text{ g}^{-1}$.

The study AC IV shown in Fig. 33 was undertaken to determine whether different heating periods in the CsF preparation were responsible for the differences between AC I and AC II shown in Figs. 31 and 32. Two samples of CsF were compared. One was prepared at 400° for 1/2 hr., the other at 400° for 1-1/2 hr. Each sample of CsF was used in the same exchange procedure with C_3F_6 as was used for other kinetic studies, except that at 20 min. the ice bath was quickly replaced by a

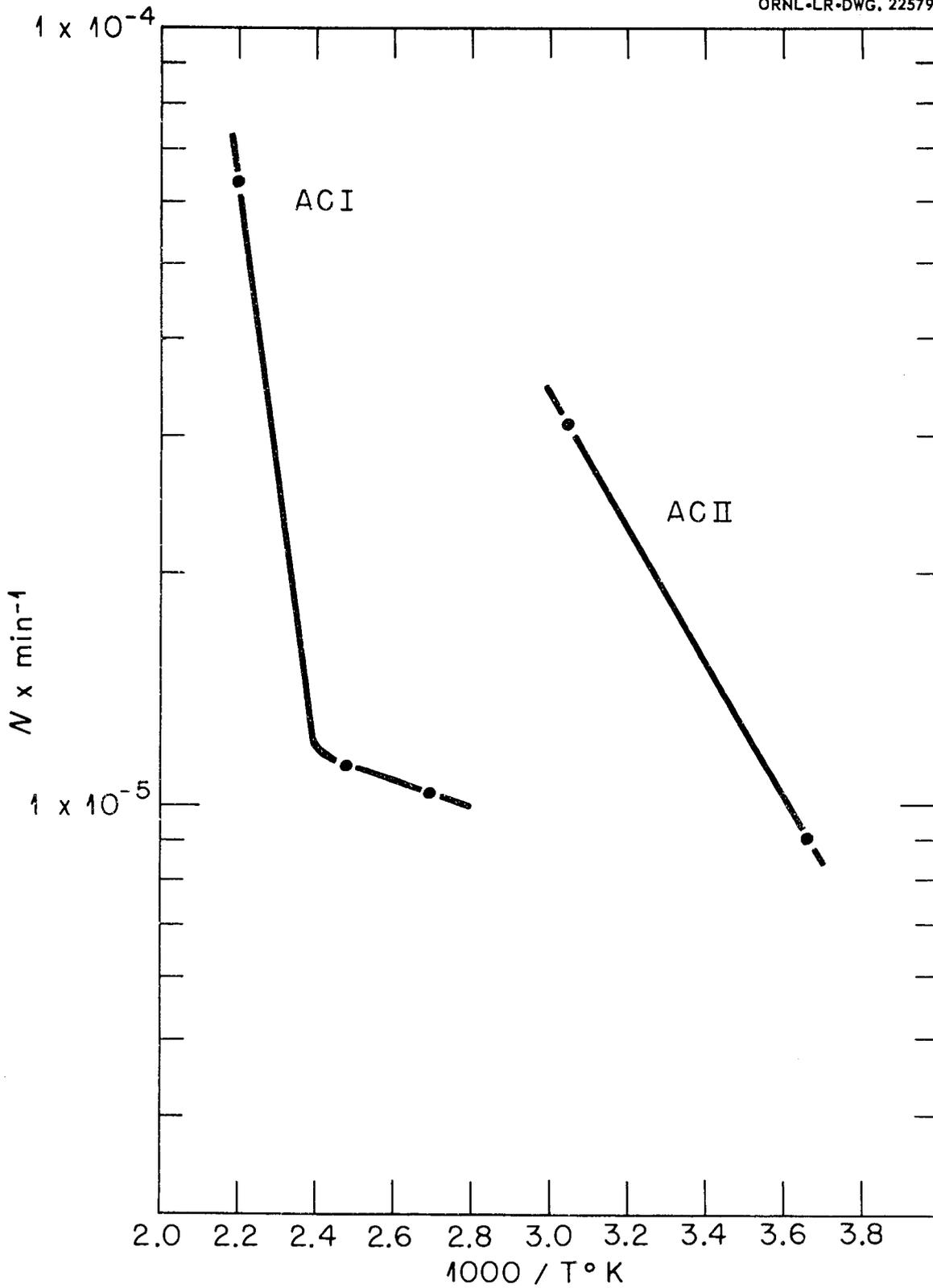


Fig. 32. RATE DATA TAKEN FROM FIG. 31

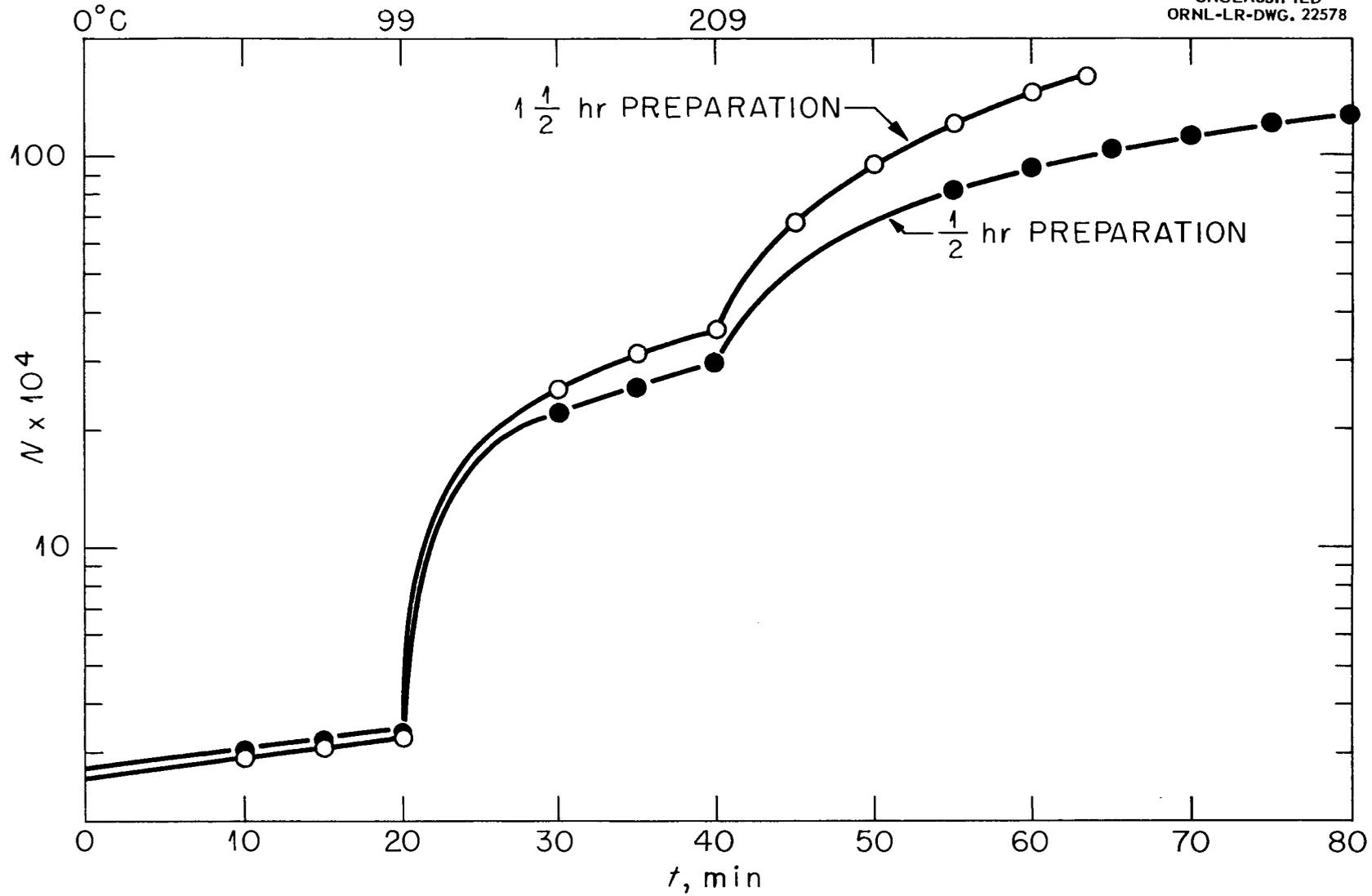


Fig.33. EFFECT OF DURATION OF CsF PREPARATION

boiling-water bath, which was subsequently quickly replaced at 40 min. by a boiling-nitrobenzene bath. The C_3F_6 was not removed between installation of different constant temperature baths, and therefore the CsF changed temperature gradually with C_3F_6 flowing constantly. The sample of CsF heated for 1-1/2 hr. during preparation produced larger values of N at the two higher temperatures. This CsF had a BET surface area of $0.11 \text{ m.}^2 \text{ g.}^{-1}$, while the CsF heated for only 1/2 hr. during preparation had $0.13 \text{ m.}^2 \text{ g.}^{-1}$. Nearly equal concentrations of CsF and C_3F_6 were used in both parts of the study.

CHAPTER VIII

DISCUSSION OF RESULTS

Fluorocarbons

The order of exchange ability was found to be $\text{CsF} > \text{RbF} > \text{KF}$, NaF , LiF regardless of which fluorocarbon was being considered. Fair agreement between high temperature and low temperature surveys as shown in Figs. 17, 23 and 36 shows that the different techniques used in preparing the alkali fluorides did not noticeably affect the results. Reproducibility of results with C_3F_6 and alkali fluorides was not affected by concentrations, which varied widely. Results could not have been induced by F^{18} radiations, since the specific activity varied by a factor of 10^5 with no apparent change in results.

The fluorocarbon survey results, expressed as the logarithm of N plotted versus reciprocal temperature, were always linear. This fact suggested that either the Arrhenius ΔE^* or Van't Hoff ΔE was being measured. The latter is more probable, since reproducible linearity is unlikely in an Arrhenius plot at a constant heating rate. Table 7 lists slopes from the survey studies and ΔE values calculated from these slopes. These slopes appear to result essentially from exchange by a fast reaction mechanism up to the highest temperatures used in the low temperature survey. Figures 23 and 36 demonstrate

TABLE 7
HEATS OF REACTION FROM SURVEY STUDIES

Materials	Run Number	Figure Number	Slope	ΔE , kcal mole ⁻¹
Low Temperature				
CF ₄ , RbF	C17a	22	-12,900	59
CF ₄ , CsF	C16a	22	-11,400	52
(C ₂ F ₅) ₂ O, LiF	C6c	21	-2,670	12
(C ₂ F ₅) ₂ O, RbF	C11a	21	-2,700	12
(C ₂ F ₅) ₂ O, CsF	C9a	21	-1,340	6
C ₄ F ₁₀ , LiF	C6b	20	-2,440	11
C ₄ F ₁₀ , KF	C3b	20	-2,440	11
C ₄ F ₁₀ , RbF	C11b	20	-2,280	10
C ₄ F ₁₀ , RbF	C17b	20	-1,910	9
C ₄ F ₁₀ , CsF	C9b	20	-2,530	12
C ₄ F ₁₀ , CsF	C16b	20	-3,770	17
C ₃ F ₆ , NaF	C1	19	-2,500	11
C ₃ F ₆ , KF	C3a	19	-3,060	14
C ₃ F ₆ , RbF	C14a	19	-1,370	6
C ₃ F ₆ , RbF	C12c	19	-1,370	6
C ₃ F ₆ , CsF	C10b	19	-1,470	7
High Temperature				
C ₄ F ₁₀ , KF	42-111	17	-7,690	35
C ₄ F ₁₀ , CsF	35-105	17	-3,510	16
C ₃ F ₆ , NaF	30-99	16	-5,400	25
C ₃ F ₆ , NaF	34-103	16	-4,710	22
C ₃ F ₆ , NaF	28-95	16	-4,780	22
C ₃ F ₆ , LiF	38-107	15	-4,550	21
C ₃ F ₆ , NaF	28-95	15	-4,640	21
C ₃ F ₆ , KF	43-111	15	-3,530	16
C ₃ F ₆ , CsF	36-105	15	-4,480	21

that the slopes become greater in the same system at higher temperatures. The same effect can be seen in Table 7. It is probable that above the Tamman temperature the magnitude of a slow reaction, which very likely is ionic self-diffusion of fluoride ions in the crystal, becomes appreciable and affects the slope. The average ΔE values calculated from the slopes of low temperature curves are about 10 kcal mole⁻¹ for $(C_2F_5)_2O$, 12 for C_4F_{10} , and 9 for C_3F_6 . The ΔE values from the kinetic studies shown in Fig. 23 for the system C_3F_6 -CsF were 8 and 6 kcal mole⁻¹ for AC I and AC II, respectively. The best value of ΔE for the fast reaction appears to be about 10 ± 2 kcal mole⁻¹ on all alkali fluorides with all fluorocarbons except CF_4 .

A fast reaction between gas and solid, close enough to equilibrium to give the linear plots summarized in Table 7 at a heating rate of $5^\circ \text{ min.}^{-1}$, has never been reported before except in surface reactions. The BET surface areas were small. The linearity of some plots extended to 20% exchange. This fast reaction must not be limited to or related to the surface area.

The crude rate studies combined with survey studies showed definitely that at least two mechanisms were involved. For example, in the combination run, which is shown in Fig. 34 (the constant temperature portion is also shown in Fig. 30), the apparent zero order rate estimated in Table 6 at a constant temperature of $203 \pm 2^\circ$ would have required about 600 minutes to produce the exchange which had occurred after only forty minutes when this portion of the experiment began.

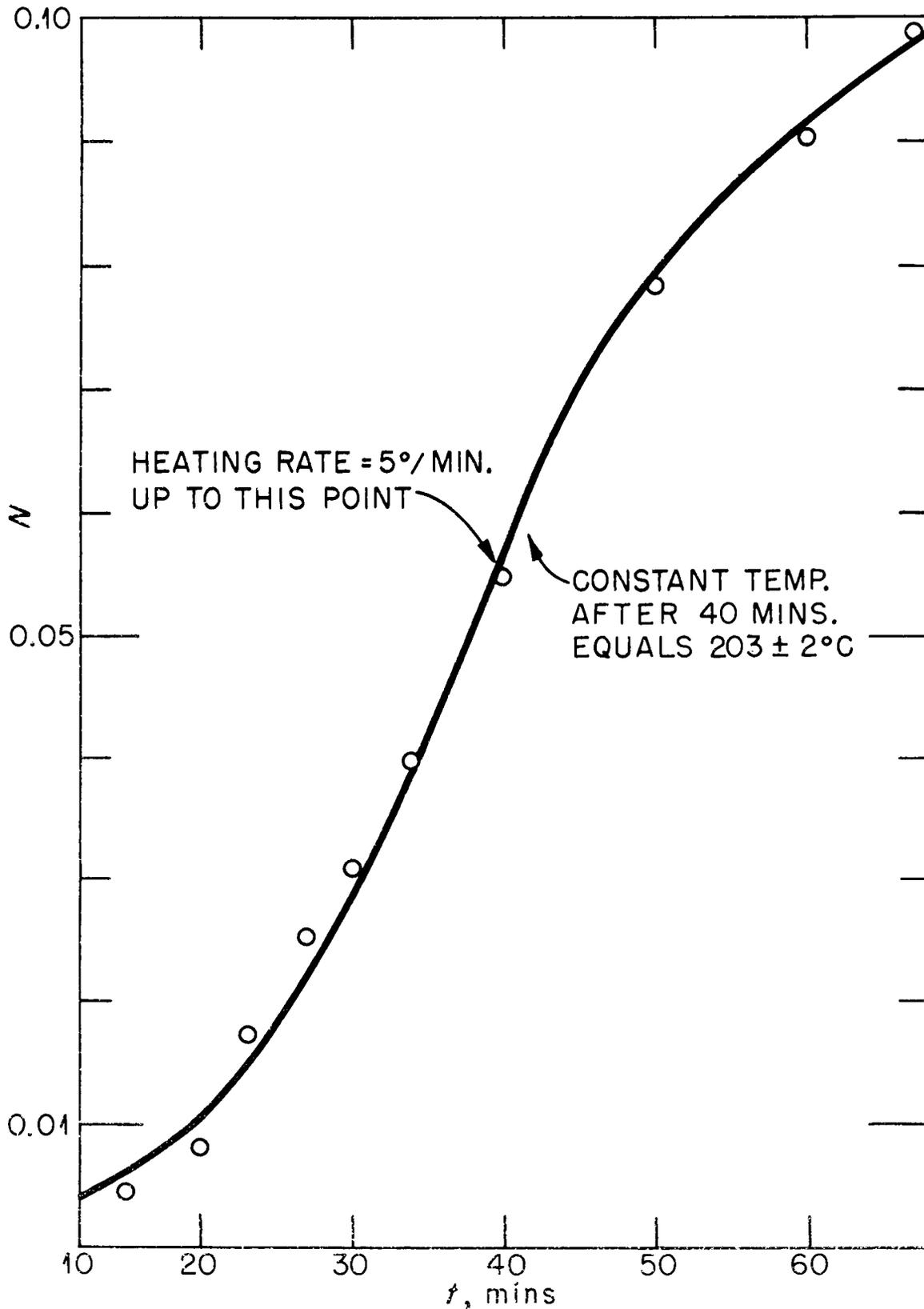


Fig.34. FRACTION OF EXCHANGE OCCURRING WITH $C_{36}F_6$ OVER CsF

The exchange observed, at least up to 200^o, occurred chiefly by the faster mechanism.

Careful kinetic studies further verified the existence of two mechanisms. Figure 31 shows that the fast process was always already close to an equilibrium value by the time of the ten minute measurement. The ordinate intercepts of Fig. 31 gave values of N for the fast reaction without any contribution from the slow reaction. When comparing these ordinate intercepts with survey results obtained with the CsF-C₃F₆ system in Fig. 23, the similarity in slopes and positions of curves indicates that the exchange observed in the surveys, at least up to 200^o, was contributed essentially by only the faster mechanism.

All of the ordinate intercept values of Fig. 31 required the exchange of C₃F₆ with several times the number of fluorine atoms available in the crystal surface, since the BET surface areas of CsF were always very close to 0.1 m.² g.⁻¹. There must have been a fast exchange reaction between the gas phase and the interior of the crystal. Figure 35 illustrates this point by demonstrating how many times the available surface would have been required to account for the values of N obtained in Study AC II. Similar curves could be drawn for all the alkali fluoride - fluorocarbon systems studied.

The activation energy of 17 kcal mole⁻¹ above the Tammann temperature estimated from Fig. 32 is very close to the activation energy of 19.6 kcal mole⁻¹ obtained by electrical conductance measurements on CsF.⁵⁸ This apparent agreement may signify that the same mechanism is

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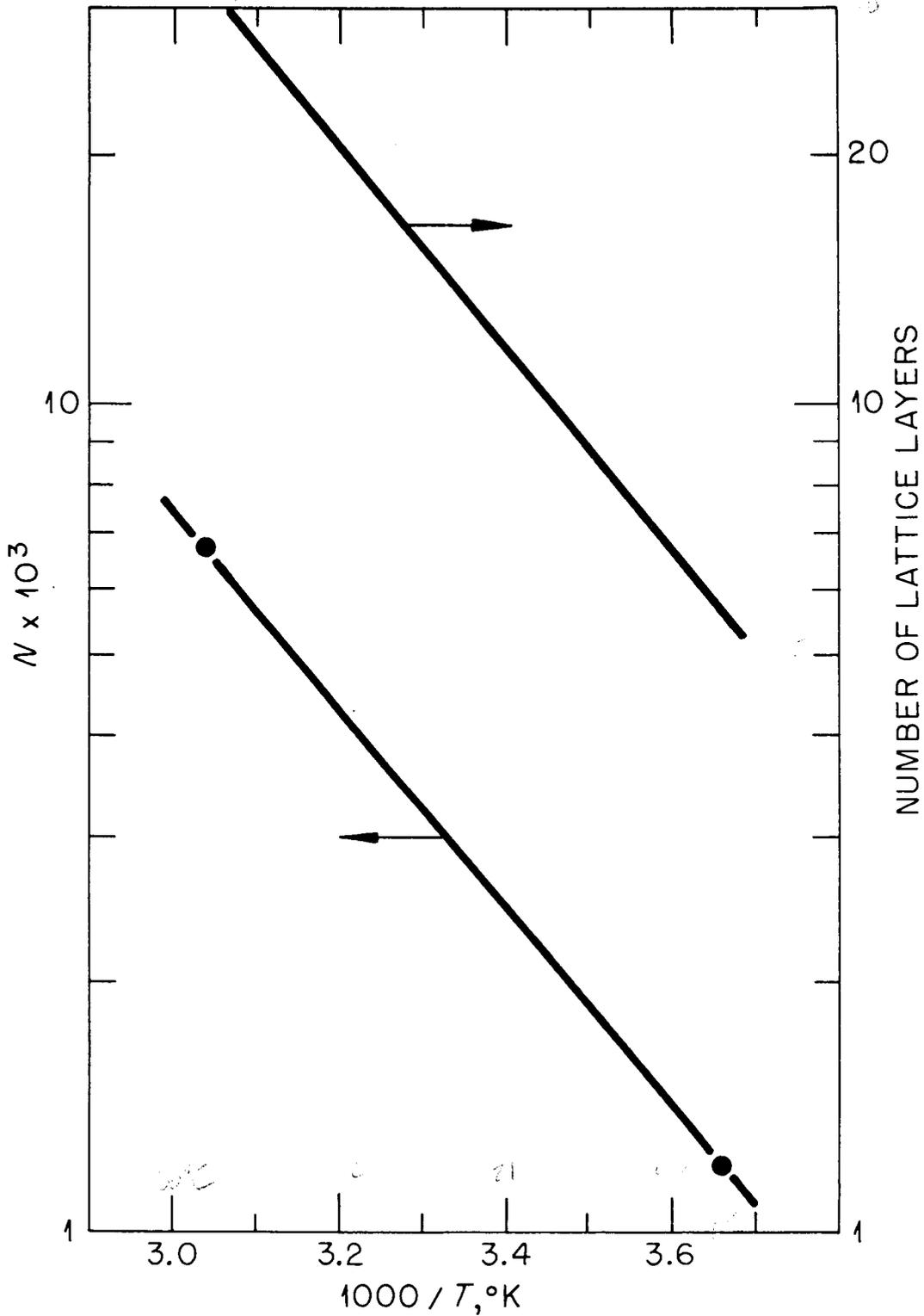


Fig. 35. NUMBER OF LATTICE LAYERS THAT WOULD BE REQUIRED TO ACCOUNT FOR VALUES OF N OBSERVED IN STUDY AcII

the major contributor to both results.

The survey study with CF_4 gave calculated values of ΔE about five times as great as others listed in Table 7. From the limited observations of exchange of C_2F_6 , CF_3H and SF_6 with alkali fluorides, it seems probable that the energy required with these gases was about as great as with CF_4 and that the exchange mechanism for these four gases was different than it was for the other fluorocarbons.

The attempted kinetic study at 100° and 209° with CF_4 and CsF produced a result which could not be predicted from the survey study of this system. From Fig. 22 it can be seen that extrapolation of the CF_4 - CsF plot to intercept an abscissa value equivalent to 100° ($1000/T$, $^\circ\text{K} = 2.68$) would give an extremely small value of N by the mechanism of this higher energy reaction. However the value of N obtained was 2×10^{-5} at both 100° and 209° . This value is of the same order of magnitude as the N values first observed near 300° in the survey study. The kinetic study value corresponded to exchange with one-twentieth of the fluoride ions on the surface as computed from the BET surface area of $0.13 \text{ m.}^2 \text{ g.}^{-1}$. Such exchange, assumed to occur with active surface sites, would not produce enough radioactivity in the gas phase to be distinguishable from the background radioactivity with the lower specific activity CsF used in the survey study. Therefore, kinetic studies with CF_4 and CsF were not feasible at these low temperatures. By use of CsF of higher specific activity, measurement of the rate of ionic diffusion of fluoride ions to the active surface

sites might be possible.

Figure 33 shows that the length of the heating period used in the preparation of CsF had some effect on results. This figure also shows the presence of a fast and a slow reaction, but the experiment was not continued long enough at a single temperature to evaluate either of these reactions. From this study it appears that the wide variation between AC I and AC II in Figs. 31 and 32 could be caused only in part by differences in heat treatment in the preparation step.

Silicon Tetrafluoride

As explained by Van Arkel, stability of complexes which can be formed from alkali fluorides is usually inversely related to the lattice energy of the particular alkali fluoride.⁵⁹ The values of the lattice energies of the alkali fluorides decrease in progressing from LiF to CsF.^{60,71} It is therefore not surprising that Fig. 25 shows no pressure decrease corresponding to formation of Li_2SiF_6 or that no Li_2SiF_6 was detected by spectrographic analysis for silicon after the experiment. However, the similarity of the LiF curve to the KF, C4c curve, where K_2SiF_6 was formed, indicates that unstable Li_2SiF_6 was also formed. The isolation of Li_2SiF_6 has been reported.⁶¹

Figure 26 compares the silicon tetrafluoride exchange study results with those of the most reactive system studied with fluorocarbons, $\text{CsF-C}_3\text{F}_6$. Comparison of slopes and curve shapes indicates that the same mechanism is involved with SiF_4 and all the alkali fluorides

studied, but that this mechanism differs from that exhibited by fluorocarbons. Logarithms of the results with SiF_4 plotted against reciprocal temperature differed greatly from similar plots with fluorocarbons, as Fig. 28 shows.

Since LiF seems to produce an unstable complex fluorosilicate at the temperature used, it may have the ability to catalyze reactions of SiF_4 at these temperatures with other gaseous materials, where such reactions are thermodynamically feasible.

These exchange data and pressure data are consistent with studies made with the alkali fluorosilicates by Caillot⁶² and by Hantke.⁶³ From the small amount of data gathered with SiF_4 , it appeared that variation in concentration affected results.

Other Work

Hydrogen fluoride failed to exchange with fluorocarbons. The only conclusion that could be drawn from the limited data in Table 5 and the preliminary high temperature survey work with PdF_2 , CrF_2 and CuF_2 was that exchange on all salts except the alkali fluorides was probably surface limited. Since NiF_2 was probably responsible for the small amounts of exchange shown in Table 4, it also appears that this surface exchange occurs as readily with the very stable SF_6 and CF_4 as it does with C_4F_{10} . While these limited results are not conclusive, it appears that a fast exchange reaction, not related to the surface, was peculiar to the alkali fluorides alone.

Fluorocarbon Exchange Mechanisms

The results defy explanation by conventional mechanisms. A fast surface reaction, followed by a slow reaction limited by the rate of ionic diffusion to the crystal surface, would be expected. However, the experimental results in all cases showed that the number of atoms exchanged in the fast reaction was much greater than the number of surface atoms. If the surface of the alkali fluoride crystals cracked, presenting more area as the temperature increased, the results would be understandable. This cannot be the true explanation, since heat treatment has been found to have very little effect on the BET surface area of the CsF. Studies made by Beeck⁶⁴ and others have shown that gases sometimes have surprising solubility in solids, but penetration of the close packed alkali fluoride crystals by the large fluorocarbon molecules appears to be impossible.

A possible mechanism, which is supported at least in part by modern solid state theories of alkali halide crystals, seems capable of explaining nearly all results. Consideration of this mechanism shows that the fluorocarbon exchange experiments may be simply providing a unique method of following reactions which take place within the crystal.

Defect sites can be introduced into alkali halides by several means.⁶⁵ Conductivity measurements as a function of temperature produce curves resembling those obtained in this exchange work with the alkali halides. Such conductivity may be correlated with defect

sites.^{65,66,67} The presence of defect sites which allow movement of fluorine atoms through the crystal at a rapid rate and whose concentrations increase in an exponential fashion with increasing temperature could explain the exchange results.

That defects exist in CsF and RbF at the temperatures of the exchange experiments was indicated by the grey discoloration that was observed during the preparation of these two fluorides. Heating of RbF or CsF at about 400° under vacuum might produce F-centers as well as other types of centers.⁶⁵ The F-centers, which require excess cations with electrons filling the vacant anion positions, might be produced if fluorine atoms were able to escape from the crystal during the preparation step. Such F-centers would probably anneal out very quickly at 400°, leaving a very small stoichiometric excess of alkali metal. A similar mechanism has been proposed to explain the catalytic activity produced in BaH₂ and CaH₂ by high temperature-vacuum treatment.⁸

If fluorine atoms could diffuse rapidly through defect sites, these atoms from the interior of the crystal might be able to exchange with adsorbed fluorocarbons, without producing any net change in fluoride concentration in the crystal. Such exchange should occur most easily at surface defects where the fluoride-cation bonding forces would be highly strained. The ΔE values of about 10 kcal mole⁻¹ might then be connected with a particular defect reaction in the alkali fluoride crystals. No contribution to ΔE would be made by the

exchange process because the products and reactants are the same.

Rapid diffusion of fluorine atoms might be expected to occur on defects, such as grain boundaries,⁶⁸ where the bonding forces between fluoride ions and cations are highly strained. The diffusion might be facilitated by the small stoichiometric deficiency of fluoride introduced by the high temperature-vacuum preparation. It is improbable that a fluorine atom actually becomes separated from its valence electron. Rather, at highly strained sites, rapid movement of fluorine atoms between alkali ions seems possible by a gradual shifting of attractive forces. Since grain boundaries can extend through a great many lattice layers, such defects may be responsible for the observed results.

An explanation based on a related mechanism can be advanced for the higher energy process which occurred with CF_4 over CsF and RbF. Since the counting rate became appreciable in the CF_4 at 300° with CsF and at 400° with RbF, the process observed may be the same process which was thought to cause discoloration, i.e., the removal of fluorine atoms from the crystal. Removal of fluorine atoms should be facilitated by surface defects. The energetic fluorine atoms might be expected to exchange homogeneously with CF_4 , leaving the F^{18} atoms in the CF_4 . The small quantity of fluorine atoms produced probably would never leave the area but would react with the walls. Use of counting rate of the CF_4 in a plot such as Fig. 22 gives the same slopes and values of ΔE as does use of N. The larger ΔE can be explained by

assuming that CF_4 does not adsorb on the surface and that the approximately 50 to 60 kcal mole⁻¹ value for ΔE includes 40 to 50 kcal g-atom⁻¹ required for removal of fluorine atoms from the crystal surface into the gas phase. Such a process would be expected to require a large amount of energy.

The active-sites surface exchange observed in the kinetic study with CF_4 and CsF appeared to be associated with a ΔE of zero, since raising the temperature did not change the counting rate in the gas. Thus, the contact required for active surface site exchange must not be sufficient for the exchange which accompanied the reaction requiring a ΔE of about 10 kcal mole⁻¹.

The slow diffusion of ions from the more ordered region of the crystals could introduce new atoms into the defects and produce the slow, apparently zero order increase in F^{18} concentration observed in the gas phase at constant temperature. Ionic diffusion can alternatively be described as the migration of defects.⁶⁹ Since equilibrium by the fast reaction is essentially achieved in five minutes, the fluorine atoms would have to diffuse to the surface rapidly. The atoms from the center of a crystal would have to cross many lattice layers. At 0°, diffusion across a single lattice layer would require an average of about an hour from the rate of the slow process observed in Study AC II.

The explanation for the order of ability to exchange with fluorocarbons in the alkali fluorides may involve the lattice energies.

The lattice energies increase in progressing through the group from CsF to LiF.^{60, 71} Therefore, defect concentration might be expected to increase in the inverse order.

The proposed exchange mechanism does not offer any simple explanation for the fact that C_3F_6 exchanged more readily than C_4F_{10} or $(C_2F_5)_2O$ or that the more volatile gases seemed to exchange only by a different mechanism requiring a greater energy. At the lower temperatures, a more favorable rate of physical adsorption and desorption would be expected with C_3F_6 , since C_4F_{10} and $(C_2F_5)_2O$ were known to be adsorbed and desorbed only slowly. However, this explanation is not compatible with the behavior of the more volatile gases, since it would require that C_3F_6 soon cease its rapid exchange as temperature increased and its physical adsorption became smaller. Since chemical bonds are involved in exchange, it is probable that chemisorption occurs on defect sites, with the order of ability to be chemisorbed being $C_3F_6 > C_4F_{10} > (C_2F_5)_2O >$ other gases studied. It should be noted that C_3F_6 was the only unsaturated fluorocarbon whose exchange behavior was studied.

Figure 36 compares high temperature and low temperature slopes of C_3F_6 . The curves with NaF and KF were first thought to exhibit scatter caused by experimental error. They were the only curves that showed this much scatter at high counting rates and the only curves which passed through the temperature region at which fluorine atoms were thought to be removed from the crystals during the CF_4 experiments. The CsF curve is a combination of two runs. These curves may

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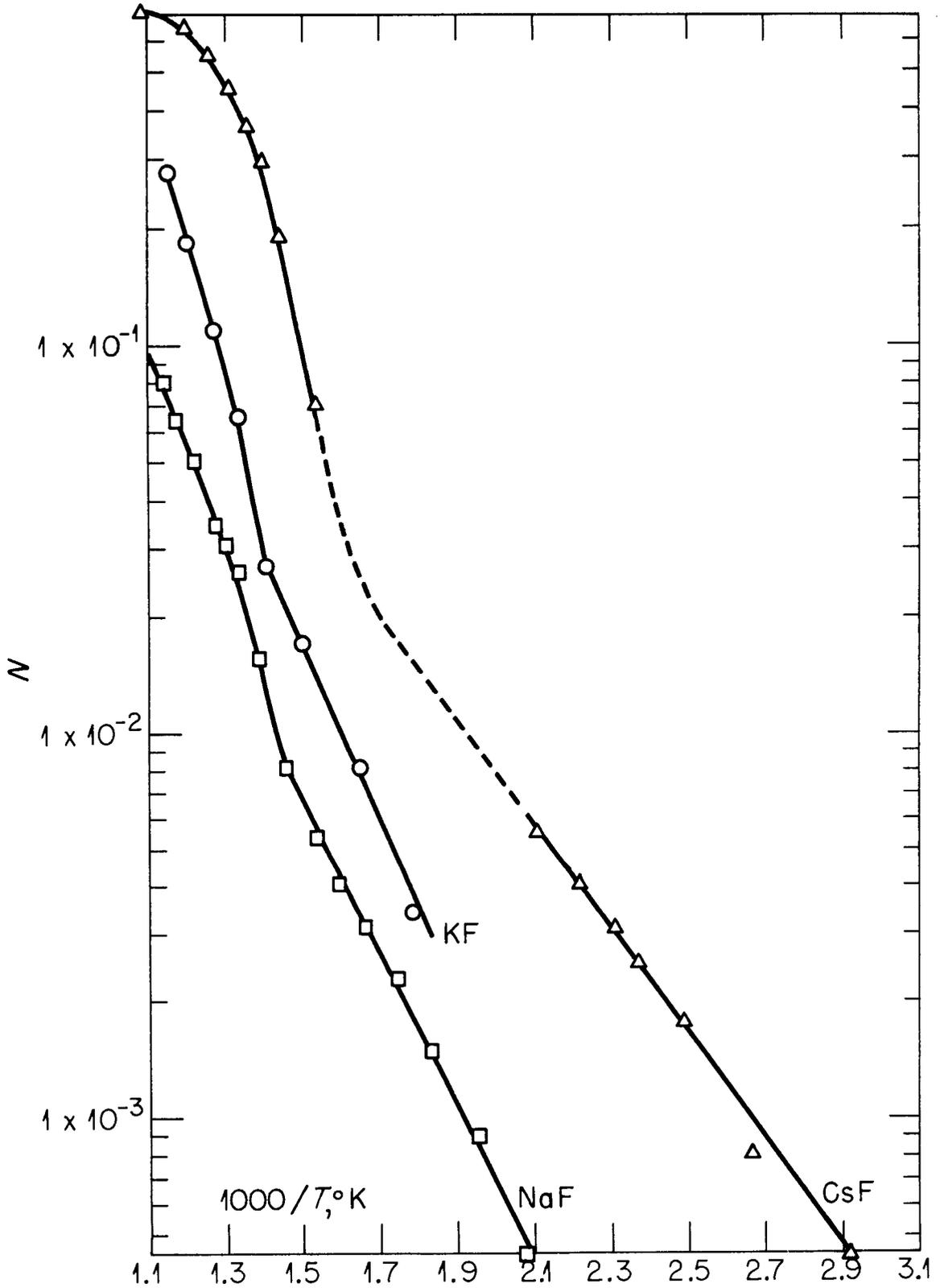


Fig.36. SECOND ORDER EFFECTS WITH C₃F₆

be exhibiting the same effect thought to be responsible for the CF_4 results.

McKay's treatment of isotopic exchange was developed for homogeneous systems. The values of N at the ordinate intercepts in Fig. 31 are thought to correspond to the number of defect sites throughout the crystal. Run AC Ic was the only run in which enough slow exchange occurred to represent the diffusion of one ion to each site. No departure from homogeneity should become apparent in the results as long as ionic diffusion from the fluorine ions closest to the defect was being measured.

The absence of any previous proposal of the rapid diffusion mechanism suggests that this mechanism may be of importance only with alkali fluorides. There exists some support for this possibility. Other halogen atoms are so much bigger⁷⁰ that it might be sterically impossible for these atoms to diffuse rapidly through defects. Despite the great electronegativity of fluorine, the electron affinity of gaseous fluorine atoms has been calculated to be about 4 kcal g-atom⁻¹ less than the electron affinity of gaseous chlorine atoms.⁷¹

This discussion of mechanism necessarily casts doubt on the interpretation of the quantity ΔE as a true thermodynamic term. If N were proportional or equal to an equilibrium constant for the reaction $\text{Salt} \rightleftharpoons \text{Defect}$, where fluorine atoms were mobile in the defects, ΔE would be a thermodynamic quantity defined by the Van't Hoff Equation. However, all of the salt is not in equilibrium with defects. Only a

specific portion of the salt is able to achieve isotopic equilibrium with the gas at each temperature, except by the much slower process of ionic diffusion. An exponential increase in the concentration of localized defect sites with increasing temperature appears to be responsible for the results.

While the proposal that fluorine atoms are very mobile in the alkali fluorides is new, much evidence indicates that mobile atoms or ions can be introduced into metals. Hydrogen has exhibited such behavior with several metals.⁷² Oxygen has been reported to be present as atoms with great mobility in zirconium at high temperature.⁷³

The proposed mechanism requires the existence of three phenomena which are compatible with, but which require some extension of, present theories of the solid state of alkali halides: great mobility of fluorine atoms in the crystal; localized nature of defects; and production of defects such as F-centers by removal of fluorine atoms from the crystal.

Suggestions for Future Work

The differences in exchange behavior among the fluorocarbons studied were not understood. More extensive studies with fluorocarbons and fluorocarbon derivatives should yield information which would help in understanding the nature of the surface intermediates involved in the exchange reaction.

It was proposed from the work with CF_4 that fluorine atoms were

removed from CsF at about 300° and from RbF at about 400° . If this interpretation of results is correct, similar threshold temperatures might be found with the remaining three alkali fluorides, probably at about 0.6 times the melting point.

Very few fluorides were studied. Others may be capable of producing exchange results with fluorocarbons such as were produced by the alkali fluorides.

If the exchange results were influenced by reactions within the crystal as has been proposed, fluorine or gaseous compounds such as fluorine-containing interhalogen compounds might produce exchange results with alkali fluorides very similar to the results from fluorocarbons.

Other approaches might yield further insight into the mechanisms of reactions in alkali fluorides. X-ray studies might correlate crystallite size with exchange ability. Experimental techniques such as are used in studying grain boundary diffusion in metals⁶⁸ might be adapted to use with alkali fluorides.

Determination of adsorption isotherms in the systems studied would be useful in establishing the exchange mechanisms.

Since rearrangement of chemical bonding forces must be involved in exchange, the alkali fluorides may be capable of catalyzing reactions to yield useful products. Simple experiments might be made to determine or characterize catalytic activity in the alkali fluorides.⁷⁴

Figure 28 demonstrates that SiF_4 produced much more exchange at

low temperature than did fluorocarbons over alkali fluorides. This great amount of exchange suggests that the study of many complex fluorosilicates may be very feasible experimentally. Other volatile fluorine-containing compounds such as BF_3 , which enters into acid-base type reactions with inorganic fluorides, might also be studied very conveniently by the same methods used with SiF_4 .

CHAPTER IX

CONCLUSIONS

Isotopic exchange between solid inorganic fluorides and gaseous fluorocarbons was observed for the first time. Rates of many of these exchange reactions were studied at temperatures as low as 0°. Of the inorganic fluorides studied, the exchange was most rapid with alkali metal fluorides. Among the alkali fluorides the rate of the exchange reaction increased markedly with increasing atomic number of the cation.

Of the gaseous fluorine-containing compounds studied, the unsaturated fluorocarbon perfluoropropene exchanged more readily than perfluorodiethylether or perfluorobutane and the latter compounds exchanged more readily than carbon tetrafluoride. No exchange was observed between fluoroform or sulfur hexafluoride and the alkali fluorides at temperatures below which decomposition occurred. Silicon tetrafluoride exchanged fluorine atoms with alkali fluorides at low temperatures. With the heavier alkali metal fluorides complex fluoro-silicates were formed at moderate temperatures. In the case of lithium fluoride, although rapid exchange occurred, no detectable stable fluoro-silicate was formed at temperatures up to 500°.

Exchange of fluorine atoms between alkali fluorides and fluorocarbons appeared to proceed by two distinct mechanisms. When fluorocarbon gas first came into contact with alkali fluoride crystals,

isotopic exchange occurred so rapidly that only quasi-equilibrium data were obtained. The number of fluorine atoms exchanging in this fast reaction was much larger in most cases than the number of fluorine atoms on the alkali fluoride surface. The fraction of the fluorine atoms in the alkali fluoride which exchanged in the fast reaction was an exponential function of the temperature. At any given temperature after the fast reaction had reached an apparent equilibrium there was further exchange at a much slower rate. It is postulated that the rate controlling step in this second stage is ionic self-diffusion of fluoride ions through alkali fluoride crystals. Although the initial rapid reaction is less well understood it is postulated that rapid transport of fluorine atoms or ions through defect sites in the alkali fluoride crystals may be involved.

Because of the short half-life of F^{18} only a few fluorine-containing compounds have been prepared heretofore in radioactive form. Many radioactive fluorine-containing compounds can now be made by the rapid isotopic exchange reactions discovered in this work. Many simple salts, several of the alkali metal fluorosilicates and silicon tetrafluoride have been made in highly radioactive form. In addition, several radioactive fluorocarbons have been prepared for the first time.

This work was undertaken as a search for inorganic fluorides which would exchange with fluorocarbons. The primary objective was attained with the discovery of the exchange behavior of the alkali

metal fluorides. Further research will be required in order to understand the mechanism of such exchange reactions. Since rearrangement of chemical bonding forces must be involved in isotopic exchange, the alkali fluorides may be capable of catalyzing reactions of fluorocarbons which yield useful products.

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