UNCLASSIFIED

AD 404 779

DEFENSE DOCUMENTATION CENTER
FOR
SCIENTIFIC AND TECHNICAL INFORMATION
CAMERON STATION, ALEXANDRIA, VIRGINIA

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

63-3-5

CATALOGED BY ASTIA
AS AD No. 404779

[redacted]

404 779

DDC
RECEIVED
MAY 27 1963
TISIA A

[redacted]

HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

Richmond Research Center
Richmond, California

STAUFFER CHEMICAL COMPANY
Richmond Research Center
Richmond, California

"HIGH ENERGY OXIDIZERS"

CONTRACT Nonr-4019(00)

Project NR 093-035

OFFICE OF NAVAL RESEARCH

WASHINGTON, D. C.

Quarterly Technical Summary Report

for the Period February 1, 1963 to May 1, 1963

Investigators

Karl O. Christe
Dr. K. O. Christe

Attila E. Pavlath
Dr. A. E. Pavlath

Department Supervisor

EGWallace
Dr. E. G. Wallace

Richmond Research Center
Richmond, California

TABLE OF CONTENTS

Page No.

Drawings

TECHNICAL REPORT DISTRIBUTION LIST

STAUFFER CHEMICAL COMPANY

Contract Nonr 4019(00) NR 093-035

Addressee	No. Copies
Advanced Research Projects Agency Propellant Chemistry The Pentagon, Room 3D165 Washington 25, D. C.	6
Defense Documentation Center Arlington Hall Station Arlington 12, Virginia	10
Chemical Propulsion Information Agency Applied Physics Laboratory Johns Hopkins University Silver Spring, Maryland	3
Dr. D. W. A. Sharp Royal College of Science & Technology Glasgow, C.1 Scotland	1
Office of Naval Research Branch Office 1000 Geary Street San Francisco 1, California Attn: Dr. P. A. Miller	1
Office of Naval Research U. S. Navy Department Power Branch, Code 429 Washington 25, D. C.	2

Summary

Qualitative and semi-quantitative proofs were obtained for the ionic structure of ClF_3 complex with Lewis acids such as BF_3, AsF_5 and SbF_5. Vapor pressure, conductivity and NMR investigations were used to arrive at this conclusion. NMR studies have to be continued in other solvents to give final quantitative proof for the existence of the ionic structure. Infrared investigations are also needed for this purpose.

Abstract

This is the first Quarterly Technical Summary Report on our investigation on the complexes of ClF_3.

The physical properties of the following three complexes were investigated: $ClF_3 \cdot BF_3$, $ClF_3 \cdot AsF_5$ and $ClF_3 \cdot SbF_5$.

A vacuum line was built to handle ClF_3 and its complexes safely with the exclusion of atmospheric moisture for vapor pressure determination, conductivity measurement and preparation of NMR samples.

Vapor pressure measurements gave indication of strong bonding with AsF_5 and SbF_5 even at room temperature. With BF_3 the complex was somewhat weaker, but still strong enough to be worth-while for further considerations.

NMR investigations were conducted with these complexes in ClF_3 as solvent. Indirect qualitative proof was obtained for the existence of the ionic structure. The results could not be evaluated quantitatively because of the rapid fluorine exchange between ClF_3 and the complexes. Other solvents such as BrF_5 and SO_3 are being investigated.

A conductivity cell was designed for measuring the conductivity of the complexes in ClF_3 as solvent. In each case a 10^{-3}-10^{-4}-fold increase was noted in the conductivity in a concentration less than 10 mol percent.

A low temperature IR cell was designed. Sodium chloride windows were found to be unsatisfactory for working with ClF_3. IRTRAN-2 windows showed no corrosion.

Introduction

Complex formation was observed in the past between halogenfluorides and Lewis acids. The subject of this project is the structure determination of the complexes formed from ClF_3 by the following Lewis acids: BF_3, PF_5, AsF_5 and SbF_5. It is supposed, based on the result of earlier work, that the complexes possess ionic structure, in which case a ClF_2^+ has to be present. If this can be proved the anion might be changed by another one, such as NO_3^-, ClO_4^-, etc. and the resulting complex would be a satisfactory high energy solid oxidizer.

Discussion

Vacuum Line

The complexes were prepared and found to be very hygroscopic. Two of them, the complexes with PF_5 and BF_3, showed essential dissociation at room temperature. Furthermore, because of the danger of explosion microscale investigation was preferred, and so a vacuum line was designed and built for handling these complexes.

Many difficulties were experienced in initial operation of the vacuum line. Even 3M's Kel-F stopcock grease was attacked by ClF_3, probably because of its SiO_2 powder content. Finally a stopcock grease was acquired from Halocarbon Corp. which was resistant to ClF_3. Another problem was the slow reaction of the ClF_3 with the mercury in the manometers, which made the reading of the pressure inaccurate. It was found that a layer of Kel-F oil on the surface of the mercury decreased the rate of reaction, but still the mercury had to be replaced even in this case after a few days of exposure to ClF_3 or the Lewis acids used in the experiments.

One of the greatest difficulties was caused by the occasional formation of ClO_2 from ClF_3 in the vacuum line which is being collected in the trap after evacuation. Once this trap was shattered to pieces by a sharp detonation while warmed up slowly at the end of an experiment. A special protective guard was designed to prevent future accidents.

Dissociation Pressure

The vapor pressure of the complexes was determined at two temperatures: 0°C. and 22°C. It was found that the stability of the complexes increased from BF_3 through AsF_5 to SbF_5, as can be seen from Table I.

Table I

Compound	Vapor Pressure (in Hg mm)	
	0°C.	22°C.
$ClF_3 \cdot BF_3$	200	total dissociation
$ClF_3 \cdot AsF_5$	10	40
$ClF_3 \cdot SbF_5$	3	10

In comparison, BF_3 boils at -101°C., AsF_5 at -53°C., SbF_5 at 149.5°C. and ClF_3 at 11.3°C. Chlorinetrifluoride has a vapor pressure of 480 Hgmm at 0°C.

All complexes were solid, except $ClF_3 \cdot BF_3$ above 0°C., where it slowly liquified and evaporated. The melting points of the components are: ClF_3 at -83°C., BF_3 at -127°C., AsF_5 at -80°C. and SbF_5 at 7°C.

The complex between ClF_3 and PF_5 was very unstable even at 0°C.; therefore, it was not investigated quantitatively any further.

These vapor pressure results indicate already more than a loose complex, especially in the case of $ClF_3 \cdot AsF_5$, where at room temperature both components would be completely evaporated at atmospheric pressure. The vapor pressure of ClF_3 and AsF_5 at 22°C. is 1.5 and 18 atm., respectively. In equimolar ratio the vapor pressure would be 9.75 atm. without any interaction between the two components, which is approximately 200 times higher than the value measured.

Nuclear Magnetic Resonance

The vacuum line was adapted to prepare samples of the complexes in excess ClF_3 as solvent for NMR investigation. The investigation was carried out at room temperature in a sealed NMR tube.

It was found that ClF_3 rapidly exchanged fluorine with the complexes under these conditions and therefore the quantitative evaluation of the results was impossible. In each case one singlet was obtained for the chlorinetrifluoride part of the complex, shifted upfield from the singlet present in the pure ClF_3. The shift varied between 800-4000 cycles/second. The singlet of the pure ClF_3 disappeared completely. In the case of the complexes with BF_3 and PF_5, no other absorption could be found which indicates a rapid fluorine interchange, not only between ClF_3 and ClF_2^+, but also between them and BF_4^- or PF_6^-. However, $ClF_2^+AsF_6^-$ and $ClF_2^+SbF_6^-$ gave another singlet too, which indicates no interaction between the anions and the solvent. This supports the theory of the ionic structure. In the case of the antimony complex the absorption was removed upfield almost by 3000 cycles/second from the original SbF_5 singlet. Since AsF_5 is a low boiling liquid its absorption could not be compared with that of its complex.

The qualitative evaluation of these results indicates a very strong interaction between ClF_3 and the Lewis acids, but another solvent should be used to prove quantitatively also the ionic structure. Theoretical considerations and known investigations seem to limit our choice to two "inert" solvents. It is stated in the literature(1), that "the fluorine atoms in BrF_5 are incapable of exchanging rapidly with other fluorides" such as HF, ClF_3 or BrF_3, while the NMR spectrum of the ClF_3 is affected by the presence of other fluorides.

---

(1) Hamer, A. N., Leece, J., Bentley, P. G., United Kingdom Atomic Energy Authority, Industrial Group, 1 GR-TN/CA-1048 p. 10

Since nothing was known on the complex forming capability of BrF_5 with the Lewis acids used in our investigation, the reaction between BrF_5 and SbF_5 was studied. It was found that a solid complex formed just as between ClF_3 and SbF_5. If this latter complex is strong enough, it can be supposed that it can be dissolved in BrF_5 without any exchange. Naturally even if ClF_3 and BrF_5 do not exchange fluorine atoms rapidly, some exchange might take place between ClF_2^+ and BrF_5. Only the actual study of the NMR spectrum of these mixtures can give a final answer.

The other solvent which might be useful to solve this problem is liquid SO_3. Some difficulties, however, might be expected here too. According to the literature BrF_3 forms a complex with sulfurtrioxide, probably $BrF_2^+SO_3F^-$ (2). Nothing is known on the complex formation between ClF_3 and SO_3. Again only the actual NMR investigation of the solution of a ClF_3-Lewis acid complex in liquid SO_3 can decide whether SO_3 can be used as solvent or not. Here SO_3 could exchange with the anion as shown in the following equation:

$$SO_3 + SbF_6^-(AsF_6^-, BF_4^-) \rightleftharpoons SO_3F^- + SbF_5(AsF_5, BF_3)$$

If none of these solvents will work chlorinetrifluoride will be used again, but at lower temperature where the literature indicates (1) no rapid exchange.

Conductivity

A conductivity cell was designed first with Pt-electrodes and W-leads. Since one of the W-leads started to burn it was reconstructed using Pt as the only metal.

The specific conductivity of the purified ClF_3 was found to be 1.7×10^{-6} ohm^{-1} cm^{-1} at -15°C. In another attempt a ClF_3 of higher purity was obtained having a sp. conductivity of 5.5×10^{-7} ohm^{-1} cm^{-1}. Earlier investigations gave a value of 3×10^{-9} ohm^{-1} cm^{-1} (3).

Table II summarizes the results obtained with different Lewis acids.

Table II

ClF_3 (mmol)	Lewis Acid (mmol)	Lewis Acid molarity	Temperature °C.	Sp. conductivity ohm^{-1} cm^{-1}	Equivalent conductivity ohm^{-1} cm^{-2}
83.8	8.4 BF_3	2.12	-20	4.2×10^{-3}	1.99
83.8	8.2 AsF_5	2.07	-15	1.1×10^{-2}	5.31
87.4	2.8 SbF_5	0.67	-15	2.1×10^{-3}	3.14

---

(2) Fialkov, Ya. A., Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk. 1954, 972, C.A. 49, 14552 (1955)

(3) Banks, A. A., Emeleus, H. J., Woolf, A. A., J. Chem. Soc. (London) 1949, 2861; Woolf, A. A., Greenwood, J., J. Chem. Soc. (London), 1950, 2200

The result with SbF_5 is probably lower than the actual value since the complex has limited solubility in ClF_3 and some undissolved solid material was left on the bottom of the conductivity cell, which could not be taken in solution. In the literature 11.8 is given for the equivalent conductivity of $ClF_3 \cdot SbF_5$ at 0°C. in a slightly lower concentration (0.564 mol/l)$^{(4)}$. A measurement was made in our case also at -78°C. where the specific and equivalent conductivity dropped to $1.7\ 10^{-3}$ and 2.30, respectively. This decrease and the increasing amount of precipitation indicated that this concentration is too high. In the case of the other complexes some definite increase could be noted in the conductivity at decreased temperature, but the changes were relatively small compared to the error of the measurement in this range; therefore, quantitative evaluation is not worth-while. A larger conductivity cell should be designed which would allow us to measure the conductivity more accurately in another range. The conductivity of the ClF_3 was found to be twice as much at -78°C. as at -15°C.

These findings indicate a strong, most probably ionic interaction between ClF_3 and the Lewis acids. The values obtained for the equivalent conductivity are lower than those of the common ionic salts, but values in different solvents cannot be compared quantitatively and therefore the lower values do not necessarily mean lower degree of ionization. The larger than 10^4 fold increase in the conductivity is a strong qualitative proof for ionization.

Infrared Spectrum

Liquid chlorinetrifluoride reacted only slowly with NaCl optical plates, but in vapor phase only the spectrum of NaF was obtained, apparently as the consequence of the following reaction:

$$3\ NaCl + ClF_3 \longrightarrow 3\ NaF + 2\ Cl_2$$

Earlier studies stated that NaCl did not react with $ClF_3$$^{(5)}$. Another article contended that both KBr and NaCl windows could be used to take the IR spectrum of ClF_3, but the description is not clear whether ClF_3 was in direct contact with the NaCl window or this latter was protected by a very thin layer of Kel-F polymer$^{(6)}$. Other investigators used Kel-F cell for infrared studies$^{(7)}$.

In the past IRTRAN-2 windows have been used successfully for taking IR spectra of corrosive materials. The exact composition of this material is not known. It was tested against liquid ClF_3 and SbF_5, but in neither case was any corrosion observed. A cell was constructed with these windows for low temperature use.

---

(4) Seel, F., Detmer, O., Z. anorg. allg. Chem. 301, 113 (1959)

(5) Ruff, O., Krug, H., Z. Anorg. allg. Chem. 190, 270 (1930)

(6) Jones, E. A., Parkinson, T. F., Murray, R. B., J. Chem. Phys. 17, 501 (1949)

(7) Pemsler, J. P., Smith, D. F., J. Chem. Phys. 22, 1834 (1954)

Experimental

Vacuum Line

A vacuum line was built and calibrated. First 3M's Kel-F grease was used but it was found to be unsatisfactory because of its slow, but definite reaction with ClF_3. The grease slowly turned yellow. Next Hooker's Fluorolub stopcock grease was applied, which did not show any sign of reaction for a few hours, but it did turn yellow after an overnight exposure to gaseous chlorinetrifluoride. Finally Halocarbon Corp.'s stopcock grease was used with success without any visible sign of attack by the ClF_3. The explanation of the different behavior is that although all of these greases are based on Kel-F polymers, the first two are thickened by SiO_2 flour, while Halocarbon use Kel-F waxes for this purpose.

The mercury in the manometers was slowly attacked by ClF_3 and the Lewis acids, which gave difficulties in the correct reading of the pressure. A high boiling Kel-F oil was acquired from Halocarbon Corp. and applied on the surface of the mercury in a layer of 30-40 mm high. Since the oil had a relatively high viscosity, care had to be taken to change the pressure slowly, otherwise the mercury would have been exposed to the corrosive atmosphere for a short period. Even in this case some slow contamination was observed because of the solubility of ClF_3 in the Kel-F oils. This effect could be minimized by heating the oil layer above the mercury gently by a hot-air blower.

The greatest difficulty was experienced with the disposal of waste ClF_3. The ClF_3 was condensed in a trap cooled with liquid N_2, at which temperature it was solid. The solid ClF_3 is pale yellow, but occasionally it is colored red. This is caused by the formation of ClO_2 which is very unstable in liquid form. The trap is allowed to warm up slowly to room temperature in a closed hood under a stream of air. Once the trap, containing waste ClF_3 and $ClF_3 \cdot BF_3$, exploded shortly after being removed from the liquid N_2 bath. The explosion took place with flame and sharp detonation. A special metal case was built in which the trap is transferred immediately from the liquid N_2 bath.

Purification

Chlorinetrifluoride was distilled in the vacuum line by trap-to-trap distillation. The distillation was repeated three times. In each case the first and last 10-15% was discarded. Finally the ClF_3 was condensed over NaF and kept at -78°C. for 1-2 days in order to remove any HF contamination.

The Lewis acids were purified by the same way save for the NaF treatment.

Dissociation Pressure

In the case of the complexes made by BF_3 and AsF_5 the Lewis acids were used in large excess while being treated with ClF_3. When the $ClF_3 \cdot SbF_5$ complex was prepared the ClF_3 was applied in an excess over the stoichiometric 1:1 ratio.

The $ClF_3 \cdot BF_3$ complex was kept at -78°C. until no more BF_3 evolved. The container was evacuated then at liquid N_2 temperature and then slowly warmed up to 0°C. After reading the pressure it was allowed to warm to room temperature (22°C.). In order to prevent the contamination of the mercury in the manometer, the system was evacuated as soon as the pressure reached 760 Hgmm.

The $ClF_3 \cdot AsF_5$ complex was kept at -42°C. until no more AsF_5 evolved. After evacuation at -78°C. the complex was heated up first to 0°C., then to 22°C. At each point the pressure reading was made after waiting an hour to reach the equilibrium.

In the case of the $ClF_3 \cdot SbF_5$ complex the container was warmed up slowly until the SbF_5 melted, but before ClF_3 boiled (m.p. of SbF_5 = 7°C.; b.p. of ClF_3 = 11°C.). Then it was cooled to -78°C. and evacuated. After all of the ClF_3 was evaporated the same procedure was followed as with $ClF_3 \cdot AsF_5$.

Nuclear Magnetic Resonance

The samples were prepared similarly as for the investigation of the dissociation pressure, but the preparation was done immediately in the NMR tubes which were connected to the vacuum line. After the preparation, ClF_3 was condensed to it until the solid went in solution at 0°C. Then the tube was sealed and stored in dry-ice until their NMR investigation. The $ClF_3 \cdot PF_5$ complex was prepared in such way that PF_5 was condensed into large excess of ClF_3, then warmed up to 0°C. The tube was sealed off at liquid air temperature. All sample tubes were cracked under their own pressure after standing two days at room temperature.

In our search for a more suitable solvent than ClF_3, another halogenfluoride, BrF_5, was investigated. Nothing was found about its complex forming capability; therefore, its reaction was investigated with SbF_5. Brominepentafluoride was cooled to 10°C. and equimolar quantity of SbF_5 was added slowly to it. The SbF_5 went into solution first, then some precipitation appeared on the bottom, and finally everything solidified in a pink crystalline mass. The solid reacted violently with water, ignited paper on contact.

Conductivity

A cell was designed according to the drawing shown and connected to the vacuum line. The cell was calibrated with 0.021 n. H_2SO_4 which gave a value of 14.2 ohm. This gave a cell constant of 11.76. The resistance was measured by the combination of a Heathkit decade resistance and RLC checker. The first cell had to be redesigned to eliminate tungsten leads, which began to burn in contact with ClF_3.

The measurement with BF_3 and AsF_5 was carried out in such a way that first known amount of ClF_3, measured volumetrically on the vacuum line, was condensed from the vacuum line into the conductivity cell and then the Lewis acid was condensed to it. The mixture was heated up to -15°C. and kept there for 20-30 minutes, then the measurement was made.

The $ClF_3 \cdot SbF_5$ complex was prepared in the cell by first introducing known amount of SbF_5 and condensing ClF_3 over it in known excess quantity. The temperature was controlled carefully between the melting point of SbF_5 (7.0°C.) and the boiling point of ClF_3 (11°C.), but still some solid precipitation was left on the bottom of the cell.

In some cases measurement was made at -78°C., but generally the changes could not be measured with good accuracy. The resistance (8-20 ohms) was very near to the lower limit of the measuring capability of the instrument (1 ohm). A cell with a lower cell constant should be built to shift these values to a more accurate range of the instrument.

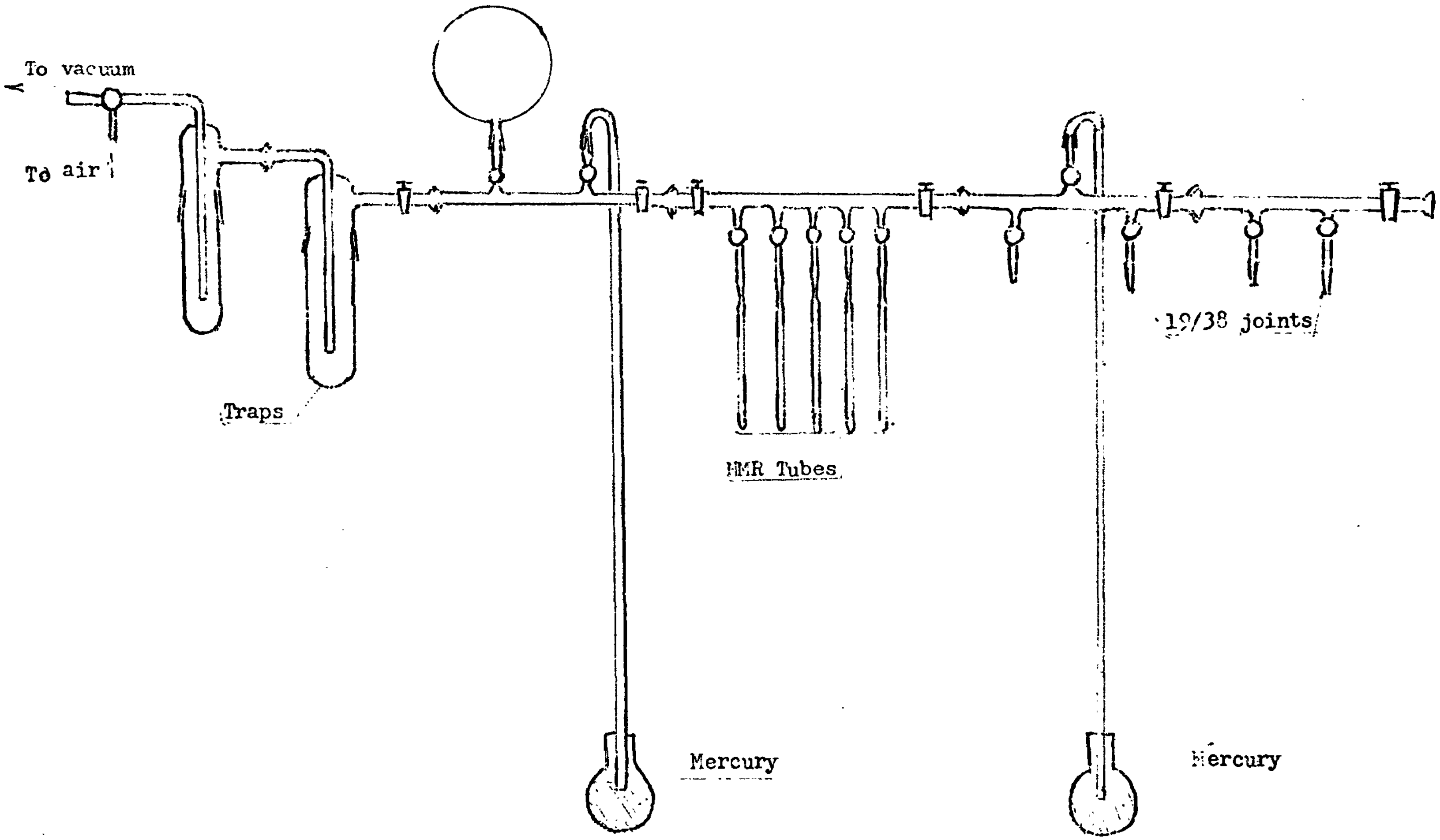
Infrared Spectrum

Both NaCl and IRTRAN-2 windows were dipped into liquid ClF_3 and kept there for 5-15 minutes. The NaCl showed slow but definite attack, while IRTRAN-2 gave no visible sign of any corrosion. When ClF_3 was used in a cell with NaCl windows only the spectrum of NaF was observed.

A special cell was designed for low temperature work according to the drawing shown. The available IRTRAN-2 windows showed too strong background; therefore, a new pair of windows was ordered.

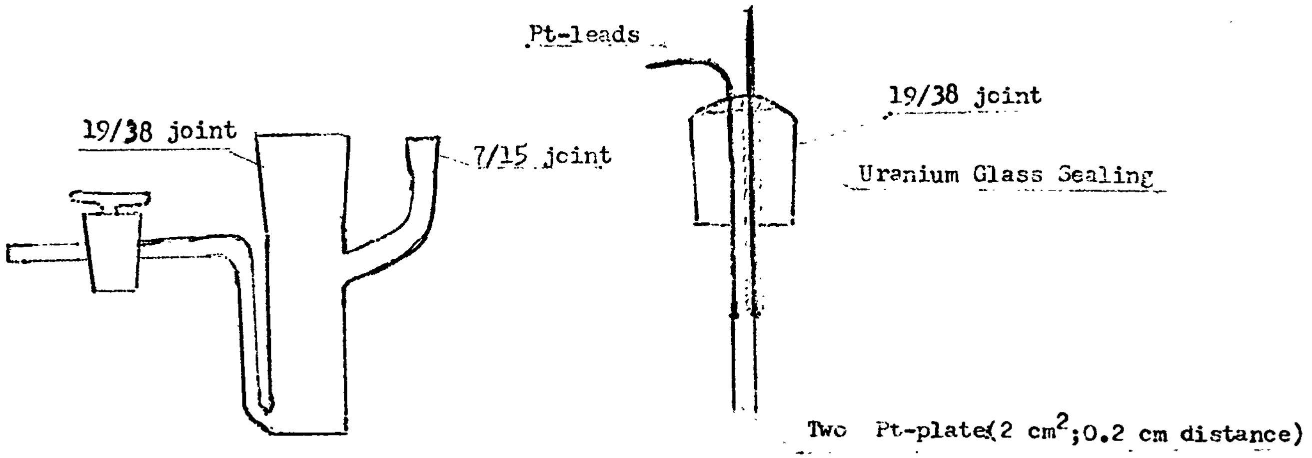
AEP:ls
May 8, 1963

DRAWING I



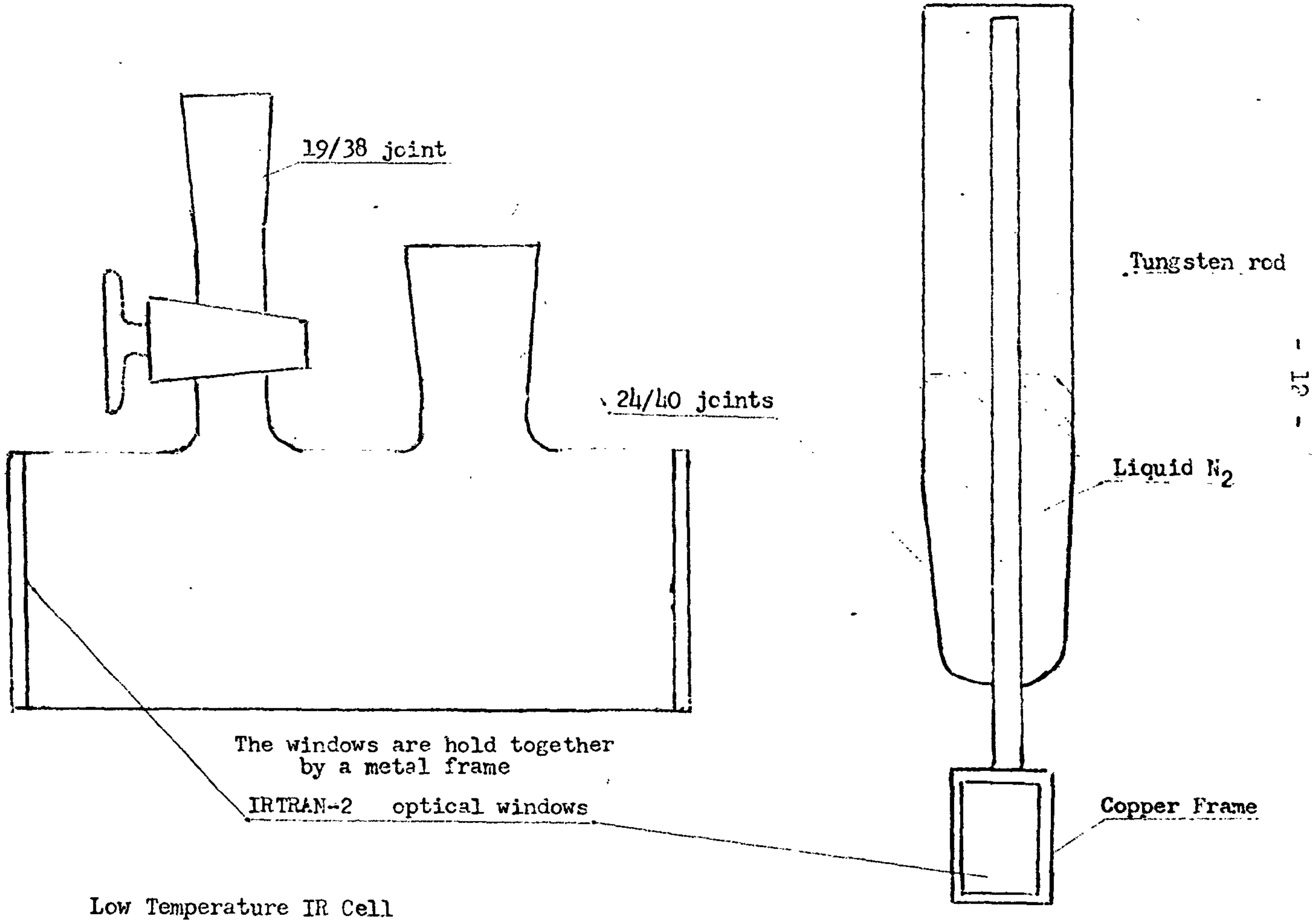
Vaacum Line

DRAWING II



Conductivity Cell

DRAWING III



Low Temperature IR Cell