Stauffer

HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

STAUFFER CHEMICAL COMPANY

Western Research Center
Richmond, California

Stauffer

HIGH ENERGY OXIDIZERS

CONTRACT Nonr-4019(00)

Project NR 093-035

STAUFFER CHEMICAL COMPANY

Western Research Center
Richmond, California

STAUFFER CHEMICAL COMPANY
Western Research Center
Richmond, California

"HIGH ENERGY OXIDIZERS"

CONTRACT Nonr-4019(00)

Project NR 093-035

ARPA No. 399-62

OFFICE OF NAVAL RESEARCH

WASHINGTON, D. C.

Quarterly Technical Summary Report

for the Period May 1, 1965 to July 31, 1965

Investigators

Karl O. Christe
Dr. K. O. Christe

Dr. J. P. Guertin

Dr. A. E. Pavlath

Department Supervisor

Dr. E. G. Wallace

Western Research Center
Richmond, California

TABLE OF CONTENTS

Page No.

Foreword i

Abstract 1

I. Introduction 2

II. Manuscript of Paper 4

III. Glow-discharge apparatus 15

IV. Correction of X-ray data on $KClF_2$, $RbClF_2$, and $CsClF_2$ 18

Technical Report Distribution List a

Foreword

This is the second Quarterly Technical Summary Report of the third year's investigation of complexes based on chlorine fluorides. It covers the period from May 1, 1965 to July 31, 1965. The work was conducted at the Western Research Center, Richmond, California, Stauffer Chemical Company, under the sponsorship of the Advanced Research Projects Agency. This work was administered by the Department of the Navy, Office of Naval Research, with Mr. R. L. Hanson serving as Scientific Officer, under ARPA No. 399-62.

This report includes (i) the first draft of a paper on the structure of the ClF_4^- anion, which will be submitted for publication, (ii) a description of our new setup for glow-discharge reactions, and (iii) additional results and a correction of the X-ray data obtained for $KClF_2$, $RbClF_2$, and $CsClF_2$.

Abstract

Infrared and conductivity measurements show that $MClF_4$ (where M is NO, Rb, or Cs) is ionic in the solid state and in solution, respectively. A square-planar structure (point group D_{4h}) is assigned to the ClF_4^- anion in $Rb^+ClF_4^-$ and $Cs^+ClF_4^-$. For the ClF_4^- anion in $NO^+ClF_4^-$ the low-temperature infrared measurement indicates a lower symmetry (at least as low as point group D_{2h}).

A vacuum line, which will enable us to run glow-discharge reactions at low temperatures and reduced pressures, was designed and built.

Density measurements on the alkali metal difluorochlorates(I) indicate that the X-ray patterns given in the preceding Quarterly Report are probably due to small amounts of alkali metal bifluorides, present as impurities.

I. Introduction

One of the objectives of this contract is to prepare and characterize new complexes based on chlorine fluorides and to resolve the ionic character and structure of these and those already known. The following ions, based on chlorine fluorides, are theoretically possible*:

$$Cl^+ \xleftarrow{-F^-} ClF \xrightarrow{+F^-} ClF_2^-$$

$$ClF_2^+ \xleftarrow{-F^-} ClF_3 \xrightarrow{+F^-} ClF_4^-$$

* The chemistry of (ClF_5) is classified.

The complex formation of ClF_3 with strong Lewis acids and bases has been reported in the literature; however, nothing was known about the nature and structure of these complexes. In the course of our contract we successfully proved the ionic character and structure of the ClF_2^+ cation. In addition to this, we succeeded in preparing the previously unknown ClF_2^- anion in form of its NO^+, K^+, Rb^+, and Cs^+ salts. These compounds were shown to be ionic and their structures were resolved. During the past quarter the structure of the ClF_4^- anion was investigated. In this way the structure of all unclassified ionic chlorine fluoride complexes was determined. We showed that they are ionic and that the ClF_2^- and ClF_4^- anions are isostructural with the isoelectronic noble gas fluorides and the ClF_2^+ anion isostructural with the isoelectronic SF_2 molecule.

Another object of this contract has been to combine the chlorine fluoride based ions with other ions of high energy content in order to obtain potential solid oxidizers. However, all attempts have failed. Therefore, experiments will be undertaken to prepare other ionic moieties, resulting in potential high-energy oxidizers. For this purpose a complex vacuum system was designed and built to include a glow-discharge unit. Our first experiments will consist of low-temperature glow-discharge reactions between $NF_3 + F_2 + AsF_5$ in an attempt to prepare $NF_4^+AsF_6^-$.

II. Manuscript of Paper

To be submitted in slightly modified form for publication.

Contribution from the Western Research Center
Stauffer Chemical Company, Richmond, California

Structural Possibilities for the Tetrafluorochlorate(III) Anion, ClF_4^-

by Karl O. Christe and Jacques P. Guertin

Abstract

Infrared and conductivity measurements show that $MClF_4$ (where M is NO, Rb, or Cs) is ionic in the solid state and in solution, respectively. A square-planar structure (point group D_{4h}) is assigned to the ClF_4^- anion in $Rb^+ClF_4^-$ and $Cs^+ClF_4^-$. For the ClF_4^- anion in $NO^+ClF_4^-$, the low-temperature infrared measurement indicates a lower symmetry (at least as low as point group D_{2h}).

Introduction

While the existence of $MClF_4$ (where M is NO, K, Rb, or Cs) is well known[1-4], no reports on the ionic character of the NOF-ClF_3

---

(1) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, J. Am. Chem. Soc., 83, 2955 (1961).

(2) D. H. Kelly, B. Post, and R. W. Mason, ibid., 85, 307 (1963).

(3) E. Whitney, R. MacLaren, C. Fogle, and T. Hurley, ibid., 86, 2583 (1964).

(4) E. Whitney, R. MacLaren, T. Hurley, and C. Fogle, ibid., 86, 4340 (1964).

adduct and on the structure of the ClF_4^- anion have been published. Asprey[3] et al. obtained the infrared spectrum of $KClF_4$; however, the absorptions reported by them occur at much higher frequencies than expected for the fundamental vibrations of the ClF_4^- anion. Therefore, they could have obtained only overtones and combination frequencies.

The structure of the ClF_4^- anion can be expected to be similar to that of the BrF_4^- anion, since both $KClF_4$[2] and $KBrF_4$[5] crystallize in the tetragonal system and have similar unit cell dimensions. Siegel interpreted the X-ray diffraction pattern of $KBrF_4$ in terms of a tetrahedral configuration of the BrF_4^- anion. However, the pattern can be interpreted in terms of a planar BrF_4^- anion[6,7] as well. The tetrafluoroiodates(III) of potassium, rubidium, and cesium have been prepared[8], but the structure of the anion has not been investigated. However, it was reported[8] that the X-ray powder diagrams are complex and that the IF_4^- compounds are probably not isostructural with the corresponding BrF_4^- compounds. Therefore, the evidence reported previously in the literature is insufficient

---

(5) S. Siegel, Acta Cryst., <u>9</u>, 493 (1956).

(6) W. G. Sly and R. E. Marsh, ibid., <u>10</u>, 378 (1957).

(7) S. Siegel, ibid., <u>10</u>, 380 (1957).

(8) G. B. Hargreaves, and R. D. Peacock, J. Chem. Soc., 2373 (1960).

to prove the structure of any of the tetrafluorohalogenate(III) anions. However, based on the known square-planar structure of the ICl_4^- anion[9] and of the isoelectronic XeF_4[10], the square-planar structure seems most likely.

The knowledge of the structure of interhalogen complexes such as the tetrafluorochlorates(III) is important for theoretical bonding considerations, since a certain symmetry of a compound could rule out certain theoretical bond models. If, for example, the tetrafluorochlorate(III) anion would be tetrahedral, the semi-ionic bond model[10] would be incorrect.

Experimental

The compounds examined were prepared as described in the literature[3,4]. The infrared spectra of $RbClF_4$, $CsClF_4$, and $NOClF_4$ were taken with a Beckman IR-9 spectrophotometer in the range 4000 - 400 $cm.^{-1}$. The spectrum of $RbClF_4$ was also recorded on a Beckman IR-11 spectrophotometer in the range 800 - 33 $cm.^{-1}$. Nujol mulls or dry powder between AgCl or polyethylene disks were employed. The low-temperature spectrum of $NOClF_4$ was taken using

---

(9) R. C. L. Mooney, Z. Krist. 98, 377 (1938).

(10) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, Chem. Rev., 65, 199 (1965).

the same technique described earlier for $NO^+ClF_2^-$ [11] and $ClF_2^+AsF_6^-$ [12]. The conductivity measurements were done using the method reported earlier[11].

Results

<u>Conductivity</u>. - The solubility of $NOClF_4$ in liquid ClF_3 at -23° was very low. Table I shows the results obtained for a saturated solution of $NOClF_4$ in liquid ClF_3.

Table I

Conductivity of $NOClF_4$ in liquid ClF_3

Compound	Temp., °C	Specific conductance, σ ohm^{-1} cm^{-1}
ClF_3	-23	9.2×10^{-9}
NOF	-79	5.4×10^{-5}
Saturated solution of $NOClF_4$ in liquid ClF_3	-23	2.1×10^{-7}

Assuming complete solubility of the $NOClF_4$ in ClF_3 (not actually the case) the solution would have had a molarity of 0.079 mole l.$^{-1}$, and thus a minimum equivalent conductance, $\Lambda = 3.69 \times 10^{-3}$ ohm^{-1} cm^2.

---

(11) K. O. Christe and J. P. Guertin, Inorg. Chem., <u>4</u>, 905 (1965).

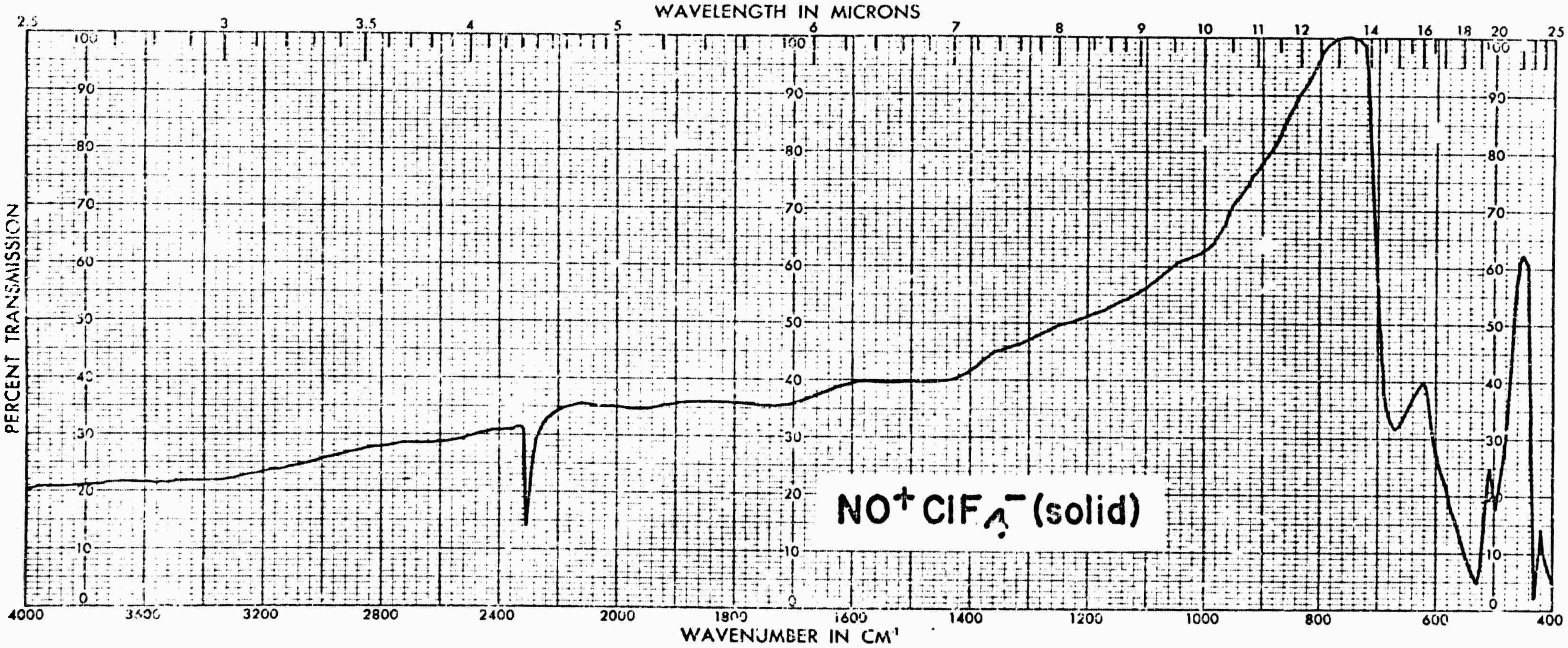
(12) K. O. Christe and A. E. Pavlath, Z. anorg. allgem. Chem., <u>335</u>, 210 (1965).

Infrared Spectra. - Table II shows the absorption frequencies of $NOClF_4$, $RbClF_4$, and $CsClF_4$. The frequencies of the pure solid starting materials, NOF[11] and ClF_3[12], have previously been reported. The $NOClF_4$ sample was prepared directly on a cold AgCl window using excess NOF or excess ClF_3. It was found more convenient to remove unreacted NOF from $NOClF_4$, due to its greater volatility. Figure 1 shows the low-temperature infrared spectrum of solid $NOClF_4$.

Table II

Infrared absorption frequencies ($cm.^{-1}$) of $MClF_4$ and vibrational assignments for $RbClF_4$ and $CsClF_4$ in point group D_{4h}

$RbClF_4$	$CsClF_4$	assignment for $RbClF_4$ and $CsClF_4$ in the point group D_{4h}	$NOClF_4$
1242 mw		$\nu_6 + \nu_7$	2298 m νNO^+
745 vs	742 vs	ν_6 (E_u)	676 ms 541 vs
486 s	478 s	ν_7 (E_u)	498 m
430 m	425 m	ν_2 (A_{2u})	434 s
118 m		lattice vibration	


WAVELENGTH IN MICRONS
2.5
3
3.5
4
5
6
7
8
9
10
11
12
14
16
18
20
25
PERCENT TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
$NO^+ ClF_4^-$ (solid)
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER IN CM⁻¹

Discussion

$NOClF_4$, Ionic Character. - Three reasonable structures for the complex are: coordination complex, $ClF_3 \cdot NOF$(I); $ClF_2^+NOF_2^-$(II); $NO^+ClF_4^-$(III). Structure I should show no significant conductivity increase in ClF_3 solution and would require an infrared spectrum similar to that of ClF_3 superimposed on NOF with perhaps some shifting of absorption bands. The NO bond in structures I and II has double bond character and should absorb at 2000-1800 $cm.^{-1}$. In structure III the NO bond has triple bond character and should absorb at 2350-2100 $cm.^{-1}$ [13]. The solution containing the complex has an increased conductivity and the infrared spectrum shows the NO absorption at 2298 $cm.^{-1}$ indicative of the NO^+ cation. In addition, considering only symmetry, structure II would have required a higher number of infrared-active vibrations, the position of which would have to have been quite different. Thus, structure III is assigned to the complex.

Structure of the ClF_4^- anion. - Table III shows the point groups taken into consideration as structural possibilities for the ClF_4^- anion and the infrared-active fundamental vibrations expected for each group.

---

(13) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, Inorg. Chem. 1, 661 (1962).

$RbClF_4$ and $CsClF_4$. - Since $NO^+ClF_4^-$ and the alkali metal tetrafluorochlorates(III) do not show the same number of asborption bonds and do not have similar frequency positions, these compounds will be treated separately. The spectra of the alkali-metal tetrafluorochlorates(III) show only three infrared-active fundamental vibrations. The absorption at 118 cm.$^{-1}$ in $RbClF_4$ is too low to be a fundamental vibration, and therefore, is assigned to a lattice vibration, in agreement with values found for K_2PtCl_4 and similar compounds[14]. The band at 1242 cm.$^{-1}$ occurs at too high a frequency to be a ClF fundamental and consequently, is assigned to a combination vibration. Therefore, since only three infrared active-fundamentals were found, a square-planar structure can be assigned to the ClF_4^- anion and the other structural possibilities can be ruled out.

A square-planar molecule of the type XY_4 has D_{4h} symmetry. The nine normal modes of vibration are classified as ($A_{1g} + A_{2u} + B_{1g} + B_{1u} + B_{2g} + 2\ E_u$). Of these, only the E_u and A_{2u} modes will be infrared active in the isolated molecule, assuming that the selection rules in the solid are the same as they would be for the free gaseous ion.

---

(14) A. Sabatini, L. Sacconi, and V. Schettino, Inorg. Chem 3, 1775 (1964).

Table III

Number of infrared-active fundamentals expected for the ClF_4^- anion in different point groups

Point group	Structure	Total number of infrared-active fundamentals	Number of infrared-active stretching vibrations	Number of infra-red-active deformation vibrations
T_d	Tetrahedral XY_4	2	1	1
D_{4h}	square-planar XY_4	3	1	2
D_{2h}	planar trans-XY_2Z_2	6	2	4
C_{2v}	non-planar XY_2Z_2	8	4	4

The bands within the range of possible fundamentals in the spectrum of $RbClF_4$, occur at 745, 486, and 430 $cm.^{-1}$. The band at 745 $cm.^{-1}$ is undoubtedly the Cl-F E_u stretching mode. Out of the two expected infrared-active deformation vibrations the in-the-plane vibration likely has a higher frequency than the out-of-plane vibration. Therefore, the bands at 486 $cm.^{-1}$ and 430 $cm.^{-1}$ are assigned to the vibration of the E_u species and the A_{2u} species, respectively. Slightly lower frequencies were obtained for these modes in $CsClF_4$. Table II contains the vibrational assignments of the observed frequencies in the point group D_{4h} for both compounds.

$\underline{NO^+ClF_4^-}$. - The low-temperature infrared spectrum of $NO^+ClF_4^-$ shows one more band in the observed range than that of the alkali-metal tetrafluorochlorates(III). In addition, the positions of the higher frequency bands differ considerably. The number of observed bands rules out the tetrahedral (T_d point group) and the square-planar (D_{4h} point group) structure. The planar trans-XY_2Z_2 structure appears to be most likely. In this case, the band at 498 $cm.^{-1}$ would be a deformation vibration. However, the band at 541 $cm.^{-1}$ is asymmetric and most spectra of $NO^+ClF_4^-$ showed a very weak shoulder at 570 $cm.^{-1}$. Based on this, and the fact that the position of the band at 498 $cm.^{-1}$ does not exclude its interpretation as a stretching vibration, the possibility of assigning the ClF_4^- anion in $NO^+ClF_4^-$ to the point group C_{2v} can not be eliminated. In any case, the symmetry of the ClF_4^- anion in $NO^+ClF_4^-$ at low temperature appears to be lower than D_{4h} found for $RbClF_4$ and $CsClF_4$.

The lower symmetry of the ClF_4^- anion in $NO^+ClF_4^-$ at low temperature might be explained by either of the following two theories, again assuming that the selection rules in the solid are the same as for the free gaseous ion.

(i) If the fluoride ion approaches the acceptor molecule, ClF_3, the attack might take place axially to the fluorine atom, right angled to the other two fluorine atoms, coaxial wit the chlorine atom. The bond strength and F-Cl-F distance of the newly formed linear F-Cl-F group would be different from the one already existing in the unreacted ClF_3 molecule. A planar trans-XY_2Z_2 molecule (point group D_{2h}) might exist at low temperature, assuming that the newly formed F-Cl-F group has identical F-Cl bonds (reasonable if based on the semi-ionic bond theory, where the singly occupied orbitals of the two fluorine atoms are overlapped by only one delocalized p orbital of the chlorine atom), which differ from those of the other non-affected F-Cl-F group and that a certain activation energy is required for the transition into four identical bonds.

(ii) The fluoride ion can attack the ClF_3 molecule nonaxially to the existing Cl-F axis. This might occur if the fluoride ion is more strongly repelled by the two free electron-pairs than by the fluorine atoms. The result would be a ClF_4^- anion of symmetry C_{2v}, which could rearrange at elevated temperature to an energetically more favored ion of higher symmetry, a square-planar ClF_4^- anion.

Conclusion

(i) The tetrafluorochlorate(III) anion in $RbClF_4$ and $CsClF_4$ is square-planar (symmetry D_{4h}).

(ii) The tetrafluorochlorate(III) anion in $NOClF_4$ at low temperature has lower symmetry than D_{4h}.

(iii) The square-planar structure found for the ClF_4^- anion in $RbClF_4$ and $CsClF_4$ is in agreement with either the semi-empirical molecular orbital model, assuming semi-ionic bonds, or the sp^3d^2-hybridization model.

(iv) The lower symmetry of the ClF_4^- anion in $NOClF_4$ may be due to the existence of stereo isomers at low temperature.

(v) Since $KClF_4$ and $KBrF_4$ are isostructural according to their x-ray data, the interpretation of $KBrF_4$ in terms of a planar rather than a tetrahedral BrF_4^- anion seems more likely.

Acknowledgment. We thank Dr. A. E. Pavlath for helpful discussions and Dr. J. Scherer and Mr. G. Bailey, of the U. S. Department of Agriculture, Albany, California, for the use of the Beckman IR-11 spectrophotometer. This work has been supported by the Advanced Research Projects Agency and the Office of Naval Research.

III. Glow-discharge apparatus

The apparatus of Schreiner et al.[rf.] has been slightly modified. We have eliminated the metal spring attached to the piston to avoid possible failure in pumping operation due to corrosion of this spring. Figure 1 illustrates the glow-discharge apparatus. The circulation pump A, B, and C, the discharge zone and following traps E, F, and O, the mercury diffusion pump P, and the McLeod gauge Q are all made from Pyrex glass. Copper tubing and Monel fittings are used wherever possible to minimize corrosion. A second mechanical pump is used solely for the purpose of eliminating any elemental fluorine (which can not be completely condensed at -196°) that had not been completely flushed out by dry helium. Exact volumes of each significant part of the vacuum line were obtained by expanding air at known volume and pressure into the system and recording the resultant pressure. The following symbols in Figure 1 are defined:

A - uni-directional ground-glass valves,

B - ground-glass tube,

C - iron (powder)-filled piston, also ground glass,

D - copper coils for ease in disassembling,

E - discharge zone with copper electrodes,

(rf.) F. Schreiner, J. G. Malm, and J. C. Hindman, J. Am. Chem. Soc., 87, 25 (1965).

F - traps for volatile material,

G - Monel Hoke bellows-seal valves (Kel-F stem, 0-200 p.s.i., No. M482M),

H - Monel Whitey valves No. M6TS6,

I - Monel high-pressure cylinders (~300 ml.),

J - Monel Helicoid gauges (-30 in. to 0 and 0 to 300 p.s.i.),

K - Monel Wallace and Tiernan gauge (0-30 in. ± 0.02 in., Model No. FA145),

L - vacuum side,

M - sample side,

N - dry helium cylinder,

O - pump traps (liquid N_2),

P - mercury diffusion pump,

Q - McLeod gauge (0-0.001 mm),

R - mechanical pumps (Halocarbon oil),

S - direction of gas flow.

Figure 2 shows the solenoid system.

Two air-cooled solenoids, S, externally surround tube B and move the piston, C, back and forth at controlled intervals. They are ~4 cm. long, ~1.5 cm. thick (including insulation), and have a hollow core ~2.3 cm. in diameter; the design (Western Electro-Mechanical Co., Oakland, Calif.) allows continuous operation on a 120 v. A.C. line without overheating. A selenium rectifier, RC, (single ph. Bridge, No. J116B1) changes A.C. to D.C. A timer, t,

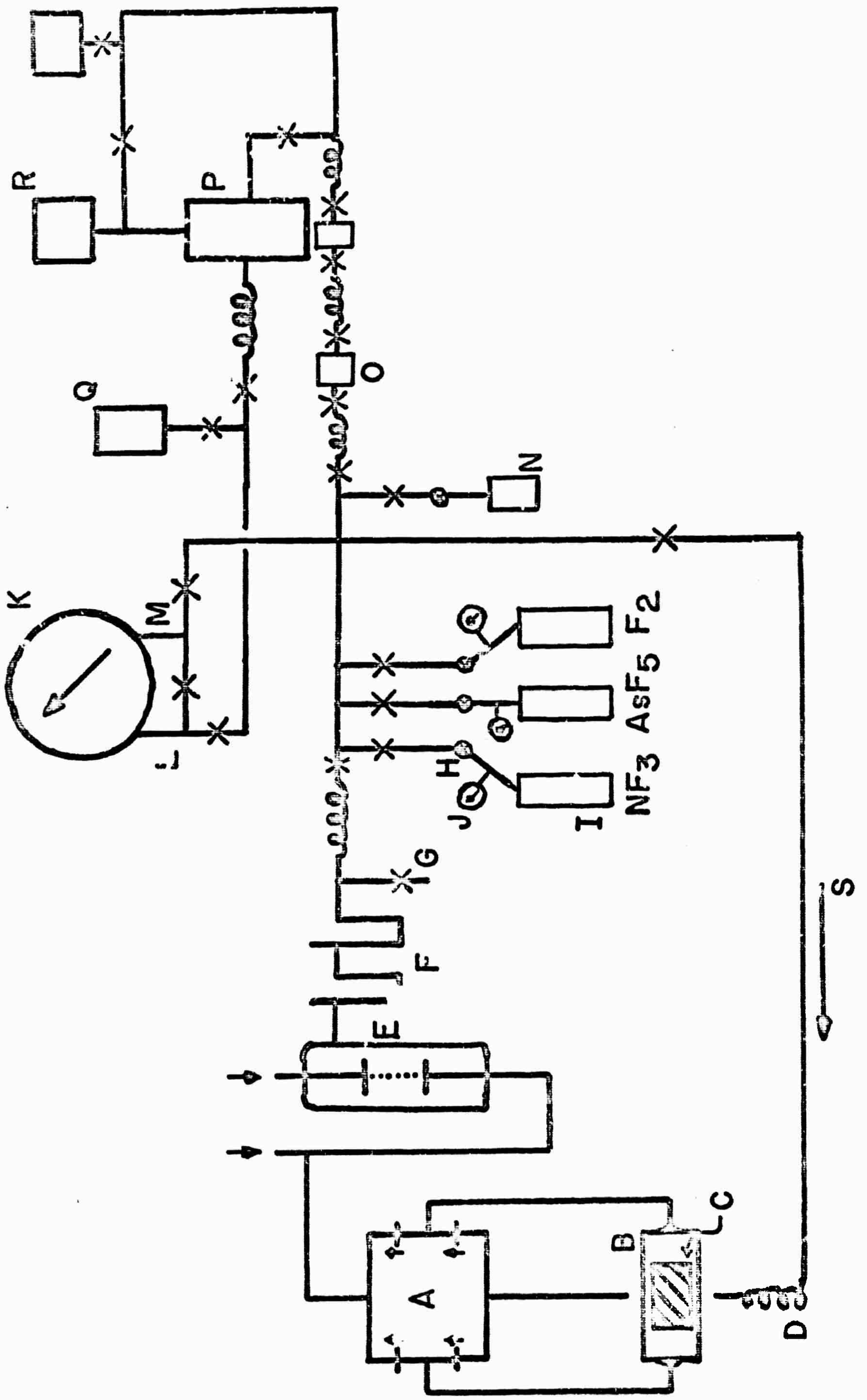


Fig. I

(Flexopulse 0-120 sec., Eagle Signal Co., Moline, Ill.) coupled with a relay, RY, (Mercury column type, 1 ma. at 115 v., Kerman Electric, Brooklyn, N. Y.) provides the means of operating one solenoid at a time for a certain period of time, i.e., when one solenoid is "on" the other is "off". We are presently operating the timer at 5 seconds "on" and 5 seconds "off".

Figure 3 shows the electrode system.

An A.C. voltmeter, V, (0-150 v., Simpson type) and an A.C. ammeter, A, (0-100 ma., Simpson type) are used to monitor the setup protected by a fuse (Littlefuse, 4 amp. and 125 V.). The transformer, TR, (Jefferson luminous tube outdoor type, primary 120 v. 60 cycles, secondary 15,000 v. 30 ma. with midpoint of secondary grounded; Jefferson Electronic Co., Bellwood, Ill.) provides the necessary voltage for the discharge. Ignition wire (Packard 440) is used throughout the high-voltage circuit.

IV. Correction of X-ray data on $KClF_2$, $RbClF_2$, and $CsClF_2$

In our last Quarterly Report we had assigned X-ray powder diffraction patterns for these compounds and on this basis had calculated unit cell dimensions for the alkali metal difluorochlorates(I). These unit cell dimensions were very similar to that of the corresponding bifluorides. Density measurements were carried out on the difluorochlorates(I) in order to decide whether these patterns arise from the difluorochlorates(I) or from small amounts of the corresponding bifluorides present as impurities. The large deviations between

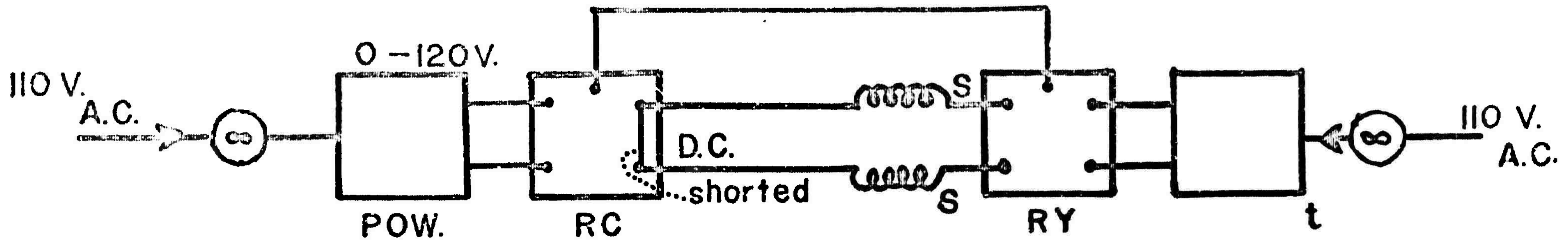

110 V.
A.C.
0 – 120 V.
POW.
RC
D.C.
...shorted
S
S
RY
t
110 V.
A.C.

Fig. 2

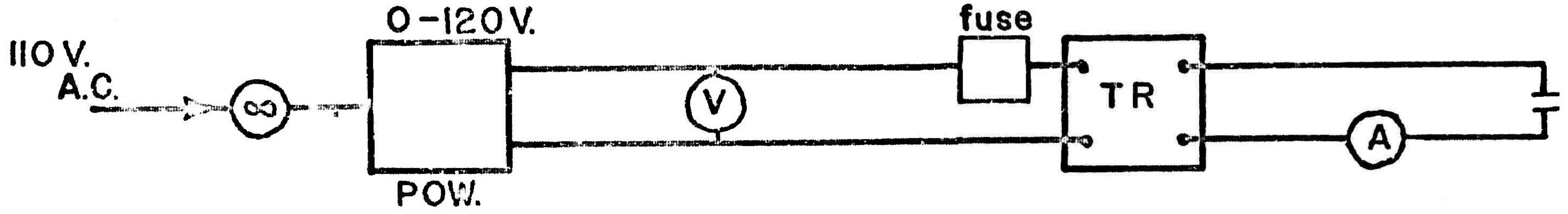

110 V.
A.C.
0 – 120 V.
POW.
V
fuse
TR
A

Fig. 3

the found and calculated densities indicate that the observed patterns are probably due to the presence of small amounts of the corresponding bifluorides. Consequently, the previously reported X-ray data for $KClF_2$, $RbClF_2$, and $CsClF_2$ should be debased.

The density measurements were carried out by the displacement method using a perfluorinated cyclic ether to fill the pycnometer, as described in the literature[3].

In addition, the statements, concerning the interaction between NOF and CsF were rephrased, since presently nothing can be said about the exact nature of the interaction between the two compounds.

ls

August 25, 1965