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1 JANUARY - 31 MARCH 1963

ELECTROCHEMICAL STUDIES IN THE
SYNTHESIS OF N-F COMPOUNDS

Contract No. Nonr-4054(00)

Research Project No. RR001-06-02

28 May 1963

T R A C O R , I N C.

1701 Guadalupe St.   Austin 1, Texas   GR6-6

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TRACOR, Inc.

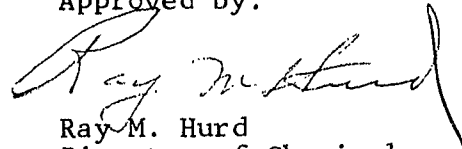Contract No. Nonr-4054(00)

Research Project No. RR001-06-02

May 28, 1963

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Abstract

The aim of this project is to determine the likelihood of obtaining ionic species containing only N and F or N, H, and F in anhydrous hydrofluoric acid (AHF) solutions. The experimental approach is based on the determination of theoretical and electrochemical properties of solution species in solutions obtained by dissolving compounds such as NF_3, NHF_2, and N_2F_4 in AHF. Constant potential techniques are planned using passivated electrodes to study the mechanism of the electrosynthesis of N - F compounds (e.g. NF_3) when NH_3 is electrolyzed in AHF. Concurrent conductance experiments will be used to determine the concentration of ionic (protonated) species in solutions of the N - F compounds in AHF. By combining the data from these two types of experiments, the extent of participation of protonated N - F species in the electrode reactions can be determined. Depending on whether the electrofluorination reaction proceeds stepwise or randomly, it can then be determined whether such species as NF_4^+, or $N_2F_5^+$ can be obtained within the limitations of solvent stability and the chemical stability of the species.

An electrochemical cell has been designed and assembled which provides for the production of solutions of the N - F compounds of known concentration. Nickel electrodes for electrolysis and for conductance measurements have been provided. The cell is refrigerated so that constant volume and temperature may be maintained during the electrolytic experiments. Polarization curves have been taken in the cell to determine the best way to passivate the various nickel electrodes so that the amount of ionic contamination of the AHF can be kept to a minimum, and as soon as a satisfactory method has been found, electrolysis experiments will begin with NH_3 solutions. Work with the hydrazines will follow completion of the NH_3 experiments.

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

I.   INTRODUCTION

The aim of this project is to determine the likelihood of obtaining ionic species in anhydrous hydrofluoric acid (AHF) which contain only N and F or N, H, and F. The emphasis of the present experimental approach is on electrochemical theory and techniques for determining properties of solution species. The data are expected to provide distinct guidelines for subsequent synthetic work. The reason for choosing AHF is because it is one of the most acid solvents known, and therefore, is the one most likely to protonate such weak bases as NF_3. In addition, electrolysis in HF produces F atoms for fluorinations without the necessity for adding special fluorinating agents. The ultimate goal is to try to produce NF_4^+ and/or $N_2F_5^+$ by electrolysis in AHF, and then to try to discover means of incorporating them in ionic crystalline solids. It is recognized, however, that ionic crystalline solids containing such species as $NH_2F_2^+$, NHF_3^+ or $N_2HF_4^+$ would also have great potential for solid rocket oxidizers, and means of incorporating these species into solids will also be sought. The work is split into two related and essentially parallel phases which have slightly different goals. The two phases comprise a conductance study in AHF, and an electrochemical mechanism study of fluorinations in AHF. It is anticipated that the major effort will be expended in the mechanism study.

## II.   CONDUCTANCE WORK IN ANHYDROUS HYDROFLUORIC ACID

The first step in this work will be the determination
of the conductance of solutions in AHF of gases, such as NHF_2,
NF_3, N_2F_4, and NH_3, to determine the extent of ionization
(protonation) by the solvent. This work will also produce an
order of base strength for the compounds which will be useful
for the other phase. Because of its solubility in concentrated
sulfuric acid, it is anticpated that NHF_2 as well as the less
highly fluorinated species will be not only quite soluble in
AHF but also strongly protonated. Consequently, experimental
measurements will be carried out on NF_3 early in the course of
this phase to determine where this compound fits the pattern.
Ammonia is of course strongly protonated in AHF and will serve
as a reference compound from which the specific conductivities
and other transport properties for the fluorinated species can
be calculated.

The culmination of this phase will be a series of con-
ductimetric titrations using such anions as BF_4^- or $ClO_3F^=$ to see
whether these ions can be used to stabilize the protonated cation
much as the highly electropositive elements stabilize the boro-
hydrides. For use as a rocket oxidizer, the best combination of
stable cation-anion will be that in which both are oxidizing, and
this will be borne in mind in choosing the anions for these experi-
ments. A series of these titrations carried out as a function
of concentration will indicate the feasibility of crystallization
of the salts from AHF.

III.   STUDY OF THE MECHANISM OF ELECTROCHEMICAL FLUORINATION
OF NITROGEN SPECIES IN AHF

The goal of this study is to identify the participating
N-F species and from this step to evaluate the possibilities
for producing NF_4^+ and $N_2F_5^+$. These goals were derived through
the following reasoning: When NH_3 is dissolved in AHF and
electrolysed to produce NF_3 (refs 1 & 2), the over-all process
involves substitution of F for hydrogens in a protonated,
cationic species

$$NH_4^+ + 2xF \cdot \rightarrow NH_{4-x}F_x^+ + xHF$$
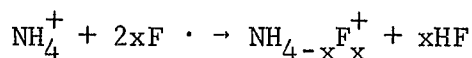
The $NH_{4-x}F_x^+$ may subsequently deprotonate and volatilize,
but the initial reactant (at the electrode) is almost certainly
the protonated cation. If NF_3 is appreciably protonated in AHF,
the logical extension of this argument leads to the conclusion,
that electrochemical generation of NF_4^+ may very well be possible
by the same type mechanism. The decomposition potential of the
solvent will have to lie beyond the potential required to tetra-
fluorinate, and, to be consistent with present knowledge about
electrosynthesis of NF, the process would have to be stepwise.
The other possibility for formation of the NF_3 electrochemically
in AHF is for the electrochemical step to be only an active F
generator and the fluorination step to be controlled by chemical,
rather than electrochemical parameters.

Relatively unsophisticated polarization experiments will
be used to determine first whether the process is stepwise and
therefore involves nitrogen species with intermediate degrees of
fluorination, or whether fluorination is brought about by
electrochemical generation of active F atoms. In order to make
observations over the widest possible range of potentials, it
will undoubtedly be necessary to use anodically passivated elec-
trodes. The nature of the passivation process will require the
use of controlled potential techniques.

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The experimental work in this phase will consist in experiments designed to yield information about the potentials required for the different stages of the electrochemical fluorination reaction, the electrode-metal dissolution reaction, the electrode passivation process, and the solvent decomposition reaction. The groundwork experiments will consist in taking constant potential polarization curves using a third, nonpolarized reference electrode. A suitable reference electrode will have to be found or developed. Depending on the information gained in these experiments, investigation of the mechanism may proceed using chronopotentiometry or allied techniques to determine whether the step-wise fluorination becomes progressively more difficult energetically or chemically, i.e., whether the NF_4^+ is attainable within the solvent limitations and the fundamental limitations of the chemical stability of the species.

The pioneering work which has been reported by the researcher at Rocketdyne has been of great value to the design of our experiment and the following description of the planned approach contains conclusions, based on a study of their reports (refs 3, 4, & 5). It should be noted that there will be at least two major differences in our approach compared to theirs. First, it is planned to use a potentiostat and to operate therefore at controlled potentials; and second, it will be necessary to have very pure AHF so that the only possible electroreactions can be kept to the following: (1) dissolution of the electrode; (2) decomposition of solvent; and (3) fluorination of the nitrogen species. The reasons for these differences will become apparent from the discussion below.

It is known from mixed potential theory that when a constant current is impressed on an electrode which is immersed in a solution such that several different electroreactions can occur simultaneously the potential assumed by the electrode will depend on a complex interaction of variables such as concentration of the various electroactive species, composition of the electrode, or solvent. For this reason, if the equilibrium potentials for the various reactions are different, as they usually are, potentiostatic control of the electrode rather than amperometric control will allow the various

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various reactions to be separated and the contribution each makes
to the data evaluated.

One of the biggest difficulties associated with electro-
chemical work in AHF is the corrosion of the electrodes, particu-
larly under anodic conditions. For this reason almost all electro-
chemical work in this solvent aimed at mechanism information will
have to deal with a mixed reaction-mixed potential situation.
Fortunately passivation has been observed for some metals in AHF
(ref 6) so that in principle working with potentiostatic control,
it should be possible to work in a potential region where the
current consumed by the electrode dissolution reaction is small
compared to the reaction under study. In some cases, as for
example on silicon in aqueous media (ref 7), it is possible to
carry out cathodic reactions on passivated electrodes at potentials
which are active compared to the primary passive potential. In
any case, it is possible to use passivated electrodes as if they
were inert if potentials are maintained in the passive region.
In addition, if the current required to maintain passivity is
very small compared to the exchange current of the reaction under
study, the observed potential and the equilibrium potential for
the reaction studies will coincide; (ref 8).

The energetics of an electroreaction and its equilibrium
potential are intimately related, so that in the case of successive
fluorination of NH_4^+ or $N_2H_5^+$, if the process is entirely electro-
chemical (as contrasted to electrochemical generation of fluorine
followed by chemical fluorination of the amine), replacement of
each successive hydrogen atom by a fluorine atom should be associ-
ated with a specific potential. If so, then by appropriate elec-
trochemical techniques, each step should be isolable for study
provided these potentials are sufficiently separated. Furthermore,
it should be possible to determine the likelihood of electrochemical
generation of cationic species containing only N and F based on a
study of the mechanism and of the occurrence potentials for the
preceding stepwise reactions. Formal thermodynamic correlations
will probably be unobtainable in AHF because of the lack of a
well defined reference electrode and of a defined potential system.

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The feasibility of these arguments is supported first of
all by the fact that NF_3 is produced by electrosynthesis in AHF
(ref 1 & 2) and secondly by the reported observation that the
products of the electrolysis are different depending on whether
active or passive electrodes are used (ref 9). It should be noted
at this point that the data which lead the Rocketdyne workers to
conclude that surface effects are of prime importance to the
nature of the products formed in the electrolysis of NH_3 in AHF,
can also be interpreted by reference to the electrode potentials
to mean that the electrode potential is very important and that
there can be an advantage to potentiostatic operations. For
example, in Figure 1, of their quarterly progress report (ref 6a)
it is noted that before passivation, a current of 10.4 amperes
produced an electrode potential of about 4.25 volts whereas a
current of only 4.5 amps produced a potential of 9.0 volts after
passivation. These results have been correctly attributed to
passivation of the nickel electrodes in the AHF, but we think
incorrectly related to the reason for the difference in the
products obtained from passive or active electrodes.

If the potential for formation of NF_3 lies in a region
which is accessible to a passive electrode, and potentiostatic
electrolysis is used, the portion of the current which goes to side
products or to metal dissolution can be very greatly reduced com-
pared to constant current electrolysis . The actual current flow
will of course be controlled by the concentration of the electro-
reactive species and the rate of stirring. The current efficiency
should be improved over that indicated in the Rocketdyne reports.

Taking all of these factors into consideration, the initial
experiments for the electrolysis phase of the project will be to
determine the potential-current relationships for nickel electrodes
as the electrodes are made more and more anodic until first passi-
vation and finally solvent breakdown occurs, i.e., to trace out an

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anodic polarization curve using potentiostatic control of the cell. The next step is to determine the characteristics of the NH_3 electrolysis and to determine whether passive electrodes can be used. After accumulation of these data, a detailed experimental approach to study the mechanism is planned. Similar experiments can then be carried out with N_2H_4.

IV.   CURRENT STATUS AND FUTURE WORK

To satisfy the electrochemical and the volume requirements, the cell depicted schematically in Figure 1 and photographically in Figure 2 was designed and assembled. Several trial runs have led to some modifications, but the basic design is the same. The most recent modifications are shown in Figures 1 and 2. The cell container is a teflon cup supported by a steel cup wrapped with refrigerant lines and insulated on the atmosphere side. The electrodes are supported by a teflon spacer ring which rests on the flange of the teflon cup. Resting on this ring is a monel conical-section with six entry ports for gases, etc. At least one of these ports is provided with a teflon blowout plug. The monel condenser rests on the conical section and all four pieces, the cell container, the electrode ring, the conical port section, and the condenser are clamped together to form a seal by means of six bolts through two retaining rings. Various traps, a dump line, an AHF input line, a nitrogen line, and a thermistor probe are attached as auxiliary equipment. A flow diagram is shown in Figure 3.

Inside the cell itself, in contact with the AHF, the following items have been provided as shown in Figure 1.
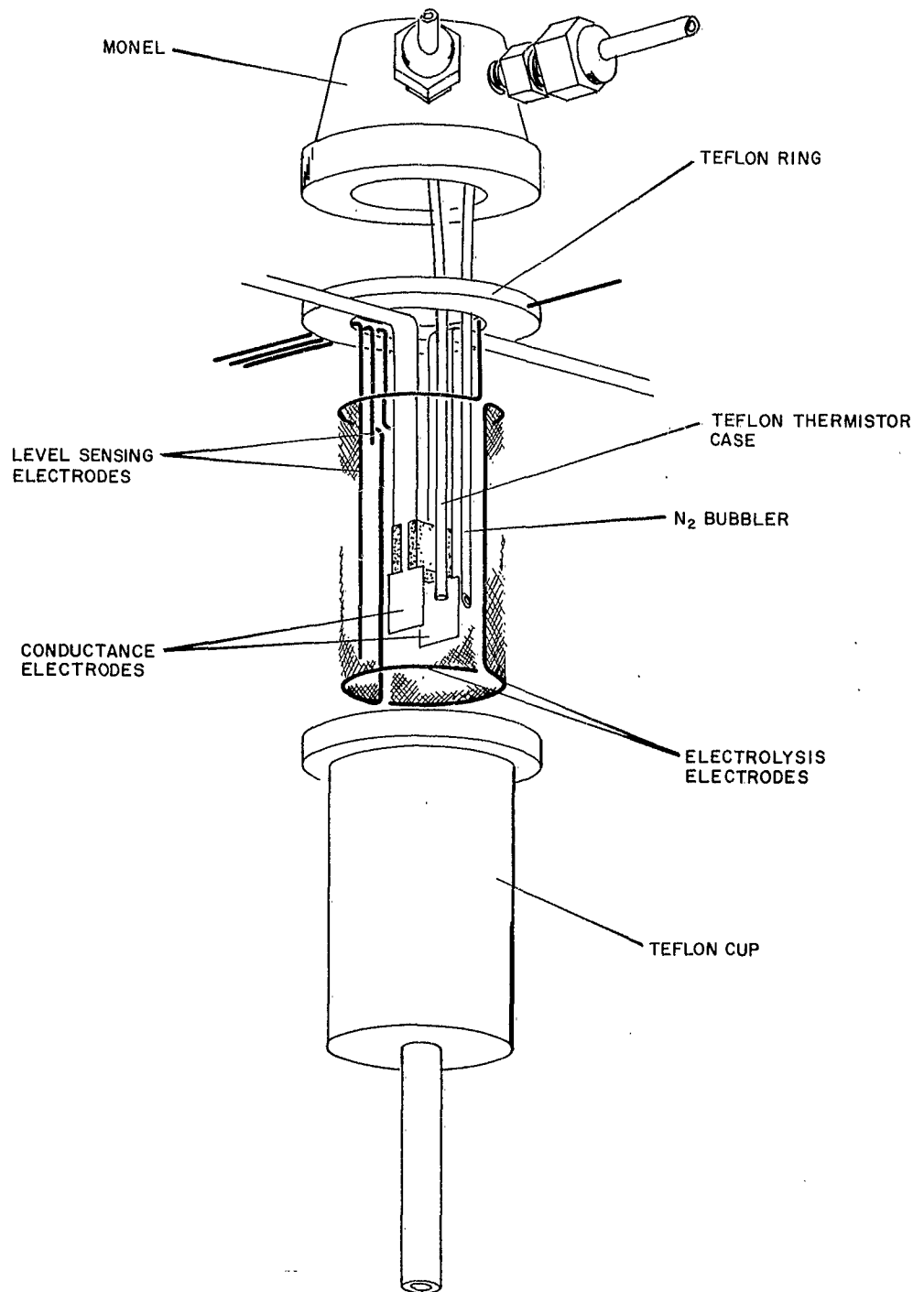
Two cylindrical nickel gauze electrolysis electrodes to be used to remove the last traces of water.

Nickel conductance electrodes which are 1 cm x 1 cm and spaced 1 cm apart.

A teflon tube for conducting nitrogen into the solution to sweep out the OF_2.

A teflon tube with a sealed end containing a thermistor probe for temperature monitoring.

Experiments using the cell have begun. The refrigeration system will be quite adequate for all of the necessary polarization curves, constant potential electrolyses, chronopotentiometric experiments, etc. Polarization curves have been taken to determine the best way to passivate the various nickel electrodes so that

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MONEL

TEFLON RING

TEFLON THERMISTOR
CASE

N_2 BUBBLER

LEVEL SENSING
ELECTRODES

CONDUCTANCE
ELECTRODES

ELECTROLYSIS
ELECTRODES

TEFLON CUP

Fig. I- CONDUCTANCE AND ELECTROLYSIS CELL
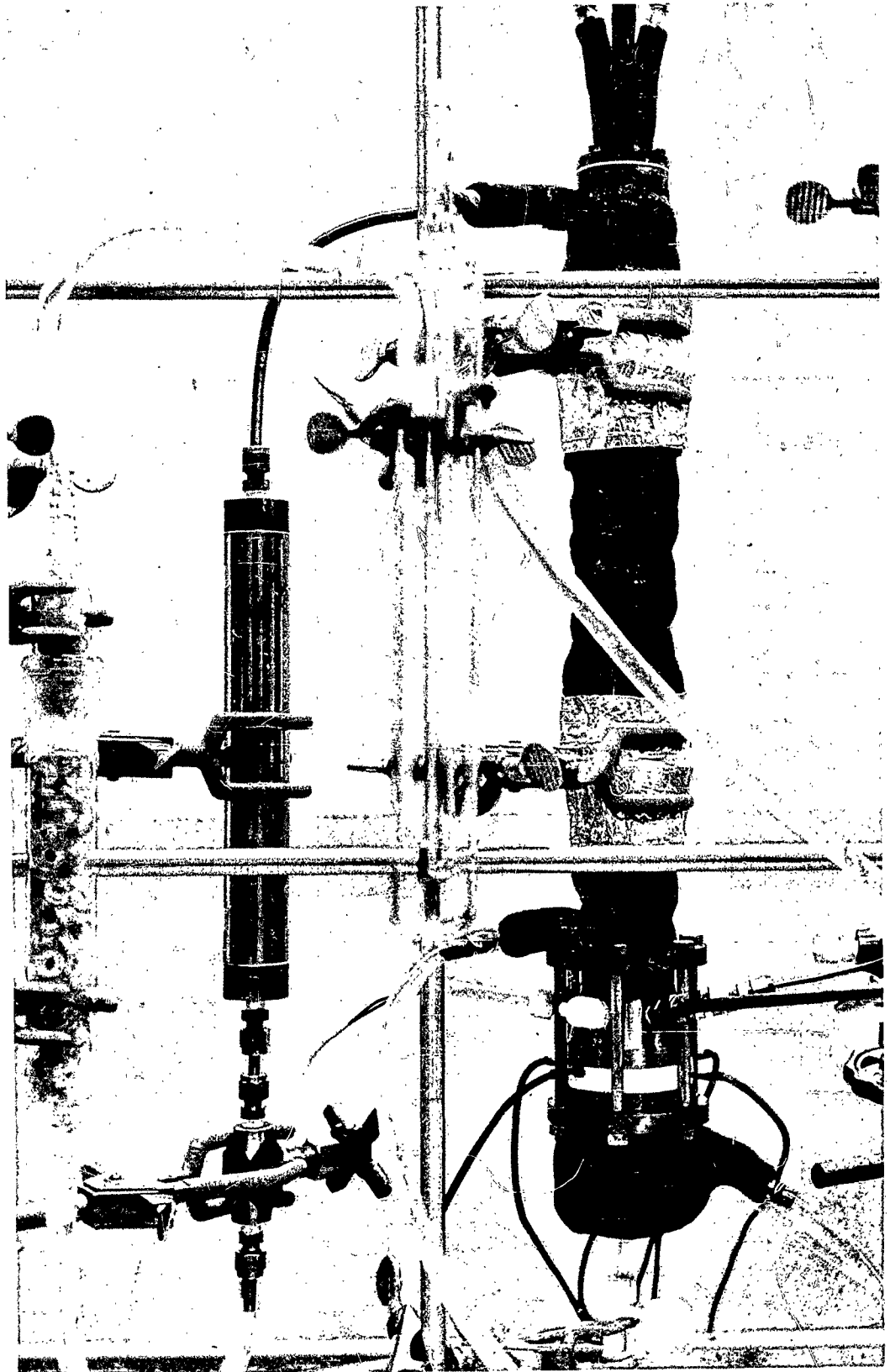
Fig. 2 – ELECTROLYTIC CELL WITH ASSOCIATED LINES
AND TRAPS
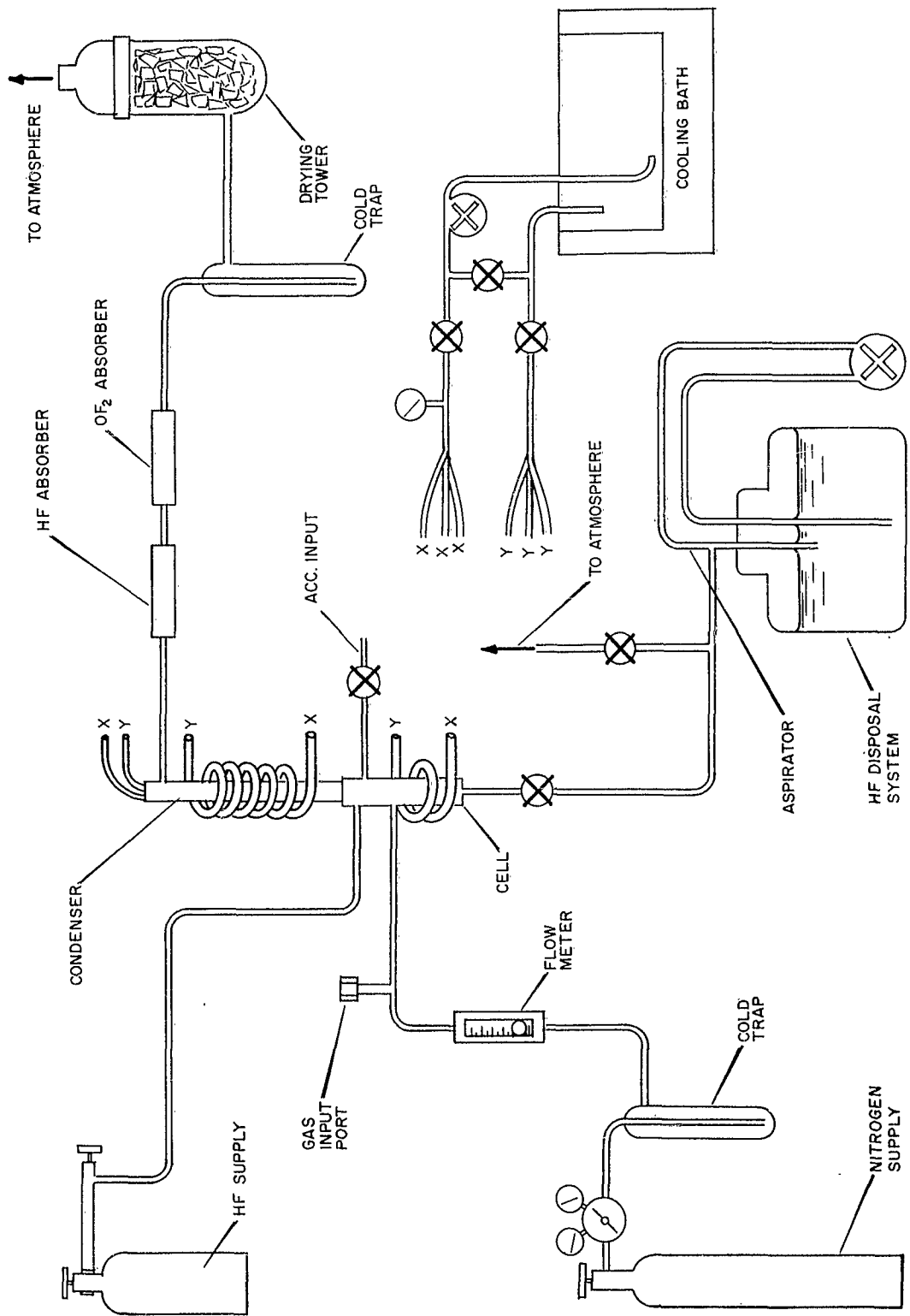
Fig. 3— FLOW DIAGRAM AHF ELECTROLYTIC CELL AND HANDLING SYSTEM

TO ATMOSPHERE

DRYING TOWER

COLD TRAP

COOLING BATH

HF ABSORBER

OF₂ ABSORBER

ACC. INPUT

X X Y X Y X

X X X

Y Y Y

TO ATMOSPHERE

ASPIRATOR

HF DISPOSAL SYSTEM

CONDENSER

CELL

FLOW METER

HF SUPPLY

GAS INPUT PORT

COLD TRAP

NITROGEN SUPPLY

the amount of ionic contamination of the AHF can be kept to a minimum. These experiments are continuing and as soon as a satisfactory method has been found, experiments will begin with NH_3. As the data develops with this compound, further experiments are planned with NF_3 and NHF_2. When the data have sufficiently outlined the mechanism of the reaction for the mononitrogen compounds, the dinitrogen compounds, N_2H_4 and N_2F_4 will be used for similar experiments.

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