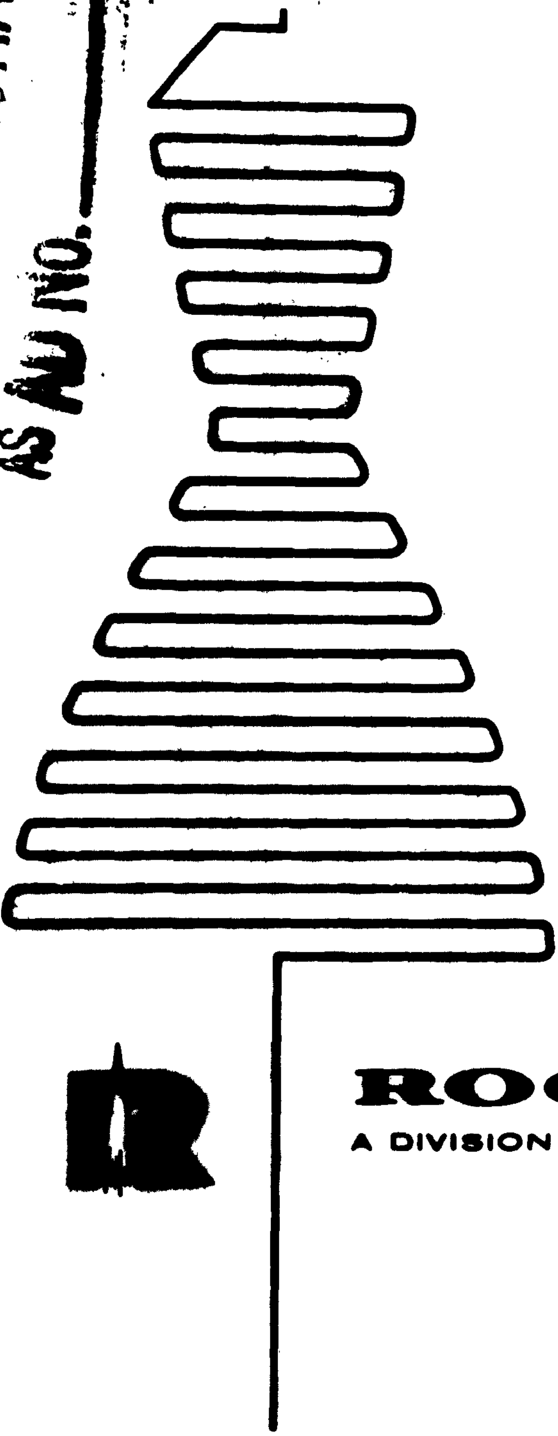

ROCKETDYNE

A DIVISION OF NORTH AMERICAN AVIATION, INC.
CANOGA PARK, CALIFORNIA

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RESEARCH IN FLUORINE CHEMISTRY, SUMMARY REPORT FOR PERIOD 16 MARCH 1961 TO 15 MARCH 1962

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ABSTRACT

The electrolysis of solutions of compounds containing nitrogen and oxygen dissolved in anhydrous HF was initiated as a means of synthesizing N-O-F compounds. Data are presented on the HF-N_2O_4 system, particularly its electrical properties; information also is presented on electrode materials.

Platinum has been found to be a satisfactory reference electrode in anhydrous HF for monitoring changes in electrode potential during electrolysis.

The electrolysis of HF-N_2O_4 and of HF-HNO_3 solutions near 0 C has yielded substantial quantities of NO_3F and OF_2. This synthesis of NO_3F demonstrates for the first time that a compound containing the - NOF group can be prepared electrochemically. At -20 C, the electrolysis of HF-N_2O_4 yielded O_3 in addition to NO_3F and OF_2. The O_3 prepared by this method showed an unusual degree of stability toward explosive decomposition. The effect of additives and of changes in experimental conditions is discussed.

The results of electrolysis on the HF-NO and HF-FNO systems are also presented. Data on the solubility of N_2O in HF are reported.

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INTRODUCTION

This program was directed toward the synthesis of new compounds containing nitrogen, oxygen, and fluorine. An additional goal was to devise new routes to existing compounds which are difficult to prepare by known routes. The approach which was chosen was the electrolysis of solutions of compounds of nitrogen, oxygen, and fluorine dissolved in anhydrous hydrofluoric acid, because it offered unique preparative possibilities. It was also capable of providing relatively large yields of products, particularly when compared to other electrical methods such as the glow discharge.

The probability of synthesizing relatively unstable N-O-F compounds by electrolysis was expected to be increased by the low temperatures of operation which were used in this work. The elimination of organic compounds, precluding the formation of stable CF_4, was also expected to materially increase the possibility of forming these compounds. This research was also aided by the presence of nitrogen-oxygen compounds where the nitrogen was already in the +2, +3, +4, or +5 valence state, compared to nitrogen-hydrogen compounds where the nitrogen formally showed negative valence. In addition, the probability of terminating the reaction prematurely with a stable intermediate, such as nitrogen, was lessened. Finally, chances of explosion both in the cell and in the traps were reduced because readily oxidizable materials were absent.

The need for the lowest possible voltages to avoid complete fluorination to NF_3 and OF_2 is apparent. A definite effort has been made to keep voltages at a minimum, thereby increasing the chances of synthesizing relatively unstable compounds. This effort was aided by the cathodic depolarizing action of the N_2O_4.

The first experiments were conducted with N_2O_4, but NO, FNO, and nitrates also were used. The electrolysis of these compounds dissolved in anhydrous HF could be expected to present corrosion difficulties not normally encountered in the electrolysis of fluorides, because of the presence of strong nitrogen oxidizers. Therefore, knowledge of metallic corrosion, under nonelectrolytic as well as anodic conditions, was considered necessary. In addition, because N_2O_4 could be expected to behave differently than those compounds previously electrolyzed in HF solution, some insight into the $HF-N_2O_4$ system and into the behavior of electrodes in such a system also was considered necessary. Therefore, to maximize the probability of success, and to avoid false starts if possible, it was decided to initiate the research program with a preliminary investigation to obtain the above information. Experiments were conducted to obtain sufficient data to reach the above objectives; a thorough interpretive analysis was not considered warranted.

The system $HF-N_2O$ has been investigated (Ref. 1). Mixtures of N_2O_4 and HF have been used for nitration (Ref. 2). According to Darmois (Ref. 3), nitric acid dissolved in HF dissociates to NO_3^- and a proton trapped between HF molecules, although he stated that this is contrary to the generally accepted view that HNO_3 acts as a base in HF. Fredenhagen (Ref. 4) reported that the addition of KNO_2 to anhydrous HF is accompanied by the evolution of nitrous gases and the formation of a colorless solution. However, solutions of KNO_2 in HF gave a violet coloration when NO was added (Ref. 5), the color being attributed to the postulated formation of $N_2O_2^+$ ion from NO^+FHF^-. Similar results were also obtained when N_2O_4, N_2O_3, and FNO were substituted for KNO_2. Much work (Ref. 6) has been done in the electrolysis of all types of heterocyclic bases and other nitrogen-containing organic compounds such as N, N-dimethylformamide dissolved in anhydrous hydrogen fluoride. No inorganic N-0-F compounds have resulted from this work, although NF_3 was often a product.

DISCUSSION

CHEMICAL AND ELECTROCHEMICAL DATA

This program was started with experiments directed toward elucidation of the HF-N_2O_4 system and its electrochemistry to obtain sufficient information to plan and to interpret preparative experiments.

Reaction of HF With N_2O_4

The addition of N_2O_4 to HF to form a colorless solution (mole ratio HF:N_2O_4 = 14:1) is accompanied by hissing and the copious evolution of fumes. When destroying these solutions by the dropwise addition of water, very little evolution of white fumes (from HF), but copious evolution of b fumes, occurs. Apparently the water displaces the N_2O_4 from the products of the HF-N_2O_4 reaction. During this work a green color formed in the solution, and the conditions of formation were investigated. The addition of 0.083 mole of ice to a cold solution of 0.036 mole of N_2O_4 in 0.52 mole of HF caused the evolution of b fumes and the formation of a blue color (probably N_2O_3) near the ice, but the solution became colorless after mixing. The further addition of 0.036 mole of ice caused a green color to appear which darkened upon the addition of more ice. This color faded very slowly over a period of several hours, with the evolution of brown fumes. The conditions of formation did not appear to be critical, and the green color was produced by several other ratios of HF, N_2O_4 and H_2O, and by HF, $NaNO_2$ and H_2O. No reference to the formation of a green color in HF has been found, although a violet HF, attributed to the formation of an $N_2O_2^+$ ion, has been reported (Ref. 5).

Current-Voltage Relationships of the Electrolytic Cell

The current between two nickel electrodes was measured as a function of the composition of HF-N_2O_4 solutions in an open Kel-F beaker. The primary objective was to find the composition or compositions at which the current was at a maximum. for a constant applied voltage.

The apparatus described in the experimental section under Electrolysis Procedure 1, was employed. Current peaks (Fig. 1) were obtained for HF-N_2O_4 at mole ratios (HF:N_2O_4) of 400:1 and 36:1. The first is thought to be a result of electrolysis of impurities in the HF, and the second a result of normal electrolysis of HF-N_2O_4 solutions. The decrease in current after the second peak is very slow and is probably a dilution effect caused by excess N_2O_4.

Thermodynamic calculations based on the free energies of reaction in this electrolysis have indicated that NO and H_2O, rather than H_2, are the most likely cathodic products of the electrolysis of HF-N_2O_4 solutions.

Corrosion Tests

Several metals were tested for corrosion resistance in a solution of N_2O_4 (3.9 milliliters, 62 m moles) in HF (47 milliliters; 2320 m moles). These were nickel, monel, Hastelloy-C, Inco A, and Type 321 stainless steel. The metal strips and rods were mounted in Teflon to prevent electrical contact, then placed in a Kel-F tube containing the solution and permitted to stand for 17 hours at about 18 C. The tube was stoppered, but no other attempt was made to exclude moisture. The amount of corrosion, as determined by weight loss, was negligible.

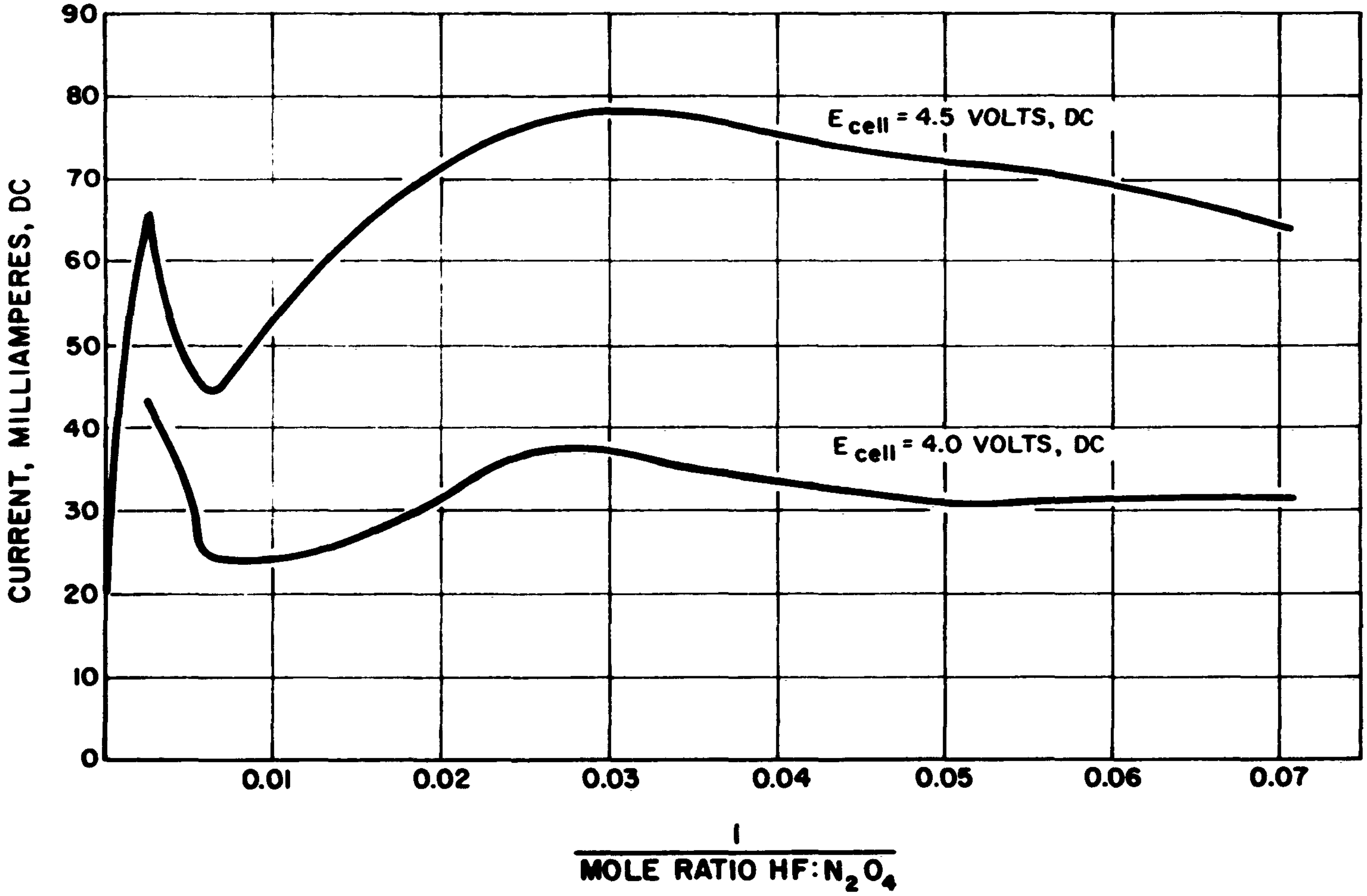

Figure 1. Cell Conductance, dc, for HF-N_2O_4 Using Nickel Electrodes

Over-all Cell Impedance

Electrical measurements using direct current on the HF-N_2O_4 system were reported above. These measurements were extended to alternating currents to minimize electrode polarization and are described below.

The measurements of over-all cell impedance at several frequencies and voltages using platinum wire electrodes were made on solutions of HF-N_2O_4 (mole ratio, 31:1) at 0 C in an open beaker. The results (Fig. 2) show the expected decrease in impedance with an increase in applied potential at frequencies below 1000 cycles.

The over-all cell impedance was measured as a function of HF-N_2O_4 ratio, at 1000 cycles, 0 C and 0.5 v rms. Minima in impedance at ratios of 48:1 and 35:1 can be seen in a plot of the data (Fig. 3). During the experiment it was observed that the readings were quite unsteady until, at approximately 35:1, fluctuations in the current readings suddenly ceased.

A rough indication of the specific conductivity of HF-N_2O_4 at 0 C was found by filling the same cell used in the above work with NaCl solution and comparing the result with the impedance when filled with HF-N_2O_4 (mole ratio, 31:1). The data indicate the specific conductivity of the HF-N_2O_4 solution of the same order of magnitude as saturated aqueous NaCl at 0 C (10^{-1} ohm^{-1} cm^{-1}).

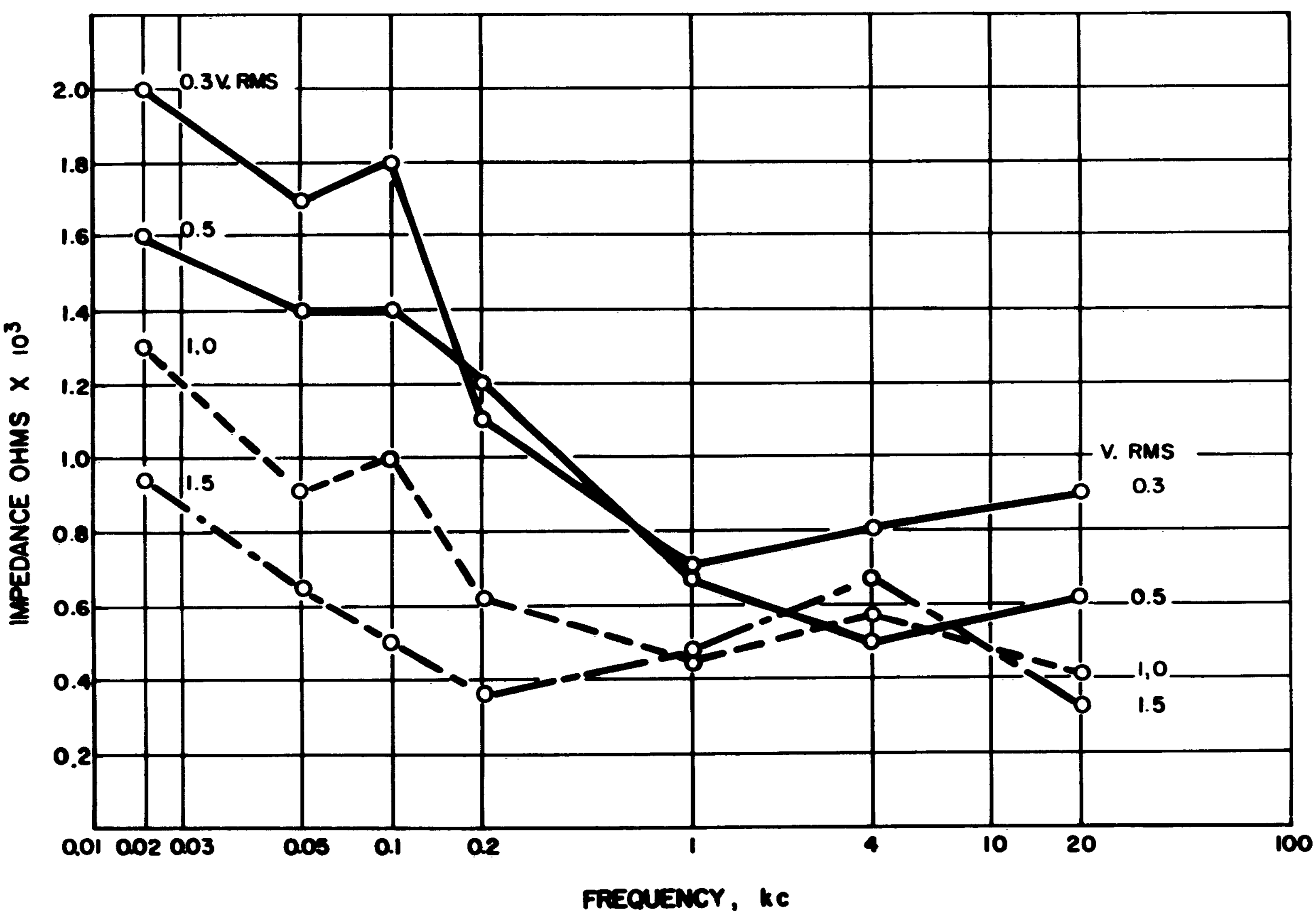

Figure 2. Effect of Frequency on Cell Impedance When Filled With HF-N_2O_4, Mole Ratio 31:1

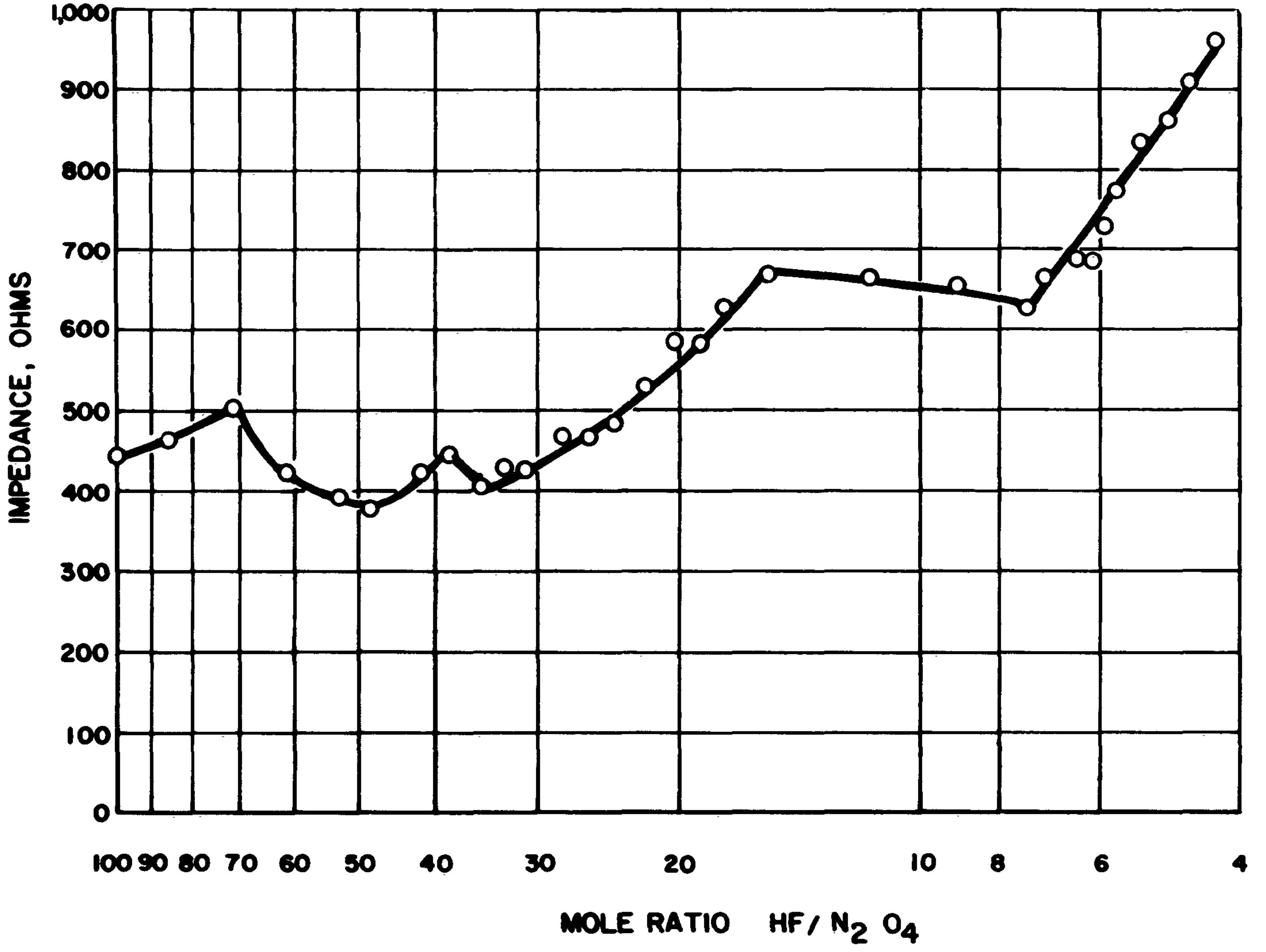

Figure 3. Effect of Mole Ratio of HF-N_2O_4 on Cell Impedance at 1000 Cycles, 0.5 Volts, rms and 0 Degrees C

Effect of Intermittent Direct Current on Apparent Cell Resistance

It was anticipated that it might prove necessary during the course of this work to conduct an electrolysis at very low current levels, primarily to decrease the amount of heating caused by the passage of current.

A transistorized pulse generator was built which has enabled cell operation at low average current and voltage levels. The effect of using this device was to reduce the power losses at a given average current. As can be seen (Fig. 4), the reduction became more pronounced at the lowest current levels. Pulse rates were usually about 5 pulses/sec and pulse widths about 20 percent of the total period.

Effect of Extended-Time Electrolysis

An electrolysis for an extended period of time was carried out on HF-N_2O (mole ratio, 31 1) in the smaller electrolysis cell without the cell cover A plot of current against time (Fig. 5) shows that after an initial rise the current decreased and leveled off until additional N_2O_4 was added. The current increased again and then proceeded to decrease. A second addition of N_2O_4 caused a much smaller rise. For the synthetic work, it would normally be desirable to cease operation of the cell when the current decreases significantly. Otherwise, interpretation of the results would be unduly complicated by the change in electrolyte composition.

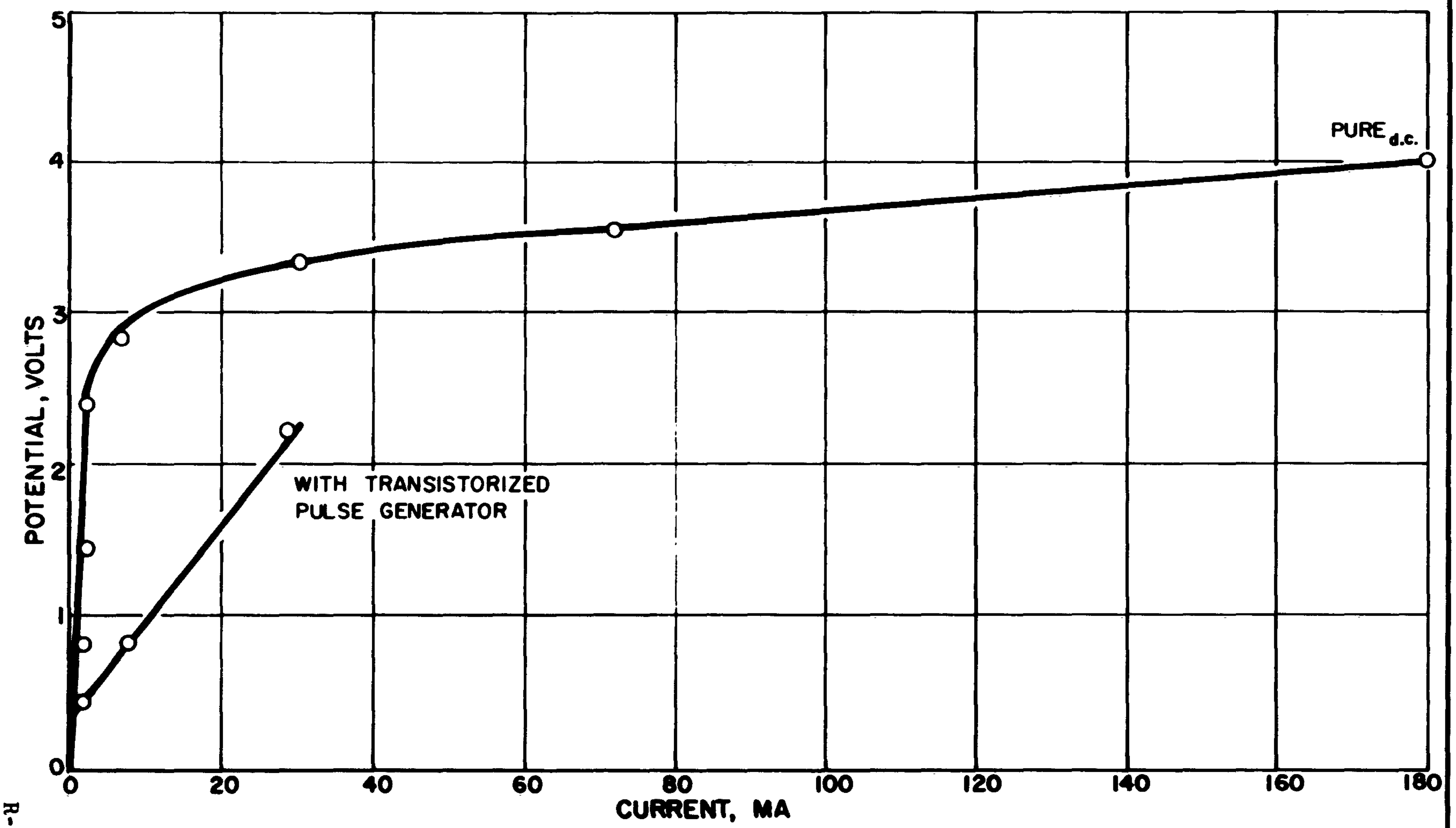

Figure 4. Comparison of Pure dc and Pulsed dc in Electrolysis of $HF-N_2O_4$ (Mole Ratio 31:1) With Nickel Electrodes in Apparatus, Fig. 11

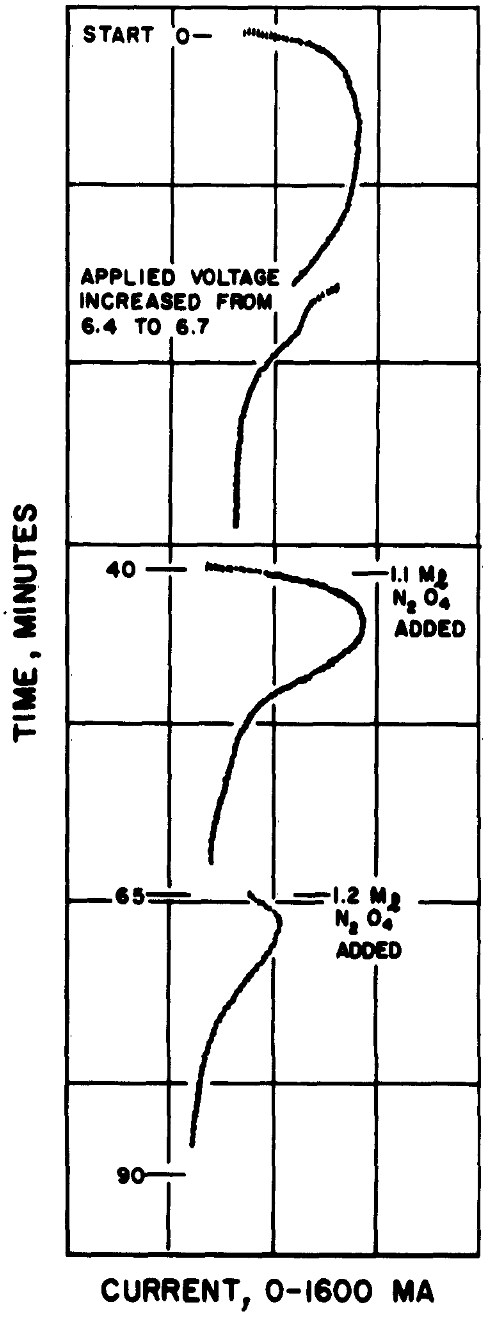

Figure 5. Extended Time Electrolysis, Effect of Adding N_2O_4

Polarization Curves of HF-N_2O_4 Solutions

Electrolysis of HF-N_2O_4 solutions, in the mole ratio of 18:1, using Electrolysis Procedure 2 with nickel electrodes in an open beaker, is shown in Fig. 6 The substitution of platinum for the nickel cathode had little effect. However, the substitution of a platinum anode caused a significant increase in current density at a given applied voltage. The use of platinum for both the anode and cathode electrodes resulted in an almost identical curve and an additional increase in cell current at a given applied voltage.

The data from an experiment using a palladium anode with a nickel cathode show a sharp break in the curve at 1.7 volts and 6 milliamperes; however, gas evolution did not start until the current was changed to 150 milliamperes at 2.0 volts. The remainder of the curve was similar to, but below, the platinum curves As might be expected from the delayed start of gas evolution, attack on the palladium was very severe.

Dissolution of both nickel and platinum also was noted, reaching 3 to 10 percent based on the current passed (assuming a valence change of two for nickel and four for platinum)

Electrolysis--Area Effects--HF-N_2O_4

Two nickel electrodes, 19.5 millimeters and 3.0 millimeters in width, were used alternately as anode and cathode (Electrolysis Procedure 1). Significantly higher currents were measured when the larger electrode was used as the anode For example, at 7.0 volts, 190 milliamperes were

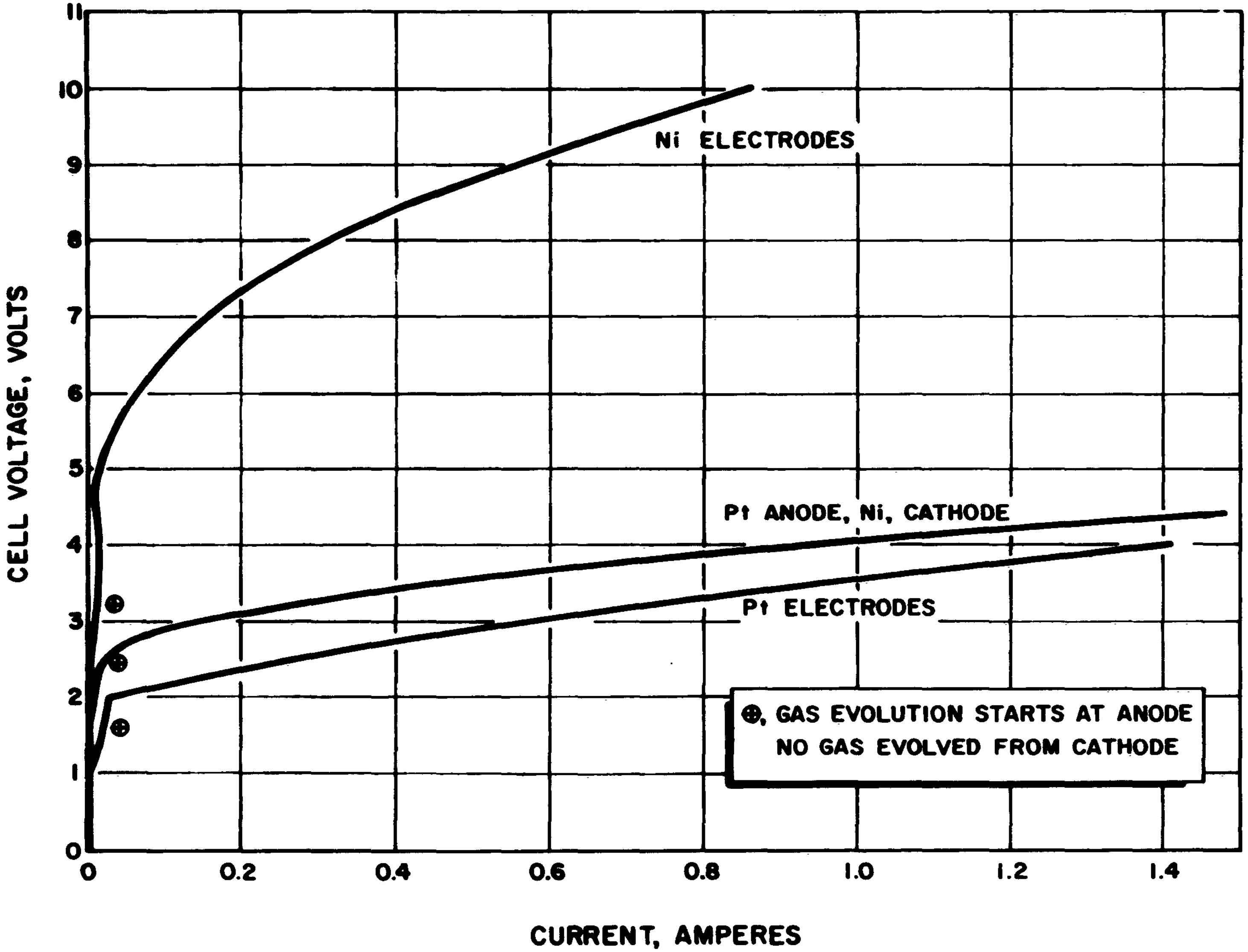

Figure 6. Electrolysis of HF-N_2O_4 (Mole Ratio 36:1)

measured with the narrow anode, and 530 milliamperes with the wide anode. With two wide electrodes, the curve was almost identical to that obtained with the wide anode and narrow cathode.

Polarization Curves of HF Solutions With Two-Electrode Systems

Data (Fig. 7) from the electrolysis of HF (open Kel-F beaker, Electrolysis Procedure 2, nickel electrodes), compared with that obtained from the electrolysis of HF-H_2O, indicate that water, a usual impurity in HF, may be responsible for the break in the HF curve at 3.6 volts. The HF-N_2O_4 system showed a similar break at 2.4 volts. It is highly significant that in this latter system, gas evolution was not observed at the cathode, consistent with the hypothesis derived from free energy data that NO and H_2O are cathodic products, as discussed previously (it was established in other experiments that NO is soluble in HF). The electrolysis of HF with platinum electrodes was included for comparative purposes. The portion of the curve that has a negative slope was correlated with an observed rapid attack of the anode.

In electrolysis work, considerable importance is usually attached to a relatively low electrode potential to prevent decomposition of desirable products. As can be seen (Fig. 6), the use of another electrode material, such as platinum, will result in milder operating conditions by permitting lower voltages to be used. On the other hand, should more severe conditions be desired, then monel, with a higher overvoltage than nickel, could be used as the anode.

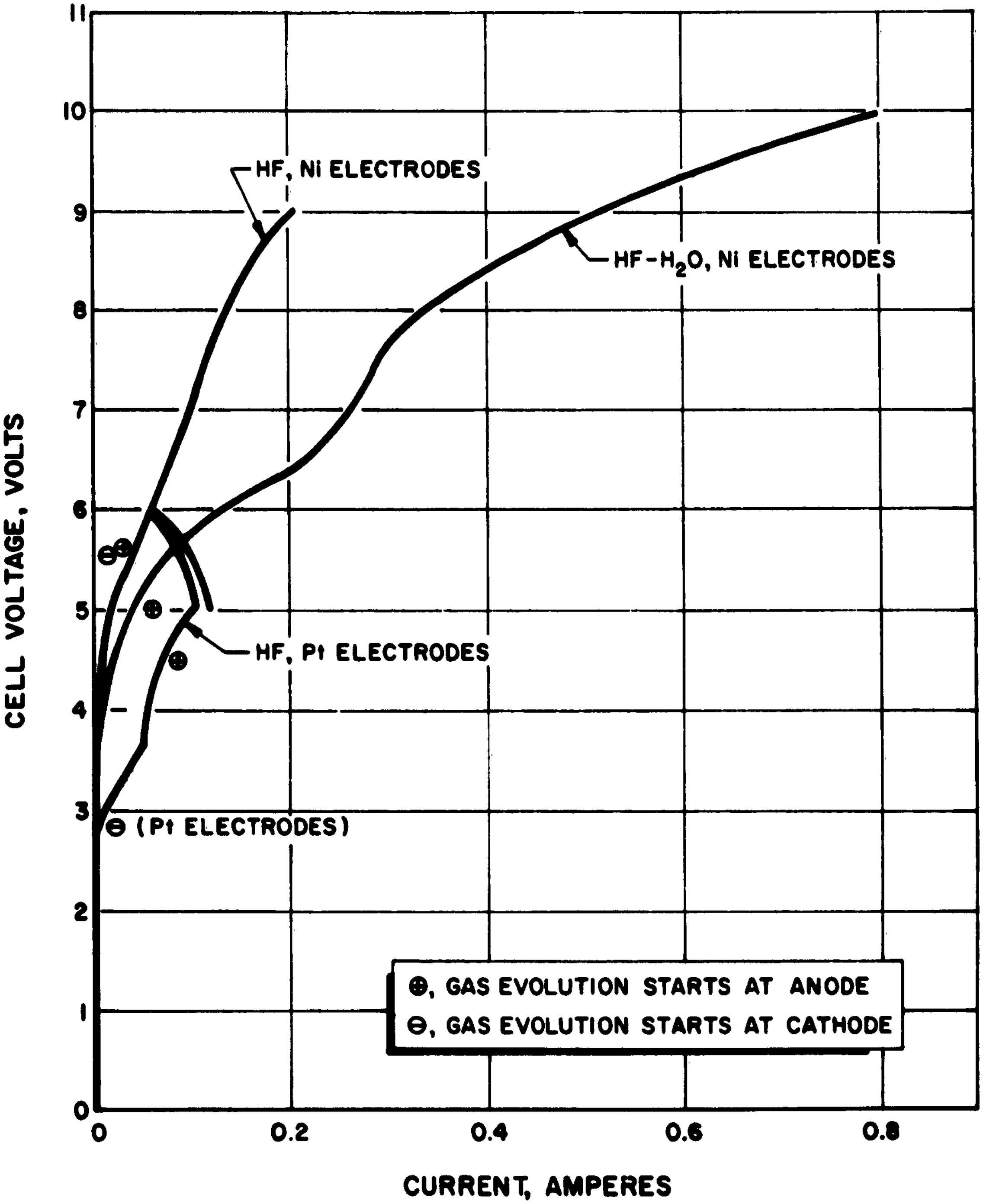

Figure 7. Electrolysis of HF and HF-H_2O (Mole Ratio 17:1)

Electrode Potential Measurements

The Two-Electrode System. It was desirable to obtain information on whether the anodic or cathodic reactions principally govern the electrolyses. Two methods have been used to effect this understanding. Figures 6 and 7 represent polarization curves obtained experimentally using two electrodes. Rate limiting processes can be assigned for specific values of applied potential However, without additional information, it is not normally possible to state with any certainty whether a particular rate controlling process is a result of oxidation or reduction (i e., anodic or cathodic process). To be sure, such information using two-electrode systems is obtained in most polarographic work Under these conditions we start with the a priori knowledge that one of the electrodes is nonpolarizable (usually the anode); i.e , one electrode is capable of supporting any current at potential studied, so that any limiting current can be assigned with certainty to a process occurring at the other electrode.

The bulk of the literature dealing with potential measurements in liquid HF is concerned with evaluation of equilibrium potentials, which are subsequently used in the evaluation of free energies The literature has little information concerning polarization measurements in liquid HF.

From the curves of applied potential vs current (Fig. 6 , upper curve, and Fig 7) we have no way of assigning the limiting processes to anode or cathode However, in auxiliary experiments (Fig. 6 , lower curves) where platinum electrodes are substituted for nickel electrodes, reasonable assurance is provided that the cathode can support any current and that all rate-limiting processes can be associated with electrode reactions occurring at the anode

<u>The Three-Electrode System</u>. The three-electrode system permits direct determination of an anodic or cathodic polarization curve. Potential is applied between the electrode being studied and an auxiliary electrode. Potentials are measured between a third, or reference electrode, and the electrode being studied.

It was our thought that a reference electrode in the conventional sense (i.e., nonpolarizable) was not necessary to obtain useful information in our systems. Rather, if an electrode could be found which would maintain a steady potential in our systems, it could be used to monitor any changes occurring at the test electrode In our measuring circuit, we are not drawing any current and so the requirement that the third electrode keep a steady potential as a function of current is obviated. It was experimentally determined that a platinum wire electrode met the above stated requirements for the third electrode. This electrode was placed (Fig. 8) in close proximity to the anode so that any contribution from IR drop would be negligible.

The potential between a platinum wire electrode and a nickel rod in anhydrous HF was found to be about 0 08 volt. A current was then passed between the nickel rod and an additional nickel rod which served as an auxiliary electrode. The current was removed, and the three electrodes were shorted so that an equilibrium condition could be achieved in a short time The open circuit potential between the nickel rod and the platinum wire electrode was found to be approximately 0.07 volt A similar experiment was conducted using a nickel wire electrode. The open circuit potential before and after electrolysis between this electrode and the test electrode was found to be approximately 0.25 volt The formation of a yellow film on the nickel wire

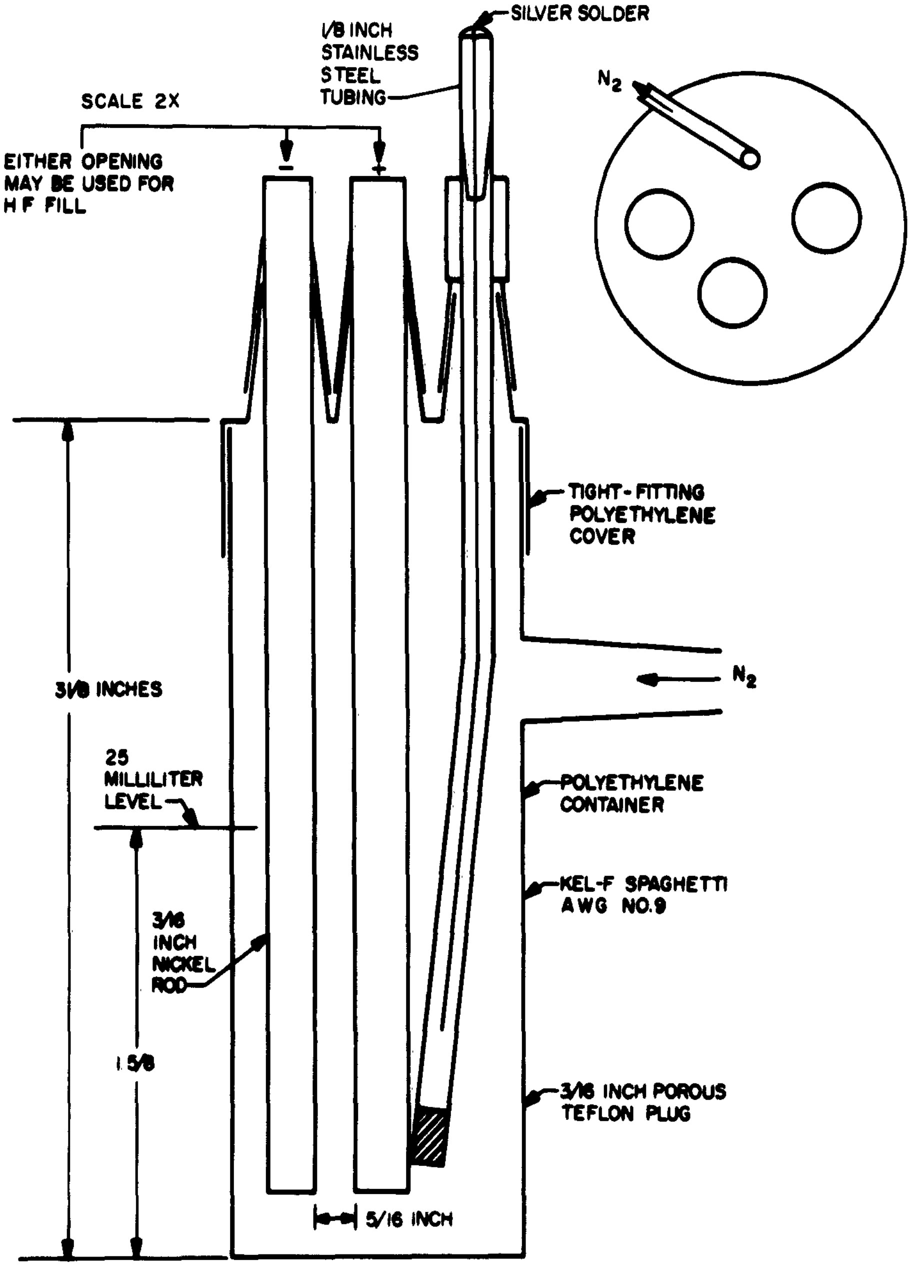

Figure 8 . Electrolytic Cell for Electrode Potential Measurements

was noted. Although either platinum or nickel would have been satisfactory for the reference electrode, platinum was selected because chemical attack on the wire, which might affect the potential, was considered less likely The reference electrode, which was immersed in anhydrous HF and separated from the cell by a porous Teflon plug, was used to determine the effect upon anode potential resulting from gradually increasing the current flow while electrolyzing anhydrous HF (Matheson, direct from cylinder). In such a system, the applied potential (E_t) can be considered to be the sum of the potentials at the anode (E_a), the cathode (E_c), and the IR drop through the solution.

$$E_t = E_a + E_c + IR \qquad (1)$$

The lower curve (Fig 9) represents the potential difference between the anode and the reference electrode Since there is no current flow between these two electrodes, it is reasonable to state that the observed changes in potential reflect the changes occurring at the anode as a result of electrolysis It is apparent that the two curves, $E_{Applied}$ and E_{Anode} are very similar Consideration of Eq. 1 leads to the conclusion that the contributions of E_c and of IR, while small, are proportional to current That the E_c and IR components are small is of primary importance since there is an implicit assertion that the cathode can support any current which would normally be used, that it is relatively nonpolarizable, and that any rate-limiting or current-determining steps are a result of processes occurring at the anode. This is in direct agreement with our work on the HF-N_2O_4 system wherein it was shown that an increase in anode area results in a decrease in observed polarization, while a change in cathode area was without effect Further, when platinum was substituted for nickel as a cathode

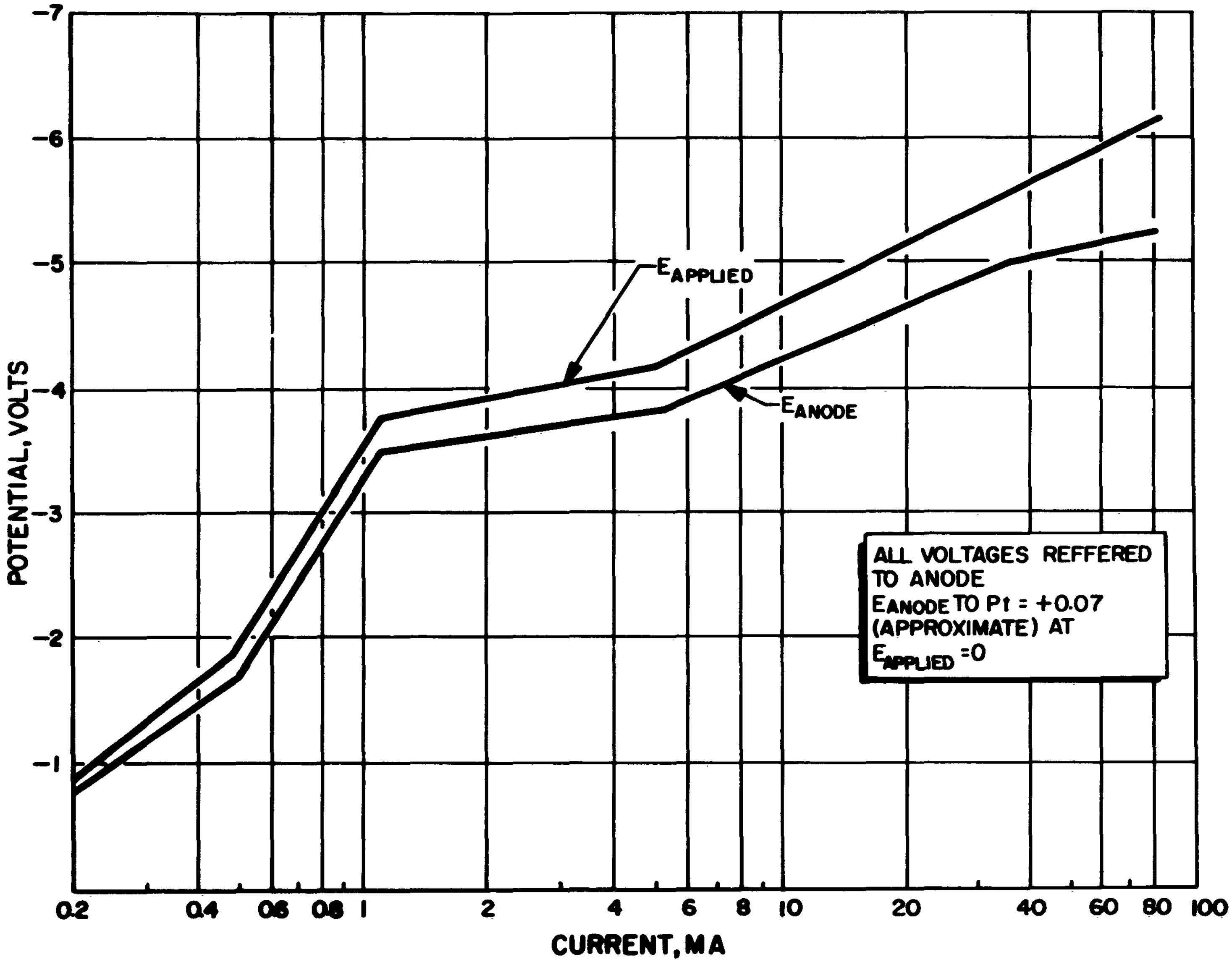

Figure 9 . Effect of Current Upon Applied Potential and Upon Anode Potential in Hydrogen Fluoride

material (nickel anode), the polarization curves were similar, again indicating that the process is under anodic control. This is shown convincingly in Fig 10 which represents the experimentally determined cathodic polarization curves. It can be seen that the cathode is virtually nonpolarized over the potential range investigated.

The potential between platinum and nickel was checked before and after cathode and anode potential measurements. In both cases, the potential dropped from an initial value of 0.1 volt to 0.07 volt, referred to the nickel electrode

It is worthwhile to assess the implications of the study using three electrodes which, perhaps, are not immediately apparent. In the system studied, the mechanistic interpretations using three electrodes are identical to those derived using the results obtained from two electrodes plus some auxiliary experiments. This is fortuitous since the cathode is relatively nonpolarizable, so that this two-electrode system can be treated qualitatively as a reference electrode (cathode) monitoring the test electrode (anode).

The two-electrode system fails, however, as we study more complicated systems; systems in which over-all processes might be under alternate anodic and cathodic control or mixed control. Such situations are more frequently encountered in electrochemical studies This is evidenced by the increasing use of three electrodes in aqueous systems. The development of a third electrode in HF systems then, in effect, opens a new avenue of approach to elucidating electro hemical mechanisms. The results of such studies would permit researchers to select the particular electrode which would be most effective in the achievement of a desired product, as well as the optimum operating conditions.

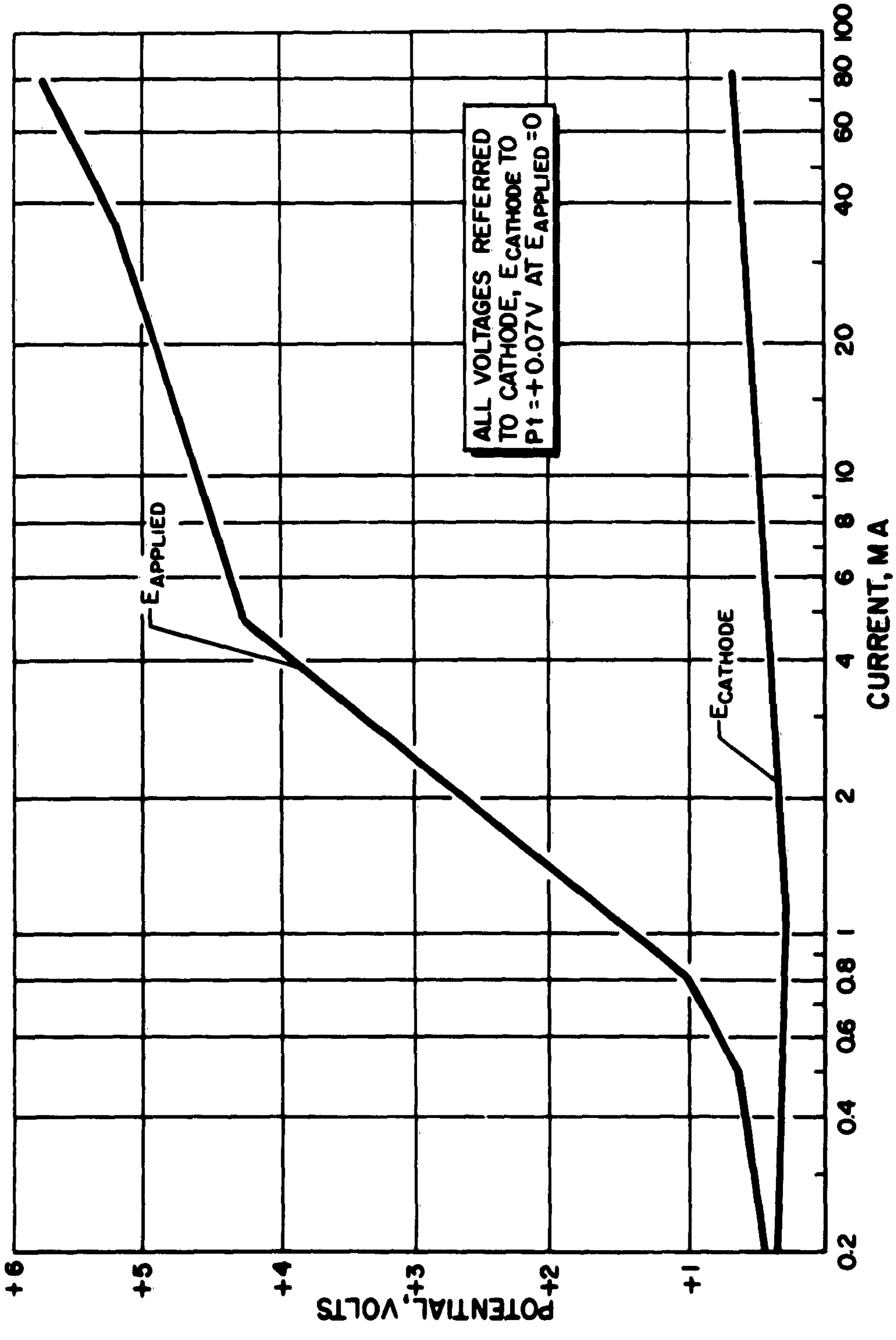

Figure 10. Effect of Current Upon Applied Potential and Upon Cathode Potential in Hydrogen Fluoride

ELECTROCHEMICAL SYNTHESIS--SMALLER CELL

The synthesis of compounds containing N, O, and F by the electrolysis of solutions of HF and N-O compounds was started in the smaller electrolytic cell (Fig 11) This work was intended to show what types of compounds could be synthesized and the effects of changes in starting materials, additives, and experimental conditions. Since the starting materials in this work were of relatively high oxygen content, it is not surprising that the products which were found invariably contained oxygen as well as fluorine.

HF-N_2O_4

Electrolyses of HF-N_2O_4 solutions at four different mole ratios were carried out. At a mole ratio of 12:1 (HF-N_2O_4), oxygen was essentially the only product; while at 24:1, a major yield of OF_2 and a minor yield of NO_3F were found At a ratio of 34:1, significant yields of both OF_2 and NO_3F were found in addition to oxygen. The 34:1 ratio was chosen because it is in the region of minimum cell impedance. At a ratio of 77:1, no NO_3F was found; OF_2, N_2O, O_2, and H_2 were the principal products The N_2O and H_2 were probably a result of continued reduction at the cathode following partial reduction of the N_2O_4. It was calculated that more than sufficient current had passed to accomplish this result The 34:1 run was repeated with electrolytically dried HF and appeared to give only a slightly improved yield of OF_2 and NO_3F.

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Figure 11. One-Amp Electrolysis Cell

$HF-N_2O_4$-Bases

The electrolysis of a solution of $HF \cdot N_2O_4$-KF (mole ratio, 33:1:0.83) resulted in reduced yields of NO_3F, although correspondingly more OF_2 was produced. The substitution of H_2O for KF, with the drying step eliminated (mole ratio $HF.N_2O_4:H_2O$, 34:1:0.67), gave OF_2 and NO_3F in about the same ratio as when the KF additive was used. The voltage required was 6.4 at 1.07 amperes, increasing to 10.0 at 0.4 ampere by the end of the run. In the other experiments, the voltage changed only slightly during the runs. The low over-all cell conductivity (high over-all cell resistance) is a considerable disadvantage, causing heating if operation at even reasonable current levels is to be maintained. Therefore, water should be considered an undesirable additive, especially in large quantities. The addition of strong bases, such as KF and H_2O, appears to deter the synthesis of NO_3F.

$HF-HNO_3$

The synthesis of NO_3F from $HF-N_2O_4$ solutions suggests the presence of nitrate according to the following equations

$$2HF + N_2O_4 = NO^+ + HF_2^- + HNO_3$$

$$2HF + HNO_3 = H_2NO_3^+ + HF_2^-$$

The $H_2NO_3^+$ ion then reacts as follows

$$3HF + 2H_2NO_3^+ = NO^+ + HF_2^- + 2H_3O^+ + NO_3F$$

A similar result should therefore be obtainable from the electrolysis of anhydrous HNO_3 dissolved in HF. In one experiment, $Pb(NO_3)_2$ was used as a source of anhydrous HNO_3 because PbF_2 is only slightly soluble in HF.

$$Pb(NO_3)_2 + 6HF = \underline{PbF_2} + 2H_2NO_3^+ + 2HF_2^-$$

The experiment (mole ratio $HF \cdot Pb(NO_3)_2 = 34:1$) yielded mostly NO_3F as well as some OF_2.

<u>HF-HNO3-Bases</u>

The substitution of the soluble base $NaNO_3$ (mole ratio $HF:NaNO_3$, 17:1) for $Pb(NO_3)_2$ caused a reduction in the yield of NO_3F compared to the yield of OF_2. The effect of water was determined by electrolyzing a solution of HF-HNO_3-H_2O (mole ratio of 17:1:0.4) obtained by dissolving white fuming nitric acid in HF. Even less NO_3F was found than when the HF-$NaNO_3$ solution was used. It seems apparent, therefore, that in the electrolysis of both HF-HNO_3 and HF-N_2O_4 solutions, the presence of base reduces the yield of NO_3F.

When the solution from the cell was poured into water, brown fumes, apparently NO_2, were evolved. Since these fumes were not evolved from the reaction of HF-HNO_3 solution with water, reduction of NO_3^- must have taken place during electrolysis. A similar reduction probably occurred in the HF-N_2O_4 experiments.

HF-NaNO_2

The electrolysis of the solution of HF-NaNO_2 (mole ratio 17:1) yielded mostly NO_2, with some $N_2$0 and a trace of FNO. It is surprising that even a small amount of FNO was detected because it is known to coordinate with the HF (Ref 7, 8, 9) and, therefore, would be expected to remain in the cell. The presence of NO_2 in quantity in the gaseous products is surprising It has, heretofore, not been detected in more than trace amounts, presumably because it would remain dissolved in the HF It is most probable, therefore, that either an unknown compound decomposed in the system, forming NO_2 as one of the products, or that oxygen was formed at the anode which reacted with NO (from NaNO_2 reaction with HF) in the gas phase to form NO_2.

ELECTROCHEMICAL SYNTHESIS--LARGER CELL

HF-N_2O_4

The first two experiments (Table 1 A104-32, -38) were intended to be essentially duplicates of previous work with the HF-N_2O_4 system to check the operation of the larger electrolytic cell and associated equipment The only significant change in reaction conditions was a reduction in coolant temperature from 0 to -20 C In addition to the lower temperature, the heat transfer characteristics of the larger metal cell were better than the smaller Kel-F cell used in the aforementioned electrolyses

TABLE 1

DETAILS OF ELECTROLYSIS EXPERIMENTS*

Run No.	Reactants	Mole Ratio	Coolant Temperature, C	Current, amperes	Voltage, volts	Length of Run, minutes	Major Products
A104-32	$HF:N_2O_4$	30:1	-20	9.6	6 6 to 5.0	77	NO_3F, OF_2, O_3
A104-38	$HF \cdot N_2O_4$	34:1	-19	9 3	6.8 to 5.1	62	NO_3F, OF_2, O_3
A104-41	$HF\ N_2O_4 \cdot BF_3$	34·1:1	-24	6 5	7.0 to 4.8	65	NO_3F, OF_2, O_3
A104-48	$HF\ N_2O_4:SbF_5$	34:1:1	-20	9.6	6.0 to 5.6	70	N_2O, NO_3F, OF_2, O_3
A104-49	$HF:N_2O_4$	4:1	-22	9.6	4.0 to 7.0	65	N_2O, N_2O_4, OF_2
A195-01	$HF:N_2O_4$	2:1	-24	8.0	4.6 to 7.0	53	N_2O, N_2O_4, NO_3F, OF_2
A195-03	$HF:NO$	36:1	-22	4.0	7.0 to 13.0	66	N_2O, N_2O_4, NO_3F, HNO_3
A195-07	$HF:NO$	45:1	-22	1.2 to 0.4	20	53	N_2O
A195-08	$HF:NO$	41:1	-22	0.8	5.8 to 6.0	184	N_2O, NO_3F, OF_2, N_2O_4 small amounts NF_3

*All runs were made with nickel electrodes having effective areas of approximately 70 cm^2 each, except run A195-07 where the anode area was reduced to approximately 7 cm^2. Helium flow in all runs was 30 to 35 cc/min.

Both experiments yielded substantial quantities of NO_3F and OF_2, as expected from our previous results In addition, large yields of ozone were also obtained which is significant because an unstable compound has now been made in substantial quantities under the new experimental conditions It might be inferred from this preparation that under the appropriate chemical environment similarly unstable N-O-F compounds might also be prepared

The preparation of ozone, by electrolytic means, is also of interest in connection with the electrolytic preparation of nitrogen trifluoride from molten ammonium bifluoride Ruff (Ref 10) has stated that explosions occurred in a trap during the collection of the gases from the electrolytic cell because of the accumulation of O_3 It would seem unlikely, however, that O_3 could have been prepared in Ruff's apparatus, because the electrolytic cell was operated at about 125 C At this temperature, ozone would undergo rapid thermal decomposition Another interesting aspect of our ozone preparation is that it has been routinely transferred by standard vacuum techniques and was observed to boil rather violently In only one instance has an explosion been observed and this happened when, inadvertently, excessive ozone pressure was permitted to build up in a trap containing about 1 or 2 milliliters of liquid ozone The explosion occurred a few moments after a valve was opened suddenly to release the pressure. One possible explanation for the observed stability is that the method of preparation would exclude any oxidizable impurities In addition, the interior surfaces of the vacuum system would be fairly inactive because of their exposure to active fluorine compounds

Previous work has indicated that the addition of bases would inhibit the synthesis of NO_3F from HF-N_2O_4. It was postulated that the addition of an acid such as BF_3 might complex the NO_2^+ ion even in HF solution so that NO_2^+ would form in preference to $H_2NO_3^+$ and NO^+ (Ref. 11).

$$N_2O_4 + 4HF = H_2NO_3^+ + NO^+ + 2HF_2^-$$

$$N_2O_4 + BF_3 = NO_2^+ (BF_3 \longleftarrow NO_2^-)$$

If the mechanism shown by the last equation also applies in an HF system, then we would not expect NO_3F as a product. An electrolysis of HF-N_2O_4--BF_3 (Table 1, A104-41) has yielded identical products to those obtained from previous runs without BF_3 The substitution of the much stronger acid SbF_5 for BF_3 (Table 1, A104-48) also yielded virtually identical products. It might, therefore, be concluded that such complexing does not take place in HF solution probably because insufficient energy is available to dissociate the HF-N_2O_4 complex In both cases, however, white solids were found in the bottom of the cell which probably were the corresponding nitronium salts Although it is possible that all the BF_3 was precipitated by the N_2O_4 from the electrolyte, a significant reduction in conductivity should have resulted; since this did not occur, apparently a large portion of both the N_2O_4 and BF_3 must have remained in solution

The strength of the HF-N_2O_4 complex was indicated by another observation. Upon adding 15 milliliters of N_2O_4 to 157 milliliters of electrolytically dried HF(-24 C), a reduction in total volume to 148 milliliters took place This observation is consistent with a paper (Ref. 1) which stated that the maximum density in the HF-NO_2 system of 1.61 g/cc at 20 C occurs at a mole ratio of 1:1. This density is higher than either HF or NO_2 at the same temperature.

In two additional runs (Table 1, A104-49, A195-01) in the HF-N_2O_4 system with large amounts of N_2O_4, ozone was not obtained. The measured applied potentials were lower in these runs than those measured for the runs in which ozone was obtained. In addition, the solution resistances of these runs were found to be greater (Fig. 3). It would be reasonable to conclude that the lower potentials observed can be ascribed to a different rate controlling reaction, probably one associated with the production of oxygen. It is interesting to note that where the initial cell potential was down to 4.0 volts, almost no fluorination occurred.

HF-NO

While NO has been found to dissolve in anhydrous HF to form a conducting solution, the rate of solution was quite slow compared to the violent reaction experienced when dissolving N_2O_4. When a solution of NO in HF was electrolyzed (Table 1, A195-03), the products found in the cold trap were NO_3F, N_2O, HNO_3 and N_2O_4. The following sequence of over-all cell reactions was thought to be responsible for the synthesis of NO_3F and OF_2 with the HF-NO electrolyte:

$$2NO = N_2O + 1/2\ O_2$$

$$2NO + O_2 = N_2O_4$$

$$N_2O_4 + 4HF = NO^+ + H_2NO_3^+ + 2HF_2$$

Thus, after all the NO was gone, the system was somewhat similar to the initial state of the HF-N_2O_4 system and some of the same products would have been expected. This hypothesis was tested in one run (Table 1, A195-08) which was conducted at a low current density. The products from the first part of the run were N_2O and N_2O_4. Nitrogen tetroxide must also have been produced in solution by the same reaction if not by direct synthesis at the anode. The products from the second part of the run were N_2O, NO_3F, and OF_2 as expected from the above hypothesis. In addition, a small amount of NF_3 was formed. This was encouraging because it showed that an N-F bond could be formed under the experimental conditions

The effect of increased current density was tested in an additional run (Table 1, A195-07) In this run, only N_2O and N_2O_4 were found, probably because the experiment ended before fluorinated products appeared. The experiment was stopped because excessively high voltages were required to maintain current flow

From the results of this and previous runs, there would seen to be a maximum current density peculiar to each system beyond which excessive polarization occurs

HF-NO· Porous Nickel Anode

A run (Table 2, A195-20) was conducted with a porous nickel anode through which gaseous NO was passed The products found were N_2O and N_2O_4, along with a large quantity of NO which passed through the cell unchanged This result is essentially identical with the first

TABLE 2

DETAILS OF ELECTROLYSIS EXPERIMENTS

Run No.	Reactants	Mole Ratio	Coolant Temperature, C		Current, amperes	Voltage, volts	Length of Run, minutes	Major Products
			In	Out				
A195-09	HF:NOCl	34:1	-24		3.2	5.5 to 15	103	N_2O, NOCl
A195-19	HF:NOF	58:1	-28	-27	0.4 0.96	6.5 7.0	160 54	SO_2F_2 (small amount)
A195-20	HF:NO	(a)	-24	-22	1.1 to 2.4	6.8 to 5.0	60	N_2O, NO, NO_2
					3.2	6.9 to 6.5		N_2O, NO
						7.4 to 8.7	54	
A195-23	HF:NO	30:1	-11	-9	0.8	6.0 to 8.5	48	N_2O, NO, NO_2

Run A195-19 was conducted with an effective electrode area of 40 to 45 cm^2.
Run A195-20, -21, and -22 were conducted using porous nickel as an anode, effective area 26 cm^2.
Run A195-23 conducted using monel anode.
(a) Mole ratios not determinable; reactant gases flowing through the porous nickel at a rate of 35 to 40 cc/min.
Helium flow in -19, and -23 was 30 to 35 cc/min.

part of a previous run (Table 1, A195-08). It could be inferred from a comparison of the two runs that, in this experiment, the reaction never passed the first stage because the anode was continuously supplied with NO.

HF-NO: Monel Anode

A Monel anode was used to electrolyze a solution of NO in anhydrous HF (Table 2, A195-23) so that the effects of an expected greater anode polarization could be ascertained The results were virtually identical to the previous run with a nickel anode (Table 1, A195-08). Although possible, it is not likely that the run was greatly influenced by the higher temperature of operation' which caused a corresponding reduction in the solubility of NO

HF-FNO

An attempt (Table 2, A195-09) was made to prepare a solution of FNO in HF by the reaction of NOCl with liquid HF (Ref 8). So much difficulty was experienced with corrosion of the stainless-steel system by the NOCl that the results of the experiment were inconclusive. Therefore, it was decided to prepare FNO by a route not involving chlorine so that severe corrosion difficulties from chlorine could be avoided. Approximately 2.5 milliliters of FNO were obtained by scaling up a laboratory

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'Caused by partial equipment failure

preparation described in the literature (Ref. 12). The electrolysis of the resulting solution in HF (Table 2, A195-19) did not yield any compounds containing nitrogen. Instead, extensive corrosion of the anode was found. This latter result is not surprising in light of the report (Ref. 7) that HF-FNO complexes dissolve most metals in Groups V, VI, VII and VIII. No attack was found on the stainless-steel cell or upon the nickel cathode; however, the solution of FNO used in this study is much more dilute than the complexes discussed in the literature. Complete decomposition and attack of FNO upon stainless steel was found, however, when 15 grams of FNO were stored for 64 hours in a stainless-steel cylinder at room temperature.

Solubility of N_2O in HF

A sample of spent electrolyte from an HF-NO run (Table 2, A195-23) was analyzed and found to contain dissolved N_2O. Since it is planned to use N_2O as a solute in future electrolysis, it was considered desirable to check the solubility of N_2O in HF because a literature survey did not yield any such data. The experimental data obtained are plotted in Fig. 12. The isotherms appear to follow Henry's law throughout the range considered; the Henry's law constants are 7×10^6 at -23 ± 1 C and 53×10^6 at 78.5 ± 1 C.

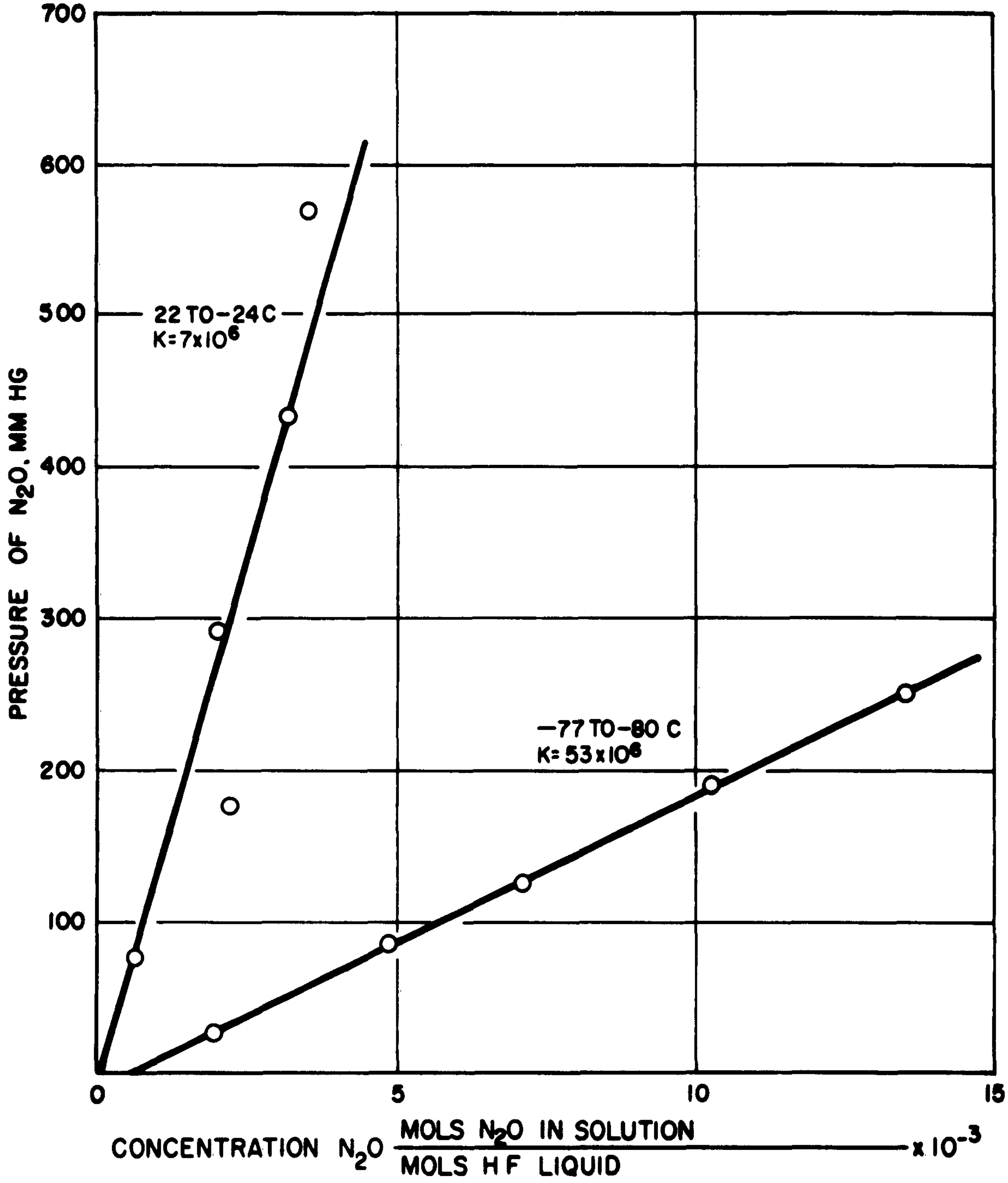

Figure 12. Solubility of $N_2O(g)$ in $HF(\ell)$

SUMMARY

In line with the objectives of the project, as stated in the introduction, work started with an investigation of the HF-N_2O_4 system. It was found that the solution had the high electrical conductivity desirable for electrolytic synthesis The variation of conductivity with changes in electrolyte composition was investigated and, from the data obtained, a working range of electrolyte composition was selected for the synthetic work Indeed, it was found that when electrolyses were conducted outside of the indicated range in the HF:N_2O_4 system, yields of NO_3F decreased markedly.

Other investigations were conducted to narrow the choice of operating conditions and to aid in the cell design For example, it was found that the choice of anode materials was restricted to nickel or platinum, but that stainless steel was a more suitable cell material because it tended to build up a film that was electrically insulating and would, therefore restrict reaction to the cell electrodes Other experiments were conducted which suggested limits for the sizes of electrodes and ranges of current densities to be used

Electrolyses conducted with the HF N_2O_4 system have generally yielded OF_2 and NO_3F as products This work appears to be the first electrochemical synthesis of NO_3F It was postulated that NO_3F probably resulted from the fluorination of HNO_3 formed when N_2O_4 was dissolved in HF The above premise was strengthened when it was found that NO_3F

could also be obtained from the electrolyses of HF HNO_3 solutions. During the electrolysis of HF N_2O_4 at a lower temperature of operation, ozone also was synthesized It is of interest that the ozone prepared by this method appears to be more stable to explosive decomposition than that prepared by the usual routes

The formation of O_3, as well as NO_3F, suggested the presence of too much oxygen in relation to the amount of nitrogen in the electrolyte for the synthesis of F-N-O compounds containing large ratios of fluorine to nitrogen Consequently, emphasis was shifted to systems with lower oxygen content Experiments with the HF NO system yielded no fluorinated products during the first part of the electrolysis. After prolonged electrolysis, however, NO_3F was again prepared It is thought that the NO was oxidized to NO_2 at the anode which subsequently reacted with the HF, forming nitric acid After a substantial quantity of NO was oxidized, it was then possible to electrofluorinate the nitric acid, forming NO_3F.

The pressure-composition relationship was determined for the HF-N_2O system and has demonstrated some solubility of N_2O in HF. It is anticipated, however, that a conductivity additive will have to be used because it is not expected that the solution will be sufficiently conductive

A series of experiments has been carried out which established the reproducibility of a platinum wire for use as a reference electrode to monitor anode potential changes during electrolysis It is expected that such measurements will aid in interpretation of experimental results.

EXPERIMENTAL DETAILS

ELECTROCHEMICAL AND CHEMICAL DATA

Reaction of HF with N_2O_4

Nitrogen tetroxide (2.5 milliliters; 40 m moles) was poured slowly into HF (4.2 milliliters; 210 m moles, Matheson) contained in a translucent Kel-F tube. All reagents and containers were cooled in ice before use. The N_2O_4 dissolved with the formation of a lemon-yellow solution, accompanied by violent hissing and initial evolution of fumes. The vapor above the solution was light brown in color.

When N_2O_4 (0.5 milliliters; 8 m moles) was added to HF (24.5 milliliters; 1210 m moles), the addition was accompanied by violent hissing. However, no hissing was noted upon the addition of more N_2O_4.

Preliminary Equipment and Procedures

Power was supplied by a continuously variable, unfiltered, full-wave rectified supply and measured by calibrated panel meters. A filtered power supply originally ordered for this work, Knight 87FX505, was substituted for the unfiltered supply. No significant difference could be found in the electrolysis of HF-N_2O_4, even though the ripple factor was reduced from 47 percent to a maximum of 1.3 percent. Two different procedures were used; in both, however, the electrodes were inserted into the open vessels from above.

The N_2O_4 was poured slowly into the HF[2]. All vessels, graduated cylinders, and reagents were cooled with ice before using, and the mixed solution was cooled for a few minutes before electrolyzing.

Electrolysis Procedure 1. A translucent Kel-F beaker, 37 millimeters ID, 65 millimeters deep, with 5-millimeter walls, was used. The strip electrodes[3], 7 millimeters in width, were immersed to a depth of about 18 millimeters in the solution and were spaced 13 millimeters apart. The beaker was immersed in an ice bath over the solution level during electrolysis.

Electrolysis Procedure 2. A transparent[4] Kel-F beaker, 26 millimeters ID, 35 millimeters deep, with 3.2-millimeter walls, was used with 10 x 10 millimeter sheet-metal electrodes. The electrodes were fully immersed into the solution and connected to the power source by an extension of the same metal, 1 to 2 millimeters wide. Spacing was 10 millimeters between electrodes.

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[2] No attempt was made to compensate for the loss of HF or N_2O_4 by vaporization.

[3] If strip electrodes were unavailable, then rods were used in such a way that an equivalent area was exposed

[4] The use of a transparent Kel-F beaker permitted the visual observation of the electrolysis and, thereby, the initiation of gas evolution.

Over-all Cell Impedance

The electrode assembly was made by inserting two 0.020-inch-diameter wires, spaced 10 millimeters apart, into a Teflon Block until the wires protruded 0.2 millimeter. The block was then placed into an ice-cooled Kel-F beaker. A Teflon-tipped stirrer was used to agitate the solution continuously.

In the measuring circuit (Fig. 13), the function of the 1N34A germanium diode was to compress the scale. With the diode connected, a reading of 1.0 represented an actual current of 5.35 milliamperes, whereas a reading of 0.25 corresponded to 0.52 milliampere.

Transistorized Pulse Generator

The pulse generator (Fig. 14) used for the intermittent direct-current experiments is an adaptation of a Power-Drive Time-Base Generator (Ref. 13), modified so that both the pulse duration and repetition rate could be controlled. In addition, a 15-ohm resistor was added to limit the peak current of the 2N1059 to prevent exceeding its maximum current rating.

Polarization Curves of HF Solutions With Two-Electrode Systems

The electrolysis of anhydrous HF (Matheson) was conducted with nickel electrodes and with platinum electrodes, using Electrolysis Procedure 2. The data (Fig. 7) also include that from the electrolysis of HF-H_2O, (mole ratio 17:1) under the same conditions.

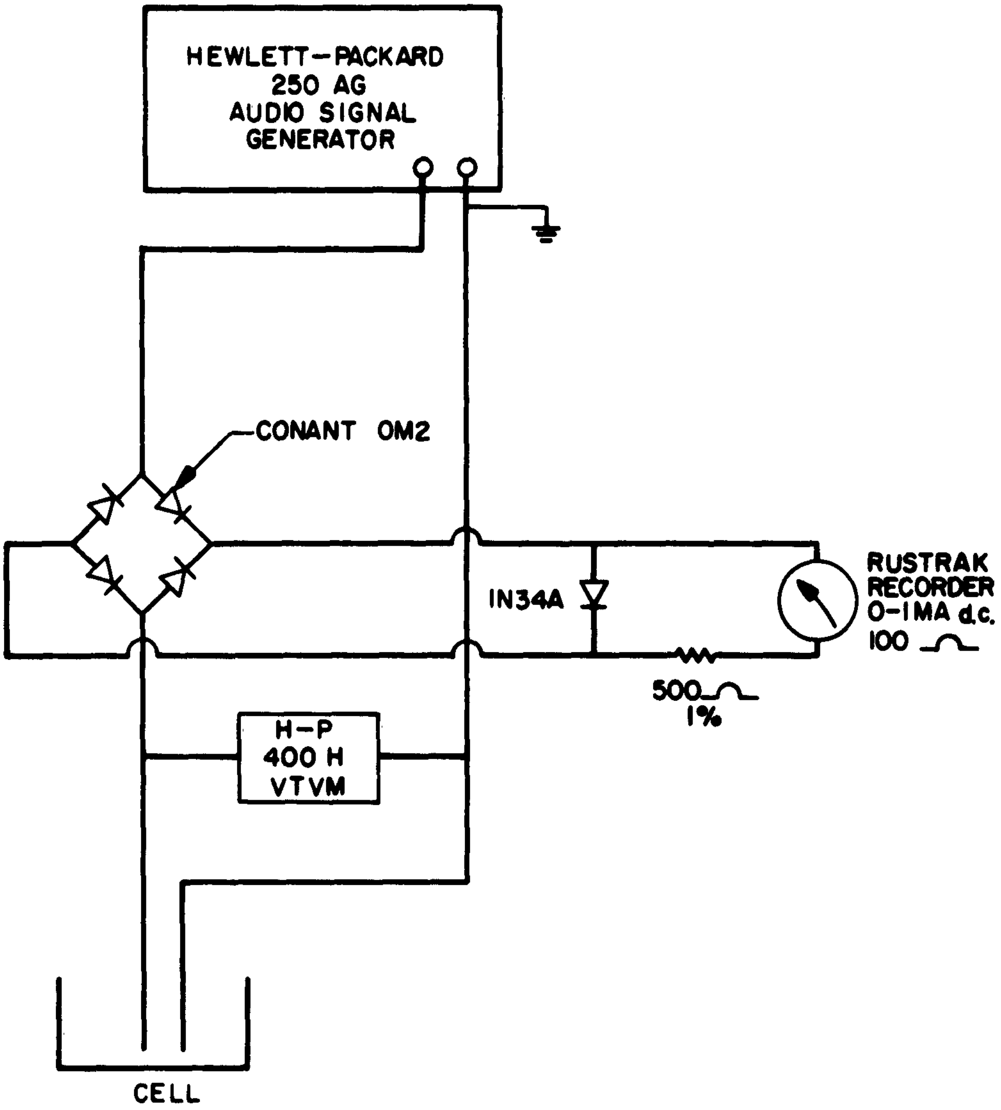

Figure 13. Impedance-Measuring Circuit

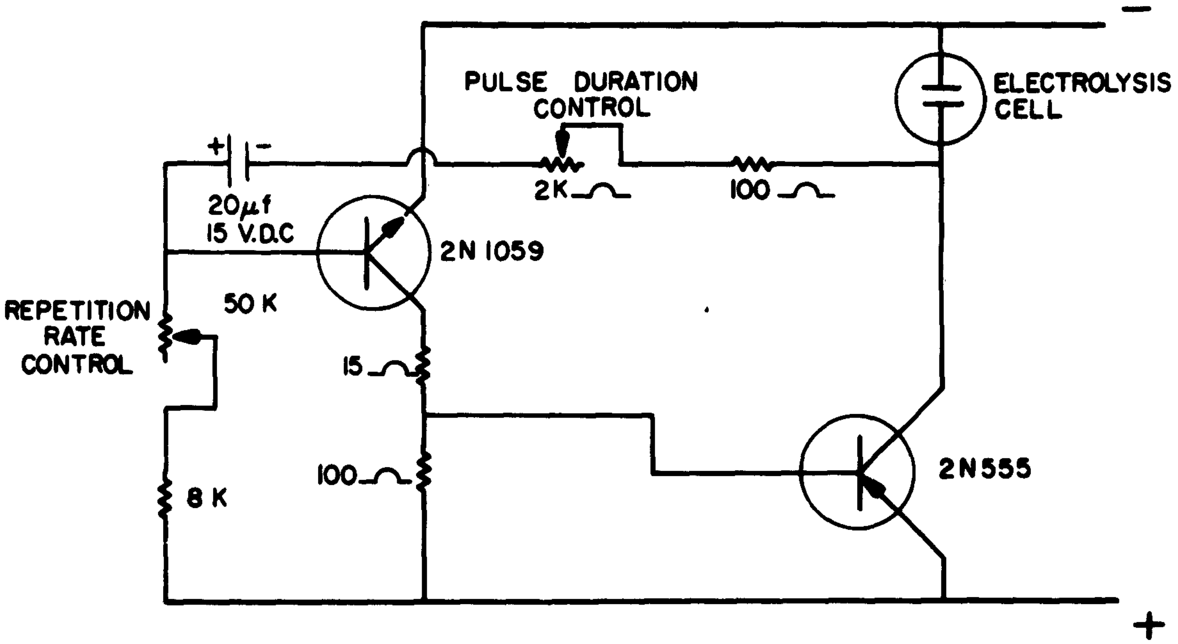

Figure 14. Transistorized Pulse Generator

Electrode Potential Measurements

The electrolytic cell used for the electrode potential measurements is shown in Fig. 8. The anode, cathode and Kel-F electrode were heat sealed into female polyethylene connectors. Male connectors were forced into holes in the polyethylene cover, forming an adequate seal. After cooling in a salt-ice slush, the cell was filled with anhydrous HF directly from a cylinder through an electrode opening (Fig. 15). After filling, the nitrogen stream was increased, the HF connector was removed, and the electrode was replaced. After sufficient HF had diffused through the porous Teflon, the platinum electrode and stainless-steel tubing were inserted into the Kel-F tube forming a sealed system. The pressure above the HF solution in the Kel-F tube was maintained essentially constant, minimizing diffusion of HF through the porous Teflon even though the HF level in the polyethylene container changed because of vaporization, chemical reaction, or bubble formation. The electrical circuitry (Fig. 15) was assembled so that the anode was connected to the electrometer ground. Both cell input voltage and reference electrode potential were measured, therefore, in reepect to the anode.

Anode Materials

Materials other than Pt and Ni have been examined for suitability as anodes in the electrolysis of HF-N_2O_4. The following were found to be soluble upon immersion in this solution: Sn, Pb, Ti, Nb, and Ta. Upon passage of an electric current, Ag, Cd, Zr, Pd, Mo, W and Mn dissolved rapidly. The insoluble metals Cu, Au, Zn, Fe, Co did not permit current to pass, undoubtedly because of the formation of an anodic film. A degree of conductivity was found for Cr and for monel. However, an alloy containing Ni and Cr in the ratio 9:1, did not permit current to pass.

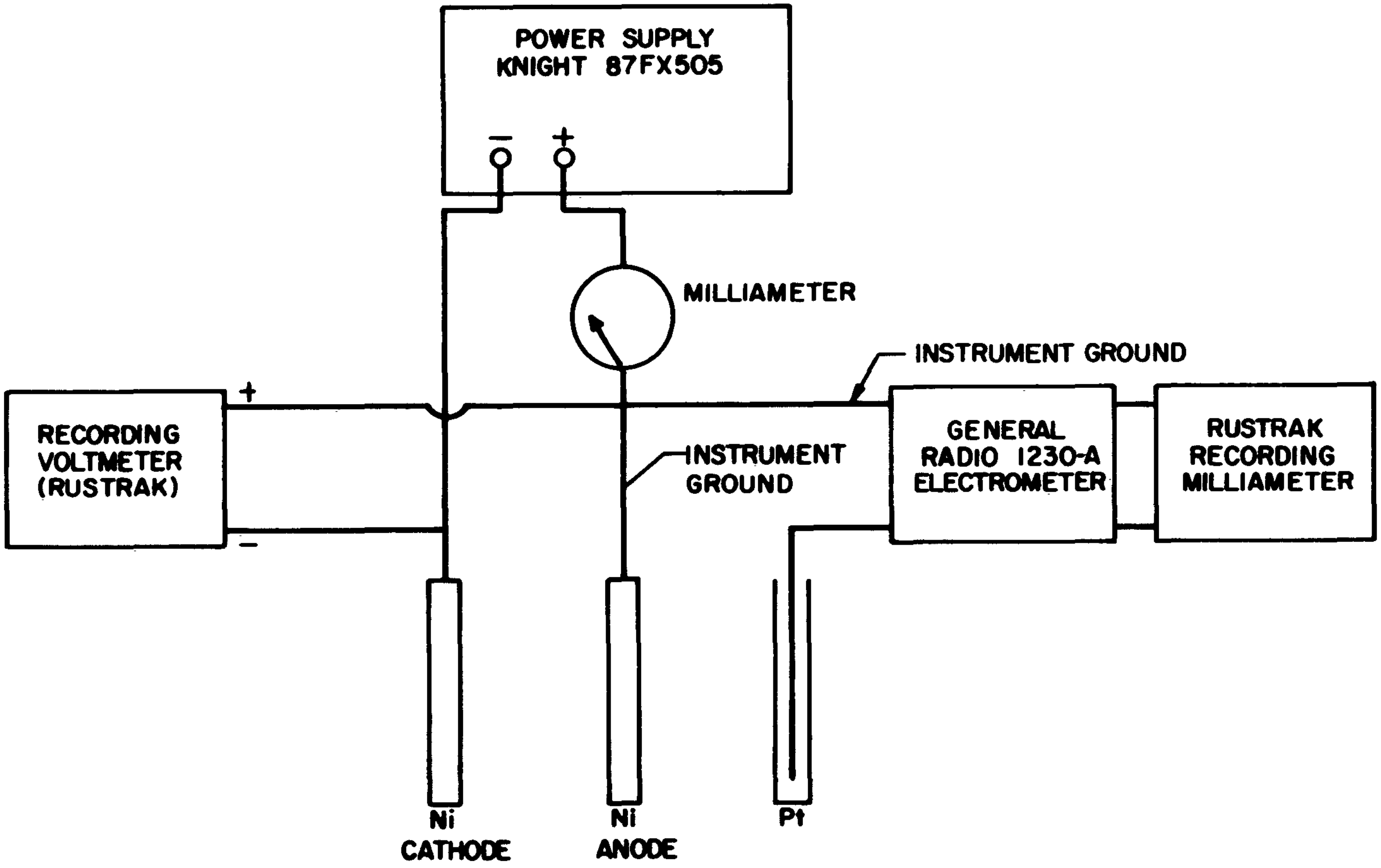

Figure 15. Electrical Circuitry for Electrode Potential Measurement

Similar behavior was found with Inco A, Hastelloy-C and Type 321 stainless steel. However, the latter two alloys and monel were found to be satisfactory as cathode materials.

The synthetic work has been based on nickel for both anodes and cathodes, except for one run where monel was used as an anode.

ELECTROCHEMICAL SYNTHESIS--SMALLER CELL

Equipment

A 1-ampere cell (Fig. 11) was used for extended electrolysis, pulse, two-electrode polarization, and synthesis experiments. The nickel electrodes were held by 3/16-inch nickel rods which had been pressed through a Kel-F plug. The 1/4-inch stainless-steel inlet and exit tubes had been previously pressed into a 7/8-inch hole in an AN814-16C plug. The body of the cell was made by drilling a 3/4-inch hole in a 1-inch Kel-F rod, and the cell was joined to the plug with an AN819-16C nut. The entire assembly was found to be vacuum tight.

Procedure

The precooled HF, which was added as a liquid to the ice-cooled cell, was dried by electrolysis before proceeding in some of the experiments. The end point of the electrolysis was indicated by no further reduction in the current through the cell. At this point, the solute was added through the funnel, the cell agitated, and electrolysis started.

Helium flow was maintained through the cell during all operations, except during the addition of reagents When it was necessary to add solids to the HF, it was done independently of the cell in a closed polyethylene bottle and subsequently poured into the cell The cell was cooled during all experiments in an ice bath

The gaseous product from the cell, mixed with He, was conducted through a stainless-steel absorber filled with NaF pellets (Harshaw) to absorb HF and then into a Kel-F U-tube cooled in liquid nitrogen At the completion of the run, the U-tube was closed off from the absorber, evacuated, and all the trapped products were permitted to vaporize into a stainless-steel collection cylinder A metal IR cell with coated[5] NaCl windows was filled directly from this cylinder During some of the experiments samples of noncondensable gas passing through the Kel-F trap were taken and analyzed in the mass spectrometer

ELECTROCHEMICAL SYNTHESIS WITH LARGER ELECTROLYTIC CELL

Details of Experiments

The details of the synthesis work are shown in Tables 1 and 2 As indicated the voltage readings reflect the cell changes which took place from the beginning to the end of the electrolyses The current flow was maintained essentially constant by the current regulator for all runs, except as noted for A195-07 -21 and -22 In run A195-07, the

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[5] NaCl windows were coated with a very thin layer of Halocarbon wax for protection against the fluorides

current density at the anode was increased by reducing its area by a factor of 10, making it impractical to maintain constant current because of excessive voltage. During runs A195-21 and -22 no attempt was made to regulate current, although an attempt was made to adhere to the current and voltage relationships normally used during the electrolytic drying operation. Constant current is not used during the drying operation because the cell resistance rises and excessive voltages would be required.

Equipment and Procedure

The experimental equipment (Fig. 16, 17, and 18) consisted of a reactant handling system, a jacketed stainless-steel electrolytic cell, condenser, fluorine absorber, and a metal and Kel-F vacuum line. Total system pressure was measured with a Pirani vacuum gauge. For measuring product pressures, a metal-bellows null indicator was employed and dried nitrogen was used to balance the diaphragm pressure as indicated by a neon bulb (O, Fig. 17). A pressure reading was obtained from a mercury manometer.

System purging was accomplished by feeding dried nitrogen through valve (M) and out valve (K). To back-purge the NaF absorber (X, Fig. 16), the flow was directed through valve (A) after disconnecting the absorber from the condenser. The coolant system, for maintaining essentially constant temperature in the cell and supplying coolant for the condenser, consisted of a refrigeration unit with a copper cooling coil, a supply tank (Fig. 16) and an immersion pump. Coolant was pumped through the condenser to the cell. Temperatures were recorded on a Bailey recorder by means of copper-constantan thermocouples (AWG No. 36) (Fig. 18) located at the entrance to the condenser and at the exit of the electrolytic cell.

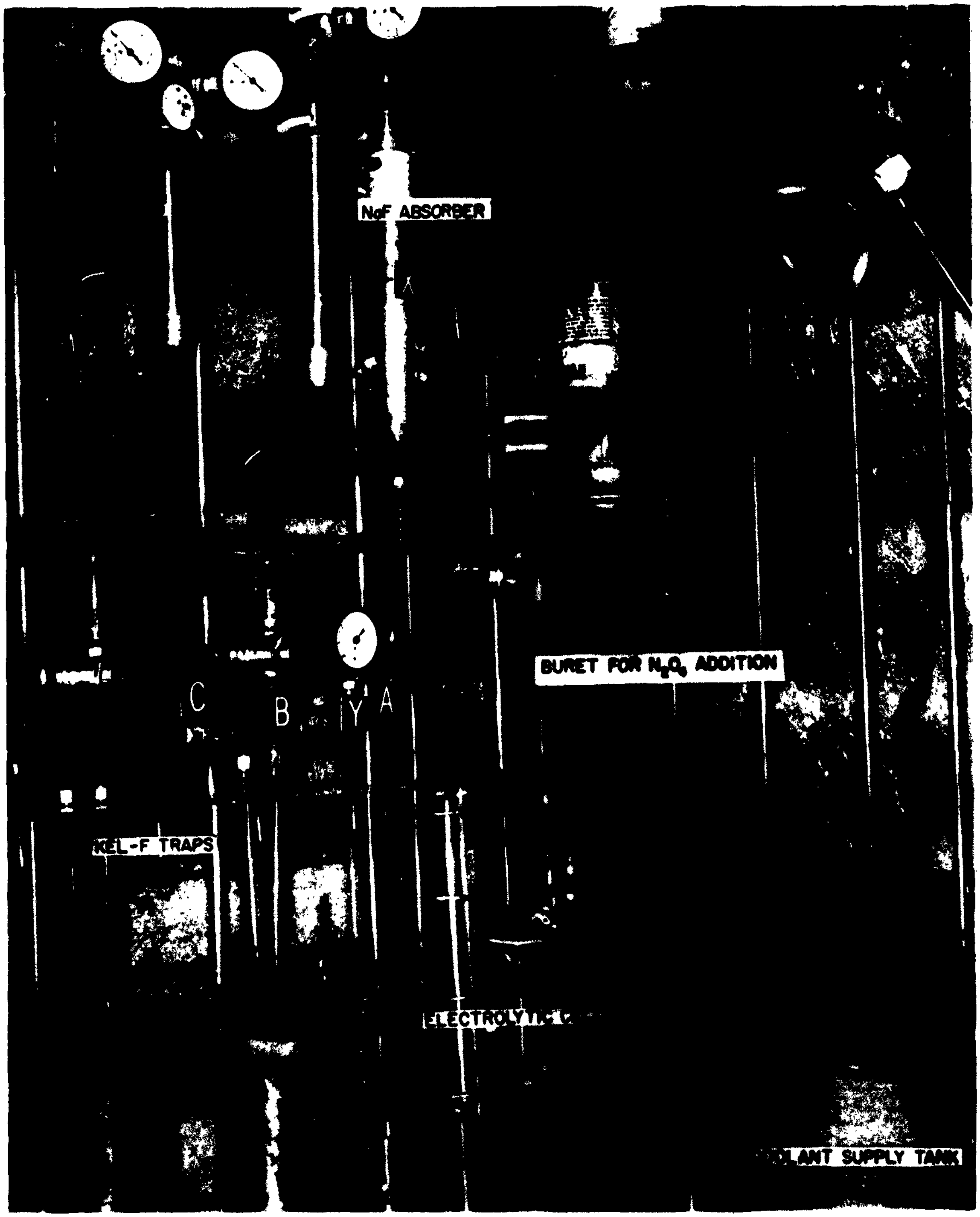

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Figure 16. Electrolysis Assembly

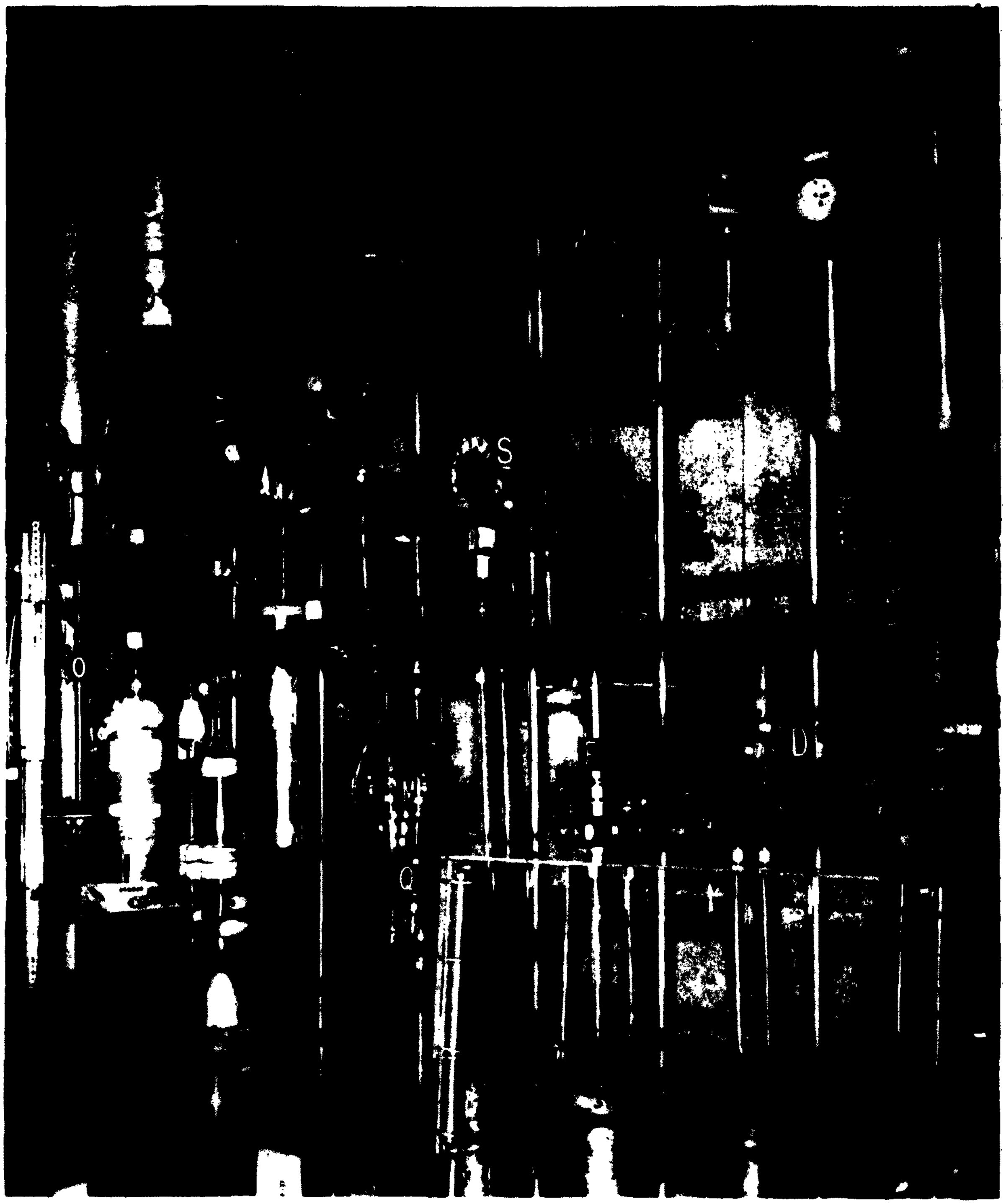

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Figure 17. Pumping, Collection, and Pressure Measuring Section of Vacuum Line

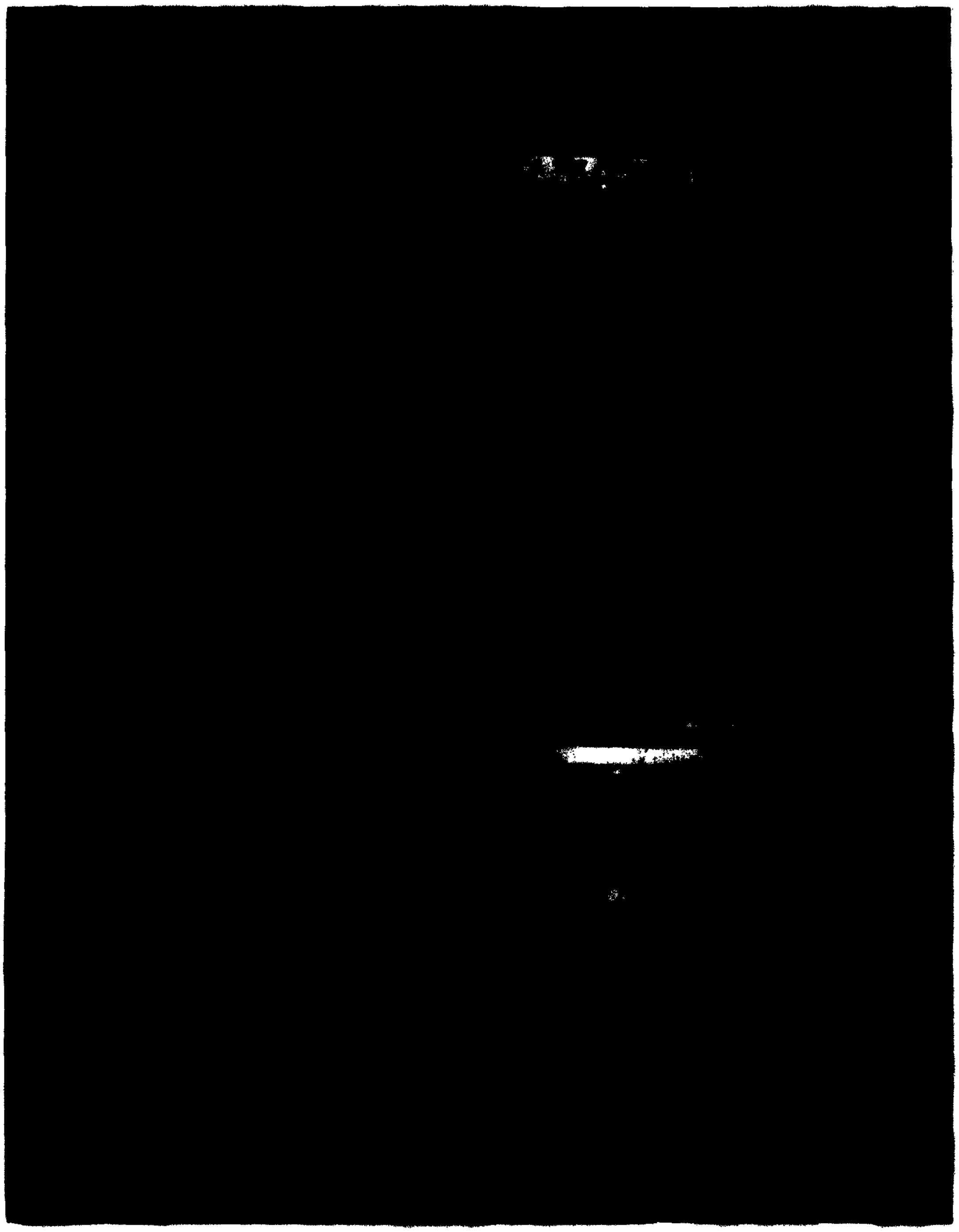

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Figure 18. Disassembled View of Electrolytic Cell and Associated Equipment

The electrolysis reactions were performed in a jacketed stainless-steel cell (Fig 18) with a useful liquid capacity between 40 and 360 milliliters. There were two inlets for introduction of reactants, an inert gas inlet, a connection to the condenser, an opening for the liquid level probe, and a bottom drain The HF was added to the cell as a liquid through polyethylene tubing from the storage cylinder (Fig. 16). A piece of Kel-F tubing was used to connect the N_2O_4 cylinder to a glass buret from which the liquid N_2O_4 was metered into the cell. When BF_3 was used, it was introduced as a gas from a cylinder (Fig. 18). The SbF_5, after distillation, was added as a liquid from a glass bulb through Kel-F tubing, at the same location used for BF_3.

The level of the liquid in the cell was found by using a piece of monel rod covered with a thin Kel-F sleeve, except for the ends, as a level detector and an ohmmeter as an indicating device Helium was used as an inert carrier gas during the experiments It was found that a flow of 50 to 60 cc/min was needed while electrolytically drying the HF to prevent, or at least to reduce. the severity of minor explosions. However, during the subsequent electrolysis the flow was reduced to 30 to 35 cc/min without any explosions occurring

Effect of Impurities

In most experiments one or more products such as CO_2, SO_2F_2, ClO_3F and NO_3F have been found Several experiments were performed to trace the source of certain of the more important impurities The NO_3F apparently resulted from the use of dilute nitric acid as a cleaning solution, a procedure which was therefore abandoned. The ClO_3F probably resulted from the decomposition of Halocarbon wax at the porous anode. The HF itself is also a source of impurities, for example, SO_2, which probably supplied the starting material for the small amounts of SO_2F_2 found.

Usually, these impurities are not troublesome when sufficient quantities of starting materials are used. When mole ratios (HF:solute) considerably less than 34:1 are used, then products resulting from fluorination of the impurities may become troublesome.

Porous Anode. A porous nickel electrode (Fig. 19) was fabricated for use as an anode in runs where one of the reactants was a gas. Preliminary tests with methanol on this electrode showed that a minimum flow of 40 cc/min (GN_2) was required to keep gas flowing, as well as to prevent liquid from backing through the porous nickel into the gas cavity.

Electrical Equipment

The circuit of the power supply and measuring circuit (Fig. 20) is relatively conventional except for the connections to the cell. As shown, the voltage readings were taken from additional terminals on the electrodes to avoid any errors from contact resistances. The recording ammeter and voltmeter were actually 0- to 1-milliameter strip-chart recorders connected with the appropriate shunts and series resistors

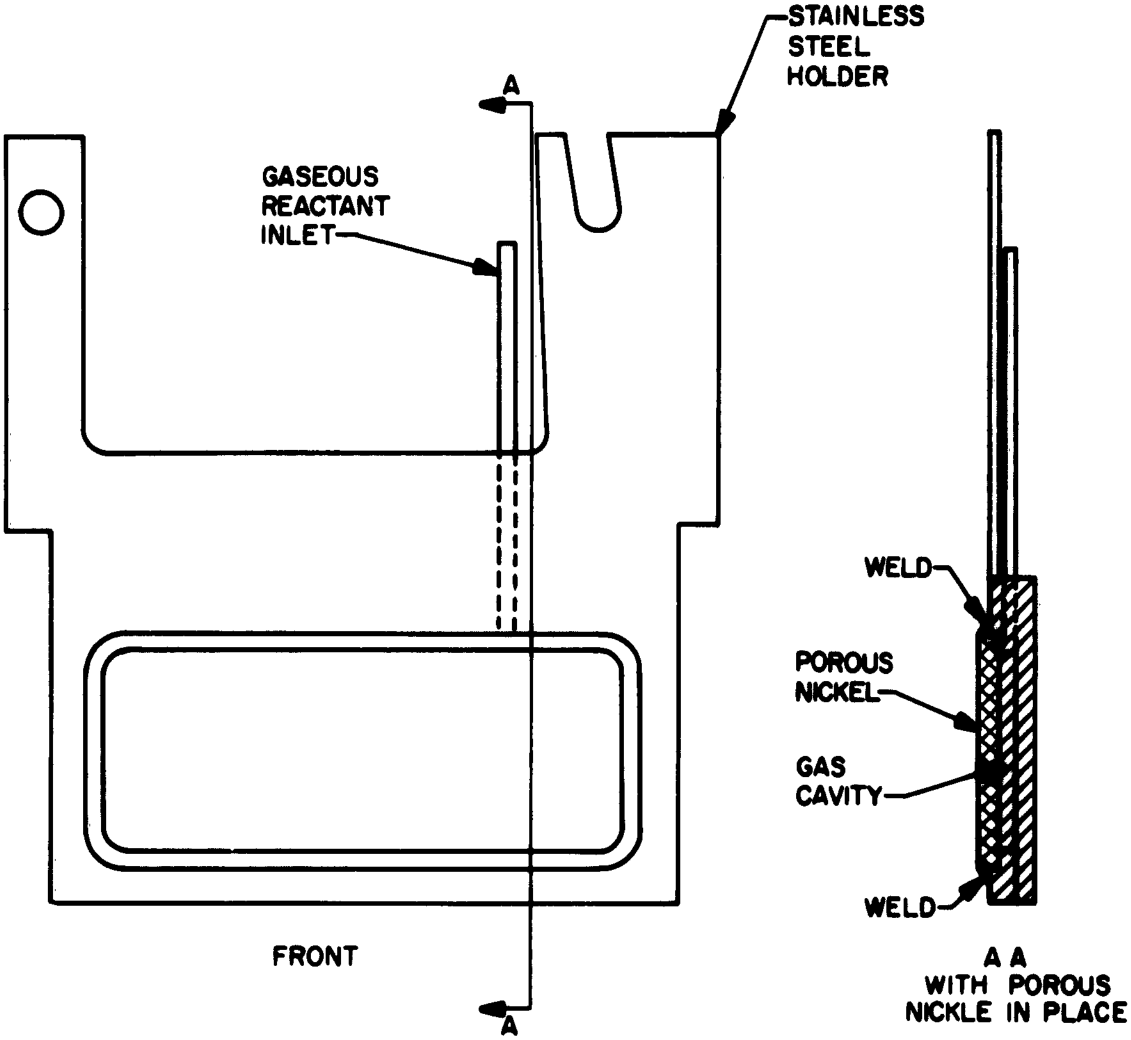

Figure 19. Details of Porous Electrode

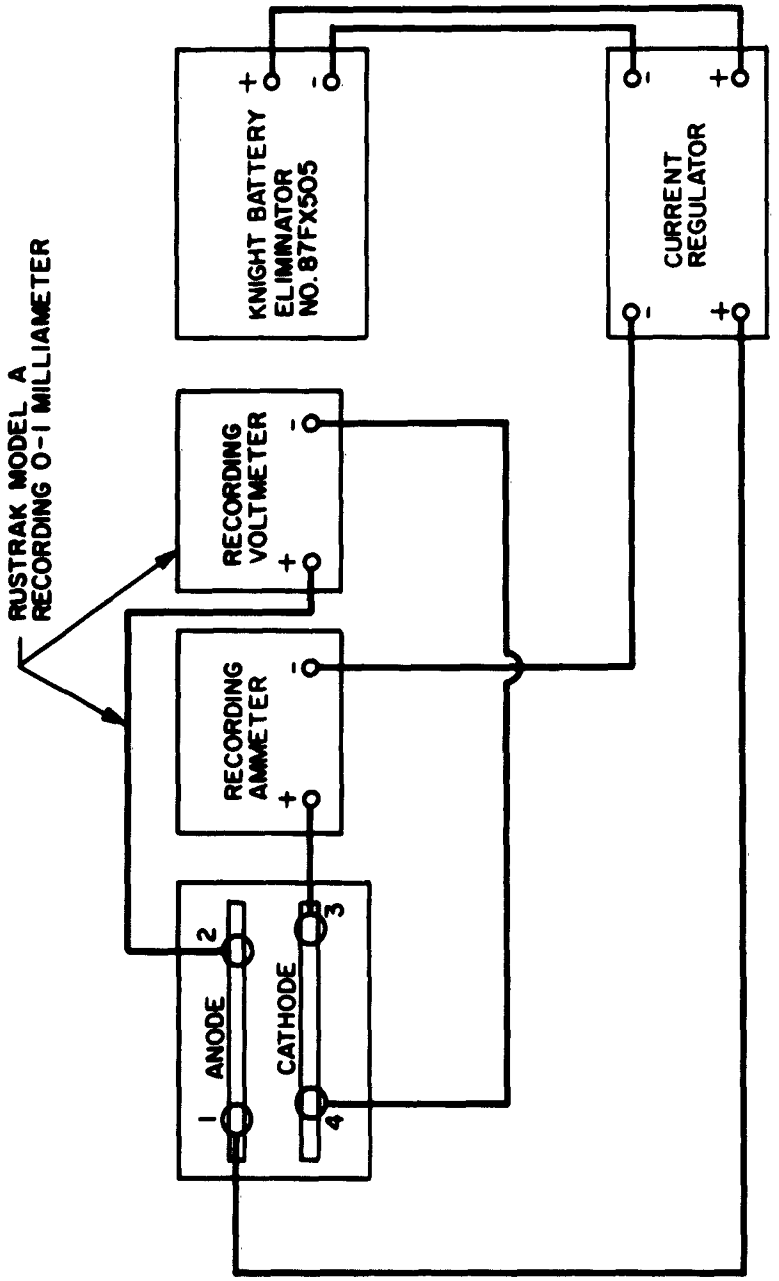

Figure 20. Power Supply and Measuring Equipment

The current regulator (Fig 21) was designed to maintain constant current to the cell regardless of cell resistance or voltage requirements. It has been found to operate satisfactorily over a range from 3 to 26 volts input potential and from 0 1- to 10-amperes output current. Minimum voltage drop through the regulator is 1 2 volts at 10 amperes. Maximum voltage drop is limited by the transistor heat dissipation and is about 7 volts at 10 amperes Considerably higher voltage drops can be tolerated at lower current levels or if forced air cooling is applied to the transistor heat sink Regulation has been found to be adequate even when operating at or near maximum current For a 600-percent change in load resistance, or a 16-percent change in input voltage, the current changed by 3 percent Changes of these magnitudes are not normally encountered in practice Certain aspects of the circuit (Fig. 21) represent changes from the usual current regulator circuit design. The No. 1141 lamp bulbs act as ballast resistors and provide a degree of current regulation permitting operation over a much wider input voltage range than would have been obtained with the usual fixed resistor The 6-ampere diodes were mounted on a small copper heat sink, and the assembly was mounted on the exterior of the regulator Long-time thermal drift problems in the diodes were virtually eliminated by this expedient.

Performance of Electrolysis Equipment

The change in operating temperature from 0 to -20 C has proved to be important in determining the nature of the products of the electrolysis. Therefore, certain aspects of the cooling system are discussed below. The refrigerating system was found capable of keeping the coolant temperature at -20 C while operating at a 50-watt input to the cell. The cooling

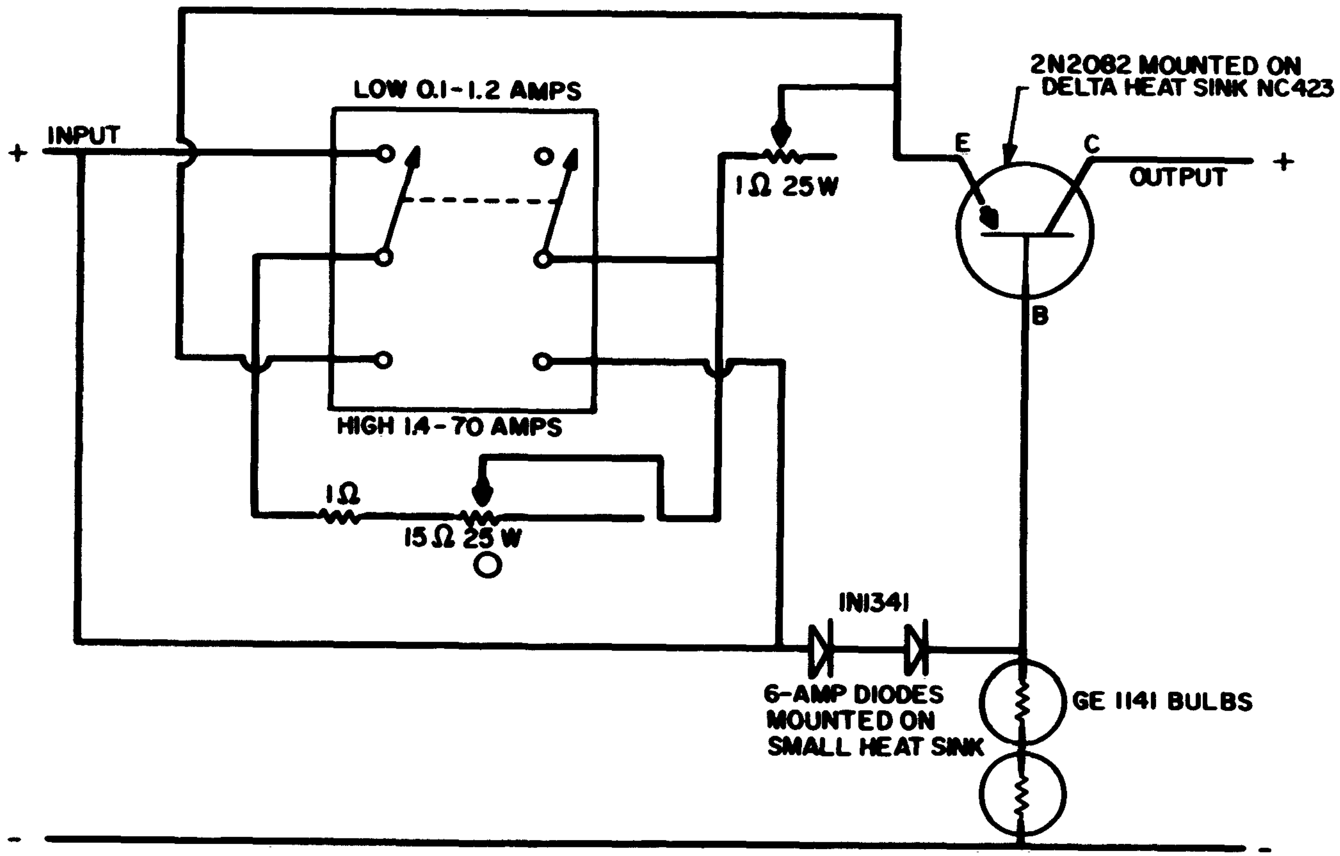

Figure 21. Current Regulator

efficiency of the new jacketed cell design was indicated by a very rapid decrease in electrolyte temperature upon interrupting the current to the cell, and by a very slow rise in electrolyte temperature upon resumption of current flow. The change in electrolyte temperature was indicated by a corresponding change in solution resistance.

FUTURE WORK

Continuation of the electrolysis of N-O compounds containing less oxygen than N_2O_4 is planned. Compounds such as FNO and N_2O, which would not be expected to lead to the formation of HNO_3, are of particular interest.

It is intended to continue to use the platinum reference electrode developed under this project to monitor the planned electrolysis experiments.

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