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# INFLUENCE OF NOBLER METAL SALT ADDITIONS UPON THE DISSOLUTION RATE OF ALUMINUM IN HYDROFLUORIC ACID

By

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A

THESIS

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# ABSTRACT

The rate of dissolution of aluminum in 2N HF upon the addition of nobler metallic salts was studied. Aluminum corrodes in HF due to the acid's ability to dissolve the protective oxide present on the surface. Rates were measured by the hydrogen evolution method.

Salt additions of $AgNO_3$, $CuSO_4$, $HAuCl_4$, and $PtCl_4$ to aluminum dissolving in 2N HF resulted in the electroless deposition of more or less coherent metals(from the salts mentioned)on the aluminum surface. The dissolution rate initially decreased in all of the cases and was attributed to the "blanketing effect" of the deposits. Ensuing increases of rate after the initial decrease was probably due to the uncovering of local cathodes beneath the inhibiting deposit. All experiments involving $PtCl_4$ were carried out in nitrogen atmospheres which caused a greater dissolution rate due to the absence of strongly protective layers. Additions of the salt solutions of $NiCl_2$, $FeSO_4$, and $CuSO_4$ gave similar rate fluctuations, but no visible deposit. It was suspected that thin invisible layers electrolessly deposited were present on the aluminum surface. Qualitative testing was performed in many of the cases to observe formation of various precipitates.

Electropotential measurements of aluminum showed that the anodic potential increased in the salt solutions mentioned above and thus supported the measured rate decreases.

Microhardness tests were performed and showed harder surfaces on the aluminum dissolving in HF with added nobler metal salts, because of Ag, Ni and Co layers present on it. These facts substantiated the theory of thin layers electrolessly deposited on the aluminum surface which inhibited the rate of dissolution.

Electron microscopy showed a difference in the etching behavior of a sample of aluminum etched in HF and an aluminum sample etched in HF in the presence of $NiCl_2$.

# ACKNOWLEDGEMENTS

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# TABLE OF CONTENTS

Electrode potential of aluminum in 2N HF and the effect of certain salt additions:

Microhardness of aluminum corroded in 2N HF on addition of:

# LIST OF FIGURES

Figures Page

## LIST OF TABLES

# CHAPTER I

# INTRODUCTION AND LITERATURE REVIEW

Aluminum is lower (more negative) in the electrochemical series than most other common metals. As a result of this, its property in corrosive environments is greatly influenced by other more noble metals which are in external contact with it.

The deposition of a metal upon the surface of a less noble metal in an electrolyte without cathodic current is known as electroless deposition.[1] The mechanism by which this occurs is a simple replacement of the less noble material in the electromotive series by the nobler metal. For example: a zinc plate immersed in a solution of copper sulfate will ionize (Zn) into the solution and copper will be replaced by it:

$$Zn + Cu^{++} \longrightarrow Zn^{++} + Cu \text{ (deposited on excess zinc)} \qquad (1)$$

By the law of electroneutrality, a net charge cannot exist in the solution. Copper ions will therefore discharge upon the only metal surface available--the zinc plate. The copper atom deposits upon the zinc surface at preferential spots where nucleation is easier. Thus the electrons needed by the cupric ions come from the zinc atoms which ionize. The surface consists of innumerable corrosion cells with copper as local cathodes. Under certain conditions, the copper may appear as a very continuous film on the zinc surface. However, the layer contains pores since some zinc always dissolves while the copper film is forming.

Electroless plating is a somewhat new method of industrial application of coats. By far the most common method of electroless plating of aluminum is the zinc immersion process.[2] The principal functions of this process are to remove the oxide film and replace it with an adherent layer of metallic zinc. A common commercial solution is a caustic soda, sodium zincate, to give a highly alkaline solution, zinc oxide, and water. Upon immersion, the oxide layer is removed, the underlying aluminum is dissolved and simultaneously replaced by an equivalent weight of zinc. When the aluminum surface is completely covered with a layer of zinc in a reaction similar to Eq. (1), action virtually ceases. A zinc layer is commonly deposited in this manner before other plating operations are carried out upon that layer, which provides an excellent surface for deposition. In 1958 Steinberg[3] reported tight adherent coats of many metals more noble than aluminum could be produced without cathodic current on the latter. De Long[4] (1960) put an adherent (non-electrolytic) coat of nickel upon aluminum using a fluoride-hypophosphite bath. He noted that the use of fluoride salts substantially increased the rate of coating formations. In 1962 electroless gold plating upon aluminum was achieved by Heilman.[5] MacCormack[6] received a U.S. patent for electroless plating of nickel, cobalt, and copper on aluminum in 1964.

Obviously a series of more noble metals can be deposited from their solutions non-electrolytically upon aluminum. Of particular interest from the viewpoint of corrosion is the deposition in acidic solutions. Electropotential and dissolution rate studies of aluminum in hydrofluoric acid were made by Wang[7] in 1954. He also studied the effect of nobler metal salt additions, but in very little detail. The various effects produced by these additions will thus be discussed in this thesis. The only acid in which very pure aluminum will dissolve at a considerable rate is hydrofluoric. This acid, therefore, was used throughout this work.

# CHAPTER II

## DISSOLUTION RATE OF ALUMINUM IN HYDROFLUORIC ACID

The initial phase of the investigation involved simply the dissolution rate study of aluminum in hydrofluoric acid.

Aluminum produces stable trivalent compounds and therefore it will react with hydrofluoric as shown:

$$2\ Al + 6\ HF \longrightarrow 2\ AlF_3 + 3\ H_2 \qquad (2)$$

### A. Materials

The aluminum used was Super-Raffinal (Swiss, Aluminum-Industrie-Alstein-Gesellschaft) and had the following composition:

| | |
|---|---|
| Silicon | 3 p.p.m. |
| Iron | 3 p.p.m. |
| Copper | 1.3 p.p.m. |
| Aluminum | balance |

The hydrofluoric acid used was 48-51% specific gravity and of reagent grade.

Certain concentrations of acid solutions (diluted with distilled water) were prepared and checked by titration with a standarized solution of sodium carbonate, using methyl orange as an indicator.

### B. Apparatus, Procedure, and Calculations

Fig. 1 is a picture of the entire dissolution rate apparatus, consisting of a constant temperature water bath, a stirring mechanism with a mercury seal, a reaction flask for holding the

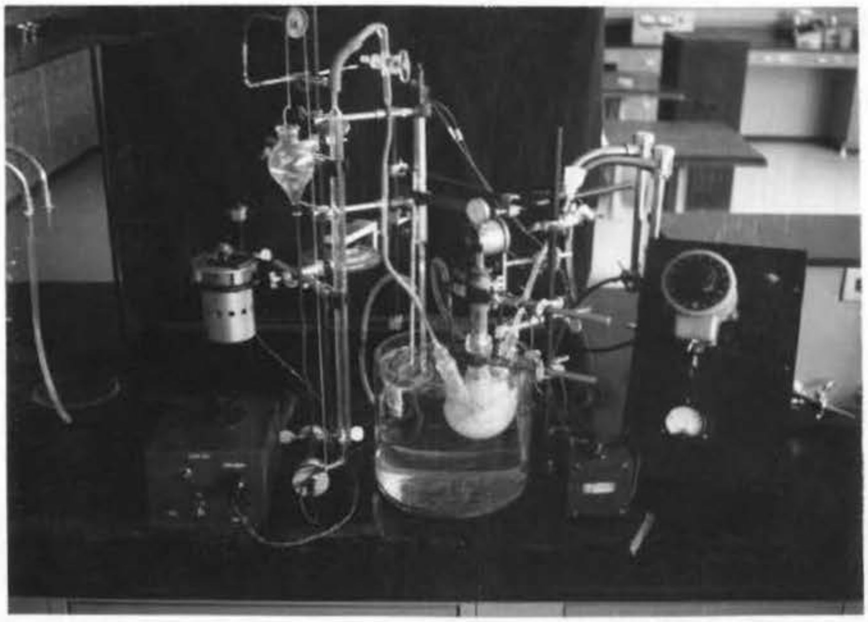


Figure 1

Dissolution rate apparatus

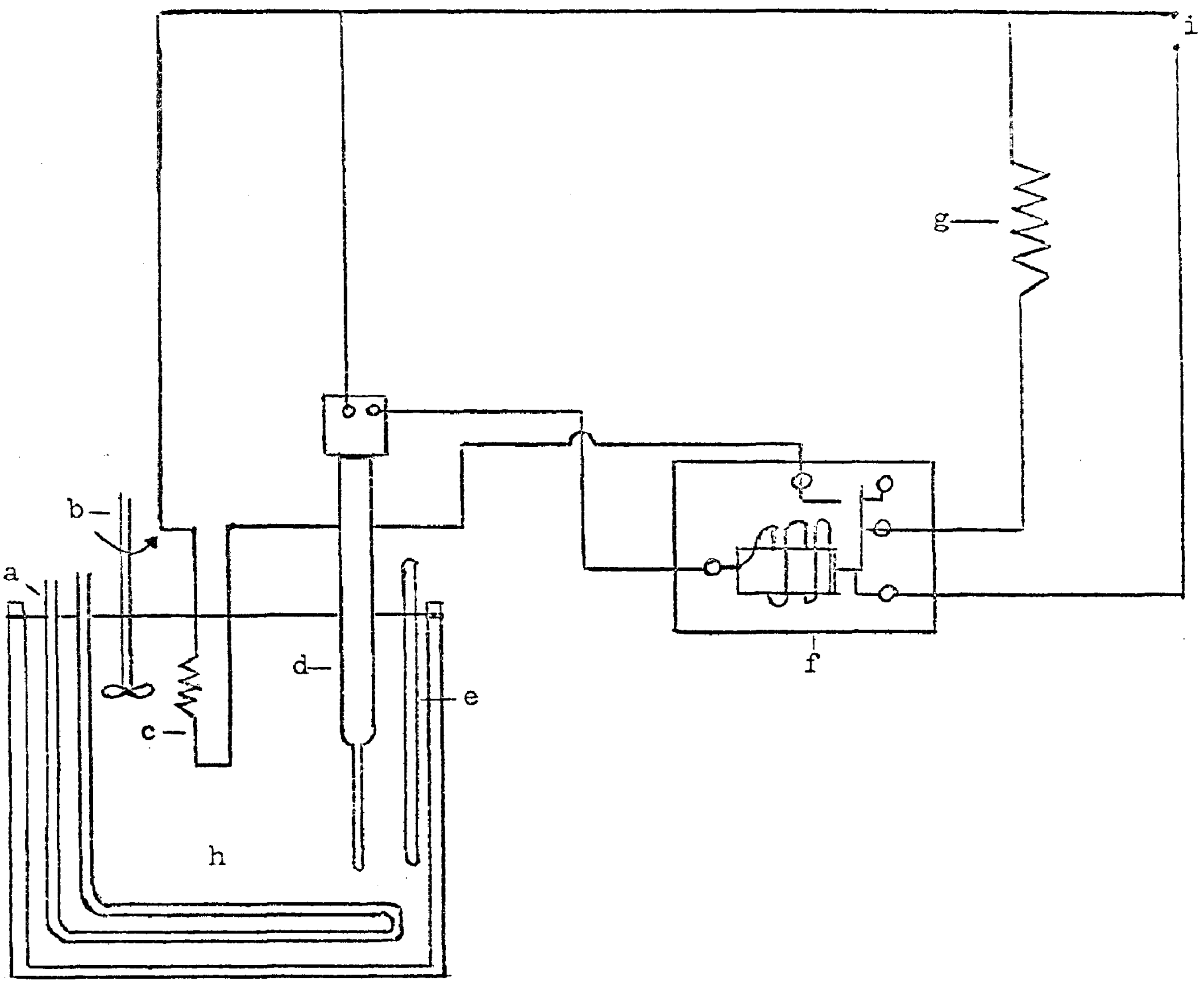
reactants, and a gas burette for collecting and measuring the amount of hydrogen displaced.

The constant temperature water bath (Fig. 2) consisted of a two gallon glass container filled with distilled water. A tubular quartz infrared lamp was used to heat the water, while a copper coil in the bath was for the passage of coolant (tap water if necessary). The temperature of the bath was controlled at 25°C ± .1° C by means of a mercury thermoregulator connected to an electronic relay and the heater.

The 500 ml. gas reaction flask had three ground glass fittings, one to allow entrance of reagents through a funnel, another to hold the stirrer and mercury seal, and the final one to allow passage of gas to the burette. The flask was submerged in the bath to assure a constant temperature. A beeswax coating was put on the inside of the flask to prevent reaction of the acid with the glass.

The belt-driven stirring mechanism with a mercury seal had, a polyvinyl-chloride specimen holder at the bottom of the stirrer (inside the flask). The drive was supplied by a constant speed motor and a constant rate of 200 rpm was maintained by means of a rheostat and reduction pulley setup.

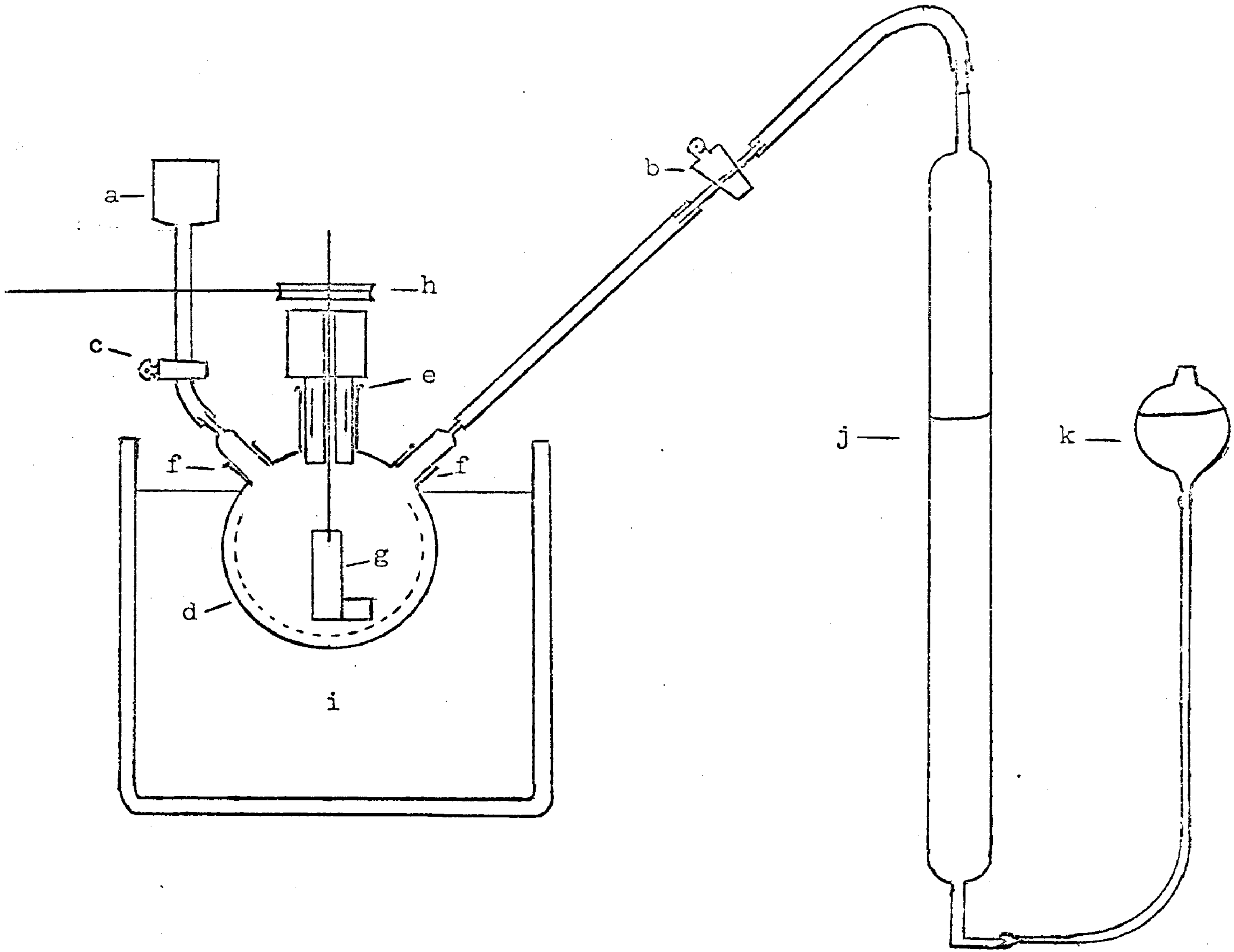
The gas burette had a capacity of 100 ml, but could be used for collecting more by opening the three-way valve (b, Fig. 3) and forcing the hydrogen out into the atmosphere by raising the



a) cooling coil
b) stirrer
c) infrared quartz heater
d) mercury thermo-regulator
e) thermometer
f) electronic relay
g) rheostat
h) water bath
i) line voltage, 110v.

Figure 2

Apparatus and wiring for constant temperature water bath



a) funnel for introduction of reagents
b) three way valve
c) valve
d) reaction flask with beeswax lining
e) mercury seal with ground glass stopper
f) ground glass fittings
g) polyvinylchloride specimen holder
h) pulley with drive belt attached
i) constant temperature water bath
j) gas burette
k) leveling bulb

Figure 3

Reaction vessel and volumetric equipment leveling bulb and then returning the valve to the initial position. Since hydrogen is not much absorbed by water, collection was made over distilled water. Equalization of hydrogen and atmospheric pressure was maintained with the leveling bulb so as the two water levels were of the same height (when reading the burette). Square specimens were cut from the aluminum sheet and accurately measured to the nearest .1 mm with vernier calipers for the surface area calculation. The aluminum was then mounted in bakelite--leaving only one surface exposed. Preparation of the surface consisted of rough grinding followed by fine polishing on a wheel with levigated aluminum oxide. Then the clean, dry specimen was fastened to the polyvinylchloride holder with beeswax and inserted into the reaction flask. Care was taken to see that all ground glass fittings were clean and had a thin layer of vacuum grease on them to assure air-tightness. The flask was inserted into the water bath at 25° C and held there with a clamp. One hundred ml of hydrofluoric acid were poured into a waxed Erlenmeyer flask and also placed into the bath so that the acid could assume water temperature. The belt was connected to the stirrer and the constant speed of 200 rpm was maintained and checked by means of a tachometer. The ground glass fittings of the reaction flask between the burette and funnel were placed carefully in their proper positions and the entire system was then checked for air tightness by raising the leveling bulb several inches above the water level in the burette. If the level changed (after 30 minutes or more) the ground glass fittings were taken apart, cleaned, and regreased until the system was air tight. The acid was now added to the flask and the water level in the burette adjusted to zero. The valve (c, Fig. 3) was opened to allow entrance of acid to the flask while at the same time the three-way valve (b, Fig. 3) was moved to a position so as to open the flask to the atmosphere. This operation was to prevent the entrance of displaced air from the flask because acid flowing into it pushed down the level in the burette. As soon as the acid was all in the flask, the valve (c, Fig. 3) was closed and the valve (b, Fig. 3) was opened permitting the passage of hydrogen into the burette. A timer was started and the measurements began. Readings of the water level were taken at certain time lapses (usually every 10 minutes). The leveling bulb water was always kept slightly below that of the burette, except during readings, so that no pressure would tend to expel the hydrogen. At the end of the experiment the belt drive was removed and the stirrer taken out of the flask. The aluminum specimen was carefully separated from its holder, washed with distilled water, dried, and observed. The condition of the solution was also observed and recorded.

As a preliminary precaution and also to become accustomed to the equipment, the following experiment was performed. A preweighed amount of zinc was completely dissolved in the reaction flask, charged with hydrochloric acid and the hydrogen displaced (Eq. 3) was measured. Several such determinations were performed.

$$Zn + 2\ H^+ \dashrightarrow Zn^{++} + H_2 \qquad (3)$$

According to Eq. (3), one mole of zinc (65.38 g) must displace one mole (22,412 ml) of hydrogen from HCL: hence, 1 ml $H_2$ will be produced by 65.38/22,412 or .002917 g Zn(all vol. STP).

A tabulation of these results appears in Table I. The deviations between experimental and theoretical values are seen to be small in all three experiments. Now attempts of duplicating past results of Wang[7] involving dissolution rates of aluminum in hydrofluoric were made. The hydrogen displaced was measured every ten minutes for rate calculations. The length of the experiment depended upon the time required for the rate to pass a maximum. A plot of rate vs. time yields a curve with three basic stages typical of faster reactions. As can be seen from Fig. 4, at first is an induction period of increasing rate followed by a maximum, leveling off. Finally is a declining period in which the rate drops slowly below that of the maximum. At this point the experiment was stopped.

The equation of rate of hydrogen evolution is:

$$R = 1000\Delta v/\Delta tA \qquad (4)$$

## TABLE I

### Theoretical and experimental displacements of hydrogen from HCl by Zn

| Run | Wt. of Zn (g) | $H_2$ produced (ml) | $H_2$ produced* (ml) | $H_2$ calc. (ml) | % |
|---|---|---|---|---|---|
| 1 | .20864 | 81.2 | 70.38 | 71.52 | 1.59 |
| 2 | .20757 | 80.7 | 69.89 | 71.45 | 2.18 |
| 3 | .21436 | 84.3 | 73.08 | 73.79 | .96 |

* reduced to STP

Avg. % deviation--1.58

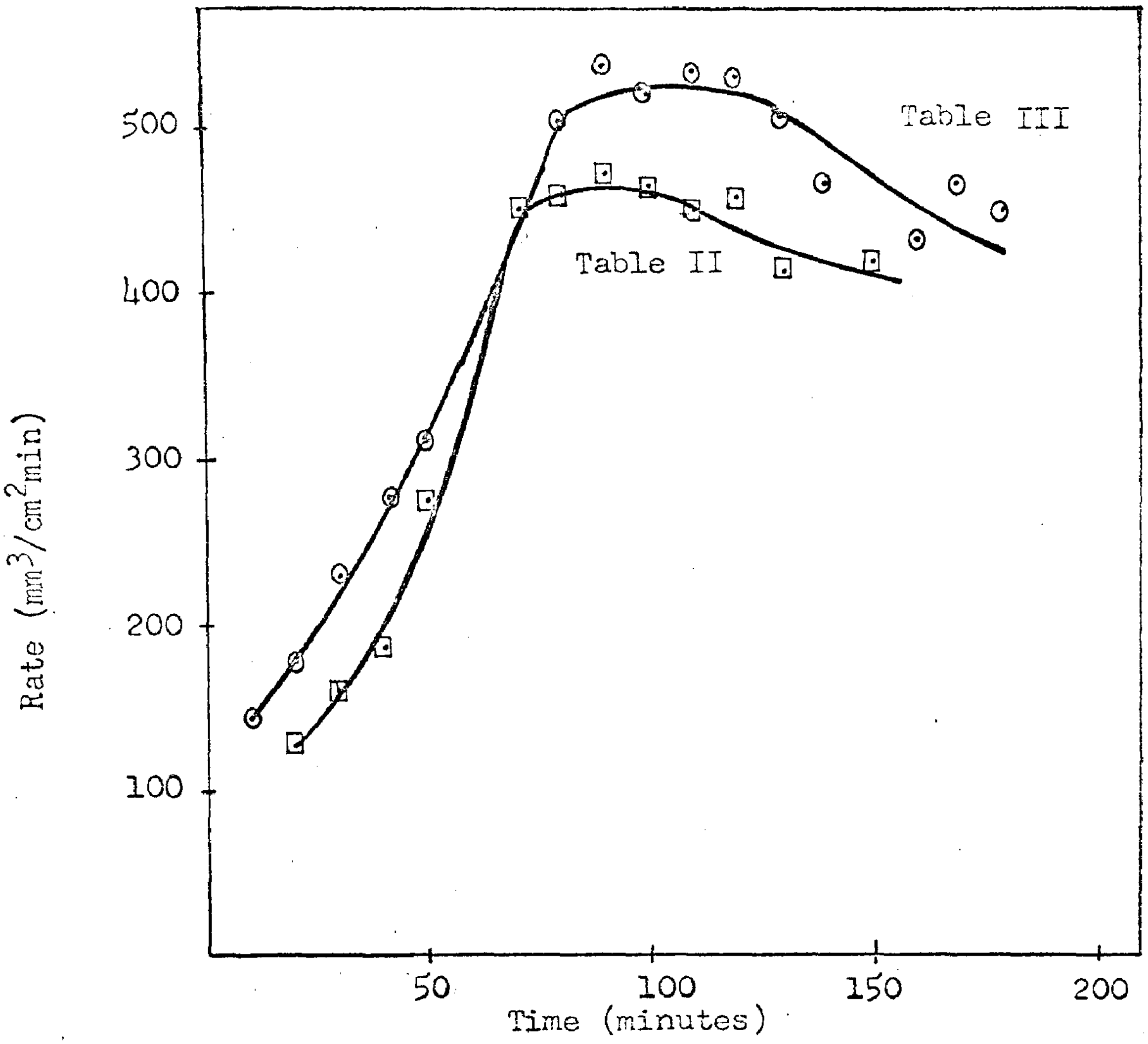


Figure 4

Hydrogen evolution rate of aluminum in 2 N HF at 25°C where:

$R$= rate of $H_2$ evolution in ml

$\Delta v$= the difference in the volume of the two hydrogen readings for a particular length of time in ml

$\Delta t$= the time interval in min

$A$= the area of the reacting Al surface in $cm^2$

Data taken from Table II show that between 80 and 90 minutes a $\Delta v$ of 5.8 ml was recorded. Multiplying this by the STP conversion factor:

$$\frac{711.6}{760} \times \frac{273}{294.1} = .869$$

will give a volume change of 5.04 ml at standard conditions. The rate of $H_2$-evolution for this time period is now calculated (knowing A is 1.065 $cm^2$):

$$R = \frac{5.04}{10} \times \frac{1,000}{1.065} = 473.2 \ mm^3/cm^2 min$$

These calculations were made for every 10 minute period and recorded. Finally the plot (Fig. 4) was drawn using Tables II and III. From Eq. (2) it is evident that 2 moles of aluminum (2 x 26.96g) produces 3 moles of hydrogen (3 x 22,412,000 $mm^3$).

Therefore 1 $mm^3$ of $H_2$ corresponds to $\frac{2 \times 26.96 \times 1,000}{3 \times 22,412,000}$ or .0008020 mg Al. This is the conversion factor of $mm^3$ of $H_2$ to mg Al. For the previously calculated example, the rate may be expressed as:

473.2 x .0008020 or .3795 mg Al/min $cm^2$

## TABLE II

Hydrogen evolution rate of Al in 2N HF at 25°C

| | |
|---|---|
| Avg. room temp: | 21.2°C |
| Avg. corrected pressure: | 711.6 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting Al surface: | 1.065 $cm^2$ |

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| 20 | 1.60 | 1.60 | 1.39 | 131 |
| 30 | 3.60 | 2.00 | 1.74 | 163 |
| 40 | 5.90 | 2.30 | 2.00 | 188 |
| 50 | 9.30 | 3.40 | 2.95 | 277 |
| 60 | 13.90 | 4.60 | 4.00 | 376 |
| 70 | 19.40 | 5.50 | 4.78 | 499# |
| 80 | 25.00 | 5.60 | 4.87 | 457# |
| 90 | 30.80 | 5.80 | 5.04 | 473# |
| 100 | 36.50 | 5.70 | 4.95 | 465# |
| 110 | 42.00 | 5.50 | 4.78 | 449# |
| 120 | 47.60 | 5.60 | 4.87 | 457# |
| 130 | 52.60 | 5.00 | 4.35 | 408 |
| 140 | 57.70 | 5.10 | 4.43 | 416 |
| 150 | 62.80 | 5.10 | 4.43 | 416 |

# Avg. maximum rate: 458 $mm^3/cm^2min$

## TABLE III

Hydrogen evolution rate of Al in 2N HF at 25°C

| | |
|---|---|
| Avg. room temp: | 21.3°C |
| Avg. corrected pressure: | 713.7 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting Al surface: | 1.070 $cm^2$ |

| Time (min) | $H_2$ vol. (ml) | $\Delta v$ (ml) | $\Delta v$ STP (ml) | Rate ($mm^3/cm^2 min$) |
|---|---|---|---|---|
| 10 | 1.80 | 1.80 | 1.57 | 147 |
| 20 | 4.00 | 2.20 | 1.92 | 179 |
| 30 | 6.80 | 2.80 | 2.45 | 229 |
| 40 | 10.50 | 3.70 | 3.22 | 301 |
| 50 | 14.70 | 3.80 | 3.11 | 309 |
| 60 | 19.70 | 5.00 | 4.36 | 407 |
| 70 | 25.10 | 5.40 | 4.70 | 439 |
| 80 | 31.30 | 6.20 | 5.40 | 505# |
| 90 | 38.00 | 6.70 | 5.84 | 546# |
| 100 | 44.40 | 6.40 | 5.57 | 521# |
| 110 | 51.00 | 6.60 | 5.75 | 537# |
| 120 | 57.50 | 6.50 | 5.66 | 529# |
| 130 | 63.70 | 6.20 | 5.40 | 505# |
| 140 | 69.40 | 5.70 | 4.96 | 464 |
| 150 | 74.70 | 5.30 | 4.70 | 431 |
| 160 | 80.40 | 5.70 | 4.96 | 464 |

# Avg. maximum rate: 524 $mm^3/cm^2 min$

Avg. maximum rate for both runs: 491 ± 33 $mm^3/cm^2 min$

## C. Results

Only one concentration of acid was used--2N HF. As an average of the maximum of the curves (Tables II, III and eight other Tables) a value of(491 ± 33)$mm^3/cm^2min$ was obtained. Wang reported a somewhat higher value of(546 ± 48)$mm^3/cm^2min$(10 runs). The length of time to achieve a maximum is noted to be somewhat shorter in Wang's thesis. Both discrepancies could be due to Wang's acids being stronger than 2N.

Thus, the maximum deviation from the average is not more than ± 33 $mm^3/cm^2min$(6.7%). Considering the difficulty of reproduction in corrosion experiments, this deviation is acceptable, especially if considered that Wang's deviation was ± 48 (8.8%). Uneven distribution of impurities may be one cause of the fluctuations.

Following careful washing with distilled water and drying, the aluminum surface was noted to have a white precipitate at the edges of the bakelite-aluminum interface. This white precipitate is aluminum fluoride, which is soluble in 2N HF to the extent of 2g $AlF_3$ per 100g saturated solution at 25°C[8]. 100 ml of 2N HF (S.G. 1.017) will weigh 101.7g. Since 100 ml of HF is used in the experiment, over 2g of $AlF_3$ may be dissolved. For every three moles of hydrogen produced (Eq. 2) there will be two moles of $AlF_3$. Thus, 3(22,413 ml) $H_2$ corresponds to 2(83.96g) $AlF_3$ or 1 ml of $H_2$ corresponds to .0024945g $AlF_3$. Since never more than 200 ml of hydrogen was displaced in any one experiment, a maximum of 200 x .0024945 or .49890 g of $AlF_3$ was ever in solution, well beneath the solubility limit. However, it is feasible that some of the $AlF_3$ formed on the surface during the reaction would not dissolve in HF as fast as it is formed, so that some would remain and build up at the aluminum-bakelite interface where the effect of stirring is less. This could also explain the fluctuation in rate.

Microscopic observation of the samples after dissolution showed a shiny, but irregular surface with gentle peaks and valleys typical of strongly etched aluminum.

# CHAPTER III

# THE INFLUENCE OF NOBLER SALT ADDITIONS UPON DISSOLUTION RATE

This investigation involved the change in the dissolution rate of aluminum in hydrofluoric acid to which additions of nobler salt solutions have been made.

## A. Materials, Apparatus, and Procedure

In addition to the acid and aluminum as mentioned, solutions of $AgNO_3$, $CuSO_4$, $FeSO_4$, $NiCl_2$, $CoSO_4$, $HAuCl_4$, and $PtCl_4$ were used. All metallic salts were at least of reagent grade. Solutions of .01 M and .1 M were prepared by diluting with distilled water the proper weights of salt or pure metal (in the case of Pt and Au). The Pt and Au were dissolved in aqua regia before dilution to correct concentration. The apparatus and calculations were the same as described in Section B of Chapter II. The only difference in the procedure was the addition of the salt solution when the dissolution rate had begun its decline (in Fig. 4) and appeared to be almost constant. Before the addition was made, the valve (b, Fig. 3) was opened to allow, by raising the leveling bulb, the level of water in the burette to return to zero (by expulsion of the collected hydrogen). The salt solution (4 ml) was premixed with the same volume of 4N HF so that the final concentration would still be 2N. The addition, at the water bath temperature, was made exactly as the acid was originally poured in (pp. 9-10). Addition of 4 ml .1 M salt plus 4 ml 4N HF to 100 ml of 2N HF resulted in a solution with a concentration of (.1) (4)/108 or .0037 M. Similarly the resultant concentration after the .01 M addition was found to be .00037 M.

Two concentrations of each salt(.01M and .1M) were used. The concentrations of the Pt additions were, however, .001 M and .01 M. Each experiment was at least duplicated. For the $PtCl_4$ additions, the air in the flask was initially displaced with nitrogen to prevent the Pt deposited on the aluminum acting as a catalyst in the combination of hydrogen and oxygen to water. The initial percent in rate change due to the addition was calculated by use of the following equation: (5)

$$\% \text{ change} = 100 \, \frac{(\text{Rate at which add. was made}) - (\text{Rate 10 min. after add.})}{(\text{Rate at which add. was made})}$$

B. Addition of $AgNO_3$

Tables IV-VII (appendix) and Fig. 5 show the effects of .01 M and .1 M $AgNO_3$ additions. Fig. 5 shows that the rate initially decreased in both cases and then increased again slowly. In the case of the weaker concentration, the increase was above that of the previous maximum (in plain HF). A dark precipitate was seen on the aluminum surface, while white flakes accumulated in the acid solution. Fig. 6 is a picture of the aluminum under magnification of 1740 X showing the dark layer which covers the aluminum surface in places.

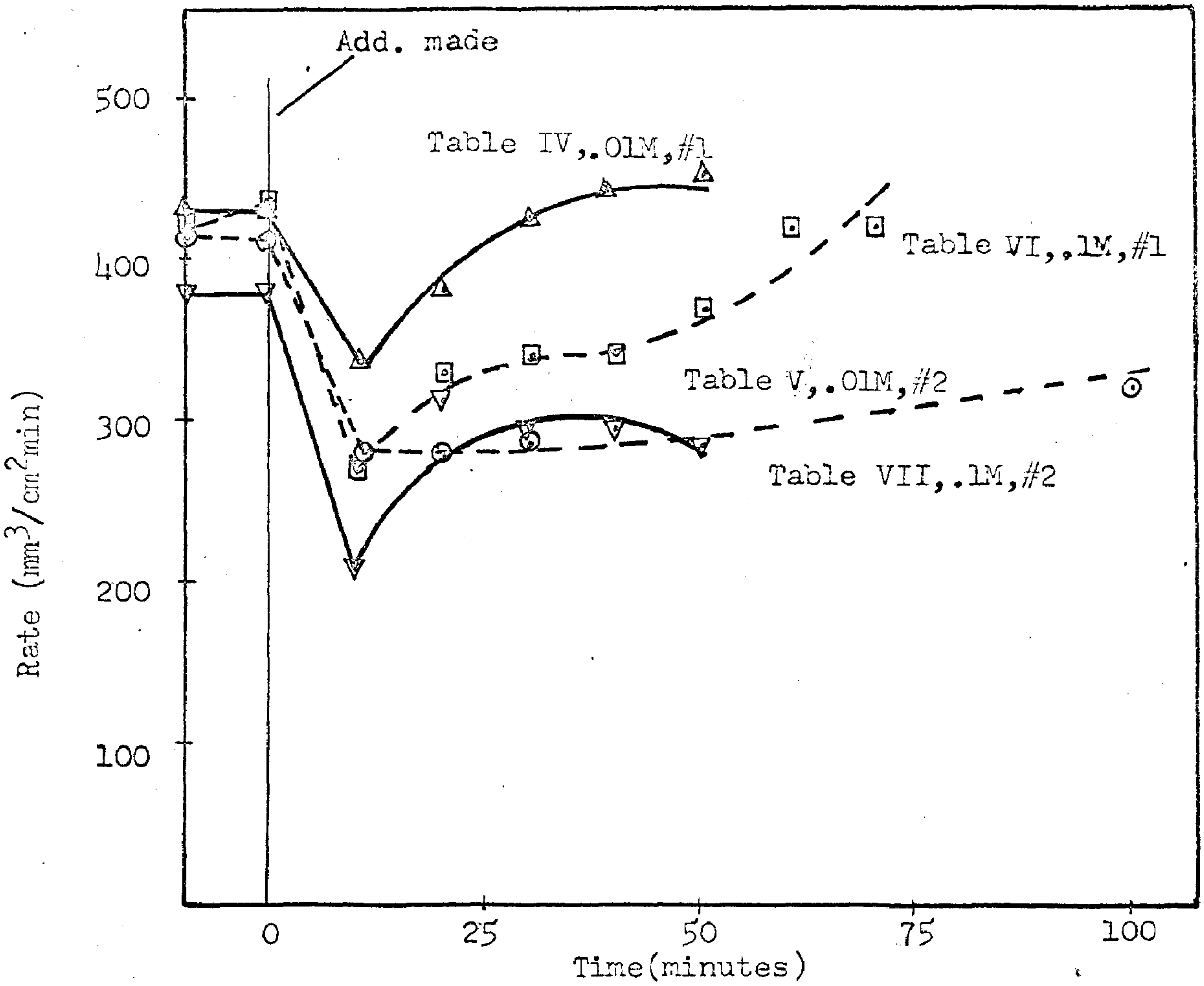


Figure 5

Hydrogen evolution rate of aluminum in 2N HF at 25°C before and upon addition of $AgNO_3$ to the acid

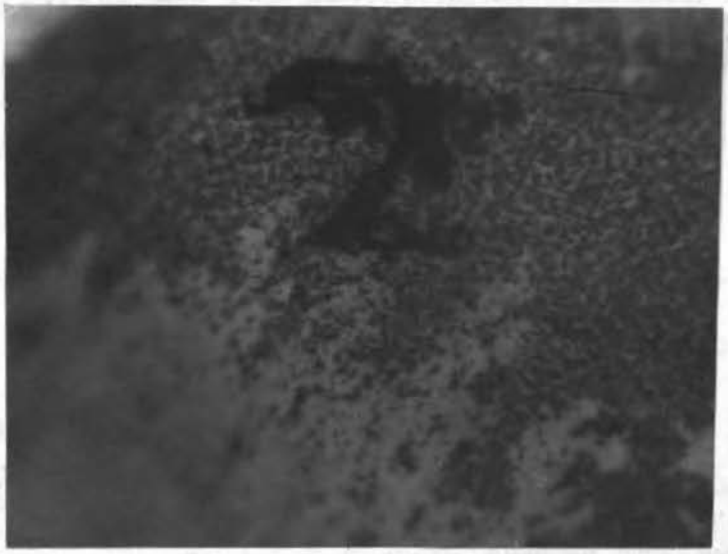


Figure 6

Aluminum sample after corrosion in 2N HF with .1M $AgNO_3$ added showing dark spots upon light aluminum surface. Magnification 1740 X

To observe the formation of the white flakes and the dark precipitate qualitative experiments involving Ag were also performed. A piece of Al was dropped into a Polyethylene beaker containing 100 ml of 2N HF and was allowed to dissolve for a period of time (one hour or more). The addition of $AgNO_3$ (4 ml $AgNO_3$ plus 4 ml 4N HF) caused an immediate dark layer to cover the entire surface and the evolution of hydrogen bubbles almost ceased. After several seconds this layer would peel off the aluminum in chunks, due to the hydrogen evolution which now again increased. As this peeled off, the precipitate floated (because of hydrogen bubbles adhering to it) until it separated completely from the aluminum. It then turned into a white flake and dropped to the bottom of the beaker. A very interesting phenomena occurred when this flake resumed even loose contact with the aluminum. It turned again darker and bubble formation resumed causing it to float until such time when contact was lost. Evidently there is an electrical contact throughout the precipitate. Samples of the white precipitate could be easily made, washed and dried for microscopic observation and x-ray analysis, which showed that it was pure silver consisting of fine metallic needles. However, the black precipitate proved much harder to gather. The only way this could be achieved was by careful removal of the aluminum with the dark deposit on it from the acid, washing, and drying of the precipitate in contact with the Al.

If the contact was lost even momentarily before it was dry, the precipitate turned white. The more brittle black precipitate seemed to be a white salt (probably $AlF_3$) with many black particles and Ag needles embedded within it. X-ray pictures were made of each precipitate. The particle size of the dark one was smaller than the white, according to the resulting x-ray patterns.

Further explanation for the formation of the dark and white precipitates will be given in the "Discussion."

### C. Addition of $FeSO_4$

Tables VIII-XI (appendix) along with Fig. 7 show the effects of $FeSO_4$ additions. The weaker concentration of the salt caused an initial decrease followed by a rapid, substantial increase to a maximum which surpassed the initial rate of dissolution and a slower decrease once more.

Microscopic examination of the surfaces failed to reveal anything but a few specks at high magnification which could have simply been impurities. Therefore, qualitative testing was performed here also to show the precipitation of iron on aluminum. Each experiment involved three phases. Three aluminum pieces were dropped into separate beakers each containing 100 ml of 2N HF and allowed to dissolve for one hour or more. 4 ml of .01 M $FeSO_4$ plus 4 ml 4N HF were added to one while the same

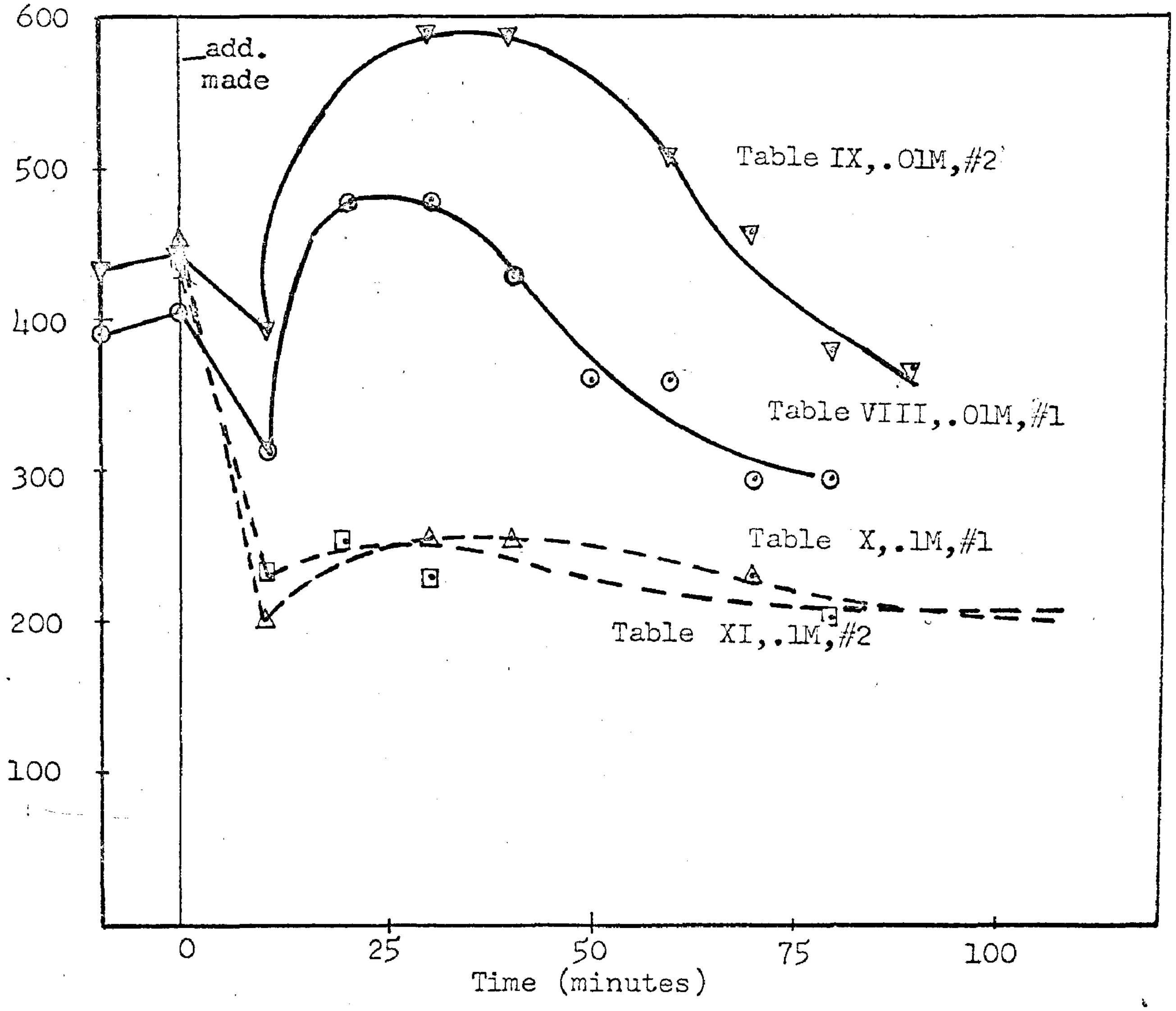


Figure 7

Hydrogen evolution rate of aluminum in 2N HF at 25°C before and upon addition of $FeSO_4$ to the acid solution with .1 M $FeSO_4$ was poured into another. Etching continued for several more minutes and all three specimens were removed, carefully washed in distilled water, and dried. Ferroxyl indicator was then applied to all three pieces and allowed to set. The experiment was repeated in this manner several times. Never did the indicator prove the presence of iron (by turning blue) upon the aluminum etched in plain HF or in HF plus .1 M $FeSO_4$. However, the aluminum etched in the HF with .01 M $FeSO_4$ did give an indication of some iron, but in only two of the six experiments. It is possible that the iron on the aluminum was cathodically protected by the latter from corroding in the ferroxyl indicator.

## D. Addition of $CuSO_4$

The results of $CuSO_4$ additions are given in Tables XII-XV (appendix) and Fig. 8. The .01 M salt addition shows an initial decrease followed by an immediate increase. The stronger concentration of the salt addition also showed a decrease followed by an increase but differed from the lower salt concentration in that a maximum was reached and a subsequent decrease occurred.

A red precipitate (presumably Cu) appeared on the aluminum surface and in the solution at the end of the experiment. Microscopic observation showed the presence of copper on the surface, especially in the stronger salt concentration, shown by Fig. 9.

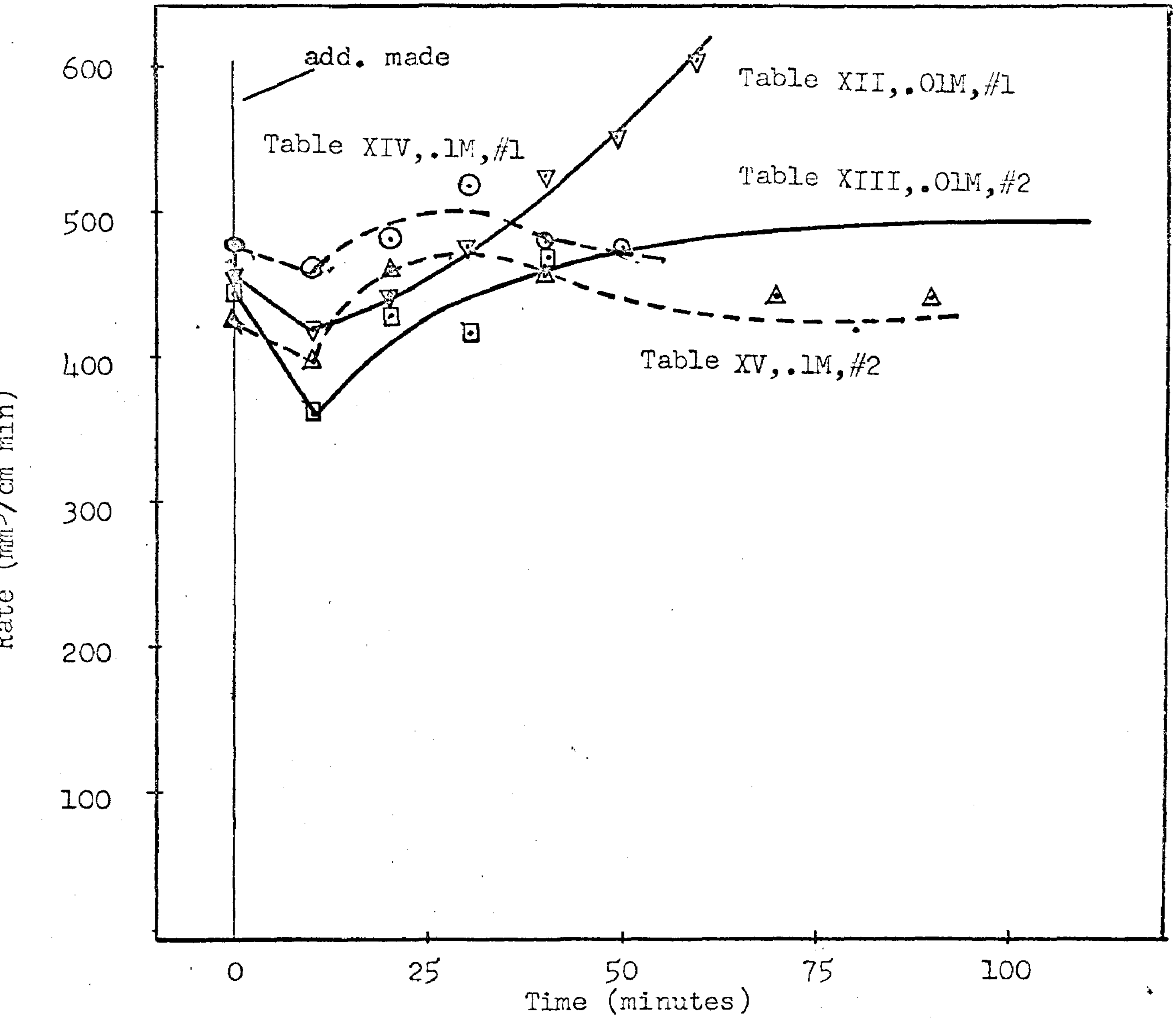


Figure 8

Hydrogen evolution rate of aluminum in 2N HF at 25°C
before and upon addition of $CuSO_4$ to the acid

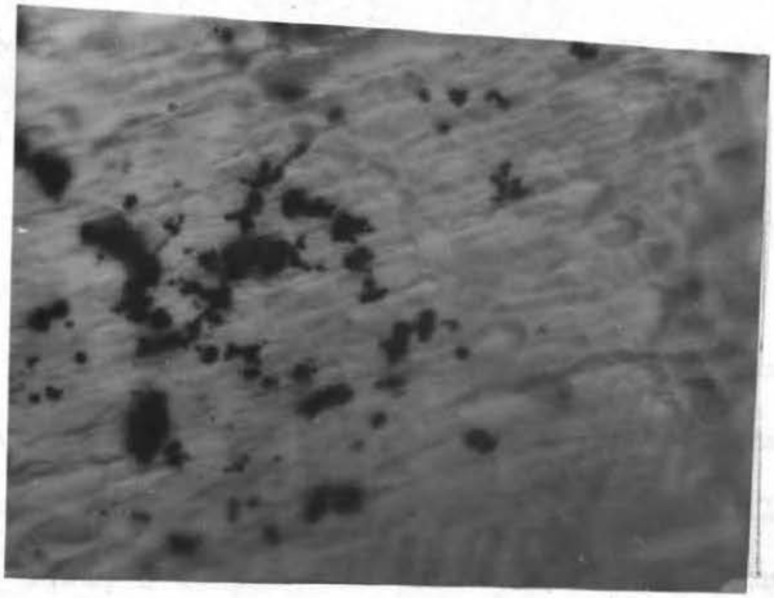


Figure 9

Red precipitate on aluminum surface dissolving
in 2N HF with addition of .1 M $CuSO_4$
Magnification 1740 X

### E. Addition of $NiCl_2$

The effect of $NiCl_2$ additions were much the same regardless of salt concentrations. A substantial decrease (Tables XVI-XIX in appendix and Fig. 10) occurred immediately and this rate became somewhat steady at this lower value.

No precipitate was seen in the solution at the end of the experiment. The surface was observed microscopically, but this revealed nothing but the apparent highly reflective surface of aluminum. Qualitative testing failed to prove the presence of nickel.

### F. Addition of $CoSO_4$

$CoSO_4$ additions created effects similar to those produced by $NiCl_2$. That is, an initial decrease occurred always, after which the stronger salt caused the rate to level off, while the weaker one brought about a substantial increase past the original rate of dissolution. The surface showed nothing upon it, and no precipitate of any kind was visible in the solution. Tables XX-XXIII (appendix) and Fig. 11 illustrate these results.

### G. Addition of $PtCl_4$

In order to study the effect of $PtCl_4$ additions, it was necessary to perform all these experiments in an atmosphere of nitrogen as already mentioned (see p. 20). Fig. 12 and Tables XXIV-XXVII (appendix) show the effects of $PtCl_4$ additions. Fig. 12

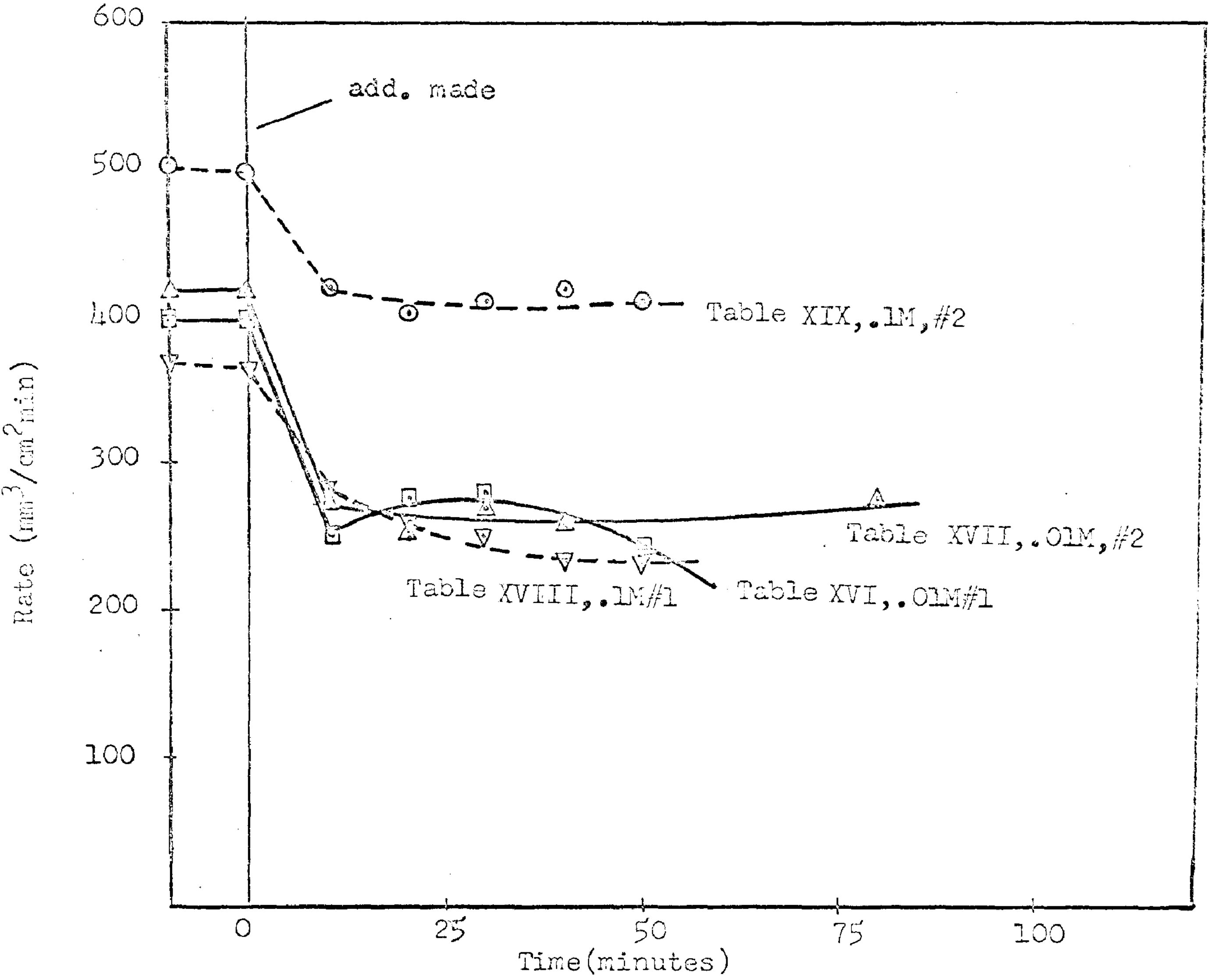


Figure 10

Hydrogen evolution rate of aluminum in 2N HF at 25° C
before and after addition of $NiCl_2$ to the acid

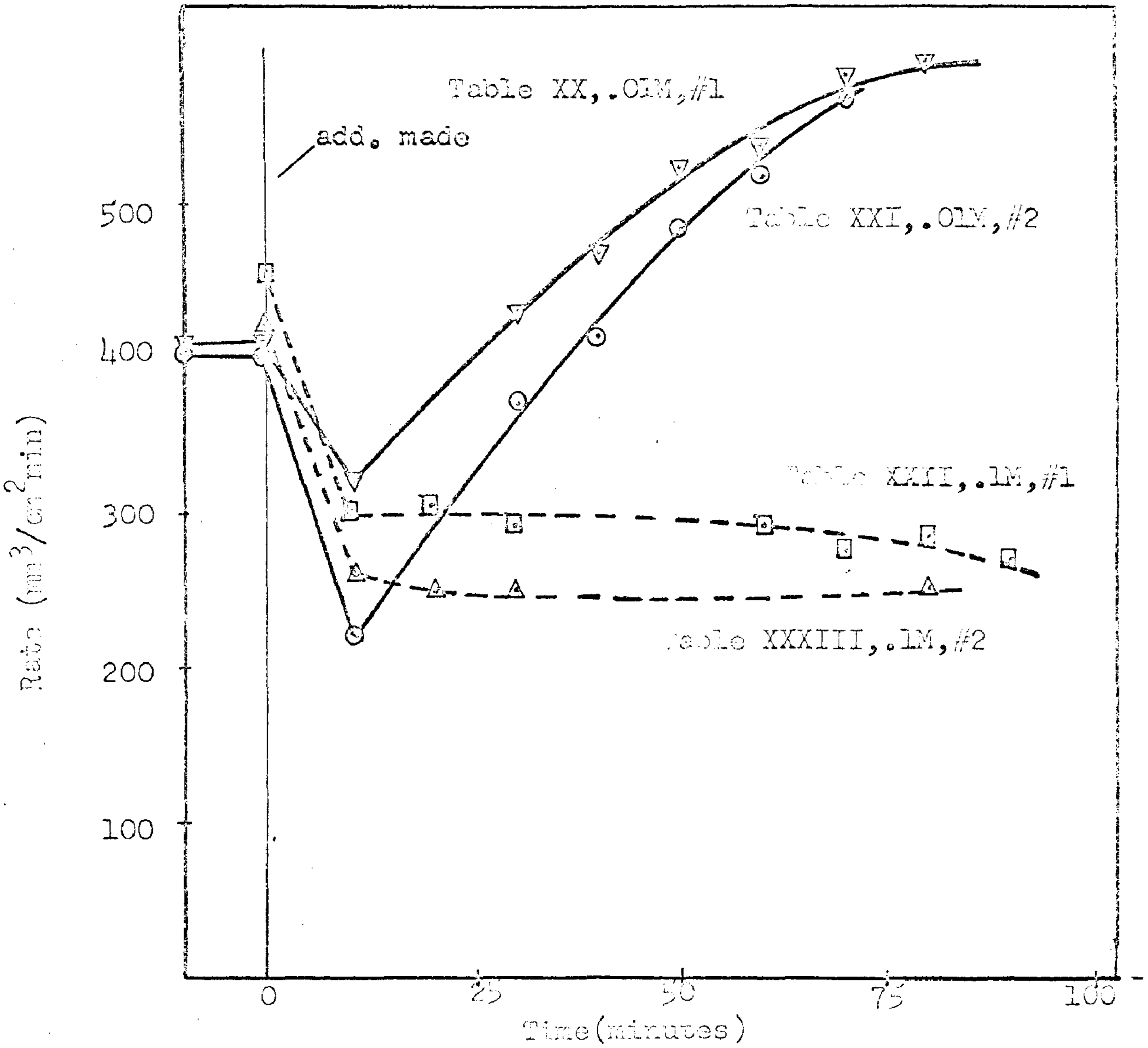


Figure 11

Hydrogen evolution rate of aluminum in 2N HF at 25°C
before and upon addition of $CoSO_4$ to the acid

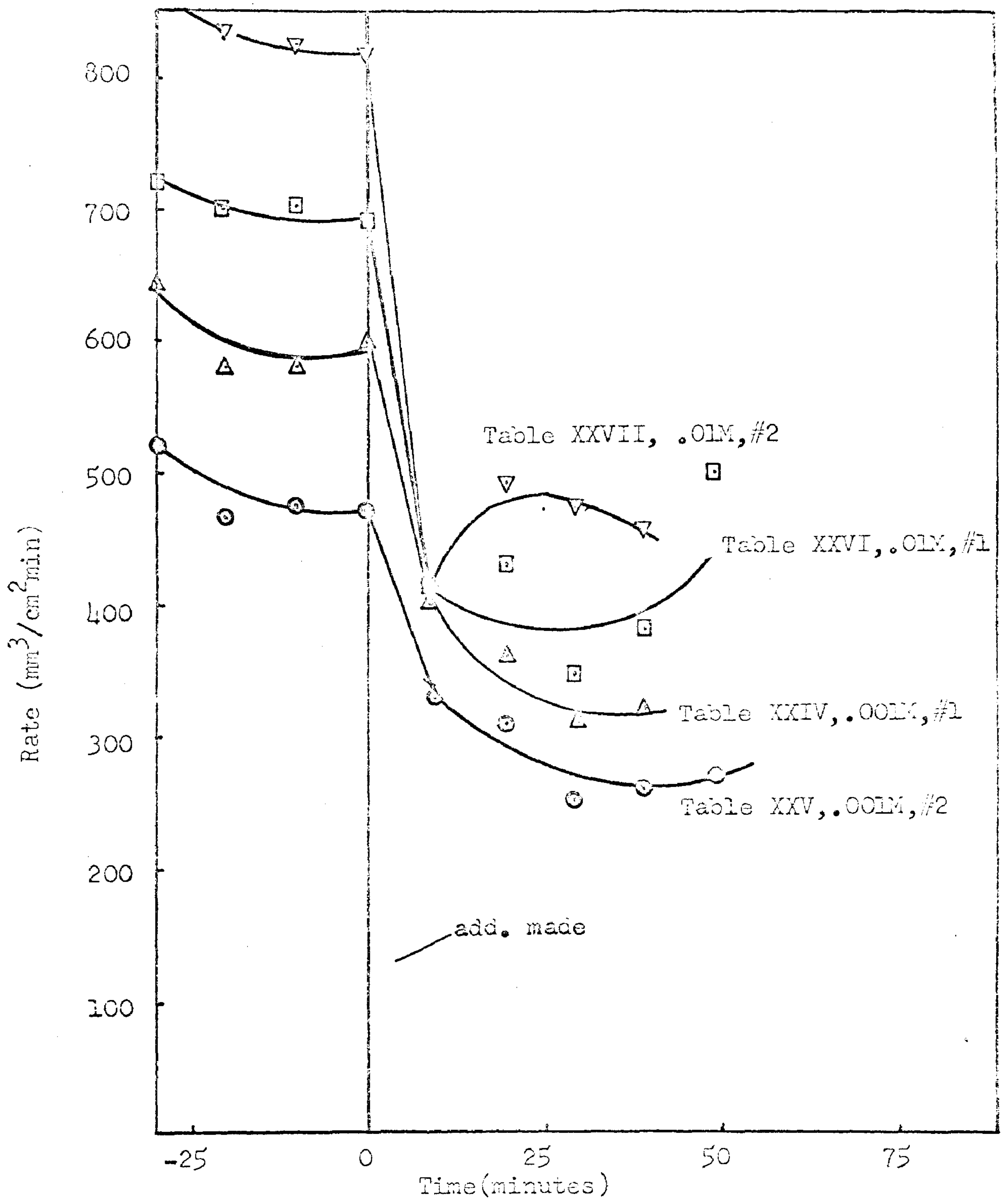


Figure 12

Hydrogen evolution rate of aluminum in 2N HF at 25° C
before and upon the addition of $PtCl_4$

also reveals a very sporadic dissolution rate of the aluminum in the nitrogen atmosphere even before the $PtCl_4$ was added. No consistency could be attained, except that all the rates were higher than in the air atmosphere experiments. Wang[7] recorded the same higher rates, but failed to mention them. It would seem the opposite should be true, namely that the rates in nitrogen would be lower. However this may possibly be explained by the presence of a weaker protective layer and will be treated in the " Discussion."

It can be seen that a very large rate decrease was observed when the .001 M Pt salt was added and a still larger one with the stronger addition. Furthermore, this decrease does not represent the true value. As soon as the salt was added, a very slightly negative rate was observed for a minute or two before recovering to a positive rate. Evidently the hydrogen was consumed faster than it was liberated. For stronger concentrations of Pt salts, the negative rate was even greater. Although care was taken, there probably was some oxygen left either in the system or it was present in the nitrogen. It is impossible to say whether the return of the positive rate was the point of all oxygen consumption or there was an increase in hydrogen evolution to such a rate as to overcome the loss. Another experiment was performed without the nitrogen atmosphere to see if oxygen in the system would indeed have an effect. When the .01 M $PtCl_4$

solution was added, the rate became very negative and continued as such for 10 minutes before becoming positive again. Even then the rate stayed at a very low value. There was, of course, plenty of oxygen to combine with the hydrogen. In all probability the Pt salt caused the rate to decrease initially (although not as much as shown) and increase slightly in the further stage of dissolution. The .001 M addition probably did not contain enough Pt for a fast combination of the hydrogen and oxygen as the .01 M solution. Therefore a more truthful curve is given in the first case.

There was a fine black precipitate formed immediately on the aluminum upon salt addition. Microscopic observation of the surface at 1740 X showed on uneven distribution of black particles.

## H. Addition of $HAuCl_4$

The results of gold additions proved to be erratic, shown by Fig. 13(Tables XXVIII-XXXI,app.). For both concentrations, one run showed a small increase and the other a small decrease. In all instances, however, a leveling off occurred at the increase or decrease. It is thus difficult to predict what will happen. The results of Wang[7] showed an increase in the rate.

A yellowish-red precipitate (probably Au) appeared on the aluminum and in the solution after dissolution. It should be noted that the addition of salts which create a visible precipitate generally caused more sporadic results to occur. This

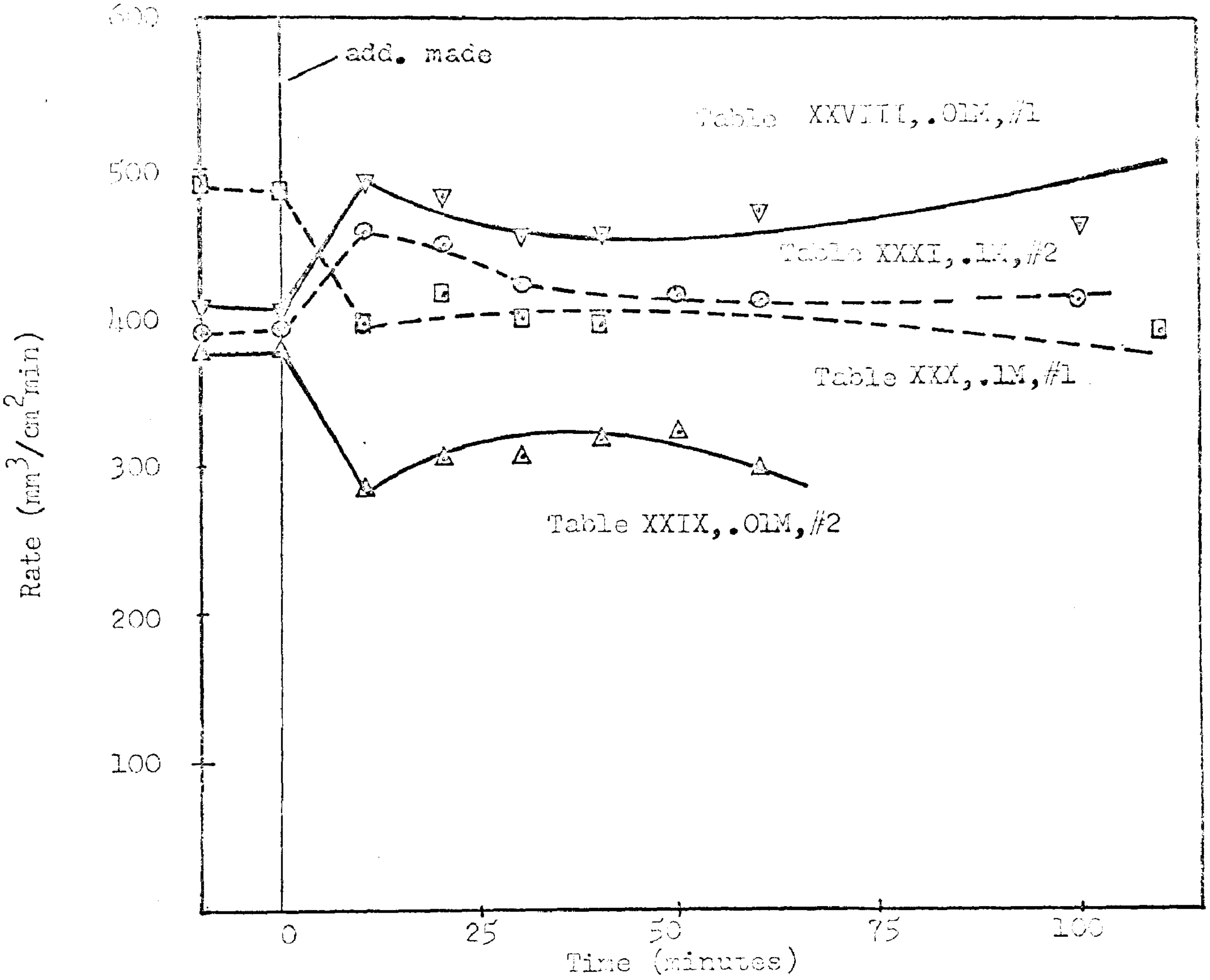


Figure 13

Hydrogen evolution rate of aluminum in 2N HF at 25°C before and upon addition of $HAuCl_4$ to the acid was probably due to the covering of the surface by the precipitate to a greater extent at some times than at other times. Microscopic examination revealed the presence of an uneven distribution of yellowish-red specks throughout the aluminum surface. The stronger salt concentrations showed coarser and larger covered areas than did the .01 M additions.

# CHAPTER IV

## THE INFLUENCE OF NOBLER METAL SALTS ON THE ALUMINUM ELECTRODE POTENTIAL

To find the reasons of inactivity of some salts of nobler metals upon aluminum and since corrosion of metals is generally electrochemical, electrode potential measurements were made. The corrosion rate expressed in Eq. (4) is a function of the potential as shown by:

$$R = v/\ tA = kz'(n - E')/r \qquad (6)$$

where:

$R$ = corrosion rate (in $mm^3/cm^2min$) of displaced $H_2$
$z'$ = average number of local cathodes per square unit
$k$ = conversion constant
$n$ = potential of the local cathode
$E'$ = anodic potential of the dissolving metal
$r$ = average resistance of local cells

The resistance of the electrolyte is a function of concentration and therefore may be considered constant at low corrosion rates. There is no way to measure the number or potential of the local cathodes. The anodic potential of the dissolving aluminum or the mixed potential of the metallic deposit-aluminum surface can, however, be measured directly with a calomel reference electrode.

### A. Apparatus and procedure

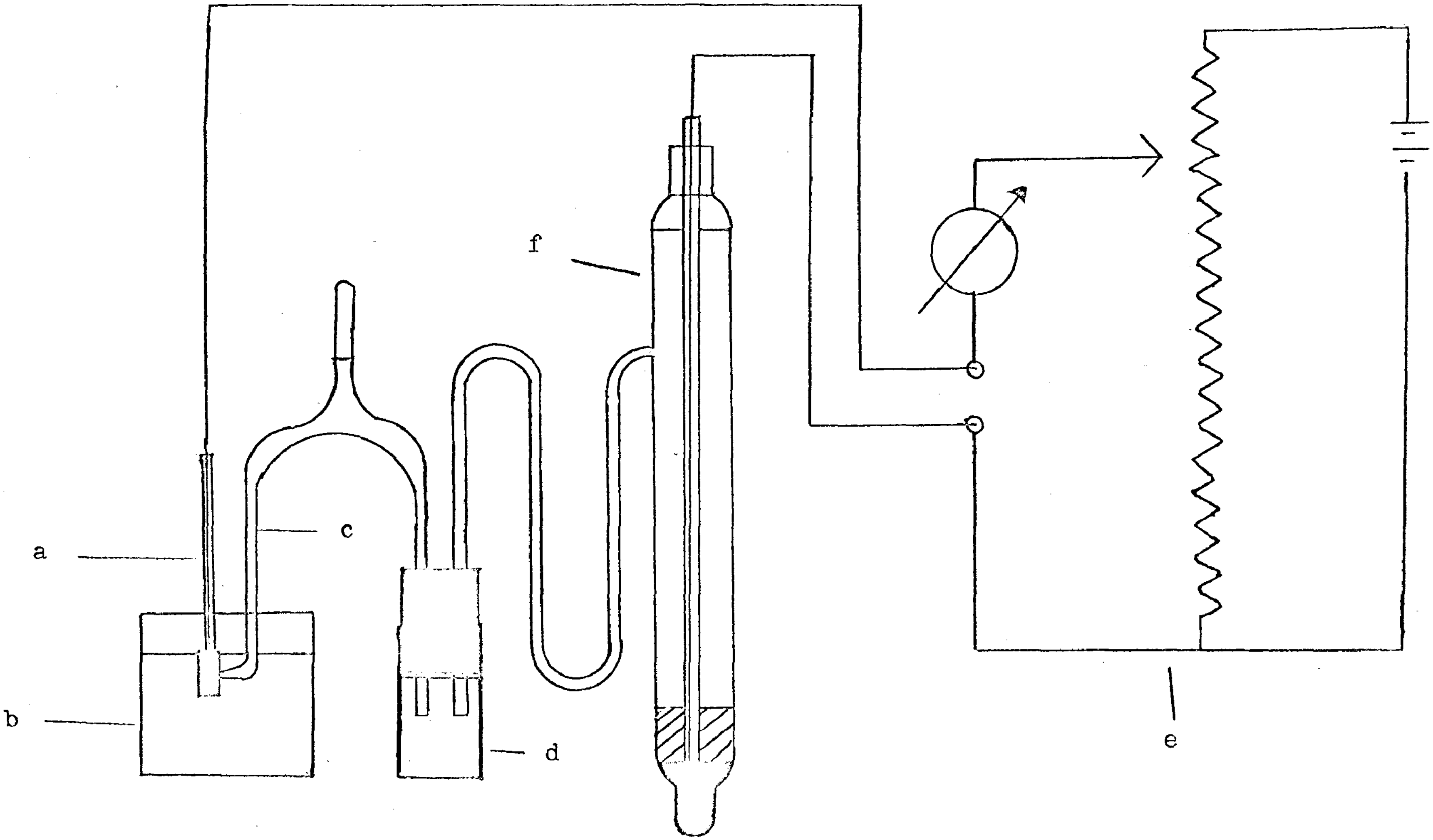
The calomel half cell ($Hg/Hg_2Cl_2$, 1N KCl) was prepared and checked against a saturated calomel electrode (Beckman) and found to be +.281 v against the normal hydrogen electrode. Therefore, subtraction of .281 from all measured values (with the calomel electrode) will yield a potential in the hydrogen scale. The potential difference of the cell:

Al/HF, 1N KCl, $Hg_2Cl_2$/ Hg

will thus be measured by means of a potentiometer. Fig. 14 is a schematic of this set-up. A salt bridge of 3.5 N KCl was utilized to eliminate junction potential.

The aluminum electrode was prepared by placing a square piece of aluminum with a screw on it (overlapping on one side) in the mounting press. Bakelite was poured on this and the mount was made. The bakelite was cut away from the screw and electrical contact between it and the aluminum was checked with an ohm-meter. After grinding and polishing the aluminum surface, a copper wire was soldered to the exposed screw and encased in a glass tube. The finished electrode (Fig. 15) was now ready for measurements after a coating of museum jar wax cement was applied to any metallic areas, besides the aluminum surface, still exposed and to as much of the glass as would be in contact with the HF.

After making the connections as illustrated in Fig. 14, 100 ml of 2N HF were poured into the Polyethylene beaker. The aluminum electrode was immersed into the acid and placed in contact with the wax-coated capillary tube from the salt-bridge. By means of the potentiometer, the potential was measured every few minutes.

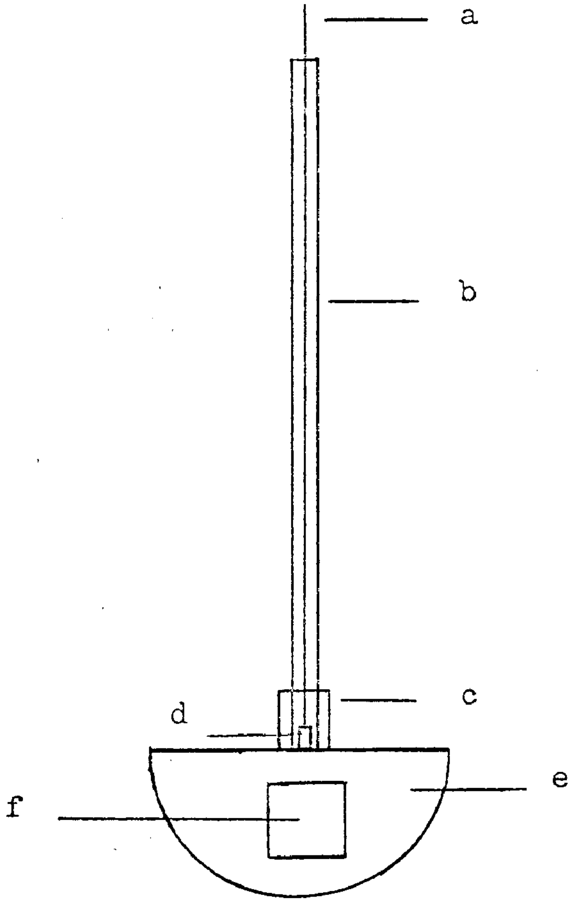


a. aluminum electrode
b. Polyethylene beaker
c. capillary tube

d. salt bridge (3.5 N KCl)
e. potentiometer
f. Calomel electrode (1 N KCl)

Figure 14

Schematic diagram for potential measurement



a. copper wire soldered to screw (d)
b. glass tubing
c. cement coating
d. screw in contact with aluminum
e. bakelite mounting
f. aluminum electrode surface

Figure 15

Aluminum electrode used for potential measurements

After observing a somewhat stable potential, the salt(4 ml noble metal salt solution plus 4 ml HF) was added and the fluctuation observed.

## B. Results

In all cases the addition of the salt caused a positive increase (or from more negative to less negative) in the measured potential. It was interesting to note that the more noble was the metal in the salt, the greater was the potential increase, as shown by Table IV. This lends belief that the surface of the aluminum has a "mixed potential" of some kind. The average potential of the aluminum before the salt addition was found to be -1.210 v ± 44 mv (Wang[7] noted an average of -1.220 v). The increase due to the salt addition was larger with the higher concentration of salt. Tables XXXII-XXXV (appendix) and Figs. 16-22 summarize and illustrate the effects of these additions on the potential.

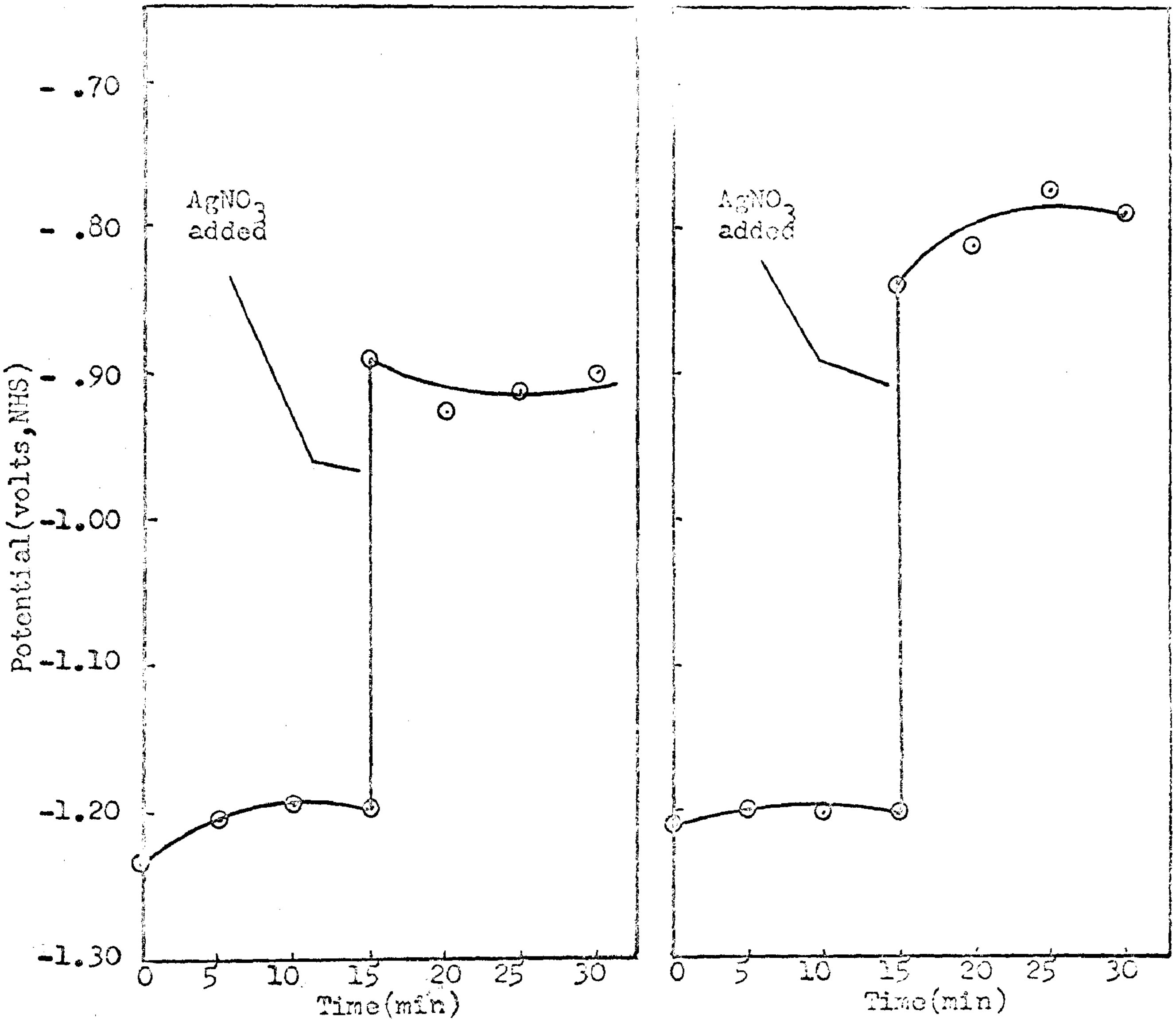
Salts of metallic elements less noble than aluminum were added to the 2N HF to see if any potential changes would occur. Solutions of .1 M NaCl and KCl were added in separate tests, resulting in an insignificant change of potential. Therefore, apparently, nothing formed on the surface.

Some potential measurements were extended for longer periods of time to see how the potential changed. The potential of aluminum

## TABLE IV

Comparison of potential increase of aluminum upon addition of metallic salts to the nobility of the metallic element of the salt

| Metallic element | Pot. increase(volts) .01M | .1M | Pot. of metallic element (volts) |
|---|---|---|---|
| Au | .405 | .517 | +1.35 |
| Pt | .407 | - | +1.20 |
| Ag | .307 | .364 | + .80 |
| Cu | .385 | .482 | + .34 |
| Ni | .048 | .189 | - .25 |
| Co | .220 | .287 | - .28 |
| Fe | .134 | .162 | - .44 |



.01 M

.1 M

Figure 16

Effect of $AgNO_3$ on aluminum electrode potential in 2N HF

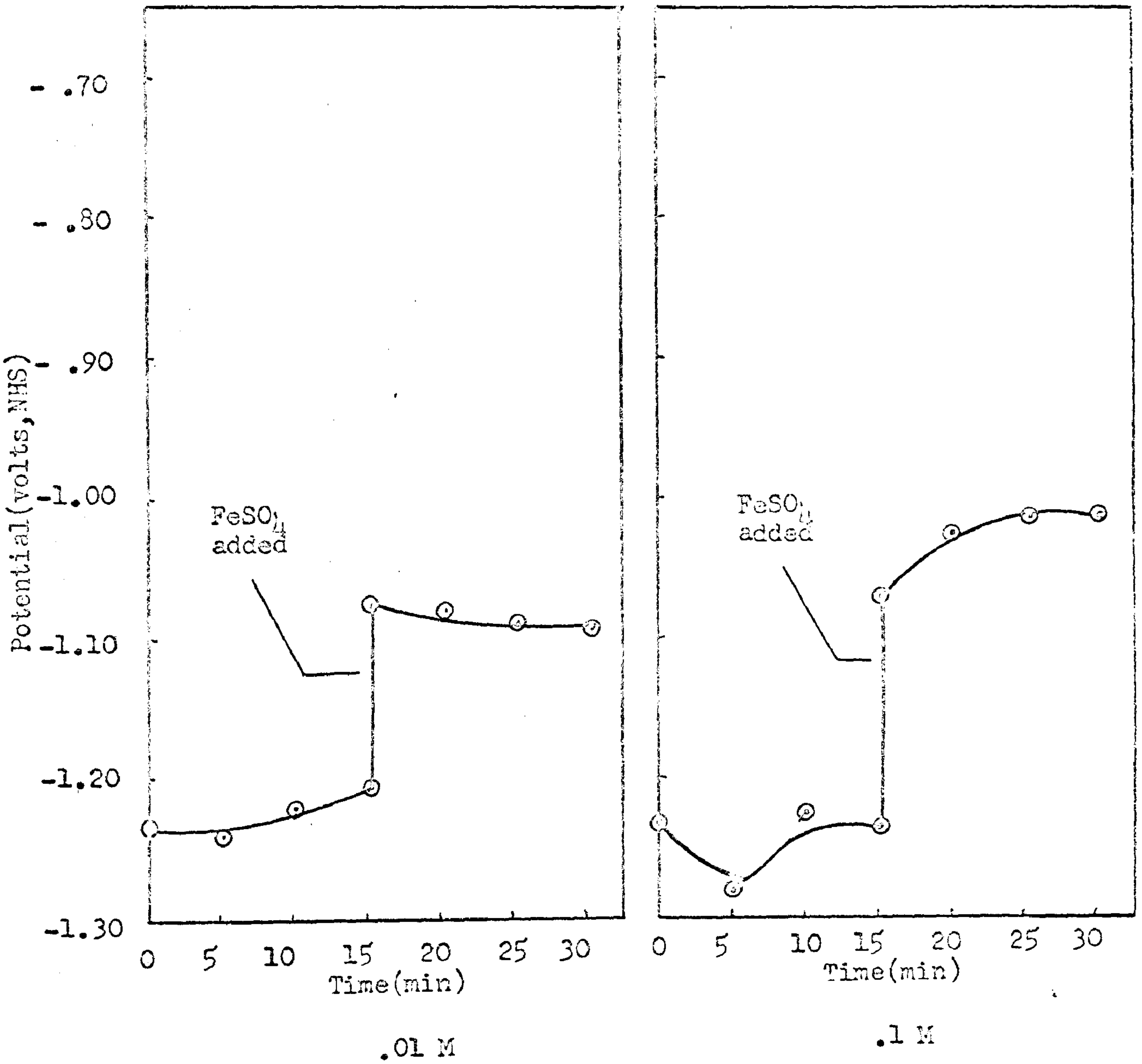
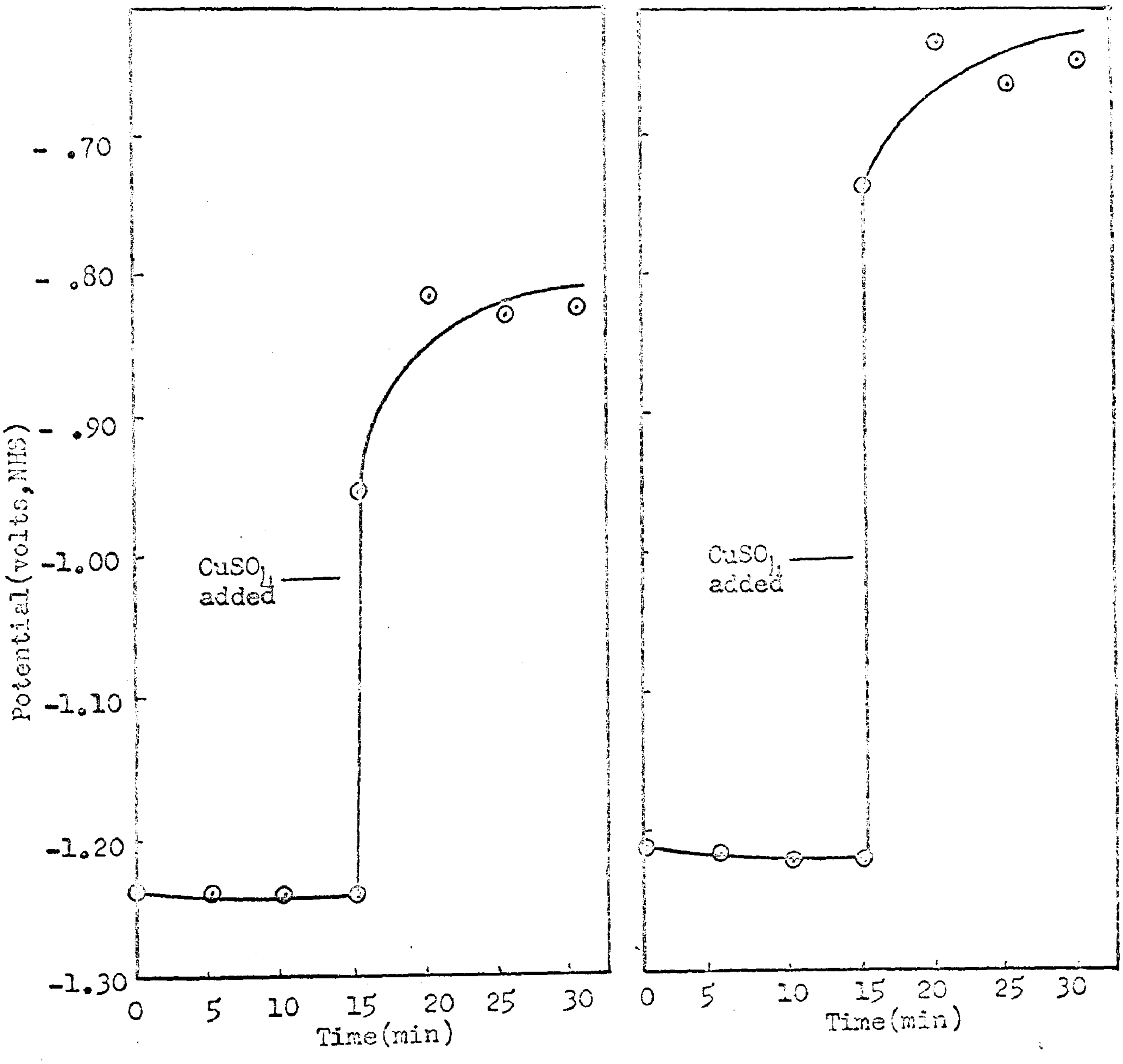


Figure 17

Effect of FeSO$_4$ on aluminum electrode potential in 2N HF



.01 M

.1 M

Figure 18

Effect of CuSO$_4$ on aluminum
electrode potential in 2N HF

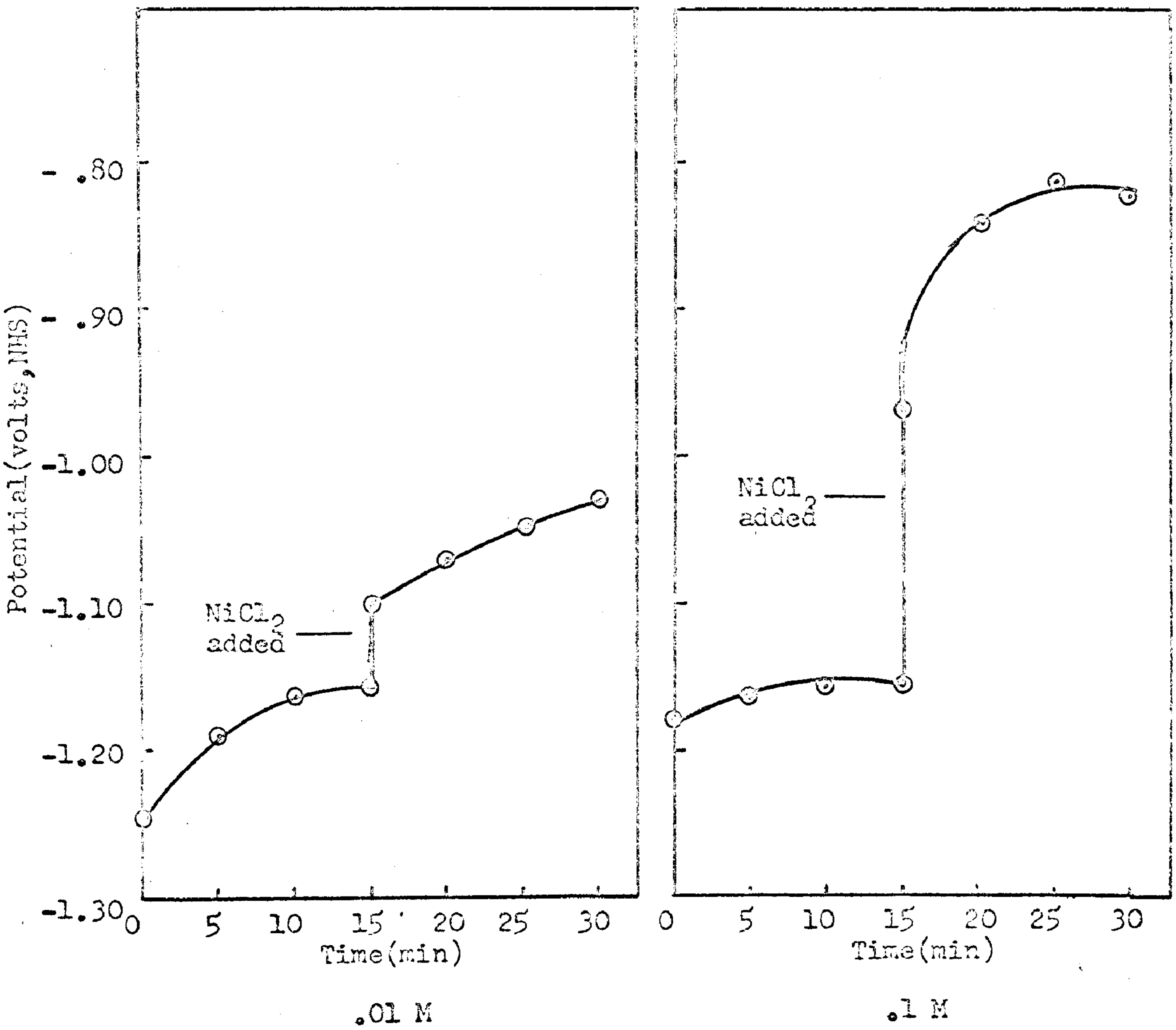


Figure 19

Effect of NiCl$_2$ on aluminum electrode potential in 2N HF

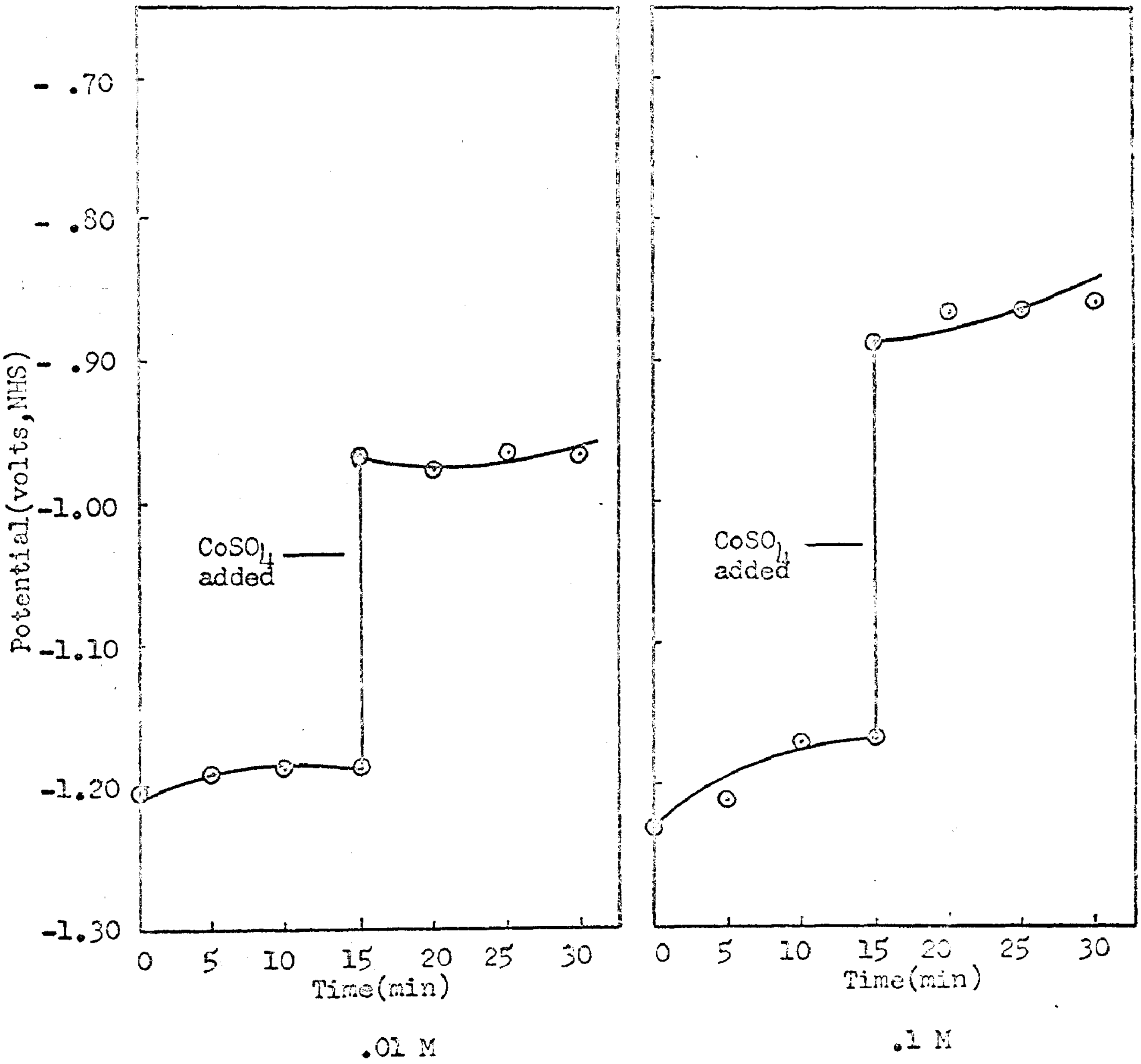


Figure 20

Effect of $CoSO_4$ on aluminum
electrode potential in 2N HF

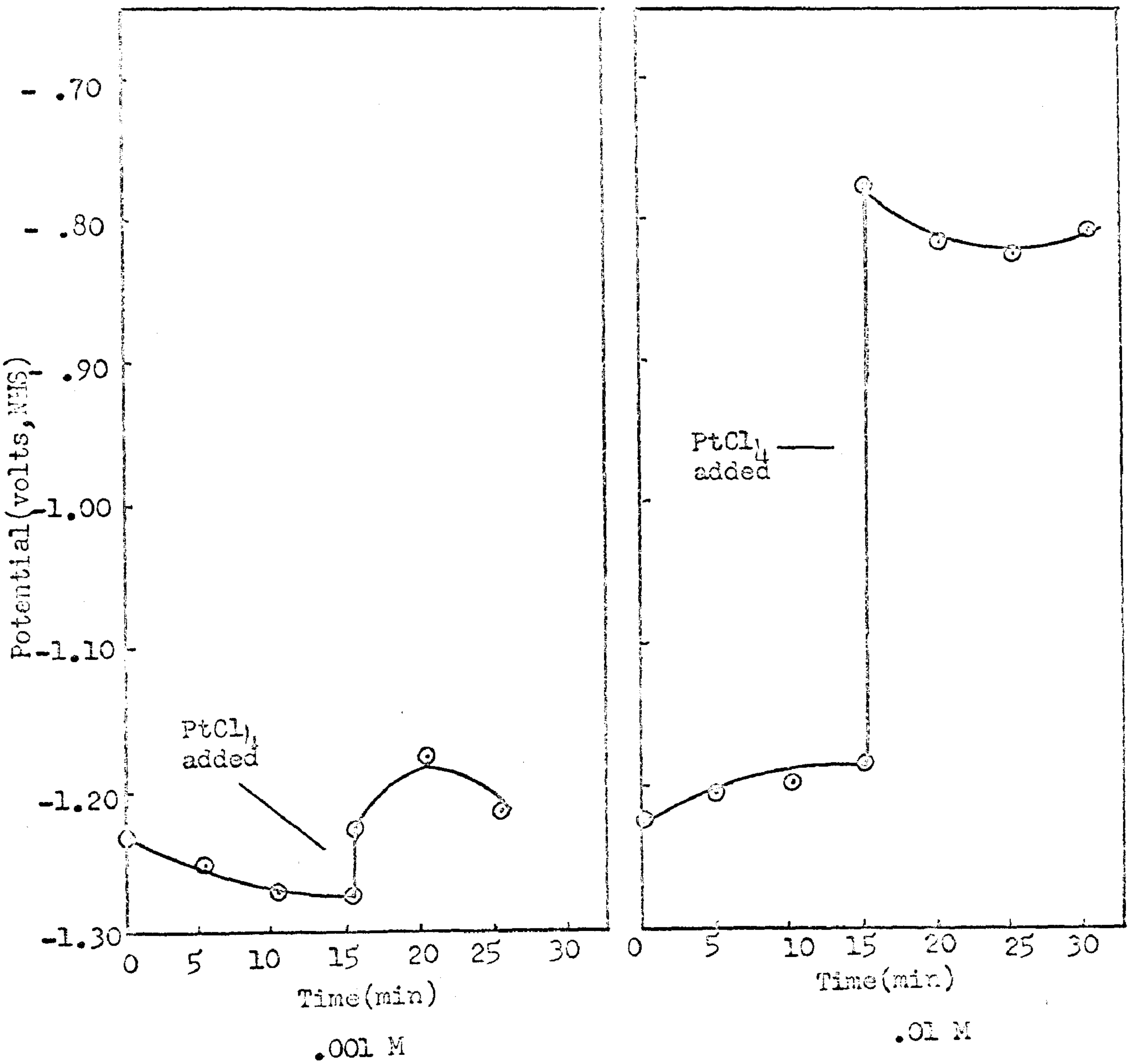


Figure 21

Effect of PtCl$_4$ on aluminum electrode potential in 2N HF

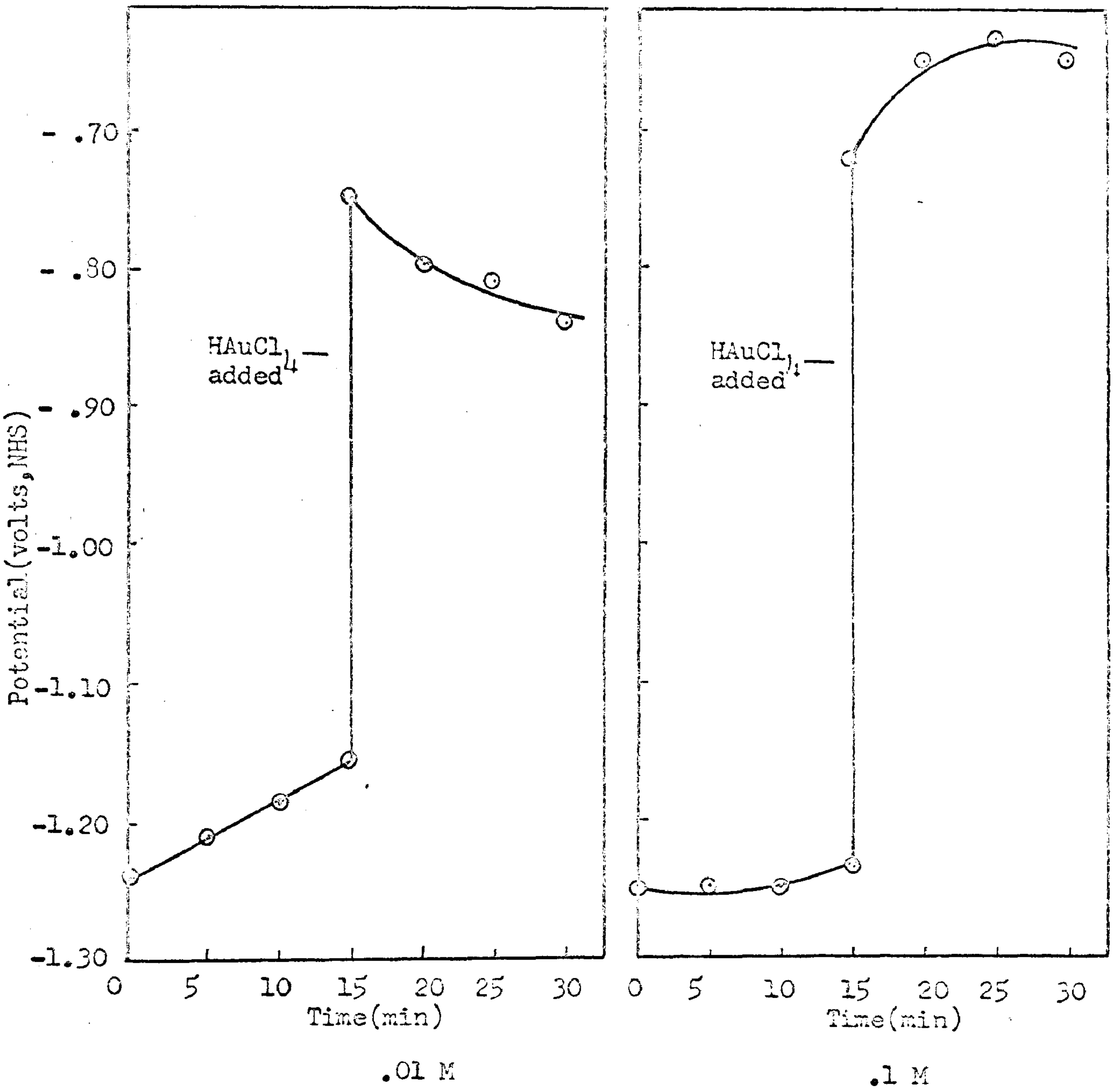


Figure 22

Effect of HAuCl$_4$ on aluminum electrode potential in 2N HF in HF plus separate additions of .01M $CoSO_4$, $NiCl_2$, and $AgNO_3$ was observed. Table V and Fig. 23 show that the potential of aluminum in HF with Ni and Ag began to decrease after a period of time, but that of Co did not until after 3 hours, and even then the decrease was slight. The original potential of aluminum even in plain HF was never reached again in any case.

Some deposit must be on the surface of the aluminum to cause the rate decrease and potential increase. The following experiment (Fig. 24) was performed to substantiate this. The aluminum electrode was immersed in HF and set up for potential measurements in the previously described manner. After several minutes, $NiCl_2$ (.1 M) was added as before and the potential increased immediately. After an interim, the electrode was removed, washed, and then immersed into a beaker containing plain 2N HF. The potential measured was considerably lower in the very beginning, but kept decreasing with time. Then the electrode was put back into the solution of HF and $NiCl_2$. The potential immediately increased to the approximate previous value. Again the aluminum was removed, washed, and this time a fine brush was used to scratch the surface. Placing the electrode back into the solution of HF resulted in a potential close to that of the beginning of the experiment. In other words, the return was faster when the surface was scratched than it was when not scratched before immersion into plain HF. As a further test, the aluminum electrode was

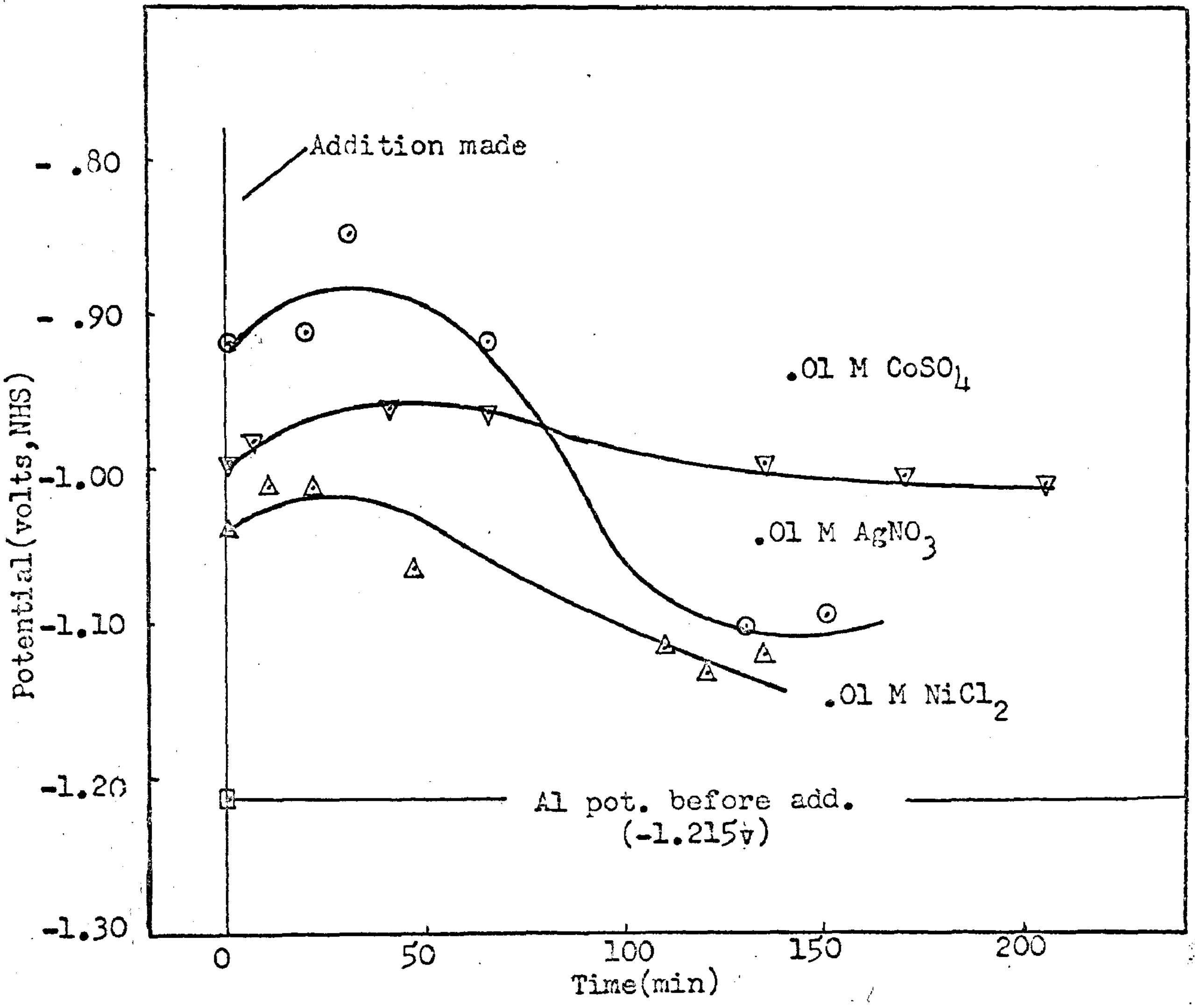


Figure 23

Extended aluminum electrode potentials in 2N HF upon addition of .01 M $CoSO_4$, $NiCl_2$, and $AgNO_3$ to the acid

# TABLE V

Extended aluminum electrode potentials in 2N HF upon addition of .01M $CoSO_4$, $NiCl_2$, and $AgNO_3$ to the acid

| .01M $CoSO_4$ | | .01M $NiCl_2$ | | .01M $AgNO_3$ | |
|---|---|---|---|---|---|
| Pot. (volts) | Time (min) | Pot. (volts) | Time (min) | Pot. (volts) | Time (min) |
| * -1.189 | | * -1.227 | | * -1.199 | |
| - .994 | 0 | -1.038 | 0 | - .919 | 0 |
| - .978 | 5 | -1.010 | 10 | - .909 | 20 |
| - .962 | 40 | -1.007 | 20 | - .848 | 30 |
| - .960 | 65 | -1.064 | 45 | - .918 | 65 |
| - .981 | 85 | -1.037 | 65 | -1.103 | 110 |
| - .994 | 135 | -1.117 | 110 | -1.101 | 130 |
| -1.005 | 170 | -1.131 | 120 | -1.094 | 150 |
| -1.009 | 205 | -1.121 | 135 | | |
| -1.020 | 235 | | | | |

* addition of 4 ml .01M salt plus 4 ml 4N HF

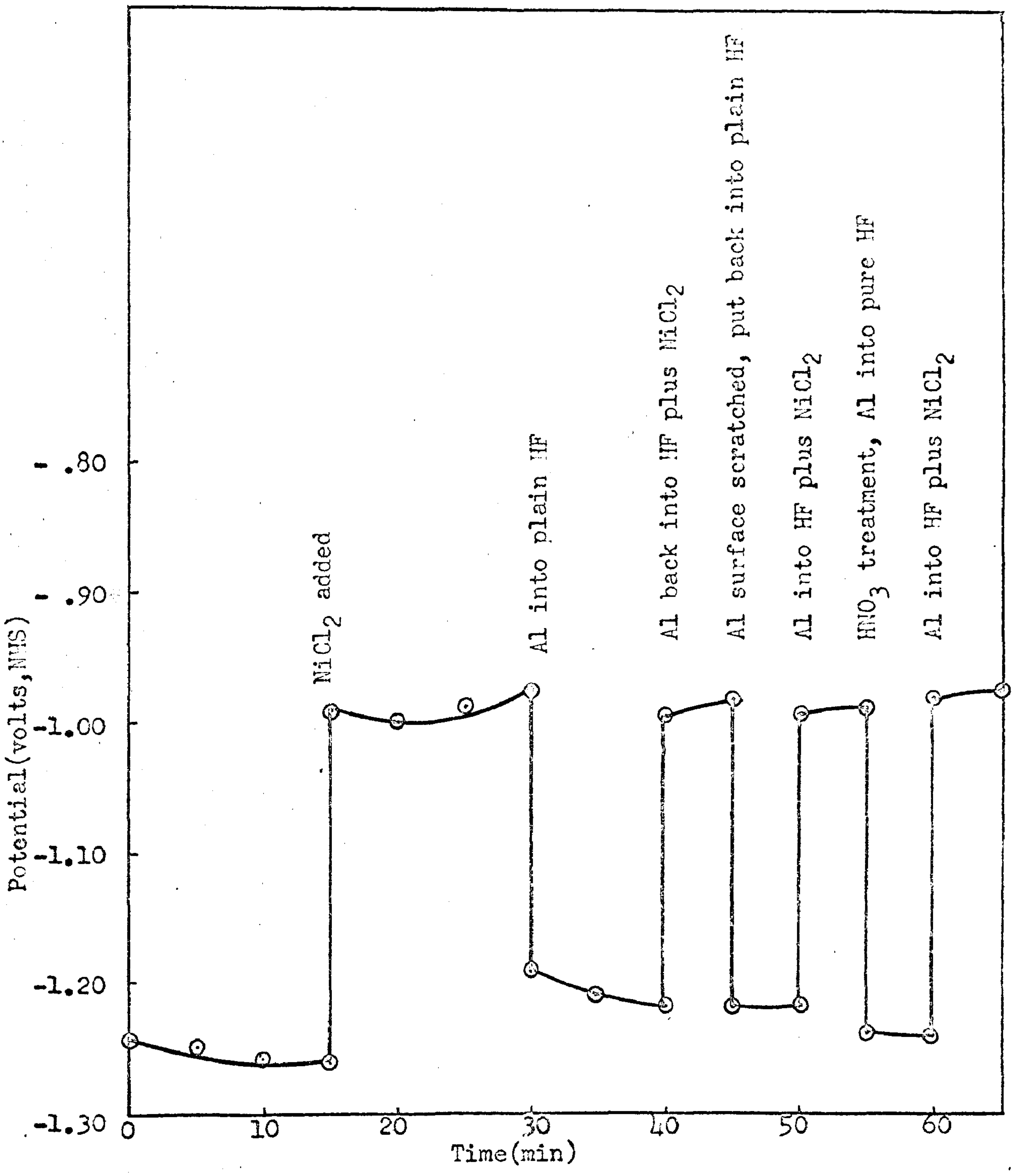


Figure 24

Effect of various treatments on aluminum electrode potential in 2N HF with .1 M $NiCl_2$ added removed from the solution of HF and $NiCl_2$ and washed. It was then treated with $HNO_3$ (to remove to possible Ni layer on the surface, if present). Upon immersion in a solution of plain HF, the potential was the same as that of the pure aluminum in plain HF at the beginning. Therefore, there was evidently something was formed on the surface of the aluminum after the $NiCl_2$ was added.

# CHAPTER V

## MICROHARDNESS TESTING OF THE ALUMINUM SURFACE AFTER DISSOLVING IN 2N HF WITH NOBLER METALLIC SALTS ADDED

Formation of Pt, Ag, Au, and Cu layers on the surface of the aluminum, which has been dissolved in HF with the respective metallic salt added, was visibly evident. However, no layer of any form can be detected upon the aluminum surface dissolved in HF in the presence of $FeSO_4$, $CoSO_4$, and $NiCl_2$. It is clear however, through dissolution rate and electropotential measurements that something should be present. Therefore, microhardness tests were performed.

Pure aluminum is a very soft metal. If even a very thin layer of another harder material were on the surface, a microhardness test might reveal it in the form of increased hardness values.

Strips of pure aluminum were cut and placed into Polyethylene beakers containing 2N HF. After some time equal amounts of .1 M $NiCl_2$, $CoSO_4$, $AgNO_3$, NaCl, and KCl were added to five of the beakers while nothing was added to the sixth. $NiCl_2$ and $CoSO_4$ were added for possible detection of Ni or Co layers on the aluminum. NaCl and KCl were added as a precaution to see that nothing formed on the aluminum, as exhibited by the electropotential measurements. The purpose of the $AgNO_3$ addition was to measure the hardness of those areas where no massive Ag deposit was evident to see if perhaps a very thin layer of Ag was present but invisible. After dissolution for several more minutes, all five pieces were removed, carefully washed, and dried. They were now ready for microhardness testing, which was performed on a Reichert Microhardness Tester with a pyramidal diamond indenter.

Hardness values were expressed as Vickers Hardness Numbers[11] ($H_V$ in kg/mm$^2$), which were calculated using the formula:

$$H_V = 1.8544\ P/d^2 \qquad (7)$$

where P is the load in kg and d is the length of the diagonal of the indentation in mm. The load chosen within the tester was 18.2 g in all cases, while the diagonal of the square-based pyramid indentation was measured with the optical micrometer. For each specimen, 10 indentation measurements were made, and the $H_V$ for each was calculated. An average of these 10 measurements was made and the standard deviation was calculated using the formula:

$$\text{Standard deviation} = \sqrt{\Sigma\Delta^2/(n-1)} \qquad (8)$$

where $\Delta$ is the difference between the average and individual $H_V$ and n is the number of measurements (10). The results are summarized in Table VI and given in more complete detail in the appendix (Tables XXXVI-XLI).

The results show that it is credible that a layer of Ni, Co, and Ag are indeed present as the hardness values are larger

## TABLE VI

Hardness of Al corroded in HF in comparison with Al corroded in HF in presence of metal salts

| Specimen | $H_v$ (kg/mm$^2$) | Stand. dev. |
|---|---|---|
| Al in HF | 32.1 | ± 2.9 |
| Al in HF with $NiCl_2$ | 42.6 | ± 3.8 |
| Al in HF with $AgNO_3$ | 40.5 | ± 2.3 |
| Al in HF with $CoSO_4$ | 41.6 | ± 2.1 |
| Al in HF with NaCl | 31.9 | ± 2.4 |
| Al in HF with KCl | 30.6 | ± 1.4 |

(since Ni, Co, and Ag are harder than Al) within the realm of the standard deviation. That is, the highest hardness value of aluminum in plain HF (32.1 + 2.9) was still lower than the lowest hardness value of the aluminum in HF plus $NiCl_2$ (42.6 - 3.8), $CoSO_4$ (41.6-2.1) and $AgNO_3$ (40.5-2.3). The hardness of aluminum dissolved in HF with NaCl added (31.9 ± 2.4) was seen to be much the same (within the limits of error) as aluminum dissolved in HF alone, showing that nothing was distorting or present on the surface.

# CHAPTER VI

# DISCUSSION AND CONCLUSIONS

When a metal corrodes in an acid, ions of that metal go into solution while an equivalent amount of hydrogen is displaced from the acid and evolved at an adjacent site of low hydrogen overvoltage. This site is commonly a very small metallic particle (of different composition than the base metal). The dissolving metal is thus the anode, while the particle is the cathode and a current is set up between them. Thus, there is an innumerable amount of these small irreversible cells. The effect of these local cathodes upon the corrosion rate is expressed in Eq. 6. The emf of such a cell is $n - E'$, where $n$ is the potential of the local cathode and $E'$ is the dissolution potential of the anode. If these local cathodes are active and exposed to the corrosive medium, it is expected that the corrosion rate would increase. However, if some metallic oxide or salt layer is covering these local elements, they would not contribute to the dissolution rate. In fact, if these layers were adherent enough and not too porous, rate of corrosion of the base metal indeed would be expected to decrease. If these layers broke down, the corrosion rate would increase as the underlying local elements would be exposed. Furthermore, if the broken down layers have a low hydrogen overpotential, they would increase still more the rate of dissolution of the base metal.

## A. Dissolution of aluminum in hydrofluoric acid

A thin but very adherent layer of $Al_2O_3$ is always present on an aluminum surface. This layer gives aluminum its desirable property of corrosion resistance. However, HF will dissolve this protective layer and hence, aluminum is corroded in this acid. The layer continuously forms during dissolution, provided oxygen is present and can diffuse through the corrosive medium to the aluminum surface. As the layer dissolves, more and more local cathodes are exposed and thus the dissolution rate increases. A maximum is reached where the local elements contribute to the rate as much as possible. The elements then begin to break off because of mechanical effects, lowering the rate so slowly that a constant value appears to have been reached. The rate also lowers to a certain extent due to the depletion of the acid. A "poisoning" of the local elements by corrosion products could also cause this. The presence of a white precipitate showed that $AlF_3$ was present and could be expected to affect the rate of corrosion. This could explain some of the experimental deviations as the $AlF_3$ could have partially blanketed the surface and thus the local elements.

## B. Dissolution rate of aluminum in hydrofluoric acid with other additions

Aluminum would be expected to displace any metal that is more electropositive from the salt solution of the latter. Thus reactions of these salts with aluminum should occur as listed:

$$Al + 3AgNO_3 \dashrightarrow Al(NO_3)_3 + 3Ag \qquad (9)$$

$$2Al + 3FeSO_4 \dashrightarrow Al_2(SO_4)_3 + 3Fe \qquad (10)$$

$$2Al + 3CuSO_4 \dashrightarrow Al_2(SO_4)_3 + 3Cu \qquad (11)$$

$$2Al + 3NiCl_2 \dashrightarrow 2AlCl_3 + 3Ni \qquad (12)$$

$$4Al + 3PtCl_4 \dashrightarrow 4AlCl_3 + 3Pt \qquad (13)$$

$$2Al + 3CoSO_4 \dashrightarrow Al_2(SO_4)_3 + 3Co \qquad (14)$$

$$Al + AuCl_3 \cdot HCl \dashrightarrow AlCl_3 + Au \qquad (15)$$

When $AgNO_3$ was added to the acid, the corrosion rate decreased simultaneously (Fig. 5) with the formation of a dark layer of silver on the aluminum surface. This layer evidently covered the active local cathodes and was not active itself. However, the layer was not staying in the original place itself and began to peel off, uncovering some of the local elements as noted by the rate increase. It was, however, observed that the layer kept reforming: the dark precipitate turning to white flakes when separated from the aluminum. This phenomenon was investigated by x-ray analysis. Within the limits of error, the diameter of the Ag (333) ring (Cu radiation) for both deposits showed no difference, proving both precipitates to be silver. However, the grain size of the black precipitate was smaller than the white, as evidenced by broader lines on the x-ray pattern. This black color is possibly caused by impurities within the silver, absorbing some aluminum, and thus creating a distortion in the lattice. This dark silver displays a decreased hydrogen overpotential. As soon as contact with the aluminum is lost, the impurities (aluminum) dissolve and the flakes turn white (recovery of the ideal lattice). Straumanis and Fang[10] reported a very similar phenomenon with silver deposited upon zinc in $H_2SO_4$. They reported that zinc and silver co-deposit on the zinc surface. The black color was attributed to the fineness of particle size. The same could have occurred here with the aluminum co-depositing with the silver. When the deposit separated from the aluminum, the aluminum in the deposit dissolved immediately, allowing the recrystallization of the silver to occur, yielding a larger grain size and thus the white color. Qualitative experiments showed clearly that upon contact of these flakes with aluminum, they turned dark again, probably due to deposition of more Ag-Al on the surface.

Additions of $FeSO_4$ and $CoSO_4$ and $NiCl_2$ all showed very similar effects to the resultant rate changes (Figs. 7, 10, and 11). In all three cases, the rate dropped considerably at first with the addition of both concentrations of salts. However, in contrast to silver, no precipitate was formed as nothing could be seen on the surface of the corroding aluminum. Therefore, there must have been a tight adherent layer of iron, cobalt, and nickel electrolessly deposited on the aluminum in so thin a layer that it could not even be microscopically detected. The .01 M addition of nickel also retained the lower rate, but the cobalt and iron showed very sharp increases right after the initial drop. The increase continued to values higher than even the previous maximum showing that the layers evidently were active themselves and, upon partial separation from aluminum, also permitted the local elements on the aluminum to contribute to the increase of the dissolution rate.

Copper additions all decreased the rate initially, but then the rate increased considerably especially with the lower concentration salt addition (Fig. 8). Copper was visibly deposited on the surface, but probably not too adherently, thus increasing the rate, as mentioned.

Gold additions brought about sporadic results, somewhat typical of all the additions which created visible precipitates (Fig. 13). The scattering was greater here than any of the other additions as the dissolution rate both increased and decreased with both additions. This variable effect was probably caused by the precipitate. If the layer of gold would adhere well, the rate decreased, but if the layer covered incompletely, the rate increased due to the effect of local elements. In either case the rate fluctuation was small.

Experiments involving $PtCl_4$ additions yielded results showing greater rates of dissolution even before the $PtCl_4$ was added. The only difference in these experiments and all others was the nitrogen atmosphere (see p. 20). This, then, must have been the cause. It would seem that the opposite would be true, that is the rate of hydrogen evolution in an inert nitrogen atmosphere would be less than one in air. However, this might be explained by the $Al_2O_3$ layer always present in the experiments carried out in air. This layer might be formed by:

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \qquad (16)$$

This oxide or a similar surface oxide layer is soluble in HF:

$$Al_2O_3 + 6HF \longrightarrow 2AlF_3 + 3H_2O \qquad (17)$$

However, with a nitrogen atmosphere, after the initial $Al_2O_3$ layer is consumed,there would be no oxygen left to combine with aluminum to make any more of the reistant oxide layer. The only one which could form would be:

$$6H_2O + 2Al \longrightarrow 2Al(OH)_3 + 3H_2 \qquad (18)$$

$Al(OH)_3$ or $AlO(OH)$ is probably thinner or at least more porous than that formed in the presence of oxygen. The $Al(OH)_3$ would combine with HF as shown:

$$Al(OH)_3 + 3HF \longrightarrow AlF_3 + 3H_2O \qquad (19)$$

If reaction (19) were faster than reaction (17), the dissolution rate would indeed be higher in the nitrogen atmosphere. A simple qualitative experiment was devised to demonstrate the protective oxide layer. Pieces of aluminum were added to two Polyethylene beakers containing 2N HF and allowed to partially dissolve.
A small amount of $HNO_3$ was added to one and chromic acid to the other. Both are good oxidizers (inhibitors) and should assist in the formation of a protective coating. $HNO_3$ greatly slowed the dissolution rate, while chromic acid stopped it altogether, proving the oxide or a similar layer was instrumental in preventing

the corrosion. $PtCl_4$ additions were seen to decrease the dissolution rate considerably, but probably not as much as shown due to the possible consumption of hydrogen in forming water (see p. ). A black precipitate resulted from the addition. This deposit probably caused the decrease in rate, but as soon as it began to loosen and drop off in the form of a black precipitate, a higher dissolution rate resulted.

## C. Electrode potential measurements

According to Eq. 6, the increase(less negative) of the anodic potential (E') and thus the decrease of emf (n - E') should cause a decrease in the dissolution rate. However, this rate reduced because of the protective metal layer formed, covering the local cathodes on the aluminum. In all potential measurements, there was an ensuing increase in potential upon the addition of the salts of more noble metals than aluminum. This supports the measured rate decreases. However, no correlation between the amount of decrease in rate and the increase in potential could be made. For example, while .01 M $NiCl_2$ only increased the potential 48 mv, a large drop (-35%) in the dissolution rate was noted. On the other hand, .01 M $CuSO_4$ caused a potential rise of 385 mv but only a small decrease in rate (-13.3%). Thus, the protective effect of the cover and not the potential change is of prime importance. This change originates probably as a mixed potential between that of the aluminum in the pores and the cathodic potential of the covering on which hydrogen is developing. A general trend of the greater potential increase with the lower hydrogen overpotential of the metallic cover has to be expected. The fact that no correlation between rate and potential change exists is explained, as already mentioned, by the decrease of the number of active local cathodes (z'), which is greater in one case than in another. The blanketing effect could also differ with the various additions, depending on the form of the precipitates present. The mixed potential approach is supported by the fact that additions of NaCl and KCl do not cause a significant potential change of the corroding aluminum, because as expected Na and K would not be displaced from their salt solutions by aluminum. Removal of the invisible nickel layer by $HNO_3$ resulted in an immediate decrease in the measured potential.

### D. Microhardness tests

Additions of $FeSO_4$, $NiCl_2$, and $CoSO_4$ yielded no visible precipitates that could be the cause of the rate decreases. The electropotential increase gives rise to the belief that a metallic layer was deposited, but so thin that it appeared to be transparent. Since these layers should be harder than the aluminum, the microhardness measurements (p.55) were used as detectors.

Indeed, the increased hardness values showed that a layer was present. This layer, although very thin, caused the hardness of the combined aluminum-electrolessly deposited metal to increase. The thin layer present on the aluminum surface caused the inhibiting effect of the rate reduction. No changes in the hardness of aluminum were observed if treated with NaCl or KCl solutions, because no deposition of the metals could occur.

A combination of electron and optical microscopy was used to examine the aluminum surface after dissolution in plain HF and the aluminum dissolved in HF in presence of $NiCl_2$. The electron microscope showed a variation in the two surfaces in the form of different etching behavior. The sample etched in HF with $NiCl_2$ added contained many diamond shaped etch pits throughout the surface, while no definite geometric arrangement in the etching of aluminum dissolved in plain HF could be detected. Careful examination with the optical microscope substantiated these results. Thus the aluminum surface etched in HF with $NiCl_2$ was covered with a nickel layer except in certain areas containing pores where the dissolution continued preferentially and produced etch pits in the form of diamonds.

# CHAPTER VII

## SUMMARY

1. The dissolution rate of aluminum in 2N HF at 25 C determined by the hydrogen evolution method was found to increase in an induction period to a maximum and then slightly drop off.

2. Addition of nobler metal salts such as $AgNO_3$, $FeSO_4$, $CuSO_4$, $NiCl_2$, $CoSO_4$, $PtCl_4$, and $HAuCl_4$ to the HF as the rate just passed the maximum decreased the dissolution rate of the aluminum appreciably.

3. Weaker additions of some of these salts created lesser decreases in rate and sometimes showed ensuing increases to points even above the previous maximum due to the uncovering of local cathodes.

4. $AgNO_3$, $CuSO_4$, $PtCl_4$, and $HAuCl_4$ additions produced deposits upon the aluminum surface which acted as blankets to inhibit the rate. $AgNO_3$ additions produced a dark precipitate (on the aluminum surface) which turned white when contact with the aluminum was lost due to the presence of co-deposited aluminum within the silver lattice.

5. Experiments involving $PtCl_4$ additions were carried out in an atmosphere of nitrogen which caused the rates to be higher due to the absence of a strongly protective oxide layer.

6. $FeSO_4$, $CoSO_4$, and $NiCl_2$ additions produced no visible precipitates, but a thin invisible layer was electrolessly deposited, the presence of which was detected with potential and microhardness measurements.

7. Electropotential measurements showed an increase in the anodic potential of aluminum upon all salt additions ( except those of Na and K).

8. Microhardness testing gave higher hardness values(at points where deposits were not visible) for the aluminum surface dissolved in HF with nobler metal salt additions than the aluminum dissolved only in HF, proving the presence of a metallic layer.

9. Electron microscopy showed a difference in the etching behavior of aluminum after dissolution in HF and aluminum after dissolution in HF with $NiCl_2$ added.

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# APPENDICES

TABLE I

Theoretical and experimental displacements
of hydrogen from HCl by Zn

| | Run #1 | Run#2 | Run #3 |
|---|---|---|---|
| Wt. Zn (g) | .20864 | .20757 | .21436 |
| Avg. temp. (°C) | 21.9 | 21.2 | 21.9 |
| Avg. cor. press.(mm Hg) | 711.6 | 711.5 | 711.6 |
| Exp. $H_2$ (ml) | 81.2 | 80.7 | 84.3 |
| Exp. $H_2$*(ml) | 70.38 | 69.89 | 73.08 |
| Theo. $H_2$ (ml) | 71.52 | 71.45 | 73.79 |
| % dev. | 1.59 | 2.18 | .96 |

* reduced to STP

Sample calculations for Run#1:

Avg. cor. press. = 733.8 - 19.70 - 2.50 = 711.6 mm Hg

Avg. temp. = $21.9^\circ$C = $294.9^\circ$K

81.2(711.6x273/760x294.9) = 70.38 ml at STP

.20864 g Zn/.002905 g Zn per ml $H_2$ = 71.52 ml

% dev. = (71.52 - 70.38)/71.52 100 = 1.59%

Avg. % dev. = 1.58%

## TABLE II

Hydrogen evolution rate of Al in 2N HF at 25°C

| | |
|---|---|
| Avg. room temp: | 21.1°C |
| Avg. corrected pressure: | 711.6 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting Al surface: | 1.065 $cm^2$ |

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| 20 | 1.60 | 1.60 | 1.39 | 131 |
| 30 | 3.60 | 2.00 | 1.74 | 163 |
| 40 | 5.90 | 2.30 | 2.00 | 188 |
| 50 | 9.30 | 3.40 | 2.95 | 277 |
| 60 | 13.90 | 4.60 | 4.00 | 376 |
| 70 | 19.40 | 5.50 | 4.78 | 499# |
| 80 | 25.00 | 5.60 | 4.87 | 457# |
| 90 | 30.80 | 5.80 | 5.04 | 473# |
| 100 | 36.50 | 5.70 | 4.95 | 465# |
| 110 | 42.00 | 5.50 | 4.78 | 449# |
| 120 | 47.60 | 5.60 | 4.87 | 457# |
| 130 | 52.60 | 5.00 | 4.35 | 408 |
| 140 | 57.70 | 5.10 | 4.43 | 416 |
| 150 | 62.80 | 5.10 | 4.43 | 416 |

\# Avg. maximum rate: 458 $mm^3/cm^2min$

## TABLE III

Hydrogen evolution rate of Al in 2N HF at 25°C

| | |
|---|---|
| Avg. room temp: | 21.3°C |
| Avg. corrected pressure: | 713.7 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting Al surface: | 1.070 $cm^2$ |

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| 10 | 1.80 | 1.80 | 1.57 | 147 |
| 20 | 4.00 | 2.20 | 1.92 | 179 |
| 30 | 6.80 | 2.80 | 2.45 | 229 |
| 40 | 10.50 | 3.70 | 3.22 | 301 |
| 50 | 14.70 | 3.80 | 3.31 | 309 |
| 60 | 19.70 | 5.00 | 4.36 | 407 |
| 70 | 25.10 | 5.40 | 4.70 | 439 |
| 80 | 31.30 | 6.20 | 5.40 | 505# |
| 90 | 38.00 | 6.70 | 5.84 | 546# |
| 100 | 44.40 | 6.40 | 5.57 | 521# |
| 110 | 51.00 | 6.60 | 5.75 | 537# |
| 120 | 57.50 | 6.50 | 5.66 | 529# |
| 130 | 63.70 | 6.20 | 5.40 | 505# |
| 140 | 69.40 | 5.70 | 4.96 | 464 |
| 150 | 74.70 | 5.30 | 4.70 | 431 |
| 160 | 80.40 | 5.70 | 4.96 | 464 |

\# Avg. maximum rate: 524 $mm^3/cm^2min$
Avg. maximum rate for both runs: 491 ± 33 $mm^3/cm^2min$

# TABLE IV

Hydrogen evolution rate of aluminum in 2N HF at 25° C
upon addition of .01 M $AgNO_3$

Avg. room temp: 20.7° C
Avg. corrected pressure: 739.5 mm Hg
Speed of stirrer. 200 rpm
Area of reacting aluminum surface: .95 $cm^2$

## Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2 min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 230 | 81.90 | 4.70 | 4.13 | 436 |
| 240 | 86.60 | 4.70 | 4.13 | 436 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 3.60 | 3.60 | 3.16 | 334 |
| 20 | 7.70 | 4.10 | 3.60 | 380 |
| 30 | 12.30 | 4.60 | 4.04 | 427 |
| 40 | 17.10 | 4.80 | 4.22 | 446 |
| 50 | 24.00 | 4.90 | 4.31 | 455 |

* 4 ml .01 M $AgNO_3$ plus 4 ml 4N HF added

% rate change -23.4

## TABLE V

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $AgNO_3$

| | |
|---|---|
| Avg. room temp: | 20.9°C |
| Avg. corrected pressure: | 718.9 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .99 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 230 | 18.10 | 4.30 | 3.78 | 382 |
| 240 | 22.40 | 4.30 | 3.78 | 382 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 2.30 | 2.30 | 2.02 | 204 |
| 20 | 6.00 | 3.70 | 3.25 | 328 |
| 30 | 9.20 | 3.20 | 2.81 | 284 |
| 40 | 12.50 | 3.30 | 2.90 | 293 |
| 50 | 15.70 | 3.20 | 2.81 | 284 |

* 4 ml .01 M $AgNO_3$ plus 4 ml 4N HF added

% rate change -46.7

Avg. % rate change for both runs -35.1

# TABLE VI

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $AgNO_3$

| | |
|---|---|
| Avg. room temp: | 20.3° C |
| Avg. corrected pressure: | 714.7 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .85 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 290 | 14.00 | 4.00 | 3.56 | 418 |
| 300 | 18.40 | 4.40 | 3.67 | 431 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 2.60 | 2.60 | 2.28 | 268 |
| 20 | 5.70 | 3.10 | 2.71 | 318 |
| 30 | 9.00 | 3.30 | 2.89 | 340 |
| 40 | 12.30 | 3.30 | 2.89 | 340 |
| 50 | 15.90 | 3.60 | 3.15 | 370 |
| 60 | 19.90 | 4.00 | 3.56 | 418 |
| 70 | 23.90 | 4.00 | 3.56 | 418 |

* 4 ml .1 M $AgNO_3$ plus 4 ml 4N HF added

% rate change -37.8

# TABLE VII

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $AgNO_3$

| | |
|---|---|
| Avg. room temp: | 20.9°C |
| Avg. corrected pressure: | 715.2 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.14 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 200 | 90.30 | 5.30 | 4.63 | 410 |
| 210 | 95.60 | 5.30 | 4.63 | 410 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 3.60 | 3.60 | 3.15 | 279 |
| 20 | 7.20 | 3.60 | 3.15 | 279 |
| 30 | 10.90 | 3.70 | 3.23 | 286 |
| . | . | . | . | . |
| 100 | 39.20 | 4.15 | 3.63 | 321 |
| 110 | 43.70 | 4.50 | 3.93 | 348 |
| 120 | 47.70 | 4.00 | 3.50 | 310 |
| 130 | 52.20 | 4.50 | 3.93 | 348 |

* 4 ml .1 M $AgNO_3$ plus 4 ml 4N HF added

% rate change -32.0

Avg. % rate change for both runs -34.9

## TABLE VIII

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $FeSO_4$

| | |
|---|---|
| Avg. room temp: | 22.1°C |
| Avg. corrected pressure: | 704.6 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.28 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2$min |
|---|---|---|---|---|
| . | . | . | . | . |
| 130 | 76.40 | 5.80 | 4.98 | 389 |
| 140 | 82.50 | 6.10 | 5.23 | 409 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.70 | 4.70 | 4.03 | 315 |
| 20 | 11.90 | 7.20 | 6.18 | 482 |
| 30 | 19.10 | 7.20 | 6.18 | 482 |
| 40 | 25.50 | 6.40 | 5.49 | 429 |
| 50 | 30.90 | 5.40 | 4.63 | 362 |
| 60 | 36.30 | 5.40 | 4.63 | 362 |
| 70 | 40.70 | 4.40 | 3.78 | 295 |
| 80 | 45.10 | 4.40 | 3.78 | 295 |

* 4 ml .01 M $FeSO_4$ plus 4 ml 4N HF added

% Rate change -23.0

## TABLE IX

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $FeSO_4$

| | |
|---|---|
| Avg. room temp: | 21.5°C |
| Avg. corrected pressure: | 708.2 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.34 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 210 | 41.70 | 6.80 | 5.86 | 439 |
| 220 | 48.60 | 6.90 | 5.95 | 445 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 6.10 | 6.10 | 5.26 | 394 |
| 20 | 14.80 | 8.70 | 7.50 | 561 |
| 30 | 24.00 | 9.20 | 7.94 | 594 |
| 40 | 33.20 | 9.20 | 7.94 | 594 |
| 50 | 42.00 | 8.80 | 7.59 | 567 |
| 60 | 49.90 | 7.90 | 6.81 | 510 |
| 70 | 57.00 | 7.10 | 6.13 | 458 |
| 80 | 62.90 | 5.90 | 5.08 | 380 |

* 4 ml .01 M $FeSO_4$ plus 4 ml 4N HF added

% rate change -11.5

Avg. % rate change for both runs -17.3

## TABLE X

### Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $FeSO_4$

| | |
|---|---|
| Avg. room temp: | 21.0°C |
| Avg. corrected pressure: | 715.0 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .945 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 270 | 29.70 | 4.70 | 4.10 | 434 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 2.50 | 2.50 | 2.18 | 231 |
| 20 | 5.40 | 2.90 | 2.53 | 268 |
| 30 | 7.90 | 2.50 | 2.18 | 231 |
| . | . | . | . | . |
| 70 | 18.00 | 2.50 | 2.18 | 231 |
| 80 | 20.20 | 2.20 | 1.92 | 204 |
| . | . | . | . | . |
| 150 | 40.90 | 2.10 | 1.83 | 194 |

* 4 ml .1 M $FeSO_4$ plus 4 ml 4N HF added

% rate change -46.9

## TABLE XI

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $FeSO_4$

| | |
|---|---|
| Avg. room temp: | 21.2°C |
| Avg. corrected pressure: | 716.8 |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .957 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 250 | 93.70 | 5.10 | 4.46 | 466 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 2.20 | 2.20 | 1.92 | 201 |
| 20 | 5.00 | 2.80 | 2.44 | 255 |
| 30 | 7.80 | 2.80 | 2.44 | 255 |
| 40 | 10.60 | 2.80 | 2.44 | 255 |
| . | . | . | . | . |
| 190 | 46.60 | 2.40 | 2.10 | 219 |

*4 ml .1 M $FeSO_4$ plus 4 ml 4N HF added

% rate change -56.9

Avg. % rate change for both runs -51.9

## TABLE XII

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $CuSO_4$

| | |
|---|---|
| Avg. room temp: | 20.6°C |
| Avg. corrected pressure: | 722.1 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .99 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 150 | 70.10 | 5.10 | 4.50 | 455 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.70 | 4.70 | 4.14 | 419 |
| 20 | 9.60 | 4.90 | 4.33 | 438 |
| 30 | 14.90 | 5.30 | 4.68 | 474 |
| 40 | 20.80 | 5.90 | 5.21 | 527 |
| 50 | 27.00 | 6.20 | 5.47 | 553 |
| 60 | 33.80 | 6.80 | 6.00 | 607 |
| 70 | 40.80 | 7.00 | 6.18 | 625 |
| 80 | 48.40 | 7.60 | 6.71 | 679 |
| 90 | 56.60 | 8.20 | 7.22 | 731 |

* 4 ml .01 M $CuSO_4$ plus 4 ml 4N HF added

% rate change -7.91

## TABLE XIII

Hydrogen evolution rate of aluminum in 2N HF at 25°C
upon addition of .01 M $CuSO_4$

| | |
|---|---|
| Avg. room temp: | 21.1°C |
| Avg. corrected pressure: | 719.3 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.05 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 215 | 10.60 | 5.30 | 4.65 | 443 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.30 | 4.30 | 3.78 | 360 |
| 20 | 9.60 | 5.30 | 4.65 | 443 |
| 30 | 14.60 | 5.00 | 4.39 | 418 |
| 40 | 20.20 | 5.60 | 4.92 | 468 |
| . | . | . | . | . |
| 170 | 95.30 | 5.80 | 5.09 | 485 |
| 180 | 5.70 | 5.70 | 5.00 | 476 |

* 4 ml .01 M $CuSO_4$ plus 4 ml 4N HF added

% rate change -18.75

Avg. % rate change for both runs -13.33

## TABLE XIV

Hydrogen evolution rate of aluminum in 2N HF at 25°C
upon addition of .1 M $CuSO_4$

| | |
|---|---|
| Avg. room temp: | 20.6°C |
| Avg. corrected pressure: | 716.1 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .875 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 290 | 18.60 | 4.80 | 4.20 | 480 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.60 | 4.60 | 4.03 | 461 |
| 20 | 9.40 | 4.80 | 4.20 | 480 |
| 30 | 14.60 | 5.20 | 4.56 | 521 |
| 40 | 19.80 | 4.80 | 4.20 | 480 |
| 50 | 24.60 | 4.80 | 4.20 | 480 |

* 4 ml .1 M $CuSO_4$ plus 4 ml 4N HF added

% rate change -3.96

## TABLE XV

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $CuSO_4$

| | |
|---|---|
| Avg. room temp: | 20.5°C |
| Avg. corrected pressure: | 718.8 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.11 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 250 | 37.60 | 5.40 | 4.74 | 426 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 5.00 | 5.00 | 4.38 | 394 |
| 20 | 10.80 | 5.80 | 5.09 | 458 |
| 30 | 17.00 | 6.20 | 5.43 | 489 |
| 40 | 22.80 | 5.80 | 5.09 | 457 |
| . | . | . | . | . |
| 70 | 43.20 | 5.60 | 4.90 | 442 |
| 80 | 48.30 | 5.10 | 4.47 | 402 |
| 90 | 53.90 | 5.60 | 4.90 | 442 |

* 4 ml .1 M $CuSO_4$ plus 4 ml 4N HF added

% rate change -7.50

Avg. % rate change for both runs -5.73

## TABLE XVI

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .ol M $NiCl_2$

| | |
|---|---|
| Avg. room temp: | 20.5°C |
| Avg. corrected pressure: | 720.2 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.06 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2 min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 240 | 24.20 | 4.70 | 4.17 | 393 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 3.00 | 3.00 | 2.66 | 251 |
| 20 | 6.30 | 3.30 | 2.93 | 276 |
| 30 | 9.20 | 2.90 | 2.57 | 242 |
| 40 | 12.50 | 3.30 | 2.93 | 276 |
| 50 | 15.30 | 2.80 | 2.48 | 234 |

* 4 ml .01 M $NiCl_2$ plus 4 ml 4N HF added

% rate change -36.1

# TABLE XVII

Hydrogen evolution rate of aluminum in 2N HF at 25°C
upon addition of .01 M $NiCl_2$

| | |
|---|---|
| Avg. room temp: | 20.9°C |
| Avg. corrected pressure | 715.1 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.08 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 220 | 95.70 | 5.10 | 4.46 | 413 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 3.40 | 3.40 | 2.97 | 275 |
| 20 | 6.60 | 3.20 | 2.80 | 259 |
| 30 | 10.00 | 3.40 | 2.97 | 275 |
| 40 | 13.20 | 3.20 | 2.80 | 259 |
| . | . | . | . | . |
| 80 | 26.60 | 3.40 | 2.97 | 275 |

* 4 ml .01 M $NiCl_2$ plus 4 ml 4N HF added

% rate change -33.4

Avg. % rate change for both runs -34.8

## TABLE XVIII

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $NiCl_2$

| | |
|---|---|
| Avg. room temp: | 26.4°C |
| Avg. corrected pressure: | 710.8 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .98 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2$ min) |
|---|---|---|---|---|
| . | . | . | . | . |
| 120 | 50.60 | 4.20 | 3.58 | 364 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 3.20 | 3.20 | 2.73 | 277 |
| 20 | 6.10 | 2.90 | 2.47 | 251 |
| 30 | 9.00 | 2.90 | 2.47 | 251 |
| 40 | 11.70 | 2.70 | 2.33 | 237 |
| 50 | 14.40 | 2.70 | 2.33 | 237 |

* 4 ml .1 M $NiCl_2$ plus 4 ml 4N HF added

% rate change - 23.9

## TABLE XIX

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $NiCl_2$

| | |
|---|---|
| Avg. room temp: | 20.8°C |
| Avg. corrected pressure: | 718.4 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.006 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 240 | 84.40 | 5.70 | 5.00 | 497 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.80 | 4.80 | 4.21 | 418 |
| 20 | 9.40 | 4.60 | 4.04 | 402 |
| 30 | 14.10 | 4.70 | 4.13 | 411 |
| 40 | 18.90 | 4.80 | 4.21 | 418 |
| 50 | 23.60 | 4.70 | 4.13 | 411 |

* 4 ml .1 M $NiCl_2$ plus 4 ml 4N HF added

% rate change -15.9

Avg. % rate change for both runs -19.9

## TABLE XX

Hydrogen evolution rate of aluminum in 2N HF at 25°C
upon addition of .01 M $CoSO_4$

| | |
|---|---|
| Avg. room temp: | 22.1° C |
| Avg. corrected pressure: | 719.7 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.50 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 200 | 49.00 | 7.00 | 6.13 | 409 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 5.50 | 5.50 | 4.81 | 321 |
| 20 | 11.90 | 6.40 | 5.60 | 374 |
| 30 | 19.30 | 7.40 | 6.48 | 433 |
| 40 | 27.30 | 8.00 | 7.08 | 468 |
| 50 | 36.30 | 9.00 | 7.88 | 526 |
| 60 | 45.50 | 9.20 | 8.05 | 538 |
| 70 | 55.50 | 10.00 | 8.75 | 585 |
| 80 | 65.60 | 10.10 | 8.84 | 596 |
| 90 | 74.40 | 9.80 | 8.56 | 572 |

* 4 ml .01 M $CoSO_4$ plus 4 ml 4N HF added

% rate change -21.5

# TABLE XXI

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $CoSO_4$

| | |
|---|---|
| Avg. room temp: | 22.9°C |
| Avg. corrected pressure: | 717.5 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.22 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 270 | 76.40 | 5.60 | 4.88 | 400 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 3.60 | 3.60 | 2.67 | 219 |
| 20 | 7.70 | 4.10 | 3.58 | 293 |
| 30 | 12.90 | 5.20 | 4.53 | 371 |
| 40 | 18.70 | 5.80 | 5.06 | 415 |
| 50 | 25.50 | 6.80 | 5.93 | 486 |
| 60 | 32.80 | 7.30 | 6.37 | 522 |
| 70 | 40.80 | 8.00 | 6.98 | 572 |
| 80 | 48.30 | 8.50 | 7.41 | 607 |

* 4 ml .01 M $CoSO_4$ plus 4 ml 4N HF added

% rate change -40.3

Avg. % rate change for both runs -30.9

## TABLE XXII

Hydrogen evolution rate of aluminum in 2N HF at 25°C

upon addition of .1 M $CoSO_4$

| | |
|---|---|
| Avg. room temp: | 22.9°C |
| Avg. corrected pressure: | 717.5 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.23 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2 min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 190 | 19.00 | 6.40 | 5.60 | 455 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.20 | 4.20 | 3.68 | 299 |
| 20 | 8.50 | 4.30 | 3.76 | 306 |
| 30 | 12.60 | 4.10 | 3.59 | 292 |
| . | . | . | . | . |
| 60 | 24.80 | 4.10 | 3.59 | 292 |
| 70 | 28.70 | 3.90 | 3.41 | 277 |
| 80 | 32.70 | 4.00 | 3.50 | 285 |
| 90 | 36.50 | 3.80 | 3.33 | 271 |

* 4 ml .1 M $CoSO_4$ plus 4 ml 4N HF added

% rate change -34.3

## TABLE XXIII

### Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .1 M $CoSO_4$

Avg. room temp: 22.4°C
Avg. corrected pressure: 716.4 mm Hg
Speed of stirrer: 200 rpm
Area of reacting aluminum surface: 1.30 $cm^2$

Run #2

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2 min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 240 | 61.00 | 6.30 | 5.49 | 422 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | . | . | . | . |
| 20 | 7.70 | 3.85 | 3.35 | 258 |
| 30 | 11.40 | 3.70 | 3.22 | 248 |
| 40 | 15.10 | 3.70 | 3.22 | 248 |
| . | . | . | . | . |
| 80 | 29.70 | 3.70 | 3.22 | 248 |
| 90 | . | . | . | . |
| 100 | 37.50 | 3.90 | 3.39 | 260 |

* 4 ml .1 M $CoSO_4$

% rate change -38.9

Avg. % rate change for both runs -36.6

## TABLE XXIV

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .001 M $PtCl_4$ in a nitrogen atmosphere

| | |
|---|---|
| Avg. room temp: | 21.3°C |
| Avg. corrected pressure: | 717.3 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .903 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 320 | 54.60 | 6.00 | 5.25 | 581 |
| 330 | 60.80 | 6.20 | 5.43 | 601 |
| * 0 | 10.40 | 0 | 0 | 0 |
| 10 | 14.50 | 4.10 | 3.59 | 397 |
| 20 | 18.20 | 3.70 | 3.24 | 359 |
| 30 | 21.40 | 3.20 | 2.80 | 310 |
| 40 | 24.70 | 3.30 | 2.89 | 320 |

* 4 ml .001 M $PtCl_4$ plus 4 ml 4N HF added

% rate change -33.9

## TABLE XXV

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .001 M $PtCl_4$ in a nitrogen atmosphere

Run #2

| | |
|---|---|
| Avg. room temp: | 21.3°C |
| Avg. corrected pressure: | 720.6 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .908 $cm^2$ |

| Time (ml) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 220 | 40.70 | 4.90 | 4.31 | 475 |
| 230 | 45.70 | 5.00 | 4.39 | 483 |
| * 0 | 13.30 | 0 | 0 | 0 |
| 10 | 16.70 | 3.40 | 2.99 | 329 |
| 20 | 19.90 | 3.20 | 2.81 | 309 |
| 30 | 22.50 | 2.60 | 2.29 | 252 |
| 40 | 25.20 | 2.70 | 2.37 | 261 |
| 50 | 28.00 | 2.80 | 2.46 | 271 |

* 4 ml .001 M $PtCl_4$ plus 4 ml 4N HF added

% rate change -31.9

Avg. % rate change both runs -32.9

## TABLE XXVI

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $PtCl_4$ in a nitrogen atmosphere

| | |
|---|---|
| Avg. room temp: | 20.5°C |
| Avg. corrected pressure: | 713.6 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .936 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 300 | 45.30 | 7.40 | 6.47 | 691 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.20 | 4.20 | 3.67 | 392 |
| 20 | 8.80 | 4.60 | 4.02 | 429 |
| 30 | 12.50 | 3.70 | 3.23 | 345 |
| 40 | 17.80 | 5.30 | 4.63 | 494 |
| 50 | 21.90 | 4.10 | 3.58 | 382 |

* 4 ml .01 M $PtCl_4$ plus 4 ml 4N HF added

% rate change -43.3

## TABLE XXVII

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $PtCl_4$ in a nitrogen atmosphere

| | |
|---|---|
| Avg. room temp: | 21.2°C |
| Avg. corrected pressure: | 711.8 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .935 $cm^2$ |

Run #2

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 220 | 58.00 | 8.90 | 7.73 | 826 |
| 230 | 66.80 | 8.80 | 7.65 | 818 |
| * 0 | 7.00 | 0 | 0 | 0 |
| 10 | 10.90 | 3.90 | 3.39 | 362 |
| 20 | 16.20 | 5.30 | 4.61 | 493 |
| 30 | 21.30 | 5.10 | 4.43 | 474 |
| 40 | 26.20 | 4.90 | 4.26 | 455 |

* .01 M $PtCl_4$ plus 4 ml 4N HF added

[illegible] change [illegible]

[illegible] change both runs -49.6

## TABLE XXVIII

Hydrogen evolution rate of aluminum in 2N HF at 25°C
upon addition of .01 M $HAuCl_4$

Avg. room temp: 23.0°C
Avg. corrected pressure: 712.8 mm Hg
Speed of stirrer: 200 rpm
Area of reacting aluminum surface: .955 $cm^2$

Run #1

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 210 | 4.50 | 4.50 | 3.89 | 407 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 5.40 | 5.40 | 4.67 | 489 |
| 20 | 10.70 | 5.30 | 4.58 | 480 |
| 30 | 15.70 | 5.00 | 4.33 | 453 |
| 40 | 20.70 | 5.00 | 4.33 | 453 |
| 50 | 26.20 | 5.50 | 4.78 | 500 |
| 60 | 31.40 | 5.20 | 4.50 | 471 |
| . | . | . | . | . |
| 100 | 52.40 | 5.10 | 4.41 | 461 |

* 4 ml .ol M $HAuCl_4$ plus 4 ml 4N HF added

% rate change +16.8

## TABLE XXIX

Hydrogen evolution rate of aluminum in 2N HF at 25°C upon addition of .01 M $HAuCl_4$

| | |
|---|---|
| Avg. room temp: | 22.9° C |
| Avg. corrected pressure: | 713.3 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.24 $cm^2$ |

Run # 1

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2$ min) |
|---|---|---|---|---|
| . | . | . | . | . |
| 250 | 28.00 | 5.40 | 4.68 | 377 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.10 | 4.10 | 3.55 | 286 |
| 20 | 8.50 | 4.40 | 3.81 | 307 |
| 30 | 12.90 | 4.40 | 3.81 | 307 |
| 40 | 17.40 | 4.50 | 3.90 | 315 |
| 50 | 22.00 | 4.60 | 3.99 | 321 |
| 60 | 26.20 | 4.20 | 3.64 | 293 |

* 4 ml .01 M $HAuCl_4$ plus 4 ml 4N HF added

% rate change -24.1

## TABLE XXX

Hydrogen evolution rate of aluminum in 2N HF at 25°C

upon addition of .1 M $HAuCl_4$

| | |
|---|---|
| Avg. room temp: | 23.3°C |
| Avg. corrected pressure: | 711.1 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | 1.12 $cm^2$ |

Run #1

| Time (min) | $H_2$ vol. (ml) | Δ v (ml) | Δ v STP (ml) | Rate ($mm^3/cm^2 min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 240 | 59.80 | 6.30 | 5.43 | 485 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 5.10 | 5.10 | 4.40 | 393 |
| 20 | 10.50 | 5.40 | 4.65 | 415 |
| 30 | 15.70 | 5.20 | 4.48 | 400 |
| 40 | 20.80 | 5.10 | 4.40 | 393 |
| 50 | 26.20 | 5.40 | 4.65 | 415 |
| 60 | 31.00 | 4.80 | 4.14 | 370 |
| . | . | . | . | . |
| 110 | 56.30 | 4.35 | 4.35 | 388 |

* 4 ml .1 M $HAuCl_4$ plus 4 ml 4N HF added

% rate change -19.0

## TABLE XXXI

Hydrogen evolution rate of aluminum in 2N HF at 25°C
upon addition of .1 M $HAuCl_4$

| | |
|---|---|
| Avg. room temp: | 22.9°C |
| Avg. corrected pressure: | 703.9 mm Hg |
| Speed of stirrer: | 200 rpm |
| Area of reacting aluminum surface: | .892 $cm^2$ |

Run # 2

| Time (min) | $H_2$ vol. (ml) | $\Delta$ v (ml) | $\Delta$ v STP (ml) | Rate ($mm^3/cm^2 min$) |
|---|---|---|---|---|
| . | . | . | . | . |
| 220 | 90.30 | 4.10 | 3.50 | 392 |
| * 0 | 0 | 0 | 0 | 0 |
| 10 | 4.80 | 4.80 | 4.09 | 457 |
| 20 | 9.50 | 4.70 | 4.01 | 448 |
| 30 | 13.20 | 4.40 | 3.75 | 420 |
| 40 | . | . | . | . |
| 50 | 22.60 | 4.35 | 3.71 | 415 |
| 60 | 26.90 | 4.30 | 3.67 | 411 |
| . | . | . | . | . |
| 100 | 44.20 | 4.30 | 4.30 | 411 |

* 4 ml .1 M $HAuCl_4$ plus 4 ml 4N HF added.

% rate change +16.6

# TABLE XXXII

Electrode potential of aluminum in 2N HF
and the effect of certain salt additions

AgNO$_3$ addition

| | | .01M | | | .1M |
|---|---|---|---|---|---|
| Time (min) | pot. (volts) | Δ pot. upon add. (volts) | Time (min) | pot. (volts) | Δ pot. upon add. (volts) |
| 0 | -1.234 | | 0 | -1.208 | |
| 5 | -1.206 | | 5 | -1.202 | |
| 10 | -1.196 | | 10 | -1.205 | |
| 15 | -1.154 | +.307 | 15 | -1.202 | +.364 |
| * 0 | - .889 | | 0 | - .838 | |
| 5 | - .926 | | 5 | - .812 | |
| 10 | - .910 | | 10 | - .775 | |
| 15 | - .899 | | 15 | - .790 | |
| | | FeSO$_4$ addition | | | |
| 0 | -1.234 | | 0 | -1.230 | |
| 5 | -1.239 | | 5 | -1.283 | |
| 10 | -1.221 | | 10 | -1.219 | |
| 15 | -1.208 | +.134 | 15 | -1.231 | +.162 |
| * 0 | -1.074 | | 0 | -1.069 | |
| 5 | -1.082 | | 5 | -1.019 | |
| 10 | -1.088 | | 10 | -1.010 | |
| 15 | -1.088 | | 15 | -1.010 | |

* 4 ml salt solution plus 4 ml 4N HF added

## TABLE XXXIII

Electrode potential of aluminum in 2N HF
and the effect of certain salt solutions

$CuSO_4$ addition

| | .01M | | | | .1M | |
|---|---|---|---|---|---|---|
| | Time (min) | Pot. (volts) | Δ pot. upon add. (volts) | Time (min) | Pot. (volts) | Δ pot. upon addition (volts) |
| | 0 | -1.241 | | 0 | -1.209 | |
| | 5 | -1.242 | | 5 | -1.214 | |
| | 10 | -1.240 | | 10 | -1.221 | |
| | 15 | -1.241 | +.385 | 15 | -1.222 | +.482 |
| * | 0 | - .956 | | * 0 | - .740 | |
| | 5 | - .817 | | 5 | - .637 | |
| | 10 | - .828 | | 10 | - .665 | |
| | 15 | - .824 | | 15 | - .646 | |

$NiCl_2$ addition

| | Time (min) | Pot. (volts) | Δ pot. upon add. (volts) | Time (min) | Pot. (volts) | Δ pot. upon addition (volts) |
|---|---|---|---|---|---|---|
| | 0 | -1.226 | | 0 | -1.179 | |
| | 5 | -1.189 | | 5 | -1.169 | |
| | 10 | -1.166 | | 10 | -1.163 | |
| | 15 | -1.158 | +.048 | 15 | -1.158 | +.189 |
| * | 0 | -1.110 | | * 0 | - .969 | |
| | 5 | -1.069 | | 5 | - .839 | |
| | 10 | -1.048 | | 10 | - .811 | |
| | 15 | -1.028 | | 15 | - .819 | |

* 4 ml salt solution plus 4 ml 4N HF added

## TABLE XXXIV

Electrode potential of aluminum in 2N HF
and the effect of certain salt solutions

$CoSO_4$ addition

| | .01M | | | .1M | |
|---|---|---|---|---|---|
| Time (min) | Pot. (volts) | Δ pot. upon add. (volts) | Time (min) | Pot. (volts) | Δ pot. upon addition (volts) |
| 0 | -1.203 | | 0 | -1.232 | |
| 5 | -1.190 | | 5 | -1.210 | |
| 10 | -1.186 | | 10 | -1.170 | |
| 15 | -1.186 | +.220 | 15 | -1.170 | +.287 |
| * 0 | - .966 | | * 0 | - .883 | |
| 5 | - .976 | | 5 | - .863 | |
| 10 | - .963 | | 10 | - .863 | |
| 15 | - .966 | | 15 | - .857 | |

$PtCl_4$ addition

| | .001M | | | .01M | |
|---|---|---|---|---|---|
| 0 | -1.230 | | 0 | -1.219 | |
| 5 | -1.249 | | 5 | -1.201 | |
| 10 | -1.271 | | 10 | -1.194 | |
| 15 | -1.269 | +.043 | 15 | -1.180 | +.407 |
| * 0 | -1.226 | | * 0 | - .773 | |
| 5 | -1.174 | | 5 | - .813 | |
| 10 | -1.213 | | 10 | - .819 | |
| 15 | - | | 15 | - .806 | |

* 4 ml salt solution plus 4 ml 4N HF added

## TABLE XXXV

Electrode potential of aluminum in 2N HF
and the effect of $HAuCl_4$ salt solutions

| Time (min) | Pot. (volts) | Δ pot. upon addition (volts) | Time (min) | Pot. (volts) | Δ pot. upon addition (volts) |
|---|---|---|---|---|---|
| 0 | -1.242 | | 0 | -1.250 | |
| 5 | -1.210 | | 5 | -1.249 | |
| 10 | -1.184 | | 10 | -1.251 | |
| 15 | -1.154 | +.405 | 15 | -1.236 | +.517 |
| * 0 | - .749 | | * 0 | - .719 | |
| 5 | - .798 | | 5 | - .650 | |
| 10 | - .811 | | 10 | - .637 | |
| 15 | - .838 | | 15 | - .649 | |

---

* 4 ml $HAuCl_4$ plus 4 ml 4N HF added

## TABLE XXXVI

Microhardness of aluminum corroded in 2N HF

$H_v = 1.8544\ P/d^2\ kg/mm^2$

$P = 18.2\ g$

| Measurement | diagonal (u) | (diagonal)$^2$ (u$^2$) | $H_v$ (kg/mm$^2$) | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|
| 1 | 34.4 | 1183.4 | 28.5 | -3.6 | 13.0 |
| 2 | 34.4 | 1183.4 | 28.5 | -3.6 | 13.0 |
| 3 | 33.6 | 1129.0 | 29.9 | -2.2 | 4.8 |
| 4 | 31.6 | 998.6 | 33.8 | +1.7 | 2.9 |
| 5 | 33.9 | 1149.2 | 29.4 | -2.7 | 7.3 |
| 6 | 31.1 | 967.2 | 34.9 | +2.8 | 7.8 |
| 7 | 30.2 | 912.2 | 37.0 | +4.9 | 2.4 |
| 8 | 29.4 | 864.4 | 39.0 | +6.9 | 6.2 |
| 9 | 34.4 | 1183.4 | 28.5 | -3.6 | 13.0 |
| 10 | 31.1 | 967.2 | 34.9 | +2.8 | 7.8 |
| | | | $\Sigma$ = 321.1 | | $\Sigma$ = 78.2 |

Avg. $H_v$ = 321.2/10 = 32.1 kg/mm$^2$

Standard dev. = $\sqrt{78.2/(10-1)} = \pm 2.9$

## TABLE XXXVII

Microhardness of aluminum corroded
in 2N HF on addition of .1M $NiCl_2$

$H_v = 1.8544\ P/d^2\ kg/mm^2$

$P = 18.2\ g$

| Measurement | diagonal (u) | $(\text{diagonal})^2$ ($u^2$) | $H_v$ ($kg/mm^2$) | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|
| 1 | 29.2 | 852.6 | 39.6 | -3.0 | 9.0 |
| 2 | 26.9 | 723.6 | 46.6 | +4.0 | 16.0 |
| 3 | 27.6 | 761.8 | 44.3 | +1.7 | 2.9 |
| 4 | 26.5 | 702.3 | 48.1 | +5.5 | 30.3 |
| 5 | 27.7 | 767.3 | 44.0 | +1.4 | 2.0 |
| 6 | 28.9 | 835.2 | 40.4 | -2.2 | 4.8 |
| 7 | 29.6 | 876.1 | 38.5 | -3.9 | 15.2 |
| 8 | 26.9 | 723.6 | 46.6 | +4.0 | 16.0 |
| 9 | 30.2 | 912.0 | 37.0 | -5.6 | 31.4 |
| 10 | 28.6 | 818.0 | 41.3 | -1.3 | 1.7 |
|  |  |  | $\Sigma = 426.6$ | $\Sigma =$ | 127.6 |

Avg. $H_v = 426.4/10 = 42.6\ kg/mm^2$

Standard dev. $= \sqrt{127.6/(10-1)} = \pm 3.8$

## TABLE XXXVIII

Microhardness of aluminum corroded in 2N HF on addition of .1M $CoSO_4$

| Measurement | diagonal (u) | (diagonal)$^2$ ($u^2$) | $H_V$ ($kg/mm^2$) | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|
| 1 | 27.6 | 761.8 | 44.3 | +2.7 | 7.3 |
| 2 | 27.6 | 761.8 | 44.3 | +2.7 | 7.3 |
| 3 | 28.6 | 818.0 | 41.2 | - .4 | .2 |
| 4 | 28.6 | 818.0 | 41.2 | - .4 | .2 |
| 5 | 28.2 | 795.2 | 42.4 | + .8 | .6 |
| 6 | 28.6 | 818.0 | 41.2 | - .4 | .2 |
| 7 | 29.1 | 846.8 | 39.9 | -1.7 | 2.9 |
| 8 | 27.7 | 767.3 | 44.0 | +2.4 | 5.8 |
| 9 | 29.6 | 876.1 | 38.5 | -3.1 | 9.6 |
| 10 | 29.2 | 852.6 | 39.6 | -2.0 | 4.0 |
|  |  | Σ = | 415.6 | Σ = | 38.1 |

Avg. $H_V$ = 415.6/10 = 41.6 $kg/mm^2$

Standard deviation = $\sqrt{38.1/(10-1)}$ = $\pm$ 2.1

## TABLE XXXIX

Microhardness of aluminum corroded in 2N HF on addition of .1M $AgNO_3$

| Measurement | diagonal (u) | (diagonal)$^2$ ($u^2$) | $H_v$ (kg/mm$^2$) | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|
| 1 | 28.6 | 818.0 | 41.2 | + .7 | .5 |
| 2 | 29.4 | 864.4 | 39.0 | -1.5 | 2.2 |
| 3 | 29.4 | 864.4 | 39.0 | -1.5 | 2.2 |
| 4 | 28.9 | 835.2 | 40.4 | - .1 | 0 |
| 5 | 27.7 | 767.3 | 44.0 | +3.5 | 12.3 |
| 6 | 29.4 | 864.4 | 39.0 | -1.5 | 2.2 |
| 7 | 30.2 | 912.0 | 37.0 | -3.5 | 12.3 |
| 8 | 28.2 | 795.2 | 42.4 | +1.9 | 3.6 |
| 9 | 27.7 | 767.3 | 44.0 | +3.5 | 12.3 |
| 10 | 29.4 | 864.4 | 39.0 | -1.5 | 2.2 |
|  |  |  | $\Sigma$ = 405.0 | $\Sigma$ = | 49.8 |

Avg. $H_v$ = 405.0/10 = 40.5 kg/mm$^2$

Standard deviation = $\sqrt{49.8/(10-1)}$ = ± 2.3

## TABLE XL

### Microhardness of aluminum corroded in 2N HF on addition of .1M NaCl

| Measurement | diagonal (u) | (diagonal)$^2$ ($u^2$) | $H_v$ (kg/mm$^2$) | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|
| 1 | 31.4 | 986.0 | 34.2 | +2.3 | 5.3 |
| 2 | 33.9 | 1149.2 | 29.4 | -2.5 | 6.3 |
| 3 | 34.6 | 1197.2 | 28.2 | -3.7 | 13.7 |
| 4 | 31.6 | 998.7 | 33.8 | +1.9 | 3.6 |
| 5 | 31.6 | 998.7 | 33.8 | +1.9 | 3.6 |
| 6 | 34.1 | 1162.8 | 29.0 | -2.9 | 8.4 |
| 7 | 31.4 | 986.0 | 34.2 | +2.3 | 5.3 |
| 8 | 31.7 | 1004.9 | 33.6 | +1.7 | 2.9 |
| 9 | 32.4 | 1050.0 | 32.1 | + .2 | 0 |
| 10 | 33.3 | 1108.9 | 30.4 | -1.5 | 2.2 |
| | | | $\Sigma$ = 319.3 | $\Sigma$ | = 51.3 |

Avg. $H_v$ = 319.3/10 = 31.9 kg/mm$^2$

Standard deviation = $\sqrt{51.3/(10-1)}$ = ± 2.4

## TABLE XLI

Microhardness of aluminum corroded
in 2N HF on addition of .1 M KCl

| Measurement | diagonal (u) | $(\text{diagonal})^2$ ($u^2$) | $H_v$ ($kg/mm^2$) | $\Delta$ | $\Delta^2$ |
|---|---|---|---|---|---|
| 1 | 32.8 | 1075.8 | 31.4 | + .8 | .6 |
| 2 | 33.6 | 1124.0 | 29.9 | - .7 | .5 |
| 3 | 33.8 | 1142.4 | 29.5 | -1.1 | 1.2 |
| 4 | 32.9 | 1082.4 | 31.2 | + .6 | .4 |
| 5 | 31.7 | 1004.9 | 33.6 | +3.0 | 9.0 |
| 6 | 34.4 | 1183.4 | 28.5 | -1.9 | 3.6 |
| 7 | 32.9 | 1082.4 | 31.2 | + .6 | .4 |
| 8 | 32.9 | 1082.4 | 31.2 | + .6 | .4 |
| 9 | 33.8 | 1142.4 | 29.5 | -1.1 | 1.2 |
| 10 | 33.4 | 1115.6 | 30.2 | - .4 | .2 |
| | | | $\Sigma$ = 306.2 | $\Sigma$ | = 17.5 |

Avg. $H_v$ = 306.2/10 = 30.6

Standard deviation = $\sqrt{17.5/(10-1)}$ = ± 1.4

# VITA

The author was born on May 13, 1944 in St. Louis, Missouri. He received his Bachelor of Science Degree in Metallurgical Engineering from the University of Missouri at Rolla in June, 1966. He enrolled in the University of Missouri at Rolla in September, 1966 as a candidate for a Master of Science Degree in Metallurgical Engineering.