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AN INVESTIGATION OF THE DISSOLUTION OF  
HAFNIUM-FREE ZIRCONIUM IN HYDROFLUORIC ACID AND  
THE EFFECT OF FLUORIDE ADDITIONS

BY

ALFRED S. NEIMAN

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A

THESIS

submitted to the faculty of the  
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI  
in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1957

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Approved by -



Research Professor of Metallurgy

90720



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## I

## Introduction

Hafnium-free zirconium has assumed great importance in commercial use in recent years. When economical methods were developed in 1950<sup>1</sup> to remove hafnium from Zr, a metal was produced which not only exhibited good corrosion resistance and desirable physical properties, but also had a very low absorption cross section for thermal neutrons. Such a metal could obviously be utilized to advantage as a structural material for nuclear reactors. This application is the most important one for Zr at present.

Good corrosion resistance to most mineral acids is one of the outstanding non-nuclear properties of Zr. Hf-free Zr has good corrosion resistance<sup>2</sup> in all mineral acids with exception of hydrofluoric acid, concentrated sulfuric and phosphoric acids, and aqua regia. The resistance of Zr to attack in concentrated nitric acid is excellent, with but negligible attack occurring in fuming nitric acid. The corrosion of Zr in hydrochloric acid<sup>3</sup> is particularly dependent on the purity of the metal. It has been shown that high carbon graphite melted Zr is severely embrittled in HCl because of selective attack of the carbides. In general, Hf-free Zr (containing less than 0.1% Hf) is more corrosion resistant than Zr containing the usual 2.5% Hf. Small percentages of

- 
- 1) Golden, L. B. in Lustman, B. and Kerze, F. Jr., "Metallurgy of Zirconium," McGraw-Hill, N. Y. (1955), p. 4
  - 2) Miller, G. L., "Zirconium," Academic Press, N. Y. (1954), p. 203
  - 3) Golden, L. B., ref. 1, p. 651



other impurities in Zr such as carbon, nitrogen, and oxygen will also decrease corrosion resistance.

It has been stated that Zr has poor corrosion resistance in HF. It was proposed that a quantitative investigation of the dissolution of Zr in HF be made to provide additional data to that already gathered on the corrosion of Zr in other mineral acids. Since the **rate** of dissolution of Zr in HF is greater than in any other mineral acid, a **study** of the rate and mechanism of the reaction and possible passivation effects might be a valuable addition to present knowledge.

## II

## Review of the Literature

The rate of dissolution of Zr in HF has been investigated both qualitatively and quantitatively, but only since 1946 has any great activity occurred. The availability of high purity Zr to researchers and the interest for nuclear applications are the basic reasons for the recent increased attention.

A. Qualitative studies of the dissolution of Zr in HF:

The work of J. J. Berzelius with amorphous Zr and of L. Troost with crystalline Zr (contaminated with aluminum) is described by Mellor<sup>1</sup>. Their studies showed that the metal dissolves rapidly in all concentrations of HF<sup>2</sup>, either hot or cold. Studies carried out with ductile iodide Zr by the Foote Mineral Co. show that Zr when tested in all dilutions of HF at 100°C is rapidly attacked. Fontana<sup>3</sup> describes tests in which the corrosion rate of Zr in HF of all concentrations at 75°C is very high. Miller<sup>4</sup> has found crystal bar Zr to be subject to rapid attack in a 14 day test in HF at 20°C. Johnson and Hill<sup>5</sup> using Hf-free Zr found that in 0.005N HF there is no weight loss observed in two days. At concentrations from 0.02-0.04 N HF an intermittent gray film was formed and slow formation of gas bubbles

- 
- 1) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, Longmans, Green & Co., N. Y. (1927), p. 115
  - 2) Uhlig, H. H., "Corrosion Handbook," Wiley, N. Y., (1948), p. 347
  - 3) Fontana, M. G., Ind. Eng. Chem., 44, (7), 71-A, (1952)
  - 4) Miller, G. L., p-1, ref. 2, p. 209
  - 5) Johnson, A. B. and Hill, G. R., Corrosion of Zr, I, Surface Area Determination and Sample Preparation Study, AECU-3000, Dec. 1, 1954, p. 3.

was observed. From 0.05 - 1.0 N HF a black surface film was formed and gas evolution was readily observed.

B. Quantitative Studies of the dissolution of Zr in HF:

The first quantitative study of the dissolution of Zr in HF was published by Baumrucker<sup>6</sup> in 1950. This investigation was an attempt to develop a method for dissolving Zr at a controlled, reproducible rate.

In this work both pure crystal bar and magnesium-reduced Zr were dissolved in 5% by volume HF. Tests were made at 3° and 18°C using both 100 ml. and 500 ml. solution volumes. Both weight loss and decrease in thickness were measured at intervals and plotted versus time. Increased attack at the edges necessitated making thickness measurements at the centers of the specimens.

It was found that the reaction rate decreased with increasing time even though fresh acid was constantly supplied and the solutions well stirred. It was suggested that the black smut formed on the Zr surface may have been instrumental in decreasing the rate. The gas evolved at the metal surface left flow lines on the surface smut after prolonged attack.

In addition it was concluded that differences in metal structure could affect the reaction rate. Also a general slope for a particular reaction temperature and material could be predicted. It was found that the higher the temperature of the HF solution the greater was the rate of dissolution.

---

6) Baumrucker, J. E., Dissolution of Zr in HF, ANL-5020, March 31, 1950

7)  
Smith and Hill have completed an extensive study of the rate of solution of Hf-free Zr in dilute HF solutions. Radioactive Zr<sup>95</sup> was employed and a scintillometer used to measure the build up of the radioactive Zr ions in solution for rate determinations. The counting meter for the scintillometer was connected to continuous recording equipment.

A plot of HF concentration versus rate was a straight line over a range from 0.0005 - 0.5 moles/liter. Tests made in the presence of O<sub>2</sub> showed that the rate was independent of O<sub>2</sub> concentration. However, since but few tests were made these results were not considered final proof. Some work was done on the effect of additions on rate. It was concluded that the rate is independent of small additions of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, K<sup>+</sup>, ClO<sub>4</sub><sup>-</sup>, F<sup>-</sup>, and HF<sub>2</sub><sup>-</sup> ions.

From an Arrhenius plot the temperature coefficient of the reaction is shown to be small, and the activation energy was calculated to be 4.0 kilocalories/mole. It was found that in an HF-HNO<sub>3</sub> solution the gaseous products of the reaction were 20% H<sub>2</sub>, 10% O<sub>2</sub>, and 70% N<sub>2</sub>O. In an HF-HCl solution the products were 20% H<sub>2</sub>, 3-4% O<sub>2</sub>, and the rest unknown. The source of the O<sub>2</sub> from the HCl reaction was not determined.

Two mechanisms of dissolution were suggested as being probable: The first was the adsorption of free HF on the surface, while the second was the reaction of HF with an adsorbed surface substance containing O<sub>2</sub>.

It can be seen that there has been very little quantitative in-

---

7) Smith, T. and Hill, G. R., Corrosion of Zr, II, A Reaction Rate Study of the Solution of Hafnium-Free Zr in HF Solutions, AECU-3002, Nov. 30, 1954

vestigation of the dissolution of Zr in HF. There has been even less study of the effect of additions on the rate of reaction, especially large additions. It was therefore decided to verify the effect of HF concentration on the rate of dissolution of Zr in HF and study the effects of larger additions.

## III

## Experimental Equipment, Procedure, and Results

A. The rate of dissolution of Zr in HF:1. Materialsa. Analysis and physical condition of Zr

The low-Hf Zr used in this investigation was obtained from the U. S. Bureau of Mines, Northwest Electrodevelopment Laboratory, Albany, Oregon. The analysis was given as:

O<sub>2</sub> - 0.11%  
 N<sub>2</sub> - 0.005%  
 Fe - 0.04%  
 Hf - 0.01%

After rolling, the Zr had been given a stress relief and annealing treatment in vacuum for 30 minutes at 700°C. The Zr sheet was approximately 1/16 of an inch thick.

b. Standardization of HF

The method used to standardize HF was developed from the principles given by Willard, Furman, and Bricker<sup>1</sup> and is outlined as follows:

## Preparation of Standard NaOH

- 1) Approximately 0.5 grams of primary standard oxalic acid were weighed.
- 2) The oxalic acid was dissolved in CO<sub>2</sub>-free redistilled water (used throughout the standardization procedure) and two drops of phenolphthalein indicator added.
- 3) A saturated solution of NaOH (obtained from the Chemistry Dept.) which did not contain CO<sub>2</sub> was used to make up a dilute, carbonate-free solution of NaOH.
- 4) The NaOH solution was titrated into the oxalic acid solution until the first pink color.

---

1) Willard, H. H., Furman, N. H., and Bricker, C. E., "Elements of Quantitative Analysis," 4th ed., Van Nostrand, N. Y., (1956).

- 5) The normality of the NaOH was calculated:  $N_{\text{NaOH}} = \frac{\text{gms. oxalic acid}}{\text{ml. NaOH (0.063035)}}$   
 0.063035 being the milli-equivalent weight of crystallized oxalic acid,  
 $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

#### Preparation of Standard HF

- 1) Since 48% concentrated HF is approximately 28N an approximate 5N HF solution was made up by diluting with distilled water.
- 2) Two drops of phenolphthalein indicator were added to 5 ml. HF in a polyethylene beaker. The HF was added from a polystyrene burette.
- 3) The HF solution was titrated with standardized NaOH to the first pink color.
- 4) The normality of the HF was calculated:  $N_{\text{HF}} = \frac{\text{ml. NaOH} \times N \text{ NaOH}}{\text{ml. HF}}$

All titrations were run several times to preclude experimental errors.

#### 2. Experimental Principles

It was decided to measure the rate of dissolution of Zr by collecting the  $\text{H}_2$  evolved in the reaction. It was then assumed that a constant ratio exists between the volume of  $\text{H}_2$  evolved and the weight of Zr dissolved. According to Straumanis and Ballass the reaction of Zr in HF is



So one gram atom of Zr will evolve two moles of  $\text{H}_2$ . Then, since one gram molecular volume of a gas at standard conditions = 22, 414.6 milliliters, the atomic weight of Zr = 91.22 grams should be equivalent to  $2 \times 22, 414.6$  ml. of  $\text{H}_2$ . One milligram of Zr should then correspond

- 
- 2) Straumanis, M. E. and Ballass, J. T., Z. anorgan. allgem. Chemie, 278, 36, (1955)

to 0.49144 ml.  $H_2$  gas at standard conditions, or one ml.  $H_2$  gas is equivalent to 2.035 mg. of Zr. It was decided to check reaction (1) once more in order to be quite sure of its validity and to check the high purity of the Zr used.

### 3. The dissolution reaction of Zr in HF

#### a. Experimental Equipment

The equipment used in this investigation is the same as that employed by Straumanis and Ballass<sup>3</sup> in their studies of the dissolution reaction of Zr in HF. The experimental arrangement is shown in Figure 1. A wax lined 125 ml. reaction flask with a ground glass aperture in the side was made. The sample was held in a small platinum crucible (B) supported by a fixture (A) which fitted through the ground glass joint in the flask. Upon turning the fixture, the Pt crucible and Zr could be dropped into the HF solution. A rubber stopper (F) hermetically sealed the reaction flask. A glass tube fitted with a stopcock served as an inlet valve (C) while another glass tube was connected to a gas burette (D) equipped with a leveling bulb. An outlet valve (E) was inserted between the reaction vessel and the gas burette.

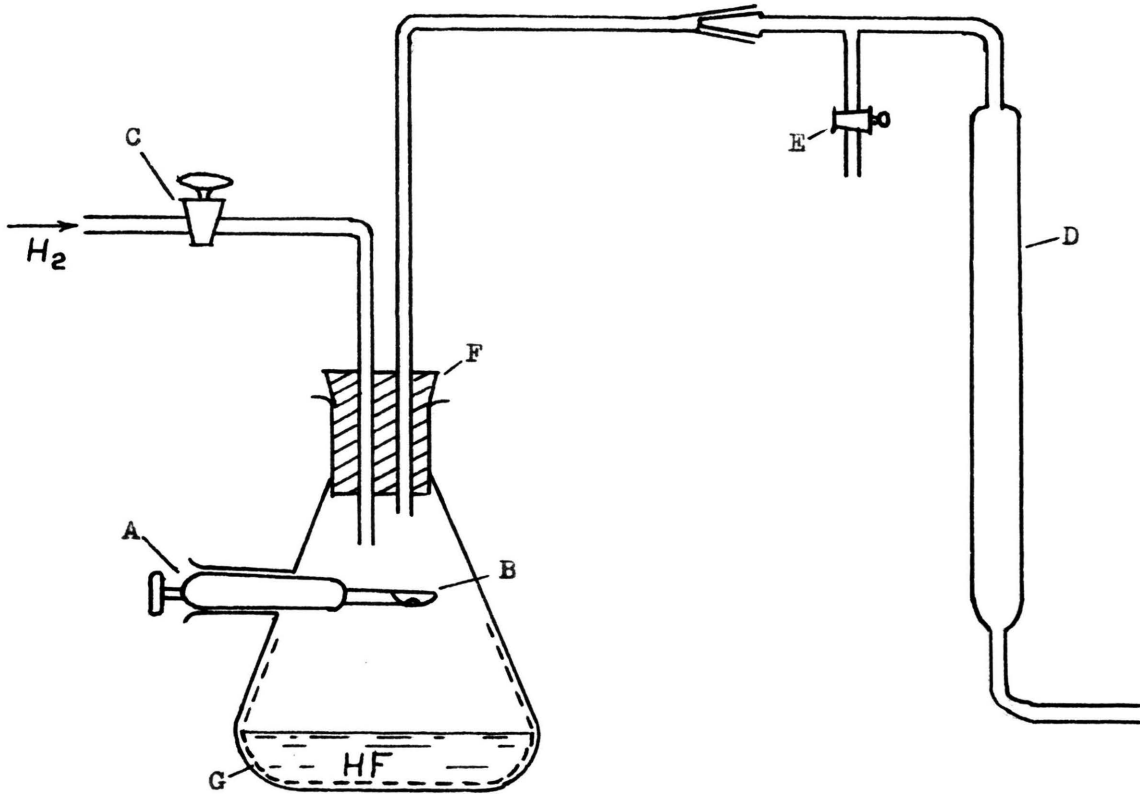
#### b. Procedure

A sample of 0.04 - 0.075 grams of Zr chips and filings was weighed. About 50 ml. of 5.0N HF were poured into the reaction vessel. The weighed Zr sample, held in the Pt crucible, was placed on the supporting fixture

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3) Straumanis, M. E. and Ballass, J. I., p-8, ref. 2, p. 34





- A - fixture for support of Zr sample
- B - Pt crucible holding Zr sample
- C - inlet valve
- D - gas burette
- E - outlet valve
- F - rubber stopper
- G - wax lining

Figure 1

Apparatus for determining the ratio between the Zr dissolved and H<sub>2</sub> evolved in the Zr - HF reaction

and inserted into the flask. Then the water level in the gas burette was adjusted to zero.

To prevent further oxidation of any intermediate oxidation states of Zr, tests were made in an  $H_2$  atmosphere. A cylinder of  $H_2$  was connected to the inlet tube (C) and the system was flushed with  $H_2$  for about 30 minutes. Both inlet and outlet valves were opened to allow flushing and both valves closed simultaneously at the end of flushing to prevent entry of air. When tests were made in the presence of air the two valves were simply closed and the  $H_2$  flushing omitted.

At this point the handle of the fixture (A) was rotated to drop the sample into the HF solution. An electromagnetic stirring device was employed to agitate the HF solution and so ensure a complete reaction. The  $H_2$  evolved was collected in the gas burette and measured. After 20 minutes if no change in the  $H_2$  volume was noted a final reading was recorded.

### c. Results

The  $H_2$  volume reading was reduced to standard conditions of temperature, pressure, and also dryness, because the  $H_2$  was collected over water in the gas burette. It was therefore necessary to subtract the vapor pressure of  $H_2O$  from the barometric pressure. This correction was obtained from Hodgman's <sup>4</sup> table as was the thermal expansion correction for mercury and the brass scale. There was no

---

4) Hodgman, C. D., "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, (1954), pp. 2140, 2292

5)

correction made for depression of the mercury capillary in the barometer since the inside diameter of the barometer used was one centimeter. These barometric pressure corrections were made throughout all experimental work involving hydrogen collection.

A sample calculation is as follows:

Weight of Zr sample = 0.0524 grams

Temperature = 28.4°C = 301.4°K

Barometric Pressure = 731.6 mm. Hg

Correction for vapor pressure = 29.02 mm. Hg

Correction due to thermal expansion of Hg and the brass scale = 3.33 mm.

Corrected pressure: 731.6 - 29.02 - 3.33 = 699.25 mm. Hg

Total volume of H<sub>2</sub> gas collected = 31.10 ml.

Volume of H<sub>2</sub> gas reduced to standard conditions:  $\frac{(699.25)(273)}{(760)(301.4)} 31.10 = 25.92$

Volume of H<sub>2</sub> calculated from reaction (1): (0.0524)(491.44) = 25.75 ml.

Percent difference from theoretical volume:  $\frac{25.92 - 25.75}{25.75} \times 100 = 0.66\%$

The results of all determinations are compiled in Table 1. The results obtained show that the assumed reaction (1) is correct and that the Zr-HF reaction has no dependence on the presence of O<sub>2</sub>. This conclusion agrees with the work of Straumanis<sup>6)</sup> and also of Smith and Hill<sup>7)</sup>.

5) Miller, D. C., "Laboratory Physics," Ginn & Co., (1932), pp. 71-72

6) Straumanis, M. E. and Ballass, J. I., p-8, ref. 2

7) Smith, T. and Hill, G. R., p-5, ref. 7

Table 1

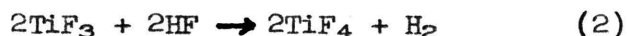
Results of H<sub>2</sub> Evolution from the Dissolution of Zr in the Zr-HF Reaction

Atmosphere	Experiment	Weight of Zr Sample(grams)	Volume of H <sub>2</sub> Collected at standard conditions (cm <sup>3</sup> )	Calculated Volume of H <sub>2</sub> (cm <sup>3</sup> )	Percent Difference
H <sub>2</sub>	1	0.0624	30.39	30.67	0.67
	2	0.0410	20.48	20.15	1.64
	3	0.0735	36.32	36.12	0.55
	4	0.0639	31.65	31.90	-0.54
	5	0.0524	25.92	25.75	-0.91
Air	6	0.0464	22.79	22.80	0.04
	7	0.0436	21.40	21.40	0.00
	8	0.0493	24.85	24.20	2.68

Note: No weight loss was observed for the Pt crucible

When the reduced H<sub>2</sub> volumes were compared with the theoretical volumes all the percent differences were under 1% with two exceptions. No reason can be given for those differences over 1%.

If a +3 intermediate oxidation state existed such as Straumanis<sup>8</sup> and Chen found in the Ti-HF reaction, a far larger percent difference should have been found for tests in a H<sub>2</sub> atmosphere. Also there was no evidence of the effect found by Straumanis and Cheng<sup>9</sup> in the Ti-HF reaction. In their findings the volume of H<sub>2</sub> collected slowly increased over a period of time because of the reaction:



Thus another conclusion can be drawn that Zr is oxidized directly to the +4 oxidation state in the Zr-HF reaction.

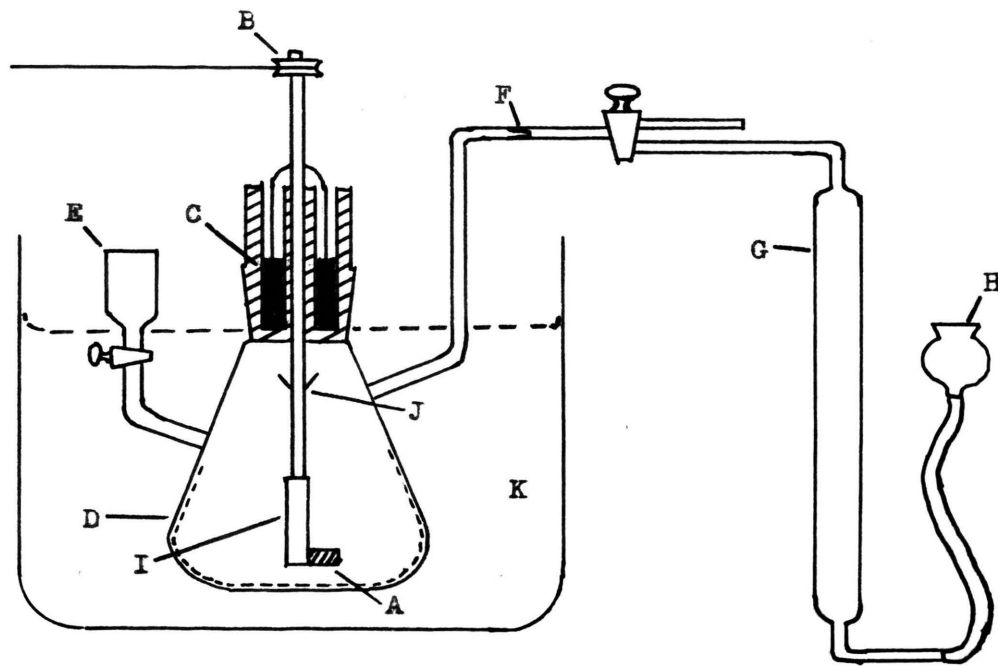
#### 4. The rate of dissolution of Zr in varying concentrations of HF

##### a. Experimental equipment

The equipment with but minor changes was the same as that used by Straumanis and Chen<sup>10</sup> in their studies of the dissolution of titanium in HF. The equipment consisted of a reaction vessel which held the HF solution, a shaft which rotated the Zr sample through a mercury seal, a gas burette, and constant temperature water bath. The overall arrangement of the essential equipment is shown in Figure 2.

The Zr sample (A) was mounted on an ebonite foot (I) which fitted on the end of a rotating shaft. The foot was made so that the Zr was

- 
- 8) Straumanis, M. E., and Chen, P. C., Corrosion, 7, 229, (1951)
- 9) Straumanis, M. E., Cheng, C. H., and Schlechten, A. W., J. Electrochem. Soc., 103, 439, (1956)
- 10) Straumanis, M. E. and Chen, P. C., p-14, ref. 8



- A - Zr sample on ebonite foot
- B - pulley for the rotating shaft
- C - mercury seal
- D - wax-lined reaction flask
- E - funnel for additions
- F - gas outlet
- G - gas burette
- H - leveling bulb
- I - ebonite foot
- J - rubber cup
- K - constant temperature water bath

Figure 2

Apparatus for determining the rate of dissolution of Zr  
in hydrofluoric acid

fixed at an angle of  $45^\circ$  as it rotated in the HF solution. At the upper end of the shaft was affixed an aluminum pulley (B) over which a drive belt would fit. Since the shaft rotated in a mercury seal (C) leakage of  $H_2$  was prevented. The mercury also functioned as a lubricant in promoting free rotation. A rubber cup (J) was fitted onto the shaft to prevent any foreign material such as eroded glass powder or Hg from falling into the HF solution.

The reaction vessel for the rate measurement was a 325 ml. wax-lined flask (D) fitted with a gas outlet (F) and a valved funnel inlet (E) to allow addition of liquid reagents. The flask had ground glass joints at its mouth and on the gas outlet. With all connections in place and valves closed the vessel was air tight.

The  $H_2$  from the reaction vessel was collected in a 100 ml. gas burette (G). As  $H_2$  displaced water in the gas burette, a leveling bulb (H) was employed to keep the  $H_2$  at atmospheric pressure.

A 1/50 H. P. direct current motor with a matching electronic speed controller was used to rotate the Zr sample in the HF solution. The controller allowed any desired speed to be set and kept constant automatically with very little deviation.

The same motor drove a stirrer which circulated the water in the temperature control bath. The control circuit and equipment for the water bath is shown in Figure 4. The water bath (G) was controlled by a bi-metal thermoregulator (A) on a D. C. control circuit. A relay in the A.C. circuit, energized by the D. C. circuit, controlled an incandescent bulb (C) which heated the water bath. Copper coils (F) served

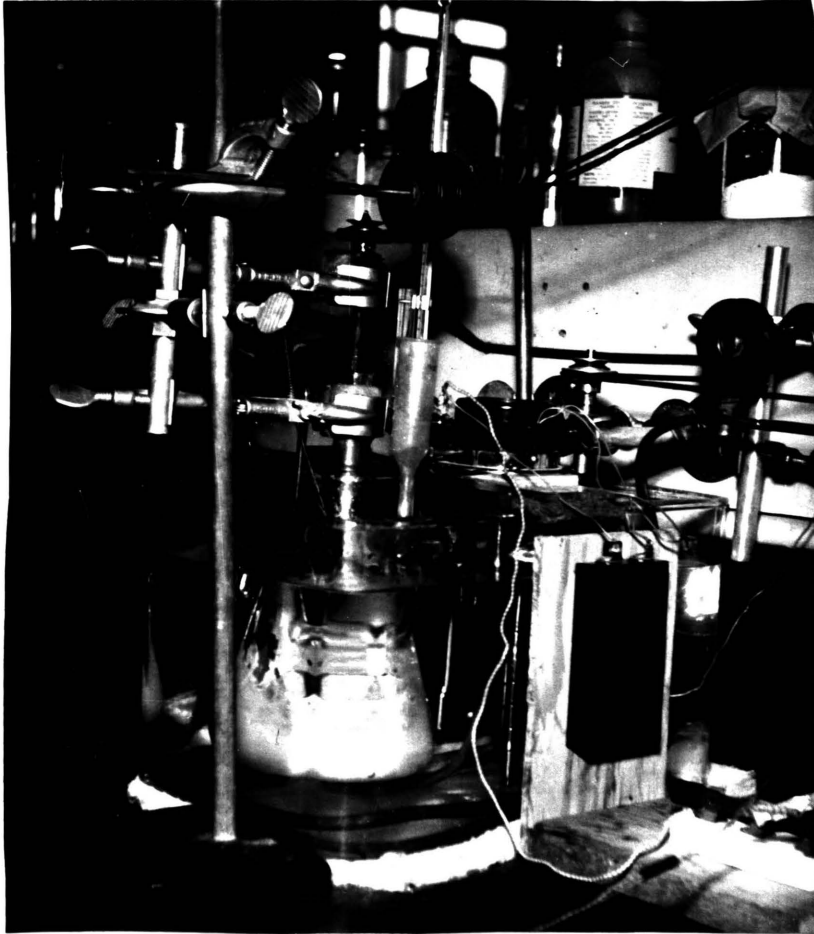
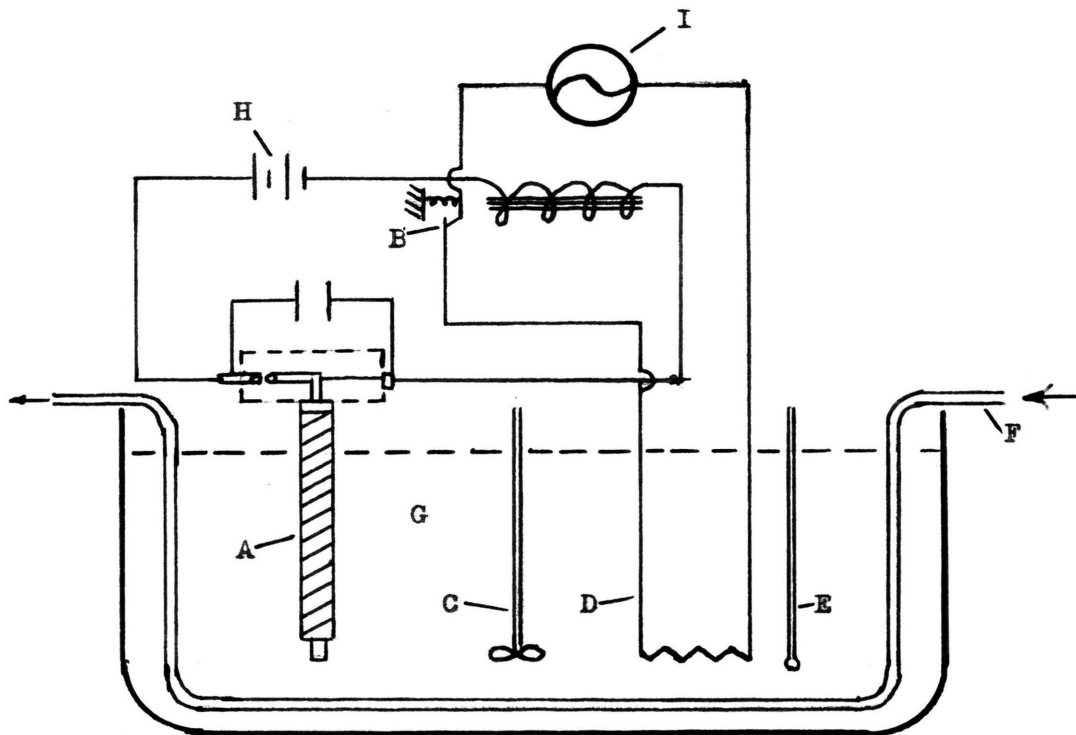


Figure 3

The arrangement of the apparatus for determining the rate of dissolution of Zr in HF





- A - bi-metal thermoregulator
- B - switch controlled by relay
- C - stirrer
- D - incandescent bulb for heating
- E - thermometer
- F - cooling coils
- G - water bath
- H - 12 volt D.C. power source
- I - 110 volt A.C. power source

Figure 4

Circuit diagram used with the thermoregulator to control the temperature of the water bath

to cool the bath when room temperature was over 25°C although the water valves were manually operated. A temperature of 25°± 0.1 C was maintained in the bath throughout all tests at any room temperature.

b. Procedure

The Zr samples were cut from sheet Zr and finished to a size of one square centimeter. Measurements were made with a vernier caliper which had an accuracy of ± 0.01 cm. The one square centimeter samples were mounted in bakelite with a standard metallographic mounting press. The circular bakelite mounting was cut down to conform with the square shape of the Zr sample. After mounting, each sample was given a standard metallographic polish using 0, 00, 000, and 0000 emery paper and stored. Immediately before a test the sample was given a final polish on a canvas lap using 600 grit silicon carbide and subsequently a billiard cloth lap using levigated alumina.

The Zr sample, after being degreased, was attached to the ebonite foot with wax. The stirring rod was lifted and held so that the Zr would clear the HF upon assembly of the equipment. The stirring rod had a vertical displacement of 2.5 cm. without breaking the mercury seal. 125 ml. of HF solution of the desired concentration were poured into the reaction flask and the equipment assembled.

The temperature control circuit for the water bath was activated and the bath stirrer turned on. The cooling coils or an immersion heater were used to help bring the temperature of the bath to 25°C quickly. Then the control circuit was used to keep the temperature constant until thermal equilibrium of the apparatus was attained.

The water level in the gas burette was adjusted to zero and the temperature and barometric pressure recorded. After checking to see that all valves were positioned correctly, the stirring rod with the Zr sample affixed to the end was lowered into the HF solution and the time recorded. The leveling bulb was adjusted so that the water levels in the gas burette and leveling bulb were equalized, and the burette reading was recorded.

The drive belt was immediately installed over the pulley and the controller set so that a constant stirring speed of 200 R.P.M. was maintained. The R.P.M.'s were checked with a tachometer. The stirring action had a very important role in the rate measurements. Stirring not only brought a constant supply of fresh acid to the sample surface and removed  $H_2$ , but also agitated the HF solution so that the temperature remained essentially constant throughout the reaction volume.

As the  $H_2$  displaced the water in the gas burette the leveling bulb was synchronously lowered so that the reaction could proceed at atmospheric pressure. After at least 120 - 140 minutes the test was ended, and the temperature and barometric pressure again recorded. These readings were averaged with readings made at the beginning of the test and used to reduce the  $H_2$  volume to standard conditions. Then  $\frac{\Delta \text{ volume}}{\text{time}} \times 1000$  equaled the rate of dissolution of Zr in  $\text{mm}^3/\text{cm}^2 - \text{min.}$

The factor of 1000 is necessary to convert from cubic centimeters in which the burette readings were taken to cubic millimeters.

### c. Results

The rate of dissolution reached a maximum from 10 - 30 minutes

after the start of a run and then decreased steadily as shown in Figure 5. This result agrees with the work of Baumrucker <sup>11)</sup> and of Smith and Hill <sup>12)</sup>. A tenacious black film was formed on all specimens with exception of the 0.01N samples on which an extremely thin, intermittent, gray film was formed. These films were also reported in the literature.

An average of the rates over a range where the rates were highest was recorded as the average maximum rate for a run. Two runs were averaged for each concentration of HF plotted in Figure 6. It can be seen that in the range from 0 - 0.25N HF there is an essentially straight line relationship between rate and HF concentration. The equation for the straight line is

$$R = 1980C$$

where R = rate in mm<sup>3</sup>/cm<sup>2</sup> - min.  
C = normal HF concentration

However, at 0.50N HF the rate showed a significant positive deviation from the linear plot. If the curve is extrapolated through the 0.50N point as shown in Figure 6, it would appear that the rate increases exponentially at higher HF concentrations.

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11) Baumrucker, J. E., p-4, ref. 6

12) Smith, T. and Hill, G. R., p-5, ref. 7

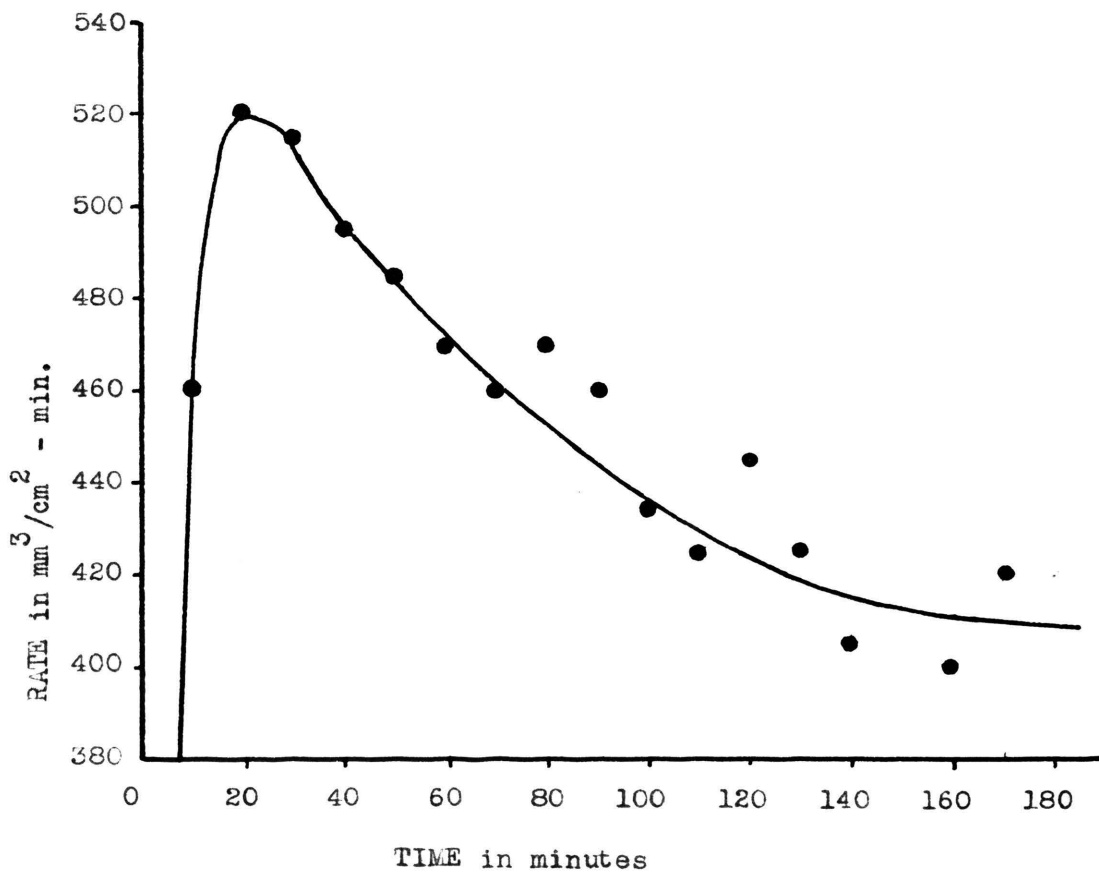


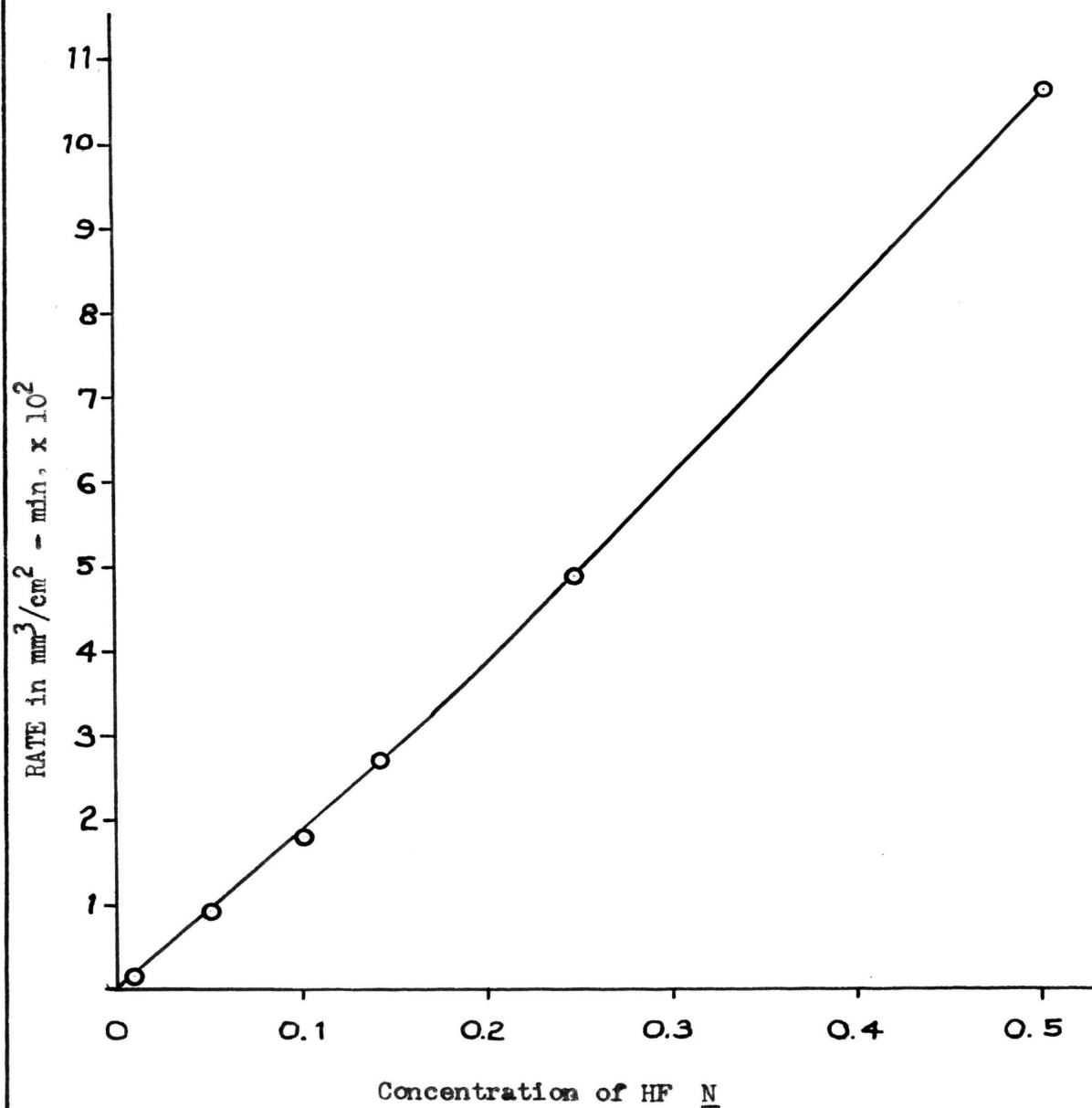
Figure 5

The rate of dissolution of Zr in 0.25N HF plotted versus time

See Table VIII

FIG. 6

THE EFFECT OF HF CONCENTRATION ON THE AVERAGE MAXIMUM  
RATE OF DISSOLUTION OF ZIRCONIUM



See Tables IV - IX

B. The effects of additions on the rate of dissolution of Zr in HF:

1. Qualitative tests

a. HNO<sub>3</sub> additions

The first addition to be tested was nitric acid. Johnson and Hill<sup>13</sup> found that a 3% HF - 30% HNO<sub>3</sub> solution did not react with Zr as violently as did solutions with higher HF concentrations. Concentrated HNO<sub>3</sub> has<sup>14</sup> caused passivation of iron by formation of an oxide film, so it was believed that a similar effect might be possible with Zr.

It was difficult to observe changes in gas evolution from Zr after an addition of 0.1N HNO<sub>3</sub> to a 0.5N HF solution. It was then decided to observe the effects of HNO<sub>3</sub> additions on the films formed on Zr in HF. Four Zr samples were placed in 0.1N HF until they had acquired the black film previously reported. The samples were removed from the HF solution, washed, and placed in 16, 8, 4, and 2N HNO<sub>3</sub> solutions respectively. No gas evolution was observed from samples in the pure HNO<sub>3</sub> solutions, so HF was added until the solutions were 0.1N with respect to HF. Gas evolution then commenced with an accompanying breakdown of the black film. However, after a short time the rate of H<sub>2</sub> evolution decreased in the four solutions with the decrease occurring first in the solution of greatest HNO<sub>3</sub> concentration. It was found that the smaller the HNO<sub>3</sub> concentration the longer was the time required for passivation. Passivation was accompanied by the appearance of a very shiny surface<sup>15</sup> which has also been reported by Johnson and Hill.

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13) Johnson, A. B., and Hill, G. R., p-3, ref. 5

14) Evans, U. R., "Metallic Corrosion Passivity and Protection," Arnold, London, (1946), p. 24

15) Johnson, A. B., and Hill, G. R., p-3, ref. 5, p. 2

The specimen which had become passivated in the 16N HNO<sub>3</sub> - 0.1N HF solution was removed and placed in a pure 0.1N HF solution. The shiny surface changed very quickly to a black film. Thus it can be seen that the shiny surface formed in HNO<sub>3</sub> - HF solutions may be stable when in contact with a solution having a high HNO<sub>3</sub>/HF ratio. If additional HF is added so that the HNO<sub>3</sub>/HF ratio is reduced below a critical value, gas evolution will start and a black film is formed once again. It is difficult to reproduce these results and find the threshold value.

Quantitative tests with the equipment described in Figure 2 were attempted using HNO<sub>3</sub> additions to 0.25N HF up to 4N HNO<sub>3</sub>. Results showed the general effect that increased HNO<sub>3</sub> concentration decreased the rate of gas evolution when HF concentration was held constant. However, the rates were not reproducible. The shiny sample surface formed in HNO<sub>3</sub> was still attacked quickly. Further tests with additions up to 8N HNO<sub>3</sub> proved to be destructive to the wax and ebonite parts of the equipment and the bakelite sample mounting. These problems could not be overcome, so the tests were given up.

b. Additions of fluorides

After some discussion and study of the literature it was decided to investigate fluoride additions. Blumenthal<sup>16</sup> states that fluorides and fluozirconates are the only halogen salts that do not react with water. These salts can be crystallized from aqueous solutions in anhydrous form. If an insoluble fluoride or fluozirconate were formed during the dissolution reaction, the possibility exists that an in-

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16) Blumenthal, W. B., Ind. Eng. Chem., 46, 530, (1954)



soluble reaction product might adhere to the Zr surface and cause passivation. The same equipment (Fig. 2), used in studies of the rate of dissolution of Zr in pure HF, was used since  $H_2$  could be the only gaseous reaction product.

At first qualitative rate studies were made to ascertain the effect of ammonium fluoride additions on the rate of dissolution of Zr in 0.1N HF. The rate of dissolution increased immediately after an initial addition of 0.1M  $NH_4F$  to the acid. Further additions of up to 4M  $NH_4F$  were made, but the only significant result noted was a change in the appearance of the sample surface. Such a sample is shown in Figure 10-A where most of the black film (formed by initial reaction in HF) is dissolved. Flow lines appear on the black film.

Since no passivation effect was noted at concentrations up to 4M  $NH_4F$ , tests were made at higher concentrations. Three samples already coated with the black film were placed in 2, 4, and 6M  $NH_4F$  - 0.1N HF solutions. Initially there was little difference in the rate of  $H_2$  evolution among the three samples. However, after several hours the  $H_2$  evolution from Zr in the 6M  $NH_4F$  - 0.1N HF solution was significantly less than from the other two samples.

Quantitative tests involving additions of fluoride to 0.1N HF solutions were then undertaken. This concentration of HF was used on the basis of results obtained from the rate studies in this acid. The rate of dissolution in 0.1N HF was small enough so that a sample was not dissolved before the end of a run. Yet, the rate was high enough to show a marked deviation upon the introduction of fluoride.

2. Quantitative studies of the effects of fluoride additions on the rate of dissolution of Zr in 0.1N HF solutions

a. Experimental equipment and procedure

The same equipment as shown in Figure 2 was utilized for investigation of the effects of fluoride additions. All operating conditions remained the same.

Precisely the same steps were followed in procedure as in the rate studies in HF solutions. However, after the Zr sample had been reacted for 100 minutes in 0.1N HF a fluoride addition was made. Initially liquid fluoride additions were made through the inlet funnel of the reaction vessel. These additions were calculated on the basis of an original reaction solution volume of 125 ml, so that the initial concentration of HF did not change. A sample calculation for a 0.1N HF and 0.1M  $\text{NH}_4\text{F}$  solution is as follows:

A 13.5M  $\text{NH}_4\text{F}$  solution provided a source of  $\text{NH}_4\text{F}$  so

$$13.5 x = 0.1 (125 + 2x) \quad (1)$$

$x$  = Volume of 13.5M  $\text{NH}_4\text{F}$  solution to be added so that the concentration becomes 0.1M in  $\text{NH}_4\text{F}$

The same volume of 0.2N HF must be added to  $\text{NH}_4\text{F}$  to make the solution 0.1N with respect to HF.

Then solving (1) for  $x$  we obtain:  $13.5 x - 0.2 x = 12.5$

$$x = \frac{12.5}{13.3} = 0.94 \text{ ml } 13.5\text{M } \text{NH}_4\text{F} \text{ to be added along with } 0.94 \text{ ml of } 0.2\text{N HF}.$$

The addition was poured into the funnel (E, Fig. 2) and the inlet valve opened. The outlet valve was then opened to allow the gas displaced by the incoming solution to escape. Upon making additions of the larger volumes of  $\text{NH}_4\text{F}$ , this method was demonstrated to be too cumbersome for practical operation.

The most efficient method proved to be a replacement of the entire reaction volume with a previously prepared solution. This premixed solution contained the proper concentration of fluoride and HF. A sample calculation for the replacement is as follows:

Calculations were made for a total volume of 125 ml to be 6M with respect to  $\text{NH}_4\text{F}$  and 0.1N in HF.

As the gram molecular weight of  $\text{NH}_4\text{F}$  = 37.08 grams then

$$\frac{x}{125} = \frac{6 (37.08)}{1000}$$

$x = 27.78$  grams  $\text{NH}_4\text{F}$  required to make 125 ml of 6M solution. The solution was made up by adding 62.5 ml. of 0.2N HF solution to the 27.78 grams  $\text{NH}_4\text{F}$  in a polyethylene beaker. Then the solution was diluted to 125 ml. with distilled water. The volume of 0.2N HF is thus diluted by half so that the total solution volume is 0.1N in HF and 6M in  $\text{NH}_4\text{F}$ .

The replacement of the reaction solution was effected by first stopping the stirrer and detaching the reaction flask (D, Fig. 2) at the gas outlet (F) and at the joint with mercury seal. The stirring rod (B) with the Zr sample affixed was lifted and held out of the solution. Then the 0.1N HF solution was poured out and the premixed solution containing fluoride was poured into the flask. The apparatus was reassembled and the stirring rod was again lowered into the HF. A burette and a time reading were recorded. The complete replacement operation was accomplished in from two to three minutes, and there was no significant change in the results when the replacement method was used. All runs were continued for approximately 100 minutes after addition of the premixed solution.

Additions were made of ammonium, potassium, and sodium fluorides. Since both  $\text{NH}_4\text{F}$  and  $\text{KF}$  are deliquescent it was necessary to dry them before weighing.  $\text{NH}_4\text{F}$  was dried at temperatures no higher than  $110^\circ\text{C}$  to avoid loss of  $\text{NH}_3$  and formation of the bifluoride.  $\text{KF}$  could be heated to somewhat higher temperatures without fear of decomposition.

b. Results

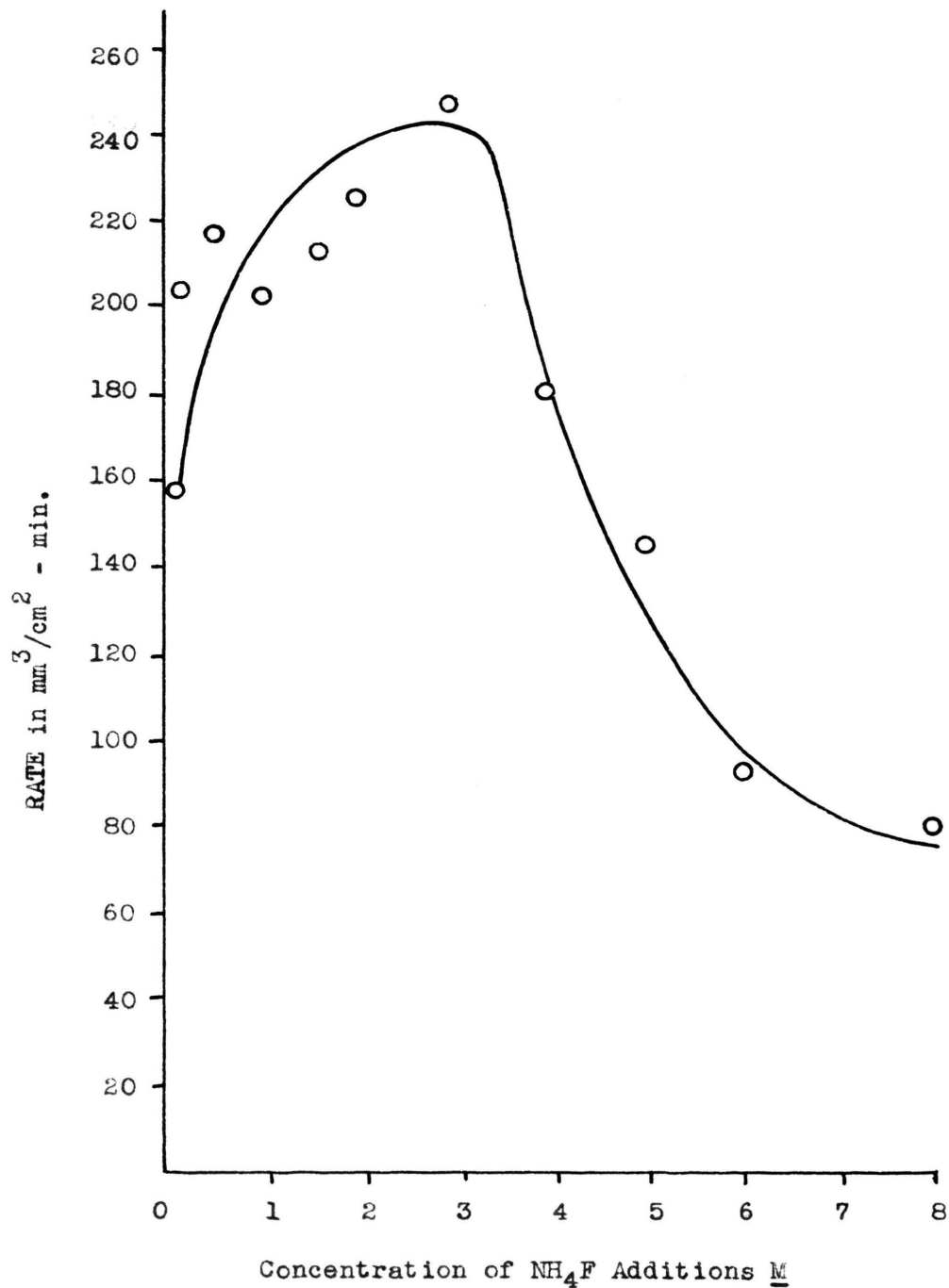
The results of the additions of  $\text{NH}_4\text{F}$ ,  $\text{KF}$ , and  $\text{NaF}$  on the rate of dissolution of Zr in 0.1N HF are shown in Figures 7, 8, and 9 respectively. The rate plotted was an average over a range from about 60 minutes after the fluoride addition to the end of the run. All points on the plots are an average of at least two runs with the following exceptions which were single runs:  $\text{NH}_4\text{F}$  - 5M, and 8M;  $\text{KF}$  - 0.72M;  $\text{NaF}$  - 0.15M. The zero fluoride concentration point on all the plots was derived by averaging ten rates of dissolution in 0.1N HF at 100 minutes.

As shown in Figure 7 the rate of dissolution of Zr increased to a maximum with additions to 3M  $\text{NH}_4\text{F}$ . However, from this point the rate decreased rapidly until at 6M  $\text{NH}_4\text{F}$  the rate was but 37% of the maximum rate. Addition of  $\text{KF}$  (Fig. 8) also caused an initial increase in the rate of dissolution of Zr. However, with an addition to 0.5M  $\text{KF}$  or more the rate decreased very rapidly to approximately 1/10 the maximum rate. An  $\text{NaF}$  addition (Fig. 9) of 0.125M  $\text{NaF}$  caused complete passivation of Zr in a 0.1N HF solution.

It is evident from Figures 7, 8, and 9 that  $\text{NaF}$ ,  $\text{KF}$ , and  $\text{NH}_4\text{F}$  in that order of effectiveness will cause passivation of Zr in a 0.1N HF solution. The minimum rates achieved by additions of  $\text{NH}_4\text{F}$ ,  $\text{KF}$ , and  $\text{NaF}$  were 80, 20, and 0  $\text{mm}^3/\text{cm}^2$  min. respectively. The minimum rates obtained by  $\text{NH}_4\text{F}$  and  $\text{KF}$  additions were obtained 110 minutes after the

FIG. 7

THE EFFECT OF  $\text{NH}_4\text{F}$  ADDITIONS ON THE RATE OF DISSOLUTION OF ZR IN 0.1N HF



See Tables X - XIX

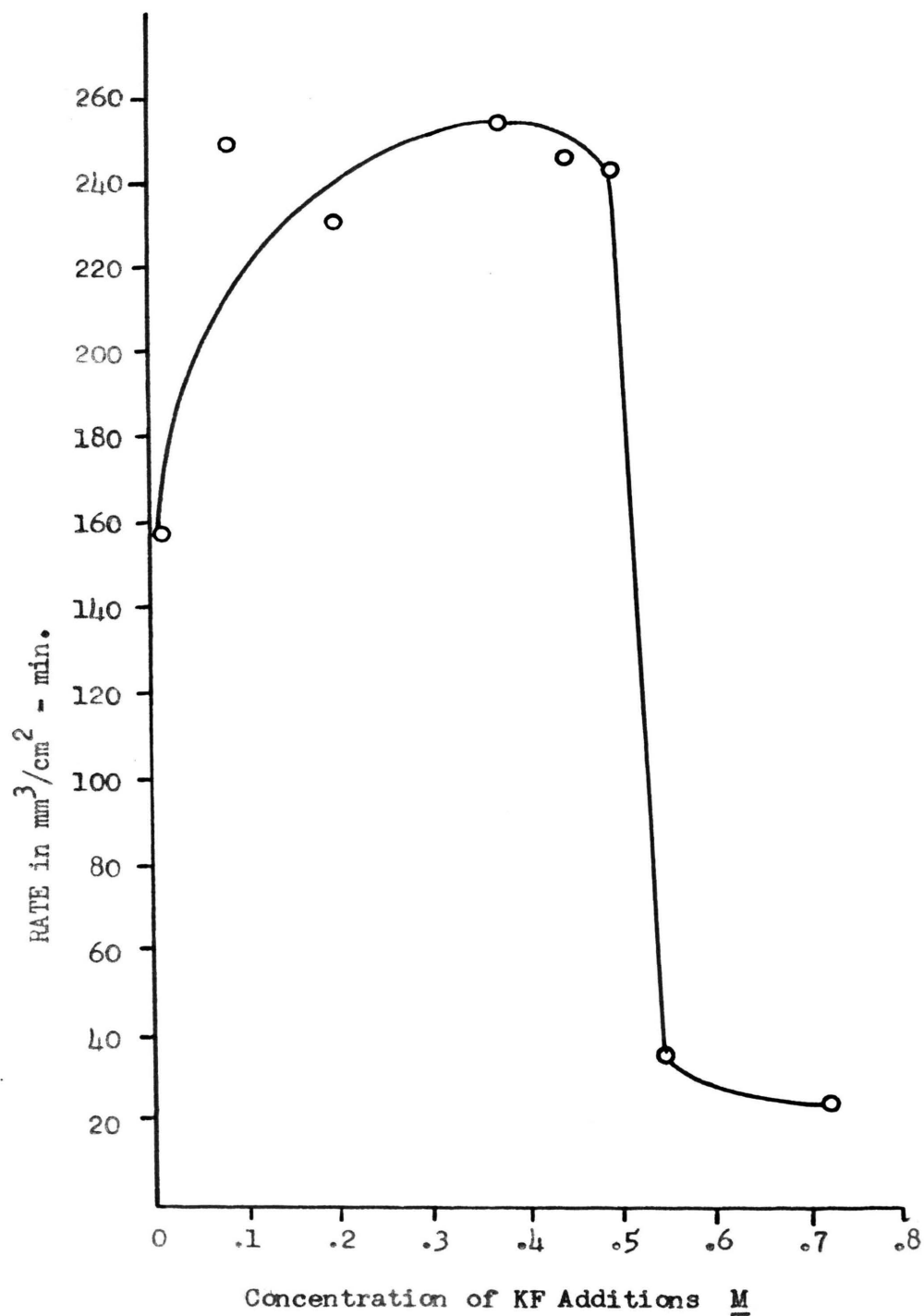


Fig. 8 The effect of KF additions on the rate of dissolution of Zr in 0.1 N HF See Tables XX - XXVI

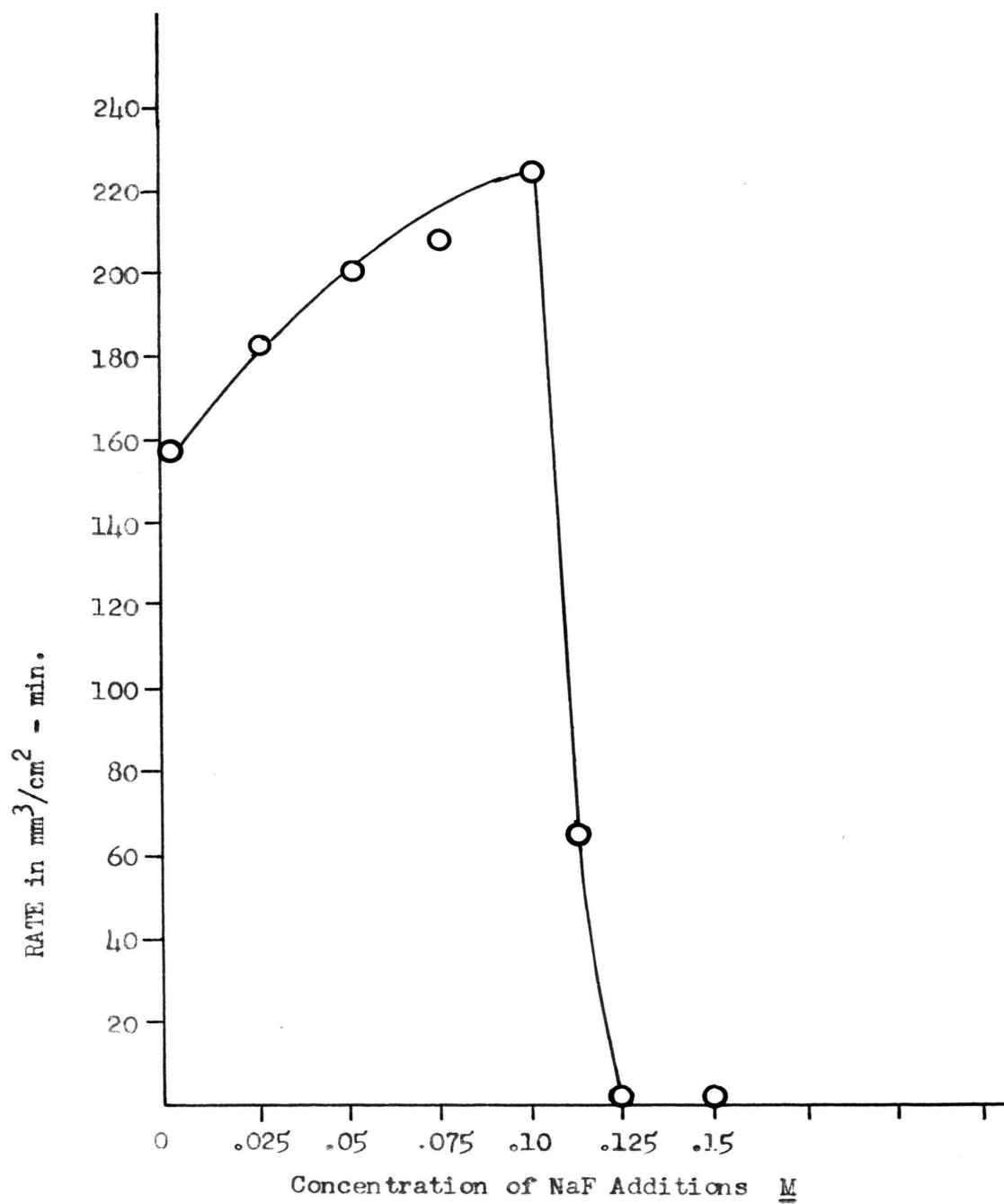


Fig. 9 The effect of NaF additions on the rate of dissolution of Zr in 0.1 N HF Tables XXVII - XXXIV

fluoride addition. However, an addition of 0.125M NaF caused complete passivation after 50 minutes. In all three cases the rate increased after addition of the fluoride until a concentration was reached at which the rate curve leveled off. Higher concentrations of the fluoride caused the rate to decrease. In general reproducibility of the rates was quite good, however, time-rate curves were not reproducible and so were not considered to have sufficient importance for discussion in this paper.

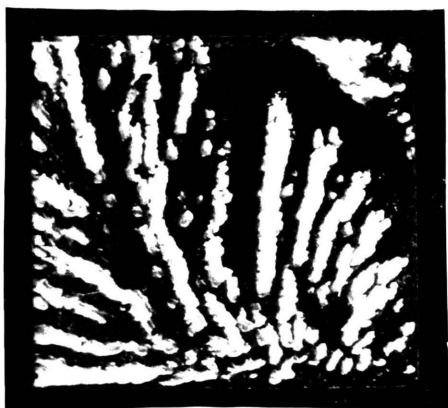
### 3. Studies of the films produced on Zr

#### a. Visual studies

The black film formed on Zr in HF solution could be removed in a saturated  $\text{NH}_4\text{F}$  solution. Evidently the tenacious black film was undermined by a salt film and was loosened. In Figure 10 samples A, B, C, and D are shown which display the breakdown and replacement of the original black film by a salt film. These samples are shown as they appeared upon removal from reaction solutions 110 minutes after addition of the fluorides. Samples A, B, C, and D are from the 3, 4, 6, and 8M  $\text{NH}_4\text{F}$  solutions respectively. Specimens A and B show flow lines in the black film. The flow lines originate from the breakdown of the black film exposing an underlying shiny, metallic surface. On specimen B nearly all of the original black film had been removed. However, on specimen C an iridescent salt film was observed with small amounts of black film remaining. On specimen D an even more complete salt film had developed with only minute remnants of black film visible. All of the films shown in Figure 10 were very tenacious.

Few flow lines were visible on specimens from the KF solutions. Upon passivation of the specimens at concentrations over 0.5M KF a grey





A  
3M KF



B  
4M KF



C  
6M KF



D  
8M KF

Figure 10

Zr specimens which have been reacted for approximately 100 minutes in 0.1N HF solutions containing varying concentrations of  $\text{NH}_4\text{F}$

salt film was formed. This film possessed none of the iridescent qualities of the film formed in  $\text{NH}_4\text{F}$ , but did appear thicker and more crystalline under microscopic examination at 50X.

The dark grey salt film formed on Zr in NaF solutions seemed to be either combined with or overlying the original black film. The thick, crystalline film was examined at 50X, and squares were observed which probably belonged to the cubic or tetragonal system.

b. X-Ray examinations

The black film formed in pure 0.1N HF was removed by placing the coated Zr sample in a saturated  $\text{NH}_4\text{F}$  solution. The film after being washed and dried was crushed to a powder. A pyrex filament, coated with grease so the powder would adhere, was used to hold the sample for the x-ray examination. Dr. James<sup>17</sup> using an x-ray powder camera obtained diffraction patterns for the black powder. He reported the film to be zirconium hydride,  $\text{ZrH}_2$ .

Studies of the passivating salt films were made while the salt films were still in place on the specimen surface. A Geiger-Muller x-ray spectrometer was used for these surface studies. No diffraction pattern could be obtained from the specimen passivated in  $\text{NH}_4\text{F}$  solution. The film was probably too thin to produce intense diffraction and was too tenacious to be removed for use in other techniques.

The diffraction pattern obtained from the specimen passivated in KF was compared with the ASTM tables<sup>18</sup>. A diffraction pattern had pre-

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17) James, W. J., Dept. of Chemistry, Mo. School of Mines & Metallurgy, private communication, June 1956

18) "Alphabetical and Grouped Numerical Index of X-Ray Diffraction Data," American Society for Testing Materials, Philadelphia, (1950)

viously been obtained from a polished Zr sample for use as a blank. Thus the Zr lines could be eliminated and the lines for the salt films could be isolated. Table II gives a comparison of the "d" values obtained from the salt film with the standard "d" values obtained from the ASTM tables. It was concluded that the film consisted of potassium fluozirconate,  $K_3ZrF_7$ , and potassium fluoride dihydrate,  $KF \cdot 2H_2O$ .

Patterns were obtained from the salt film on the specimen passivated in NaF both by surface and powder camera techniques. However, when compared with the ASTM tables no similar compound could be found listed. The absence of a standard pattern for sodium fluozirconate is regrettable. The formation of this compound would be most probable if the passivation mechanism is similar to that in the KF solution.

#### C. Potential measurements of Zr in HF:

It was considered necessary to investigate the potential-time curves of Zr in HF solutions. The reasons for this further study are summarized by Evans<sup>19</sup> who states that "the main object of potential-time curves is to ascertain whether the potential falls (indicating breakdown of a protective film) or rises (indicating repair)."

##### 1. Experimental equipment

The overall experimental arrangement shown in Figure 11 consisted of a cell  $Zr | \text{acid, saturated KCl, 1N KCl, Hg}_2\text{Cl}_2 | Hg$  and of a potentiometer (F). The cell thus consisted of the Zr electrode in HF and of the calomel reference electrode. The potentiometer measured the potential difference of the whole cell. Then the potential of the Zr | acid electrode could be calculated from the potential difference of

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19) Evans, U. R., p-24, ref. 14, p. 759

Table II

Data from an x-ray diffraction pattern of the passivating salt film formed on Zr in a KF solution

Zr	Standard principal "d" values <sup>18</sup>			"d" values from the experimental diffraction pattern		
	K <sub>3</sub> ZrF <sub>7</sub>	KF·2H <sub>2</sub> O	I/I <sub>0</sub>	Specimen	Observed	I/I <sub>0</sub> (relative intensity)
1.36			15	1.37		17
1.46			18	1.46		100
1.61			18	- *		-
	1.83		50	1.83		35
1.88			18	1.89		93
	2.24		50	2.24		35
2.44			100	2.45		17
2.56			20	2.60		98
		2.58	75	Obscured by Zr line above		
2.78			31	- *		-
		3.01	100	2.96		100
	3.18		100	3.15		100
		4.42	63	4.43		53

\* The two missing Zr lines can be seen in patterns obtained from a polished Zr surface

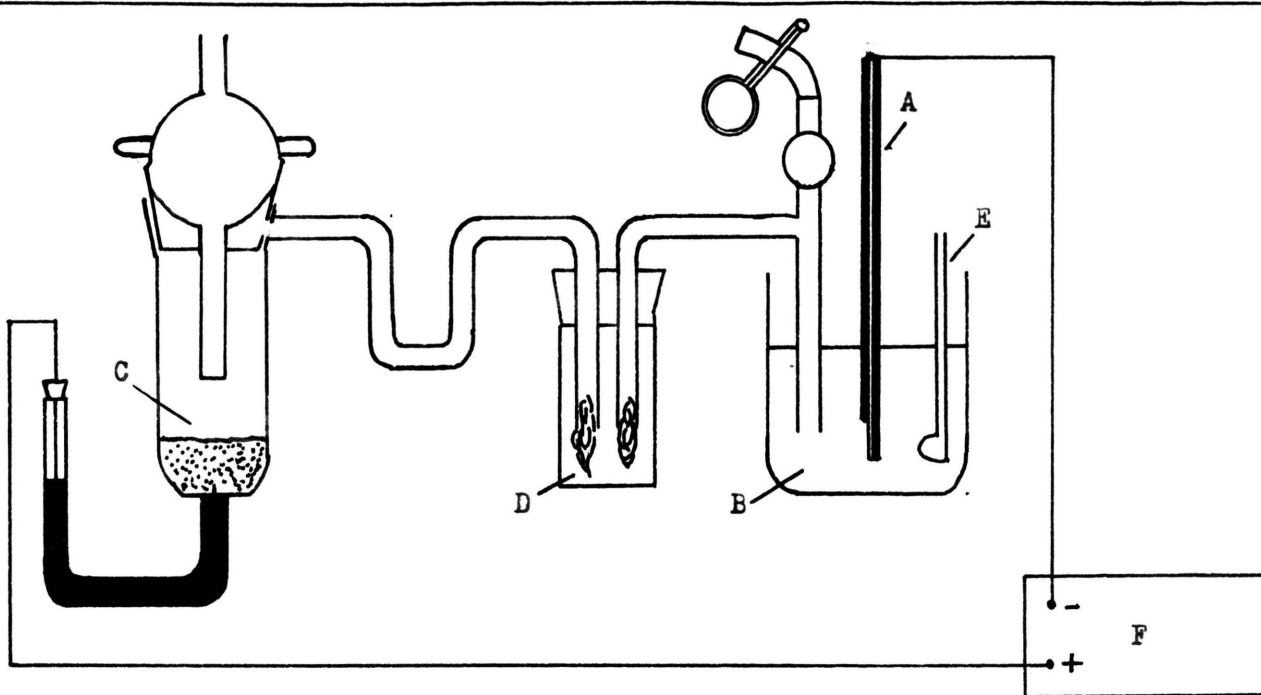


Figure 11

- A - Zirconium electrode insulated except for one cm<sup>2</sup> area immersed in HF
- B - HF solution
- C - 1 normal calomel electrode
- D - saturated KCl solution
- E - stirrer
- F - potentiometer

The experimental arrangement for the potential measurement of Zr in HF solutions.

the cell and the 1N calomel cell potential.

A stirrer (E) was used to agitate the HF solution (B) thus reproducing to some extent conditions in the reaction vessel. Dissolution of solid fluoride additions was also aided by agitation. A saturated KCl solution (D) served as a salt bridge. Cotton was stuffed into the ends of the half cell connecting tubes to reduce mixing and thus prevented contamination of the cells.

The 1N standard calomel cell was made up according to Palmer's<sup>20</sup> instructions. The accuracy of the calomel cell was compared with the standard value of 0.280 volts at 25°C given by Evans<sup>21</sup>. A cell for comparison was made up following the arrangement shown in Figure 11. Pure cadmium replaced the Zr while 1M CdSO<sub>4</sub> took the place of the HF solution. The calculation is as follows:

The potentiometer reading = 0.713 volts at 25°C was found to be the potential difference of the cell. Cd | 1M CdSO<sub>4</sub>, saturated KCl, 1N KCl, Hg<sub>2</sub>Cl<sub>2</sub> | Hg,

Then it followed that

$E_{\text{Cd}} = \text{Cell potential difference} + \text{potential of 1N calomel cell at } 25^{\circ}\text{C}$

$E_{\text{Cd}} = - 0.713 + 0.280 = - 0.433 \text{ volts}$

$E_{\text{Cd}}^{\circ}$ , the normal electrode potential of Cd, is then found

$$E_{\text{Cd}}^{\circ} = E_{\text{Cd}} + 2.3 \frac{RT}{nF} \log \frac{a_{\text{Cd}}}{a_{\text{Cd}^{++}}}$$

$a_{\text{Cd}^{++}} = \text{activity of Cd}^{++} \text{ in 1M CdSO}_4$

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20) Palmer, W. G., "Experimental Physical Chemistry," Cambridge University Press, (1941), pp. 202-205, 214-215

21) Evans, U. R., p-24, ref. 14, p. xxv

$a_{\text{Cd}^{++}} = f c$                        $f =$  activity coefficient of  $\text{Cd}^{++}$  in 1M  $\text{CdSO}_4$   
 $c =$  molar concentration of  $\text{CdSO}_4$

$f$  for  $\text{Cd}^{++}$  in 1M  $\text{CdSO}_4$  at  $25^\circ\text{C} = 0.041$ <sup>22</sup>

$a_{\text{Cd}^{++}} = 0.041$  (1)                      So substituting

$$E_{\text{Cd}}^\circ = -0.433 + \frac{0.06014 \log \frac{1}{0.041}}{2} = -0.433 + 0.0417$$

$$E_{\text{Cd}}^\circ = -0.391 \text{ volts}$$

Evans<sup>23</sup> gives  $E_{\text{Cd}}^\circ = -0.402$  volts

so  $\frac{-0.402 - (-0.391)}{-0.402} \times 100 = 2.7\%$  difference from the standard value.

This small error will not affect the results to any significant degree.

## 2. Procedure

A Zr electrode was cut from sheet Zr to a size of one centimeter in width and about four inches long. Before each potential-time measurement, the area of the electrode to be immersed was polished with 0 and 00 emery paper. Both wax and Pyseal were utilized to cover the entire electrode surface except for a one square centimeter area on one end for immersion and a place on the opposite end for electrical contact. The Zr - acid interface could then be entirely submerged in the solution.

A polyethylene beaker was used to hold the acid solution. The tube connecting the salt bridge and the acid solution was filled with 0.14N HF. This concentration was the lowest that possessed sufficient conductivity to provide adequate potentiometer sensitivity. Therefore 0.14N HF was used in the connecting tube for all potential measurements. No difficulties were encountered from dilution or concentration of the

22) Kortum, G., and Bockris, J. O'M., "Textbook of Electrochemistry," Vol. II, Elsevier, Houston, (1951), p. 666

23) Evans, U. R., p-24, ref. 14, p. xxiv

cell acid from the 0.14N HF.

The copper lead wire from the calomel cell was connected to the plus post on the potentiometer while the wire from the Zr was connected to the minus post. After the potentiometer had been balanced the Zr electrode was placed in the HF solution so that the entire one square centimeter surface was well below the level of the acid solution. Potential-time measurements in varying concentrations of HF were carried on for 75 - 135 minutes.

Before fluoride additions were made the Zr electrode was allowed to dissolve in a 0.1N HF solution for 75 minutes. At this time either a solid fluoride addition was made or the 0.1N HF was replaced by a solution having the desired fluoride and HF concentration. Calculations for the additions were made in the same way as in the studies of the effect of fluoride additions on rate. Potential measurements after the addition of fluorides were continued for up to 24 hours or longer.

### 3. Results

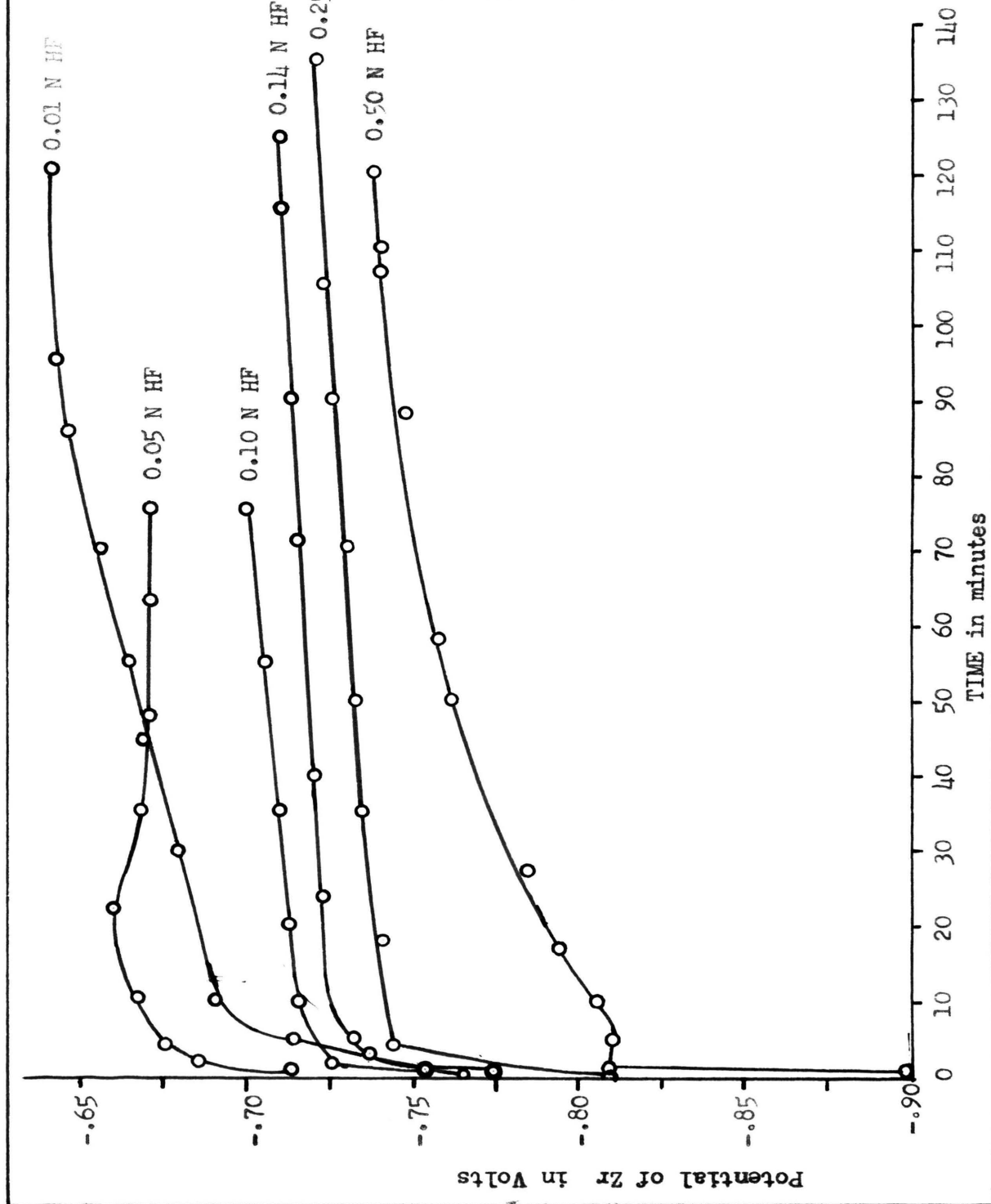
A set of potential-time curves for varying concentrations of HF is shown in Figure 12. Initially the potential quickly became more positive, but later only a gradual increase in potential occurred. It can be seen that the higher the HF concentration the more negative is the potential of Zr at all points on the curves. At first the curve for 0.01N HF does not follow this pattern. However, the extremely low conductivity of the solution and the different type of film formed in 0.01N HF may cause an anomalous effect. The potential-time curves in HF appear hyperbolic with the potential of the Zr becoming more positive with increasing time.

The effects of fluoride additions on the potential-time curves of Zr in HF are shown in Figures 13, 14, and 15. The concentrations of



Fig. 12

Potential-Time Curves of Zr in Varying Concentrations of HF  
See Table XXXV



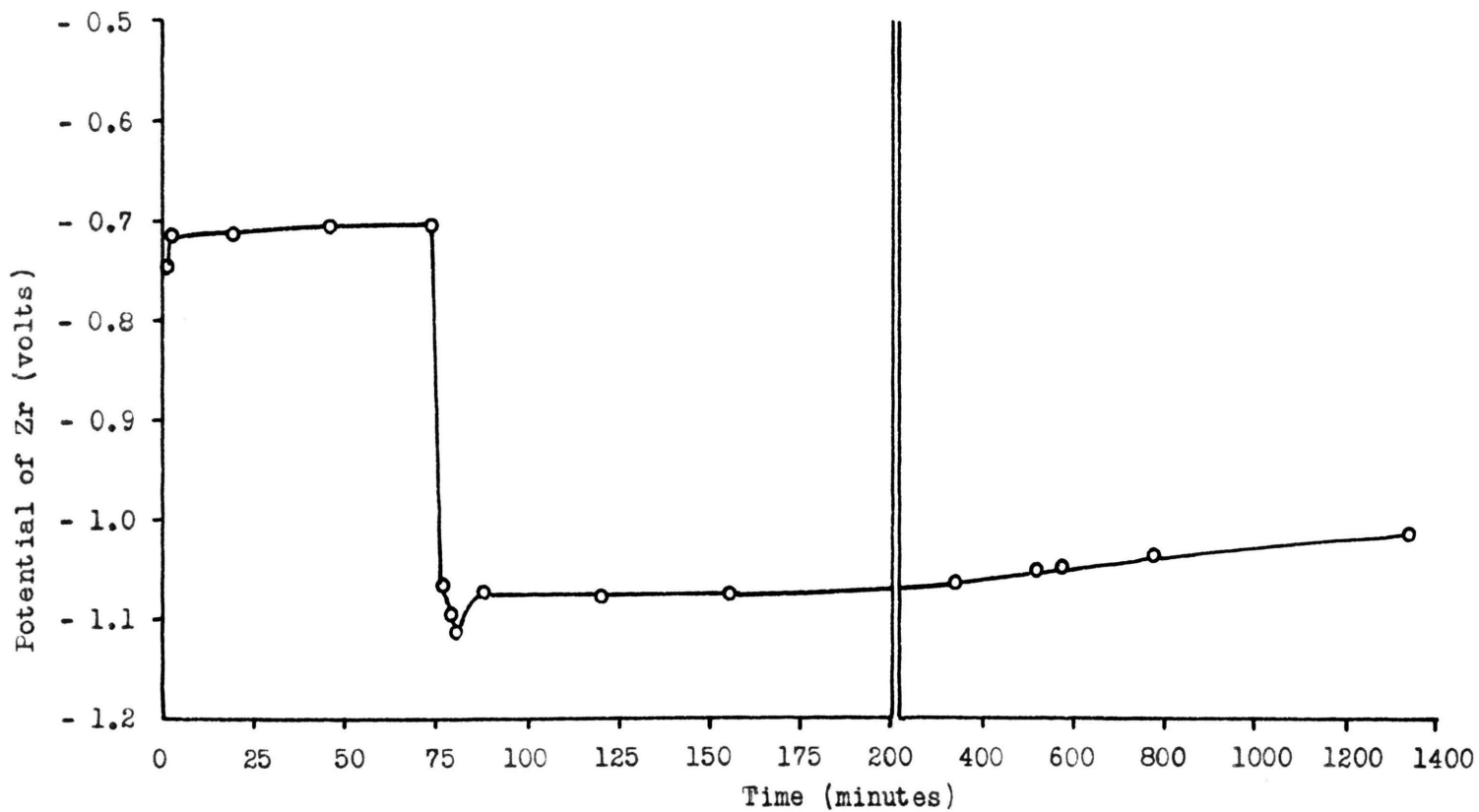


Figure 13

Potential - time curve of Zr in 0.1N HF showing the effect of an addition of 6.5M NH<sub>4</sub>F after 75 minutes. ( See Table XXXVI )

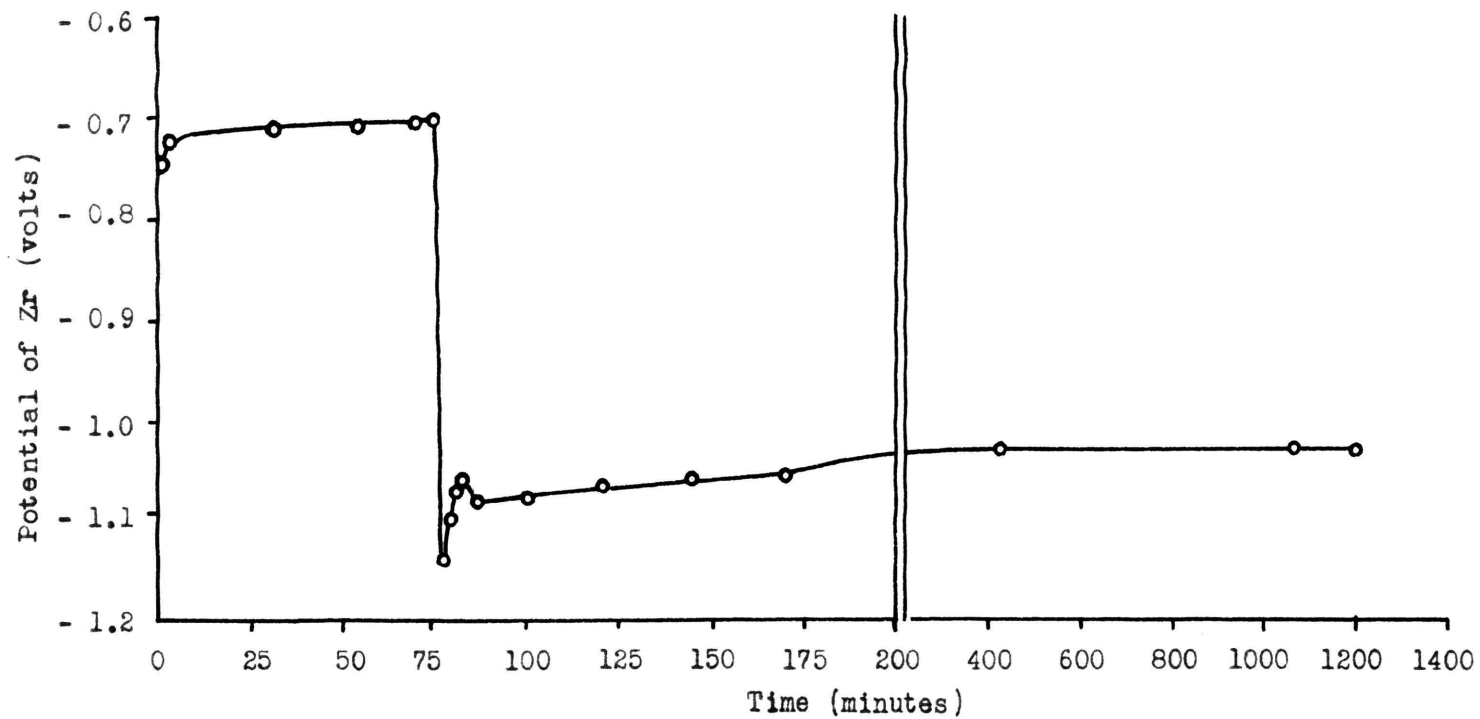


Figure 14

Potential - time curve of Zr in 0.1N HF showing the effect of an addition of 0.71M KF after 75 minutes. ( See Table XXXVIII )

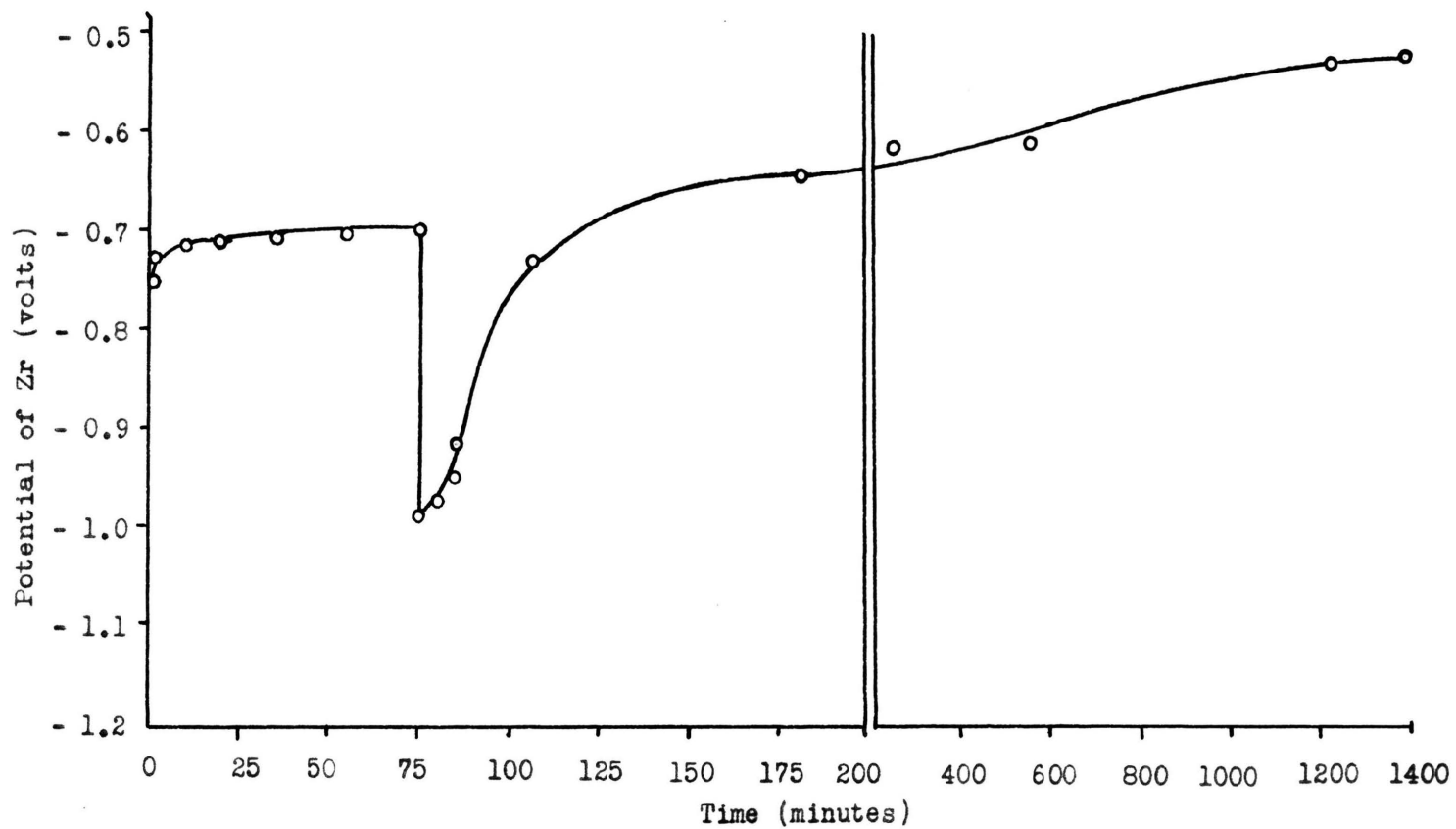


Figure 15

Potential - time curve of Zr in 0.1N HF showing the effect of an addition of 0.15M NaF after 75 minutes ( See Table XL )

fluorides added were such that passivation of the Zr would be produced. It was therefore possible to observe through potential-time curves the breakdown of the black,  $ZrH_2$  film and the subsequent build up of the passivating salt film, as shown below.

An addition of 6.5M  $NH_4F$  (Fig. 12) caused a sharp decrease in potential indicating the start of a breakdown of the hydride film. Over an extended period of time the breakdown of the black film could be observed visually. Immediately after the fluoride addition an increase in the rate of  $H_2$  evolution from the Zr was noticed. The evolution of  $H_2$  steadily decreased so that at 515 minutes only localized gas evolution occurred at the edges. After the initial sharp decrease in potential to - 1.112 volts there was a very quick increase in potential to - 1.076 volts. Apparently there is an almost immediate transition of the hydride film to a film that has passivating characteristics. After the reading at - 1.076 volts the potential gradually became more positive reaching a steady potential of - 1.015 volts at 1340 minutes.

An addition to 3M  $NH_4F$  produced a potential-time curve similar to that of 6.5M  $NH_4F$ . The steady potential of Zr in 3M  $NH_4F$  became more positive than in the 6.5M solution and  $H_2$  evolution did not noticeably decrease even at 1080 minutes. This  $H_2$  evolution occurring at 1080 minutes was far greater than was observed in the 6.5M  $NH_4F$  solution after the same period of time. This result is in accordance with the rate measurements previously described.

The potential-time curve of Zr in a 0.71M KF - 0.1N HF solution (Fig. 14) is somewhat similar to the curve obtained in the  $NH_4F$  solution. The potential dropped immediately to a minimum after the addition of KF, but very quickly became more positive again. However, ten to twenty

minutes after the addition of the KF the potential again became more negative. This effect is unique among the potential-time curves studied here and is reproducible. In runs with additions of 1.37M KF this effect is even more intense. From this second minimum the curve steadily became more positive until a steady potential of - 1.030 volts was reached after 420 minutes. Of the two minima, the second is smaller in magnitude.

The potential-time curve of Zr in a 0.15M NaF - 0.1N HF solution (Fig. 15) is quite similar to the  $\text{NH}_4\text{F}$  curve. However, the minimum potential is less negative, only - 0.988 volts. The steady potential of - 0.528 volts is far more positive than the potential in either the KF or  $\text{NH}_4\text{F}$  solutions. This more positive potential can account in part for the complete passivation of Zr by small additions of NaF. Seven minutes after addition of the NaF,  $\text{H}_2$  evolution from the sample had ceased.

The reproducibility of the potential-time curves, all shown in Figures 13, 14, and 15, was very good.

## IV

## Discussion and Conclusions

A. Comparison with previous quantitative studies of the dissolution of Zr in HF:

This investigation is not entirely in agreement with the two published quantitative studies of other authors. A tenacious black film was formed on Zr when dissolved in low concentrations of HF. However, Baumrucker<sup>1</sup>, who used a much higher HF concentration (2.5N), described the film as a loose black smut. Evidently HF concentration will affect the adherence of the black film to Zr. The data collected showed (Fig. 5) that the rate of H<sub>2</sub> evolution from Zr in HF decreased, (after an initial increase) with increasing time. This result agrees with Baumrucker's weight loss versus time curves as described in Chapter II.

The work by Smith and Hill<sup>2</sup> offers some very interesting points for comparison. In their studies it was found, though not conclusively, that O<sub>2</sub> has no effect on the rate of reaction. The effect of O<sub>2</sub> on the reaction was therefore checked once again and was found to cause no change in the amount of gas evolved in the Zr-HF reaction (Table I). Therefore it is probable that O<sub>2</sub> has no influence on the rate of reaction.

The results obtained from the effect of HF concentration on rate are in partial agreement with the studies of Smith and Hill, who found a linear relationship from 0 - 0.5M HF. Our results show that the plot of HF concentration versus rate (Fig. 6) is linear from 0 - 0.25N HF. However, the rate at 0.5N HF increased slightly from the straight line plot.

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1) Baumrucker, J. E., p-4, ref. 6

2) Smith, T., and Hill, G. R., p-5, ref. 7

It is possible that at concentrations greater than 0.25N HF the rate may increase exponentially with increasing HF concentration. Further studies should be made to establish whether a linear relationship exists between rate and HF concentrations over 0.5N. The quantitative rate measurements agree quite well with the data published by Smith and Hill.

Smith and Hill also stated that  $K^+$ ,  $F^-$ , and  $NO_3^-$ , (among others) had no effect on the reaction rate. However, Figure 8 shows a definite effect of KF additions on the rate of dissolution of Zr in 0.1N HF. Additions of over 0.5M KF caused passivation of Zr. ~~NO~~ $NO_3$  additions qualitatively appeared to reduce the rate of dissolution, although quantitative conclusions were difficult to make. Therefore, a valid comparison could not be made with the work of Smith and Hill on the effect of  $NO_3^-$  on rate.

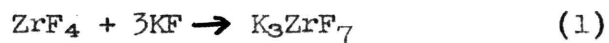
#### B. Passivation mechanisms:

Additions of NaF, KF, and  $NH_4F$  caused Zr to become passivated in 0.1N HF. In all three cases passivation was accompanied by formation of a salt film. The film covered the sample surface and replaced the hydride film. All potential-time curves became more negative immediately after addition of fluoride. This drop in potential indicated a breakdown of the initial hydride film. However, a subsequent, gradual increase in potential pointed to a build up of a passivating film.

X-ray studies (Table II) of the salt film, deposited on Zr after additions of over 0.5M KF, established the film to be potassium heptafluozirconate,  $K_3ZrF_7$ . The  $KF \cdot 2H_2O$  also found in the x-ray diffraction pattern of the film was probably entrapped during deposition of the  $K_3ZrF_7$ . The  $KF \cdot 2H_2O$  probably has no role in the passivation effect.



According to Hampson and Pauling<sup>3</sup> crystals of  $K_3ZrF_7$  were grown by dissolving  $ZrF_4$  in a hot solution containing a large excess of KF and then allowing the solution to crystallize slowly. The reaction would be:



It is known that  $ZrF_4$  is produced in the dissolution reaction of Zr in HF by the following reaction:



$ZrF_4$  was not present in the premixed replacement solution, but was rapidly produced by reaction (2) which continued because of the HF present in the premixed addition. It is probable that with increasing KF concentration a series of fluozirconates is formed. Mellor<sup>4</sup> describes the crystallization of  $KZrF_5$  and  $K_2ZrF_6$  from solutions containing KF and  $ZrF_4$ .

The passivating film formed on Zr after  $NH_4F$  additions of 6M was not identified, but it will be assumed by analogy that the film is ammonium heptafluozirconate,  $(NH_4)_3ZrF_7$ . Von Hevesy, Christiansen, and Berglund<sup>5</sup> stated that when ammonium fluozirconate was crystallized in the presence of excess  $NH_4F$ ,  $(NH_4)_3ZrF_7$  was formed instead of  $(NH_4)_2ZrF_6$ . This effect would establish  $(NH_4)_3ZrF_7$  to be the most probable film formed on Zr in solutions containing an excess of  $NH_4F$ .

The literature does not list the compound,  $Na_3ZrF_7$ . However, Mellor<sup>6</sup> describes the crystallization of sodium fluozirconate,  $Na_2ZrF_6$ , from a

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3) Hampson, G. C., and Pauling, L., J. Am. Chem. Soc., 60, 2702, (1938)

4) Mellor, J. W., p-3, ref. 1, p. 140

5) Hevesy, G. V., Christiansen, J. A., and Berglund, V., Z. anorgan. allgem. Chemie, 144, 69, (1925)

6) Mellor, J. W., p-3, ref 1, p. 139-140

solution containing one to two parts of NaF and fourteen parts of  $ZrF_4$ . Mellor also describes the work of De Marignac who prepared  $Na_5Zr_2F_9$  by double decomposition of sodium chloride and ammonium fluozirconate.

The effectiveness of  $NH_4F$ ,  $KF$ , and  $NaF$  additions in passivation may be explained by the relative solubilities of the fluozirconates. (It has now been assumed that all the salt films are fluozirconates) Table III gives the data for solubilities of fluozirconates that are available in the literature. While this table is not complete it does provide a basis for qualitative interpretations.

It can be seen from Table III that the normal fluozirconates of the general formula  $R_2ZrF_6$  decrease in solubility in the order of  $NH_4^+$ ,  $K^+$  and  $Na^+$ . It can be assumed that heptafluozirconates,  $R_3ZrF_7$ , have the same order of decreasing solubilities.

Von Hevesy<sup>7</sup> has published a plot of the solubility of  $(NH_4)_3ZrF_7$  versus  $NH_4F$  concentration. This plot shows that the solubility of  $(NH_4)_3ZrF_7$  decreases with increasing  $NH_4F$  concentration. Up to 4M  $NH_4F$  the solubility of  $(NH_4)_3ZrF_7$  decreased sharply and after that point remained constant even up to 10M  $NH_4F$ . In reference to Figure 7 it can be seen that the rate of dissolution of Zr began decreasing with additions of over 3M  $NH_4F$ . However, since the solubility of the  $(NH_4)_3ZrF_7$  film does not decrease further with increased  $NH_4F$  concentration, then passivation of the Zr may not be completed. The rates of dissolution of Zr with additions of 6M and 8M  $NH_4F$  were nearly the same, indicating that film solubility is probably the critical factor in passivation of Zr in HF by fluoride additions.

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7) Hevesy, G. V., Christiansen, J. A., and Berglund, V., p-50, ref. 5

Table III

The solubilities of fluozirconates at 20°C

Fluozirconate	Solvent	Solubility (moles/liter)
$(\text{NH}_4)_3\text{ZrF}_7$	water	0.55 <sup>7</sup>
$(\text{NH}_4)_2\text{ZrF}_6$	water	1.05
$\text{K}_3\text{ZrF}_7$	-	-
$\text{K}_2\text{ZrF}_6$	water	0.053 <sup>6</sup>
	0.125N HF	0.0655 <sup>7</sup>
	5.890N HF	0.1297
$\text{Na}_3\text{ZrF}_7$	-	-
$\text{Na}_2\text{ZrF}_6$	-	far less soluble than $\text{K}_2\text{ZrF}_6$ <sup>8</sup>

8) Missenden, J., The Chemical News, 124, 327, (1922)

C. Discussion of the possibility of local currents:

In referring to the literature concerning the dissolution of Ti in HF certain similarities to this work were noted. Straumanis and Gill<sup>9</sup> found that  $\text{NH}_4\text{F}$  caused passivation of Ti in  $\text{H}_2\text{SO}_4$  and HF. Their passivation curve was quite similar to Figure 7. Straumanis and Gill also showed the effect of  $\text{NH}_4\text{F}$  additions on the potential-time curve of Ti in HF. This curve is very similar to Figure 13. Straumanis and Chen<sup>10</sup> have proven the importance of local currents in the mechanism of dissolution of Ti in HF. Upon considering the similarity between the results of this investigation and the findings of Straumanis and Gill it appears quite possible that local currents may also play a part in the mechanism of dissolution of Zr in HF.

If this is so then it is possible that, in addition to salt film formation, the emf of the local elements is decreased by the increased overpotential of the local cathodes, as it was in the case of Ti<sup>11</sup>. In the light of this interpretation the local cathodes on Zr would be blocked much faster by a salt film (with simultaneous increase of overpotential) in the case of NaF than in the case of  $\text{NH}_4\text{F}$  additions.

D. Discussion of the potential-time curves:

The potential-time curves of Zr in pure HF (Fig. 12) displayed a sharp initial rise in potential. This rise in potential, according to

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9) Straumanis, M. E., and Gill, C. B., J. Electrochem. Soc., 101, 10, (1954)

10) Straumanis, M. E., and Chen, P. C., p-14, ref. 8

11) Straumanis, M. E., and Gill, C. B., ref. 9

Evans, is due to the formation of a film. By visual observation a black, hydride film is observed to form (except in very low HF concentrations) on Zr thus causing a more positive potential. The initially film free metal had a very negative potential which quickly became more positive upon formation of the porous, hydride film. As the film grew in thickness the pores became smaller in size with the potential slowly becoming even more positive.

The film did not appear to grow in thickness continually, probably being soluble to some extent in the acid. Thus, the potential should not have continued to become more positive indefinitely. This prediction was substantiated by the steady potentials approached by the curves in Figure 12.

The immediate effect of fluoride additions on the potential-time curves of Zr in HF (Figs. 13, 14 and 15) was to cause a sharp decrease in potential. A minimum value was reached from one to six minutes after the addition. According to Evans, this decrease in potential would indicate a breakdown of the black, hydride film. While it was difficult to see a breakdown, the black film was later replaced by a grey salt film.

From the minimum point the potential-time curves quickly became much more positive, but later increased only gradually until a steady potential was reached. This section of the curve shows that another film began to form immediately after the breakdown of the hydride film. At first the pores of the film (formed from deposition of fluozirconate) were quite large. As the film continued to grow in thickness, the pores decreased in size and the potential became more positive. The steady potential

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12) Evans, U. R., p-24, ref. 14, pp. 757-759

reached after an extended period of time could be attributed to several factors. These factors might include film solubility and increased local current density among others.

## V

## Summary

This investigation of the dissolution of hafnium-free zirconium in hydrofluoric acid was begun by studying the dissolution reaction. It was found by experiment that the reaction:



as described in the literature was correct.

The rate of dissolution of Zr in HF was measured by using the principle of hydrogen collection. The equipment was designed so that all variables were kept constant except acid concentration. A linear relationship was found between rate of dissolution and HF concentration from 0 - 0.25N. At 0.5N HF the rate showed a slight increase from the linear plot.

Fluoride additions, when present in sufficient concentration, caused passivation of Zr after 60 - 110 minutes. However, the immediate effect of the fluoride addition was to increase the rate. Also, if the fluoride concentration was not great enough to cause passivation, dissolution continued at a higher rate than in pure HF. NaF, KF, and NH<sub>4</sub>F in order of decreasing effectiveness caused passivation of Zr in 0.1N HF.

From x-ray studies of the passivating salt films, it was concluded that the films were fluozirconates. Potassium heptafluozirconate, K<sub>3</sub>ZrF<sub>7</sub> was positively identified as the salt film which caused passivation of Zr in a KF solution. A study of the solubilities of the fluozirconates showed that they have very low solubility, even in HF solutions. In addition the solubilities are related to the effectiveness of the fluozirconate film in causing passivation. Thus the sodium fluozirconate, which has the lowest solubility, is most effective in causing passivation.

Potential measurements of Zr in various concentrations of HF showed that the higher the HF concentration, the more negative was the potential. The potential-time curves were hyperbolic with the potential becoming more positive with increasing time.

Fluoride additions caused the potential of Zr in HF to quickly become far more negative. The potential gradually became more positive until a steady potential was attained. The steady potential reached after  $\text{NH}_4\text{F}$  and KF additions was far more negative than the potential resulting from an NaF addition.



## Appendix

Preface

This appendix includes tables containing all data for the rate and potential measurements.

Data for rate measurements

The hydrogen volumes listed are reduced to standard conditions of temperature, pressure, and dryness. The average maximum rate of dissolution of Zr in pure HF was taken over an arbitrary range which might vary depending upon the particular case. Each value (in the range over which the average was taken) was marked with #.

Data for potential measurements

$E_{Zr}$  is the potential of Zr reduced to the hydrogen scale.

Table IV

The rate of dissolution of Zr in 0.01N HF

Run No. 1

Average corrected pressure: 709.3 mm Hg

Average room temperature: 25.8°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
30	0.45	0.45	15 #
45	0.75	0.30	20 #
60	0.90	0.15	10 #
75	1.20	0.30	20 #
90	1.35	0.15	10 #
105	1.70	0.35	23.3 #
120	1.90	0.20	13.3 #
170	2.30	0.40	8

# Average maximum rate for first run = 16 mm<sup>3</sup>/cm<sup>2</sup>min

Run No. 2

Average corrected pressure: 709.5 mm Hg

Average room temperature: 25.6°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
30	0.35	0.35	11.7
60	0.90	0.55	18.3 #
90	1.30	0.40	13.3 #
120	2.05	0.75	25.0 #
150	2.40	0.35	11.7 #
180	2.80	0.40	13.3
210	3.05	0.25	8.4
240	3.50	0.45	15.0
300	4.25	0.75	12.5
330	4.50	0.25	8.3
360	4.75	0.25	8.3

Average maximum rate for second run = 17.1 mm<sup>3</sup>/cm<sup>2</sup> min

Average maximum rate for both runs = 16.55 mm<sup>3</sup>/cm<sup>2</sup> min

Table V

The rate of dissolution of Zr in 0.047N HF

Run No. 1

Average corrected pressure: 700.2 mm Hg

Average room temperature: 30.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
15	0.70	0.70	46.7
30	1.80	1.10	73.5 #
45	3.60	1.80	120.0 #
60	5.00	1.40	93.3 #
75	6.35	1.35	90.0 #
90	7.60	1.25	83.4
105	8.90	1.30	86.8
120	10.10	1.20	80.0

# Average maximum rate for first run: 94.2 mm<sup>3</sup>/cm<sup>2</sup> min

Run No. 2

Average corrected pressure: 712.4 mm Hg

Average room temperature: 25.0°C

Time (minutes)	Volume (cm <sup>3</sup> )	Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
20	1.65	1.65	82.5 #
30	2.65	1.00	100.0 #
45	3.95	1.30	86.7 #
60	5.55	1.60	106.8 #
80	7.15	1.60	80.0 #
95	8.40	1.25	83.4
110	9.65	1.25	83.4
125	10.90	1.25	83.4

# Average maximum rate for second run: 91.2 mm<sup>3</sup>/cm<sup>2</sup> min

Average maximum rate for both runs: 92.7 mm<sup>3</sup>/cm<sup>2</sup> min

Table VI

The rate of dissolution of Zr in 0.0984N HF

Run No. 1

Average corrected pressure: 710.1 mm<sup>3</sup> Hg

Average room temperature: 26.2°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	1.55	1.55	155
20	3.40	1.85	185 #
30	5.80	2.40	240 #
40	7.85	2.05	205 #
50	9.80	1.95	195 #
60	11.50	1.70	170 #
72	13.55	2.05	170 #
80	15.10	1.55	155
92	17.05	1.95	163
100	18.40	1.35	169
110	20.10	1.70	170
120	21.55	1.45	145

# Average maximum rate for first run: 196 mm<sup>3</sup>/cm<sup>2</sup> min

Run No. 2

Average corrected pressure: 709.7 mm Hg

Average room temperature: 26.6°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	1.00	1.00	100
20	2.90	1.90	190 #
30	4.25	1.35	135 #
40	6.90	2.65	265 #
50	8.60	1.70	170 #
60	10.30	1.70	170 #
70	11.90	1.60	160
80	13.80	1.90	190
90	15.40	1.60	160
100	16.85	1.45	145

# Average maximum rate for second run: 185 mm<sup>3</sup>/cm<sup>2</sup> min

Average maximum rate for both runs: 190.5 mm<sup>3</sup>/cm<sup>2</sup> min

Table VII

The rate of dissolution of Zr in 0.14N HF

Run No. 1

Average corrected pressure: 706.4 mm Hg

Average room temperature: 25.6°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	2.80	2.80	280 #
20	5.90	3.10	310 #
30	8.90	3.00	300 #
40	11.90	3.00	300 #
50	14.35	2.45	245 #
60	16.90	2.55	255 #
70	19.60	2.70	270 #
85	22.85	3.25	217
90	24.05	1.20	240
100	26.30	2.25	225
120	31.35	5.05	252.5
130	33.45	2.10	210.0
140	35.75	2.30	230.0

# Average maximum rate for first run: 280 mm<sup>3</sup>/cm<sup>2</sup>min

Table VII (Continued)

The rate of dissolution of Zr in 0.14N HF

Run No. 2

Average corrected pressure: 705.7 mm Hg

Average room temperature: 26.4°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	2.30	2.30	230 #
20	5.15	2.85	285 #
30	8.55	3.40	340 #
40	11.45	2.90	290 #
50	14.25	2.80	280 #
60	16.75	2.50	250 #
70	19.55	2.80	280 #
80	22.45	2.90	290 #
90	24.80	2.35	235
100	27.40	2.60	260
110	29.90	2.50	250
120	32.45	2.55	255

# Average maximum rate for second run: 287.9 mm<sup>3</sup>/cm<sup>2</sup>minAverage maximum rate for both runs: 284 mm<sup>3</sup>/cm<sup>2</sup>min

Table VIII

The rate of dissolution of Zr in 0.25N HF

Run No. 1

Average corrected pressure: 702.2 mm Hg

Average room temperature: 28.2°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	4.60	4.60	460 #
20	9.80	5.20	520 #
30	14.95	5.15	515 #
40	19.90	4.95	495 #
50	24.75	4.85	485 #
60	29.45	4.70	470
70	34.05	4.60	460
80	38.75	4.70	470
90	43.35	4.60	460
100	47.70	4.35	435
110	51.95	4.25	425
120	56.40	4.45	445
130	60.65	4.25	425
140	64.70	4.05	405
160	68.70	4.00	400
170	72.90	4.20	420

# Average maximum rate for first run: 495 mm<sup>3</sup>/cm<sup>2</sup>min

Table VIII (Continued)

The rate of dissolution of Zr in 0.25N HF

Run No. 2

Average corrected pressure: 702.9 mm Hg

Average room temperature: 29.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	4.60	4.60	460 #
20	10.05	5.45	545 #
30	15.05	5.00	500 #
40	20.10	5.05	505 #
50	24.95	4.85	485 #
60	29.80	4.85	485 #
70	34.40	4.60	460
80	38.80	4.40	440
90	43.40	4.60	460
100	47.80	4.40	440
110	52.25	4.45	445
120	56.55	4.30	430
130	60.95	4.40	440
140	65.15	4.20	420

# Average maximum rate for second run: 493.7 mm<sup>3</sup>/cm<sup>2</sup>minAverage maximum rate for both runs: 494.2 mm<sup>3</sup>/cm<sup>2</sup>min



Table IX

The rate of dissolution of Zr in 0.50N HF

Run No. 1

Average corrected pressure: 702.3 mm Hg

Average room temperature: 30.4°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	10.40	10.40	1040 #
20	21.30	10.90	1090 #
30	31.90	10.60	1060 #
40	42.45	10.55	1055 #
50	52.60	10.15	1015
60	62.60	10.00	1000
70	72.40	9.80	980
80	81.80	9.40	940
85	86.10	4.30	860

# Average maximum rate for first run: 1061.3 mm<sup>3</sup>/cm<sup>2</sup>min

Run No. 2

Average corrected pressure: 705.6 mm Hg

Average room temperature: 27.8°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	10.75	10.75	1075 #
20	22.05	11.30	1130 #
30	32.55	10.50	1050 #
40	43.10	10.55	1055 #
50	53.35	10.25	1025
60	63.55	10.20	1020
70	73.60	10.05	1005
80	83.25	9.65	965
90	92.80	9.55	955
100	102.05	9.25	925
110	111.05	9.00	900
120	120.05	9.00	900
130	128.75	8.70	370

# Average maximum rate for second run: 1077.5 mm<sup>3</sup>/cm<sup>2</sup>minAverage maximum rate for both runs: 1069.4 mm<sup>3</sup>/cm<sup>2</sup>min

Tables IV-IX See Figure 6

Table X

The effect of an addition of 0.1M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 703.8 mm Hg

Average room temperature: 29.2°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
10	0.90	0.90	90
20	2.50	1.60	160
30	4.35	1.85	185
66	10.50	6.15	170.5
75	12.10	1.60	178
90	14.65	2.55	170
100	16.20	1.55	155

Addition of 0.1M  $\text{NH}_4\text{F}$

0	16.20	1.55	155
10	18.10	1.90	190
20	20.65	2.55	255
30	22.80	2.15	215
40	24.90	2.10	210 #
50	27.15	2.15	215 #
60	29.25	2.10	210 #
70	31.35	2.10	210 #

# Average rate for first run: 211  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table X (Continued)

The effect of an addition of 0.1M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure:

Average room temperature:

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
10	0.70	0.70	70
45	5.70	5.00	143
75	11.20	5.50	183
100	15.05	3.85	154

Addition of 0.1M  $\text{NH}_4\text{F}$

0	15.05	3.85	154
6	16.25	1.20	200
20	19.30	3.05	218
30	21.45	2.15	215
40	23.80	2.35	235
45	24.75	0.95	190 #
55	26.85	2.10	210 #
75	30.60	3.85	183 #
85	32.50	1.90	190 #

# Average rate for second run:  $196 \text{ mm}^3/\text{cm}^2 \text{ min}$

Average rate for both runs:  $203.5 \text{ mm}^3/\text{cm}^2 \text{ min}$

Table XI

The effect of an addition of 0.5M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 700.8 mm Hg

Average room temperature: 30.4°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
10	0.85	0.85	85
20	2.75	1.90	190
30	5.00	2.25	225
40	6.90	1.90	190
55	9.45	2.55	170
60	10.35	0.90	180
70	12.30	1.95	195
80	14.30	2.00	200
90	16.20	1.90	190
100	17.70	1.50	150

Addition of 0.5M  $\text{NH}_4\text{F}$

0	17.70	1.50	150
10	20.00	2.30	256
20	22.25	2.25	225
50	29.25	7.00	233
60	30.90	1.65	165 #
71	33.20	2.30	209 #
80	34.95	1.75	195 #
90	37.30	2.35	235 #
95	38.40	1.10	220 #

# Average rate for first run: 214  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XI (Continued)

The effect of an addition of 0.5M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 699.7 mm Hg

Average room temperature: 29.8°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
16	1.40	1.40	88
25	2.85	1.45	162
50	7.40	4.55	182
65	10.00	2.60	174
76	11.85	1.85	168
85	13.35	1.50	167
100	15.85	2.50	167

Addition of 0.5M  $\text{NH}_4\text{F}$

0	15.85	2.50	167
10	18.10	2.25	225
30	22.75	4.65	233
41	24.80	2.05	187
50	27.20	2.40	267
60	29.70	2.50	250 #
70	31.90	2.20	220 #
80	34.10	2.20	220 #
91	36.50	2.40	218 #
100	38.45	1.95	217 #

# Average rate for second run: 219  $\text{mm}^3/\text{cm}^2 \text{ min}$

Average rate for both runs: 216.5  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XII

The effect of an addition of 1.0M NH<sub>4</sub>F on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 704.1 mm Hg

Average room temperature: 29.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
40	6.95	6.95	174
50	7.75	0.80	80
61	9.45	1.70	154
70	10.60	1.15	128
80	11.75	1.15	128
90	13.60	1.85	185
100	15.10	1.50	150

Addition of 1.0M NH<sub>4</sub>F

0	15.10	1.50	150
10	17.10	2.00	200
20	19.45	2.35	225
30	21.65	2.20	220
40	23.70	2.05	205
50	25.75	2.05	205
60	27.90	2.15	215 #
70	29.85	1.95	195 #
80	31.65	1.80	180 #
95	34.55	2.90	193 #
110	37.10	2.55	170 #

# Average rate for first run: 184 mm<sup>3</sup>/cm<sup>2</sup> min

Table XII (Continued)

The effect of an addition of 1.0M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 700.8 mm Hg

Average room temperature: 30.6°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
11	0.85	0.85	78
30	4.15	3.30	174
45	6.80	2.65	177
60	9.45	2.65	177
80	12.95	3.50	175
100	16.25	3.30	165

Addition of 1.0M  $\text{NH}_4\text{F}$

0	16.25	3.30	165
7	17.70	1.45	207
15	18.80	1.10	138
30	23.35	4.55	303
57	29.90	6.55	243
65	31.75	1.85	231 #
80	35.10	3.35	224 #
90	37.25	2.15	215 #
101	39.55	2.30	210 #

# Average rate for second run: 216  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XII (Continued)

The effect of an addition of 1.0M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 3

Average corrected pressure: 701.4 mm Hg

Average room temperature: 30.7°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
12	0.90	0.90	58
30	2.50	1.60	89
45	4.40	1.90	127
60	6.00	1.60	107
75	8.00	2.00	134
92	10.55	2.55	150
100	11.95	1.40	175

Addition of 1.0M  $\text{NH}_4\text{F}$

0	11.95	1.40	175
5	12.95	1.00	200
16	15.60	2.65	241
30	18.90	3.30	236
50	23.05	4.15	208
60	25.15	2.10	210 #
72	27.35	2.20	184 #
85	30.10	2.75	212 #
96	32.50	2.40	218 #
106	34.40	1.90	190 #

# Average rate for third run: 201  $\text{mm}^3/\text{cm}^2 \text{ min}$

Average rate for three runs: 200.3  $\text{mm}^3/\text{cm}^2 \text{ min}$



Table XIII

The effect of an addition of 1.5M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 704.8 mm Hg

Average room temperature: 28.2°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
8	0.75	0.75	94
18	2.70	1.95	195
33	5.45	2.75	183
48	8.10	2.65	177
58	9.70	1.60	160
78	13.25	3.55	177
88	14.90	1.65	165
100	17.05	2.15	179

Addition of 1.5M  $\text{NH}_4\text{F}$

0	17.05	2.15	179
20	20.75	3.70	218
31	23.25	2.50	237
43	25.90	2.65	221
59	29.35	3.45	216 #
78	33.35	4.00	211 #
88	35.40	2.05	205 #
98	37.35	1.95	195 #
108	39.35	2.00	200 #

# Average rate for first run: 204  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XIII (Continued)

The effect of an addition of 1.5M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 707.7 mm Hg

Average room temperature: 26.6°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
4	0.30	0.30	75
34	5.70	5.40	180
67	11.80	6.10	185
91	15.15	3.35	140
100	16.75	1.60	178

Addition of 1.5M  $\text{NH}_4\text{F}$

0	16.75	1.60	178
4	17.45	0.70	234
14	19.70	2.25	225
36	25.00	5.30	241
46	27.35	2.35	235
63	31.35	4.00	235 #
69	32.65	1.30	217 #
81	35.60	2.95	246 #
98	39.50	3.90	230 #
106	40.85	1.35	169 #

# Average rate for second run: 221  $\text{mm}^3/\text{cm}^2 \text{ min}$

Average rate for both runs: 212.5  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XIV

The effect of an addition of 2.0M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 702.1 mm Hg

Average room temperature: 29.8°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
15	1.60	1.60	107
30	4.15	2.55	170
45	6.85	2.70	180
65	10.85	4.00	200
81	13.40	2.55	160
90	15.15	1.75	195
100	16.95	1.80	180

Addition of 2.0 M  $\text{NH}_4\text{F}$

0	16.95	1.80	180
20	19.30	2.35	261
30	21.55	2.25	225
40	24.25	2.70	270
56	28.30	4.05	253 #
70	31.80	3.50	250 #
80	34.15	2.35	235 #
91	36.65	2.50	227 #
100	38.75	2.10	233 #
110	40.85	2.10	210 #

# Average rate for first run: 232  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XIV (Continued)

The effect of an addition of 2.0M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Average corrected pressure: 697 mm Hg

Average room temperature: 31.6°C

Run No. 2

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
20	0.70	0.70	57
30	2.30	1.60	160
55	6.65	4.35	174
70	9.30	2.65	177
80	10.70	1.40	140
90	12.30	1.60	160
100	14.05	1.75	175

Addition of 2.0M  $\text{NH}_4\text{F}$

0	14.05	1.75	175
7	15.20	1.15	230
21	18.50	3.30	236
40	23.10	4.60	242
56	26.85	3.75	234
61	28.00	1.15	230 #
90	34.45	6.45	223 #
100	36.55	2.10	210 #
110	38.70	2.15	215 #
120	40.95	2.25	225 #

# Average rate for second run: 219  $\text{mm}^3/\text{cm}^2 \text{ min}$

Average rate for both runs: 225.5  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XV

The effect of an addition of 3M  $\text{NH}_4\text{F}$  on the rate of dissolution in 0.1N HF

Run No. 1

Average corrected pressure: 704.4 mm Hg

Average room temperature: 28.2°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
5	0.50	0.50	100
28	4.60	4.10	178
40	6.95	2.35	196
65	11.10	4.15	166
81	15.10	4.00	250
100	18.50	3.40	179

Addition of 3M  $\text{NH}_4\text{F}$

0	18.50	3.40	179
7	19.60	1.10	275
20	23.80	4.20	323
32	27.40	3.60	300
52	33.10	5.70	285
60	35.10	2.00	250 #
72	38.55	3.45	288 #
80	40.55	2.00	250 #
91	43.45	2.90	264 #
102	46.05	2.60	237 #
105	46.80	0.75	250 #

# Average rate for first run: 260  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XV (Continued)

The effect of an addition of 3M  $\text{NH}_4\text{F}$  on the rate of dissolution in 0.1N HF

Run No. 2

Average corrected pressure: 704.4 mm Hg

Average room temperature: 28.2°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
30	4.20	4.20	140
40	6.20	2.00	200
52	8.40	2.20	184
65	10.40	2.00	154
85	13.80	3.40	170
100	16.40	2.60	173

Addition of 3M  $\text{NH}_4\text{F}$

0	16.40	2.60	173
3	16.60	0.20	200
10	18.75	2.15	308
20	21.55	2.80	280
30	24.95	3.40	262
41	28.40	3.45	431
52	31.45	3.05	381
66	35.65	4.20	300 #
80	39.55	3.90	279 #
90	42.10	2.55	255 #
105	44.80	2.70	180 #
110	45.85	1.05	210 #

# Average rate for second run: 232  $\text{mm}^3/\text{cm}^2 \text{ min}$

Average rate for both runs: 246  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XVI

The effect of an addition of 4M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 701.4 mm Hg

Average room temperature: 29.5°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
10	1.15	1.15	115
25	4.40	3.25	217
35	6.20	1.80	180
45	8.05	1.85	185
60	10.75	2.70	180
75	13.20	2.45	164
85	14.85	1.65	165
100	16.90	2.05	137

Addition of 4M  $\text{NH}_4\text{F}$

0	16.90	2.05	137
20	18.40	1.50	214
35	21.15	2.75	183
45	23.15	2.00	200
55	25.25	2.10	210 #
75	28.95	3.70	185 #
85	30.75	1.80	180 #
95	32.50	1.75	175 #
105	34.25	1.75	175 #

# Average rate for first run: 180  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XVI (Continued)

The effect of an addition of 4M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 700.9 mm Hg

Average room temperature: 28.9°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
11	1.10	1.10	100
31	5.65	4.55	227
46	8.15	2.50	167
60	10.85	2.70	193
82	14.90	4.05	184
100	18.10	3.20	178
Addition of 4M $\text{NH}_4\text{F}$			
0	18.10	3.20	178
11	20.10	2.00	250
22	22.25	2.15	195
39	25.80	3.55	209
52	28.40	2.60	200
60	31.05	1.65	206 #
75	33.85	2.80	187 #
91	36.75	2.90	181 #
102	38.80	2.05	186 #
111	40.40	1.60	178 #

# Average rate for second run: 184  $\text{mm}^3/\text{cm}^2 \text{ min}$



Table XVII

The effect of an addition of 5M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 698.8 mm Hg

Average room temperature: 29.7°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
18	1.65	1.65	92
66	9.85	8.20	171
84	12.85	3.00	167
100	15.25	2.40	150

Addition of 5M  $\text{NH}_4\text{F}$

0	15.25	2.40	150
9	15.80	0.55	92
19	17.10	1.30	130
29	18.55	1.45	145
49	21.60	3.05	153
63	23.65	2.05	147 #
74	25.25	1.60	146 #
88	27.25	2.00	143 #
100	28.95	1.70	142 #
110	29.40	1.45	145 #

Average rate for run: 144  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XVIII

The effect of an addition of 6M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 707.1 mm Hg

Average room temperature: 27.6°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
10	1.10	1.10	110
25	3.65	2.55	171
35	5.70	2.05	205
57	9.40	3.70	168
85	14.15	4.75	170
100	16.10	1.95	130

Addition of 6M  $\text{NH}_4\text{F}$

0	16.10	1.95	130
15	16.80	0.70	58
30	17.85	1.05	70
50	19.05	1.20	60 #
70	20.75	1.70	85 #
88	21.95	1.20	67 #
98	22.70	0.75	75 #
105	23.40	0.70	100 #

# Average rate for first run: 78.5  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XVIII (Continued)

The effect of an addition of 6M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 702.1 mm Hg

Average room temperature: 29.7°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
17	2.05	2.05	120
30	4.80	2.75	211
50	8.55	3.75	187
80	14.25	5.70	190
100	17.65	3.40	170

Addition of 6M  $\text{NH}_4\text{F}$

0	17.65	3.40	170
15	18.55	0.90	75
31	21.10	2.55	160
45	23.35	2.25	161
60	24.00	0.65	43.5
71	25.15	1.15	105 #
80	26.20	1.05	117 #
98	28.05	1.85	103 #
111	29.45	1.40	108 #

# Average rate for second run: 107.5  $\text{mm}^3/\text{cm}^2 \text{ min}$

Average rate for both runs: 93  $\text{mm}^3/\text{cm}^2 \text{ min}$

Table XIX

The effect of an addition of 8M  $\text{NH}_4\text{F}$  on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 705 mm Hg

Average room temperature: 29.5°C

Time (minutes)	Volume $\text{H}_2$ ( $\text{cm}^3$ )	$\Delta$ Volume ( $\text{cm}^3$ )	Rate ( $\text{mm}^3/\text{cm}^2 \text{ min}$ )
0	0	0	0
5	0.35	0.35	70
38	3.50	3.15	96
65	6.70	3.20	119
80	8.50	1.80	120
100	11.40	2.90	145

Addition of 8M  $\text{NH}_4\text{F}$

0	11.40	2.90	145
11	11.40	0	0
29	12.90	1.50	84
46	14.60	1.70	100
55	15.35	0.75	84 #
68	16.20	0.85	66 #
75	16.80	0.60	86 #
90	17.95	1.15	77 #
100	18.75	0.80	80 #
112	19.90	1.15	96 #

# Average rate for run: 80  $\text{mm}^3/\text{cm}^2 \text{ min}$

Tables X - XIX See Figure 7

Table XX

The effect of an addition of 0.073M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 702.1 mm Hg

Average room temperature: 29.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	ΔVolume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
35	5.25	5.25	153
50	7.90	2.65	177
73	11.85	3.95	172
100	16.25	4.40	163

Addition of 0.073M KF

0	16.25	4.40	163
23	22.30	6.05	263
35	25.65	3.35	279
53	30.40	4.75	264
59	32.00	1.60	267 #
80	37.35	5.35	255 #
102	42.65	5.30	241 #
110	44.55	1.90	238 #

Average rate for first run: 246 mm<sup>3</sup>/cm<sup>2</sup> min

Table XX (Continued)

The effect of an addition of 0.073M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 696.0 mm Hg

Average room temperature: 31.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	$\Delta$ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
7	0.40	0.40	57
72	12.75	12.35	185
100	16.95	4.20	150

Addition of 0.073M KF

0	16.95	4.20	150
13	18.85	1.90	155
42	26.90	8.05	278
66	32.75	5.85	244 #
90	38.90	6.15	256 #
101	41.65	2.75	250 #
111	44.20	2.55	255 #
117	45.60	1.40	234 #

# Average rate for second run: 252 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 249 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXI

The effect of an addition of 0.18M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 699.8 mm Hg

Average room temperature: 30.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
8	0.30	0.30	37
37	5.45	5.15	178
91	14.85	9.40	174
100	16.15	1.30	145

Addition of 0.18M KF

0	16.15	1.30	145
5	16.65	0.50	100
31	23.40	6.75	260
47	27.50	4.10	256
57	30.00	2.50	250 #
71	33.35	3.35	239 #
86	36.90	3.55	237 #
97	39.55	2.65	241 #
111	42.65	3.10	222 #

# Average rate for first run: 234 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXI (Continued)

The effect of an addition of 0.18M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 699.6 mm Hg

Average room temperature: 31.5°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
74	10.80	10.80	146
100	15.10	4.30	164

Addition of 0.18M KF

0	15.10	4.30	164
7	15.75	0.65	90
32	20.85	5.10	204
46	24.95	4.10	293
64	29.15	4.20	233 #
68	30.20	1.05	263 #
81	33.50	3.30	254 #
97	36.80	3.30	206 #
105	38.40	1.60	200 #
111	39.85	1.45	242 #

# Average rate for second run: 228 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 231 mm<sup>3</sup>/cm<sup>2</sup> min



Table XXII

The effect of an addition of 0.36M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 698.9 mm Hg

Average room temperature: 30.7°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
12	1.35	1.35	113
30	5.30	3.95	219
40	7.45	2.15	215
51	11.75	4.30	390
78	15.40	3.65	215
100	19.25	3.85	175

Addition of 0.36M KF

0	19.25	3.85	175
5	19.40	0.15	75
18	22.70	3.30	254
45	30.70	8.00	296
60	34.75	4.05	270 #
70	37.40	2.65	265 #
80	39.95	2.55	255 #
99	44.85	4.90	257 #
105	46.10	2.25	375 #

Average rate for first run: 275 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXII (Continued)

The effect of an addition of 0.36M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 696.2 mm Hg

Average room temperature: 31.7°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	0.40	0.40	40
51	7.15	6.75	165
73	10.85	3.70	168
95	14.40	3.55	162
100	15.25	0.85	170

Addition of 0.36M KF

0	15.25	0.85	170
15	16.90	1.65	137
26	19.45	2.55	232
36	21.00	1.55	155
58	26.95	5.95	270 #
66	28.80	1.85	231 #
77	31.40	2.60	236 #
93	35.05	3.65	228 #
100	36.80	1.75	250 #

Average rate for second run: 234.5 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 250 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXIII

The effect of an addition of 0.43M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 701.8 mm Hg

Average room temperature: 29.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	$\Delta$ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
5	0.10	0.10	20
38	5.70	5.60	170
81	13.05	7.35	171
100	16.20	3.15	166

Addition of 0.43M KF

0	16.20	3.15	166
5	16.70	0.50	100
36	24.35	7.65	247
51	29.15	4.80	320
65	31.85	2.70	193 #
83	36.30	4.45	247 #
94	39.00	2.70	245 #
107	42.20	3.20	246 #

# Average rate for first run: 247 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXIII (Continued)

The effect of an addition of 0.43M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 696.6 mm Hg

Average room temperature: 33.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	$\Delta$ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
36	5.95	5.95	165
55	9.30	3.35	176
72	12.30	3.00	177
89	14.95	2.65	156
100	16.95	2.00	182

Addition of 0.43M KF

0	16.95	2.00	182
8	18.35	1.40	175
20	21.15	2.80	233
52	29.60	8.45	264
64	32.55	2.95	246 #
79	36.50	3.95	263 #
91	39.25	2.75	229 #
110	43.80	4.55	239 #

# Average rate for second run: 245 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 246 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXIV

The effect of an addition of 0.49 M KF on the rate of dissolution of Zr in 0.1 N KF

Run No. 1

Average corrected pressure: 702.8 mm Hg

Average room temperature: 28.7°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	$\Delta$ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
12	0.95	0.95	79
64	10.45	9.50	183
100	17.15	6.70	186

Addition of 0.49M KF

0	17.15	6.70	186
8	19.30	2.15	267
23	24.00	4.60	307
41	29.15	5.15	286
58	33.70	4.55	267 #
82	39.85	6.15	256 #
100	44.15	4.30	239 #
108	45.95	1.80	225 #

# Average rate for first run: 245 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXIV (Continued)

The effect of an addition of 0.49M KF on the rate of dissolution of Zr in 0.1N KF

Run No. 2

Average corrected pressure: 692.6 mm Hg

Average room temperature: 33.4°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
24	4.80	4.80	200
38	7.70	2.90	207
69	13.55	5.85	189
100	19.15	5.60	180

Addition of 0.49M KF

0	19.15	5.60	180
8	20.35	1.20	150
21	23.90	3.55	273
30	26.45	2.55	284
41	29.25	2.80	255
51	32.00	2.75	275
61	34.50	2.50	250 #
74	37.80	3.30	254 #
95	42.90	5.10	243 #
108	45.90	3.00	231 #

# Average rate for second run: 243 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 244 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXV

The effect of an addition of 0.54M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 699.2 mm Hg

Average room temperature: 30.6°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
7	0.35	0.35	50
42	7.45	7.10	203
78	15.00	7.55	209
100	18.10	3.10	141

Addition of 0.54M KF

0	18.10	3.10	141
9	19.05	0.95	136
38	22.95	3.90	135
50	23.60	0.65	54
57	23.95	0.35	50 #
72	24.55	0.60	40 #
105	25.85	1.30	40 #

# Average rate for first run: 39.6 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 35.5 mm<sup>3</sup>/cm<sup>2</sup> min

Run No. 2

Average corrected pressure: 697.4 mm Hg

Average room temperature: 31.2°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
58	10.00	10.00	172
100	18.20	8.20	195

Addition of 0.54M KF

0	18.20	8.20	195
16	22.55	4.35	272
24	23.90	1.35	169
36	24.75	0.85	71
47	25.05	0.30	27
60	25.35	0.30	23 #
97	26.45	1.10	30 #
114	27.05	0.60	35 #

Table XXVI

The effect of an addition of 0.72M KF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 702.8 mm Hg

Average room temperature: 29.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
34	5.35	5.35	158
47	7.65	2.30	177
100	16.40	8.75	165

Addition of 0.72M KF

0	16.40	8.75	165
23	16.40	0.0	0
37	16.75	0.35	25
68	17.45	0.70	23 #
86	17.95	0.50	28 #
99	18.20	0.25	19 #
109	18.45	0.25	26 #

Average rate for first run: 24 mm<sup>3</sup>/cm<sup>2</sup> min

Tables XX - XXVI See Figure 8



Table XXVII

The effect of an addition of 0.025M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 704.3 mm Hg

Average room temperature: 27.4°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	$\Delta$ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	0.95	0.95	95
25	3.75	2.80	186
40	6.20	2.45	175
60	9.40	3.20	160
75	11.75	2.35	157
90	13.70	1.95	130
100	15.20	1.50	150

Addition of 0.025M NaF

0	15.20	1.50	150
6	15.95	0.75	167
10	16.90	0.95	238
25	19.40	2.50	167
40	22.70	3.30	220
55	25.70	3.00	200
65	27.60	1.90	190 #
80	30.70	3.10	207 #
95	33.65	2.95	197 #
110	36.60	2.95	197 #
120	38.50	1.90	190 #

# Average rate for first run: 198 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXVII (Continued)

The effect of an addition of 0.025M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 698.5 mm Hg

Average room temperature: 30.2°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	$\Delta$ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
5	0	0	0
20	2.70	2.70	180
35	5.70	3.00	200
50	8.60	2.90	193
65	10.90	2.30	153
80	13.80	2.90	193
100	17.10	3.30	165

Addition of 0.025M NaF

0	17.10	3.30	165
5	17.95	0.85	170
20	20.60	2.65	177
35	23.90	3.30	220
50	26.80	2.90	193
65	29.35	2.55	170 #
85	32.35	3.00	150 #
100	35.00	2.65	177 #
115	38.10	3.10	207 #

# Average rate for second run: 175 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 186.5 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXVIII

The effect of an addition to 0.05M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 706.3 mm Hg

Average room temperature: 26.8°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	$\Delta$ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	1.90	1.90	190
25	4.65	2.75	183
40	7.30	2.65	177
55	10.00	2.70	180
70	12.55	2.55	170
85	14.75	2.20	147
100	17.15	2.40	160

Addition of 0.05M NaF

0	17.15	2.40	160
5	18.40	1.25	250
15	21.10	2.70	270
25	23.55	2.45	245
35	26.00	2.45	245
45	28.15	2.15	215
55	30.35	2.20	220
65	32.50	2.15	215 #
75	34.65	2.15	215 #
85	36.65	2.00	200 #
95	38.60	1.95	195 #
105	40.45	1.85	185 #
115	42.60	2.15	215 #
120	43.65	1.05	210 #

# Average rate for first run: 203 mm<sup>3</sup>/cm<sup>2</sup> min

Table XVIII (Continued)

The effect of an addition of 0.05M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 705.4 mm Hg

Average room temperature: 27.5°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	1.30	1.30	130
20	3.05	1.75	175
30	4.65	1.60	160
45	7.25	2.60	173
60	10.15	2.90	193
75	12.35	2.20	147
95	15.20	2.85	143
100	15.95	0.75	150

Addition of 0.05M NaF

0	15.95	0.75	150
10	18.40	2.45	245
25	22.25	3.85	257
35	24.45	2.20	220
45	26.70	2.25	225
55	28.60	1.90	190
65	30.80	2.20	220 #
76	33.25	2.45	223 #
86	35.15	1.90	190 #
95	36.75	1.60	178 #
105	38.80	2.05	205 #
115	40.65	1.85	185 #

# Average rate for second run: 197 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 200 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXIX

The effect of an addition of 0.075M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 703.2 mm Hg

Average room temperature: 29.1°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
5	0.15	0.15	30
10	0.85	0.70	140
35	5.25	4.40	176
45	6.60	1.35	135
70	10.60	4.00	160
85	12.70	2.10	140
100	15.05	2.35	157

Addition of 0.075M NaF

0	15.05	2.35	157
5	15.90	0.85	170
15	18.75	2.85	285
25	21.40	2.65	265
35	23.90	2.50	250
50	27.65	3.75	250
60	30.00	2.35	235 #
70	32.45	2.45	245 #
80	34.60	2.15	215 #
95	37.80	3.20	214 #
105	40.15	2.35	235 #
115	42.15	2.00	200 #

# Average rate for first run: 221 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXIX (Continued)

The effect of an addition of 0.075M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 703.2 mm Hg

Average room temperature: 28.2°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
5	0.60	0.60	120
20	2.70	2.10	140
35	4.80	2.10	140
50	7.20	2.40	160
65	9.40	2.20	147
80	11.40	2.00	134
95	13.15	1.75	117
100	13.85	0.70	140

Addition of 0.075M NaF

0	13.85	0.70	140
5	14.85	1.00	200
15	17.45	2.60	260
26	20.30	2.85	259
35	22.20	1.90	211
45	24.55	2.35	235
55	26.65	2.10	210
65	28.50	1.85	185 #
76	30.95	2.45	223 #
85	32.55	1.60	178 #
95	34.80	2.25	225 #
105	36.50	1.70	170 #
120	39.15	2.65	177 #

# Average rate for second run: 194 mm<sup>3</sup>/cm<sup>2</sup> minAverage rate for both runs: 207.5 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXX

The effect of an addition of 0.1M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 692.7 mm Hg

Average room temperature: 32.6°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	0.80	0.80	80
23	2.80	2.00	154
42	6.50	3.70	195
56	8.95	2.45	175
70	11.15	2.20	157
88	14.00	2.85	159
100	16.05	2.05	171

Addition of 0.1M NaF

0	16.05	2.05	171
11	18.25	2.20	200
18	20.05	1.80	257
36	24.10	4.05	225
42	25.75	1.65	275
54	28.85	3.10	255 #
70	32.45	3.60	225 #
80	34.60	2.15	215 #
90	37.00	2.40	240 #
100	39.15	2.15	215 #
110	41.00	1.85	185 #
120	43.05	2.05	205 #

# Average rate for first run: 215 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXX (Continued)

The effect of an addition of 0.1M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 706.7 mm Hg

Average room temperature: 26.0°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
3	0.35	0.35	116
15	2.55	2.20	183
40	5.15	2.60	104
55	8.00	2.85	190
70	10.60	2.60	174
91	14.35	3.75	179
100	15.65	1.30	145

Addition of 0.1M NaF

0	15.65	1.30	145
10	19.45	3.80	380
25	24.20	4.75	317
40	28.25	4.05	270
55	32.50	4.25	283 #
65	34.95	2.45	245 #
80	38.85	3.90	260 #
95	42.30	3.45	230 #
110	45.10	2.80	187 #
115	46.50	1.40	280 #

# Average rate for second run: 233 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 224 mm<sup>3</sup>/cm<sup>2</sup> min



Table XXXI

The effect of an addition of 0.1125N NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 700.1 mm Hg

Average room temperature: 28.4°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
5	0.85	0.85	170
20	3.85	3.00	200
35	6.45	2.60	173
50	9.00	2.55	170
65	11.50	2.50	167
80	13.95	2.45	163
95	16.20	2.25	150
100	17.05	0.85	170

Addition of 0.1125N NaF

0	17.05	0.85	170
5	17.70	0.65	130
21	22.30	4.60	287
35	25.75	3.45	247
50	28.40	2.65	177
65	29.90	1.50	100
80	30.60	0.70	47 #
100	30.60	0.0	0 #
115	30.60	0.0	0 #

Average rate for first run: 14 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXXI (Continued)

The effect of an addition of 0.1125N NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 700.5 mm Hg

Average room temperature: 28.2°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	0.95	0.95	95
25	3.70	2.75	184
40	6.75	3.05	203
55	9.80	3.05	203
70	12.60	2.80	187
85	15.20	2.60	173
100	17.95	2.75	184

Addition of 0.1125N NaF

0	17.95	2.75	184
5	19.05	1.10	220
20	23.15	4.10	273
35	26.60	3.45	230
50	30.00	3.40	227
65	32.75	2.75	184 #
80	35.45	2.70	180 #
100	37.50	2.05	102.5 #
110	38.60	1.10	110 #
120	39.10	0.50	50 #

# Average rate for second run: 115 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 70 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXXII

The effect of an addition of 0.125M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 1

Average corrected pressure: 695.7 mm Hg

Average room temperature: 30.6°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	1.05	1.05	105
20	2.70	1.65	165
60	10.20	7.50	187
75	12.70	2.50	167
90	15.10	2.40	160
100	16.80	1.70	170

Addition of 0.125M NaF

0	16.80	1.70	170
5	17.05	0.25	50
15	19.10	2.05	205
30	20.00	0.90	60
45	20.00	0	0
60	20.00	0	0 #
75	20.00	0	0 #
90	20.00	0	0 #

# Average rate for first run: 0 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXXII (Continued)

The effect of an addition of 0.125M NaF on the rate of dissolution of Zr in 0.1N HF

Run No. 2

Average corrected pressure: 705.8 mm Hg

Average room temperature: 27.8°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
3	0.10	0.10	33
20	3.15	3.05	180
35	6.15	3.00	200
50	8.50	2.35	157
70	10.85	2.35	117
85	13.80	2.95	197
100	16.25	2.45	163

Addition of 0.125M NaF

0	16.25	2.45	163
5	17.15	0.90	180
15	17.90	0.75	75
25	18.25	0.35	35
35	18.40	0.15	15
50	18.40	0	0 #
65	18.40	0	0 #
80	18.40	0	0 #
85	18.40	0	0 #

# Average rate for second run: 0 mm<sup>3</sup>/cm<sup>2</sup> min

Average rate for both runs: 0 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXXIII

The effect of an addition of 0.15M NaF on the rate of dissolution of Zr in 0.1N HF

Average corrected pressure: 703.2 mm Hg

Average room temperature: 26.8°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
10	1.40	1.40	140
25	4.30	2.90	194
40	7.05	2.75	184
55	9.85	2.80	187
70	12.55	2.70	180
85	14.80	2.25	150
100	17.15	2.35	157

Addition of 0.15M NaF

0	17.15	2.35	157
5	17.75	0.60	117
20	18.45	0.70	47
30	18.80	0.35	35
45	19.00	0.20	13
60	19.10	0.10	7 #
75	19.25	0.15	10 #
90	19.30	0.05	3 #
105	19.35	0.05	3 #

# Average rate for run: 5.6 mm<sup>3</sup>/cm<sup>2</sup> min

Table XXXIV

The effect of an addition of 0.2M NaF on the rate of dissolution of Zr in 0.1N HF

Average corrected pressure: 701.6 mm Hg

Average room temperature: 27.3°C

Time (minutes)	Volume H <sub>2</sub> (cm <sup>3</sup> )	Δ Volume (cm <sup>3</sup> )	Rate (mm <sup>3</sup> /cm <sup>2</sup> min)
0	0	0	0
5	0.75	0.75	150
20	3.95	3.20	213
35	6.60	2.65	177
50	9.65	3.05	203
65	12.15	2.50	167
80	14.80	2.65	177
95	17.00	2.20	147
100	17.70	0.70	140

Addition of 0.2M NaF

0	17.70	0.70	140
5	18.10	0.40	80
20	19.15	1.05	70
35	19.25	0.10	7
50	19.70	0.45	30
65	19.70	0.00	0#
80	19.70	0.00	0#
95	19.70	0.00	0#

# Average rate for run: 0 mm<sup>3</sup>/cm<sup>2</sup> min

Tables XXVII - XXXIV See Figure 9

Table XXXV

Data for potential-time curves of Zr in varying concentrations of HF

See Figure 12

0.01N HF	
Time (minutes)	$E_{Zr}$
0	-0.768
1	-0.742
2	-0.728
3	-0.713
4	-0.706
5	-0.704
10	-0.691
20	-0.687
30	-0.679
45	-0.668
55	-0.664
70	-0.656
85	-0.646
95	-0.642
120	-0.641

0.05N HF	
Time (minutes)	$E_{Zr}$
0	-0.713
2	-0.686
4	-0.676
10	-0.668
22	-0.660
35	-0.668
47	-0.671
63	-0.670
75	-0.670

0.10N HF	
Time (minutes)	$E_{Zr}$
0	-0.754
2	-0.726
10	-0.715
20	-0.712
35	-0.709
55	-0.705
75	-0.700

Table XXXV (Continued)

Data for potential-time curves of Zr in varying concentrations of HF

See Figure 12

0.14N HF

Time (minutes)	$E_{Zr}$
0	-0.774
2	-0.745
3	-0.737
5	-0.732
24	-0.728
40	-0.720
71	-0.714
90	-0.712
115	-0.709
125	-0.708

0.25N HF

Time (minutes)	$E_{Zr}$
0	-0.810
2	-0.768
3	-0.748
4	-0.744
5	-0.744
18	-0.741
35	-0.735
50	-0.733
70	-0.730
90	-0.725
105	-0.722
135	-0.719

0.50N HF

Time (minutes)	$E_{Zr}$
0	-0.900
1	-0.806
2	-0.810
4	-0.812
5	-0.812
10	-0.806
17	-0.794
27	-0.780
50	-0.762
58	-0.757
88	-0.747
107	-0.740



Table XXXVI

The effect of an addition of 6.5M  $\text{NH}_4\text{F}$  on the potential-time curve of Zr in 0.1N HF

Time (minutes)	$E_{\text{Zr}}$
0	-0.742
1	-0.720
3	-0.716
19	-0.714
48	-0.711
62	-0.709
75	-0.707
Addition of 6.5M $\text{NH}_4\text{F}$	
77	-1.062
78	-1.070
79	-1.092
80	-1.112
81	-1.112
88	-1.076
103	-1.076
120	-1.076
155	-1.075
335	-1.064
515	-1.052
575	-1.050
770	-1.040
1340	-1.015
1535	-1.015
1655	-1.015

See Figure 13

Table XXXVII

The effect of an addition of 3.0M  $\text{NH}_4\text{F}$  on the potential-time curve of Zr in 0.1N HF

Time (minutes)	$E_{\text{Zr}}$
0	-0.760
1	-0.730
2	-0.730
10	-0.720
51	-0.713
70	-0.710
75	-0.710
Addition of 3.0M $\text{NH}_4\text{F}$	
76	-1.074
77	-1.055
79	-1.043
103	-1.046
150	-1.035
220	-1.015
360	-0.992
540	-0.955
1080	-0.929

Table XXXVIII

The effect of an addition of 0.71M KF on the potential-time curve of Zr in 0.1N HF

Time (minutes)	$E_{Zr}$
0	-0.744
1	-0.733
2	-0.727
18	-0.709
35	-0.706
60	-0.702
75	-0.702
Addition of 0.71M KF	
78	-1.133
80	-1.095
82	-1.064
83	-1.057
87	-1.075
100	-1.077
120	-1.061
140	-1.053
170	-1.050
420	-1.030
1065	-1.029
1200	-1.028

See Figure 14

Table XXXIX

The effect of an addition of 1.37M KF on the potential-time curve of Zr in 0.1N HF

Time (minutes)	$E_{Zr}$
0	-0.742
2	-0.726
11	-0.714
20	-0.711
30	-0.710
70	-0.702
75	-0.702
Addition of 1.37M KF	
76	-1.136
77	-1.108
79	-0.958
82	-0.940
95	-0.966
107	-0.984
118	-0.992
128	-0.997
180	-0.996
195	-0.994
270	-0.969
320	-0.948
390	-0.942
480	-0.941
630	-0.940

Table XL

The effect of an addition of 0.15M NaF on the potential-time curve of Zr in 0.1N HF

Time (minutes)	$E_{Zr}$
0	-0.754
2	-0.726
10	-0.715
20	-0.712
35	-0.709
55	-0.705
75	-0.700
Addition of 0.15M NaF	
76	-0.988
77	-0.972
79	-0.974
81	-0.959
85	-0.917
105	-0.728
180	-0.642
210	-0.626
240	-0.616
550	-0.611
1215	-0.528
1380	-0.522
1460	-0.541
1515	-0.528
1530	-0.528

See Figure 15

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